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THE PLACE OF TRANSITION METALS IN ORGANIC SYNTHESIS

Editor
D. W. Slocum

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THE PLACE OF TRANSITION METALS IN ORGANIC SYNTHESIS*

Editor and Conference Chairman
D. W. SLOCUM

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INTRODUCTORY REMARKS

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One might ask why it is necessary to hold a separate conference on transition metal organic chemistry. There have been many organometallic conferences in the past: Gordon conferences, international organometallic conferences, and numerous American Chemical Society symposia. Only recently, however, has the spotlight turned toward utilization of such reagents in organic synthesis. In some of these conferences, synthesis itself has been stressed but not organic synthesis per se. In organizing this conference, it was our intent to focus on the real and potential uses of transition metal complexes in organic synthesis, whether as catalysts, as stoichiometric agents in their own right, or as compounds of utility in any situation in between.

I believe that the first 25 years of organometallic chemistry have belonged essentially to the inorganic chemist. Bridging and cluster compounds, structures that were inconceivable not too long ago, have become commonplace today. But since the discovery of ferrocene, the organic chemist has generally remained relatively ignorant of the potential uses of transition metal complexes in synthesis. I just as firmly believe that the time has arrived for the organic chemist to be involved in this fascinating field.

It is particularly timely that the senior author of that remarkable initial paper on the subject of this conference, Prof. Peter Pauson, will present the first talk at this meeting. Prof. Pauson, as many of you probably know, began research in the field at Duquesne University in Pittsburgh, Pennsylvania in 1951. The historic paper on $C_{10}H_{10}Fe$ appeared in *Nature* just 25 years ago. Since then, Prof. Pauson has published well over 100 papers in this area of chemistry.

Lastly, I personally thank the staff of The Academy, particularly Mrs. Ellen Marks, and Dr. Jerome Fredrick and Prof. Edwin Abbott of the Conference Committee. It is a long time between the gleam in a scientist's eye at the prospect of a potential conference and the reality of a room filled with approximately 200 people. The aforementioned people not only made the conference possible but also greatly simplified the organizational process to make it a *relative* pleasure; organizing things is never a *total* pleasure.

USES OF COBALT-CARBONYL ACETYLENE COMPLEXES IN ORGANIC SYNTHESIS*†

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Condensations of acetylenes with themselves and with carbon monoxide have frequently been observed when acetylenes were treated with metal carbonyls. The most extensive information in the literature relates to iron carbonyls, from which a vast range of complexes have been obtained, the organic ligand of which is rarely the unchanged acetylene but, rather, is usually composed of one to three acetylene units with or without incorporation of one or two carbonyl groups. Interesting structures are made in this way from these simple fragments. Whereas many of the iron complexes formed are too stable to be of obvious promise as intermediates in organic synthesis, one of the earliest reactions studied by Reppe,[1] that which leads to hydroquinones from two acetylene and two carbon monoxide molecules, continues to hold at least potential practical interest.

At the outset of the present work, we considered that the somewhat less extensively explored reactions of cobalt carbonyl[2] might prove more rewarding as synthetic tools for the following reasons:

Simple acetylene hexacarbonyldicobalt complexes (**1**) are readily formed from octacarbonyldicobalt and all acetylenes so far examined.

The further transformations known also proceed cleanly in a single direction.

At least one useful catalytic reaction that gives otherwise inaccessible products is known,[3] that between acetylenes and carbon monoxide under pressure to give the bifurandiones of type (**2**).

Apart from substitution of carbon monoxide groups or acetylenes by other ligands, the following reactions of complexes (**1**) are known:

Conversion to the tetranuclear complexes of type (**3**) is of no further interest in the present context.

Reaction with carbon monoxide under pressure to yield the lactone complexes[4,5] of type (**4**) is clearly of interest in understanding the formation of the dilactones (**2**).

Reaction with acids restricted to complexes of the terminal acetylenes (e.g., **1c**) yields[6,7] the trinuclear complexes of type (**5**) (also accessible from *gem*-trihalides), the chemistry of which has been extensively studied by Seyferth *et al.*[8] at the Massachusetts Institute of Technology and by Penfold and Robinson[9] in New Zealand.

Reaction with excess of acetylene results in its cyclotrimerization.[10,11] Although octacarbonyldicobalt is only one of several efficient cyclotrimerization catalysts, isolation[10] and structure determinations[12,13] of intermediates that incorporate three molecules of the acetylenic precursors shed significant light on the reaction path. The first such structure was obtained[12] for complex (**6**) from $(C_2H_2)Co_2(CO)_6 + 2Bu^tC_2H$ and shows clearly that its formation involves separate

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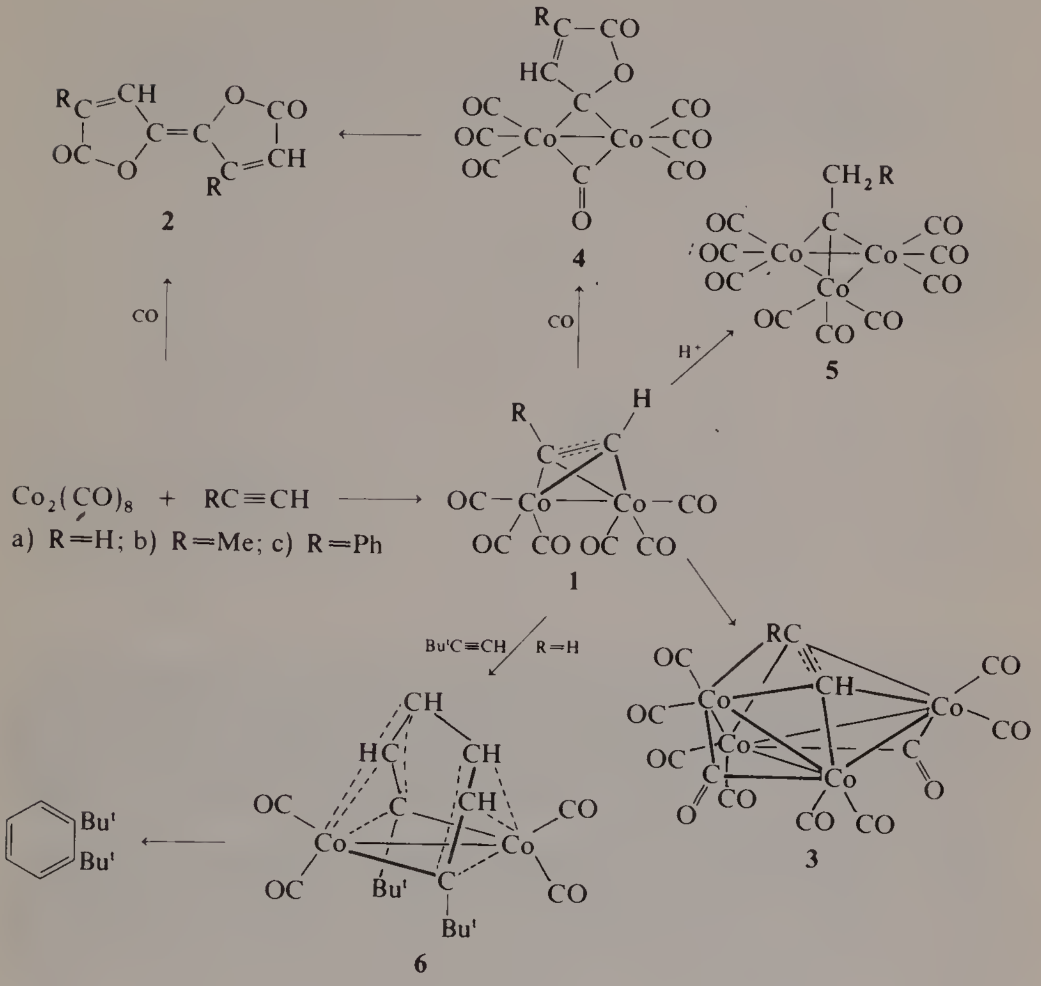
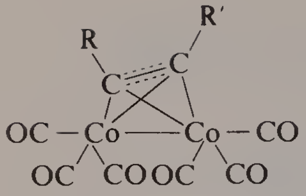
* Organo cobalt complexes, part XII.

† Supported by the Science Research Council.



insertion of two molecules of the alkyne into cobalt—carbon bonds. Apparently, the new carbon—carbon bonds are preferentially formed between unsubstituted carbons, presumably because of lesser steric hindrance.

On the basis of the last reaction, we chose to study whether sufficiently reactive alkenes would insert in a similar manner. As our first alkene, we selected norbornadiene (bicyclo[2.2.1]heptadiene), whose reactivity is enhanced by ring strain and which had been compared to acetylenes regarding, for example, its ability to undergo nickel carbonyl-catalyzed carboxylation.[14] Indeed, it reacted under mild conditions with the acetylene complexes (**1**) and yielded the ketones (**7**) as the principal organic products. Before demonstrating the wider applicability of this reaction for synthesis of cyclopentenones, we will discuss some other aspects. The organocobalt compounds that accompany these ketones depend on the solvent used. Reaction in arenes yields[15,16] the previously unknown arene tetracobalt cluster compounds, $(ArH)Co_4(CO)_9$. Their composition suggested a close relationship to dodecacarbonyl tetracobalt, which was supported by simple preparation on heating the latter with arenes, and the structure (**8**) was confirmed by x-ray crystallographic



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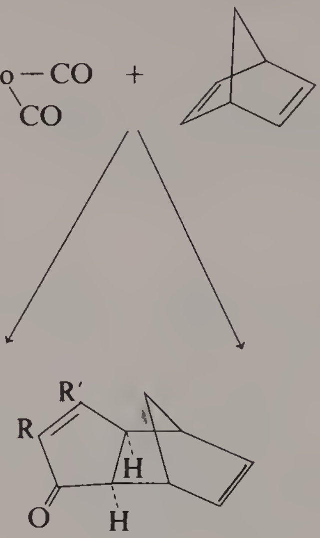
a) R=R′=H
b) R=Me; R′=H
c) R=Ph; R′=H
d) R=R′=Ph



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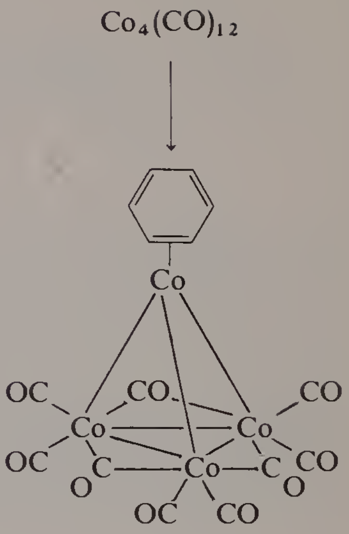

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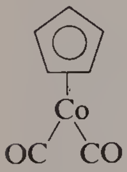

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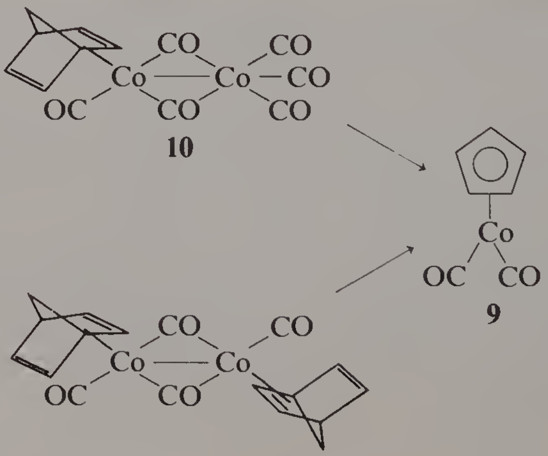
study.[17] In inert solvents, most of the cobalt was recovered as cyclopentadienyldicarbonylcobalt (**9**). This compound can only have resulted from a reverse Diels-Alder reaction, splitting norbornadiene to yield cyclopentadiene and acetylene. Such cleavage must have been powerfully catalyzed by the cobalt complex(es), because the uncatalyzed reaction is known to require temperatures at least 100 °C higher than the temperature we used.

The two norbornadiene-carbonylcobalt complexes (**10** and **11**)[18] were found to undergo a similarly facile retro-Diels-Alder reaction, again yielding the complex (**9**). The trinuclear complex (**5a**) also promotes this cleavage but less readily and smoothly: It reacts with the diene under mild conditions to give the complex (**12a**) by simple replacement of two carbonyl groups, but somewhat more vigorous conditions give the biscyclopentadienyl derivatives (**13a**) in low yield.[15]



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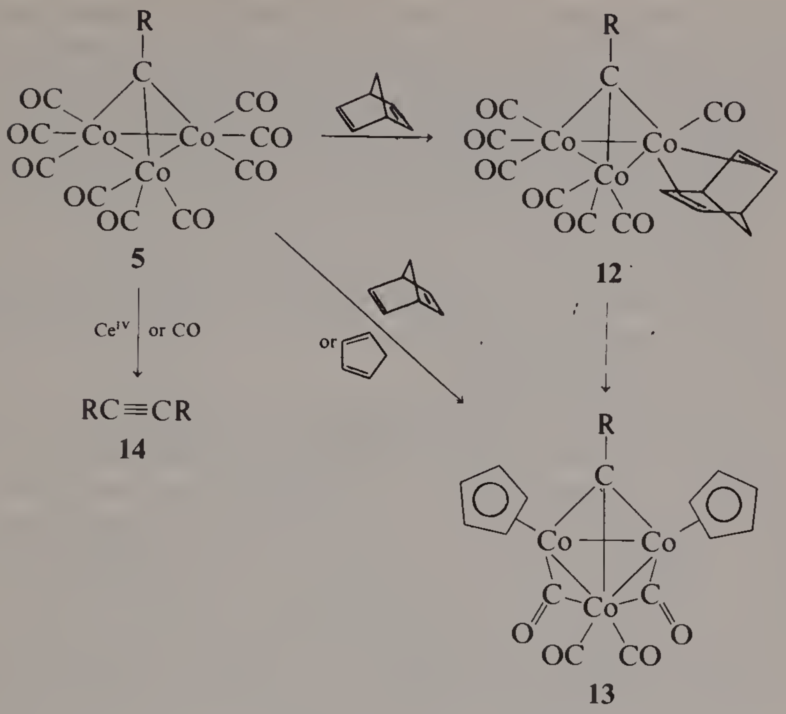
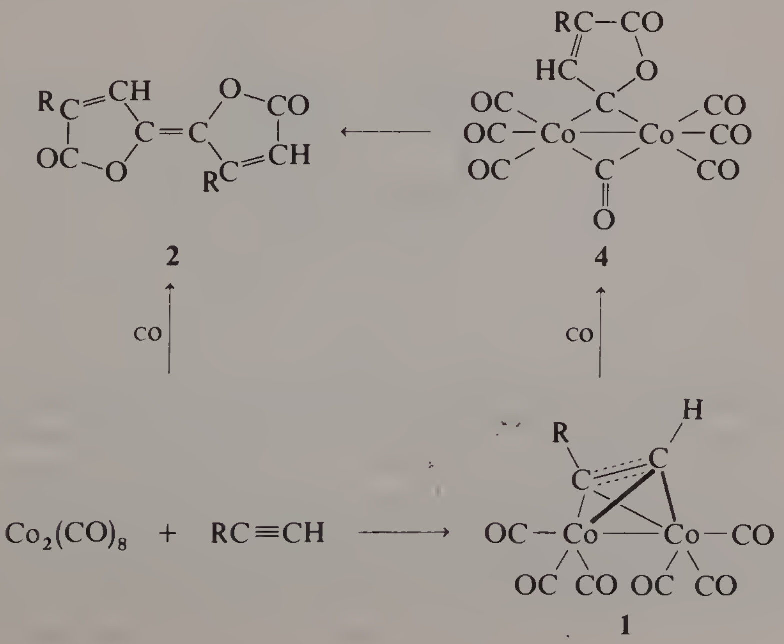


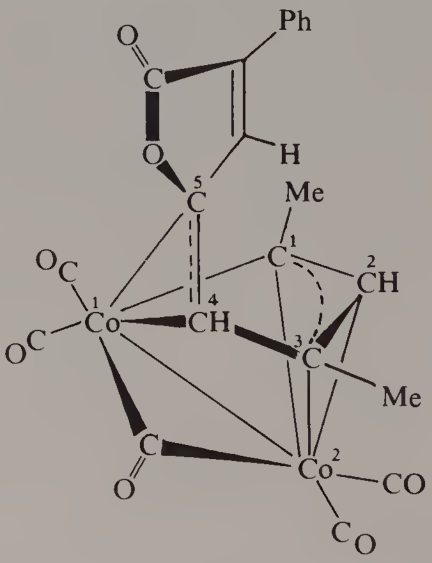
We made one other observation about these trinuclear complexes (**5**) that is relevant to synthetic utility.[19] Both on attempted carbonylation and on ceric salt oxidation, they give appreciable quantities of the symmetric acetylenes (**14**) derived from two RC units. Despite modest yields, the overall conversion $RC{\equiv}CH \rightarrow RCH_2C{\equiv}CCH_2R$ is so simple that it must be an attractive route in some cases.

For the lactone complexes (**4**), a similar coupling of organic residues would lead to symmetric bifurandiones of type (**2**), provided that the complexes themselves were homogeneous, whereas Albanesi[20] has shown that the catalytically formed



products have unsymmetrically substituted structures (**2**) when derived from terminal alkynes. We were able to demonstrate that these alkynes do yield lactone complexes (**4**) regiospecifically, with substituents always on the carbon adjacent to the organic carbonyl group. Thus, the bifurandiones cannot arise by coupling of two separately preformed lactone residues. Pyrolysis of the lactone complex (**4**, R = Ph) did afford a trace of the symmetric bifurandione, and this trace amount could be the source of the minute yields of symmetric products observed in the catalytic process. The same complexes (**4**), however, reacted with acetylenes under carbon monoxide pressure to give, in fair yield, the unsymmetric bifurandiones (**2**). We regard this result as strong evidence that these complexes (**4**) are, indeed, intermediates that provide one of the furanone rings but that the second such ring is produced by a series of further insertion reactions.

The structure of the bifurandiones (**4**) can only arise if such insertions involve successive incorporation of a carbon monoxide, an acetylene, and a second carbon monoxide molecule. No intermediates in this sequence could be isolated, however. It was known that acetylenes react with the lactone complexes without carbon monoxide but with incorporation of more than one and normally two acetylene units. Again, no product of a single insertion could be detected, so that there can be no direct correlation between this reaction and the bifurandione synthesis. Nevertheless, the nature of the bis-acetylene adduct appeared of interest. The initially amorphous complexes proved difficult to handle until one of our coworkers detected that they could be separated into two isomeric crystalline complexes by careful and repeated thin-layer chromatography. As a result, it has now been possible to demonstrate[22] the structure (**15**) crystallographically for one of the isomers obtained from the complex (**4**, R = Ph) on insertion of two molecules of propyne. Again, we recognize that insertion of two acetylenes into cobalt—carbon bonds has occurred, here less symmetrically than in the insertion into the acetylenedicobalt hexacarbonyls (**1**). The product further illustrates the complexity of structures that result from such reactions and also exemplifies a variety of bonding types, as it has cobalt atoms formally σ-bonded to carbon and π-bonded to a double bond and to an allyl system. The second isomer is still under investigation, but on



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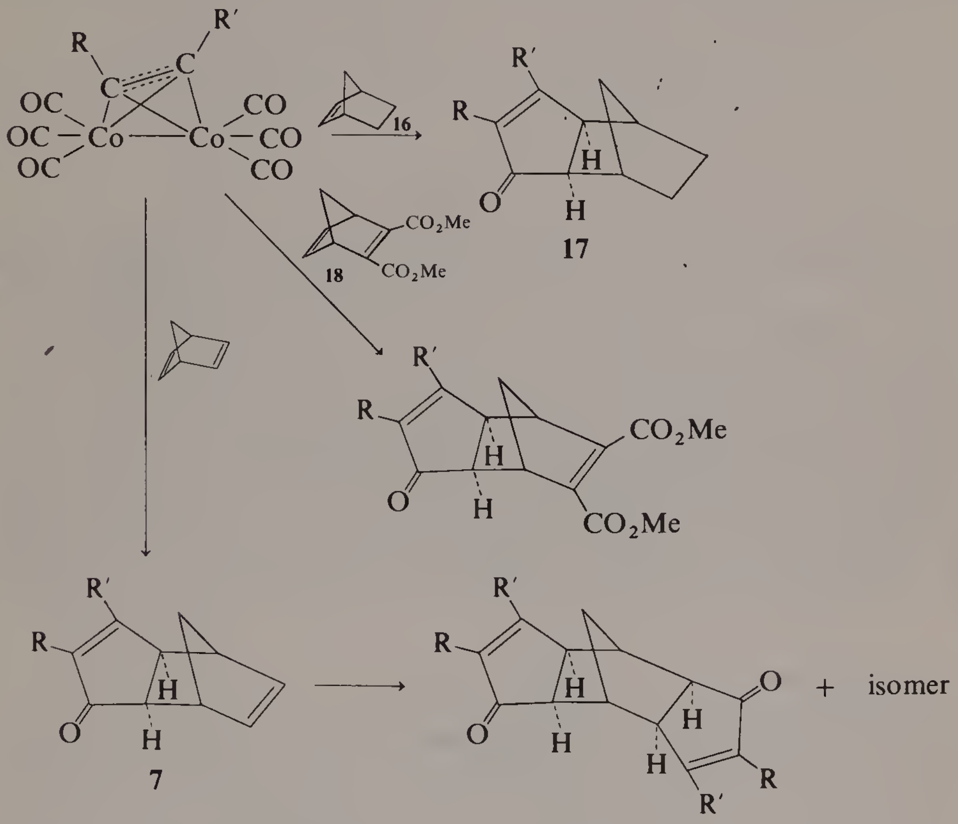
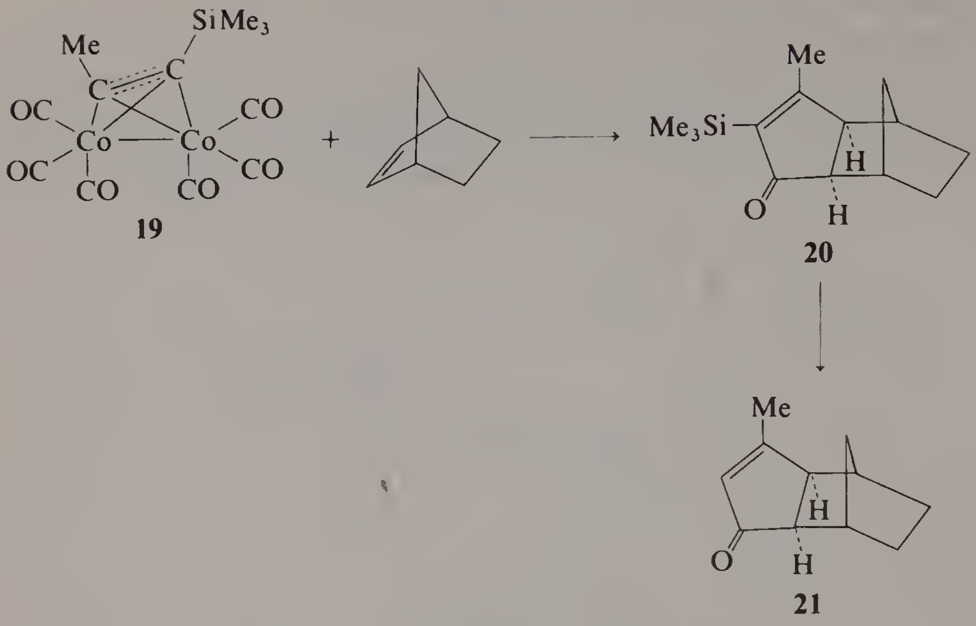
spectroscopic grounds, we favor a structure with the same carbon skeleton but a different metal—carbon bond distribution.

While these investigations were in progress, we continued studies on the reaction between the acetylene complexes (7) and norbornadiene, and the remainder of this survey will concentrate on the organic products of such reactions. We have mentioned the formation of the ketone (7). It was readily shown that norbornene (**16**) reacts similarly under equally mild conditions (~60 °C), as do such derivatives as dicyclopentadiene, the diester (**18**), and the ketone (7) itself.[23] Thus, only one double bond is required for the anneation to occur; apparently, however, activation of this bond by angle strain is important, because alkenes like cyclohexene failed to react with the acetylene complexes (**1**) at similar or slightly higher temperatures. With norbornene and norbornadiene, the reaction could be performed catalytically with the alkene, carbon monoxide, and the free acetylene with only a few mole percent of octacarbonyldicobalt. Insertion of these reactive alkenes into the initially formed acetylene complex (**1**) must therefore compete effectively with insertion of excess acetylene. Moreover, the reaction was found to be both stereospecific, giving only products with the "*exo*" ring fusion shown, and regiospecific or at least highly regioselective with respect to the 2- and 3-substituents derived from the acetylene.[23,24]

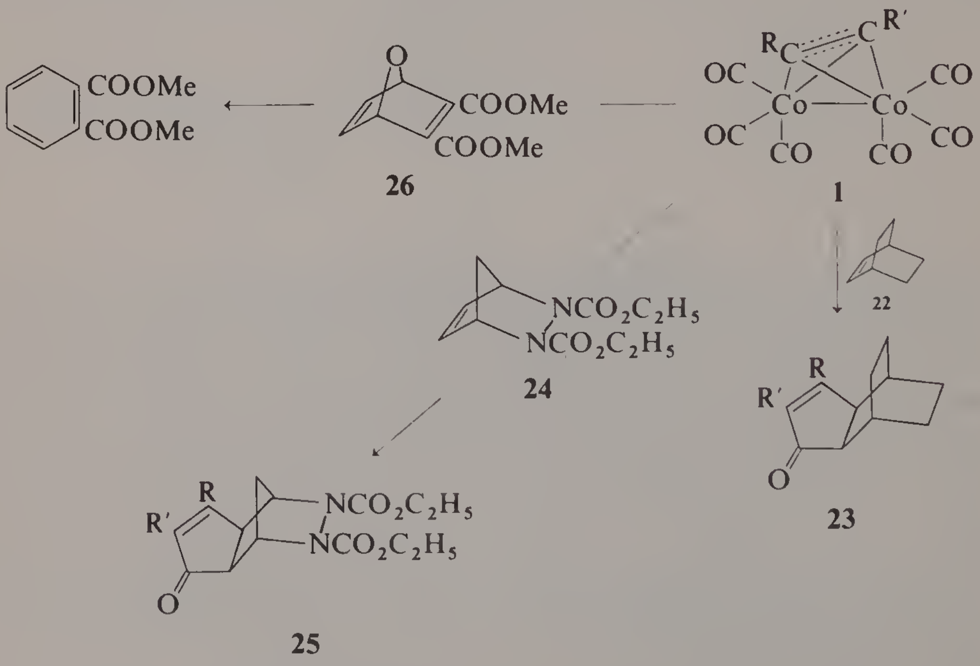


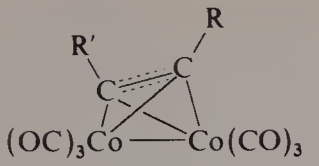
When complexes (**1**) of terminal alkynes were used, only ketones substituted in the 2-position were obtained; in rare cases[25] where a second isomer, probably the 3-substituted ketone, was isolated, it was only found in trace amounts. When two substituents were present, the larger one was always attached at position 2 and the smaller one at position 3. Thus, whereas the propyne complex (**1**, R = Me; R' = H)



reacted with norbornene to give the 2-methyl-substituted ketone (**17**, R = Me; R′ = H), we were able to employ a bulky protecting group, conveniently trimethylsilyl, to make the 3-substituted isomer (**21**) via intermediates (**19**) and (**20**).[24]

In addition to simple norbornene derivatives, the reaction succeeded with the less strained bicyclooctene (**22**) and also with the diaza analog (**24**), but the oxygen-bridged alkene (**26**) underwent deoxygenation and yielded dimethyl phthalate. To illustrate the applicability of the reaction to other types of strained alkenes, we chose two readily accessible cyclobutene derivatives (**27**) and (**28**), which were found to react with at least equal ease and regio- and stereospecificity.[26] The stereostructures shown for the product ketones (**29**) and (**30**), respectively, were deduced from their





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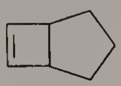

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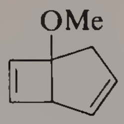

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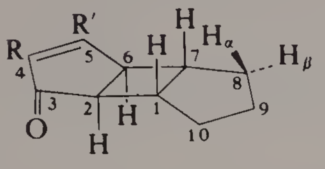

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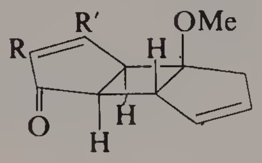

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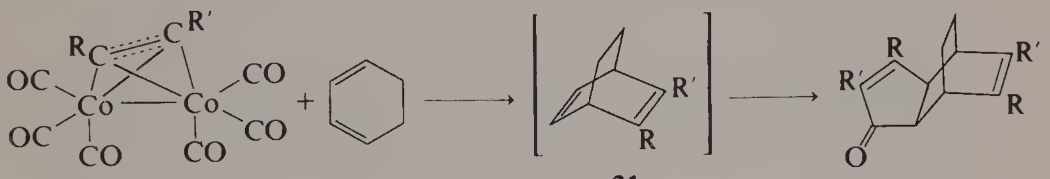
^{1}H nuclear magnetic resonance (nmr) spectra with the aid of "Eufod" shift reagent, which complexed with the carbonyl group of the former but with the methoxy group of the latter ketone.

In a search for other types of alkenes that might behave similarly, we found that cyclohexa-1,3-diene gave ketones whose spectral properties, indeed, resembled those of ketones obtained from the norbornene derivatives. But their compositions, as determined by analysis, nmr, and mass spectroscopy showed incorporation of



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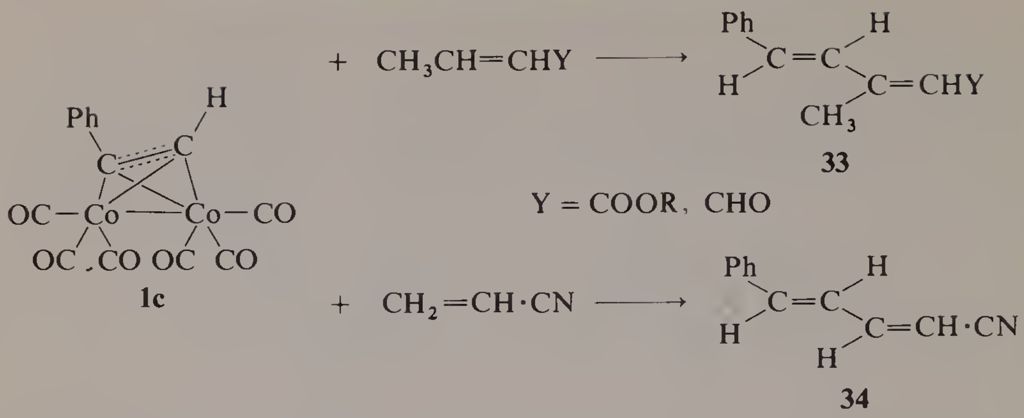
two acetylene units from each of the complexes (**1**) used. The most probable structure that we could postulate was therefore one that would result from initial Diels-Alder addition, generating a bicyclooctadiene (**31**) as the intermediate, which then reacted further, according to the now familiar scheme, to give the ketone (**32**). The unsubstituted compound (R = R′ = H) was readily hydrogenated to a tetrahydro derivative, identical with the dihydro derivative of the previously mentioned product (**23**), thus proving its structure.

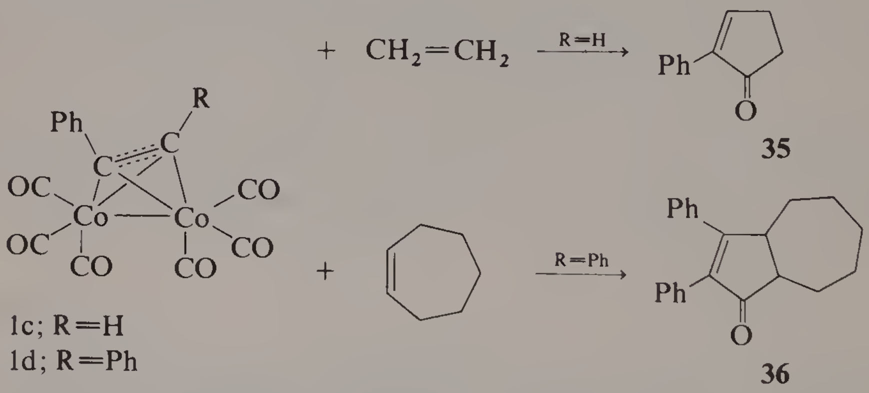
Because the initial Diels-Alder addition step does not occur readily between the two free hydrocarbons, it is clear that the cobalt complex catalyzes certain Diels-Alder reactions as well as the retro reactions. It also catalyzes isomerization of 1,4- to 1,3-dienes, so that cyclohexa-1,4-diene and the unconjugated isomer give the same products.

A new variation of the reaction was encountered when we examined alkenes that bear strong electron-withdrawing groups (CN, CO_2Et). These alkenes reacted, for example, with the phenylacetylene complex (**1c**), to give conjugated dienes rather than ketones.[27] Thus, ethyl crotonate yielded the ester (**33**, Y = CO_2Et), and acrylonitrile gave the cyanide (**34**), both as mixtures of *trans,trans* and *2-cis,4-trans* isomers.

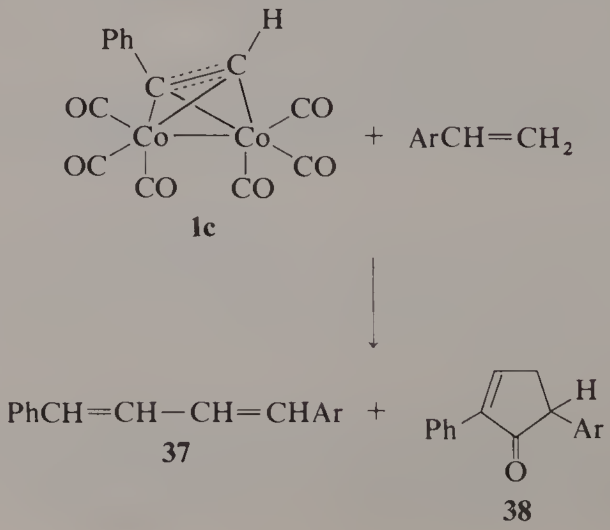
Only after obtaining these results were we encouraged to reexamine the behavior of simple alkenes under rather more severe conditions. Indeed, on increasing the temperature to approximately 120 °C, we found that simple alkenes, including cycloalkenes, react fairly smoothly to give cyclopentenones.[25] Very volatile or



gaseous alkenes are used in an autoclave; others are employed conveniently in refluxing toluene. Thus, ethylene with the complex (**1c**) yields 2-phenylcyclopent-2-enone (**35**), and even the relatively unreactive tolan complex (**1d**) reacts with cycloheptene to give the octahydroazulenone (**36**) in better yield than obtained with previous multistage methods.

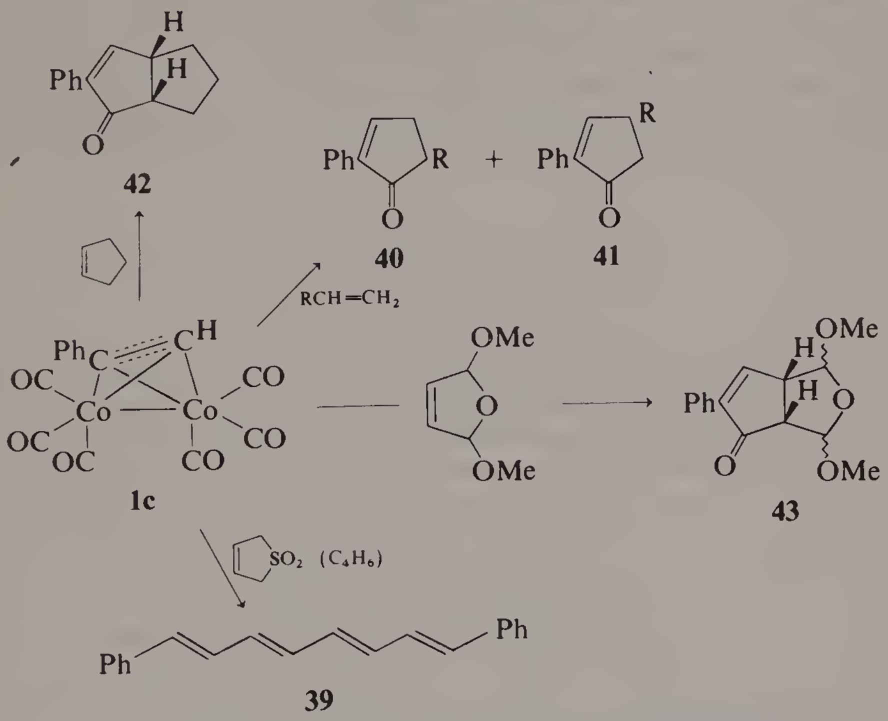


When styrene or substituted styrenes were used as the alkene, both the diarylbutadienes (**37**) and the 2,5-diarylcyclopentenones (**38**) were produced.[25] Thus, substitution of alkenes with weak electron-withdrawing aromatic groups leads to



behavior intermediate between that of simple alkenes and that of alkene derivatives with stronger electron-withdrawing groups. We would like to postulate that these two reaction pathways involve a common intermediate, formed by first coordinating the alkene to one of the cobalt atoms and then linking the alkene and alkyne fragments while still bonded to the metal. Thereafter, hydrogen transfer leads to the diene or insertion of one of the carbonyl groups yields the ketone.

We are still studying the effect of styrene substituents and reaction conditions on the relative importance of the two pathways. The results available do not reveal any simple pattern. Indeed, we find that vinylferrocene yields the diene (**37**, Ar = ferrocenyl) and only traces of ketone, although the ferrocenyl group generally behaves as a much better electron donor than does the phenyl group. We also find that butadiene behaves similarly, and unlike cyclohexadiene. Both ends of the molecule react to give, with complex (**1c**), the diphenyloctatetraene (**39**). The reaction is rather inefficient with the free diene, apparently because of its polymerization; it proceeds much more smoothly when 3-sulfolene ("butadiene sulfone") is used, from which the diene is released gradually at the reaction temperature employed.



Whereas the butadiene and styrene reactions are highly regioselective with respect to the alkene and alkyne components, reactions with other alkenes are found to be unselective. Thus, propene and 1-octene give approximately equimolar mixtures of the 4- and 5-alkylcyclopentenones (**40**) and (**41**). Also, alkenes with bulky substituents are rather unreactive. This relative lack of reactivity may explain why we have been able to employ complexes (**1**) in which the acetylene moiety bears olefinic groups conjugated with or one carbon removed from the triple bond without competition between these groups and the added alkene.

The most useful examples, however, would appear to be the reactions with symmetric alkenes. Among the cycloalkenes used, cyclohexene proved to be the least reactive, whereas cyclopentene, for example, reacts as smoothly as the previously mentioned cycloheptene and yields the hexahydropentalenones (**42**). Finally, the reaction with 2,5-dimethoxy-2,5-dihydrofuran illustrates the potential for introducing functional groups. The product (**43**) is a mixture from which we have isolated three stereoisomers, but because these stereoisomers are all acetals of the same dialdehyde, this complexity does not significantly reduce the utility of the product for further synthetic use. Our exploration of these methods is continuing, particularly regarding their use in natural product syntheses.

EXPERIMENTAL METHODS

The majority of the reactions mentioned in this paper have been reported in the publications cited. Those with cyclic conjugated dienes and with styrene derivatives will be the subject of separate reports. The following sections will therefore give details on reactions with four heterocyclic alkenes.

The general conditions were the same as in previous work.[24–27] All reactions were conducted under nitrogen. Light petroleum refers to the fraction with a boiling point of 40–60 °C.

*Reaction of the Diazanorbornene (**24**) with Propynehexacarbonyldicobalt (**1b**)*

The mixture of the diester (**24**, 1 g, 4 mmol) and the complex (**1b**, 2 g, 6 mmol) in toluene (150 ml) was warmed to 80–90 °C with stirring for 6 hr. The solvent was then removed under reduced pressure, the residue was extracted with light petroleum and then with benzene, and the combined extracts were chromatographed on neutralized alumina. Light petroleum eluted the unchanged propyne complex (**1b**, 80 mg), which was followed by an additional metalcarbonyl-containing fraction (45 mg). Benzene then eluted toluenenonacarbonyltetracobalt (60 mg). Finally, chloroform eluted the ketone (**25**, R = H; R′ = CH_3) as a colorless oil (0.25 g, 20%); its structure follows from its ^1H nmr spectrum, which shows signals (in $CDCl_3$) at τ2.82 (1H, m, H-3), 5.45 (2H, br.d., H-4 and H-7), 5.85 (4H, q, OCH_2), 6.86 (1H, m, H-7a), 7.24 (1H, br.d, H-3a), 8.22 (3H, t, CH_3 at C-2), 8.55 (2H, br.s, CH_2), and 8.71 (6H, t, CH_3CH_2).
(Found: M,308.1356. $C_{15}H_{20}N_2O_5$ requires M,308.1372.)

*Reaction of Diazanorbornene (**24**) with Phenylacetylenehexacarbonyldicobalt (**1c**)*

The diester (**24**, 2.5 g, 10 mmol) and the complex (**1c**, 5 g, 13 mmol) were heated in benzene (150 ml) at 60–70 °C for 10 hr. Workup, as in the preceding experiment, gave the ketone (**25**, R = H; R′ = C_6H_5) as a colorless crystalline solid (1.37 g, 36%), melting point of 92–93 °C (from light petroleum-benzene), signals (in $CDCl_3$) at τ 2.35 (3H, m) and 2.67 (3H, m, H-3 and C_6H_5), 5.32 (2H, br.d., H-4 and H-7), 5.76 (4H, q, OCH_2), 6.70 (1H, m, H-7a), 7.02 (1H, br.d., H-3a), 8.43 (2H, br.s., CH_2), and 8.69 (6H, t, CH_3CH_2). (Found: C, 64.7; H, 6.35; N, 7.1%; M,370.1526. $C_{20}H_{22}N_2O_5$ requires C,64.8; H,6.0; N,7.6%; M,370.1529.)

Reaction of the Oxanorbornadiene (**26**) *with the Complex* (**1c**)

The diester (**26**, 0.5 g, 2 mmol) and the complex (**1c**, 2 g, 5 mmol) were heated in toluene (150 ml) at 70–80 °C for 6 hr. Workup, as in the previous experiments, gave (on elution of the chromatogram with chloroform) dimethyl phthalate (0.15 g), boiling point of 90–100 °C/0.5 mm identified by its ^{1}H nmr spectrum and by infrared spectral comparison with an authentic sample. No ketonic product could be detected.

Formation of All-trans-*1,8-diphenyl-1,3,5,7-octatetraene* (**39**)

3-Sulfolene (1.8 g, 15 mmol) and the complex (**1c**, 4.0 g, 10 mmol) were refluxed in toluene (150 ml) for 6 hr (bath temperature of 130–140 °C). The initially red color changed to yellowish brown. After removal of toluene under reduced pressure, the residue was extracted with light petroleum and then with benzene, and the combined extracts were chromatographed on neutralized alumina. Light petroleum eluted the unreacted complex (**1c**, 90 mg), and benzene-chloroform eluted the hydrocarbon (**39**, 0.5 g, 19%) whose spectral (infrared and nmr) and other properties [bright yellow crystals, melting point of 234–236 °C (lit: 235–237 °C); Found: C,92.8; H,6.9%. M,258.1402. Calc. for $C_{20}H_{18}$: C,93.0; H,7.0%. M,258.1408] agreed with the structure (**39**).

The same product was isolated in very low yield (accompanied by much polymer) when the reaction was conducted in an autoclave with butadiene (in excess) instead of 3-sulfolene. 1,2,7,8-*Tetraphenyl*-1,3,5,7-*octatetraene* (0.42 g, 12%) was obtained similarly from 3-sulfolene (1.6 g, 14 mmol) and the tolan complex (**1**, R = R′ = Ph; 4.0 g, 9 mmol). It formed a yellow, microcrystalline powder with a melting point of 263–265 °C (from benzene). (Found: C,93.6; H,6.1. $C_{32}H_{26}$ requires C,93.7; H,6.3%.)

Preparation of the Keto-acetal (*43*)

2,5-Dimethoxy-2,5-dihydrofuran (2.6 g, 20 mmol) and the complex (**1c**, 4.0 g, 10 mmol) were refluxed in toluene for 6 hr (bath temperature of 140–150 °C); the initial red color changed to brownish black during this period. Removal of toluene under reduced pressure was followed by extraction of the residue with light petroleum and then with benzene and chromatography of the combined extracts on neutralized alumina. Unreacted complex (**1c**, 200 mg) was eluted with light petroleum, and another metalcarbonyl-containing fraction (100 mg) was eluded with benzene. A mixture of benzene and chloroform (1 : 8) then eluted a light brown oil (750 mg, 30%) that distilled at 160–170 °C (bath temperature)/0.1 mm. (Found: C,69.2; H,6.5. $C_{15}H_{16}O_4$ requires C,69.2; H,6.2%.) When light petroleum was added to a benzene solution of this oil, an off-white, nonketonic (infrared) solid (~100 mg) deposited first. On refrigeration, the mother liquors slowly deposited one isomer (**A**) of the acetal (**43**) as colorless crystals with a melting point of 98–99 °C (90 mg, 4%). (Found: C,69.1; H,6.1%.) Concentration and further slow crystallization then successively gave a second isomer (**B**, 70 mg, 3%) with a melting point of 59–60 °C and finally a third isomer (**C**, 50 mg, 2%) with a melting point of 80 °C. (Found: C,69.5; H,6.1%.) These isomers melted sharply and were clearly distinguishable by their infrared spectra. Because the dihydrofuran used is a mixture of readily interconvertible *cis* and *trans* isomers (cf., for example, Reference 28), four isomers, all of which have *cis*-fused rings (but which differed in orientation of the OCH_3 groups), are possible. Their structures are further supported by their nmr spectra, which, however, do not readily permit specific stereochemical assignments to individual isomers.

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ORGANIC SYNTHESIS WITH POLYMER-ATTACHED HOMOGENEOUS CATALYSTS*

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INTRODUCTION

Transition metals and their compounds have played an enormous role in organic synthesis for 100 years. Heterogeneous metal and metal oxide catalysts[1] and reagents, such as CrO_3 and $KMnO_4$, are widely applied. More recently, homogeneous transition metal complexes have been found to catalyze a wide range of organic reactions,[2] including oxidations,[3] hydrogenations,[4] oligomerizations,[5] carbonylations,[6] and decarbonylations.[7] Because these homogeneous complexes are frequently expensive and often difficult to separate from the products, many recent studies have been directed at heterogenizing them such that they may be readily separated from products or used as fixed-bed catalysts. One promising route to heterogenize transition metal complexes is to anchor them to organic resins.[8,9] In this way, the catalyst might still operate mechanistically as if it were still in a homogeneous solution. Therefore, the ability to tailor selectivity by changing ligands and to operate at mild conditions (advantages of homogeneous complexes) would be maintained.

Several advantages, other than the ease of catalyst recovery, have already been reported for polymer-bound catalysts over their soluble analogs. For example, the catalyst hydrogenation activity for polymer-bound titanocene was found by Grubbs *et al.*[10] to be enhanced because of immobilization by the polymer of the active bound titanocene molecules. Thus, titanocene dimerization, which destroys the active catalytic species in solutions, was retarded on the polymer. Pittman *et al.*[11] observed that the hydrogenation activity of polymer-anchored $Ir(CO)Cl(PPh_3)_2$ was greater than that of its homogeneous analog at low P/Ir ratios. The positional selectivity in olefinic hydrogenation was greater for polymer-anchored $RhCl(PPh_3)_3$ than for its homogeneous application.[12] Likewise, this anchored catalyst promoted more rapid hydrogenation of small olefins than of large ones.[13] Similarly, initial studies of enhanced normal/branched ratios in the hydroformylation of terminal olefins, catalyzed by polymer-anchored $RhH(CO)(PPh_3)_3$, have appeared.[14] The use of a nickel catalyst, produced by reduction of polystyrene-anchored $NiCl_2(PPh_3)_2$ with $NaBH_4$, resulted in the highly selective dimerization of butadiene to (E,E)-1,3,6-octatriene.[15] The corresponding homogeneous catalyst was far less selective. Polymer-attached $RhCl(CO)(PPh_3)_2$ has now been used as a regeneratable reagent in ketone syntheses.[16] Finally, multistep sequential reactions have been performed with two different polymer-anchored catalysts in the same reaction vessel.[17,18]

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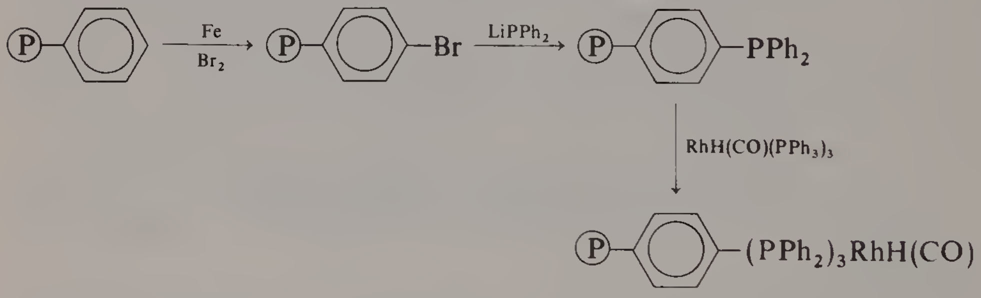
RESULTS AND DISCUSSION

Metal-Ligand Equilibrium. Effect of Polymeric Ligand

The equilibrium between dissolved ligand and metal complex is a key feature in determining the selectivity of many homogeneously catalyzed processes. We postulated that the position of such equilibria could be drastically altered by attaching the ligand and the metal complex to a polymer matrix.[14] For example, if a phosphine was attached along a polymer backbone, its ability to undergo reversible addition to a metal complex would depend on the swellability of the polymer, the density of phosphine sites present, the cross-link density of the polymer, the chain mobility of the polymer, and the P/metal ratio present.

Consider the following example. A polystyrene-1% divinylbenzene resin (200–400 mesh bead size) was functionalized with diphenylphosphine groups according to the route shown below. This route randomly distributes phosphine sites throughout the volume of the swollen resin beads. The complex $RhH(CO)(PPh_3)_3$ was then anchored by thermal phosphine exchange, and the PPh_3, which was displaced by the polymeric Ⓟ$-C_6H_4-PPh_2$ groups, was removed by continuous extraction:

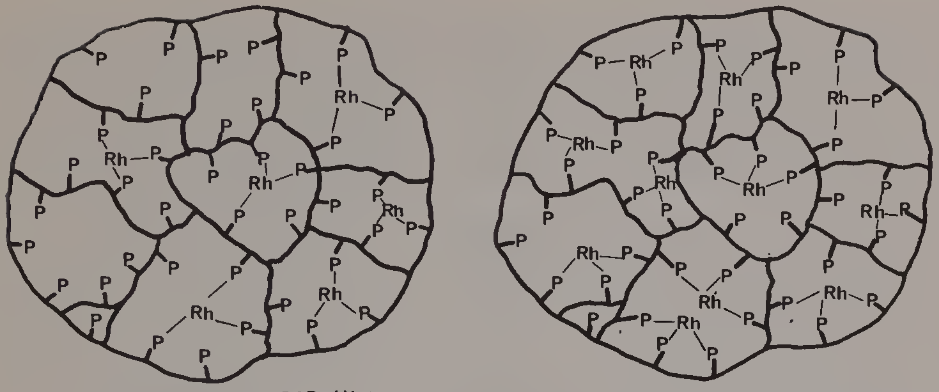


(1)

1

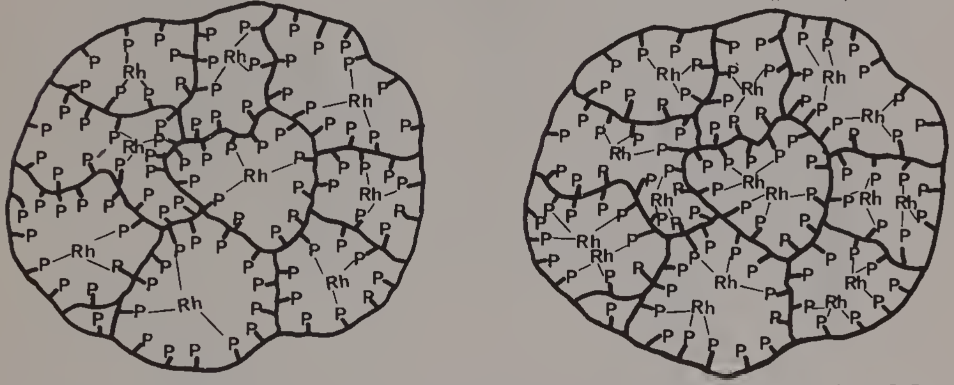
The polymer may be phosphinated to any given average loading level. The phosphine loading is most conveniently expressed in terms of the percentage of the polymer's phenyl rings that are phosphinated (a term preferable to milliequivalents per gram or simple percent phosphorus because it provides a much clearer picture of the concept of phosphine loading and separation in the resin). At either high or low phosphine loadings, the amount of catalyst introduced is controlled simply by regulating the reaction stoichiometry. Thus, the P/Rh ratio is easily tailored for the example shown in reaction 1.

A variety of resin systems with various phosphine loadings and P/Rh ratios have been made in order to study the possible effects of the resin in hydroformylation of terminal olefins. Four cases are protrayed in FIGURE 1. Both cases **A** and **B** have low phosphine loadings; however, case **A** has a high P/Rh ratio, whereas case **B** has a low P/Rh ratio. In case **A**, more ligand is available to compete for coordinatively unsaturated rhodium in the equilibrium, $P + RhH(CO)P_x \rightleftharpoons RhH(CO)P_{x+1}$, but the position of the equilibrium will tend to be shifted to the left if both phosphine loading and the polymer's chain mobility are low. In other words, many of the phosphine sites simply cannot encounter given rhodium sites due to restrictions imposed by the polymer's structure. In cases **C** and **D**, the phosphine loading is high; case **C** has a high P/Rh ratio, while case **D** has a low loading. In both cases **C** and **D**, the equilibria will be shifted more to the right than in cases **A** and **B**, because the local phosphine concentration near a given rhodium atom is high. In fact, proximity effects and entropy factors could cause large changes in the position of the equilibria



Case A: Low % PSR, High P:Rh

Case B: Low % PSR, Low P:Rh



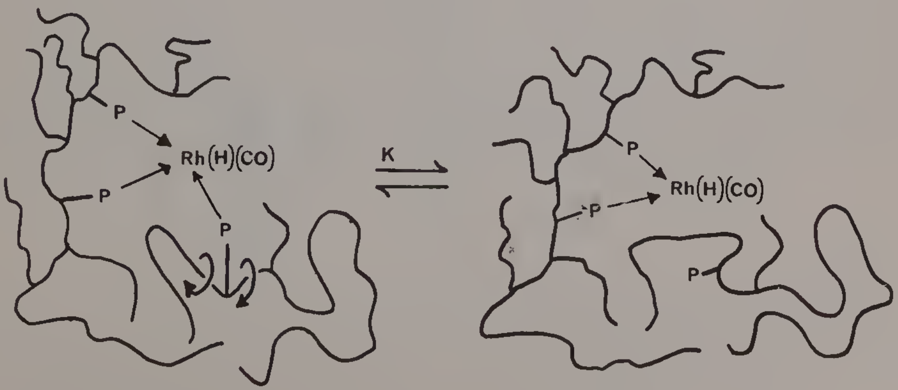
Case C: High % PSR, High P:Rh

Case D: High % PSR, Low P:Rh

FIGURE 1. Phosphine accessibility in swellable resins. Examples of low and high phosphine loadings at both low and high P/Rh ratios.

(relative to the same equilibria at similar concentrations in homogeneous solutions).

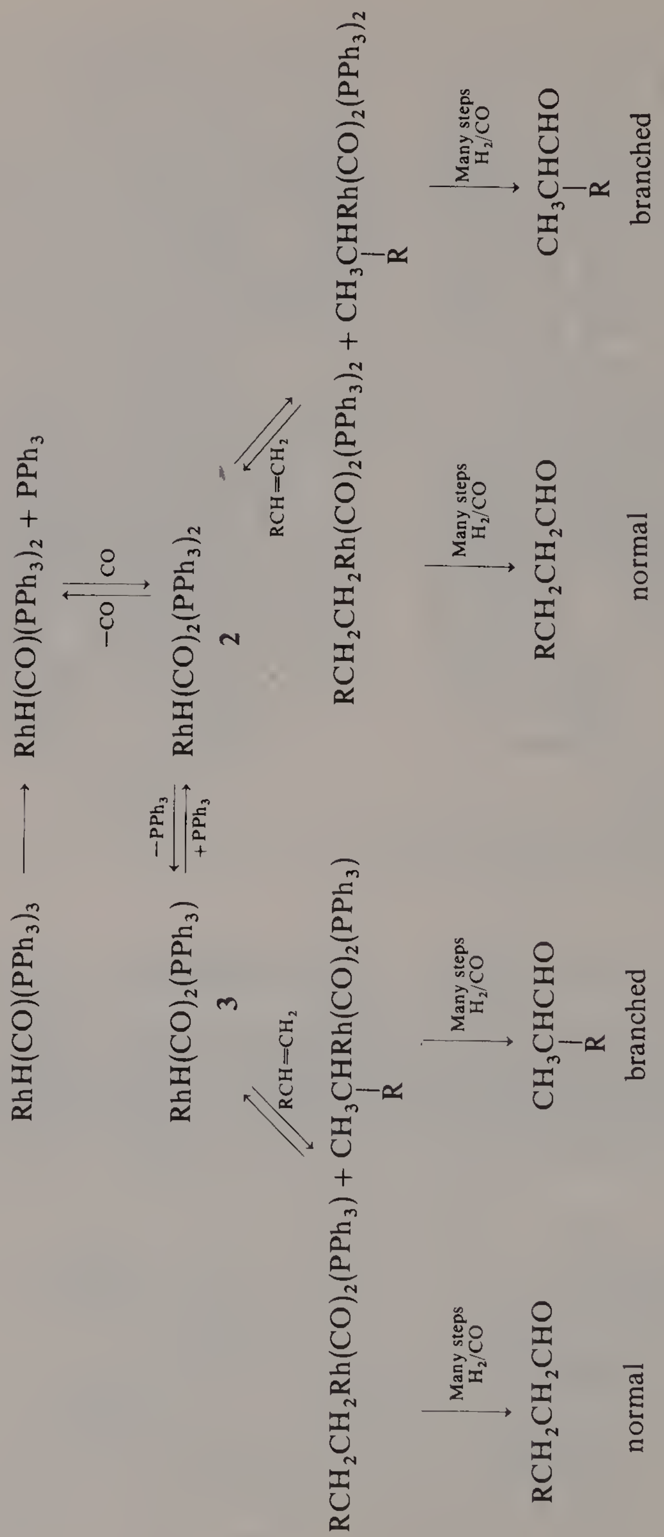
In a resin with a low phosphine loading, dissociation of a phosphorus-rhodium bond may permit a series of very favorable chain rotations that would make it difficult to reestablish the particular P—Rh bond. This problem is illustrated in FIGURE 2. The dissociation of the P—Rh bond shown is entropically favored



UNFAVORABLE CONFORMATION

PREFERRED CONFORMATION

FIGURE 2. Entropy-favored dissociation equilibrium within resin.


RhH(CO)(PPh3)3
RhH(CO)(PPh3)2 + PPh3
−CO
CO
RhH(CO)2(PPh3)2
2
−PPh3
+PPh3
RhH(CO)2(PPh3)
3
RCH=CH2
RCH2CH2Rh(CO)2(PPh3) + CH3CHRh(CO)2(PPh3)
R
RCH2CH2Rh(CO)2(PPh3)2 + CH3CHRh(CO)2(PPh3)2
R
Many steps
H2/CO
RCH2CH2CHO
normal
CH3CHCHO
R
branched

SCHEME 1

because the swollen polymeric geometry required in the presence of that bond is entropically unfavorable. Many such "unfavorable" P—Rh bonds could exist during the long reaction periods when the catalyst is formed, where free PPh_3 groups are being continually removed, leaving only the polymer-attached $—PPh_2$ groups to coordinate with the metal. Under hydroformylation conditions, hydrogen, olefin, and carbon monoxide are all present, and they may compete with phosphine for metal coordination sites.

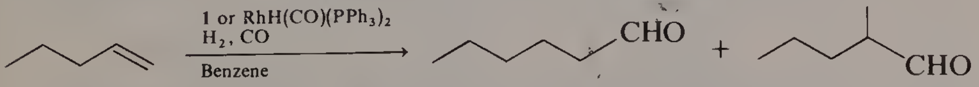
A decision was made to study the hydroformylation of terminal olefins with anchored $RhH(CO)(PPh_3)_3$ because the selectivity of this reaction in homogeneous solutions is particularly sensitive to the concentration of phosphine and to the P/Rh ratio.[19] At high phosphine concentrations and P/Rh ratios, normal/branched selectivity is high. The selectivity decreases at low phosphine concentrations and P/Rh ratios. Wilkinson *et al.*'s classic studies of the mechanism of this reaction (SCHEME 1) provide the currently accepted explanation for this selectivity dependence.[19–21] On dissolution, $RhH(CO)(PPh_3)_3$ dissociates 1 mol of PPh_3 and then adds 1 mol of carbon monoxide to give the biscarbonyl bisphosphine species **2**. Species **2** is in equilibrium with the biscarbonyl monophosphine species **3**. Either **2** or **3** may coordinate olefin, followed by rhodium hydride addition to the double bond. This step determines product selectivity. Thus, the observed selectivity is a function of the individual selectivities of **2** and **3**, the position of equilibrium between **2** and **3**, and the rate constants for rhodium hydride addition by **2** and **3**.

Species **2** is more selective toward terminal addition of rhodium because of the greater importance of steric hinderance, due to the presence of two bulky triphenylphosphine groups. Species **2** is also more terminally selective based on electronic considerations. Thus, any factor that shifts the equilibrium between **2** and **3** toward **2** will increase the normal/branched (n/b) selectivity. This explains why phosphine concentrations and high P/Rh ratios lead to greater n/b selectivity.

We reasoned that the selectivity should be high when a polymer-anchored catalyst was employed that had a high phosphine loading and a high P/Rh ratio (case **C**). In fact, for a series of polymeric catalysts, such as those illustrated in FIGURE 1, the n/b product ratio should follow the order **C** > **D** > **A** > **B**. To test this concept, a series of polymers with various phosphine loadings and P/Rh ratios were prepared, and hydroformylations of 1-pentene were performed.

Hydroformylation Catalyzed by Polymer-Anchored $RhH(CO)(PPh_3)_3$

The hydroformylation of 1-pentene with the anchored catalyst **1** was compared to analogous reactions with the homogeneous catalyst (reaction 2). Conditions for this comparison were as close to identical as could be readily achieved. In this way, a search could be made to see if the polymer exhibited any "special" effects on the catalytic process, such as those that might arise from drastic shifts in the equilibria portrayed in SCHEME 1. Furthermore, reactions were performed over a pressure range of 100–800 psi and a temperature range of 60–140 °C:



(2)

The resins prepared are listed in TABLE 1, which summarizes their phosphine loadings and P/Rh ratios. The selectivity of several of these resins was studied as a function of temperature and pressure. The results, shown in FIGURE 3, demonstrate that hydroformylation is more selective when the resin has higher phosphine

TABLE 1

SUMMARY OF RESIN-ANCHORED $RhH(CO)(PPh_3)_3$ CATALYSTS PREPARED

Resin	% P	% Rh	% Phosphine Loading*	P : Rh
A	6.2	1.1	40	19
B	6.0	1.6	40	12
C	3.3	0.5	20	23
D	6.0	1.3	32	16
E	2.1	2.0	8.5	3.6
F	1.3	1.9	2.3	6.2
G	3.6	1.9	13	6.3
H	8.1	4.1	52	5.9

* The percentage of the resin's phenyl rings that are derivatized with PPh_2 groups.

loadings. At low phosphine loadings and low P/Rh ratios, the reaction is less selective. This result was found for all pressures studied and is illustrated for pressures of 100 and 400 psig in FIGURE 3.

These results may be interpreted in terms of Wilkinson *et al.*'s[19–21] mechanism (SCHEME 1). At high phosphine loadings, the equilibrium between polymer-anchored **2** and polymer-anchored **3** is shifted toward **2**. Thus, the more selective associative mechanism is increasingly favored at the expense of the dissociative pathway. This phenomenon is readily seen by comparing the selectivity of resin A [phosphine loading (PL) = 40%, P/Rh = 19] with that of resin E (PL = 8.6, P/Rh = 3.6) in FIGURE 3.

When polymer-anchored catalysts were directly compared to their homogeneous analogs under the same conditions, the anchored catalysts were *significantly more selective* as long as the resin had a *high* phosphorus loading. For example, in

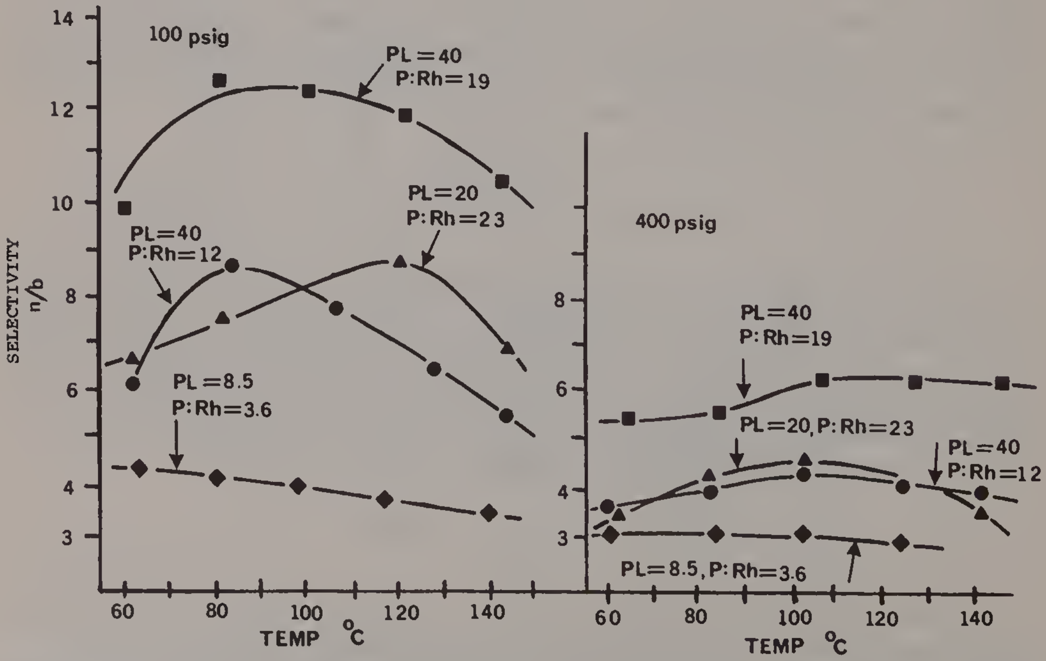


FIGURE 3. Selectivity of polymer-anchored resins as a function of phosphine loading and P/Rh.

FIGURES 4 and 5, the reactions catalyzed by the anchored catalysts are more selective at all pressures and all temperatures. In each of these cases, the phosphine loading of the resin was greater than 20%. On the other hand, when the phosphine loading was *very low* (for example, resin **E**, PL = 8.6), the selectivity of the anchored catalyst was *somewhat lower* than that of the homogeneous catalyst. This difference is illustrated in FIGURE 6. In this situation (i.e., an example of case **B** in FIGURE 1), where P/Rh is also low, the phosphine sites are more isolated within the resin, and a given rhodium atom will see a small local phosphine concentration. Thus, the equilibrium between anchored **2** and **3** (SCHEME 1) will favor **3**. Thus, the dissociative process is favored relative to the associative process. In the analogous homogeneous process, however, every phosphine is free to contribute to the equilibrium.

Many anchored-catalysts exhibited *unusual dependencies* of selectivity on temperature. In sharp contrast to homogeneous systems, the selectivity increases with temperature and then decreases with further temperature elevation with resins **A–C** (see FIGURES 4 & 5). The shape of the selectivity-temperature plots depended on the resin's phosphine loading, P/Rh ratio, and cross-link density and on pressure.

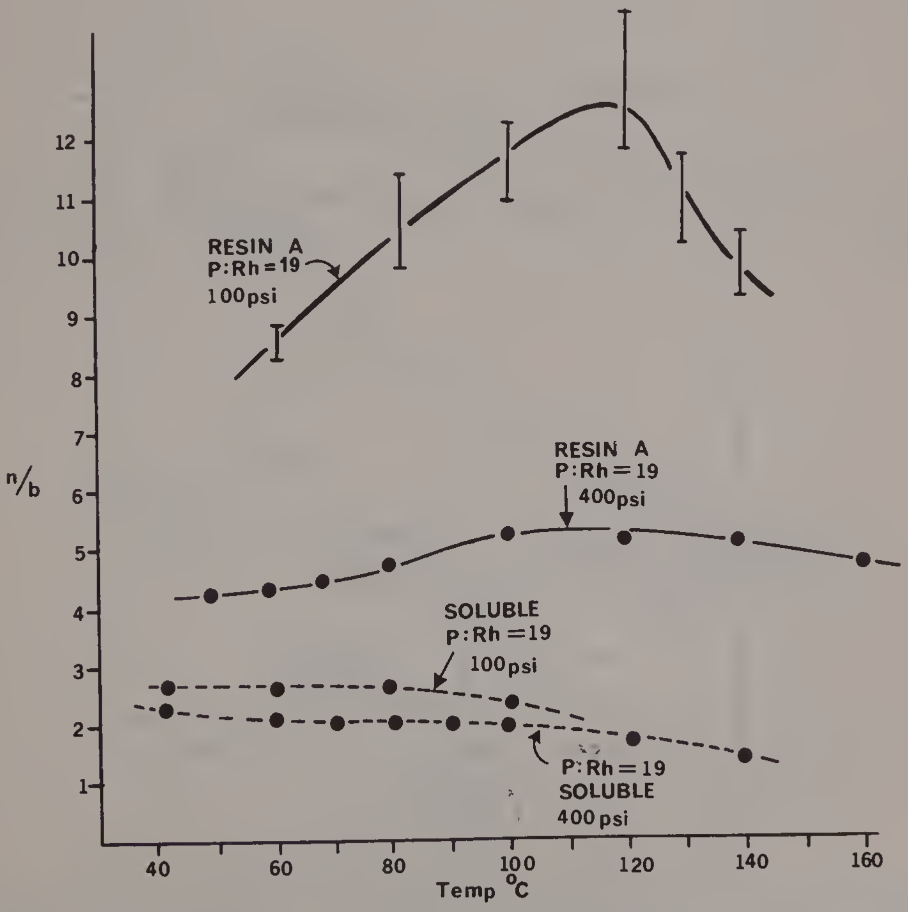


FIGURE 4. Greater selectivity of polymer-anchored $RhH(CO)(PPh_3)_3$ in 1-pentene hydroformylations. $[Rh] = 4.6 \times 10^{-3}$ M.

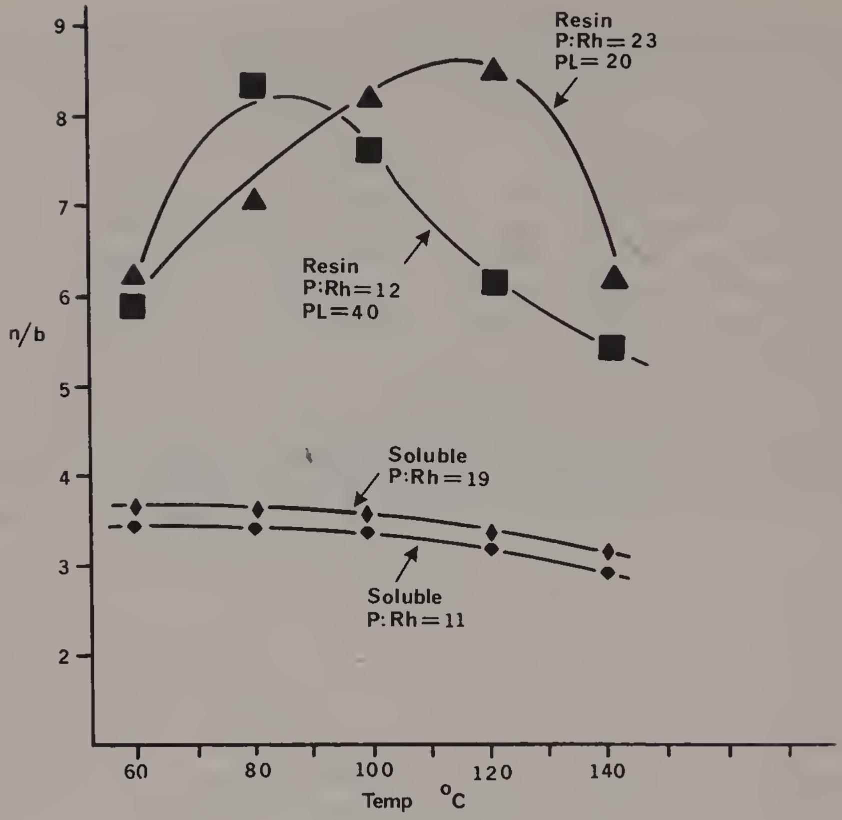


FIGURE 5. Greater selectivity of polymer-anchored $RhH(CO)(PPh_3)_3$ in 1-pentene hydroformylations at 100 psig, 1 : 1(H_2/CO). 1-Pentene/Rh = 400. Solvent = Benzene. [Rh] = 4.58 mM.

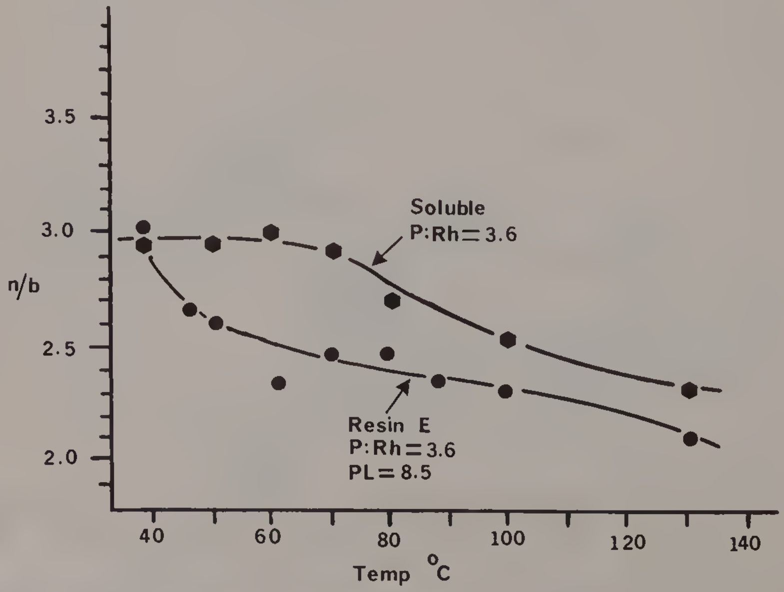


FIGURE 6. Lower hydroformylation selectivity of polymer-anchored $RhH(CO)(PPh_3)_3$ at low phosphine loadings at 800 psig, 1 : 1 (H_2/CO). 1-Pentene/Rh = 100. [Rh] = 0.187 mM.

Pressure Dependence of Selectivity

A *remarkable difference* in the pressure dependence of the selectivity was observed on comparing anchored versus homogeneous systems (see FIGURE 7). In the homogeneous case, at P/Rh = 19, selectivity increased from 2.8 to 3.3 as the pressure was reduced from 800 to 100 psi (1 : 1, CO/H_2) at 100 °C. Under the same conditions with resin A, the increase in selectivity was far more pronounced, from 4.3 to 12.1 over the same pressure range. This phenomenon appears to be a general one in resins with low or high phosphine loadings. For example, resin A exhibits a similar sharp pressure dependence at 140 °C, as does resin E, which has a low loading (8.6%) and low P/Rh (3.6%) (FIGURE 7).

Possible explanations for the strong pressure dependence of the selectivity involve the equilibria postulated in reactions 3 and 4. At high carbon monoxide partial pressures, the equilibrium of reaction 3 would be displaced toward the right. The tricarbonyl species, **4**, would be less selective, if it does participate in the rhodium hydride addition step (for which there is no direct evidence). From reaction 4, it is

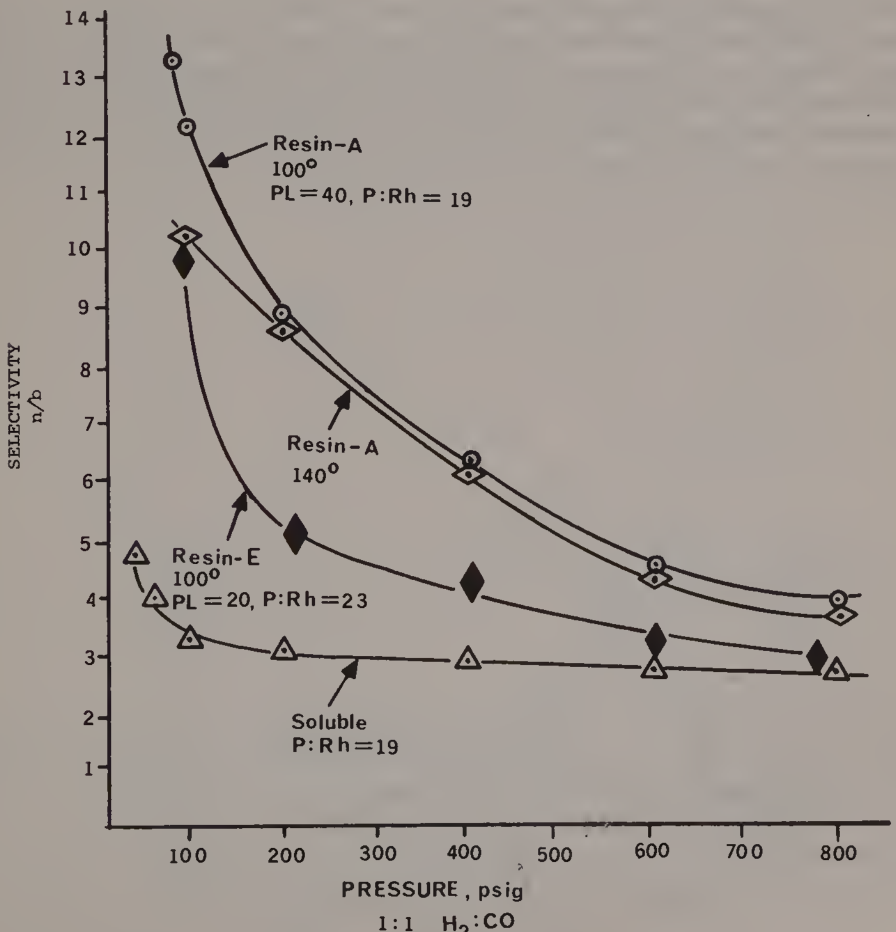


FIGURE 7. Pressure dependence of selectivity. Comparison of 1-pentene hydroformylation catalyzed by resin-anchored versus homogeneous $RhH(CO)(PPh_3)_3$. In all cases, 1-pentene/Rh = 400. [Rh] = 4.58×10^{-3} M for resins A and E and 4.45×10^{-3} M for the soluble case.

$$\underset{\mathbf{2}}{(PPh_3)_2RhH(CO)_2} \xrightleftharpoons[\substack{+PPh_3\\-CO}]{\substack{-PPh_3\\+CO}} \underset{\mathbf{4}}{(PPh_3)RhH(CO)_3} \tag{3}$$

$$\underset{\mathbf{2}}{(PPh_3)_2RhH(CO)_2} \xrightleftharpoons[+CO]{-CO} \underset{\mathbf{5}}{(PPh_3)_2RhH(CO)} \xrightleftharpoons[-PPh_3]{+PPh_3} \underset{\mathbf{6}}{(PPh_3)_3RhH(CO)} \tag{4}$$

apparent that low carbon monoxide partial pressures would shift the equilibrium away from the dicarbonyl species, **2**, to monocarbonyl species, **5** and **6**. If $(PPh_3)_2RhH(CO)$ could undergo rhodium hydride addition to olefins, it might be more selective than $(PPh_3)_2RhH(CO)_2$. Wilkinson *et al.*, however, claimed that when both $(PPh_3)_2RhH(CO)$ and $(PPh_3)_2RhH(CO)_2$ are present in solution, only the dicarbonyl adds to ethylene. Because the dicarbonyl is readily formed, even at 1 atm of carbon monoxide, it should be predominant at the pressures used in our studies (FIGURE 7).

In view of all of the trends observed, it is now possible to tailor a process, with anchored catalysts, to give very high selectivities. By using high phosphine loadings and P/Rh ratios, low or moderate total pressures, and low partial pressures of carbon dioxide, an n/b selectivity of 64 was readily obtained. This result is illustrated in FIGURE 8, where the H_2 : CO ratio was increased at 100 °C, holding the total pressure constant at 200 psig. Interestingly, the reaction rate of this system increases as the selectivity rises.

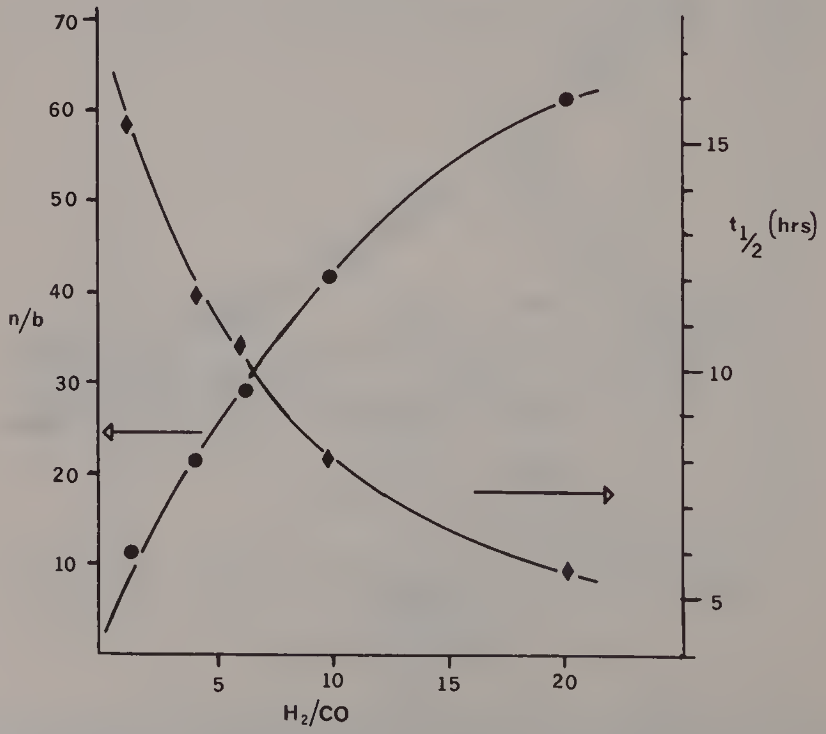
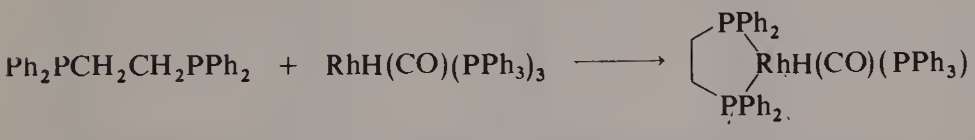


FIGURE 8. Dependence of n/b selectivity and rate on H_2/CO by use of anchored catalyst. P loading = 40%; P/Rh = 19 : 1; 100°C, 200 psig. Half-time of reaction designated by $t_{1/2}$.

Hydroformylation of 1-Pentene with Anchored cis-*Chelated Rhodium Catalyst*

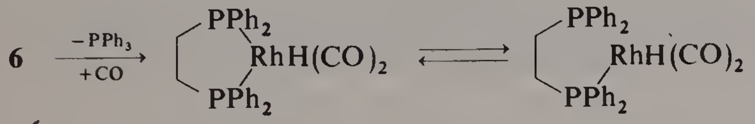
Hydroformylations catalyzed by *cis*-chelated rhodium complexes have not been well discussed in the literature. We prepared compound **6** by simple ligand exchange (reaction 4). This complex should readily dissociate 1 mol of triphenylphosphine



$$Ph_2PCH_2CH_2PPh_2 + RhH(CO)(PPh_3)_3 \longrightarrow \begin{array}{l} PPh_2 \\ \quad RhH(CO)(PPh_3) \\ PPh_2 \end{array} \qquad (4)$$

6

and acquire 1 mol of carbon monoxide under hydroformylation conditions. Because the equilibrium between **7a** and **7b** should greatly favor **7a** over **7b**, perhaps **7** would

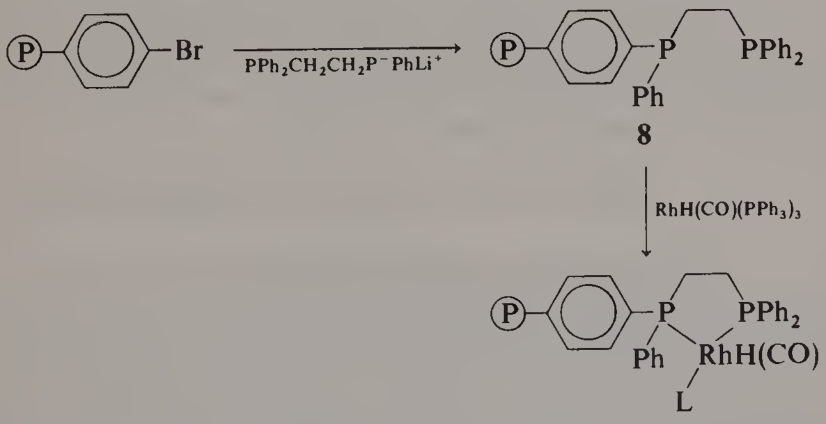


$$6 \xrightarrow[+CO]{-PPh_3} \begin{array}{l} PPh_2 \\ \quad RhH(CO)_2 \\ PPh_2 \end{array} \rightleftarrows \begin{array}{l} PPh_2 \\ \quad RhH(CO)_2 \\ PPh_2 \end{array} \qquad (5)$$

7a **7b**

be an exceptionally selective catalyst for olefinic hydroformylation. This conclusion would follow if **7a** behaved as an analog of **2** in hydroformylations via the associative process.

To test this idea, brominated styrene-divinylbenzene resins were derivatized as shown in reaction 6. The polymer-anchored analog of **6** was prepared from **8** by ligand exchange. Two polymers were made: resin **9A** had a phosphine loading of 5.7% and a P/Rh ratio of 2.1; resin **9B** had a phosphine loading of 22.2% and a P/Rh ratio of 20.9. Hydroformylations of 1-pentene were performed with each catalyst at a series of temperatures (60–120 °C) and pressures (100–800 psig, 1 : 1, H_2/CO). These results are summarized in TABLES 2 and 3. Clearly, neither **9A** nor **9B** is very selective to the normal products. Over the entire matrix of conditions, the selectivity varies from 1.0 to 2.7. Thus, the *cis* configuration of the phosphine substituents in **9** causes a distinct loss of selectivity relative to the $RhH(CO)(PPh_3)_3$ (or its anchored analogs **2**).



(6)

The loss of selectivity was readily explained on examining the product distribution as a function of conversion for hydroformylations catalyzed by **9A**. Both normal and branched products are formed competitively from the beginning before

TABLE 2

SELECTIVITIES (n/b) IN HYDROFORMYLATIONS OF 1-PENTENE CATALYZED BY RESIN **9A** (PL = 5.7%, P/Rh = 2.1)*

psig \ °C	60°	80°	100°	120°
100	2.7	0.9	1.2	1.0
200	2.7	1.0	1.0	1.0
400	2.2	1.0	1.1	1.0
800	1.2	1.0	1.1	1.0

* Each reaction was run for 21 hr. Each reaction contained 0.09 mmol of Rh, 1 ml of 1-pentene, and 8 ml of benzene.

TABLE 3

SELECTIVITIES (n/b) IN HYDROFORMYLATIONS OF 1-PENTENE CATALYZED BY RESIN **9B** (PL = 22.2%, P/Rh = 20.9)*

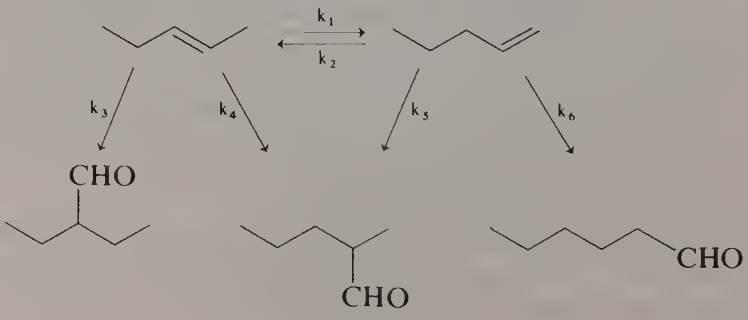
psig \ °C	60°	80°	100°	120°
100	2.0	2.0	2.1	1.2
200	2.0	2.1	2.2	1.0
400	2.0	2.1	2.1	1.0
800	1.0	1.0	1.0	1.0

* Each reaction was run for 21 hr. Each reaction contained 0.09 mmol of Rh, 1 ml of 1-pentene, and 8 ml of benzene.

significant 2-pentene is observed. In addition, significant concentrations of 2-pentene were observed (at conversions from 33 to 65%, more than 25% of the reaction mixture was 2-pentene at 400 psig and 80 °C). Thus, catalyst **9A** has a low inherent n/b selectivity and a high isomerization activity.

Hydroformylation of 2-Pentene with Anchored cis-*Chelated Rhodium Catalyst 9*

The high isomerization activity of catalysts **9** suggested that such *cis*-chelated catalysts might be superior for the hydroformylation of internal olefins. If the hydroformylation of the internal isomer is slow relative to that of the terminal isomer and if the rate of olefinic isomerization is fast, the products of terminal double bond hydroformylation might predominate. In addition, if the n/b ratio for the terminal isomer were favorable, a route to terminal aldehydes from internal double bonds would result (see SCHEME 2). Therefore, a series of 2-pentene hydroformylations were performed with resins **9A** and **9B**:



SCHEME 2

TABLE 4

SELECTIVITIES (n/b) IN HYDROFORMYLATIONS OF 2-PENTENE CATALYZED BY RESIN **9B** (PL = 22.2%, P/Rh = 20.9)

°C psig	60°	80°	100°	120°
100	0.11	0.11	0.16	0.29
200	0.08	0.09	0.12	0.28
400	0.06	0.07	0.10	0.28
800	0.03	0.06	0.13	0.22

* Each reaction was run for 21 hr. Each reaction contained 0.09 mmol of Rh, 1 ml of 2-pentene, and 8 ml of benzene.

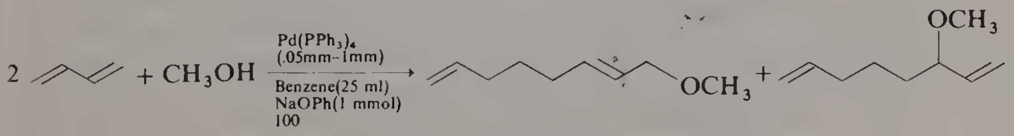
These hydroformylations proceeded smoothly and gave high yields. The more highly phosphine loaded catalyst, **9B**, gave rapid hydroformylation, but at all conditions studied (60–120 °C and 100–800 psig), low n/b ratios were obtained (the highest n/b ratio was 0.3). These results are summarized in TABLE 4. However, higher n/b ratios were obtained with resin **9A** (PL = 5.7, P/Rh = 2.1) at 100–160 °C. Thus, n/b ratios of 0.7 were obtained from 2-pentene with catalyst **9A** at 140 °C and 100–400 psig. This value corresponds to 43% terminal aldehyde from the internal olefin. This result is quite encouraging in view of a recent patent[22] in which various rhenium complexes were employed at 200 °C and about 2500–3000 psig (1 : 1, H_2/CO) to give a maximum yield of about 38% terminal products (see FIGURE 9).

Studies of product distribution as a function of conversion detected only small amounts of 1-pentene (less than 1%) during reactions performed at 80 °C and 400 psig. At 80 °C and 200 psig, as much as 5% 1-pentene was found early in the reaction, but this level decreased steadily during the reaction. Thus, terminal reactivity is greater than that of the internal double bond. Unfortunately, the inherent n/b selectivity during terminal hydroformylation at 100–140 °C is about unity. Therefore, even if 100% of the reaction occurs on the terminal olefin, no more than 50% of the normal products can be expected.

Dimerization-Methoxylation of 1,3-Butadiene

The catalytic dimerization of butadiene followed by the capture of a nucleophile has been studied by Smutny,[23] Takahashi *et al.*,[24] Tsuji *et al.*,[25] Shields and Walker,[26] and Berger and Reichel.[27] However, the mechanism of this reaction is the subject of controversy.

While investigating the kinetics of the dimerization-methoxylation of butadiene in benzene, catalyzed by tetrakis(triphenylphosphine)palladium, we found that increasing the catalyst concentration beyond very low values resulted in no increase in rate:



(7)

Reactions were performed with an excess of butadiene to determine the order in methanol and in palladium complex. The disappearance of methanol and the appearance of the dimers were monitored by VPC internal standard techniques. Under these pseudo first-order conditions, the rate was found to be first order in

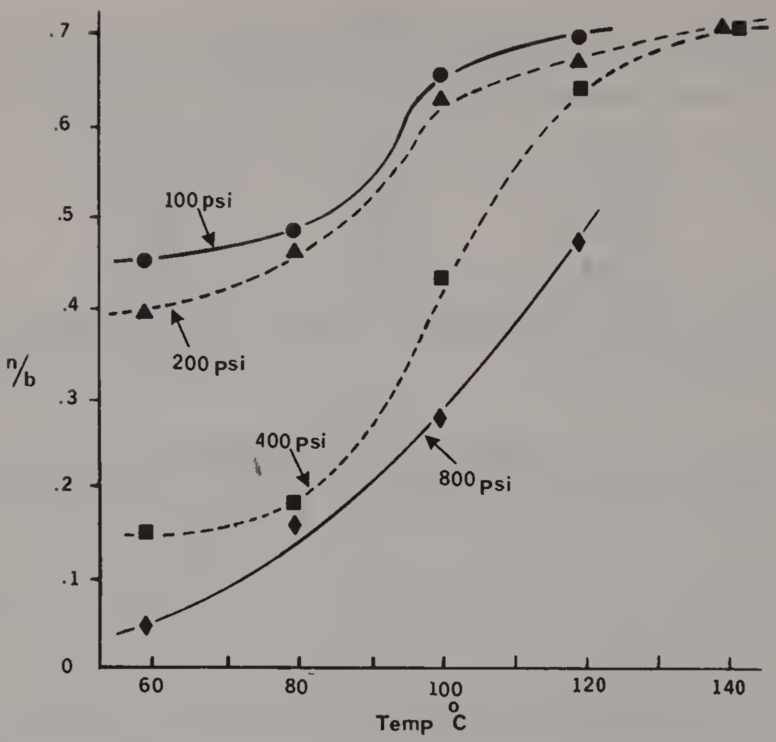


FIGURE 9. Selectivity in hydroformylation of 2-pentene catalyzed by *cis*-chelating resin catalyst **9A** (PL = 5.7; P/Rh = 2.1; Rh = 0.09 mmol; 1 ml of 2-pentene, 8 ml of benzene).

methanol. Plots of $t = 1/k \ln \dfrac{[\mathrm{CH_3OH}]^\circ}{[\mathrm{CH_3OH}]^\circ - X}$ (where X is the amount of methanol consumed at time t) were straight lines, and the rate constants were evaluated as the reciprocal of the slope for the first 10% conversion.

In FIGURE 10, the pseudo first-order rate is plotted versus catalyst concentration for two homogeneous reactions. In the case where P/Pd = 4, no extra triphenylphosphine was added. Where P/Pd = 8, 4 mol of PPh_3 were added for each mole of $Pd(PPh_3)_4$. As the catalyst concentration increases, rate rapidly levels off in both cases. This finding suggests that an equilibrium is limiting the concentration of active catalytic species to an upper limit.

We reasoned that catalytic sites might be isolated from one another by anchoring the palladium complex to a polymer. Thus, it might be possible to increase the concentration (or amount) of active catalytic species if one could suppress the equilibrium processes responsible for the upper limit of activity in the homogeneous cases. It was not considered likely that all such equilibria could be eliminated. Chain mobility within swellable resins (such as styrene-1% divinylbenzene) is extensive. Crowley and Rapoport[28] have argued that complete site isolation in swellable resins cannot be achieved. To achieve a high percentage of site isolation on the "surface" of macroporous (20% divinylbenzene macrorecticular resins) polymers could be a self-defeating proposition, because the low surface loadings that are required would not permit high catalyst concentrations in the reactor. For the above reasons, $Pd(PPh_3)_4$ was anchored to a diphenylphosphinated styrene-1% divinylbenzene resin that contained phosphine substitution on 48% of the resin's phenyl rings.

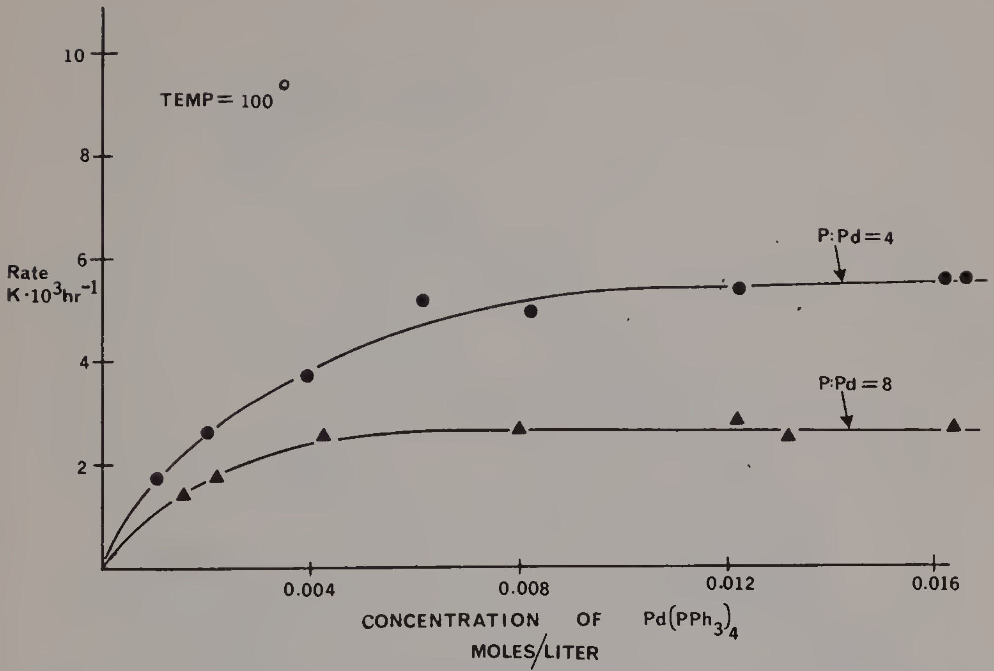


FIGURE 10. Dependence of rate of homogeneous dimerization-methoxylation of 1,3-butadiene on concentration of $Pd(PPh_3)_4$.

Several resin-anchored catalysts were prepared in which the P/Pd ratio varied from 2.5 to 4.0. Addition of palladium introduces further cross-linking sites into the resin and, presumably, further restricts chain mobility. Dimerization-methoxylation reactions of butadiene were then performed at the same stoichiometries and conditions employed in the homogeneous runs. Again, the rate of product formation was first order in methanol. Rate constants were determined at several different catalyst concentrations for each polymeric catalyst. These studies are summarized in FIGURE 11, where the rates may be compared for both the homogeneous and polymer-attached catalysts. At *all catalyst concentrations*, the anchored catalysts *are more active* than homogeneous systems. Apparently, some degree of site isolation has occurred that allows a higher fraction of palladium to remain active.

Several features of FIGURE 11 are worth noting. As the P/Pd ratio decreases, for both polymer-anchored and homogeneous catalysts, the observed rate constants increase. The anchored catalysts continue to give rate increases at higher catalyst concentrations than do the homogeneous systems. The rate of curvature of these plots also decreases as the P/Pd ratio is lowered. FIGURE 12 is a plot of the rate constant ratios of the anchored and homogeneous systems. It further illustrates the fact that the active parity between the two catalyst systems becomes greater as the concentration increases.

The n/b methoxyoctadiene ratio was similar for the homogeneous and anchored systems (3.5 for the homogeneous systems and 3.3–2.4 for the anchored catalyst as the P/Pd ratio was varied from 3.1 to 4.0, respectively). This similarity suggests that the reaction probably follows the same mechanistic pathway inside the swollen polymer network that it does in solution.

The process that causes the leveling off of rates with increasing catalyst concentration is not known. Because the rate decreases on addition of phosphine and

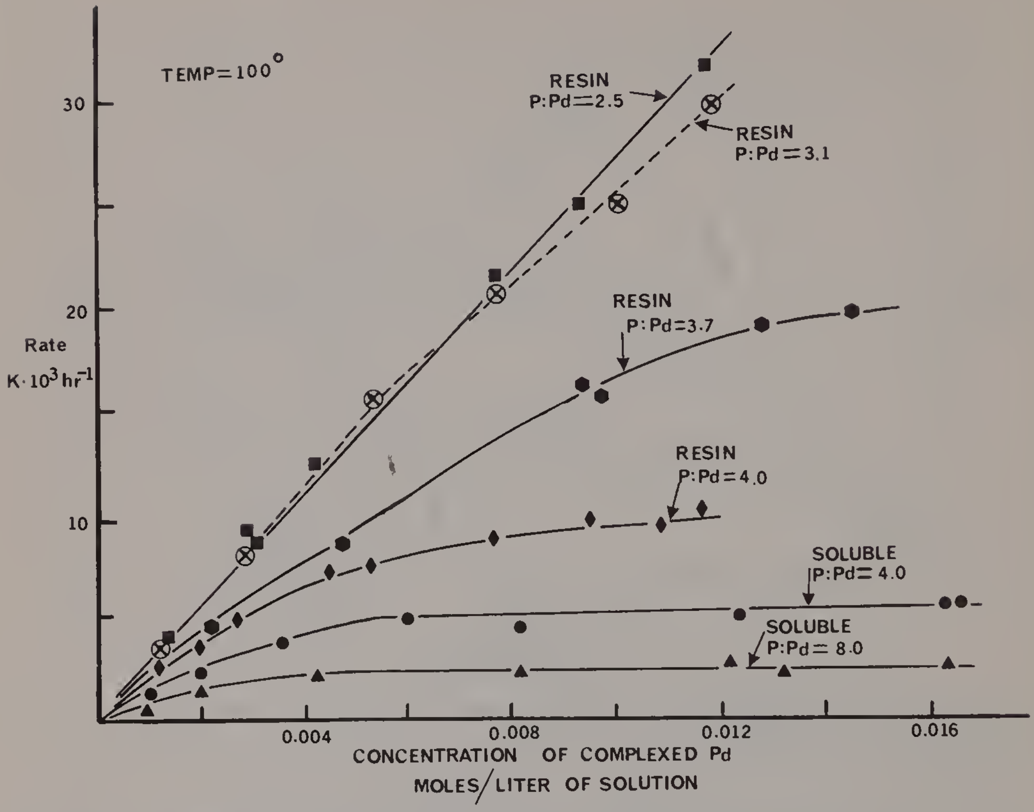


FIGURE 11. Dependence of rate of resin-catalyzed dimerization-methoxylation of 1,3-butadiene on concentration of complexed Pd. Comparison with homogeneous reactions.

the rate per mole of palladium decreases with increasing catalyst concentration, it seems likely that the active catalytic species is formed by phosphine dissociation (reaction 8). If the active species is a mono- or bisphosphine complex, an increase in the concentration of phosphine would shift the equilibria to the left, decreasing

$$X(PPh_3) + (PPh_3)_4Pd \rightleftharpoons (PPh_3)_3Pd + (X+1)(PPh_3)$$
$$\rightleftharpoons (PPh_3)_2Pd + (X+2)(PPh_3) \quad (8)$$

the concentration of the active species. Within the matrix of a resin, the limitations on mobility caused by cross-linking and other factors reduce the fraction of phosphine available to a given palladium atom. Thus, polymer-anchored phosphine is not as effective at shifting the above equilibria to the left, and a larger fraction of the palladium present exists as the active species. This rationale is probably a gross simplification, but it serves as a model from which one may predict that the activity per palladium atom should increase at low phosphine loading in the resin and low P/Pd ratios. These predictions are now being tested in our laboratories. However, the goal of achieving large overall rates with high catalyst concentrations appears to be readily obtained. Going to resins with low phosphine loadings requires the use of lower palladium concentrations.

The rate enhancements achieved by polymer anchoring are actually more dramatic than FIGURES 10–12 would appear to indicate. Note that the concentration of palladium complex is plotted versus rate. This is a true concentra-

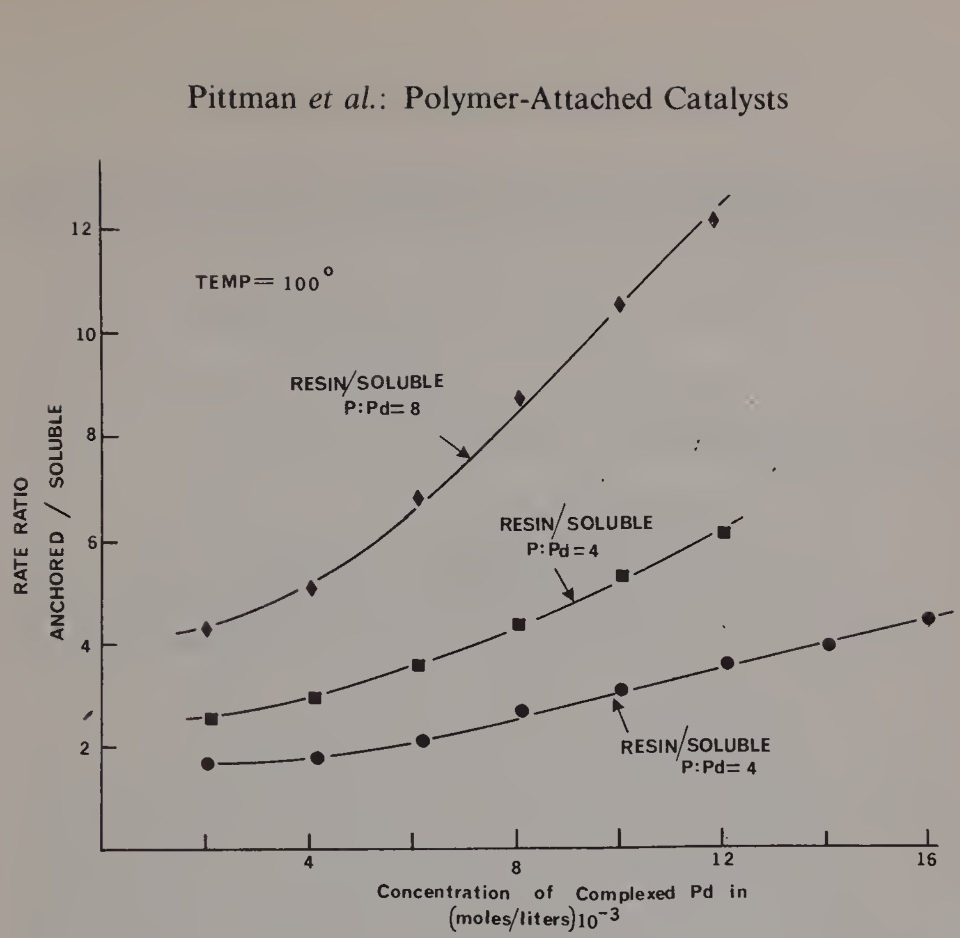


FIGURE 12. Dimerization-methoxylation of 1,3-butadiene. Rate ratio of resin/soluble catalyzed reactions as a function of catalyst concentration.

tion in the homogeneous reactions. However, for the anchored systems, the moles of palladium complex per liter of reaction solution do *not* represent the *actual* concentration, because the resin, to which the catalyst is attached, actually occupies only a small fraction of the total reaction solution volume. For example, in a total reaction solution volume of 50 ml, the swollen volume of 0.5 g of the catalyst resin occupies less than 10% of that 50 ml.

Because all of the catalyst is confirmed within the volume of the swollen resin particles, the true concentration of palladium complex is actually a minimum of 10 times greater than the values indicated on the abscissas of FIGURES 10–12. It is possible to add more resin until the swollen volume of the resin is about 70–80% of the total reaction volume (packing fraction considerations prevent attainment of 100%). Another phenomenon prevents an easy comparison of the soluble and anchored systems. In most previous studies of polymer-anchored catalysts, diffusional limitations appeared to lower the activity of the anchored catalyst relative to that of its homogeneous analog. It is not known what role diffusional limitations play in the butadiene dimerization-methoxylation reaction or if diffusion masks some of the rate enhancement achieved by site separation.

EXPERIMENTAL METHODS

Infrared, nuclear magnetic resonance (nmr), and mass spectra were obtained on Beckmann IR-33, Varian Associates HA-100, and Perkin-Elmer-Hitachi RMU-6M instruments, respectively. Analyses were performed by Schwarzkopf Microanalytical

Laboratories, Woodside, N.Y. Analytic vpc was performed on a Hewlett-Packard model 5501A gas chromatograph, and preparative runs were done on a Varian model 90-P.

Preparation of Anchored Catalysts, Resins **A–H**

These resins were prepared by the method described previously,[17,29] and the preparation and detailed analyses of these specific resins have been thoroughly described by Hanes.[30]

Hydroformylatons of 1-Pentene by Resin-Anchored Catalysts

Hydroformylations were performed in 150-cm^3 stainless steel pressure bombs that had been dried at 120 °C overnight and purged with nitrogen while cooling. The appropriate amount of resin catalyst (0.183 mmol of Rh) was added with benzene (8 ml) and 1-pentene (2.0 ml, 18.3 mmol). The bomb was cooled in an ice bath, pressurized to 400 psig with carbon monoxide, and allowed to equilibrate 5 min before venting to atmospheric pressure; this procedure was repeated twice. The bomb was then pressurized to the desired pressure with equal amounts of hydrogen and carbon monoxide (or the appropriate amounts of each in cases where a 1 : 1 ratio was not used). The bomb was placed in a preequilibrated oil bath at the proper temperature and shaken, vigorously, with a wrist action shaker for the desired reaction time. The reactions were conducted at a constant pressure by connecting the reaction bomb to a gas reservoir via coiled stainless steel tubing (coiled to permit shaking) and a pressure control valve. In this way, the pressure to the bomb remained constant, while the pressure in the gas reservoir dropped steadily. Kinetics were easily monitored by measuring the pressure change in reservoir (known volume) by means of a pressure transducer, which was, in turn, connected to a recorder. Thus, pressure versus time plots were directly obtained during the reaction. This system is described elsewhere in detail.[30]

On completion, the bomb was cooled, and gases were then vented. The reaction solution was analyzed, quantitatively, by vpc. The resin was recovered by filtration; it was washed (extracted) and dried under vacuum before being recycled. The products, hexanal and 2-methylpentanal, were isolated by preparative vpc and analyzed by nmr and infrared spectra. They were found to be identical with authentic samples.

Comparison of Homogeneous and Resin-Anchored Catalysts

The polymer-anchored and homogeneously catalyzed reactions were compared by use of an equal volume of solution for equivalent amounts of rhodium at the same 1-pentene/Rh ratios and at the same 1-pentene/benzene ratios. The reactions were always compared at equal temperatures, pressures, P/Rh ratios, and H_2/CO ratios. However, the reactions, even when conducted in this way, are not completely analogous. This problem arises because the swollen volume of the resin does not fill the entire solution volume. Thus, the rhodium atoms and phosphine sites were confined to the swollen polymer's volume in the anchored catalyst runs as opposed to the entire solution volume in the homogeneous runs. For this reason, the selectivity was directly compared at equivalent "concentrations" in several cases.

In one case, where resin **A** occupied 14% of the reaction solution's volume, the concentration of rhodium in the homogeneous reaction was increased by a factor of six (to 2.74×10^{-2} M Rh). In this comparison, the local concentration of phosphine and rhodium in the resin was quite close to that in the homogeneous reaction. At 80 °C and 400 psig, $H_2/CO = 1:1$, resin **A** was still far more selective (n/b = 5.6 versus 3.6 for the homogeneous case).

Preparation of $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$

The title compound was prepared from phenylphosphine and diphenylvinylphosphine sulfide by base-catalyzed addition of $C_6H_5PH_2$ across the vinyl group, followed by $LaAlH_4$ reduction of the sulfide according to method of King *et al.*[31] A 40% yield, with a boiling point of 210–215 °C (0.2 mm), was obtained of a product that had an nmr spectrum identical with that reported.[32]

Preparation of cis-*Chelated Resin Catalyst* **9**

A dry THF solution (100 ml) that contained $C_6H_5P(H)CH_2CH_2P(C_6H_5)_2$ (15.7 g, 49 mmol) was added slowly to a suspension of potassium metal (14 g, 359 mmol) in dry THF (100 ml) under nitrogen. A yellow precipitate appeared immediately. Stirring was continued for 2 days at 22 °C under nitrogen, and unreacted potassium was then removed. The solution was transferred, under nitrogen, to a rapidly stirred THF slurry of brominated styrene-1% divinylbenzene resin beads (6.4 g, 20.78% Br, 34% of rings brominated, 16.6 mg of bromine atoms per gram). This reaction was stirred under nitrogen for 72 hr, and unreacted $KP(C_6H_5)CH_2CH_2P(C_6H_5)_2$ was hydrolyzed in deoxygenated acetone-water (3 : 1, 1 1). The resin beads were washed successively in 1 liter each of the following nitrogen-purged solvents: acetone, water, benzene, and methanol. The beads were dried at 22 °C (0.1 mm) for several days. Analysis found 7.71% P, which corresponded to 22.2% of the phenyl rings containing a bound $P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ group. Aliquots of the polymer were then swollen in benzene and reacted with the desired amount of $RhH(CO)(PPh_3)_3$ to effect phosphine exchange. By use of various ratios of polymer to $RhH(CO)(PPh_3)_3$, the P/Rh ratio of the resin could be varied. The resultant polymers (i.e., **9A** and **9B**) were then extracted (soxhlet) with benzene and dried under vacuum. Hydroformylations of 1-pentene or 2-pentene, by use of **9A** or **9B**, were performed as described above for resins **A–H**.

Preparation of Polymer-Anchored Palladium Complexes

Tetrakis(triphenylphosphine)palladium was prepared according to the method of Coulson[33] from palladium chloride, triphenylphosphine, and hydrazine hydrate in dimethylsulfoxide at 140 °C. The resultant yellow crystalline powder was added to a deoxygenated benzene suspension of the swollen diphenylphosphinated styrene-divinylbenzene resin and refluxed. By varying the molar ratio of anchored $-PPh_2$ groups to $Pd(PPh_3)_4$, a variety of P/Pd ratios could be prepared.

To 5.0 g of phosphinated polystyrene-divinylbenzene resin (% P = 7; PL = 47.6%; 12.4 mmol of P) in a 250-mol round-bottomed flask was added $Pd(PPh_3)_4$ (4.0 g, 2.94 mmol). Dried benzene (50 ml) was added after deoxygenating with nitrogen, and the reaction mixture was refluxed for 3 days. The resultant resin was extracted (soxhlet) with benzene, under nitrogen, for 24 hr, filtered, dried *in vacuo* for 24 hr, and stored under nitrogen. (Found: % P = 5.69; % Pd = 4.86, which corresponds to P/Pd = 4.0.)

Dimerization-Methoxylation of 1,3-Butadiene

Reactions were conducted in Fischer-Porter glass aerosol compatibility tubes equipped with shutoff valves and stainless steel "dip needles" and valving for periodic sample removal while reacting under pressure. The resin catalyst (0.5 g, 0.23 mmol of Pd; PL = 47.6%; P/Pd = 4) was charged to the tube along with sodium phenoxide (0.12 g, 1.0 mmol) and benzene (25 ml) that contained 25 mmol of methanol. After two freeze-thaw degassing cycles, 1,3-butadiene (8.1 g, 150 mmol) was condensed into the tube. The contents were brought to 25 °C where the total solution volume was 50 ml. The reaction was heated at 100 °C. At intervals of 5–10 hr, 0.3-ml aliquots were withdrawn for vpc analysis (OV-17, 8% on DMCS Chrom.-W, 6 ft × $\frac{1}{8}$ in., temperature programmed from 60 °C for 2 min to 120 °C at 16 °C/min, by use of mesitylene as an internal standard). After the run was completed, products were collected by preparative vpc (OV-17, 10% on DMCS Chrom.-W, 6 ft × $\frac{1}{4}$ in., isothermal, 120 °C). [Found for 1-methoxy-2,7-octadiene: ir (cm^{-1}), 3080, 3020, 1650, 1385, 1130, 990, 970, and 914; nmr ($CDCl_3$, δ) 1.5 (m, 2, $-C\underline{H}_2-$), 2.1 (m, 4, $-C\underline{H}_2-CH{=}$), 3.3, (s, 3, $C\underline{H}_3O$), 3.9 (d, 2, $OC\underline{H}_2CH{=}$), 5.0 (m, 2H, $-C\underline{H}{=}C\underline{H}-$), 5.6 (m, 3, $C\underline{H}_2{=}C\underline{H}-$); mass spec., parent ion, *m/e* = 140. For 3-methoxy-1,7-octadiene: ir (cm^{-1}) 3080, 3020, 1640, 1450, 1100, 990, 910 (no internal *trans* double bond, i.e., 970 cm^{-1}); mass spec., parent ion *m/e* = 140.] These spectra agree with published spectra of the two isomers.[23,24,26,27]

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ARENE-METAL COMPLEXES IN ORGANIC SYNTHESIS

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In the 20 or so years that have passed since the study of π-arene-metal complexes began in a general way, hundreds of stable organometallic compounds with arene ligands have been prepared (for comprehensive reviews of the subject, see Reference 1). The structures and chemical properties are now well established, but application of π-arene complexes to organic synthesis has lagged many years behind the inorganic interest. Recent developments, however, suggest that this situation is changing, that new areas of arene chemistry are becoming available that involve selective reactions on or adjacent to metal-complexed aromatic rings. This paper focuses on the aromatic ring; it attempts to summarize the changes in reactivity induced by metal coordination, the examples of conversions with significance for organic synthesis, and the patterns of reactivity that portend valuable synthetic methods.

In general, with new methods of synthesis that involve transition metals, three aspects must be examined: introduction of the activating metal unit, induction of the appropriate organic transformation at the ligand of interest, and removal of the metal unit. This paper begins with a summary of the techniques available for formation of arene-metal complexes and for eventual release of the modified arene unit. The emphasis is on transformations of the coordinated arene.

Formation of Arene-Metal Complexes

Two techniques seem to have some general application in the formation of arene-metal bonds. Direct thermal replacement of other ligands on the metal is a process that can be efficient and mild, requiring reaction temperatures from 25°C [for the formation of η^6-benzene-η^4-norbornadienerhodium(I)[2]] to over 100°C [for conversion of chromium hexacarbonyl to η^6-benzenetricarbonylchromium(0)[3]]. This process has been particularly useful for preparation of the many η^6-arene-tricarbonylmetal(0) complexes, especially those of chromium, molybdenum, and tungsten, and for arenes with quite varied substituents.[1] Direct thermal reaction may be especially useful when considering metal complexes of the polyfunctional arenes of interest in natural product synthesis. The chief advantage is the nonpolar, neutral medium (dioxane, heptane); the yields are not always good, but optimum reaction conditions often have not been determined.

Lewis acid-promoted attachment of arene rings to metals is a general method for preparation of cationic arene-metal complexes.[1] Preparation can be accomplished by direct attachment of ligands without change in oxidation state of the metal. For example, reaction of iron(II) with benzene in the presence of aluminum bromide at 80°C produces bis(η^6-benzene)iron(II).[4] The original Fisher-Hafner method for preparation of arene-metal complexes employs a Lewis acid and a reducing agent, such as aluminum metal, and involves reduction of the metal during the process.[1,5] For example, a chromium(III) salt leads to bis(η^6-benzene) chromium(I), which, in turn, can be reduced to bis(η^6-benzene)chromium(0). A powerful method for preparation of η^6-benzene-η^5-cyclopentadienyliron(II) proceeds by Lewis acid-promoted exchange of a cyclopentadienyl unit for an arene starting from ferrocene.[6] A difficulty with the Lewis acid reactions is that many useful or necessary functional groups will undergo serious side reactions; few functionalized arenes have been converted to π-arene complexes by use of this general method.

CLEAVAGE OF ARENE-METAL BONDS

The stability of arene-metal bonds depends on the structure of the metal, the nature of the other ligands, the oxidation state of the metal, and the structure of the arene itself. For use in synthesis, the arene complexes should be quite stable thermally but should release the arene when treated with reagents or under conditions that do not affect common functional groups. Generally, separation of the arene is possible under mild conditions, by use of irradiation[7] or oxidizing agents, such as cerium(IV)[8] and iodine.[3] Direct ligand displacement with donor ligands, such as amines,[9] phosphines,[10] or halogen anions,[11] also effects separation of the arene from the metal, with required temperatures depending on the metal unit. Removal of the arene after synthesis objectives have been accomplished is unlikely to present problems, even when highly functionalized complex arenes are involved.

GENERAL EFFECTS ON ARENE REACTIVITY OF COORDINATION WITH A METAL UNIT

FIGURE 1 summarizes the five general changes in arene reactivity that have been observed when a metal is coordinated with the arene π-system: stabilization of side-chain cation sites (benzyl and phenethyl cations), stabilization of side-chain anion sites, enhanced acidity of arene ring hydrogen substituents, steric effects of the coordinated metal units, and nucleophilic aromatic addition and substitution reactions. The first three effects have not yet been developed significantly for organic synthesis, but the last two are ready for application.

Coordination of benzyl alcohol derivatives with metals is accomplished by direct displacement of ligands from a metal unit[12] but more generally arises through metal hydride reduction or Grignard addition to π-benzoyl ligands.[3,13] The number

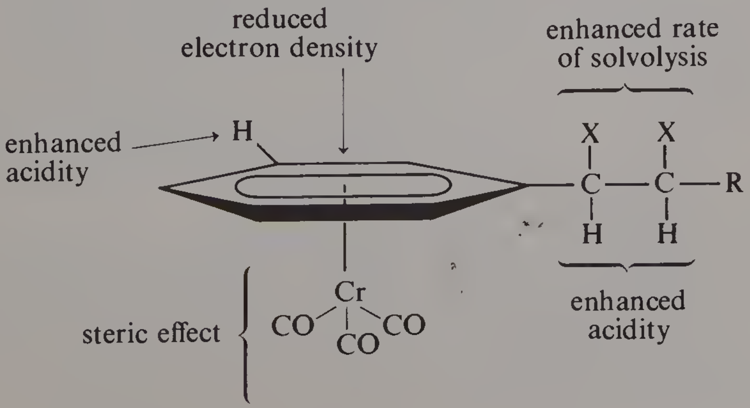
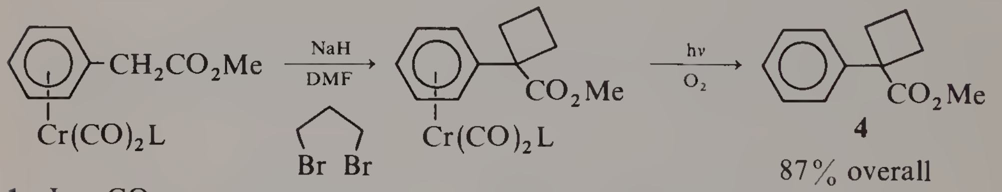


FIGURE 1. Effects on arene reactivity of metal coordination.

of such complexes is small, limited to derivatives of η^6-benzene-η^5-cyclopentadienyliron(I) and η^6-benzenetricarbonylchromium(0). Ionization of the carbon—oxygen bond in π-benzyl alcohol metal complexes is much easier than in the corresponding free benzyl alcohol.[14] In the same way, η^6-(chloromethylbenzene)-tricarbonylchromium(0) undergoes solvolysis 10^5 times faster than does benzyl chloride under the same conditions. The stability constant for π-benzyl cation is 10^7 greater than that for the benzyl cation itself. The mechanism of stabilization has not been resolved; direct through-space interaction is postulated.[16,17]

The most dramatic effect of metal coordination with an arene is the powerful withdrawal of electron density from the aromatic ring, much like the effect of a nitro substituent in the σ-framework. This factor appears to be responsible for significant enhancement of the acidity of benzylic hydrogens in η^6-(alkylarene)metal complexes. The effect has been reported for two types of metal units, the tricarbonylchromium complexes[16] and the bis(η^6-arene)iron(II) species.[17] Complexation by tricarbonylchromium results in activation of benzylic protons by a factor of 100.[18] Direct applications of this effect in synthesis are beginning to appear. Methyl phenylacetate fails to react with sodium hydride/methyl iodide at 25°C, but the corresponding methyl(tricarbonylchromium-η^6-phenyl)acetate (**1**) reacts rapidly under the same conditions to give methyl(tricarbonylchromium-η^6-phenyl)-dimethylacetate in 97% yield.[19] A second application is shown in equation 1, with exposure to sunlight in air giving the organic product (**1**) in 87% yield overall.[19] An important "fine tuning" of reactivity is demonstrated in this work. Complex **2** reacts more rapidly than **1**; both give efficient dialkylation. However, **3** reacts more slowly [$(PhO)_3P$ is a weaker electron acceptor than is CO] with sodium hydride/methyl iodide and gives the monomethylated product rather selectively.[19] In the same way, η^6-acetophenonetricarbonylchromium is converted to η^6-isopropiophenonetricarbonylchromium in 90% yield. With the powerful basic medium of potassium *tert*-butoxide in dimethyl sulfoxide, η^6-(ethylbenzene(tricarbonylchromium reacts with methyl iodide; after decomplexation of the arene ligand, isopropylbenzene (71%) and *tert*-butylbenzene (8%) are obtained. An intriguing possibility for future work is the use of π-styrene metal derivatives (e.g., **5**) as receptors for nucleophilic attack, in a process related to the Michael reaction. One example has appeared,[20] illustrated by reaction 2; the process is complicated in this case by products attributed to further nucleophilic additions by the proposed intermediate anion, **6**.

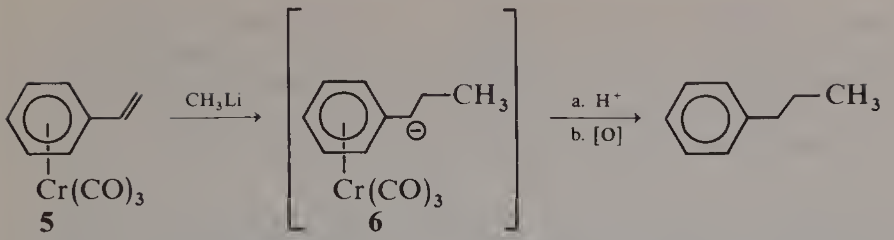


(1)

1 L = CO
2 L = CS
3 L = $(PhO)_3P$

Enhanced acidity of the ring hydrogens in arene metal complexes allows formation of π-complexed aryl lithium species by direct proton obstraction.[21] This feature has been used in the preparation of η^6-arenetricarbonylchromium complexes not readily available by the usual procedures,[21d] but no general applications in organic synthesis have appeared.

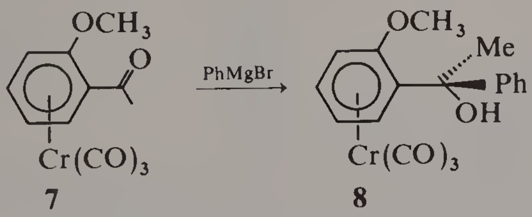
The tricarbonylchromium unit has been found to exert a large steric blocking effect, which has begun to be exploited, primarily by Jaoen *et al.*, in asymmetric



(2)

organic synthesis. Preparation of products with high enantiomeric purity can be achieved by selective reaction (asymmetric induction) from a chiral arene-metal complex (for some of the numerous examples of optically pure mono- and disubstituted arene-chromium tricarbonyl complexes, see Reference 22).

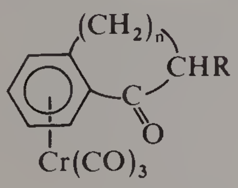
In open-chain examples, such as substituted alkylphenyl ketones coordinated with tricarbonylchromium (e.g., complex **7**), the stereochemistry and efficiency of attack by nucleophiles generally depend on the size of substituents on the arene ring and the nature of the incoming anion,[13d,23] but good selectivity is often observed, as illustrated in equation 3. The alcohol (**8**) can be separated from its



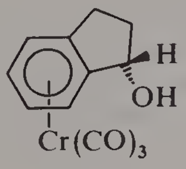
(3)

diastereoisomer by chromatography and the ligand, 100% optically pure, can be separated from the chromium in 100% yield.

When the functional group undergoing reaction is included in an alicyclic ring fused *ortho* to the π-complexed arene (e.g., in **9** and **10**), reactions occur exclusively from the side *exo* to the tricarbonylchromium group. For example, hydride reduction of π-indanonetricarbonylchromium (**9**) produces exclusively the *endo* alcohol, **11**.[13c] Even with complex **12**, hydride reduction is exclusively *exo*, producing the *trans*-indanol **13** after decomplexation.[24] Even with the more remote effect that operates in η^6-(2-indanone)tricarbonylchromium, hydride reduction proceeds to give a 93/7 mixture that favors *exo* over *endo* addition.[24]



9 $n = 1$, R = H
10 $n = 2$, R = H
12 $n = 1$, R = $t-$Bu



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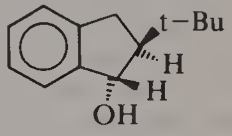
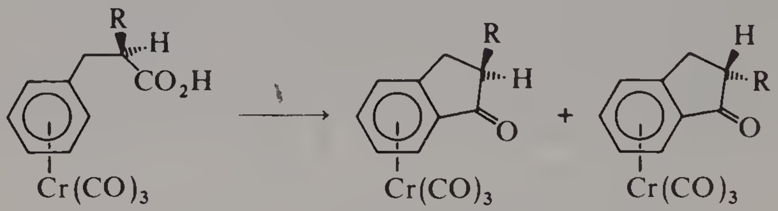


13

In the same way, alkylation of the enolate anions derived from the tricarbonylchromium complexes of 1- and 2-indanone and 1-tetralone proceeds with selective *exo* attachment. For example, reaction of complex **9** with sodium hydride/methyl iodide produces exclusively the *exo*-2-methylindanone complex. Presumably *exo-endo* equilibration of the product occurs rapidly in the basic medium, so preference for the *exo* product is likely to be the result of thermodynamic control in this case. The same selectivity occurs in the alkylation of

η^6-(1-carbomethoxyindane)tricarbonylchromium by use of sodium hydride/*N*,*N*-dimethylformamide or phase-transfer catalysis to generate the stabilized carbanion.[25]

Two practical points make these stereochemical control features particularly exciting for organic synthesis. First, numerous common functional group manipulations and carbon—carbon bond-forming reactions can be performed with the tricarbonylchromium unit attached. For example, a variety of 3-(η^6-tricarbonylchromium)phenylpropionic acid derivatives, with 2-alkyl substituents, have been observed to cyclize to η^6-indanone complexed under acid-dehydrating conditions. A mixture of isomers (**14a** and **14b**) is obtained, separable by chromatography. The carbonyl group can be reduced (as above), and the resultant alcohol can be reoxidized with manganese dioxide, one of the few oxidation reactions that does not disturb the metal—arene bond.



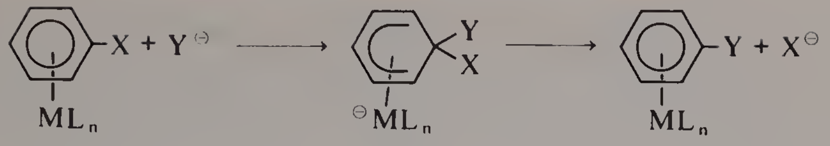
14a **14b**

R = methyl, ethyl, isopropyl, *t*-butyl

Second, these maneuvers have allowed Jaoen and Meyer[27] to work out a procedure for optical resolution of η^6-(1-tetralone)- and η^6-(1-indanone)tricarbonylchromium (i.e., **10** and **9**). Resolution of the acid succinate of η^6-(1-indanol)-tricarbonylchromium, followed by hydrolysis and oxidation, produces optically pure **9**. Then, stereospecific alkylations at the 2-position or attack of nucleophiles at the carbonyl group in **9**, followed by decomplexation by exposure to air and sunlight, leads to derivatives of indanone or indanol of high optical purity.[28,29]

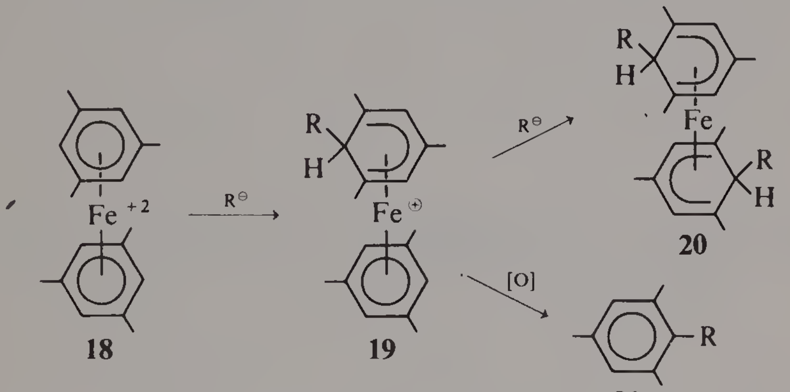
The concept of polarity inversion, or *ümpolung*, is a popular way of organizing certain organic synthesis methods and has stimulated much new chemistry.[30] Such methods rely on reversible modification of a functional group to reverse the polar driving force usually involved in reactions at that group. The powerful electron-withdrawing effect of π-bonded metal units and the easy reversibility of attachment of the metal suggest a means of polarity inversion for aromatic rings, which are usually considered as nucleophilic species. Nitro groups and other electron-withdrawing substituents are well known to reverse the reactivity pattern of aromatic rings, allowing addition of nucleophiles under mild conditions to form cyclohexadienyl anions, the Meisenheimer complexes.[31] The mechanism of classic nucleophilic aromatic substitution has been exhaustively studied, but applications in complex organic synthesis are few. An important limitation is the lack of mild and direct methods for attaching and removing the activating groups, usually nitro.

By now, hundreds of examples of addition of nucleophiles to π-arene ligands are known, generally proceeding according to reaction 4, where the starting complex can have a formal charge of 0, +1, or +2. In certain cases, loss of a substituent (*X* in **15**) produces the substituted arene complex (**17**). These two steps, addition followed by elimination, are parallel with the established mechanism for nucleophilic aromatic substitution: the π-cyclohexadienyl complex (i.e., **16**) is the transition metal analog of the classic Meisenheimer anion. Examples are known with most types of hydride,[32] oxygen,[3] nitrogen,[33] sulfur,[34] phosphorus,[35] and carbon nucleophiles as unit *Y* in reaction 4. Emphasis in the discussion below is on carbon nucleophiles.



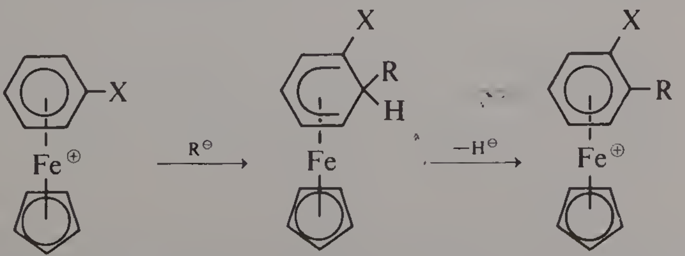
15 **16** **17** (4)

Helling *et al.* report that carbanions, such as the nitromethane anion, add to one ring of bis(η^6-mesitylene)iron(II) to give **19**; more reactive anions (phenyl, vinyl, and *tert*-butyllithium) can be controlled to add once or twice (to give **20**). The formation of **18** occurs within minutes at 25°C. The reaction is likely to be general, but few analogs of **18** are known, none with halogen substituents. Nevertheless, the products from formal nucleophilic aromatic substitution can be obtained by mild oxidation of **19**; a hydrogen substituent departs from the cyclohexadienyl ligand, and the iron is oxidized to cause release of the arene ligand (**21**). The yield of phenylmesitylene (**21**, R = phenyl) by this sequence of addition and oxidation is 35%. Unfortunately, the harsh conditions currently used to obtain such complexes as **18** (ferrous chloride, aluminum chloride at 80°C)[4] will limit application in complex organic synthesis.



18 **19** **20** **21**

Similar reactions have been worked out for η^6-arene-η^5-cyclopentadienyliron(II) fluoroborate complexes, and here more than 75 arene-substituted derivatives are available,[1b] generally prepared by Lewis acid-promoted exchange of arene for cyclopentadiene in ferrocene.[6,32] In studies with hydride[32,36] and methyllithium[37] additions to such derivatives as **22**, certain general directing effects of substituents were observed. Complex **22a** leads to preferential *ortho* substitution (o:m:p = 4:1:0 with CH_3Li), while the toluene complex (**22b**) produces more or less statistical mixtures of *ortho*, *meta*, and *para* substitution. With heteroatomic nucleophiles,



22 a: X = Cl
b: X = CH_3 (*meta*, *para* also)

23

24
(*meta*, *para* also)

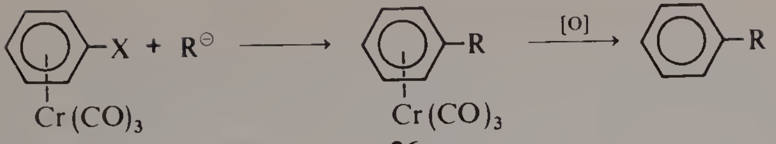
such as methoxide, reaction with the chlorobenzene complex (**22a**) leads to substitution, producing **24** (R = OCH_3; X = H).[34] Kinetic studies show that the activating influence of the cyclopentadienyliron cation unit is greater (by 2 kcal/mol in activation energy) than a *p*-nitro substituent.[34] Parallel with intermediate **19**, hydride is abstracted from **23** by such agents as *N*-bromosuccinimide and triphenylmethyl cation[38]; the product is **24**. No general procedure has been presented for separating the arene from **24**.

The arene ligand in η^6-arenetricarbonylmanganese(I) complexes is also reactive toward addition of nucleophiles,[35] but several other reaction paths can occur, depending on the nature of the nucleophile. Donor molecules, such as iodide ion or acetonitrile, can displace the arene ligand or a carbon monoxide.[39] Amines[40] and sodium methoxide[35] add to the carbon monoxide ligand, leading to an acyl complex. Many carbanions (methyllithium,[41,42] phenyllithium,[42] and malonate[35]) add to the arene ligand rapidly at 25°C to produce η^5-(alkylcyclohexadienyl)-tricarbonylmanganese(I) derivatives in moderate yield. No general technique has been presented for removal of a hydrogen from the cyclohexadienyl intermediate to give the product that corresponds to nucleophilic aromatic substitution. The directive effects of substituents on the arene ligand have been examined with η^6-(chlorobenzene)-, η^6-(anisole)-, and η^6-(*N*,*N*-dimethylaniline)tricarbonylmanganese(I) in reaction with methyl- and phenyllithium.[42] The selectivity is greater than that of corresponding reactions with **22a** and **22b**, but the trends are the same. The electron donor effect is suggested to favor attack by the carbanions at the *meta* position; with the dimethylamino substituent, the selectivity is greater than 95%. Competing influence of the inductive effect with the chlorine substituent is suggested to be responsible for the *ortho* preference ($o{:}m = 2{:}1$). Substitution for halogen in η^6-(haloarene)tricarbonylmanganese(I) complexes has not yet been reported.

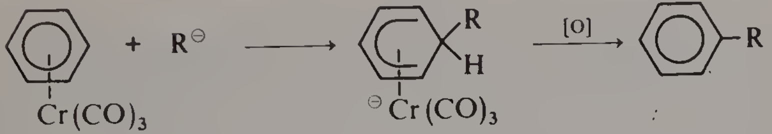
The neutral η^6-(arene)tricarbonylchromium(0) complexes are currently the most attractive of the arene metal species to be considered as intermediates for organic synthesis because of several points of operational convenience. (1) Hundreds of examples are already known,[1b] some with rather complex arene substitution patterns. (2) They can be prepared under neutral conditions by simply heating $L_3Cr(CO)_3$ with the arene, where $L = CO$, CH_3CN, or NH_3. By use of either excess arene or excess $L_3Cr(CO)_3$, the yields are excellent, regularly in the range of 80–90%. Some are commercially available. (3) They are air-stable solids, readily amenable to solution spectroscopy and chromatographic purification/analysis. (4) Mild reaction conditions are available for removal of the arene ligand from the metal. For example, aqueous Ce(IV) or iodine induces rapid release of the arene at 25°C.[3,8]

Two distinct methods have been worked out in detail: the addition/elimination route, which gives overall substitution of chlorine or fluorine[43] according to reaction 5, and an addition/oxidation technique, which provides overall substitution of a nucleophile for hydrogen (reaction 6).[8,44] The scope and limitations of carbon—carbon bond formation by both of these processes are under study; the current state of the project is outlined below, based partly on unpublished observations.

A variety of carbanions have been found to substitute for halogen in complex **25** according to reaction 5. TABLE 1 presents the successful examples. In general, highly stabilized anions (malonate and phenoxide) and reactive, tertiary anions (entries 1–6 in TABLE 1) give smooth substitution for halogen, producing the substituted arene complexes (e.g., **26**) within 15–20 hr at 25°C; then, oxidation with excess iodine at 25°C gives the free substituted arene, carbon monoxide, and Cr(III). With the anion of isobutyronitrile [R = $C(CH_3)_2CN$], complex **26** was isolated in 78% yield,[43] but the best yields of the substituted arene are obtained



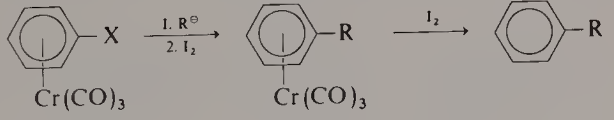
25 **26** (5)



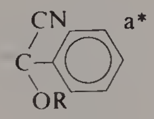
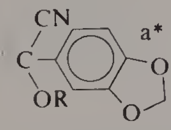
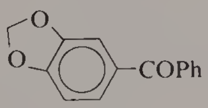
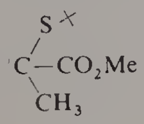
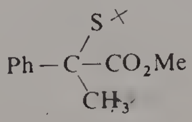
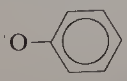
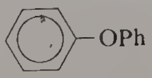
27 **28** (6)

TABLE 1

COUPLING OF CARBANIONS WITH η^6-(HALOBENZENE)TRICARBONYLCHROMIUM



29 **26**

Complex **29**	Anion	Product	Yield (%)
1. $X = Cl$	$^{\ominus}C(CH_3)_2CN$	$PhC(CH_3)_2CN$	85
2. $X = Cl$	$^{\ominus}C(CH_3)_2CO_2Et$	$PhC(CH_3)_2CO_2Et$	71
3. $X = Cl$	$^{\ominus}C(CH_3)_2CO_2^{\ominus}$	$PhC(CH_2)_2CO_2H$	63
4. $X = Cl$	 a*	PhCOPh (88)	88
5. $X = Cl$	 a*	 (90)	90
6. $X = F$	$^{\ominus}CH(CO_2Me)_2$	$PhCH(CO_2Me)_2$	95
7. $X = F$		 (94)	94
8. $X = Cl$		 (72)	72

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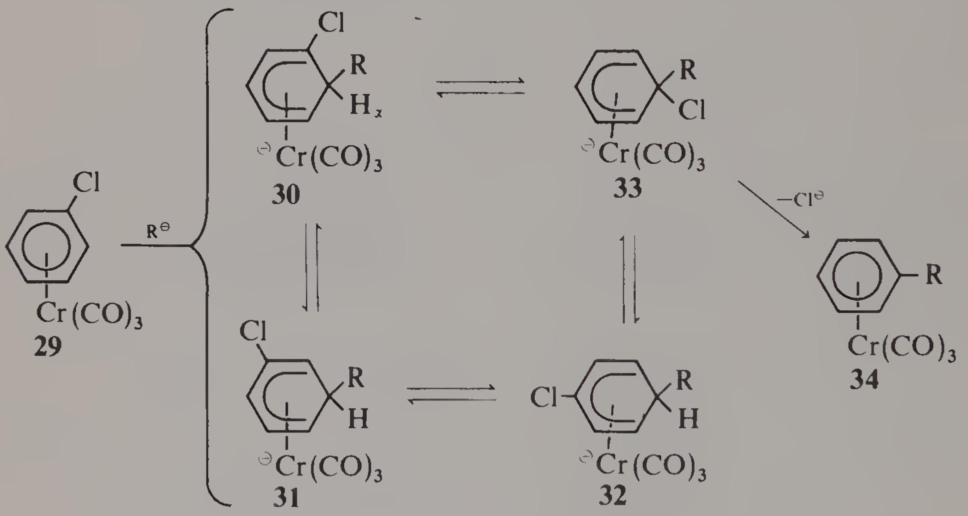
* R = $CH(CH_3)OCH_2CH_3$; the isolation procedure included hydrolysis of the acetal and conversion of the resultant cyanohydrin back to the carbonyl compound.[49]

by oxidation of the crude intermediate. Reaction of isobutyronitrile anion with η^6-(*p*-chlorotoluene)tricarbonylchromium, followed by oxidation, produces a single product, *p*-polylisobutyronitrile.[45] The absence of *m*-tolylisobutyronitrile supports the addition/elimination mechanism via η^5-[1-chloro-1-(2-cyano-2-methylethyl)-cyclohexadienyl]tricarbonylchromium(0) instead of a pathway that involves a transient aryne; a similar conclusion had been reached from kinetic considerations in reaction of **25** with heteroatomic nucleophiles.[32,46]

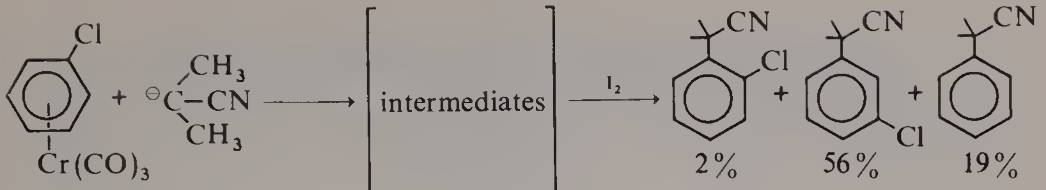
The most significant parts of TABLE 1 are the "missing" carbanions, the ones that were tested and failed: 1, $LiCH_2CO_2Me$; 2, $LiCH(CH_3)_2CO_2Me$; 3, $LiCH_2COC(CH_3)_3$; 4, $LiCH_2CN$; 5, $LiC{\equiv}CH$; 6, 2-lithio-1,3-dithiane; 7, phenyllithium; 8, methyllithium; 9, *n*-butyllithium; 10, Me_2CuLi; 11, $PhCOCH_2HgCl$; 12, CH_3MgBr; 13, allyl-MgBr; 14, $(CH_3)_3CMgBr$. These anions fall into two groups. Anions 1–9 react rapidly with **29** at −78°C but fail to give substitution for chloride, even after many hours at 25°C and above.[45] Anions 10–14 fail to react with **29** at moderate temperature (up to 25°C) and lead to slow decomposition on heating. It now appears that the more reactive lithio carbanions (TABLE 1, entries 1–7, and anions 1–9) add to the arene ring of **29** to produce η^5-cyclohexadienyl derivatives (one or more of **30–33**). When R is one of the tertiary anion units from TABLE 1 (entries 1–7), isomerization among isomers **30–32** is rapid at 25°C, and irreversible loss of chloride from **33** gives the observed product (SCHEME 1).



SCHEME 1

Anions 1–9 clearly react with **29** to give **30–32**, but there is a barrier to isomerization that prohibits formation of **33** at moderate temperatures. The less reactive anions (10–14) fail to add to the arene at low temperatures and suffer unspecified side reactions on warming. Stabilized anions, such as malonate and phenoxide, fail to give observable amounts of **30–32** [proton magnetic resonance (pmr)] but apparently low concentrations are formed, perhaps in equilibrium with **29** until **33** appears and leads (irreversibly) to **34**.

Indirect evidence for this hypothesis was obtained by adding iodine to the mixture shortly after mixing isobutyronitrile anion with **29** at 0°C or below. Presumably, the iodine removes the *endo* hydrogen (e.g., H_α in **30**) and oxidizes the chromium, causing release of the arene unit. No chlorobenzene was detected, consistent with complete conversion of the starting complex; the presence of *o*- and



29

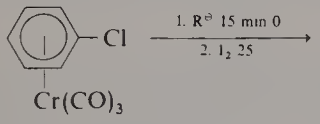
(*m*-chlorophenyl)isobutyronitrile supports the suggestion that **30** and **31** are important intermediates.[43] TABLE 2 shows similar experiments with a variety of anions.[45] The distribution of products for entries 1 and 2 change as the reaction (before iodine quenching) increases; the substitution for chloride increases. For entries 3–6, no important change in distribution of products is observed at longer reaction times; substitution for chloride is never significant, except for entry 5.

Direct evidence for intermediates, such as **28** and **30–32**, was obtained by solution spectroscopy on the reaction mixtures from complex **27** with $LiCH_2CN$, $LiCH(SPh)_2$, and $LiC(CH_3)_2CH$.[47] Addition to the arene ligand is complete within minutes at −78°C in tetrahydrofluorenone (THF) (monitored by pmr); absorptions for **28** are closely parallel with corresponding data for η^5-cyclohexadienyl complexes with other metals.[38,40] Double resonance experiments confirmed the assignments; the *exo* orientation of the anion units is assumed, based on a few well-established analogies.[48]

The reactivity of η^5-(alkylcyclohexadienyl)tricarbonylchromium(0) intermediates, such as **29**, has been probed in some detail and offers significant potential for organic synthesis. TABLE 3 shows the results of a series of experiments in which carbanions were allowed to react with η^6-benzenetricarbonylchromium (**28**) for a few minutes at 0°C in THF (or THF-HMPA mixtures) after which the mixture was quenched with excess iodine, according to reaction 6 (above).

TABLE 2

REACTION OF CARBANIONS WITH $(C_6H_5Cl)Cr(CO)_3$ FOLLOWED QUICKLY BY IODINE OXIDATION



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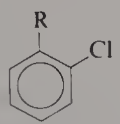
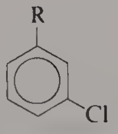
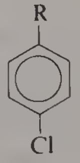
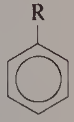
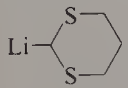
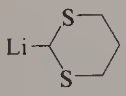
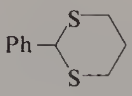
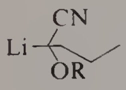
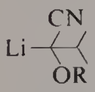
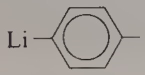
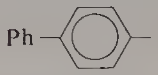
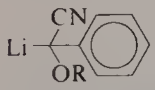
				
Anion	Product Yields (%)			
1. $LiC(CH_3)_2CN$	2	56	0	19
2. $LiC(CH_3)_2CO_2$-tBu	1	64	0	1
3. $LiCH(CH_3)CO_2$-tBu	30	52	1	0
4. $LiCH_2CO_2$-tBu	39	19	0	0
5. 	27	45	0	25
6. $LiCH_2COC(CH_3)_3$	71	21	0	0

TABLE 3

COUPLING OF CARBANIONS WITH η^6-BENZENETRICARBONYLCHROMIUM

Carbanion	Product	Yield (%)
1. $LiC(CH_3)_2CN$	$PhC(CH_3)_2CN$	94
2. $LiCH_2CN$	$PhCH_2CN$	68
3. 		93
4. 	$PhCO(CH_2)_2CH_3$	90*
5. 	$PhCOCH(CH_3)_2$	88*
6. $LiCH(SPh)_2$	$PhCH(SPh)_2$	84
7. $LiC(CH_3)_3$	$PhC(CH_3)_3$	97
8. 		71
9. $LiCH_2CO_2R$	$PhCH_2CO_2R$	87
10. $LiCH(CH_3)CO_2R$	$PhCH(CH_3)CO_2R$	88
11. $LiC(CH_3)_2CO_2R$	$PhC(CH_3)_2CO_2R$	88
12. $LiCH_2COC(CH_3)_3$	$PhCH_2COC(CH_3)_3$	0
13. *n*-BuLi	Ph-Bu	0
14. CH_3Li	Ph-CH_3	0
15. 	PhCOPh	0*

* R = $-CH(CH_3)OCH_2CH_3$; isolation included aqueous acid to hydrolyze the acetal and aqueous base to convert the cyanohydrin to the ketone.

Two important limitations are revealed in these experiments. Anions less reactive than ester enolates fail to convert **28** to the required η^5-cyclohexadienyl intermediates (entries 12 and 15). In general, ketone enolates fail in this procedure. Certain alkyllithium species (entries 13 and 14) fail because proton abstraction from the arene ligand becomes important; quenching with iodine gives mainly iodobenzene.

Generally consistent with the selectivity observed by Pauson *et al.* with arene-iron[36] and arene-manganese[37] complexes, we find that methoxy substituents on the arene strongly direct the incoming anion to the *meta* position (TABLE 4), while a methyl substituent (TABLE 5) and chlorine (TABLE 3) allow substantial attack at both the *ortho* and the *meta* sites. More bulky anions tend to give a higher preference for *meta* substitution in all examples. Remarkably, substitution in the *para* position never accounts for more than 3% of the mixture.

A simple rationale for the *meta*-directing effect of chloro, methyl, and methoxy substituents begins with the assumption that the transition state that leads to the η^5-cyclohexadienyl intermediate has some of the character of a pentadienyl anion. Then, these substituents, all capable of electron donation, have the least destabilizing effect when they sit at the 2-position (*meta*) on the cyclohexadienyl system, the position of lowest electron density.

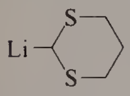
TABLE 4

COUPLING OF CARBANIONS WITH η^6-ANISOLETRICARBONYLCHROMIUM

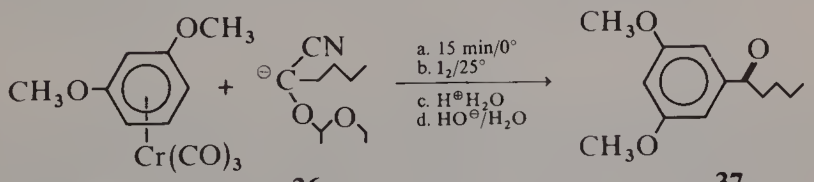
Anion	Product Yields (%)		
	Ortho	*Meta*	*Para*
$LiCH_2CN$	1	37	0
$LiC(CH_3)_2CN$	3	79	0
$LiCH_2CO_2$-tBu	5	74	0
$LiCH(CH_3)CO_2$-tBu	3	91	0
$LiC(CH_3)_2CO_2$-tBu	0	76	0

TABLE 5

COUPLING OF CARBANIONS WITH η^6-TOLUENETRICARBONYLCHROMIUM

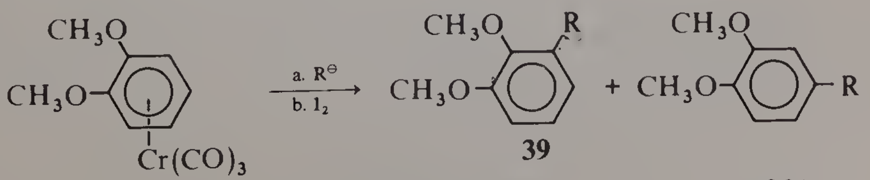
Anion	Product Yields (%)		
	Ortho	*Meta*	*Para*
$LiCH_2CN$	30	56	2
$LiC(CH_3)_2CN$	1	92	2
$LiCH_2CO_2$-tBu	25	64	0
$LiC(CH_3)_2CO_2$-tBu	3	93	0
	49	43	2

The complex (**35**) from 1,3-dimethoxybenzene reacts rapidly with the cyanohydrin acetal anion **36**; quenching with iodine, followed by acid and base treatment, affords exclusively the 1,3,5-isomer (**37**), in 84% yield. This product can be converted to olivetol in an obvious way, establishing the first route to the olivetol substitution pattern via direct addition of carbanions.



35 **36** **37**

The isomeric complex (**38**) from 1,2-dimethoxybenzene reacts in the usual way with $LiCH_2CN$ to give a single product, the 1,2,3-isomer, **39**.[45] The more bulky anion from isobutyronitrile affords both 1,2,3- and 1,2,4-isomers but with an 85 : 13 preference for the 1,2,3-isomer (**40**).

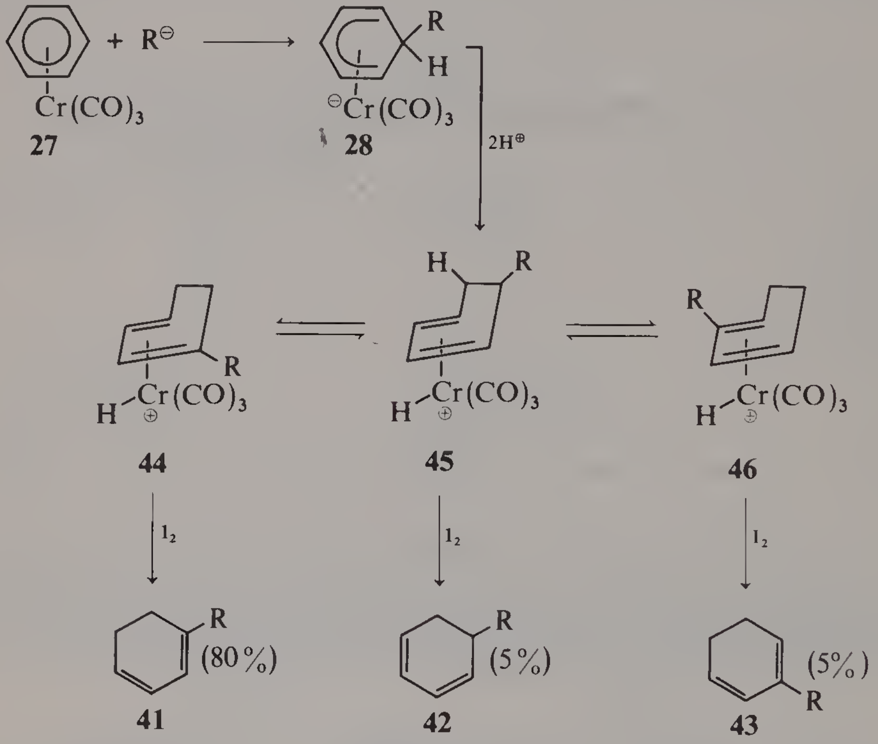


39

R = CH_2CN 48% 0%

R = $C(CN_3)_2CN$ 85% 13%

The η^5-cyclohexadienyl intermediates (e.g., **28**) have another mode of reaction of potential utility for organic synthesis. Addition of excess strong acid (trifluoroacetic) at −78°C, followed by warming to 0°C and removal of chromium with iodine oxidation, produces a mixture of 1,3-cyclohexadienes (**41**–**43**) in the yields indicated (Scheme 2). The mixture of diene isomers (**41**–**43**) may result from isomerization of the olefin units while attached to the metal (in **44**–**46**, scheme ii). The products do not isomerize under the acidic and oxidation conditions. Preliminary experiments suggest that this procedure for converting an arene into an alkyldihydroarene is general whenever the η^5-(alkylcyclohexadienyl) complexes can be obtained.[45,47]

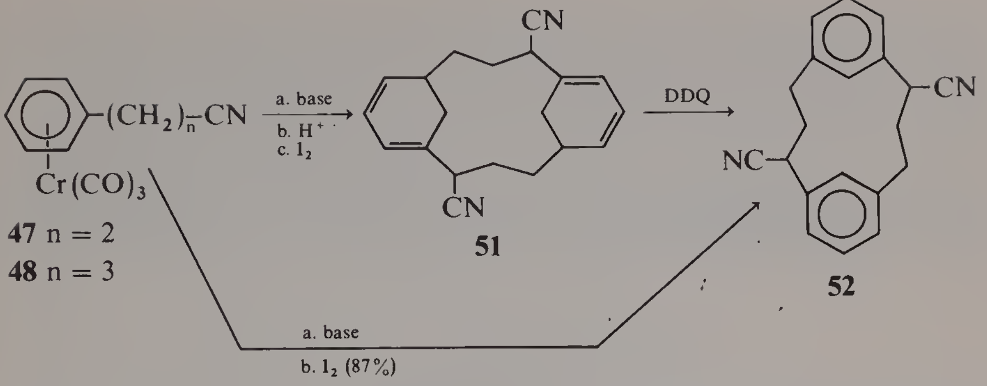


Scheme 2

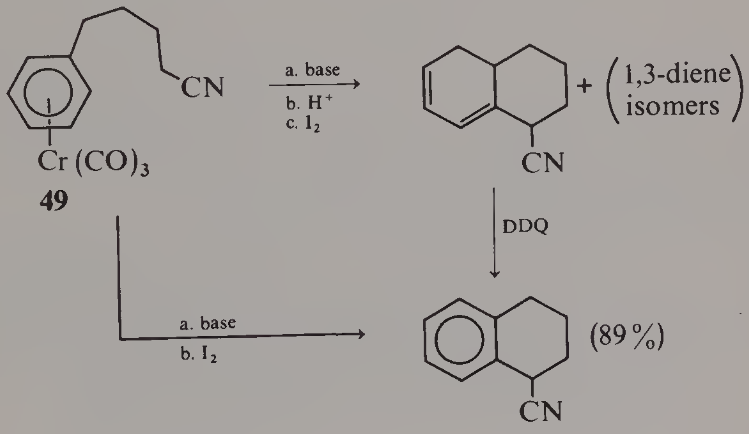
The acid-quenching technique is particularly useful in studies with intramolecular nucleophilic aromatic substitution. A series of arene chromium complexes (**47**–**50**) have been prepared with anion-stabilizing groups on a side chain.[45] Each was treated with lithium diisopropyl amide at −78°C to generate the cyano-stabilized anions and then quenched with excess trifluoroacetic acid, followed by iodine, or quenched directly with excess iodine.[45]

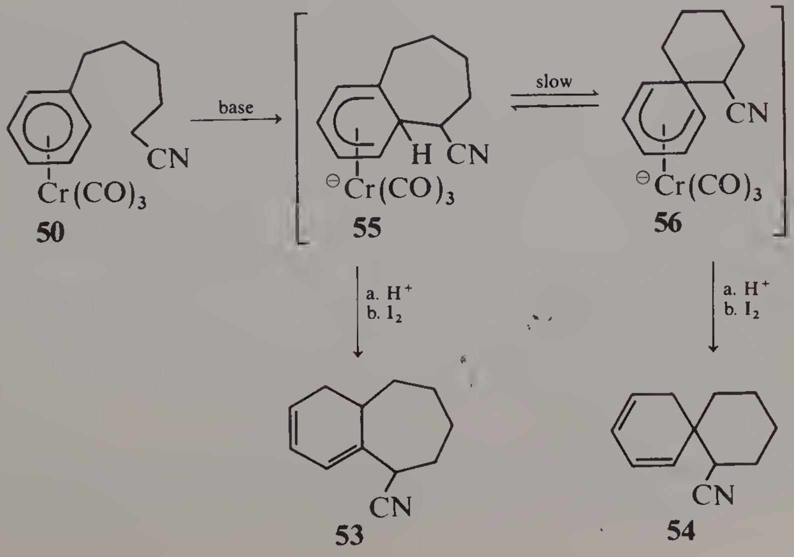
With the C_2 side chain (**47**), only high-molecular-weight products were obtained under a variety of reaction and quenching conditions. The next higher homolog (**48**), under normal concentration conditions (~ 0.1 M), led to the tetrahydro[3.3]-metacyclophane (**51**) with acidic quenching and to the [3.3]metacyclophane (**52**) with oxidative quenching. The tetrahydro derivative (**51**) was dehydrogenated to **52** by use of dechlorodicyanoquinone (DDQ) under forcing conditions.

With the C_4 side chain (**49**), similar procedures lead to fused-ring monomers as the only products obtained. Now, DDQ treatment of the dihydro arene product gives efficient, rapid formation of the arene.



The next higher homolog (**50**) gives evidence of kinetic versus thermodynamic control over the mixture of products. After treatment with base for only 0.5 hr at −78°C, acidic quenching produces an 80 : 20 mixture of fused-ring (**53**) to spiro-ring (**54**) isomers. At longer times before quenching, the spirocycle (**54**) becomes more abundant, until, after 24 hr at 0°C, the product mixture is 2 : 98 for **53** : **54**. Presumably, the fused-ring intermediate (**55**) forms first but slowly rearranges to the spirocyclic intermediate (**56**).





In summary, methods are now available by use of η^6-arenetricarbonylchromium(0) complexes that allow substitution for aryl halogen or hydrogen by carbon nucleophiles under mild conditions. Overall comparison of arene-metal species establishes that the cationic complexes of iron and manganese offer much stronger activation of the arene ligand relative to neutral arene-chromium complexes; nucleophilic addition occurs with a wide variety of carbanions and heteroatomic anions. The challenge now is to work out efficient general syntheses of the cation-arene complexes and to make the nucleophilic aromatic substitution reactions catalytic in the metal.

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MECHANISM OF OXIDATIVE ADDITION OF ORGANIC HALIDES TO GROUP-VIII TRANSITION METAL COMPLEXES*

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INTRODUCTION

Organic transformations that are catalyzed by transition metals take place by a series of steps, producing reactive intermediates, at least one of which contains a carbon-metal σ bond. One important reaction by which an intermediate that contains a carbon—metal σ bond is formed is the oxidative addition reaction, and the most versatile synthetic method is through cleavage of a carbon—halogen bond in alkyl, aryl, vinyl, and acyl halides.[1] In these reactions, the increase in the oxidation state of the metal is usually accompanied by an increase in the coordination number, and the propensity to undergo oxidative addition is characteristic of group-VIII metal complexes of the d^8 and d^{10} electronic configurations. The reactivity of group-VIII metals toward oxidative addition increases from right to left in the periodic table, down in a given group, and with decreasing initial oxidation number; the mechanism of the reaction also changes. The ligands on the metal are of special importance, because with the same metal, different dissociation constants, σ-donor or π-acceptor properties, geometries, and sizes will affect both the reactivity and the reaction mechanism. The following text discusses the stereochemistry and mechanisms of the oxidative addition reactions of benzyl halides to palladium(0), nickel(0), and rhodium(I) complexes and the conditions necessary for development of these reactions to useful, catalytic, synthetic organic transformations.

STEREOCHEMISTRY

The stereochemistry of the oxidative addition reaction of optically active benzyl halides to various phosphine palladium(0) complexes was determined by a reaction sequence in which only the oxidative addition stereochemistry was unknown. The remaining steps in the sequence either did not affect the active center or had a known stereochemistry. Thus, the oxidative addition reaction was followed by carbonylation, in which the carbon monoxide "insertion" into the carbon—palladium σ bond is known[2,3] to proceed with *retention* of configuration at carbon, and the decomposition to ester was completed by the solvent, a reaction that does not affect the asymmetric center (SCHEME 1). Because the absolute configuration and purity of the alkyl halides and the ester products could be determined from their optical rotations, the stereochemistry of the oxidative addition reaction could be assessed.

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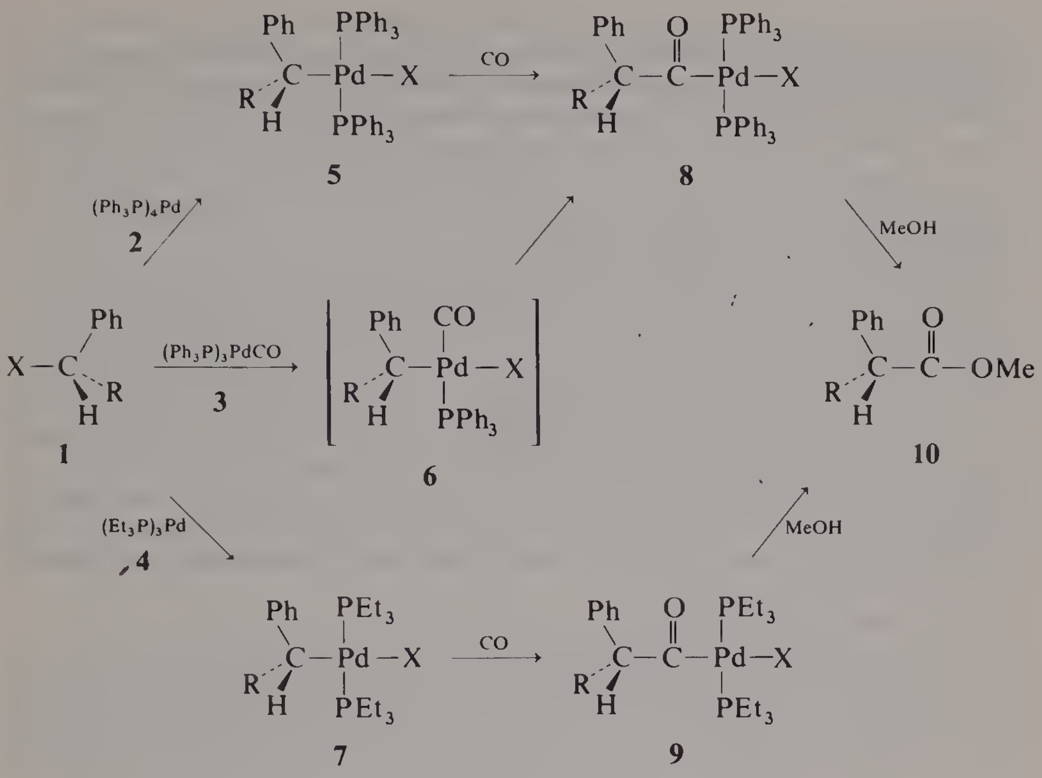


SCHEME 1

The reaction proceeds with predominate *inversion* of configuration at carbon.[4–9] In some examples, 100% net inversion of configuration occurs, whereas in one instance, only 30% enantiomeric excess of one oxidative addition product was obtained (TABLE 1).

Complexes **5** and **7** (R = D) could be isolated as stable complexes, because they do not contain hydrogen β to palladium, and optical rotations of the more soluble complexes **7** and **9** (X = Cl or Br) could be observed. Because of the tendency for **5** (R = CH_3) to undergo β-elimination, it could not be isolated from the reaction but was converted directly to **8**, either by use of carbonyl complex **3** or by the presence of carbon monoxide during the oxidative addition.

TABLE 1
OXIDATIVE ADDITION OF BENZYL HALIDES TO PALLADIUM(0)

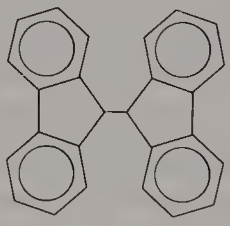
Pd(0) Complex	R	*X*	Net Inversion	Relative Rate
$(Et_3P)_3Pd$ (**4**)	D	Br	30*	10^3
	D	Cl	72	5×10^2
$(Ph_3P)_4Pd$ (**2**)	D	Cl	74	3
$(Ph_3P)_4Pd$ (**2**)†	D	Cl	100	
$(Ph_3P)_3PdCO$ (**3**)	D	Cl	100	2
$(Ph_3P)_4Pd$ (**2**)†	CH_3	Br	90	1.5
$(Ph_3P)_3PdCO$ (**3**)	CH_3	Br	90	1
$(Ph_3P)_4Pd$ (**2**)	CF_3	Cl	< 10	very slow

* Racemic coupling product, PhCHDCHDPh, also formed.
† Carbon monoxide present during the oxidative addition reaction.

It is apparent that tetrakis(triphenylphosphine)palladium(0) (**2**) and carbonyltris(triphenylphosphine)palladium(0) (**3**) behave differently than tris(triethylphosphine)palladium(0) (**4**). Although the net inversion of configuration in oxidative addition could be improved either by the use of the carbonyl complex (**3**) or by completing the reaction in the presence of carbon monoxide, the optical yields could not be similarly improved in the additions to **4**, because this complex reacts rapidly with carbon monoxide to give inert carbonyltris(triethylphosphine)palladium(0) and other carbonylated palladium(0) complexes.

The loss of stereochemistry in the oxidative addition of **1** (R = D) to **2** can be accounted for, in part, by the partial racemization of **1** (R = D) under the reaction conditions employed, because **1** (R = D) recovered from an oxidative addition reaction suffered a 10% loss of its optical activity. Over longer periods of time, the reaction of excess **1** with **2** led to complete racemization of **1**. However, the optical activity of **7** was unchanged under the reaction conditions. In all of these reactions, no CIDNP could be observed, and in the reactions of **2** with **1**, the presence of radicals could not be detected by chemical means. Thus, a nucleophilic exchange process that involves **5** (R = D) and **2** is a plausible explanation for racemization. Rapid transformation of alkyl complex **5** to acyl complex **8** would suppress racemization.

In the absence of carbon monoxide, complex **5** (R = CH_3) decomposes to styrene, ethylbenzene, and bis(triphenylphosphine)palladium bromide. The reaction of 9-bromofluorene or ethyl α-bromophenylacetate with **2** at 0°C yields the coupled products **11** and **12**, respectively, and bis(triphenylphosphine)palladium bromide. In the latter case, a mixture of *erythro*- and *threo*-2,3-diphenylsuccinate is obtained. Although higher temperatures are usually required for the coupling reaction, the greater reactivity of 9-bromofluorene and ethyl α-bromophenylacetate accounts for the lower reaction temperatures. For example, **5**(R = H; X = Cl) undergoes a reaction with benzyl chloride at 80°C to give bibenzyl.[8] In all of these reactions, no CIDNP could be observed, but chemical tests indicated the presence of radicals.



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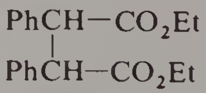
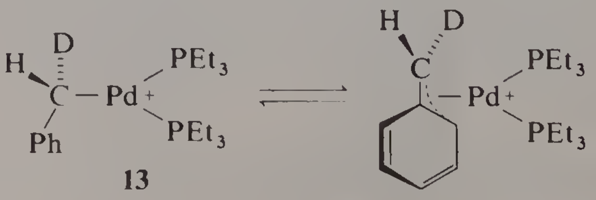


$$\begin{array}{l}\mathrm{PhCH{-}CO_2Et}\\ \quad | \\ \mathrm{PhCH{-}CO_2Et}\end{array}$$

12

The oxidative addition product (**7**) is configurationally stable in solution over long periods of time, and its optical activity is unaffected by the presence of **1**, **4**, or triethylbenzylphosphonium chloride, another product present when **1** (R = D; X = Cl) reacts with **4**. Thus, racemization in this reaction cannot be attributed to a nucleophilic exchange between **4** and **7**. In addition, the π-benzyl complex (**14**) maintains its configurational integrity in solution. Even though CIDNP could not

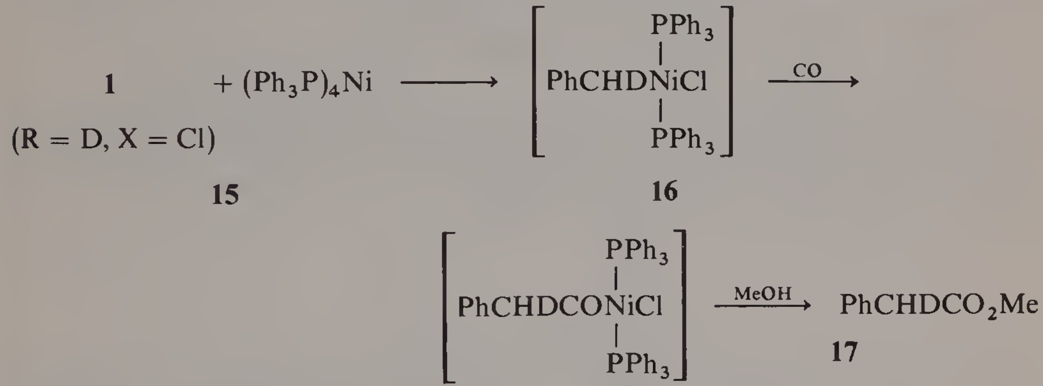


13 **14**

be observed from the reaction of **1** ($R = H$; $X = Cl$ or Br), the possibility that racemization is occurring either by an oxidative addition reaction that involves a benzyl radical or by the dissociation of the oxidative product **7** into a radical pair, followed by rotation of the benzyl group, cannot be excluded. Only in the reaction of **7** ($R = D$; $X = Br$) with **4** is any coupling product, racemic dideuteriobibenzyl, obtained.

The inversion of configuration at carbon, the order of reactivity [$PhCH_2Br > PhCH_2Cl > PhCHCH_3Br > PhCHCH_3Cl > PhCHCF_3Cl$ and $(Et_3P)_3Pd > (Ph_3P)_4Pd > (Ph_3P)_3PdCO$], and the inability to detect free radicals during the oxidative addition reaction of the optically active benzyl halides clearly are in favor of a nucleophilic displacement mechanism. Radical species probably particpate only during the decomposition of the oxidative addition product, and, depending on the characteristics of the alkyl group of the organic halide, alternative pathways for the decomposition of the oxidative adduct are possible.

Application of the same stereochemical test to the reaction of optically active α-benzyl chloride (**1**, $R = D$; $X = Cl$) to tetrakis(triphenylphosphine)nickel(0) (**15**) resulted in racemic products.[10] The nickel(II) σ-bonded complex (**16**) was formed immediately at low temperature (−60°C); the addition of carbon monoxide, followed



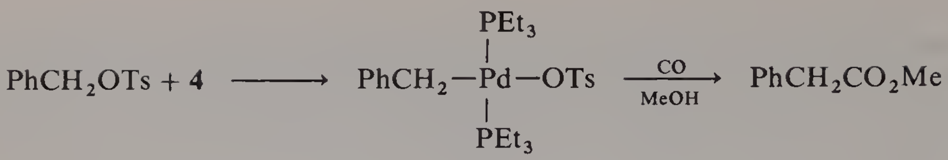
$$\underset{(R = D, X = Cl)}{\mathbf{1}} + \underset{\mathbf{15}}{(Ph_3P)_4Ni} \longrightarrow \underset{\mathbf{16}}{\left[PhCHD\overset{PPh_3}{\underset{PPh_3}{Ni}}Cl \right]} \xrightarrow{CO}$$

$$\left[PhCHDCO\overset{PPh_3}{\underset{PPh_3}{Ni}}Cl \right] \xrightarrow{MeOH} \underset{\mathbf{17}}{PhCHDCO_2Me}$$

by the addition of methanol, gave the ester (**17**). The intermediate σ-bonded complex is unstable and cannot be isolated. The reaction cannot be performed in the presence of carbon monoxide, because complex **15** reacts to form nickel carbonyls (which are unreactive in oxidative addition reactions) faster than it reacts with **1**.

SYNTHETIC UTILITY

The oxidative addition-carbonylation sequence is an attractive method for the synthesis of a variety of carboxylic acid derivatives, because it occurs at low temperatures and is stereospecific. The difference in the behavior of various group-VIII metal complexes and the alkyl groups places numerous limitations on the syntheses, however. The utilization of halides subject to β-elimination can be realized if oxidative addition is conducted in the presence of carbon monoxide. The relatively low reactivity of alkyl halides, other than benzyl halides, can be overcome by higher reaction temperatures, probably at the expense of optical yield, or by the introduction of better leaving groups and more reactive metal complexes. The oxidative addition reaction of benzyl tosylate to tris(triethylphosphine)palladium(0) occurs rapidly to give **18**, which can be carbonylated to yield the ester. Certainly tosylates are more adaptable to the synthesis of asymmetric carboxylic acid derivatives because of the ease of their preparation from the resolved or naturally occurring chiral alcohol.



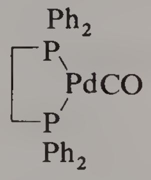
$$PhCH_2OTs + 4 \longrightarrow PhCH_2{-}\overset{\displaystyle PEt_3}{\underset{\displaystyle PEt_3}{Pd}}{-}OTs \xrightarrow[MeOH]{CO} PhCH_2CO_2Me$$

18

The ester synthesis would be especially useful if it could be applied to an organic substrate stereospecifically under strictly catalytic conditions. Because the decomposition of the acyl-palladium complexes regenerates palladium(0), the reaction does have the potential for a catalytic reaction, provided that a base is present to remove halogen acid product. A catalytic turnover of 20 can be obtained with tetrakis(triphenylphosphine)palladium(0) (**2**) when a base is present. The low turnover is a result of a disproportionation reaction of bis(triphenylphosphine)palladium(0),

$$\begin{array}{rcl}
PhCH_2Cl + PdL_4 & \longrightarrow & PhCH_2PdL_3Cl + 2L \\
PhCH_2PdL_2Cl + CO & \longrightarrow & PhCH_2COPdL_2Cl \\
PhCH_2COPdL_2Cl + MeOH & \longrightarrow & PhCH_2CO_2Me + HCl + PdL_2 \\
PdL_2 + 2L & \longrightarrow & PdL_4 \\
HCl + B & \longrightarrow & BH^+Cl^- \\
\hline
PhCH_2Cl + CO + MeOH + B & \xrightarrow{PdL_4} & PhCH_2CO_2Me + BH^+Cl^-
\end{array}$$

producing metallic palladium. To avoid this reaction, the coordinatively unsaturated carbonylethylenebis(diphenylphosphine)palladium(0) catalyst (**19**) was introduced, resulting in a 40-fold turnover. In this case, the bisligated palladium(0) species (**20**) does not undergo disproportionation as readily.



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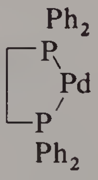

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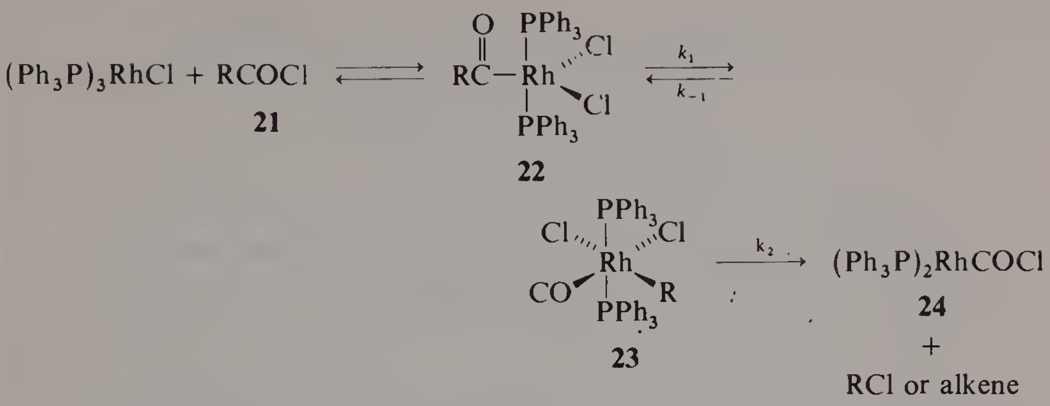
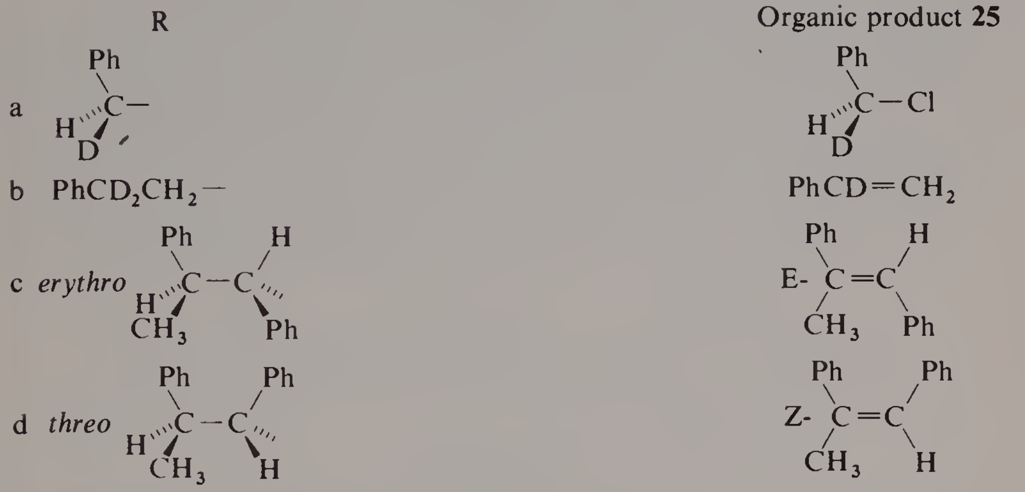
Reductive Elimination

The decarbonylation of acid chlorides with chlorotris(triphenylphosphine)-rhodium(I) yields alkyl chlorides or alkenes and hydrogen chloride, depending on the presence of a β-hydrogen in the acid chloride and, therefore, on the carbon β to the carbon—rhodium σ bond in the reductive elimination step.[11–14] The reaction proceeds through a series of intermediate complexes, **22** and **23**, each of which can be isolated. When R is benzyl, $k_1/k_{-1} \simeq 7 \times 10^{-2}$, and $k_2 \simeq k_{-1}$; when R is 2-phenylethyl, approximately the same relative rates are observed. Decarbonylation of **21b** showed a primary isotope effect of about 7; carbonyl intermediate **23** could be detected but not isolated. Decarbonylations of **21c** and **21d** are stereospecific, with overall 100% *cis*-elimination. These results are consistent with the concept of an acyl-alkyl rearrangement (**22** → **23**), with retention of configuration at carbon, followed by a *cis*-β-hydride elimination (**23** → **25**). This mechanism is supported by the observed retention of configuration at carbon in the decarbonylation of aldehydes with rhodium and by the fact that acyl-alkyl rearrangements that involve other group-VIII metals proceed with retention and that metal hydride elimination is *cis*.





Because of the large primary isotope effect, this mechanism is somewhat uncomfortable, and consequently an alternative, a concerted elimination (**22** → **25** directly), had been suggested.[14]

Somewhat surprisingly, *S*-α-deuteriophenylacetyl chloride (**21a**) underwent decarbonylation to *S*-benzyl-α-*d*-chloride (**25a**) with 20–27% net *retention* of configuration at carbon. If the acyl-alkyl rearrangement step (**22** → **23**) does, indeed, proceed with retention of configuration at carbon, the *reductive elimination step* (**23** → **25**) also occurs *with retention of configuration at carbon.* The same stereochemistry has been observed in the decarbonylation of aldehydes with chlorotris(triphenylphosphine)rhodium(I). The reverse reaction, oxidative addition, should also proceed (microscopic reversibility) with retention of configuration at carbon, although this hypothesis is difficult to confirm, because benzyl chloride will not oxidatively add to **24**. These results are somewhat perturbing because they disagree with results obtained in the oxidative addition reactions of palladium(0). Nevertheless, the reaction provides a useful stereospecific method for the conversion of acids to alkenes.

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EXAMPLES OF THE USE OF CHROMIUM TRICARBONYL—ARENE COMPLEXES IN ORGANIC SYNTHESIS

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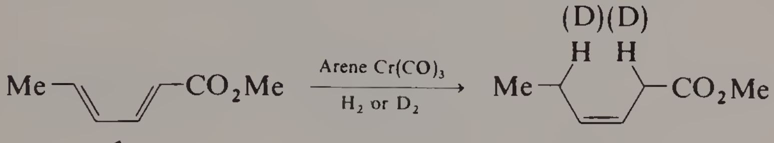
Arene complexes of transition metals have recently been shown to be useful catalysts, reagents, and intermediates in organic synthesis. Catalytic, but not stoichiometric, applications of these complexes have been extensively reviewed.[1] A typical example of the catalytic behavior of π-arene chromium tricarbonyl derivatives is the homogeneous regioselective 1,4-hydrogenation of dienes (**1**) to *cis*-monoenes(**2**).[2] This reaction is of particular interest in view of the high stereospecificity of the products (Scheme I). Furthermore, the readily available and air-stable naphthalene-chromium tricarbonyl complex allows hydrogenations in coordinating solvents at ambient temperatures and pressures.[3]

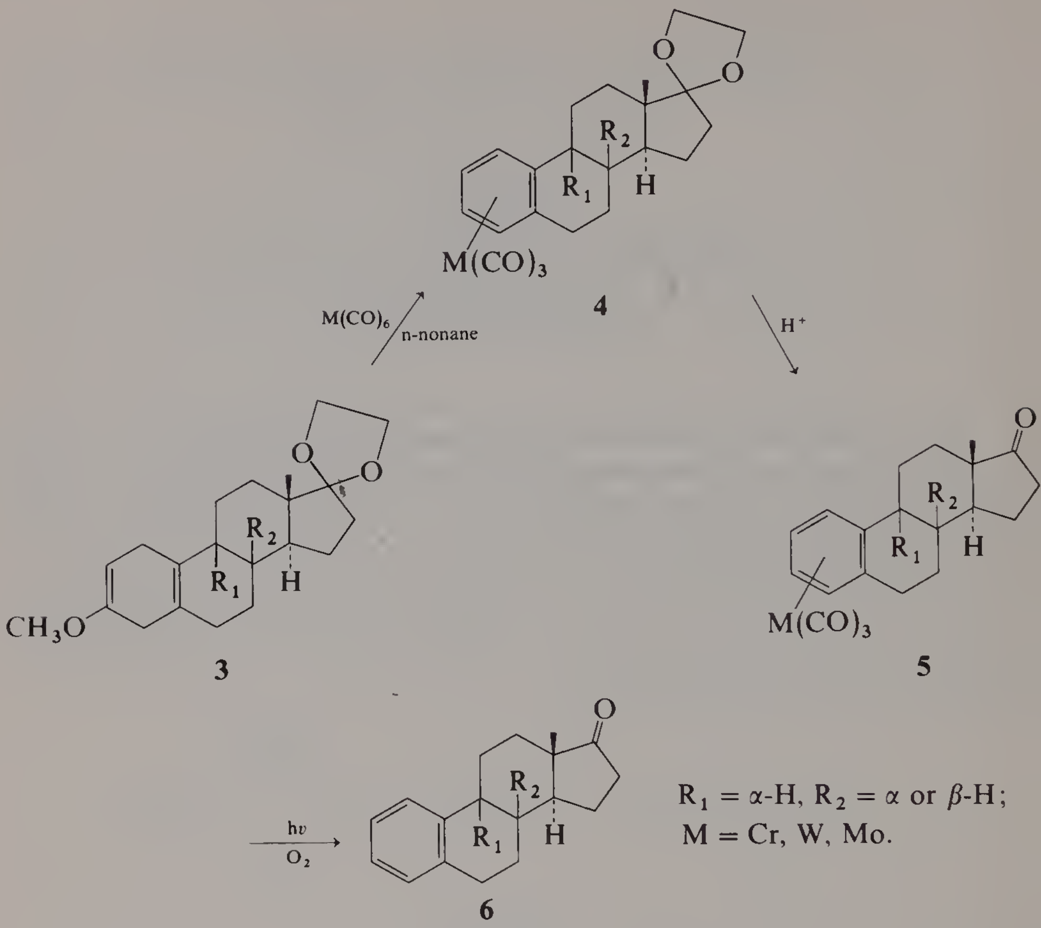


1 **2**

Scheme I

However, the stoichiometric reactions of arene complexes have been neglected so far; this aspect of such complexes will be emphasized here. One of the first examples of arene complexes utilized in stoichiometric synthesis was reported by Birch *et al.* in 1965.[4] The aromatization, which involves loss of a methanol residue, on condensation of 1-methoxycyclohexa-1,4-dienes with $M(CO)_6$ (M = Cr, Mo, W), has been extended to steroid compounds (Scheme II). In particular, several steroids in which ring A possesses a 3-methoxy-2,5-diene structure (**3**) may be converted into aromatic steroids (**6**) with an overall yield of 70%.[5] The intermediates, such as **5**, may be decomplexed by the combined action of light and air.

Similarly, in 1970, Helling and Braitsch[6] reported a method of arene synthesis that involved nucleophilic attack on hydrogen in an electron-rich aromatic nucleus via a cationic iron intermediate (Scheme III). $(Mesitylene)_2Fe(PF_6)_2$(**7**), readily available from ferrous chloride and mesitylene, reacts with phenyl, *tert*-butyl, and vinyllithium in an *exo* fashion to give either compound **8** or the pseudoferrocene derivative (**9**), according to the stoichiometry of the reaction. Thermal or oxidative decomplexation of **8** and **9** occurs with loss of hydrogen, giving, in the first case, an equimolar mixture of mesitylene and substituted mesitylene. This method, which makes use of temporary activation of the arene substrate, appears to be the best available for the synthesis of this type of compound (e.g., for **9a**, the overall yield of 35% with phenylmesitylene, with all steps included, is much greater than the yield obtained with methyl magnesium bromide, bromobenzene, and cobaltous chloride, which does not exceed 15%[7]).



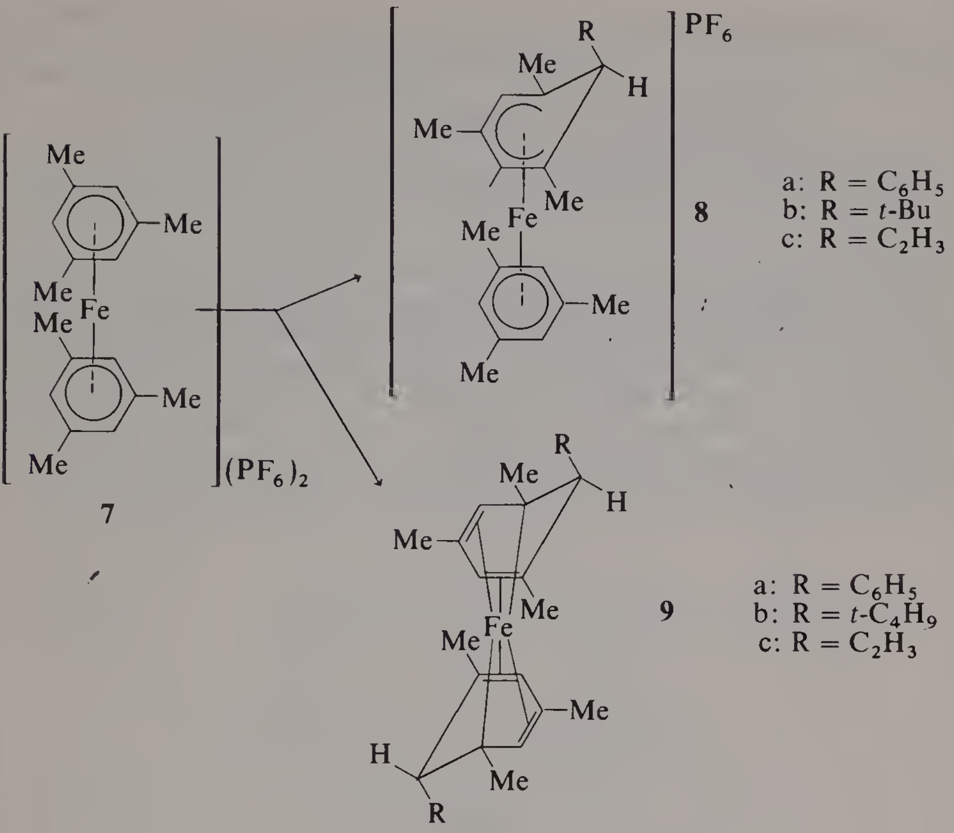
$R_1 = \alpha$-H, $R_2 = \alpha$ or β-H;
M = Cr, W, Mo.

SCHEME II

From the above-mentioned examples, it appears that the general procedure for these stoichiometric syntheses usually consists of three stages: complexation of the aromatic moiety by a transition metal; utilization of the alteration in steric and electronic factors, or in the symmetry of the ligand, to effect the desired reaction; and destruction of the metal—ligand bond and isolation of the organic derivative.

A certain number of prerequisites must be met if this scheme is to be useful in synthesis. The metal used must be the least expensive possible (e.g., iron or chromium). Complexation must be facile and as quantitative as possible and must give an organometallic derivative that is easy to manipulate. Finally, the methods used for decomplexation must be mild but quantitative. (Benzene)chromium tricarbonyl (**10**, benchrotrene) and its derivatives provide an example where all of the above conditions are satisfied, and, indeed, such complexes have found great use in organic synthesis. They therefore warrant more detailed study, and this discussion will be limited to examples that use this complex and its derivatives.

Complexation reactions are, in general, well known and require no further comment.[8] Except for arenes substituted by a nitro group, a strong electron-withdrawing group, it may be considered that each substituted arene compound has a corresponding chromium tricarbonyl derivative.

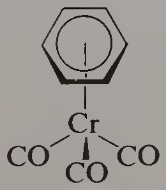


Scheme III

Decomplexation reactions, the last step in Scheme III, are much more commonly found in the literature. Mild oxidation of the metal is generally employed, and several methods have been developed in the last few years for organometallic complexes.

Chemical decomplexation may be accomplished with ceric salts,[9,10] dilute potassium permanganate,[6] ferric chloride,[11] silver salts,[12] halogens,[13,14] oxygenated water,[15] peracids,[15] *N*-oxides,[16] and cupric chloride[17]; photochemical decomplexation may be achieved in the presence of air.[18] In the particular case of benchrotrene compounds, ceric salts,[10] iodine,[14] and photochemical decomplexation[18] have been used successfully with nearly quantitative yields.

When the ligand is unstable under oxidizing conditions or when syntheses that involve ligand transfer between organometallic species are being performed, it is necessary to liberate the organic ligand under nonoxidizing conditions. As dis-



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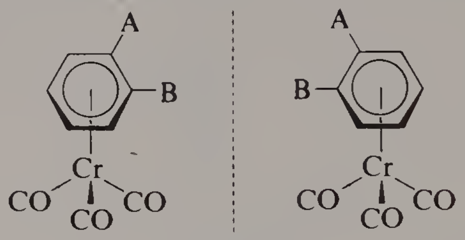
placing agents, arene ligands may be used in the series of (cycloheptatriene)-chromium tricarbonyl,[19] dihydropyridine chromium tricarbonyl,[20] or α-alcohol arene chromium tricarbonyl by creation of a carbonium ion α to the complexed ring.[21] In the last case, the metal-arene bond is sufficiently weakened by this procedure to allow ligand transfer to occur under mild conditions.

However, a ready decomplexation becomes an advantage only if the modification due to the temporary complexation induces a radical alteration of the reactivity of the ligand.

For the chromium tricarbonyl group, the modifications of the arene ligand are both chemical and stereochemical in nature. The first stereochemical consequence of complexation is shown in Scheme IV. Arene derivatives that contain different *ortho* or *meta* substituents are chiral, and there are numerous examples of the resolution of benchrotrene derivatives into optical isomers.[27,51] Another factor related to the three-dimensional structure of the coordinated molecule is the possibility of two modes of attack (*endo* or *exo*) for the reagent, whether from the same or the opposite side of the chromium tricarbonyl unit, respectively.



Scheme IV

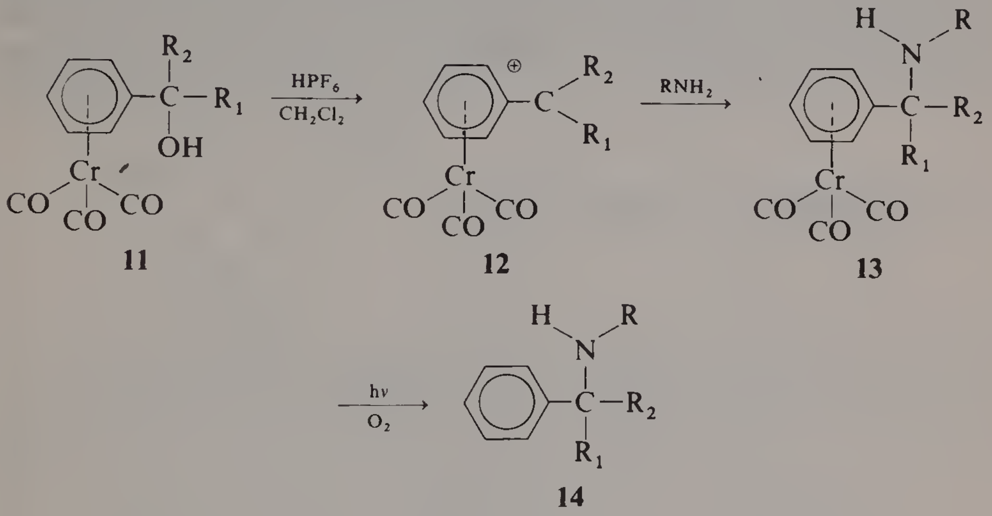
The intimate nature of the arene—chromium tricarbonyl bond has been the subject of much debate in the last few years. On the basis of arguments taken from studies of reactivity,[23–28] measurements of dissociation constants[29,30] and dipole moments,[31] molecular orbital calculations,[32–34] and nuclear magnetic resonance (nmr) spectra,[35–38] a strong electron-attracting character, compatible with the presence of a *para*-nitro group, has been postulated for the complexed chromium tricarbonyl moiety. In contrast, it has been shown by other means that the transmission of resonance effects in arene complexes is unchanged when compared with that of the free ligand,[39–42] whereas the great stability of carbonium ions α to the complexed moiety has been explained in terms of the electron-donating property of the chromium tricarbonyl group.[43,44] This apparent contradiction has been reconciled by Gubin *et al.*[45] These different effects may be explained by the postulate that complexation by chromium tricarbonyl results in a net diminution in σ-electron density on the aromatic skeleton, while little perturbation of the π-electron density of the ring occurs. A simple hypothetical example would be an analogy between the effects of the (benzene)chromium tricarbonyl substituent and those of the halogen group. In a manner analogous to the halogens, the (benzene)chromium tricarbonyl (BCT) group provides a strong attractive inductive effect and a resonance effect, the magnitude of which greatly depends on the nature of the reactive center.

Thus, complexation results in a modification of the reactivity of both the ring itself and its attached substituents. Examples of changes in properties, above all those useful in organic synthesis, will now be presented.

USE OF CARBONYL CHROMIUM GROUPS FOR SELECTIVE ACTIVATION OF ARENE SUBSTITUENTS

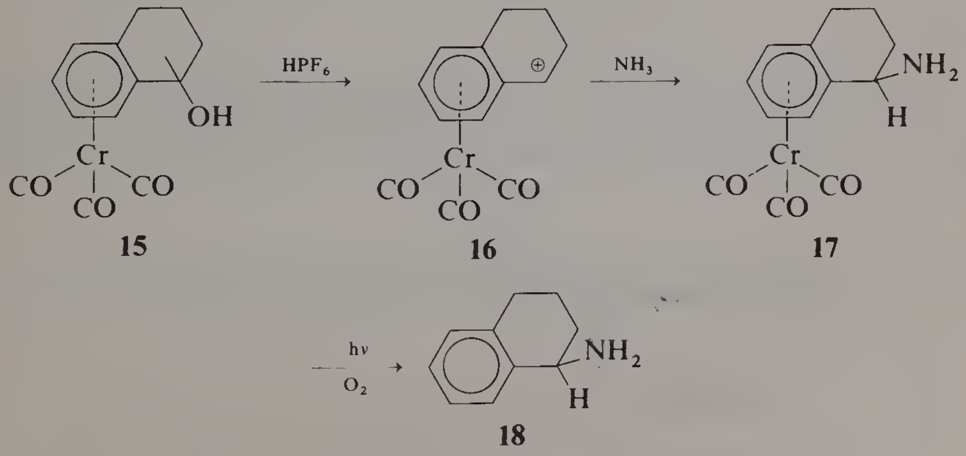
Consequences of Stabilization of α-Carbonium Ions

Synthetic applications of the extraordinary stabilization of α-carbonium ions ($pK_{R^+}BCTCH_2{}^+ = -11.8$ vs $pK_{R^+}C_6H_5CH_2{}^+ < -17.3$)[46] have not yet been investigated thoroughly. Nevertheless, as an example, SCHEME V outlines the facile preparation of amines (yields ≃ 70–80%) from primary, secondary, or tertiary benchrotrene alcohols. Carbonium ions are generated at low temperature (−40°C) by anhydrous HPF_6. The ions are stable enough to react with gaseous ammonia, amines, or alcohols (to yield ethers) prior to decomposition.



SCHEME V

The stereochemistry of the reaction may be seen in SCHEME VI. Starting from optically active *endo*-1-tetralol tricarbonyl chromium (**15**), addition of ammonia gives, stereospecifically, the "*exo*" complex (**17**), while decomplexation produces the free amine (**18**) of known absolute configuration.

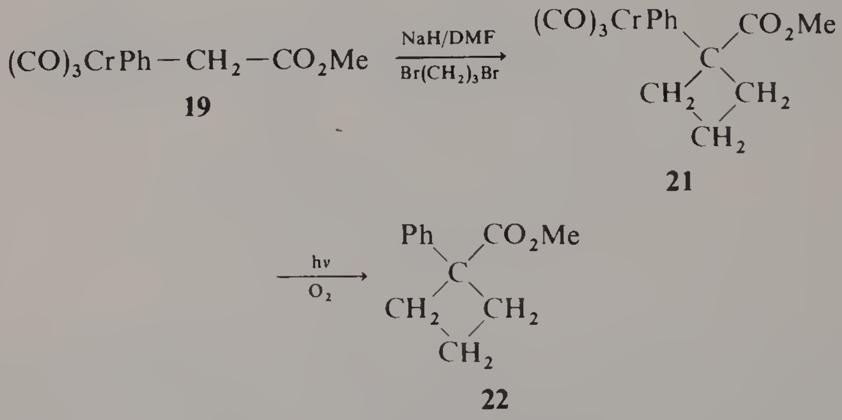


SCHEME VI

Action of Alkylating Reagents

Of the two contrasting properties of the chromium tricarbonyl group, namely, donor or acceptor activity, with respect to an aromatic side chain, the inductive acceptor effect has been more widely explored with regard to its synthetic consequences. In particular, temporary complexation of an arene substrate increases its susceptibility to proton abstraction from a carbon chain. This increased tendency toward anion formation thus permits alkylation of substrates whose free ligands have little or no reactivity.

Consider, for example, the remarkable difference in reactivity toward alkylating agents between free and complexed methyl phenylacetate.[47] Whereas the free ligand is practically inert to methyl iodide and sodium hydride at 15°C in $HCONMe_2$, the tricarbonyl chromium complex (**19**) rapidly gives $Cr(CO)_3PhMe_2CO_2Me$ (**20**, 97%) under these conditions. Small alicyclic compounds may also be formed by double attack at the α position of **19**. The reaction sequence described below has been employed at an overall yield of 87%, including photochemical decomplexation in air.

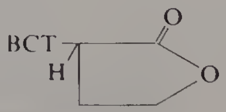
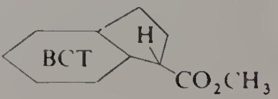


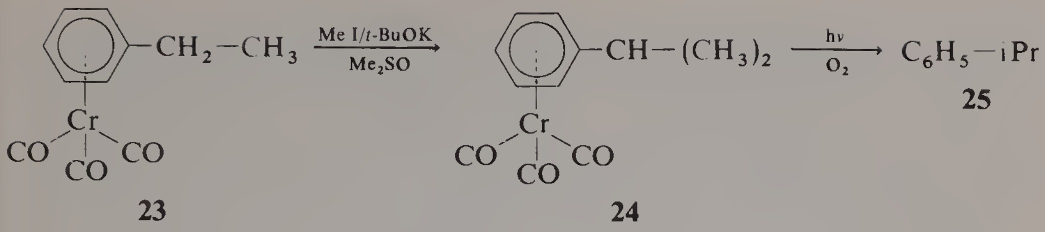
SCHEME VII

Boudeville and des Abbayes[48] recently used this type of arylacetic ester alkylation for synthesis of pharmacologically important compounds. In all of the models employed, it was possible to increase temporarily the acidity of the hydrogen atom α to the ester function by the use of a complexation procedure (TABLE 1). The yields were quantitative.

In the preceding examples, the presence of electron-withdrawing ester groups also favors the reaction; therefore, the participation of the chromium tricarbonyl group must not be the only consideration. Under similar conditions, however,

TABLE 1

RX	CH_3I, $C_6H_5CH_2Br$, $CH_2{=}CH{-}CH_2Br$, $CH{\equiv}C{-}CH_2Br$, $BrCH_2CO_2CH_3$
Substrates	BCT $CH(CH_3)CO_2CH_3$,  BCT O H  BCT H CO_2CH_3



SCHEME VIII

C_6H_5-iPr (**25**) is obtained (71%), together with *tert*-butylbenzene (8%), from the complex $Cr(CO)_3(PhEt)$ (**23**) by use of methyl iodide and *tert*-butyl potassium oxide in dimethyl sulfoxide (SCHEME VIII).

Previously, under similar conditions, Trahanovsky and Card[10] succeeded, by use of d^6-dimethyl sulfoxide, in deuterating the α-position of the complex $BCTCH_2CH_2C_6H_5$ in less than 15 min.

$$\underset{\mathbf{26}}{\mathrm{BCT{-}CH_2{-}(CH_2)_3{-}\varnothing}} \xrightarrow[\mathrm{d^6DMSO}]{t\text{-BuOK}} \underset{\mathbf{27}}{\mathrm{BCT{-}CD_2{-}(CH_2)_3\varnothing}}$$

$$\xrightarrow{\mathrm{Ce^{IV}}} \underset{\mathbf{28}}{\mathrm{C_6H_5{-}CD_2{-}(CH_2)_3{-}\varnothing}}$$

SCHEME IX

The activating power of the chromium carbonyl group may also be changed by photochemical replacement of one of the carbonyl groups by, for example, carbon sulfide, triphenylphosphine, $P(OPh)_3$ by published methods.[49] Polarographic and pK_a data indicate the following order of activating ability of the $Cr(CO)_2L$ units:

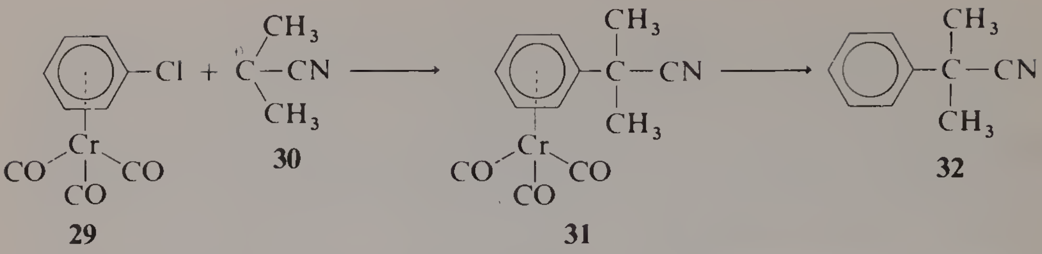
$$Cr(CO)_2CS > Cr(CO)_3 > Cr(CO)_2P(OPh)_3 > Cr(CO)_2P(Ph)_3$$

These different units may be used to increase reactivity, enhance selectivity, or protect the substituents of complexed arene rings with respect to alkylation.[47]

REACTIVITY OF AN AROMATIC MOIETY COMPLEXED BY CHROMIUM TRICARBONYL

While theory predicts a slight difference in behavior of free and complexed arenes with respect to electrophilic attack, few studies have been devoted to this problem. On the contrary, shortly after the preparation of the first benchrotrene compounds, it was reported that (chlorobenzene)chromium tricarbonyl undergoes rapid nucleophilic substitution with methoxy ion to give (anisole)tricarbonyl chromium.[23, 50–53] This finding led Semmelhack *et al.*[14, 54] to investigate the synthetic applications of the phenylation of carbanions via benchrotrene complexes. The introduction and displacement of activating groups are problems that are not easily solved in organic chemistry. Therefore, methods that involve nucleophilic addition are rarely used for fixation of carbon substituents in synthesis of aromatic natural products. The ease of complexation and displacement of the chromium tricarbonyl group makes it a reagent of choice in such syntheses.

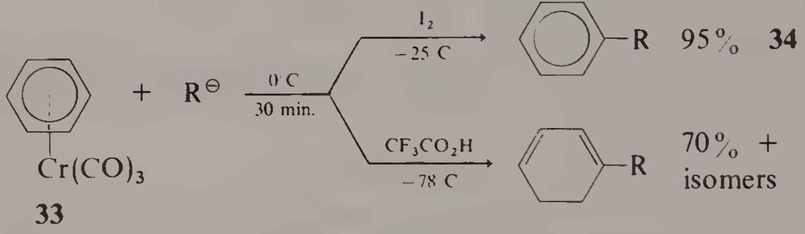
SCHEME X outlines such an approach, showing a very simple case: reaction of the anion of isobutyronitrile (**30**) with chlorobenchrotrene (**29**, 25°C, 20 hr) to



SCHEME X

give the alkylbenchrotrene (**31**) in high purity (95%, 78% yield). Cleavage of the organometallic intermediate is quantitative with iodine in ether at 0°C.

To date, most of the interest in such syntheses has been in the nucleophilic substitution reaction of benchrotrene (**33**) itself to give aromatic products **34** (SCHEME XI).

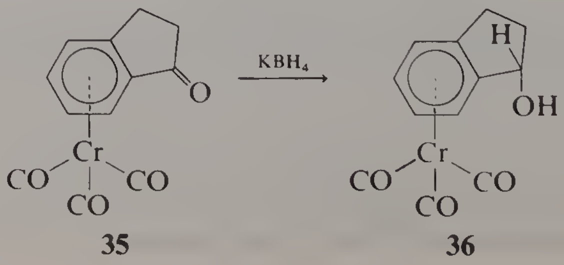


SCHEME XI

This new method of carbanion phenylation would seem to be quite useful, because only mild conditions (0°C) are necessary. Recently, a much improved synthetic method for benchrotrene has been reported.[55] It may also be noted that it is possible to utilize the enolates of primary and secondary esters.

STEREOCHEMICAL CONSEQUENCES OF TRANSITION METAL COMPLEXATION OF AN ARENE

It has previously been stated that attack by nucleophiles on cationic arene complexes occurs stereospecifically in an *exo* fashion. Stereospecificity has been observed in the metal hydride reduction of a carbonyl group situated α to a complexed ring but included in a rigid structure (e.g., indanone, **35**). Regardless of which reducing agent is used, only the *endo* isomer (**36**) is obtained.



This total stereospecificity has been interpreted in several ways. Jackson and Mitchello[56] attribute this phenomenon essentially to steric control by the chromium tricarbonyl group of the direction of attack. These conclusions are based on the fact that reduction of (2-tetralone)chromium tricarbonyl, in which the carbonyl group is more remote from the chromium tricarbonyl group, leads to 5–7% of the alcohol. At the same time, this result may also be interpreted in terms of a partial electronic control of the direction of the attack, because remoteness of the carbonyl group from the 2-position may diminish the electronic influence of the chromium tricarbonyl group. The large dipole moment of this group (5D)[31] seems to suggest that electronic control of attack is at least as important as steric control. In support of this postulate, the reduction of (2-*tert*-butyl-1-indanone)chromium tricarbonyl[57] is equally stereospecific, although an examination of molecular models indicates that the *tert*-butyl group should have a greater steric influence on the ketone function than should the chromium tricarbonyl group.

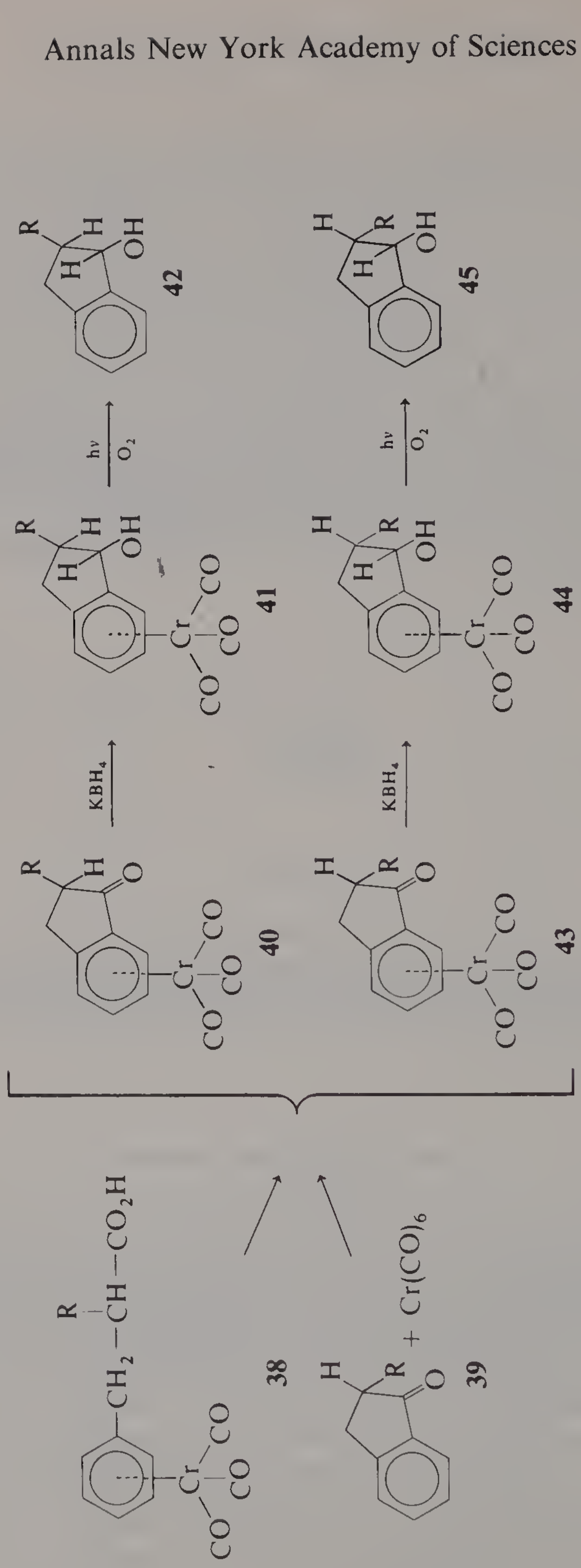
The same argument holds for electrophilic attack of a carbanion created α to the indane carbonyl (**37**):

35 **37**

These properties have been utilized for synthesis of derivatives of indanone and tetralone to obtain compounds with known configurations, both in racemic and in optically active series.

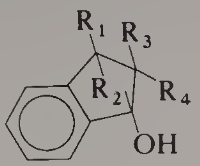
Synthesis of Substituted Indanols

No common route of access exists for the synthesis of *cis*- and *trans*-alkylindanols. Reduction of certain of these ketones by metal hydrides leads to mixtures whose compositions have not been always determined accurately. However, reduction is not stereospecific for indanones regardless of the nature or position of the substituent bonded to the alicyclic ring.[58] The indanols obtained in such reactions always possess the alcohol function in a position *cis* to the chromium tricarbonyl group. Thus, decomplexation leads quantitatively to indanols of well-defined configurations. This procedure has been utilized for synthesis of several indanols substituted in the 2- or 3-position by various alkyl groups. The precursor (indanone)-chromium tricarbonyl is prepared either by cyclization of the corresponding propionic acid derivative (**36**) or by direct complexation. Separation of the two stereoisomers (**40** and **43**) is followed by reduction with potassium borohydride. The pure *cis*- (**45**) or *trans*- (**42**) indanols may be recovered after decomplexation. SCHEME XII summarizes these different steps for the synthesis of the 2-alkyl-substituted indanols. The method leads to overall yields of the order of 60%.



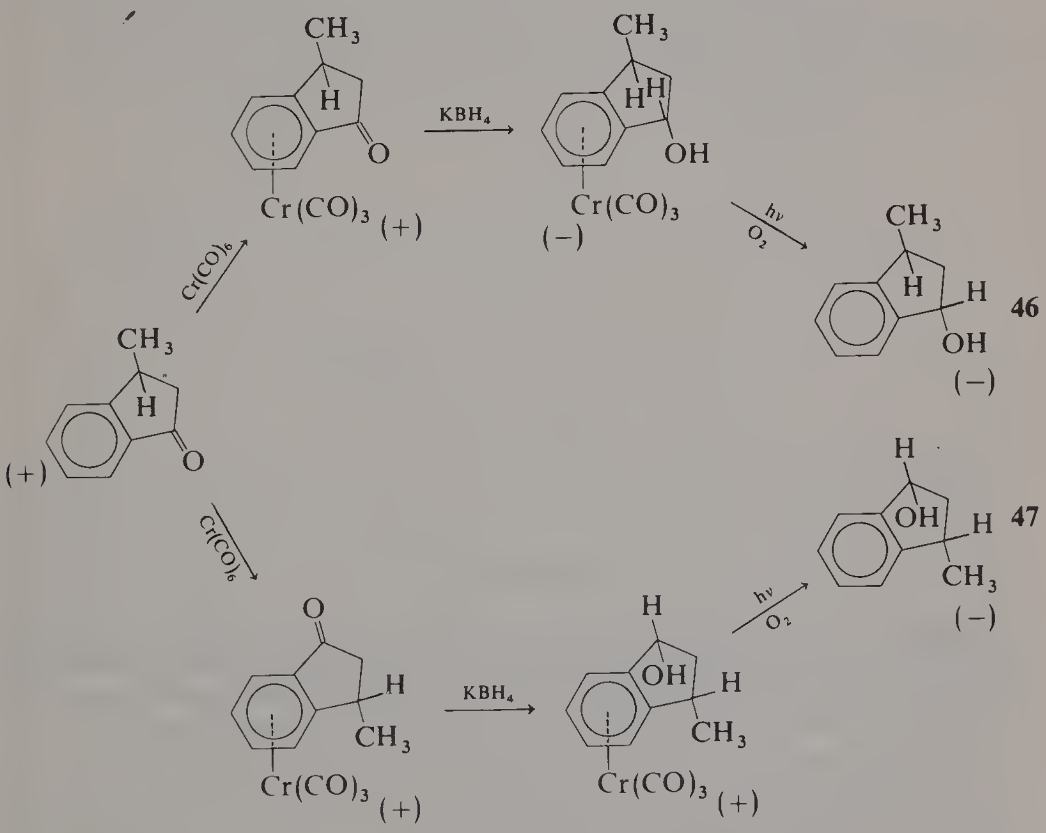
SCHEME XII

These syntheses have been applied to the following cases:



$R_1 = CH_3, C_2H_5, CH(CH_3)_2$ with $R_2 = R_3 = R_4 = H$
$R_2 = CH_3, C_2H_5, CH(CH_3)_2$ with $R_1 = R_3 = R_4 = H$
$R_3 = CH_3, C_2H_5, CH(CH_3)_2, C(CH_3)_3$ with $R_1 = R_2 = R_4 = H$
$R_4 = CH_3, C_2H_5, CH(CH_3)_2, C(CH_3)_3$ with $R_1 = R_2 = R_3 = H$

The preceding methods may be applied not only to the synthesis of racemic indanols but also to that of optically active indanols that have an optical purity of 100%. The first example reported in the literature involved preparation of optically pure 3-methyl-1-indanols (**46** and **47**, Scheme XIII).[18]

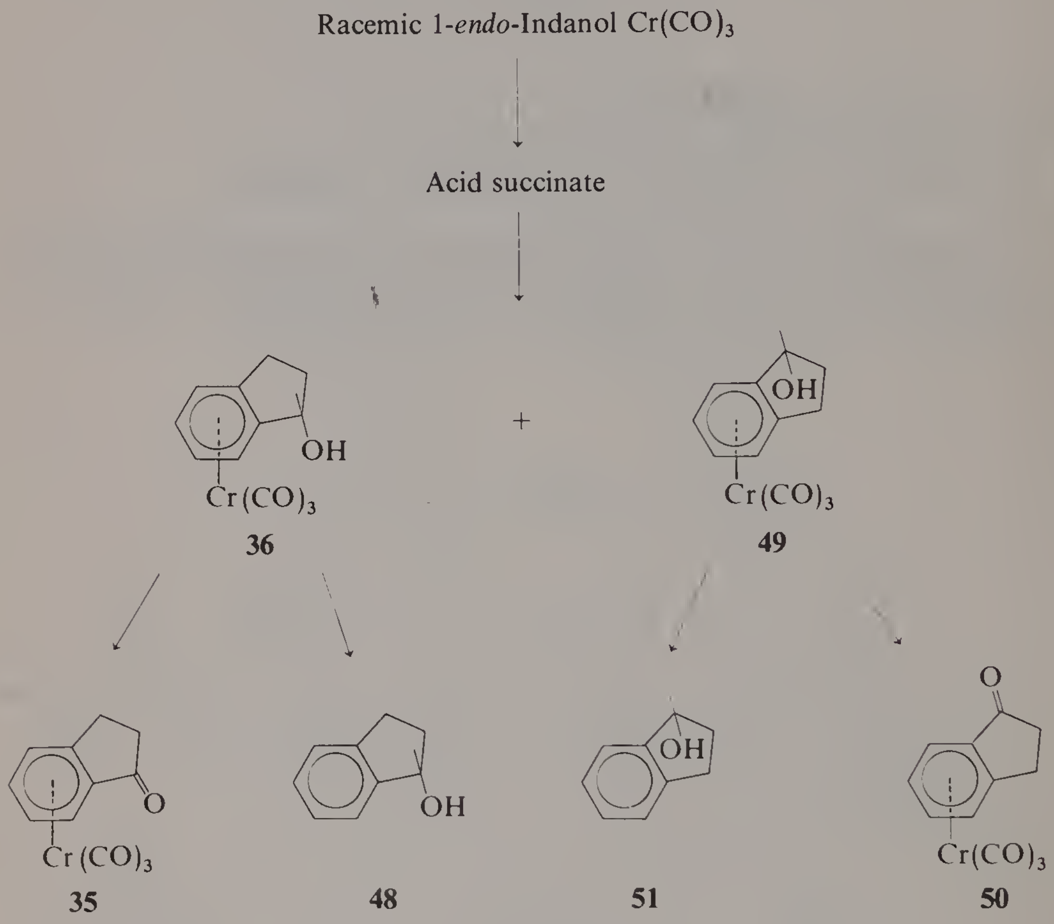


Scheme XIII

Access to Optically Active Indanones and Tetralones

Another method for preparation of optically active 2-alkylindanones has recently been developed[59] and has been extended for obtaining 2-alkyltetralones.

The stereospecificity of electrophilic attack of a carbanion created α to the ketonic group of the (indanone)- or (tetralone)chromium tricarbonyl is again utilized. However, the inherent difficulty in these syntheses is essentially the access to optically active (indanone)- or (tetralone)chromium tricarbonyl complexes. This difficulty may be overcome by use of the method outlined in SCHEME XIV for indanones.

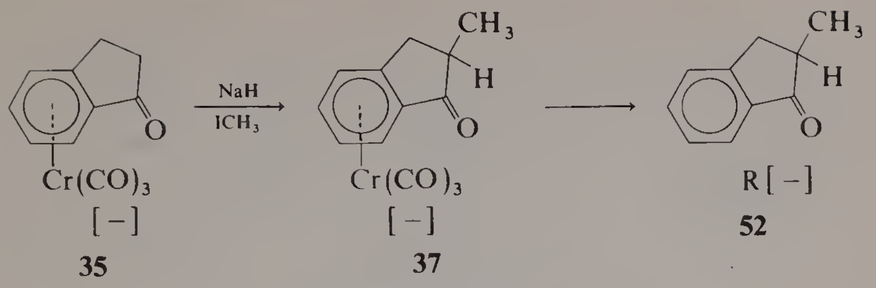


SCHEME XIV

Optically pure 1-indanone is obtained by oxidation of the corresponding 1-*endo*-indanol tricarbonyl chromium with manganese dioxide (yield of about 70%). This secondary alcohol is itself prepared in an optically active state by fractional crystallization of the cinchonidine salt of its acid succinate in acetonitrile.

The optical purity and absolute configuration of these derivatives can easily be ascertained by displacement of the chromium tricarbonyl group from the active alcohol. From SCHEME XIV, it is apparent the central chiralities of **48** and **51** are interrelated, because the *endo* nature of alcohols **36** and **49** is well established. Thus, the two types of chirality, planar and central, that coexist in **36** and **49** are not independent of one another.

An identical procedure may be used to obtain (tetralone)chromium tricarbonyl from the optically active tetralol. These optically active compounds have been applied to new syntheses. The first example is the preparation of optically active 2-methyl-1-indanone (**52**, SCHEME XV) and 2-methyl-1-tetralone. Preparation of optically active ketones remains tedious and becomes even more troublesome when



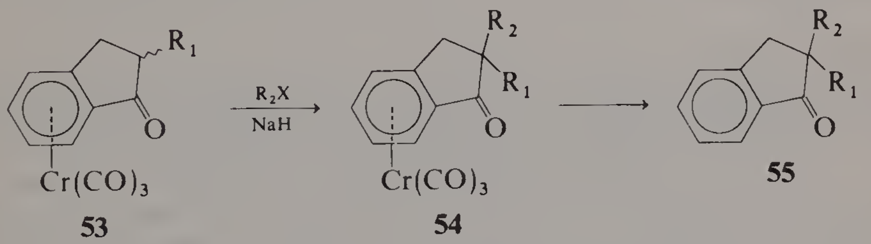
35 **37** **52**

Scheme XV

the asymmetric center α to the carbonyl group possesses a hydrogen atom, thus adding a risk of racemization. Scheme XV shows how the use of tricarbonyl chromium derivatives overcomes this difficulty.

These monomethylation reactions occur stereospecifically in an *exo* manner. Only the *exo* derivative (**37**) is obtained, despite a basic medium that favors an *exo-endo* equilibrium. However, formation of the dimethylated derivative occurs. Decomplexation gives 2-methylindanone (**52**) with an optical purity of 100%.

The following example illustrates the total control over stereochemistry exercised by the chromium tricarbonyl group during the formation of a new asymmetric center α to a ketonic carbonyl. The reaction sequence is shown in Scheme XVI.



53 **54** **55**

Scheme XVI

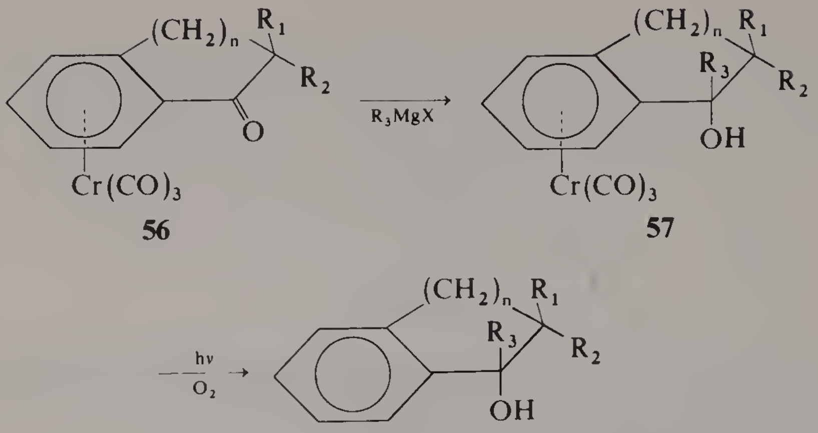
For compounds like **53**, it is not necessary to employ the pure isomer: an *exo-endo* mixture may be used. The second attack occurs stereospecifically in an *exo* manner only on the *endo* isomer present in the basic reaction medium by equilibrium through the enolic form. Thus, the enantiomer of **55** may be obtained simply by a change in the introduction of the substituents. Then, from the same optically active ketone, it may be possible to obtain various enantiomeric molecules. This method has been applied to the case where $R_1 = CH_3$ and $R_2 = CH_2C_6H_5$.

There are therefore vast synthetic possibilities for the preparation in high yields (~80%) of indanone and tetralone derivatives disubstituted in the 2-position.

Access to Optically Active Secondary and Tertiary Alcohols

Cyclic Series

Optically active alcohols are generally obtained by resolution of their acid phthalates, but the procedures are often complicated by dehydration or racemization,[60] particularly for tertiary alcohols. These difficulties may be avoided by utilizing the stereospecificity observed in the reduction of ketones by potassium borohydride and in the addition of Grignard reagents. The "*endo*" alcohol derivatives are always obtained (Scheme XVII).



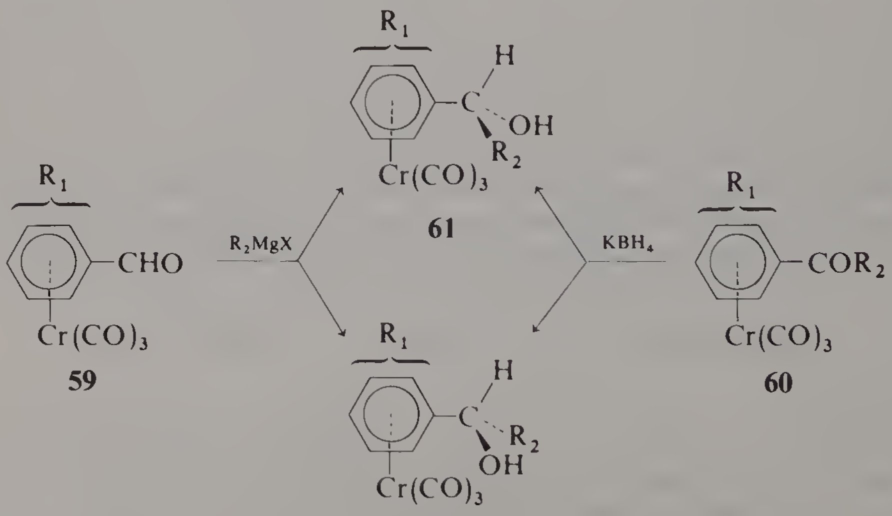
56 57 58

Scheme XVII

Ready, quantitative decomplexation with sunlight in air destroys the induced planar chirality, and the optically active aromatic ligand may be recovered. A totally asymmetric synthesis may thus be accomplished.

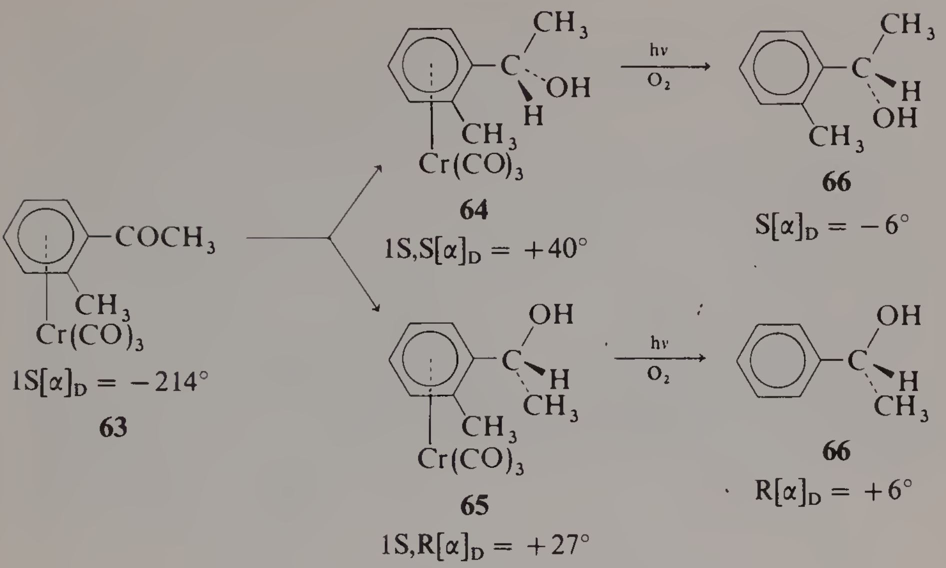
Open-Chain Series

Optically active secondary alcohols have been prepared by the highly stereoselective reduction of ketones complexed by chromium tricarbonyl or by the addition of Grignard reagents to substituted benzaldehydes complexed by chromium tricarbonyl.[61] The complexed benzaldehydes (**59**) and aromatic ketones (**60**) are obtained from the corresponding acids.[22d–f,62] Reduction of ketones **60** with potassium borohydride or reaction of benzaldehyde **59** with the appropriate Grignard reagent leads to the same diastereoisomeric alcohols (**61** and **62**), which are separable by chromatography. Finally, decomplexation yields the optically active alcohols, at an optical purity of 100%.



61 59 60 62

Scheme XVIII



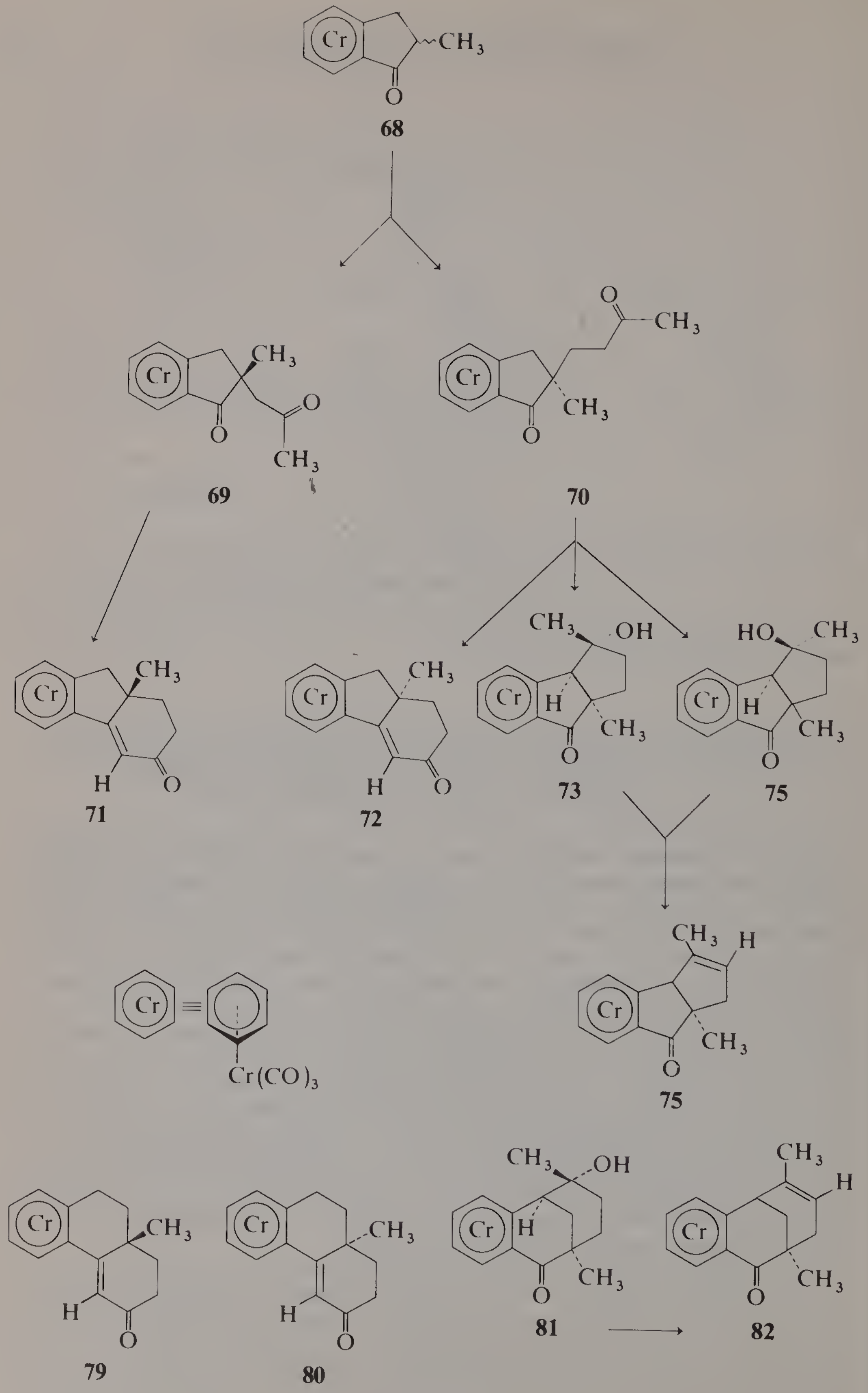
SCHEME XIX

As an example, consider the reduction of (*ortho*-methylacetophenone)chromium tricarbonyl (**63**) outlined in SCHEME XIX.[63]

A NEW ANNULATION REACTION BY USE OF THE STEREOSELECTIVE ACTIVATION OF "BENZYLIC" PROTONS IN CHROMIUM TRICARBONYL COMPLEXES OF INDANONE AND TETRALONE DERIVATIVES

In the syntheses of natural products, the methods of formation of additional 5- and 6-membered rings from a preexisting cyclic ketone have undoubtedly attracted a great deal of attention. Problems involved in annulation and the stereochemistry of molecules derived from the "indanone" and "tetralone" skeletons have been discussed extensively.[64] Modifications of these skeletons by temporary complexation by the chromium tricarbonyl unit allow a new type of annulation reaction.[65] SCHEME XX outlines such an unusual cyclization for the (indanone)-chromium tricarbonyl series. Starting from either ("*endo*"-2-methyl-1-indanone)-chromium tricarbonyl or the *exo* isomer or a mixture of these derivatives (**68**), the vapor-phase introduction of methyl vinyl ketone gave **69** (13%) and **70** (87%) in a highly stereoselective reaction. Base treatment of **69** gave the α-enone (**71**). Under the same conditions, **70** underwent two competitive cyclizations: the first one led to the expected α-enone (**72**, 5–10%), whereas the second, largely predominant, process (>90%) yielded the keto-alcohols **73** and **74** (ratio **73**/**74** ≃ 45/55). The configurational assignments of **73** and **74** have been ascertained by means of combined nuclear magnetic resonance techniques.

This unusual annulation provides a new example of stereospecific activation of the methylene protons α to the complexed ring by chromium tricarbonyl. Ceccon and Catelani found that complexation results in an addition by a factor of the order of 10^2 with respect to formation of a carbanion center α to the ring.[66] Both the stereochemistry at C-2 and the stereoelectronic effects of chromium tricarbonyl govern the course of ring closure. In **69**, the only possibility is the normal aldol condensation, which produces the α-enone (**70**), whereas in **70**, the



SCHEME XX

exo face of the molecule is not hindered, and an *exo* attack on the activated C-3 predominates.

In addition, treatment of keto-alcohols **73** and **74** with thionyl chloride in pyridine produced the same ketone (**75**).

An identical annulation sequence has been performed with (2-methyl-1-tetralone)-chromium tricarbonyl (**76**) to yield the two Michael adducts (**77**, *exo*-methyl, and **78**, *endo*-methyl; ratio **77**/**78** ≃ 1/6.5). Annulation of the major product (**78**) gave the remarkable cyclization as well. In this step (**78** → **81**), it should be noted that only a 6-membered ring compound (**81**) is formed due to attack at the chromium tricarbonyl-activated C-4. The keto-alcohol (**81**) is easily converted by dehydration into the nonconjugated enone (**82**).

These reactions have also been applied to optically active substrates, leading to optically pure organic derivatives after photochemical decomplexation. The above sequences provide striking examples in which the reaction pathways change entirely on conversion of a benzene ring into a benchrotrene unit and yield products that are not available via other routes.

Chiral 2,2′-Spirobiindanes from Optically Active (1-Indanone)Tricarbonyl Chromium

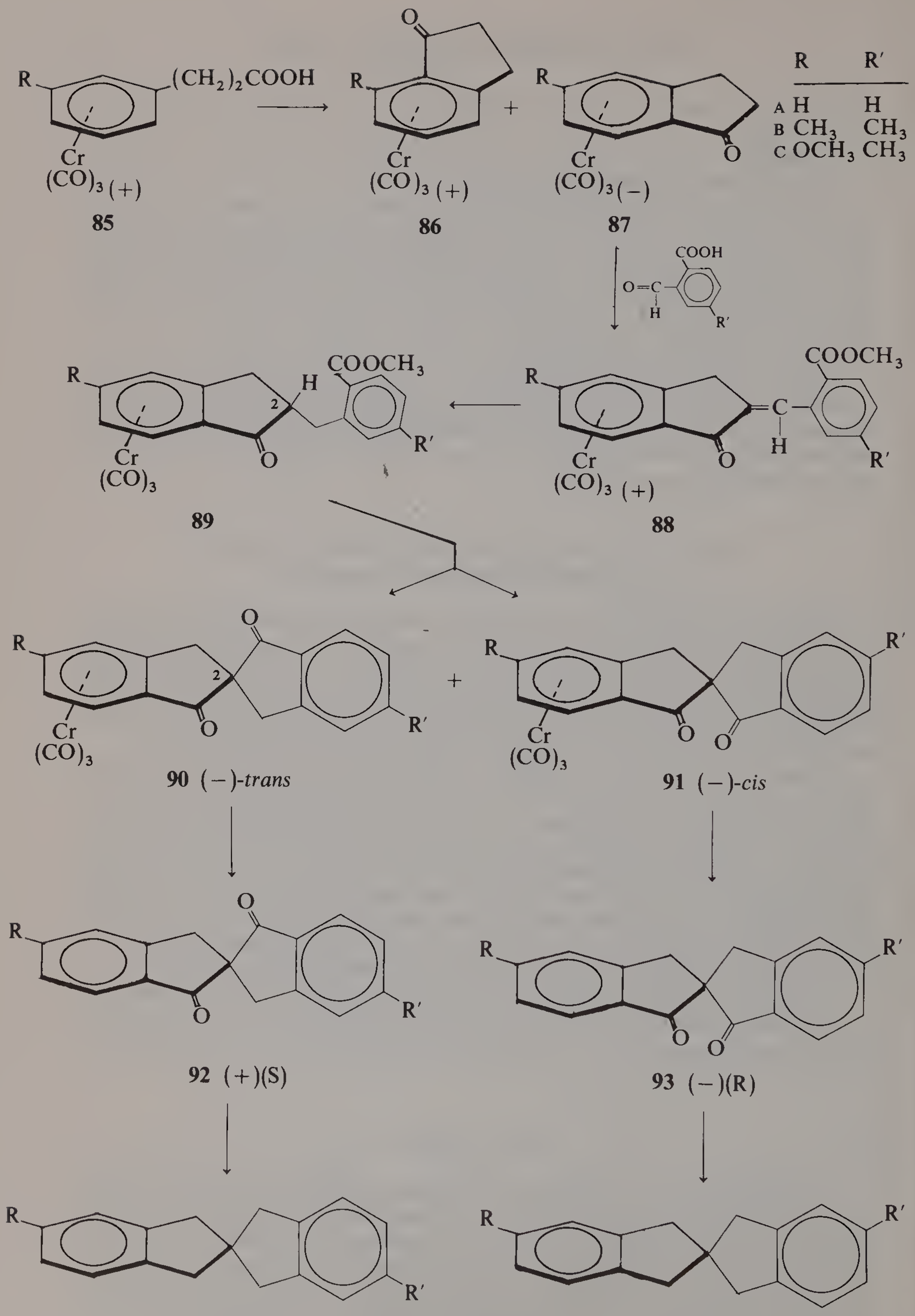
Chiral arene spiranes possess a topologic analogy with chiral allenes of symmetry C_2. Because their skeletons are rigid, they appear to be good models to study the benzene chromophore and to check Ruch's theory of the chirality functions. However, a general method of preparation combined with knowledge of the absolute configuration of these derivatives is required. The use of benchrotrene derivatives has been found to be the only available method that satisfies these criteria.[67]

Scheme XXI shows the synthesis of 2,2′-spirobiindanes from 5-substituted (indanone)chromium tricarbonyls (**87**) whose absolute configurations have been ascertained.[22,59] The condensation of diverse phthalaldehyde acids, followed by catalytic hydrogenation with Raney Nickel Catalyst®, gives the *endo* derivative (**89**). Cyclization of **89** with polyphosphoric acid yields the two diastereoisomers (**90** and **91**) in various proportions, depending on the substituents. After photochemical decomplexation of **90** or **91**, catalytic reduction (lead/charcoal) of the ketone functions leads to the optically active 2,2′-spiroindanes (**83** or **89**). While the optical purity of the starting indanones (**87**) is 100%, derivatives **83** and **84** are also optically pure.

From these models, it has been found that the effects of the ring substituents are in good agreement with Ruch's theory.[68] This method may be extended to 6-membered ring spiranes and to spiranes that have only one arene chromophore.

Conclusions

Due to the effects of activation and selectivity, this type of reaction, which involves the temporary presence of a metal atom, will become more and more a part of the armamentarium of the classic organic chemist. Although certain areas, such as stabilization of labile species by complexation[20] and nucleophilic attack, have been greatly explored, other fields, such as the use of anionic arene complexes or stabilization of carbonium ions, remain relatively open to investigation. Despite the increased sophistication recently attained for determining organic structure, the total synthesis of a product of biologic interest via an arene complex in order to control its stereochemistry still has not been performed. However, further new



$[\alpha]_D^{20}$ (CHCl$_3$)

Scheme XXI

advances and interpretations of the results obtained may be anticipated. They will require a thorough knowledge of the metal's role at different stages of the reactions, mainly in relation to alterations of the properties of coordinated ligands and the precise geometry of bonded ligands.

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MECHANISM OF RHODIUM COMPLEX-CATALYZED CARBONYLATION OF METHANOL TO ACETIC ACID

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Many rhodium compounds in conjunction with various forms of iodide have been reported[1,2] to catalyze the carbonylation of methanol to acetic acid. Although it has been speculated,[2] on the basis of reaction rates and product distributions, that various sources of rhodium and iodide may form the same active catalytic species, no direct evidence has been provided as to the specific nature of reactive intermediates, either with any given catalyst precursor or with a variety of catalyst precursors. This work represents an attempt to define the various rhodium species present in the catalytic cycle when one particular compound, namely, a rhodium(III) halide, is charged to the reaction as the catalyst precursor.* We present a pathway for the reaction that is consistent with the observed[2] independence of the overall reaction rate on carbon monoxide pressure and methanol concentration.

RHODIUM(I) SPECIES

It has been recognized[2] that formation of a rhodium(I) species capable of oxidative addition of methyl iodide is an important part of any catalytic cycle for synthesis of acetic acid. The catalyst precursors chosen for study in this work, the rhodium(III) halides, react with carbon monoxide in hydroxylic media with excess halide to give the rhodium(I) species, $[Rh(CO)_2X_2]^-$.[3,4]

With this complex as the starting point, we propose the reaction pathway illustrated on page 80.

METHYL IODIDE ADDITION

The oxidative addition of alkyl halides to d^8 and d^{10} complexes has been extensively studied recently.[5,6] Generally, addition simply results in formation of a metal-alkyl σ bond. We find that when a solution that contains $[Rh(CO)_2X_2]^-$ ions (with a variety of cations) reacts with excess methyl iodide at room temperature, the infrared spectrum of the reaction solution shows that the carbonyl stretching modes at 2064 and 1989 cm^{-1} [for the $Rh(CO)_2I_2^-$ ion] are replaced by bands at 2062 and 1711 cm^{-1}, as the reaction proceeds. The band at 1711 cm^{-1} can only be reasonably explained as an acetyl frequency and formation of intermediate **3** is being observed. It seems reasonable to assume that compound **2** is formed as an intermediate, but this dicarbonyl species is unstable and isomerizes to **3**.

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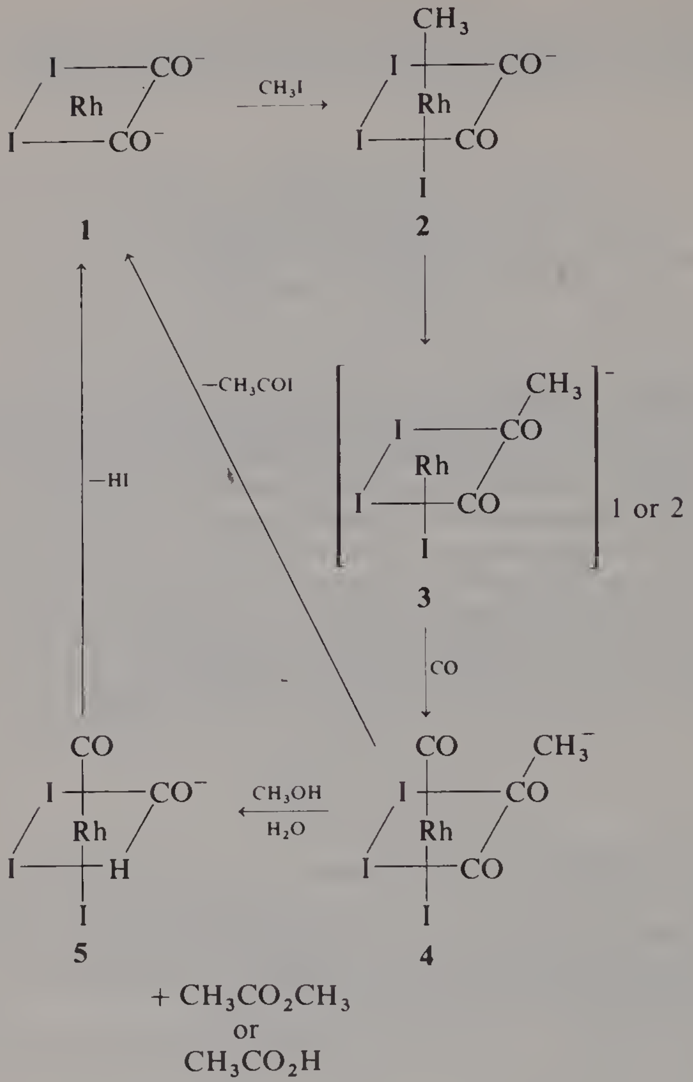
* It is not known whether similar intermediates or catalytic cycles are generally applicable.



ISOLATION OF INTERMEDIATE 3, A RHODIUM ACETYL SPECIES

$[Rh(CO)_2Cl]_2$ (0.20 g) and $(CH_3)_3(C_6H_5)NI$ (0.28 g) were heated together at 40°C in a mixture of methyl iodide (2 ml) and nitro-methane (2 ml) for 20 min. On cooling the reaction solution to 0°C, orange-brown crystals formed and were filtered off and air dried. [*Anal.* Calcd. for $C_{12}H_{17}I_3NO_2Rh$ (i.e., $[(CH_3)_3(C_6H_5)N]$-$[RhI_3(CO)(COCH_3)]$): C, 20.85; H, 2.61; I, 55.12; O, 4.63. Found: C, 21.03; H, 2.42; I, 54.89; O, 4.79.] (Note that halide exchange is complete on the rhodium within the time of this reaction.) The infrared spectrum of this material in the carbonyl region is identical with the species observed in the solution reaction of CH_3I with the $Rh(CO)_2I_2^-$ ion.

The structure of this material has been determined by x-ray diffraction methods and reported elsewhere.[7] The structural study showed that the intermediate (**3**) anion is dimerized through a weak rhodium—iodine bridge.

The reversibility of the conversion of **1** to **3** has been demonstrated by vacuum distillation of $[(C_6H_5)_4As]_2[Rh_2I_6(CO)_2(CH_2CO)_2]$ at 200°C. The residue was extracted with CH_3NO_2, and the resultant solution showed carbon monoxide stretching frequencies of $[Rh(CO)_2I_2]^-$.

OBSERVATION OF INTERMEDIATE 4

On bubbling carbon monoxide through solutions of the rhodium acetyl complex **3** dissolved in a variety of solvents (CH_3OH, $CHCl_3$, CH_3NO_2, $C_6H_5NO_2$, C_6H_5Cl, CH_2Cl_2) at room temperature, very rapid formation of a new species is observed, with carbon monoxide stretching frequencies at 2141 (w) and 2084 (vs) cm^{-1} and an acetyl frequency at 1708 (s) cm^{-1}. This species decomposes slowly at room temperature, giving $[Rh(CO)_2I_2]^-$.

The observations that the initial formation of an acetyl complex (i.e., intermediate **3**) occurs in the absence of carbon monoxide and that **3** reacts with carbon monoxide at 1 atm pressure provide an explanation for the lack of rate dependence[2] on the carbon monoxide partial pressure.

ELIMINATION STEP

The scheme outlined above contains two elimination steps, one via solvolysis and formation of a rhodium hydride species (**5**), analogous to the mechanism for carboxylation of alkyl halides by cobalt catalysts proposed by Heck and Breslow.[8] However, it is found that the carbonylation ($p_{CO} \sim 3$ atm) of anhydrous methyl iodide at 80°C with $[(C_6H_5)_4As][Rh(CO)_2X_2]$ ($X = Cl$, Br, or I) as catalysts (for several hours) gives significant quantities of acetyl iodide (identified by nuclear magnetic resonance, infrared, and reaction with methanol). Reductive elimination of an acyl halide by carbonylation of a rhodium(III)-phosphine acyl complex has been reported recently.[9] In regard to this step of the reaction, no oxidative addition between $Rh(CO)_2X_2^-$ species and acetyl chloride or bromide is observed during 24 hr at 50°C.

Thus, reductive elimination of acetyl iodide ($\mathbf{4} \rightarrow \mathbf{1}$) is the favored final step in the reaction sequence. Although no supporting evidence is available, a solvolytic mechanism may become important at high temperatures in hydroxylic solvents.

Kinetic data presented elsewhere[2] show that the reaction is first order with respect to the concentration of both rhodium and methyl iodide, which strongly suggests that the methyl iodide addition step is rate determining.

DIRECT SPECTROSCOPIC OBSERVATIONS ON A REACTING SOLUTION

To confirm the mechanism proposed above for the carbonylation reaction, we attempted to make some direct spectroscopic observations on reaction solutions by use of the high-pressure high-temperature spectrophotometric cell developed by Morris and Tinker of our laboratories.[10] The following species were charged to a thick-walled glass reactor: $RhCl_3 \cdot 3H_2O$ (0.15 g), heptanoic acid† (45 ml), methanol

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† Heptanoic, rather than acetic, acid was used in this study for two reasons: it absorbs much less strongly in the 1900–2200 cm^{-1} region than does acetic acid, and analytic proof of acetic acid formation becomes easier.

(2.5 ml), methyl iodide (1.0 ml), and water (1.0 ml). The reactor was heated to 100°C, and 6 atm of carbon monoxide were introduced. After 30 min, the solution, which was yellow, was fed into the high-pressure high-temperature spectrophotometric cell, and the infrared spectrum was observed at 100°C and 6 atm pressure. The spectrum contained two strong bands at 1996 and 2067 cm^{-1}, characteristic of the $[Rh(CO)_2I_2]^-$ ion in this medium. Gas chromatographic analysis of the reaction solution at this point showed that methyl acetate and acetic acid were present. This observation indicates that under these conditions, with this catalyst system, the rate-determining step in the catalytic cycle is probably oxidative addition of methyl iodide to the $[Rh(CO)_2I_2]^-$ ion.

SUMMARY

A detailed mechanism for the rhodium iodide-catalyzed carbonylation of methanol to acetic acid is presented. The molecular rhodium species involved in the catalytic cycle are described, and spectroscopic studies of the sequential steps of the reaction are presented. A key intermediate in the cycle has been isolated, and its structure has been determined. A direct spectroscopic measurement on a reacting solution under pressure is used to confirm a key feature of the mechanism.

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ORGANIC CHEMISTRY OF METAL VAPORS. π-COMPLEXES TO SOLVATED METALS TO METAL CLUSTERS*

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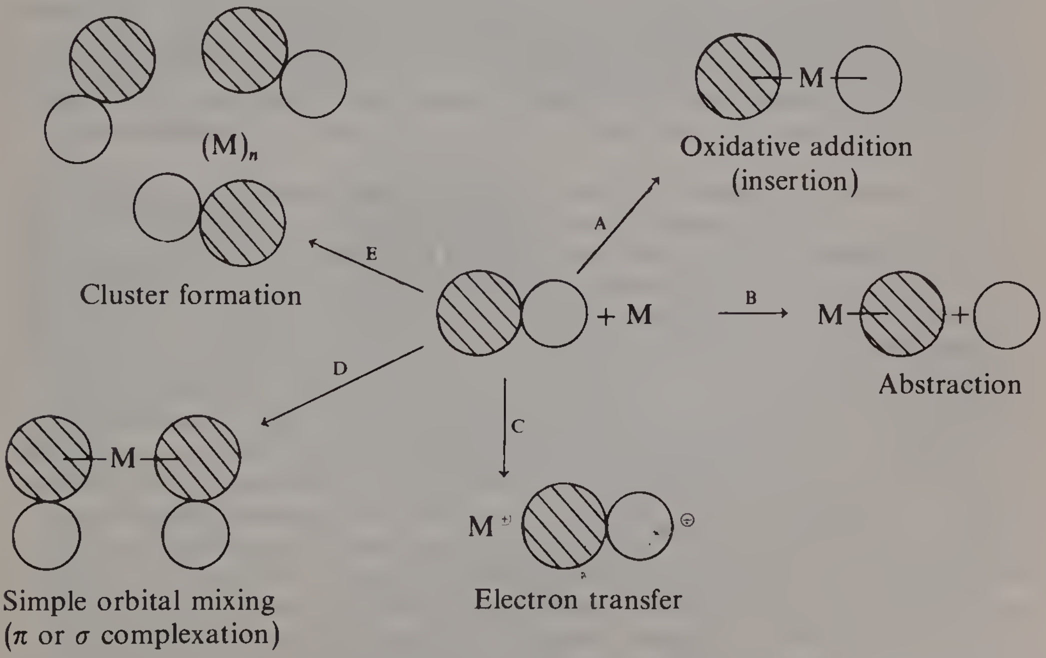
Recent literature[1] has demonstrated that the metal atom technique is now an established synthetic method in organometallic chemistry. Simply described, the metal atom technique involves the simultaneous codeposition of metal vapor with vapors of organic or inorganic compounds at low temperature. A solid low-temperature matrix (usually $-196°C$) forms, whereupon reaction occurs due to the high chemical potential of the individual metal atoms (the more energy it takes to vaporize the metal, the more dissimilar the chemistry of the individual atoms will be compared to that of the bulk element, for example, carbon atoms or platinum atom chemistry[2]; atoms have readily available orbitals for complexation and essentially no steric requirements for reaction).

When a metal atom finds itself dispersed in a solid matrix surrounded by excess organic ligand, several reaction possibilities exist, as indicated by SCHEME 1.

These reaction types (A–E, SCHEME 1) are general and are shown only for demonstration purposes. In this scheme, [▨○] represents some organic molecule with some functional group. Primary products are shown. There can be inter-



SCHEME 1. Metal atom reaction types.

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* Supported by National Science Foundation Grant GP-42376.

conversions between products. Two examples are illustrated: one in which the product of A goes directly to the product of B and one in which the products of C and D are interconvertible.

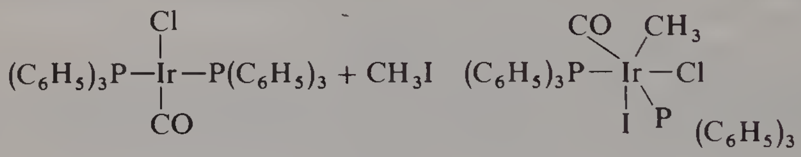
The products of reactions A–E are more interesting than are the reactions themselves. These products, made under low-temperature nonsolvated matrix conditions afforded by the metal atom technique, have very interesting properties and high reactivity due to coordinative unsaturation or weak ligand stabilization.

This paper will consider each reaction type (A–E) that has been observed in our laboratory and with the products, their structures, and reactivities. For the most part, unpublished work will be discussed, although for the sake of clarity and comprehensiveness, some published work will be described.

Reaction Type A: Oxidative Addition to Metal Atoms

Transition metals exhibit such interesting chemistry and unusual catalytic abilities for one primary reason, that is, their ability to undergo oxidative elimination and oxidative addition reactions. A particularly heralded example of oxidative addition to a transition metal complex by an alkyl iodide is shown below for Vaşka's complex[3]:

general $\quad M + X{-}{-}Y \qquad X{-}M{-}Y$

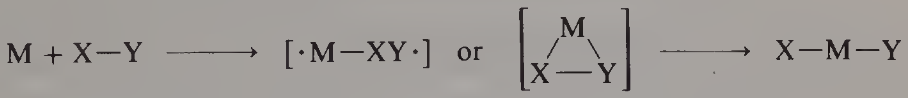


Detailed studies on such reactions have been prevalent in recent years, particularly mechanistic studies that utilized kinetic and stereochemical probes.[4] The results of these studies indicate a very complex situation, in which the exact mechanism of the addition (direct insertion, Sn2, Sn1, free radical pair, or free radical chain) is quite dependent on M, ligands attached to M, and on X—Y. Even a simple change from one alkyl halide (X—Y) to another can cause a change in mechanism.[5]

Our interest in oxidative addition studies of metal atoms (or, alternatively, "oxidative insertion" by metal atoms) comes from three considerations. First, we had earlier discovered that the M atom + RX → RMX reaction could be performed at low temperature in the absence of complicating donor ligands or solvents.[6,7] This reaction allows the production of new reactive RMX species, some of which had been proposed as important reaction or catalysis intermediates but never before prepared and characterized. Many of these species for the transition metals are highly coordinatively unsaturated and show a very interesting chemistry. Second, knowledge of the mechanism of M atom + RM → RMX reaction would have implications that may be important in mechanistic understanding of oxidative addition to metal atoms on surfaces or of solution oxidative addition studies. Finally, we wanted to determine which bonds are most susceptible to oxidative insertion (e.g., C—Cl, C—Br, C—X, Si—Cl, Si—H, and P—Cl) and to determine something about the chemistry of the reactive X—M—Y species formed.

The importance of systematic studies in this area should be emphasized. A great many X—Y and M combinations are possible, and so we have chosen to study in some detail one metal (palladium) with many X—Y species and then other metals with X—Y species that show the most promise.

We have performed numerous experiments related to the mechanism of the atom + X—Y → X—M—Y reaction. The data are complicated and difficult to interpret and will not be discussed here.[8] However, it appears that the mechanism does not involve a radical chain process but, rather, a close radical pair or direct insertion mechanism. In some cases, even the ultraviolet radiation from the metal crucible has a beneficial effect.



$$\mathrm{M + X{-}Y \longrightarrow [\cdot M{-}XY\cdot]\ \text{or}\ \left[\begin{array}{c} \mathrm{M} \\ / \quad \backslash \\ \mathrm{X{-}Y} \end{array}\right] \longrightarrow X{-}M{-}Y}$$

In the last six years, we have studied literally dozens of metal atom—alkyl halide or —aryl combinations (M + RX).[16,9] When the codeposition of metal vapor and organic halide is performed, a dark-colored matrix usually forms; on warming this matrix from −196°C, physical appearance generally changes appreciably.

Some of the more interesting RMX compounds we have prepared are shown below. The first category represents RMX species that were formed (in some cases presumably) at low temperature and decomposed below room temperature. Evidence for their existence was obtained by low-temperature trapping experiments with added ligands to stabilize the RMX species and/or by observation of decomposition products that result from RMX.

From Table 1 it is clear that perfluoro ligands yield the most stable "coordinatively unsaturated" RMX compounds. In particular, C_6F_5PdBr and CF_3PdI are of interest. Addition of donor ligands (L) to these compounds results in immediate formation of the ligand-stabilized form $L_2Pd(R_f)X$. Almost any ligand adds quantitatively ($L = NR_3$, SR_2, PR_3, AsR_3, NH_3, dienes).[12]

Table 1

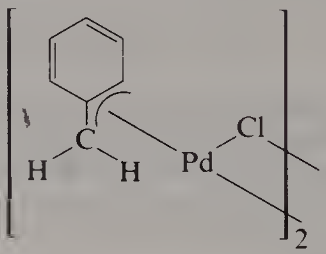
Unstable and Stable Isolated RMX (RCOMX) Species Produced

RMX	Comments	References
Unstable Species		
CF_3ZnI	CF_2 formation	6
$(CF_3)_2CFZnI$	readily hydrolyzed	6
$CF_3CF{=}CCaF(CF_3)$	eliminates CaF_2	10
C_6F_5CaF	readily hydrolyzed	10
$C_6H_5PdBr(Cl)$	stable at < −100°C	9
$(CF_3)_2CFPdI$	could not be trapped	9
$CH_3PdBr(I)$	stable at < −100°C	9
C_2H_5PdI	stable at < −100°C	9
$C_6F_5NiCl(Br)$	trapped at −80°C	11
$CF_3NiBr(I)$	trace trapped at −80°C	11
CH_3NiI	CH_4 formation during deposition	11
C_2H_5NiI	CH_4 or H_2 formation during deposition	11
Stable Species		
$C_6F_5PdBr(Cl)(I)$	reacts with many ligands	9, 12
CF_3PdI	very labile, weakly coordinates toluene	9, 12
CF_3CF_2PdI	very stable in acetone	9
$CF_3CF_2CF_2PdI$	very stable in acetone	9
$C_6H_5CH_2PdCl$	decomposes at 105°C	13, 14
C_6F_5PtBr	reacts with Et_3P to give *cis* and *trans* adducts	1b, 15

One particularly interesting feature was noted for CF_3PdI, which weakly coordinated toluene.[16] Arene coordination has turned out to be quite important with these type of species, as we will see in later discussion.

h^3-*Benzylpalladium Chloride and Substituted Analogs*

One of the more intriguing RPdX compounds that shows good stability is the benzylpalladium chloride derivative.[13] It is the only nonfluorinated RPdX that we found isolable and readily characterizable. There seems little doubt at this time that this interesting compound exhibits h^3 bonding and is dimeric.



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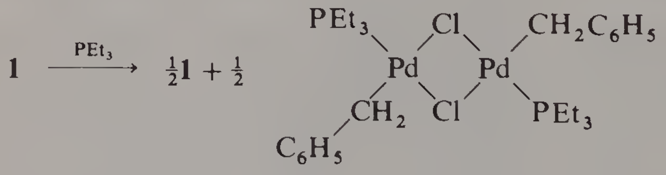
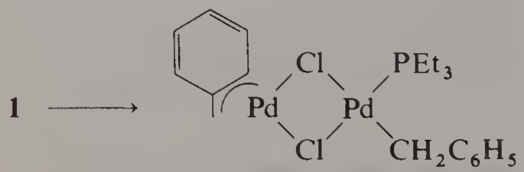
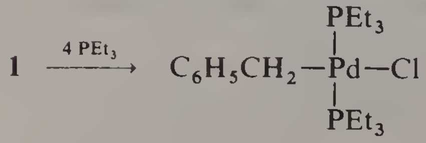
This conclusion about the bonding was based on the following reasoning. (1) The unusual stability of **1** versus C_6H_5PdCl (105°C vs < -100°C, respectively).[13] (2) There is some literature precedent for h^3-benzyl bonding,[17,18] such as in $(C_6H_5CH_2)Mo(C_5H_5)(CO)_2$. (3) Incremental addition of Et_3P to **1** in solution indicated that two equivalents of Et_3P (one per palladium atom) resulted in a rearrangement (loss of h^3 bonding), thus causing the CH_2 protons to be split into a doublet (by phosphorus)[13] and the *ortho* protons to be shifted downfield into the normal region for aryl protons in such σ-bonded compounds, that is, $(Et_3P)_2Pd(Cl)$-$CH_2C_6H_5$ (**2**). Addition of two equivalents of Et_3P resulted in the formation of **2**, and analogous results were obtained with pyridine-d_5 in place of Et_3P.[14] These results are similar to those found for Et_3P additions to allyl-bonded compounds, except



or possibly

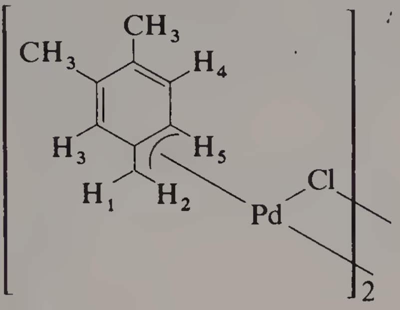




$$1 \xrightarrow{4\,PEt_3} C_6H_5CH_2-\underset{PEt_3}{\overset{PEt_3}{Pd}}-Cl$$

2

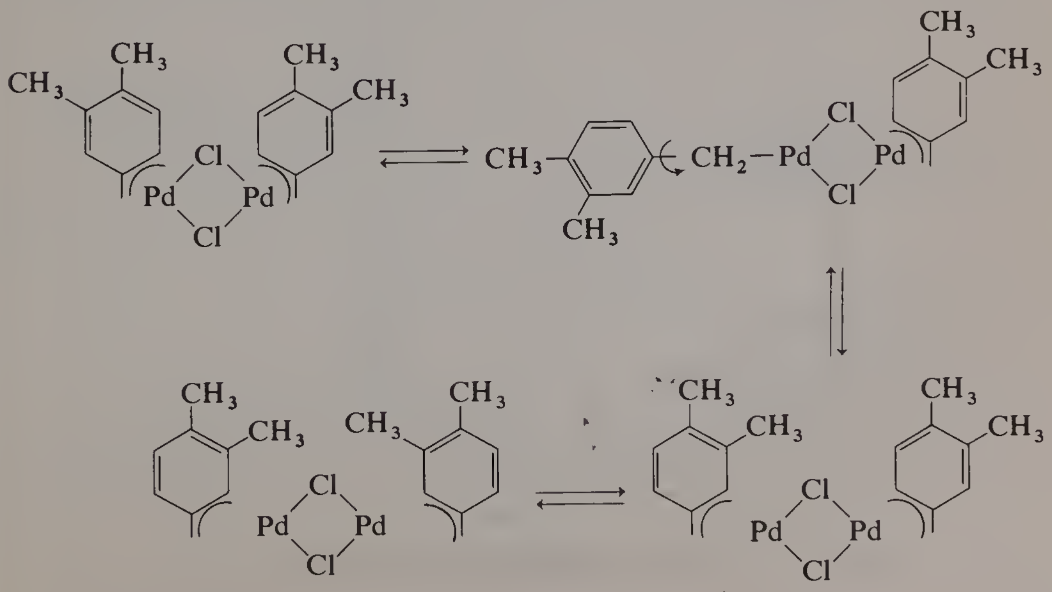
for one important feature: in allyl systems, the halogen bridge is cleaved *first*, *then* rearrangement occurs. (4) The proton magnetic resonance (pmr) spectrum of **1** is compatible with allyl-type bonding. Thus, the spectrum of **1** is very similar to that reported by Stevens and Shier[19] for $[(Et_3P)_2PdCH_2C_6H_5]^+$. The *ortho* protons are shifted upfield substantially: pmr [**1** in CD_2Cl_2, δ (ppm)] 7.92, 7.78, 7.65 (*meta* and *para* protons), 7.11, 7.00 (*ortho* protons), and 3.58 (benzylic protons). For **1**, no preferred conformations could be detected by pmr at a probe temperature variance of 40 to −85°C. *However*, for a substituted version of **1** (3,4-dimethylbenzylpalladium chloride, **3**) temperature-dependent pmr was observed (FIGURE 1).[14]



3

For the *ortho* protons, the doublet (proton 3) moves upfield and the singlet (proton 5) moves downfield with decreasing temperature. In pmr studies of palladium-allyl complexes, the proton closest to the palladium atom are generally the most shielded and absorb furthest upfield.[20] These results imply, not unexpectedly, that the most stable low-temperature configuration for **3** is that form in which the methyl groups are furthest from palladium.[14] At lower temperature, the two benzylic protons become nonequivalent.

The *ortho* protons continue to become more widely different in their chemical shifts. These concurrent changes in chemical shift imply that only one equilibrium process is being slowed and thus must explain both effects (benzylic proton and *ortho* proton changes). One such process would be a $\pi \rightarrow \sigma \rightarrow \pi$ equilibrium, with a σ-bonded benzyl group as a short-lived higher-energy intermediate. Because a



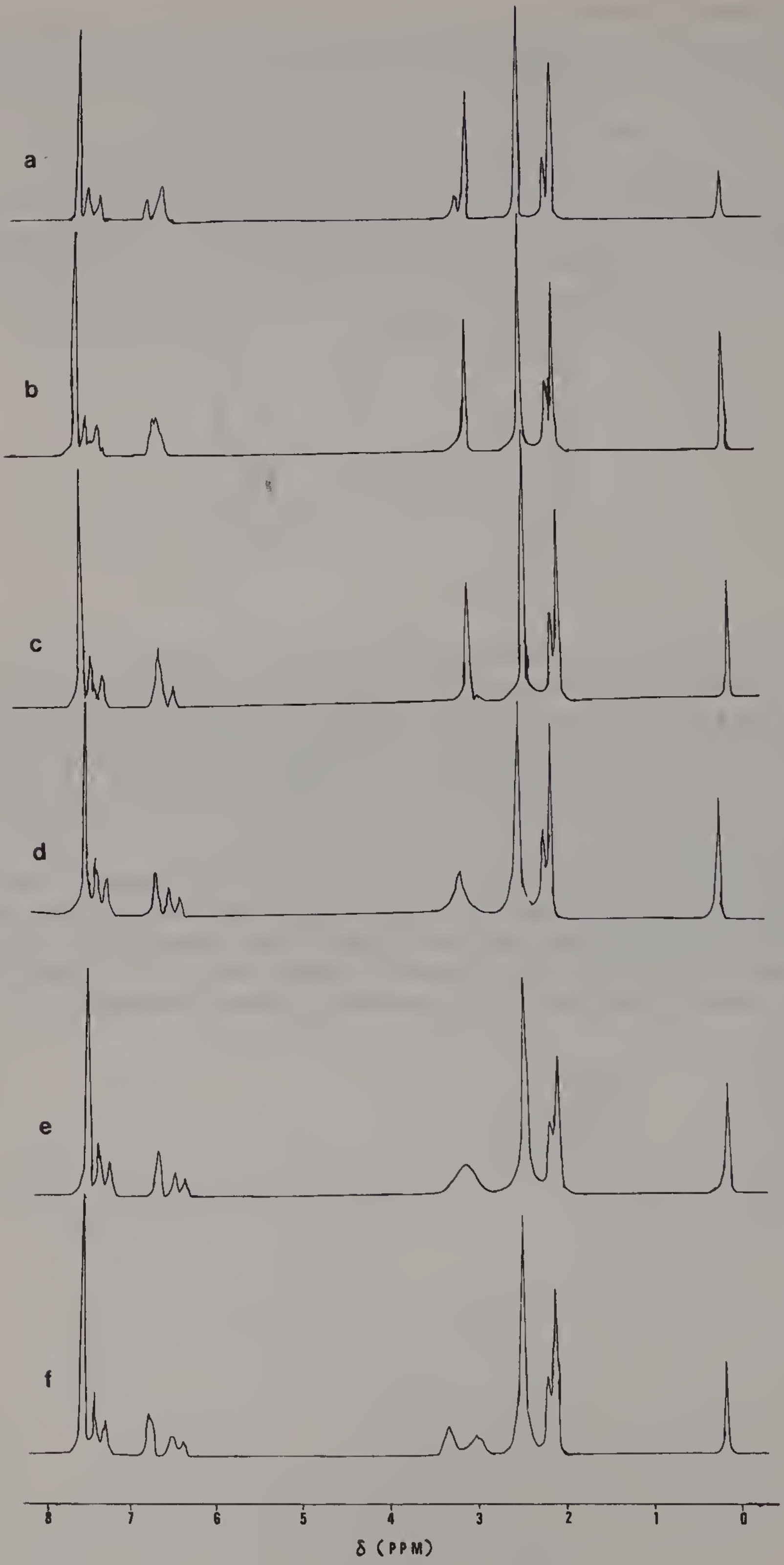
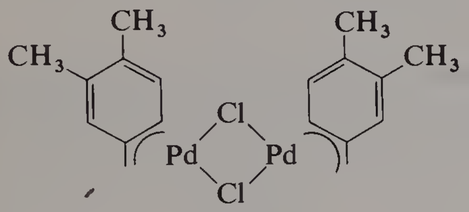
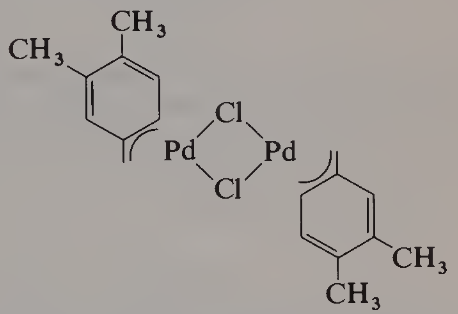


FIGURE 1. Temperature-dependent pmr spectra for compound **3**.

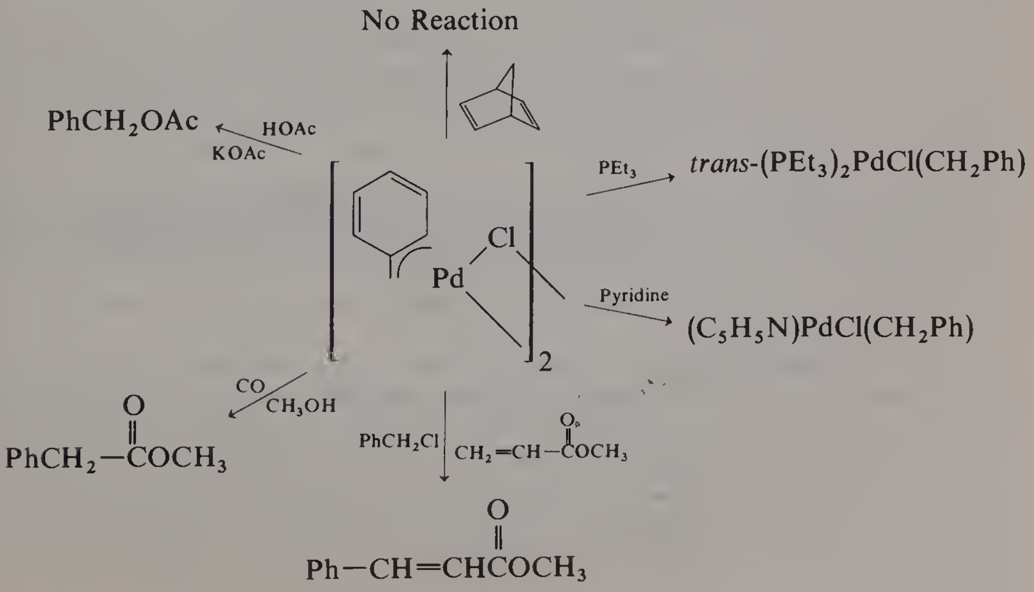
$C_1—C_2$ rotation would be rapid, H_1 and H_2 would be equivalent on a nuclear magnetic resonance (nmr) time scale as long as the $\pi \rightarrow \sigma \rightarrow \pi$ rearrangement was rapid. As the temperature is lowered, it would become more difficult for such a process to occur, and, in this case, a preferred conformation would become favored. The π system with the methyl groups farthest away from palladium would be expected to be sterically favored and would finally become so favored at very low temperatures that H_A and H_B would become nonequivalent. A $C_1—C_2$ rotation in the π-bonded species would not necessarily occur, even at room temperature, when H_1,H_2 equivalence is indicated, according to this proposal.

It seems unlikely that these low-temperature pmr results could be explained by the occurrence of favored *cis* or *trans* isomers of these dimers, because, in either case, the two halves can be related by simple symmetry operations.





In general, these low-temperature pmr results strongly support the h^3-benzyl type of bonding. And it is interesting to note that only the nonsymmetric benzyl systems we have studied show temperature-dependent pmr. (5) Other spectroscopic investigations of **1** seem to support the h^3-bonding scheme. In the ultraviolet, large changes are observed between the ultraviolet spectrum of $C_6H_5CH_2Cl$ ($\lambda_{max} = 2600$ Å), **2** (2650 m, 3100 sh, 3440 s), and **1** (2380 s, 2900 m, 3850 w). Infrared spectra indicate that bands that would be attributed to aryl C—H in-plane bending or stretching modes for **2** (1155 and 1180 cm^{-1}) and benzyl chloride (1158 and 1182 cm^{-1}) were either not observed or significantly shifted for 1. The aryl C—C stretching frequencies for **1** are either missing or shifted for **1** (1448 and 1482 cm^{-1}) when



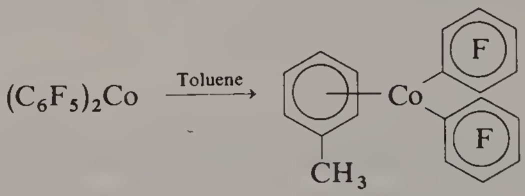
this infrared spectrum is compared to that for either benzyl chloride (1588, 1498, and 1452 cm^{-1}) or **2**. These changes in spectroscopic properties indicate that the aromatic character of the phenyl rings in **1** is greatly different from that of either benzyl chloride or **2**.

The chemistry of h^3-benzylpalladium chloride is quite interesting. It is reactive, readily combining with donor ligands, carbonylating, and serving as a catalyst for benzylation of methyl acrylate.[14]

Sometimes, we have found that RMX disproportionates to R_2M and MX_2. This phenomenon occurs for $[C_6F_5CoBr]$ (never trapped or isolated) and C_6F_5NiBr (has been trapped).[11,12,21] The chemistry of these reactive R_2M species is also

$$[C_6F_5CoBr] \longrightarrow (C_6F_5)_2Co + CoBr_2$$
$$[C_6F_5NiBr] \longrightarrow (C_6F_5)_2Ni + NiBr_2$$

quite interesting. Most intriguing is the ability of **4**[21] and **5** to coordinate toluene in an h^6 fashion,[21,22] thus yielding the first examples of R_2M—arene complexes. An x-ray structure determination of h^6-$C_6H_5CH_3Co(C_6F_5)_2$ (**6**) was undertaken.[21]



6

The molecular structure, depicted in FIGURE 2, consists of a cobalt atom bonded to two *F*-phenyl ligands and π bonded to one toluene ligand. The Co—C_1 bond distance is 1.931 (5) Å and the C_1CoC_1' bond angle is 88.3 (3) Å. The Co atom is 1.627 (2) Å from the plane of the toluene ligand, and the average Co—C π-bond distance of 2.141 (7) Å is similar to that found in $(C_6H_5)CCo_3(CO)_6 \cdot \pi\text{-}C_6H_3(CH_3)_3$, 2.15 (3) Å. The toluene ligand makes an angle of 86.3° with the plane defined by cobalt and the two σ-bonded carbons.

The molecule has m (Cs) symmetry that is fully utilized crystallographically. The carbon framework of both *F*-phenyl ligands remains planar, and the normal trend in bond angles for electron-donating and -withdrawing substituents is observed. Carbon—carbon bond lengths in the *F*-phenyl ligand average 1.373 (8) Å, and the observed C—F distance is 1.349 (7) Å. The average C—C length in the toluene ligand is 1.391 (8) Å.

This compound is paramagnetic and at room temperature exhibits a broad featureless electron spin resonance spectrum but shows fine structure at low temperature.

The analogous nickel compound forms in higher yield, and x-ray studies indicate the same space group as **6**.

The arene ligands in both the cobalt and nickel complexes are quite labile and are exchangeable at room temperature (toluene complex ⇄ benzene complex). Both complexes serve as hydrogenation catalysts for benzene or toluene at room temperature and 1500 psi, although the turnover rate is low (<20) before decomposition of the complex occurs.[22] Competition hydrogenations show that benzene is hydrogenated slightly more rapidly than is toluene. In a planned toluene-cyclohexene competition, addition of cyclohexene immediately caused decomposition of the nickel complex.

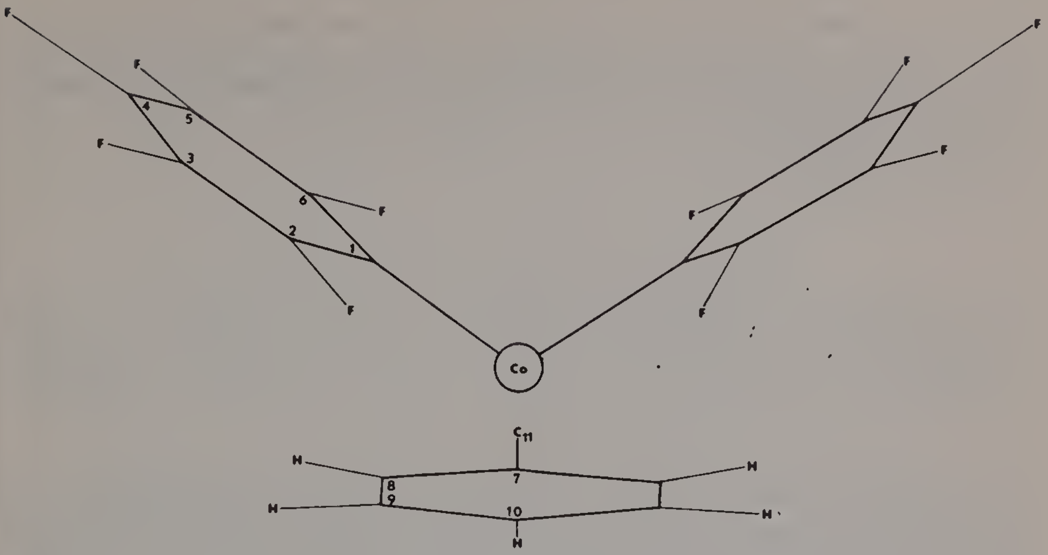
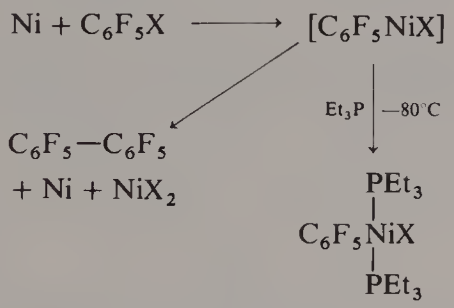
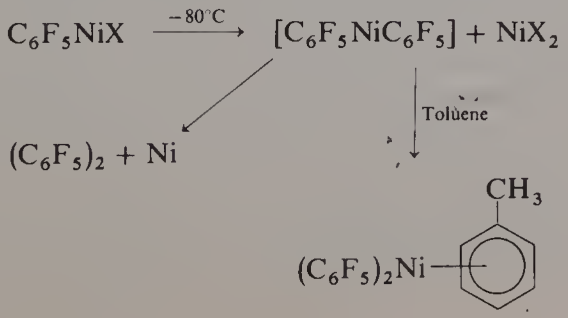


FIGURE 2. Structure of [h^6-$C_6H_5CH_3(C_6F_5)_2Co$]. The crystallographic mirror plane contains cobalt, C_7, C_{10}, C_{11}, and H_{10}. (From Anderson *et al.*[21] By permission of *Journal of the American Chemical Society*.)

The perfluorophenyl (C_6F_5) group is the only unit we have found to date that stabilizes these R_2Co—arene and R_2Ni—arene complexes. Attempts with CF_3, C_6H_5, and 2,4,6-$C_6H_3(CH_3)_3$ have failed. We have conducted low-temperature trapping experiments with Et_3P to determine the thermal stability of the reactive intermediates involved. The initial reaction of nickel atoms with C_6F_5Cl or C_6F_5Br apparently is insertion to yield C_6F_5NiX, which can be trapped by Et_3P at $-80°C$ or lower. Warming in the absence of toluene or Et_3P yields NiX_2, Ni, and



Ph_f—Ph_f. However, warming in the presence of toluene yields the toluene—$Ni(C_6F_5)_2$ adduct.[22] The most rational sequence is formation of C_6F_5NiX, followed by disproportionation above $-80°C$ to $(C_6F_5)_2Ni$ and NiX_2. In the absence of toluene,



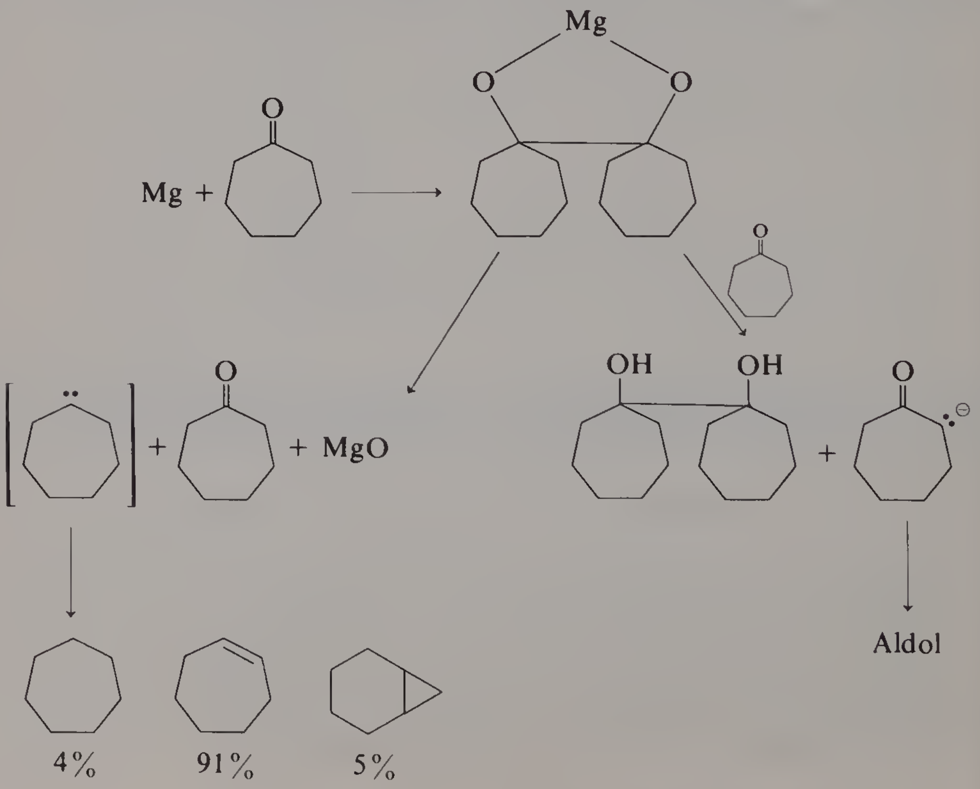
which can stabilize the $(C_6F_5)_2Ni$ species, this compound decomposes the $C_6F_5{-}C_6F_5$ and nickel metal. The analogous cobalt system $[(C_6F_5)_2Co]$ does not decompose to $C_6F_5C_6F_5$, even on warming to room temperature. Subsequent addition of toluene produces the $(C_6F_5)_2Co$—toluene adduct, and very little $C_6F_5C_6F_5$ is formed.

REACTION TYPE B: ABSTRACTION PROCESSES

Early work with Na—K vapor[23] and copper, silver, and gold vapors[24–26] showed that metal atoms were capable of halogen abstraction from alkyl halides. The intermediacy of a resultant free alkyl radical seemed reasonable, and subsequent

$$\mathrm{M} + \mathrm{X{-}R} \longrightarrow \mathrm{MX} + \mathrm{R}\cdot$$

coupling of these radicals yielded useful products in some instances. However, no organometal compounds had been produced in this way. We believed that RCu, RAg, or RAu compounds might be accessible by this technique and were encouraged by Timms' study in which he coupled optically active halides and obtained 70% optical retention.[26] This experiment indicated that some type of complexation of M with RX or R· was important (completely "free" radicals were not formed). Thus, we began an investigation of R_fI and C_6F_5Br with copper, silver, and gold vapors in hopes of producing R_fM or C_6F_5M compounds. We were successful in our initial work, and C_6F_5Cu and C_6F_5Ag were prepared and worked up in toluene and pentane solvents[27] (these known compounds were previously prepared in coordinating solvents).[28] We also prepared $(CF_3)_2CFAg$, $CF_5CF_2CF_2Ag$, and CF_3Ag. For $(CF_3)_2CFAg$, we conducted a study on yield of product versus $(CF_3)_2CFI/Ag$



ratio in the matrix. Surprisingly, the higher the ratio (lower the silver concentration in the matrix), the higher the yield of $(CF_3)_2CFAg$.[2] This result seemed to contradict the presumed mechanism, whereby AgI and $R_f\cdot$ would first be formed and $R_f\cdot$ would migrate in the matrix until a silver atom was encountered. This apparent paradox led us to propose the presence of an R_fI—Ag complex at low temperature, which would slowly decompose on warming with $R_f\cdot$, obtaining silver from another R_fI—Ag complex. The low silver concentration simply favored efficient formation of R_fI—Ag complex.[27]

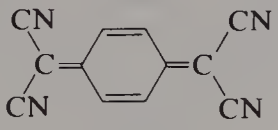
We have recently observed a deoxygenation abstraction reaction by metal atoms.[29] Magnesium, titanium, iron, nickel, and aluminium were condensed with cyclic ketones, and products characteristic of deoxygenation and coupling were observed.

Magnesium with cycloheptanone was studied most intensively, primarily because Friedman and Schechter[30] have reported that carbenacycloheptane yields cycloheptene (82%) and norcarane (18%). Thus, the presence of norcarane in the products of a magnesium-cycloheptanone reaction would be indicative of the formation of carbenacycloheptane. Indeed, norcarane was produced, along with cycloheptene, cycloheptane, 1,1′-dihydroxydicycloheptyl, and aldol-type products. The following mechanism was proposed[29]:

REACTION TYPE C: CHARGE TRANSFER

It has been reported that cesium and aluminium vapors condensed with TCNQ yield the corresponding $M^{+}TCNQ^{\cdot -}$ salts. We are studying this reaction with

transition metals and have shown that anhydrous $Ni^{2+}(TCNQ^{\cdot -})_2$ can be produced by condensing nickel vapors with TCNQ vapors (employing a special apparatus for producing TCNQ vapor with nickel vapor simultaneously).



TCNQ

The study of borderline cases where π complexation *or* charge transfer can occur could have some importance. Metal films, that of vanadium in particular, have changed transition temperatures for superconductivity when exposed to arene ligands, such as anthracene, 1,4,5,8-tetrachloroanthraquinone, and other similar ligands.[32] Electronegativity of the ligand versus the metal appears to be quite important for such effects. A clearer understanding of the interactions of the metal film with the ligands might be gained by detailed studies of M atom—ligand interactions (charge transfer vs π complexation), with variance in electron acceptor properties of the ligands. In support of such a proposal, we previously reported on the differences in stability of transition metal M—benzene as compared to M—hexafluorobenzene complexes.[33] With nickel, we found that hexafluorobenzene formed the more stable complex and attributed this result to the better "π-acceptor" properties of hexafluorobenzene than of benzene.[33]

REACTION TYPE D: SIMPLE ORBITAL MIXING (π OR σ COMPLEXATION)

Because metal atoms have readily available orbitals and essentially no steric restrictions for reaction, simple complexation with π and σ donors is a very efficient process. The vast majority of metal atom studies can be categorized under this reaction type. Important examples include M—phosphine,[34] M—CO,[35] M—diene,[36] M—olefin,[37] M—alkyne,[38] and M—arene[38] complexations. We have had a special interest in M—arene complexes, particularly those with the more electron-demanding arenes.[33,39] Two aspects of our recent collaborative work in this area are of interest: structural effects of F and CF_3 substituents on bis(arene)—V and bis(arene)—Cr sandwich complexes (as studied by x-ray crystallography with Radonovich *et al.*[40]) and substituent effects on one electron oxidation potentials of bis(arene)—Cr complexes (as studied by polarography with Treichel and Essenmacher[41]).

The x-ray structure determination of bis(1,4-difluorobenzene)vanadium(0) showed two unusual features. First, a slight boat deformation of the arene ligand was found, along with substantial bond lengthening of C_2—C_3 and C_5—C_6 bonds. In other words, a definite tendency of vanadium to bond more strongly to C_2, C_3, C_5, and C_6 was elucidated (C_1—C_2 1.386 (4) Å, C_2—C_3 1.415 (4) Å). Second, the molecule crystallized as a racemic compound (two of each enantiomer in the unit cell), with each molecule possessing D_2 symmetry. The carbons were very nearly completely eclipsed.

Although a direct comparison between $(p\text{-}C_6H_4F_2)_2$—V and —Cr has not yet been possible (because of double crystal problems), $(m\text{-}C_6H_4F_2)_2$—Cr does not show the ring distortions that $(p\text{-}C_6H_4F_2)_2$—V does. These distortions are also not found in the CF_3-substituted bis(arene)—Cr compounds we have studied.

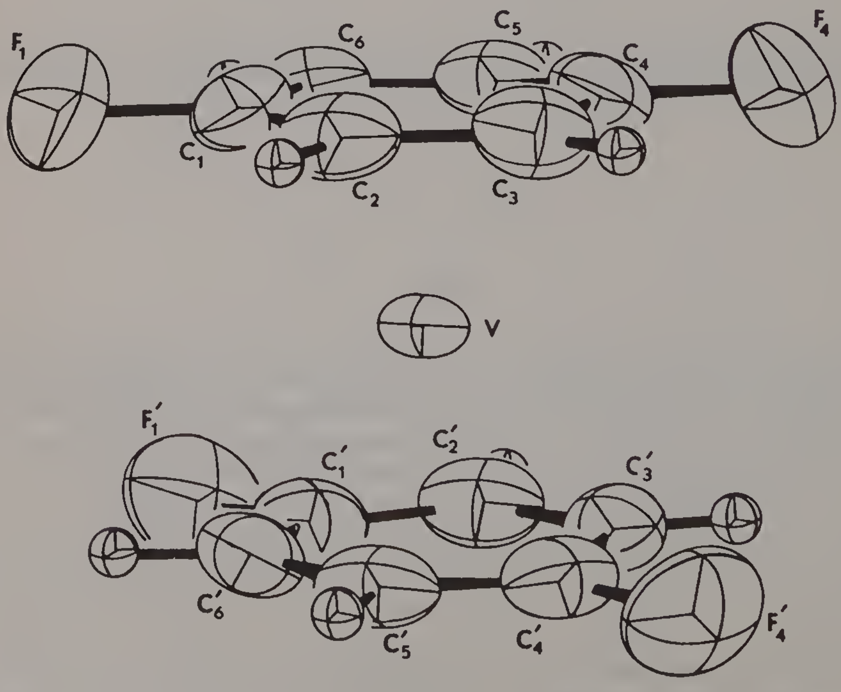


FIGURE 3. An ORTEP drawing of $(C_6H_4F_2)V$. Hydrogen atom size has been reduced deliberately for clarity. (From Radonovich *et al.*[40] By permission of *Inorganic Chemistry.*)

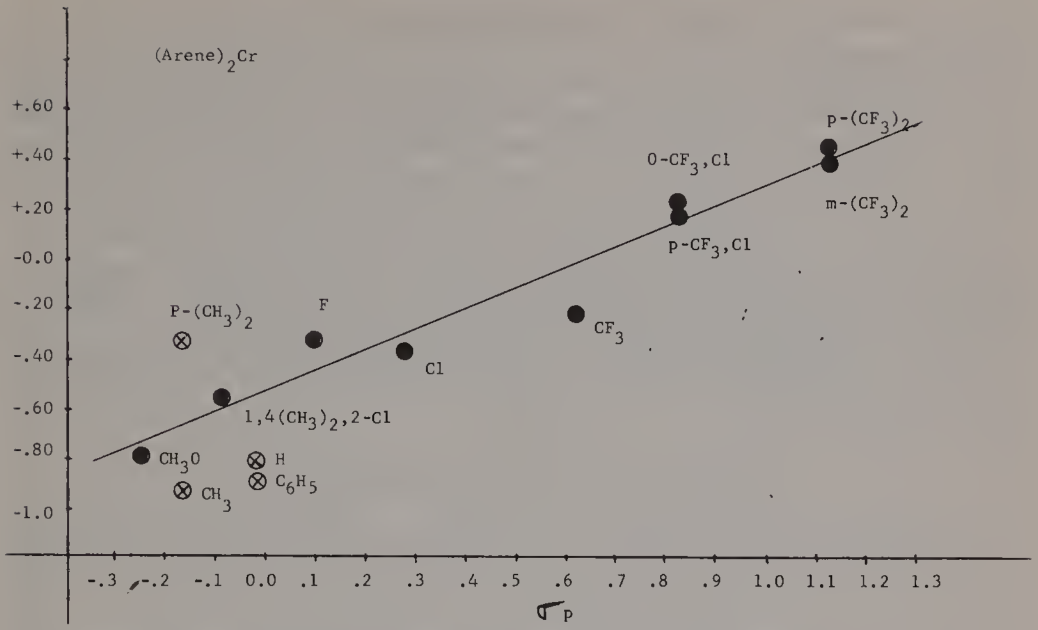


FIGURE 4. Plot of $E_{1/2}$ versus σp (cf. TABLE 2).

However, one unusual feature in $[p\text{-}C_6H_4(CF_3)_2]$—Cr is its nearly staggered carbon ring network.

Attached substituents in bis(arene)—Cr complexes have remarkable effects not only on physical properties[39] but also on one electron oxidation potentials. In collaboration with us, Treichel and Essenmacher[41] polarographically determined these oxidation potentials, finding inordinately large substituent effects for such measurements. FIGURE 4 plots these values against σp (Hammett's total polar constants) and reveals an unexpectedly good correlation. The quality of the

TABLE 2
HALF-WAVE POTENTIALS, $E_{1/2}$, FOR OXIDATION OF SUBSTITUTED BIS(ARENE)CHROMIUM(0) COMPLEXES AND σp FOR ATTACHED SUBSTITUENTS*

Arene	$E_{1/2}$ for Complex	σp for Substituent
$C_6H_5OCH_3$	−0.767	−0.27
—F	−0.367	0.06
—Cl	−0.336	0.23
—CF_3	−0.190	0.54
—1, 4-$(CH_3)_2$, 2-Cl	−0.516	−0.11
p-CF_3, Cl	0.125	0.77
o-CF_3, Cl	0.165	0.77
m-$(CF_3)_2$	0.385	1.08
p-$(CF_3)_2$	0.337	1.08
—H	−0.81†	0.0
—CH_3	−0.91†	−0.17
—$(CH_3)_2$	−0.87†	−0.34
—C_6H_5	−0.75†	−0.01

* From Reference 41. $E_{1/2}$ determined in acetonitrile.
† Data from References 53 and 54.

correlation implies a significant involvement of the ring's α framework in the metal—ring bond formation.[41]

Of the first-row transition metals, only titanium,[42] vanadium,[39] and chromium[38,39,43] form stable bis(arene) complexes. The latter metals yield arene—metal complexes employing the metal atom method, but these materials decompose on matrix warm-up. The temperatures of the decompositions depend on the metal—arene pair involved, and these temperatures are sometimes high enough that metal—arene solutions are formed on melt-down.[44] These weakly complexed metal atoms, sometimes called solvated metal atoms,[44] are useful organometallic reagents.[45] Because they are only weakly complexed, they are reactive with a variety of reagents,[44,45] yielding other organic or organometallic products.

These solvated metal atoms are also intermediates en route to clusters, the topic of the next section.

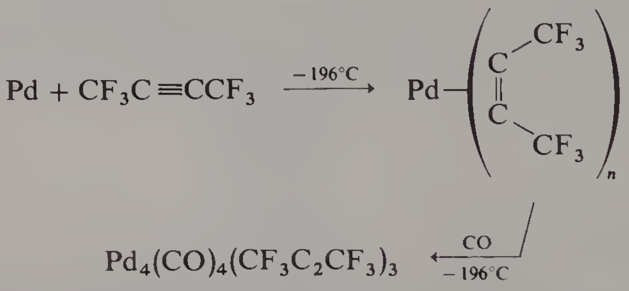
REACTION TYPE E: CLUSTER FORMATION

Metal atoms can be dispersed in several organic media that are weakly complexing and inert to oxidative addition, abstraction, or electron transfer processes (reaction types A–C).[44] Each medium serves to isolate the metal atoms at low temperature, but on warming, metal atom clusters can form. In some cases, cluster formation can stop at a small size that may be kinetically or thermodynamically favorable.[44] Or it may be possible to trap very small clusters by addition of the proper ligands before cluster size becomes large.

Small Discrete Clusters

Nickel atoms condensed with excess hexafluoro-2-butyne yield a dark matrix at −196°C. Subsequent addition of carbon monoxide, followed by slow warming, yields mainly the known[46] $Ni_4(CO)_4(CF_3C{\equiv}CCF_3)_3$ cluster. A small amount of the monomer, $Ni(CO)_2CF_3C_2CF_3$, is also formed.

We used an analogous reaction sequence to prepare the previously unknown $Pd_4(CO)_4(CF_3C_2CF_3)_3$ cluster.



Monomer formation also occurred in this case, although to a very small degree.

A similar platinum vapor reaction did not yield the analogous platinum cluster but did produce a complex mixture of $Pt_n(CF_3C_2CF_3)_m$ clusters. Similar results were obtained with cobalt and nickel when deposited with only $CF_3C_2CF_3$, followed by slow warming.[47] Apparently, the butyne by itself encourages cluster formation but stabilizes the clusters before they reach large sizes. Currently, we are attempting to sort out some of these cluster products. We believe that these techniques hold great promise for synthesis of new discrete metal—organometallic clusters.

Warming solvated metals causes $(M)_n$ crystallite (large cluster) formation. As these large clusters grow, there must be a stage where $(M)_n$ is small and could be trapped by addition of proper ligands at the temperatures at which clustering is occurring. Our first attempts with this approach have been with known cluster systems and will be reported at a later date.

Large Metal Clusters (metal-solvent slurries)

If free cluster formation is allowed (no trapping ligand added), the metal crystallites grow from the respective solvent to a thermodynamically favorable size. As mentioned before, the final metal particle size and shape were found to depend on the solvent employed.[44] This crystallite growth process from inert but weakly complexing organic media had never been studied before. Our work has shown that the process can be used to prepare active metal powders of activities that vary according to the solvent employed and for deposition of very small metal crystallites on catalyst supports.[44] In some cases, a great deal of solvent remains adhered to the metal particles, even after high-vacuum pump-down. These species

$$\text{M—solvent} \longrightarrow \text{(M)}_n\text{—solvent}$$

are actually pseudometal—organic compounds.

The metal—solvent slurries formed on warm-up vary considerably in their physical properties. Some are storable and so fine that they are totally syringeable.

Moving from left to right on the periodic table, metal—solvent slurries are discussed below.

Nickel

This metal has proven to be one of the most interesting ones. We have examined the reactivity of various nickel—solvent slurries and the physical properties of the black powders obtained after solvent pump-off[44] (Scheme 2).

$$\begin{tikzcd}
 & \text{M vapor + solvent vapor} \arrow[r, "-196^\circ\text{C}", "\text{cocondense}"'] & \text{M-solvent complex (colored)} \arrow[d, "\text{melt}"] \\
 {} & \text{(M)}_n\text{-solvent slurry (black)} \arrow[l, "\text{vaporize excess}", "\text{solvent 25°C}"'] & \text{M solution} \arrow[l, "\text{further}", "\text{warming}"'] \\
 \text{(M)}_n\text{-solvent adduct (black, small crystallites)} \arrow[r, "\text{pyrolysis}"] & \text{(M)}_n + \text{organics} &
\end{tikzcd}$$

Scheme 2. Solvated nickel atom—nickel cluster stages.

Table 3 illustrates some of the properties. Data were collected by scanning electron microscopy, x-ray powder diffraction, BET measurements of surface area, pyrolysis desorption, and chemical methods.

Nickel-alkanes. Because the ability of nickel atoms to migrate and cluster in a low-temperature matrix should be proportional to the solvent's permeability (glassiness or visiosity) and ability to complex, we undertook a study of a series of alkanes with nickel. Here, very similar weak complexation would occur, and so any differences in particles obtained should simply be dependent on matrix per-

TABLE 3
PHYSICAL DATA ON METAL PARTICLES

M (solvent)	Solvent/Metal Ratio*	Surface Area (m^2/g)†	Particle Size‡ and Shape (μm)
Ni (hexane)	1 : 25	45	5 × 20, rough pieces§
Ni (toluene)	1 : 40	100	0.5–0.8, spheres
Ni (THF)	1 : 3	400	0.5–1.5, spheres
Raney Ni¶	—	80–100	90%, 2–40

* Determined by desorption of organics on pyrolysis.

† BET methods used, except with Ni-THF, where solvent and gas desorption was employed to calculate surface area.

‡ Crystallite sizes could not be determined quantitatively due to the large line broadenings observed. These wide lines indicate crystallite sizes of less than 100 Å, a region where the Scherrner equation does not apply. Relative crystallite sizes were determined by comparing the broad line coincident with the 111 reflection (*d* spacing, 2.01 Å) for commercial nickel powder by utilizing copper Kα radiation: Raney Ni (2θ broadening of 2°) > Ni-hexane (3° broadening) > Ni-toluene (4° broadening) > Ni-THF (8° broadening) > commercial Ni powder (0.5° broadening). More detailed analysis of Ni-toluene showed only the one broad line coincident with the 111 reflection, whereas Ni-THF showed two very broad lines, one corresponding to the 111 reflection and the other at lower angle with a *d* spacing of about 4 Å.

§ Very rough edges and an average size.

¶ Grace no. 28.

meability. We did find differences. However, it now appears that these differences are not necessarily due to the alkane employed but, rather, to the *amount* of alkane deposited with the nickel vapor. If large portions of pentane are deposited with nickel (nickel/pentane molar ratio = 0.57%), the resultant black powder obtained is composed of nonferromagnetic very small crystallites.[48] If less pentane is employed, larger crystallites that are ferromagnetic are obtained.[48] The nonferromagnetic particles must be less than 100 Å crystallites, and the ferromagnetic ones must be larger than 300 Å, so quite a size range is evident.[49] (It is extremely difficult to determine exact crystallite sizes for these powders because BET and chemisorption methods give erratic results due to adherring solvent. X-ray powder methods are poor for such small particles.)

These particles serve as very active hydrogenation catalysts for benzene and cyclohexene. The powders are pyrophoric and reactive with alkyl halides, even after removal of excess solvent under vacuum at room temperature (several hours pumping down to 5×10^{-3} Torr).

Nickel-aromatics. Nickel-benzene[33] and -toluene[44] slurries have been prepared. The black powder from nickel-toluene is in the form of tiny spheres, which are reactive with alkyl halides but fairly unreactive as a hydrogenation catalyst. The particles are ferromagnetic or nonferromagnetic, depending on the nickel/toluene ratio employed.

Nickel-THF. A yellow matrix forms on codeposition that consists of a reactive low-temperature stable Ni(0)-etherate.[44] Warming of the Ni-THF complex results in black streams of Ni-THF flowing to the bottom of the reactor. The resultant Ni-THF slurry is very finely divided and totally syringeable. After removal of THF under high-vacuum pumping for several hours at room temperature, a fine Ni-THF powder is formed that is fairly unreactive as a hydrogenation catalyst but that is a very good catalyst for cyclohexane disproportionation to benzene and cyclohexane. A great deal of residual THF is strongly bound and can only be displaced by strong ligands, such as triethylphosphite, but not by excess amines, alkenes, or

TABLE 4
PRODUCTS OF REACTIONS OF NICKEL-THF SLURRIES WITH ORGANOHALIDES (AFTER REFLUX AT 55–60°C FOR SEVERAL HOURS; YIELDS BASED ON ORGANOHALIDE CONVERTED)

Organohalide	Products
Allyl bromide	propene (19%), 1,5-hexadiene (23%), 1,4-hexadiene (21%)
Allyl iodide	propene (47%), 1,5-hexadiene (8%), 1,4-hexadiene (5%)
Benzyl chloride	bibenzyl (33%), toluene (2%)
Iodobenzene	biphenyl (6%)
Bromobenzene	biphenyl (0%)
Chlorobenzene	biphenyl (0%)
1-Bromobutane	butane (21%), 1-butene (7%), *C*-2-butene (2%), *t*-2-butene (1%)
2-Bromobutane	butane (4%), 1-butene (0.6%), *C*-2-butene (0.6%), *t*-2-butane (0.5%)
2-Iodopropane	propane (17%), propene (9%)
1-Bromopropane	propane (15%), propene (7%)

ethers. The particles are surprisingly uniform as tiny spheres, which, on strong heating, release organics (THF, 45%; butyraldehyde, 20%; 1-butanol, 30%; furan, 5%), with formation of larger nickel crystals.

The Ni—THF slurry refluxed with alkyl halides quickly yields NiX_2 and reduction products of the alkyl halide, the necessary hydrogen coming apparently from THF. TABLE 4 summarizes some of these studies.

Zinc

Active slurries of zinc in THF, diglyme, toluene, and hexane have been prepared. Alkyl bromides react in any of these solvents to yield dialkyl zinc compounds. This is the first report that active zinc in both polar and nonpolar solvents is available.[50]

Cadmium

We have described the first examples of direct reaction of cadmium metal with alkyl halides in both polar and nonpolar solvents.[50] Cadmium slurries in diglyme, dioxane, THF, hexane, and toluene were prepared in 9-g batches of cadmium and allowed to react with alkyl halides to yield R—Cd compounds in yields of 55–83%, with the diglyme slurry giving the highest yield.

Aluminum

Aluminum—diglyme and —dioxane slurries react readily with C_6H_5X (X = Cl, Br, I) to form $(C_6H_5)_2AlX$.[51]

Indium

Indium—diglyme and —dioxane slurries react readily with C_2H_5I to form $(C_2H_5)_2InI$ and InI.[51]

Tin

Tin—THF slurries react with CH_3I to yield a mixture of CH_3SnI_3, $(CH_3)_2SnI_2$, and $(CH_3)_3SnI$. Of more interest is the reaction of CF_3I with Sn/THF, which yields $(CF_3)_2SnI_2$.[51] With CF_3Br, a mixture of $(CF_3)_3SnBr$, CF_3SnBr_3, and $(CF_3)_2SnBr_2$ was obtained, while C_6F_5Br yielded $(C_6F_5)_3SnBr$. Reaction of C_6H_5I with Sn/THF yielded only SnI_4, however.

Lead

Lead slurries in THF or diglyme react with CH_3I, yielding $(CH_3)_3PbI$, as the first example of a direct lead metal—alkyl halide reaction.[51] Further work with CF_3I and $BrCH_2CO_2Et$ is in progress and appears promising.

Tellurium

This element vaporizes very readily as tellurium telomers. By use of a refluxing tellurium-pentane slurry, CH_3I reacts to form $(CH_3)_2TeI_2$ in 80% yield. Similarly, a tellurium/pentane—C_2H_5I reaction yielded $(CH_3)_2TeI_2$ in 30% yield.[52]

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PHOTOCHEMICAL STUDIES ON ORGANIC DERIVATIVES OF TITANIUM, ZIRCONIUM, AND HAFNIUM*

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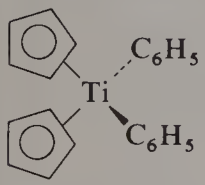
Photochemical reactions of organometallic compounds have been observed for more than 85 years,[1] but only in the past 20 years have they been extensively explored. In the transition metal area, photochemically induced reactions of the metal carbonyls have been studied in detail in recent years,[2] although only scattered reports have appeared dealing with photolytic reactions of organotransition metal compounds that contain σ-bonded substituents.[3–16] Most of these reports have considered irradiation of transition metal compounds that contain both carbonyl and σ-bonded organic ligands. In many of these cases, the carbonyl groups are labilized, while the σ-bonded substituent is not affected.

In 1974, we briefly reported results of some photochemical studies on σ-bonded organotransition metal compounds of the type $(\eta^5\text{-}C_5H_5)_2M(CH_3)_2$, where M = Ti, Zr, or Hf.[17] These compounds, to which we can give the trivial names dimethyltitanocene, -zirconocene, and -hafnocene, respectively, are readily available from recent synthetic studies by Samuel and Rausch[18] and others.[19,20] In this paper, we will summarize some of our recent studies in this area and will describe extensions to diphenyltitanocene and certain η-indenyl and η-fluorenyl analogs.

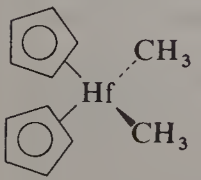
X-Ray Crystallographic Studies

Several dimethyl- and diphenylmetallocene derivatives of group-IVB metals have been examined recently by single-crystal x-ray diffraction techniques, and these results are summarized below:



(Reference 21)

$Ti{-}C_6H_5 = 2.272\ (14)$ Å (average)
$C_6H_5{-}Ti{-}C_6H_5 = 97.3°$



(Reference 22)

$Hf{-}CH_3 = 2.318\ (8)$ Å; $2.382\ (7)$ Å
$CH_3{-}Hf{-}CH_3 = 94.8°$

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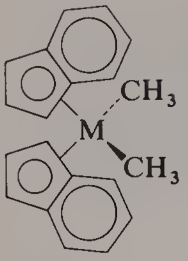


(Reference 23)

	Ti	Zr	Hf
	Bond Lengths (Å)		
M—C(σ)	2.21 (2)	2.251 (6)	2.332 (12)
M—C(η^5) (average)	2.44	2.55	2.53
	Bond Angles (degrees)		
C(σ)—M—C(σ)	92.8 (12)	96.9 (3)	96.0 (6)
Cent—M—Cent	119.8 (14)	120.8 (5)	121.0 (9)

The results clearly illustrate that the four organic ligands bonded to the central metal atom are arranged in a pseudotetrahedral manner, with the cyclopentadienyl or indenyl substituents *pentahapto* bonded and the methyl or phenyl groups *monohapto* bonded to the metal.

PHOTOLYSIS STUDIES ON DIMETHYLMETALLOCENE DERIVATIVES

When dimethyltitanocene, -zirconocene, or -hafnocene are irradiated in either hexane or benzene solution in a Pyrex® Schlenk tube ($\lambda > 300$ nm) for 6–8 hr, the solutions darken, and gas formation is evident. In the case of photolysis of dimethyltitanocene in hexane solution, for example, gas chromatographic analysis of the gas indicates its composition to be primarily methane (99%), together with smaller amounts of ethane (0.5%) and ethylene (0.05%). Dark, exceedingly reactive precipitates are formed during these photolyses in hexane, and total elemental analyses of these products indicate that they have the general composition $(C_{10}H_{10}M)_n$, where M = Ti, Zr, or Hf.

Attempts to more fully characterize these group-IVB metallocenes by use of physical and spectroscopic techniques have been severely hampered by their noncrystallinity, lack of volatility, and generally low solubilities in non-coordinating solvents. Mass spectral studies have not been successful on zirconocene (M = Zr) or halfnocene (M = Hf), while mass spectral studies on titanocene (M = Ti) produced by this photochemical method indicate that it is not as volatile as is titanocene produced by other methods.[24] At 180°C, however, a spectrum can be obtained that is similar to that previously reported for titanocene.[24] The most intense peak at *m/e* 178 can correspond either to $(C_{10}H_{10}Ti)^+$ or a doubly charged dimer ion. In addition, peaks at masses appreciably above $(C_{10}H_{10}Ti)_2{}^+$ are observed, including a peak at *m/e* 452, which could correspond to the ion $[(C_5H_5)_4Ti_4]^+$, produced either by recombination in the mass spectrometer or by fragmentation of an oligomer.

Solution molecular weight studies on titanocene (cryoscopic in benzene) indicate that the benzene-soluble portion (~70–80%) gives averaged values for a tetramer of composition $(C_{10}H_{10}Ti)_4$. Presumably, the remainder of the material is of higher molecular weight.

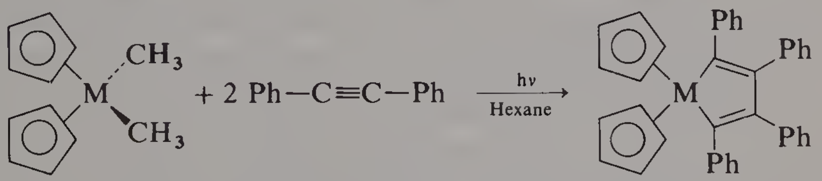
Infrared studies on these group-IVB metallocenes are perhaps the most revealing in terms of physical data. When recorded in Nujol®, the spectra are virtually identical and exhibit only absorptions that are characteristic of η^5-cyclopentadienyl—metal complexes. It is important to note that photochemically generated titanocene does not show any absorptions in the vicinity of 1230 cm^{-1}, which have previously been attributed to bridging metal—hydrogen—metal bonds in titanocene prepared by other methods.[24] Furthermore, in contrast to titanocene prepared by chemical methods, our photochemically generated titanocene exhibits carbon—hydrogen bending vibrations at 800 and 1015 cm^{-1}, which appear as sharp, unsplit bands and give further evidence for the presence of η^5-cyclopentadienyl rings.

Reactions of photochemically generated titanocene with either hydrogen chloride in toluene at −78°C or with bromine in toluene at −78°C have been performed. The major products are titanocene dichloride and titanocene dibromide, respectively. In both of these compounds, the cyclopentadienyl rings are well known to be symmetrically bonded to the titanium atom.

Various deuteration experiments have been performed on the photolysis of dimethyltitanocene by use of specifically deuterated derivatives, such as $(C_5H_5)_2Ti(CD_3)_2$ and $(C_5D_5)_2Ti(CH_3)_2$, and deuterated solvents. The studies were performed by photolyzing the appropriate materials and then analyzing the methane produced for deuterium content, by use of mass spectrometry and low ionizing voltages. The data collectively indicate that the methane that is produced in these photolyses derives hydrogen from either a second methyl group or from a cyclopentadienyl substituent but *not* from the solvent. The experiments also indicate that there is a significant deuterium isotope effect in the formation of methane in these systems.

The photolysis of dimethyltitanocene in the presence of anthracene was undertaken to determine if the reaction was radical in nature. In addition to the expected photodimer of anthracene (80% yield), 9-methylanthracene was also isolated in 8% yield. This experiment implicates the transient existence of methyl radicals in these photochemical processes; however, the results are not conclusive, because the presence of anthracene could change the course of this photochemical reaction. Nevertheless, the photochemically induced decomposition of dimethyltitanocene produces products that are symptomatic of intermediate species that possess radical-like character, although these species are most certainly not "free" radicals. A similar suggestion, previously made[25] for the thermolysis of $(C_5H_5)_2Ti(CH_3)Cl$, that the radical was within the coordination sphere of the titanium atom appears to best explain the data.

When the dimethyl derivatives of titanocene, zirconocene, or hafnocene are photolyzed in solution in the presence of acetylenes, metallocycles are frequently the major products. Photolysis in the presence of diphenylacetylene, for example, produces the corresponding metallocycles in 35–50% yields:

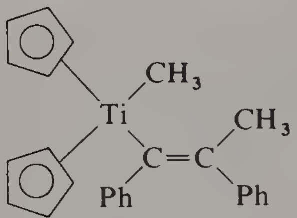


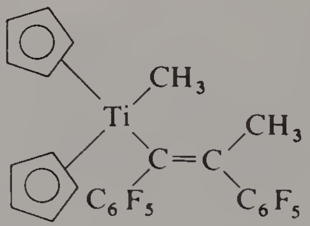
M	Color	$[M]^+$	τ Cp (CCl_4)
Titanium	green	534 (^{48}Ti)	3.77
Zirconium	orange	576 (^{90}Zr)	3.70
Hafnium	yellow	666 (^{180}Hf)	3.78

These photochemical methods currently represent the most facile route for preparing these group-IVB metallocycles. The procedure seems to be a rather general one, and recent studies have indicated that metallocycles that contain substituents other than phenyl can also be obtained. We are, likewise, also currently studying the chemical reactivity of these metallocyclic systems.

In collaboration with Prof. Jerry Atwood of the University of Alabama, we have recently completed a single-crystal x-ray crystallographic investigation of the above-mentioned titanacycle, 1,1-bis(η^5-cyclopentadienyl)-2,3,4,5-tetraphenyltitanole, and of its hafnium analog.[26] These studies have confirmed that the configuration of each species is that of a metallocyclopentadiene ring system. Within each five-membered ring, the π-electron framework is largely localized. For the titanium structure, the values of the two crystallographically independent Ti—C (σ) bond lengths are 2.172 (5) and 2.141 (5) Å, while for the hafnium structure, the Hf—C (σ) bond lengths are 2.18 (2) and 2.22 (2) Å.

Detailed studies on the photolysis of dimethyltitanocene in the presence of diphenylacetylene have revealed the formation of a second organometallic product, in addition to the titanacycle. This product is formulated as methyl(1,2-diphenylpropenyl)titanocene on the basis of its mass spectrum, its diagnostic nuclear magnetic resonance spectrum, and its conversion under acidic conditions into methane and *cis*-1,2-diphenylpropene.

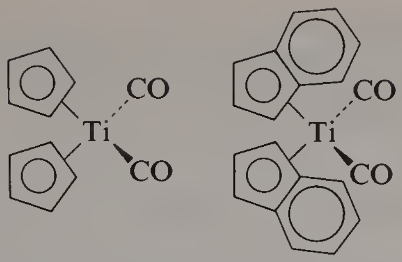




The photolysis of dimethyltitanocene in the presence of the highly fluorinated acetylene bis(pentafluorophenyl)acetylene yielded only one isolable product, methyl-(1,2-bispentafluorophenylpropenyl)titanocene (see above), the structure of which was confirmed by elemental analysis, mass spectrometry, and proton magnetic resonance spectrometry. It is interesting to note that in this reaction, the expected perfluorinated metallocycle was not detected.

The isolation and characterization of these two methylpropenyltitanocenes are of special importance to an understanding of Ziegler-Natta catalysis, because it has long been postulated that this industrially important process involves initial coordination of ethylene to the titanium atom, followed by insertion of the coordinated ethylene into a titanium—alkyl σ bond. The present result, which represents a definitive example of the insertion of an unsaturated hydrocarbon into a carbon—titanium σ bond, thus provides further verification for one of the important steps in this mechanism.

As mentioned previously, photochemically generated titanocene is highly reactive. For example, it reacts readily with dinitrogen in THF solution to form a dark purple nitrogen-containing complex. It reacts readily with carbon monoxide in benzene solution to form titanocene dicarbonyl, $(\eta^5\text{-}C_5H_5)_2Ti(CO)_2$, in essentially quantitative yield. A simpler procedure for the production of this interesting group-IVB metal carbonyl is merely to photolyze dimethyltitanocene in hexane solution while simultaneously bubbling carbon monoxide through the solution. In this way, titanocene dicarbonyl can be prepared in isolated yields of about 60%. This photolysis technique is also extendable to the formation of bis(indenyl)titanium dicarbonyl from dimethyl bis(η^5-indenyl)titanium.[27] Now that a convenient route to these interesting group-IVB metal carbonyls has been developed, we are currently investigating their chemistry.



Again in collaboration with Prof. Atwood, we have recently completed a single-crystal x-ray diffraction study on titanocene dicarbonyl.[28] The four ligands are arranged in a pseudotetrahedral array around the titanium atom, and the titanium—carbonyl bond length is 2.030 (11) Å, while the C—Ti—C bond angle is 87.6 (6)°. A comparison with similar metal—carbonyl distances of other metal carbonyls of the first transition series reveals that the metal—carbon separations agree very well with those predicted from metallic radii data, whereas only a slight bond length increase was noted in the early transition metal complexes.

Photolysis Studies on Diaryltitanocene Derivatives

The photochemically induced reaction of diphenyltitanocene in benzene solution also proceeds cleanly, with removal of the phenyl substituents and formation of titanocene. The latter appears to be similar in nature to titanocene produced in dimethyltitanocene photolyses. Surprisingly, however, the only organic product detected in this process is biphenyl, which was formed in 61% yield on the basis of two equivalents of phenyl radicals generated. This result is in striking contrast to the thermal degradation of diphenyltitanocene, either in the solid state or in solution. In these cases, benzene was the *only* organic decomposition product observed, and biphenyl specifically was not formed.[29] To ascertain the source of the biphenyl, the photolysis of diphenyltitanocene was also conducted in hexadeuterated benzene. Analysis of the biphenyl by mass spectrometry in this experiment indicated that 46% biphenyl-d_0 and 54% biphenyl-d_5 were present. On this basis, more than 90% of the phenyl groups originally bonded to titanium can be accounted for.

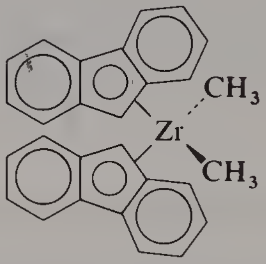
The data also suggest two simultaneous pathways for this photolytic degradation process. One pathway would involve the formation of phenyl radicals, which could then react with the solvent to yield biphenyl. The second would involve reductive elimination of biphenyl from the titanium species. Of course, other variations on these two pathways are also possible.

The photolysis of di(*p*-tolyl)titanocene in benzene solution has produced further evidence for these photochemically induced degradative pathways. In addition to titanocene, 4,4′-dimethylbiphenyl, 4-methylbiphenyl, and toluene were identified as products, in yields of 48, 10, and 11%, respectively. Again, 4,4′-dimethylbiphenyl could arise from reductive elimination of the *p*-tolyl substituents from di(*p*-tolyl)-titanocene, and the 4-methylbiphenyl could arise from attack of *p*-tolyl radicals on the solvent. Toluene is undoubtedly formed by abstraction of hydrogen from the photochemically generated aryl radical.

Additional evidence for the generation of aryl radicals in these photochemical processes has been obtained from the photochemically induced reaction of diphenyltitanocene in the presence of anthracene, a known radical-trapping reagent. In addition to the expected photodimer of anthracene, both 9-phenylanthracene and 9,10-dihydroanthracene have been obtained in low yield. The isolation and identification of these products, again, provide evidence for the intermediate formation of phenyl radicals in processes of this type.

FORMATION AND PHOTOLYSIS OF BIS(FLUORENYL)DIMETHYLZIRCONIUM

Our interest in the formation and photolytic decomposition of σ-bonded derivatives of the early transition metals has recently prompted us to study certain bis(fluorenyl) derivatives. Bis(fluorenyl)dimethylzirconium has been prepared from fluorene, methyllithium, and zirconium tetrachloride by a new and convenient route.[30]



The hafnium analog has been prepared in an analogous manner, starting with hafnium tetrachloride; however, it is much less stable thermally. Proton magnetic resonance of Flu_2ZrMe_2 shows that the coordinated methyl groups exhibit a resonance at τ 12.06, which indicates that the protons of these substituents are highly shielded. Photolysis of Flu_2ZrMe_2 in hydrocarbon solvents leads to cleavage of the methyl groups. Both methane and a bis(fluorenyl)-type compound of possible polynuclear nature are produced. Infrared studies on specifically deuterated analogs have shown that this process occurs, at least in part, by intramolecular proton abstraction from the π—coordinated fluorenyl rings.

CONCLUSIONS

Photochemically induced reactions of σ-bonded alkyl and aryl derivatives of the early transition metals offer many exciting possibilities in both organic and organometallic syntheses. Photolytic reactions of these types produce organic and organometallic intermediates of high reactivity and synthetic value.

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BASE EFFECTS ON SELECTED ZIEGLER-TYPE CATALYSTS

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INTRODUCTION

Ziegler-type catalysts are generally considered to consist of a reducing alkyl metal compound from groups I–III with a reducible transition metal compound from groups IVB–VIII. The enormous variety of catalyst compositions makes possible the synthesis of products that range from dimers to oligomers to stereoregular high polymers, starting from olefins, diolefins, and vinyl monomers. With the number of publications and patents running into the tens of thousands, some general references are appropriate.[1–5] The elegant work by Wilke *et al.* on cyclooligomerization of dienes is outside the scope of this paper, although low-valence, or zero-valence, group-VIII metal catalysts may be prepared from Ziegler-type combinations.

After a brief illustration of some types of uses for Ziegler-type catalysts in polymerization reactions, this paper will present three different effects of Lewis bases and attempt to relate the effects to the catalyst structures. Catalyst site structures and mechanisms are proposed to explain the steric defects and inversions that occur during polymerization of α-olefins to isotactic polymers.

POLYMER SYNTHESIS WITH ZIEGLER-TYPE CATALYSTS

With the many variations in both the alkyl metal and the transition metal components, there are literally hundreds of thousands of combinations possible for use in polymer synthesis. In practice, the number of useful catalysts is much more limited but still very large. By far the most useful alkyl metal is aluminum, although lithium, magnesium, and zinc alkyls have also found application. For the transition metal component, the salts of titanium and vanadium are outstanding, with uses for zirconium, chromium, molybdenum, and tungsten falling far behind.

Industrially, large quantities of aluminum trialkyl, dialkylaluminum chloride, and monoalkylaluminum dichloride are used in combination with titanium trichloride, titanium tetrachloride, and vanadium oxychlorides to prepare plastics and elastomers from olefins and diolefins. For example, polypropylene production in the United States is now in excess of 1,200,000 tons per year. Most of this polypropylene is made by use of Et_2AlCl in combination with δ-$TiCl_3 \cdot xAlCl_3$ catalyst. The discovery and development of the commercial polyolefin catalysts have been reviewed by Tornqvist.[6]

The diversity of products made with Ziegler-type catalysts is remarkable not only because so many different monomers may be used but also because so many different products can be obtained from each monomer (TABLES 1 & 2). This diversity is generally achieved by changing catalyst composition, monomer concentration, or polymerization temperature.

Table 1

Polyolefin Products Made with Ziegler-Type Catalysts

Monomer	Catalyst Type	Polymer Type
Ethylene	AlR_3/Ni salt	butenes
Ethylene	$Al_2R_3Cl_3/TiCl_4$	branched oils (low pressure)
Ethylene	$AlCl_2/Zr(OR)_4$	α-olefins (high pressure)
Ethylene	AlR_3/IVB-VIB MX_n	polyethylene
α-Olefins	$AlRCl_2/TiCl_3$	oils
α-Olefins	$AlR_2NR_2/TiCl_3$	atactic
α-Olefins	AlR_2Cl/VCl_3	stereoblock
α-Olefins	$AlR_2Cl/TiCl_3$	isotactic
α-Olefins	AlR_2Cl/VCl_4(−78°C)	syndiotactic

As shown in Table 1, ethylene can be converted into 1- and 2-butene, liquid products, or polyethylene plastic. When oligomerization catalysts are used at low monomer concentrations or high temperatures, one obtains branched oils that are attractive lubricating oils. At high ethylene concentrations, the oligomerization catalysts produce linear α-olefins.

In the polymerization of propylene and higher α-olefins, one also can vary stereoregularity to change product properties. Each side chain attachment along the polymer chain results in a chiral center. Random R and S placements produce atactic, noncrystalline polymers. Long sequences of either R or S placements produce isotactic, crystalline polymers. When the R and S sequences are separated by atactic sequences, the result is a "stereoblock" polymer, which is elastomeric by virtue of its short crystalline "cross-links." Finally, a regular alternation of R and S placements is called "syndiotactic," and this product is, again, crystalline. Isotactic polymers are obtained at 25–100°C by use of catalysts with chiral sites. Syndiotactic polymers, on the other hand, are produced at low temperatures (−78°C), where steric control is due to the last unit of the growing chain end rather than the catalyst site. There is also evidence in syndiospecific polymerizations that chain propagation occurs mainly with secondary insertion.[7]

The melting points of isotactic poly-α-olefins are plotted in Figure 1 as a function of the number of carbons in the side chain. Polymer melting points decrease from 176°C (polypropylene) to −55°C [poly(1-hexene)], then increase gradually. Up to poly(1-hexene), the crystallinity is derived from the polymer backbone, whereas the higher polyolefins reflect side chain crystallinity.

Table 2

Diene and Cycloolefin Polymers

Monomer	Catalyst Type	Polymer Structure
Butadiene	$AlR_3/Ti(OBu)_4$	1,2-isotactic
Butadiene	$AlR_3/CoCl_2 \cdot 2$ pyridine	1,2-syndiotactic
Butadiene	AlR_3/TiI_4	1,4-*cis*
Butadiene	$AlR_2I/TiI_3 \cdot$base	1,4-*trans*
Cyclobutene	$Al(Hex)_3/VCl_4$	Diisotactic polycyclic
Cyclobutene	$AlR_2Cl/V(AcAc)_3$	disyndiotactic polycyclic
Cyclobutene	$AlR_3/TiCl_4$	*cis*—C=C—C—C—
Cyclobutene	$AlR_3/TiCl_3$	*trans* —C=C—C—C—
Cyclopentene	AlR_3/WCl_6	*trans* —C=C—C—C—C—
Cyclopentene	$AlR_3/MoCl_6$	*cis* —C=C—C—C—C—

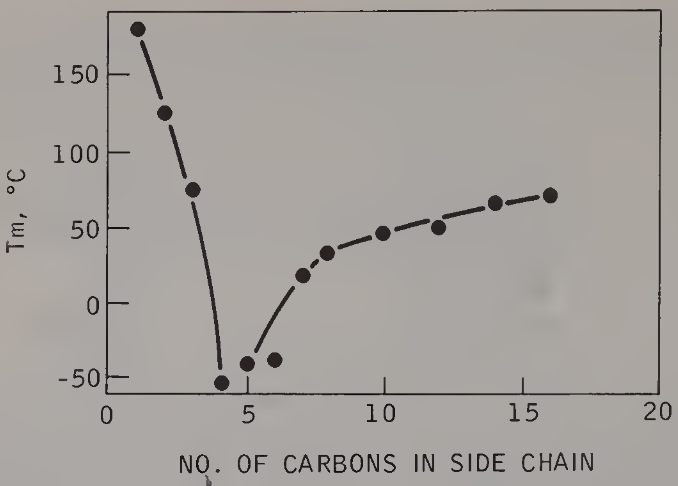


FIGURE 1. Melting points of isotactic poly-α-olefins.

When the olefin contains substituents on C-3 or C-4, the polymer side chains are more bulky and make the isotactic polymer helices more rigid and better capable of crystallization, resulting in higher melting points. Examples include poly(3-methyl-1-butene) (300°C), poly(4-dimethyl-1-pentene) (350°C), polystyrene (240°C) and polyvinylnaphthalene (360°C). Thus, polyolefins cover the range from amorphous, low-melting, or rubbery solids to hard, crystalline, high-melting plastics.

Equally remarkable control of product structure is shown in TABLE 2 for diene and cycloolefin polymerization. In addition to the expected isotactic and syndiotactic polymers, cycloolefins also undergo ring opening polymerization to *cis* and *trans* unsaturated polymers. Even more complex and sophisticated product structures have been prepared selectively from higher dienes and from polar monomers.[8]

Other uses that have been discovered for Ziegler-type catalysts include metathesis of olefins, isomerization, hydrogenation, and alkylation.

BASE EFFECTS

The modification of Ziegler-type catalysts by addition of electron donor compounds has been reviewed extensively by both Jordan and Hoeg in their chapters in Ketley.[4] The general conclusion was that Lewis bases react in two different ways: poison the exposed, less stereospecific catalyst sites by complexation and activate stereospecific catalyst sites electronically by adsorption in the vicinity of the stereospecific sites. Boor[9,10] proposed these two processes on the basis of extensive studies with various types of bases in combination with selected Ziegler-type catalysts. Though both processes certainly occur, Boor's interpretation is somewhat questionable, because much weight was placed on the assumption that diethylzinc did not form stable complexes with Lewis bases, such as triethylamine or pyridine. It is now known that the 1 : 1 complexes are stable, isolable compositions,[11] and the stability of alkylaluminum—base complexes is well established. Thus, one should expect a strong effect on both the alkyl metal and the transition metal components. Dissociation of alkylmetal—base complexes is to be expected with weak complexes but not with very strong complexes, so different mechanisms must be operative.

Several specific effects of bases on the alkylmetal component have been reported. Zambelli *et al.*[12,13] have shown that strong bases can disproportionate an excess of $EtAlCl_2$ into $Et_2AlCl + AlCl_3$—base. Caunt[14] has shown that the rate of polymerization is inversely proportional to the amount of $EtAlCl_2$ present and proposed that the increased activity on addition of bases is due to the removal of $EtAlCl_2$ by complexation. In the reaction of titanium trichloride with triethylaluminum in the presence of Lewis bases, Takashi[15] found that the rate of alkylation of titanium trichloride was greatly increased by addition of pyridine up to 1 mol per mole of triethylaluminum, and it was completely inhibited by a slight excess of pyridine. He concluded that no complex between titanium and pyridine is involved as an intermediate in the alkylation. Instead, the triethylaluminum-base complex reacts with the titanium trichloride, probably via double-salt formation, such that the base is coordinated adjacent to an active site where it improves stereospecificity.

The acidity and acid strength of titanium trichloride have been measured before and after reaction with triethylaluminum by Tanabe and Watanabe[16] by use of a butylamine titration method developed by Tamele,[17] Johnson,[18] and Benesi.[19,20] They found a distribution of strong acid sites for both types of catalyst. Unfortunately, the total acidity was greater than calculated for a surface monolayer, making questionable any conclusions regarding surface sites. A similar result was obtained in the author's laboratory with trimethylamine, which penetrated the lattice to complex the underlying titanium atoms. Cationic aspects of Ziegler-Natta catalysts have been reviewed with respect to monomer coordination, catalyst mechanism, and stereospecificity.[21]

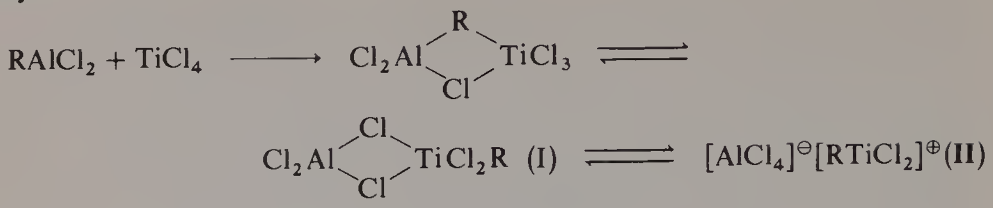
It is clear from the preceding discussion that the complexation of bases with Ziegler-type catalysts is, indeed, complex. Both product type and stereoregularity are strongly influenced by addition of Lewis bases to Ziegler-type catalysts. This paper will illustrate selected base effects in ethylene oligomerization (molecular weight control). butadiene polymerization (*cis-trans* control), and propylene polymerization (isotacticity control). These examples were taken from work performed at Exxon laboratories, although many other examples could be cited. An attempt is made to interpret the effects in terms of possible catalyst structures and stereoregulation mechanisms.

Ethylene Oligomerization

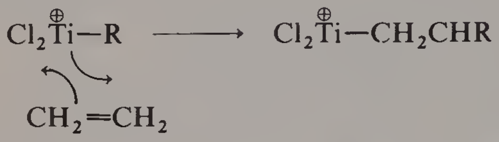
High-purity linear α-olefins from C_4 to C_{500} are prepared by catalytic oligomerization of ethylene by use of a soluble alkylaluminum chloride—group-IVB metal chloride catalyst.[22,23] Halide-free transition metal compounds may be used, particularly in zirconium-based catalysts, but exchange with the chlorides in the excess alkylaluminum chloride component is necessary for activity.[24] The steps involved in catalyst formation and oligomerization are illustrated for titanium tetrachloride catalyst.

The available evidence supports an ion-pair catalyst of the type shown. Both monomer insertion and chain transfer (displacement by monomer) are facilitated by the positive charge on the titanium. As expected from this mechanism, there is no effect of ethylene concentration on molecular weight, because the same monomer can either insert or displace the chain. These two possibilities result in random growth and chain transfer, which yield a product with $\overline{M}_w/\overline{M}_n = 2$. Molecular weight decreases with decreasing temperature and with increasing solvent polarity due to increased ion pairing.

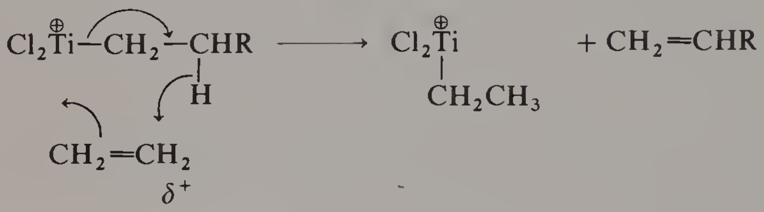
Catalyst Formation



Oligomerization



Chain Transfer



Addition of HMPA (hexamethylphosphoramide), a strong Lewis base, or hexamethylbenzene, a strong π base, causes the various effects shown in TABLE 3.[25,26] Less than equimolar amounts of HMPA, based on titanium tetrachloride, increase activity, whereas hexamethylbenzene decreases activity substantially. Both increase molecular weight, although the π-base effect is greater. Polyethylene yield increases sharply with HMPA but not at all with hexamethylbenzene (the 2% value is actually the high-molecular-weight tail end of the olefin distribution).

Bearden *et al.* interpret these effects as follows. The strong Lewis base selectively complexes the aluminum chloride component of the catalyst, which is replaced by the excess $EtAlCl_2$. Because $EtAlCl_2$ is a weaker acid than aluminum chloride, complex **III** is less ionic than **II**, and chain transfer is less favorable, resulting in

TABLE 3
BASE EFFECTS ON ETHYLENE OLIGOMERIZATION
(5-6 $AlEtCl_2/TiCl_4$, *n*-HEPTANE, 45 atm, 35°C)

Mole Percent of Base on $TiCl_4$	Grams of Product/Grams of $TiCl_4$/hr	α-Olefins, $\overline{M}_n$	Polyethylene (%)
0	135	181	1.0
60 HMPA*	167	225	3.0
100 HMPA	193	255	6.0
115 HMPA	130	315	14.6
0	176	187	<1
33 C_6Me_6†	167	270	<1
100 C_6Me_6	67	400	2.0

* Hexamethylphosphoramide.
† Hexamethylbenzene.

higher-molecular-weight olefins. The $\text{HMPA}\cdot\text{AlCl}_3$ complex was recovered and identified. Polyethylene results from more extensive alkylation of titanium, which decomposes to the heterogeneous Ziegler catalyst.

$$\mathbf{I} \xrightarrow{\substack{\text{HMPA}\\ \text{RAlCl}_2}} \text{HMPA}\cdot\text{AlCl}_3\downarrow + [\text{RAlCl}_3][\text{RTiCl}_2] \qquad \mathbf{(III)}$$

On the other hand, when a π base is added, it complexes the titanium component, decreasing the positive charge, which also increases molecular weight but decreases activity. An analogous crystalline ternary complex of this type, but with the alkyl group replaced by chlorine, was isolated and characterized ($\text{C}_6\text{Me}_6\cdot\text{TiCl}_3{}^+\text{AlCl}_4{}^-$). This finding supports the concept of an equilibrium that leads to complex **IV**.

$$\mathbf{II} \xrightleftharpoons{\pi\ \text{base}} [\text{AlCl}_4]^{\ominus}[\text{RTiCl}_2\cdot\pi\ \text{base}]^{\oplus} \qquad \mathbf{(IV)}$$

Both base effects have therefore been fully characterized. In this system, clearly the Lewis base reacts selectively with the most acidic aluminum component, and the π base reacts selectively with the transition metal component. Although this catalyst is a soluble one, as opposed to the heterogeneous catalysts used for propylene polymerization, it supports the idea that an important base effect is the removal of RAlCl_2 poison from the TiCl_3 surface.

Butadiene Polymerization

Another catalyst in which base effects are both useful and informative is the cocrystallized $\text{TiI}_3\cdot x\text{AlI}_3$ system used with AlEt_3 for butadiene polymerization. Tornqvist and Cozewith[27,28] have conducted extensive work developing catalysts that permit nearly complete control over the polybutadiene *cis-trans* microstructure. These catalysts, which contain excess aluminum iodide, dissolve in benzene and react with triethylaluminum to give the mixed dimer $\text{EtTiI}_2\cdot\text{Et}_2\text{AlI}$ (**V**) plus excess Et_2AlI.

$$\text{TiI}_3\cdot n\ \text{AlI}_3 + (2n+1)\ \text{AlEt}_3 \longrightarrow 3n\ \text{Et}_2\text{AlI} + \text{EtTiI}_2\cdot\text{AlEt}_2\text{I} \qquad \mathbf{(V)}$$

The polymer prepared with this catalyst contains more than 95% *cis* unsaturation. When a strong base, Et_3N, is added, there is little effect on activity until the amount exceeds the total aluminum present, at which point it drops to very low levels (FIGURE 2). The *trans* unsaturation begins to increase at this point. It is clear that the strong base first forms a 1 : 1 complex with the alkylaluminum iodides and then complexes the titanium sites to the exclusion of monomer.

When a weak base, tetrahydrothiophene (THT), is added, the catalyst activity remains high, even at very high ratios of base to catalyst (FIGURE 3). Again, the *trans* unsaturation increases once all the aluminum has been complexed, but now it is possible to attain any *trans* content up to about 90% while maintaining high polymerization rates.

Tornqvist's interpretation of the base effects can be summarized by the equations below.

$$\begin{array}{l}
\mathbf{V}\ \ + 3n\ \text{Et}_2\text{AlI} + 3n\ \text{base} \rightarrow \mathbf{V} + 3n\ \text{Et}_2\text{AlI}\cdot\text{base}\\
\mathbf{V}\ \ + \text{base} \rightarrow \text{base}\cdot\text{EtTiI}_2\cdot\text{Et}_2\text{AlI} \quad \mathbf{(VI)}\\
\mathbf{VI} + \text{excess weak base} \rightarrow \quad \mathbf{VI}\\
\mathbf{VI} + \text{excess strong base} \rightarrow \text{inactive.}
\end{array}$$

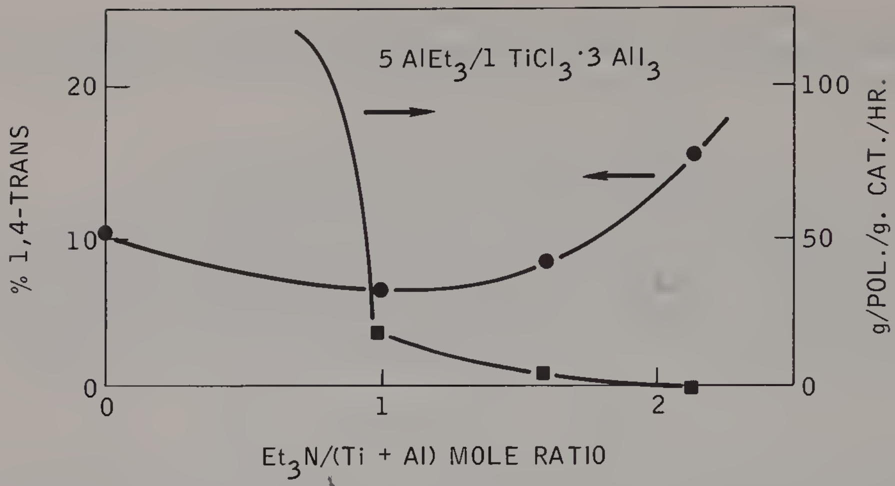


FIGURE 2. Effect of triethylamine on butadiene polymerization (benzene, 25°C).

The site structures proposed for **V** and **VI** are shown along with their product type (FIGURE 4).

Examination of models suggests that these site structures could well explain the *cis*-1,4 and *trans*-1,4 additions. The structure of **VI** is interesting in that all prior base molecules added to the system selectively complexed Et_2AlI, but the last base molecule added to **V** preferred to complex titanium rather than the last Et_2AlI. It requires that the iodide bridges in **V** be stronger than the iodide bridges in Et_2AlI dimer. Also, the acidity of **VI** should be weaker than that of **V**. This is consistent with the suggestion that additional strong base can destroy activity by blocking the remaining vacancy, but weak base does not.

Similar types of sites will be discussed in the next section on polypropylene catalysts, in which stereospecificity will be related to the stability of the R_2AlX complex with the titanium site.

The conclusions from the butadiene polymerization catalyst studies are the same

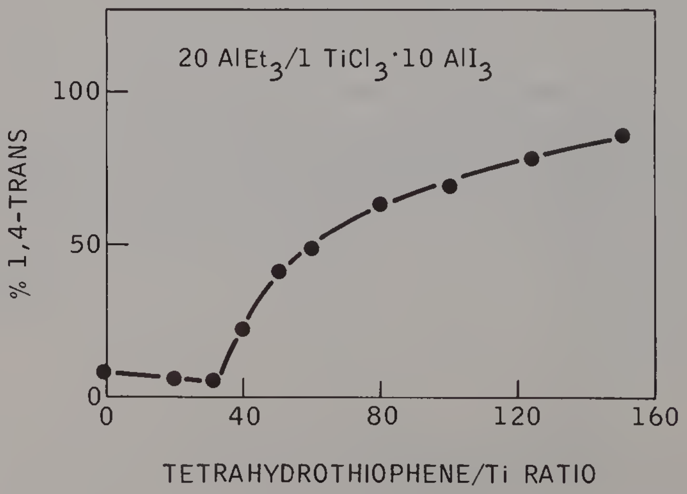
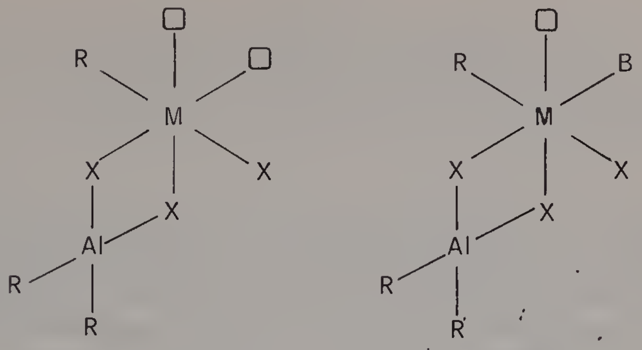


FIGURE 3. Effect of tetrahydrothiophene on butadiene polymerization (benzene, 25°C).



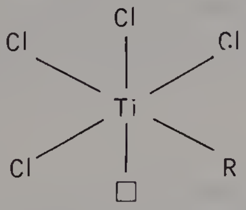
(V) CIS-1,4 **(VI)** TRANS-1,4

FIGURE 4. Proposed *cis* and *trans* site structures for diene polymerization.

as those from the oligomerization catalyst studies; that is, Lewis bases preferentially complex the alkylaluminum species, an excess of strong base kills activity by complexing the transition metal sites, and weak or soft bases interact with the transition metal to modify its properties and site structures.

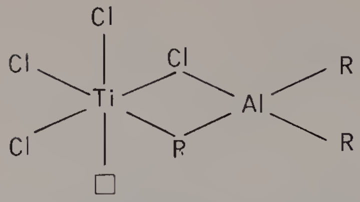
Propylene Polymerization

In the stereospecific polymerization of propylene to isotactic polymer by use of an alkyl metal—titanium trichloride catalyst system, the most widely cited catalyst structure and mechanism are contained in a series of papers by Cossee and Arlman.[29–32] The active site is essentially a five-coordinate alkyl titanium in an octahedral environment on the edge of a layer lattice structure (**VII**). It is claimed to be sufficiently chiral to be capable of making stereoregular polymers. It is primarily appealing because of its simplicity.



(VII)

However, it has long been this author's belief that a Cossee site does not explain a great many experimental observations, and, in fact, it is probably responsible for atactic or low-tacticity polymer. The same conclusions were published by Rodriguez and Van Looy,[33] who discussed a variety of objections. One of the most pertinent objections cited was that titanium dichloride also generates stereospecific sites; yet, alkylation at the edge would produce a symmetrically placed alkyl between two titanium atoms such that insertion could occur from either side and would make atactic polymer. Another major objection is that experimentally every alkyl metal cocatalyst used with titanium trichloride yields different stereospecificity, a fact that is difficult to reconcile with a simple alkylated titanium site. To account for the influence of the alkyl metal component, Rodriguez and Van Looy proposed that sites were formed from edge titaniums that had two vacancies. After alkylation, one could obtain a bimetallic site with a bridging alkyl group (**VIII**).



(VIII)

Other workers have also concluded that a simple alkylated transition metal site is insufficient to explain the data.[34,35] In particular, the elegant work on stereoselectivity and stereoelectivity by Pino *et al.* (cited in Chien[3]) provides convincing evidence that the alkyl metal component is present at the active site. Support for this conclusion can be found in studies of various alkyl metal compounds with $TiCl_3$ catalyst that show that polypropylene isotacticity decreases in the following orders: $AlEt_2I > AlEt_2Br > AlEt_2Cl > AlEt_3$[36]; $AlEt_3(85)$* $> Al(C_6H_{13})_3(64) > Al(C_{16}H_{33})_3(59)$[37,38]; $BeR_2 > AlR_3 > MgR_2 > ZnR_2$.[39] Clearly, the alkyl metal component must be part of the active site. Zambelli and Tosi[7] have reviewed the convincing evidence that isotactic stereoregularity arises from chiral catalyst sites. In the remainder of this paper, data are presented that suggest that an alkyl metal component is an integral part of the chiral site and that inversions in isotactic polymers occur by dissociation without the polymer chain.

The data in TABLE 4 show the effects of doubling alkyl metal concentration and of adding HMPA to these catalysts. Activity increased in each case. The total product density increased, indicating higher stereoregularity, and this finding is confirmed by extraction studies. The amounts soluble in boiling pentane and heptane decrease in this series as the heptane-insoluble fraction increases. Thus, both increased alkyl metal concentration and HMPA addition decrease the fraction of atactic and stereoblock polymer. Of even greater significance is the fact that the density (crystallinity, therefore stereoregularity) increased at the same time, despite increased molecular weight, which adversely affects crystallization. The different degrees of stereoregularity, even in the most isotactic fractions, is not consistent with a single, stable, isospecific site structure.

These results show that both higher alkyl metal concentration and addition of Lewis bases not only decrease the proportion of nonstereospecific sites but also further increase the stereospecificity of the isospecific sites. It is difficult to reconcile

TABLE 4

POLYPROPYLENE COMPOSITION

($AlEt_3TiCl_3$-HA, XYLENE, 85°C, 1 hr, 1 atm C_3H_6)

HMPA/Al/Ti (mM)	0/4/8	0/8/8	4/8/8	4/4/8
g/hr/g of $TiCl_3$	120	174	221	166
Density (g/cm^3)	0.8874	0.8989	0.9006	0.9007
n-Pentane soluble (%)*	17.9	7.8	4.0	—
n-Heptane soluble (%)*	19.1	9.9	5.6	—
n-Heptane insoluble (%)*	63.0	82.3	90.4	—
Density (g/cm^3)	0.9003	0.9036	0.9045	—
Molecular weight ($\times 10^{-3}$)	355	542	680	~1100

* Soxhlett extraction, 48 hr for each solvent.

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* The numbers in parentheses represent the percentages of polymer insoluble in boiling heptane, a measure of stereoregularity.

TABLE 5
PI BONDING IN HMPA-Al COMPLEXES
(HMPA/Al/$TiCl_3$-HA, XYLENE, 85°C, 2 hr, 50–55 g of C_3H_6)

Alkyl Metal	Polymer Yield (g)
$AlEt_2Cl$	29
HMPA·$AlEt_2Cl$	47
$AlEt_2O$-*t*-Bu	43
HMPA·$AlEt_2O$-*t*-Bu	0.1
$AlEt_2NEt_2$	50
HMPA·$AlEt_2NEt_2$	1.7

these results with Boor's mechanism, in which bases simply block isolated nonstereospecific sites. Our interpretation is that the active sites undergo exchange reactions or structural changes that affect stereospecificity and that these changes involve alkyl metal participation. The data suggest that both higher alkyl metal concentrations and Lewis bases decrease the frequency of exchange reactions by increasing site stability.

The increase in stereospecificity with increasing triethylaluminum concentration is opposite to that reported by Natta and Pasquon[40] for $AlEt_2Cl$ concentration. We cannot account for the difference between these two alkyl metal compounds. However, the molecular weights of the octane residues were not reported, so it is possible that the lower octane residues obtained at higher $AlEt_2Cl$ concentration may have been due to lower molecular weight rather than stereoregularity.

In the next set of experiments, we can relate stereospecificity directly to the strength of the complex between alkyl metal and titanium trichloride (TABLES 5 & 6). Pi bonding between heteroatom and aluminum should increase in the order $AlEt_2Cl < AlEt_2OR < AlEt_2NR_2$ and should thereby decrease the Lewis acidity. (Note: pi bonding in the related compound bis(dimethylamino)beryllium has been verified by x-ray diffraction studies.[41]) Polymerizations were performed with these compounds and also their preformed complexes with HMPA (TABLE 5). All three were active when used alone, but only $AlEt_2Cl$ was active in the presence of HMPA. The weakened acidity caused by π bonding in the alkoxide and amide allows dissociation of HMPA, which blocks all active sites. The $AlEt_2Cl$ experiments demonstrate that the base-$AlEt_2Cl$ complex does not dissociate and that the complex is capable of generating active sites. Our interpretation is that the complex is adsorbed on the titanium trichloride edges, where adjacent titanium atoms are

TABLE 6
PI-BONDING GROUPS DECREASE ISOTACTICITY
(Al/2 $TiCl_3$-HA, XYLENE, 85°C, 2 hr, 60% C_3H_6)

$AlEt_2X$	Decreasing Lewis Acidity	Polymer Density (g/cm^3)*
$AlEt_2Cl$	↓	0.903
$AlEt_3$		0.892
$AlEt_2OEt$		0.876
$AlEt_2NEt_2$		0.866

* Data correlated at 500,000 molecular weight to eliminate the effect of molecular weight on the rate of crystallization in compression-molded pads.

exposed. It then dissociates, and each component reacts with only one titanium. The alkylated titanium active site cannot be poisoned by the base—aluminum complex because there is no adjacent titanium available to assist in cleaving the complex.

In Table 6, the aluminum compounds are listed in order of decreasing Lewis acidity. Polymer density (isotacticity) decreases in the same order, with the π-bonding groups causing a major decrease in stereospecificity. These data are considered strong evidence that the alkyl metal component is an integral part of the isospecific active site and that the frequency of inversions during isotactic polymerization is directly related to the tendency of the alkyl metal component to dissociate from the site.

Another way to decrease the complexing ability of the alkyl metal component is to increase the amount of steric hindrance. Alkyl groups longer than hexyl or alkyls with branching on the β carbon are known to increase the dissociation of aluminum trialkyl dimers because of steric crowding,[42] and the same effect should also occur with their base complexes. Table 7 summarizes atmospheric pressure propylene polymerizations by use of aluminum trioctyl and aluminum triethyl with or without HMPA. Aluminum trioctyl is active, but the 1 : 1 complex is not. In contrast, aluminum triethyl was active in both experiments. Similar results were obtained when HMPA was added to an active polymerization. However, the aluminum triethyl in solution was able to complex most of the HMPA before it could poison all of the sites. Only when the amount of HMPA exceeded the aluminum triethyl in the system was the catalyst completely poisoned.

These results can be interpreted to mean that the aluminum triethyl complex with the strong base is not significantly dissociated, whereas the hindered aluminum trioctyl complex is dissociated sufficiently for the free base to poison sites. Polymer tensiles (roughly related to isotacticity) show that the octyl groups decrease and that the Lewis base increases polymer stereoregularity, as noted previously. We can therefore conclude that large alkyl groups decrease isotacticity by weakening the alkyl—metal complex at the titanium trichloride site. The more frequently dissociation occurs, the greater the number of inversions and the lower the isotacticity.

The base effect cannot be interpreted so easily, but if we assume that a base merely modifies the alkyl metal inversion mechanisms, it suggests that the alkyl metal becomes more firmly complexed to the site by virtue of the electron donation

Table 7
Steric Hindrance in HMPA-Al Alkyl Complexes
($\text{HMPA/Al/2 TiCl}_3\text{-HA}$, xylene, 85°C, 1 hr, 1 atm C_3H_6)

Alkyl Metal		Polymer Rate	Polymer Tensile (MPa)
Al(octyl)_3		115 g/g of TiCl_3/hr	15.7
$\text{HMPA}\cdot\text{Al(octyl)}_3$		0	—
$\text{Al(octyl)}_3 + C_3H_6$	→	active	—
+ 1 HMPA	→	dead in 15 min	—
AlEt_3		173 g/g of TiCl_3/hr	24.5
$\text{AlEt}_3\cdot\text{HMPA}$		166 g/g of TiCl_3/hr	30.8
$\text{AlEt}_3 + C_3H_6$	→	2 liters/min absorption	—
+ 1 HMPA	→	0.5 liters/min absorption	—
+ 2 HMPA	→	dead	—

at an adjacent site. Alternatively, the base could block adjacent titanium sites that would otherwise participate in alkyl metal—catalyst exchange reactions and produce inversions.

Still another way to affect complexing ability would be to attach (anchor) the alkyl metal to the surface by means of another functional group. Experiments were performed as described in TABLE 6, except that the following X groups were compared in Et_2AlX: phenoxy versus *ortho*-methoxyphenoxy and ethoxy versus β-dimethylaminoethoxy. Polymer density at 1 million molecular weight increased from 0.886 to 0.895 and from 0.874 to 0.892 in the two sets of experiments as a result of the added base functionality. We can only speculate on the reasons for increased stereospecificity, but these results are consistent with less frequent dissociation of the alkyl metal. Thus, the most plausible explanation appears to be that the base functionality in these alkyl metal compounds ties the alkyl metal more strongly to the surface by complexing to an adjacent titanium site.

Site Structure and Polymer Microstructure

From the various data presented, we have concluded that polypropylene isotacticity correlates with the stability of the complex between the alkyl metal and the titanium site. Factors that favor stable complexes include high Lewis acidity, low steric hindrance, low oxidation product solubility, anchoring functionality on the alkyl metal, and a more basic titanium chloride site from base complexation to other surface locations, particularly to an adjacent titanium. We can now arrange the alkyl metals in various series that reflect both stability of the alkyl metal—titanium chloride complex and catalyst stereospecificity: Lewis acidity of the alkyl metal, $BeR_2 > AlR_3 > MgR_2 > ZnR_2$; $AlR_2I > Br > Cl > F > OR > NR_2$; low steric hindrance, $AlEt_3 > Al(C_8H_{17})_3 > Al(C_{16}H_{33})_3$; low solubility of oxidation product, $CdEt_2 > ZnEt_2$ (EtCdCl insoluble, EtZnCl soluble)†; anchoring the alkyl metal to the $TiCl_3$ site, $Et_2AlOCH_2CH_2NMe_2 > Et_2AlOCH_2CH_3$ (Base: $MR_n > MR_n$).

The last item uses the word "anchoring" in the general sense that the strength of the alkyl metal complex is increased by interactions at adjacent sites.

We can now propose site structures in which dissociation of the alkyl metal component would lead to inversions in the polymer's microstructure. Inversions could occur by several different mechanisms: exchange of the growing polymer group between titanium sites of opposite chirality,[40] changing the chirality of a site by moving the location of the alkyl metal complex, converting an isospecific site to a nonspecific site by dissociating the alkyl metal, and by errors in the introduction of monomer units at a stable, nonexchanging site. The first mechanism will not be considered for reasons discussed later. The other three mechanisms are shown in FIGURES 5–7 together with the polymer microstructure to be expected from each. The titanium trichloride edge structure is that which Rodriguez and Van Looy found experimentally to produce active sites, that is, the face parallel to the sides of the titanium hexagon (110 plane). We have also started with the doubly vacant titanium site, which they suggested.

FIGURE 5 shows the formation of a Rodriquez and Van Looy site that contains a bridging polymer group, but we have extended it to show that the placement of AlR_2X can lead to both R and S chiralities on the same titanium. In a system in

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† See Reference 11, pp. 124 and 144.

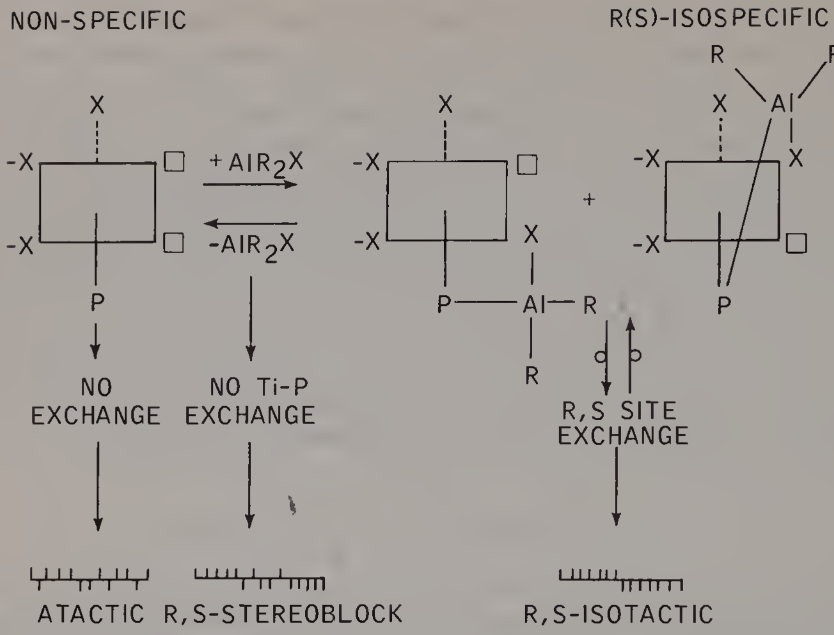


FIGURE 5. Site structures and polymeric microstructure. I. Bridging polymer.

which the AlR_2X can dissociate and recomplex, the chirality of the site can be changed without physically moving the polymer group to a different site. Without necessitating polymer group exchange between titanium sites, the uncomplexed site would still produce atactic polymer because the monomer approach is not restricted to a single side. The equilibrium between the complexed and uncomplexed sites would produce stereoblock polymer in which blocks of R and S would be separated by segments of atactic polymer, which is designated as "R,S"-stereoblock structure. If the alkyl metal never leaves the site but is mobile enough to change the

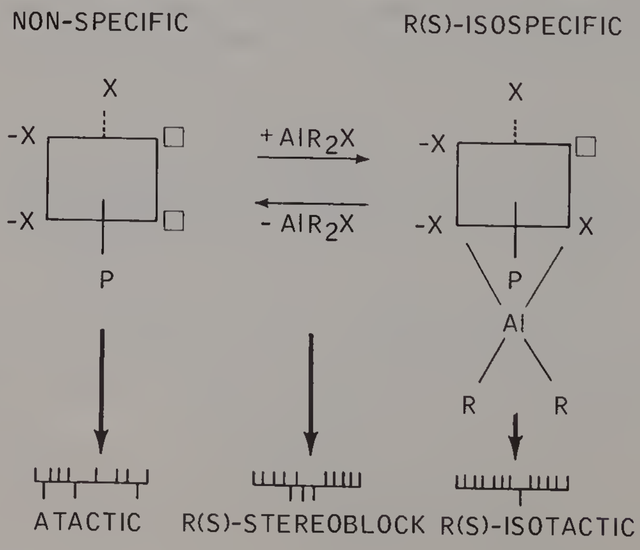


FIGURE 6. Site structures and polymeric microstructure. II. Nonbridging polymer with bottom chloride layer exposed.

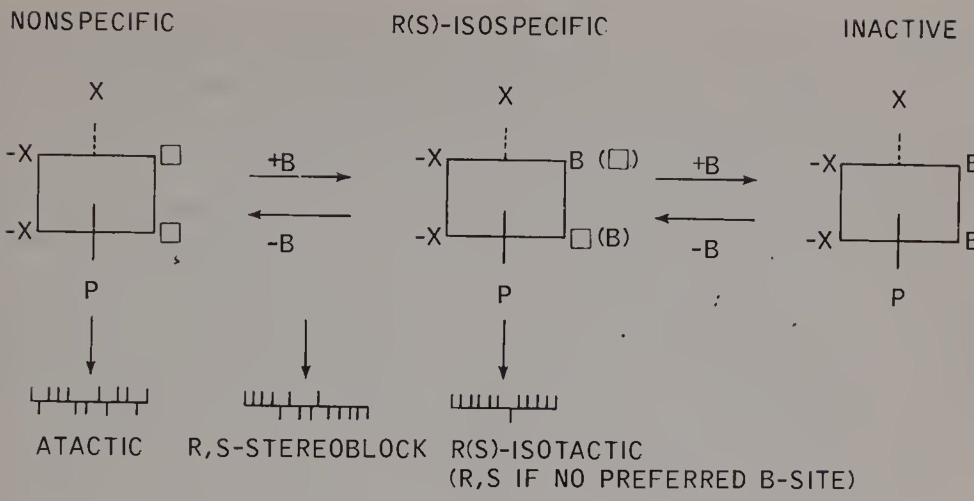


FIGURE 7. Site structures and polymeric microstructure. III. Base effect.

coordination position of the X group, one would obtain alternating blocks of R and S isotactic units. The average length of the isotactic segments in both the stereoblock and the isotactic polymers would increase with increasing stability of the Al—Ti complex. We have thus shown how the stereoregulating ability of a bridging polymer site would be determined by the stability of the alkyl metal—titanium complex.

An alternative inversion mechanism could involve dissociation of AlR_2P and complexation at another titanium site that has opposite chirality. This mechanism would also produce R,S-isotactic polymer. However, this mechanism considered improbable because it would be, in effect, the reverse of the titanium alkylation reaction and should be energetically unfavorable.

There are two very strong objections to sites that contain bridging polymer groups: (1) long-chain or bulky alkyl groups are not stable bridging groups in the aluminum alkyls,[42] and there is little reason to expect that they would be much more stable in bridging aluminum to titanium; (2) two halogen bridges should be more stable than one halogen and one alkyl by analogy to AlR_2Cl dimeric structure.

For the $AlEt_2Cl$ cocatalyst, Natta and Pasquon[40] proposed that inversion of the steric configuration is caused by exchange reactions between the catalyst—polymer bond and $AlEt_2Cl$ from solution. This mechanism seems unlikely because it would require that the large polymer molecule by physically moved from one site to another and that it be done frequently without drastic loss of molecular weight. The molecular weight reduction caused by exchange reactions with added $ZnEt_2$ suggests that it is unlikely for a polymer alkyl metal to return to a site once it has become detached. Furthermore, this mechanism would predict the wrong order for $AlEt_2Cl$, $AlEt_2OR$, and $AlEt_2NR_2$, because exchange occurs with a monomeric alkyl metal.[43] The more strongly dimerized amide should have given the fewest inversions, rather than the most.

Therefore, we prefer the nonbridging site structure shown in FIGURE 6. In this case, the aluminum is coordinated to titanium through two chloride bridges. Coordination could occur at the top or bottom of the site, depending on which chloride layer is exposed. For example, on a growth spiral on the surface of a chloride layer, only the top of the site would be exposed to permit formation of the aluminum complex. When dissociation of AlR_2X occurs from this site, the stereoblock product will be a mixture of atactic and R *or* S segments, because the original chirality will be regained when the aluminum complex is reformed. If no dissociation occurs, only R or S isotactic structure [designated "R(S)" isotactic] will be produced, except for an occasional error, which would return immediately to the preferred chiral structure.

The preferred mechanism by which base increases stereospecificity is by augmenting the stability of the AlR_2Cl complex by complexing an adjacent titanium and increasing the basicity of edge Ti—Cl sites. An additional possibility is shown in FIGURE 7, in which one molecule of base could block one of the two vacancies in an atactic site. The same reasons discussed for FIGURE 6 also apply here for a preferred position for the base to complex, so one would expect the R or S isotactic structure. Of course, the site is inactive when both vacancies are blocked by bases.

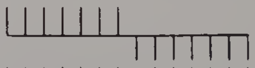
Pasquon *et al.*[35] found that the stereoblock polymer sometimes contains syndiotactic blocks, in addition to atactic blocks, between the isotactic blocks. In the sites presented above, we have described the doubly vacant site as an atactic site, but it should also be capable of producing syndiotactic polymer under the proper conditions of temperature and monomer concentration. Therefore, these sites in equilibrium with an alkyl metal species are capable of generating all of the known predominantly isotactic polymer structures.

The site structures and inversion mechanisms presented above were developed from doubly vacant titanium edge sites. One can also generate site structures from alkylated titanium sites that have a single vacancy in which the dissociation of the alkyl metal component would affect stereospecificity. Additional complexity could be introduced by invoking site structures in which the two adjacent edge titanium atoms cooperate to form a single site. Regardless of the real site structure, we have presented a mechanism by which the alkyl metal component could control stereospecificity by the stability of its complex at the site. This mechanism is preferred over all other proposals that require physical movement of a growing polymer chain from one titanium to another to explain configurational inversions. It is also consistent with observations that AlR_2Cl complexes reversibly at the active centers.[44,45]

TABLE 8 summarizes the more important catalyst implications that can be made from the polymer structure. We can now address the question whether the structure

TABLE 8

CATALYST IMPLICATIONS FROM POLYMER STRUCTURE

Isotactic		(I)
Isotactic		(II)
Stereoblock		(III)

I and II require chiral sites
I requires R-S site exchange
II requires growth at a single site; single inversions are accidents
III requires low-chirality site or chiral-achiral site interconversion

determined by nuclear magnetic resonance (nmr) allows us to select or eliminate any of the mechanistic proposals. The data obtained on highly isotactic polymer fractions have been interpreted most recently by Stehling and Knox[46] to contain only R or S structure, except for 1–5% isolated "errors" (type II). This interpretation supports the nonbridging polymer site of the type shown in FIGURE 6. It is a stable site structure that cannot be "racemized" by dissociation of the alkyl metal component and that would not undergo the site exchange reactions available to a bridging polymer site.

However, it would be premature to conclude that type-I polymer structure and bridging polymer sites (FIGURE 5) are absent, because only the most isotactic polymer fractions prepared with the best isospecific catalysts have been thoroughly studied by nmr. Only if nmr examination of the less stereoregular polymer fractions prepared by use of several different types of low-specificity catalysts showed that type-I structure is absent would we be prepared to eliminate from consideration such site structures as that illustrated in FIGURE 5. This research is in progress.

ACKNOWLEDGMENTS

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TRANSMETALATION: ORGANIC SYNTHESIS VIA TRANSFER OF ORGANIC GROUPS FROM ONE METAL TO ANOTHER

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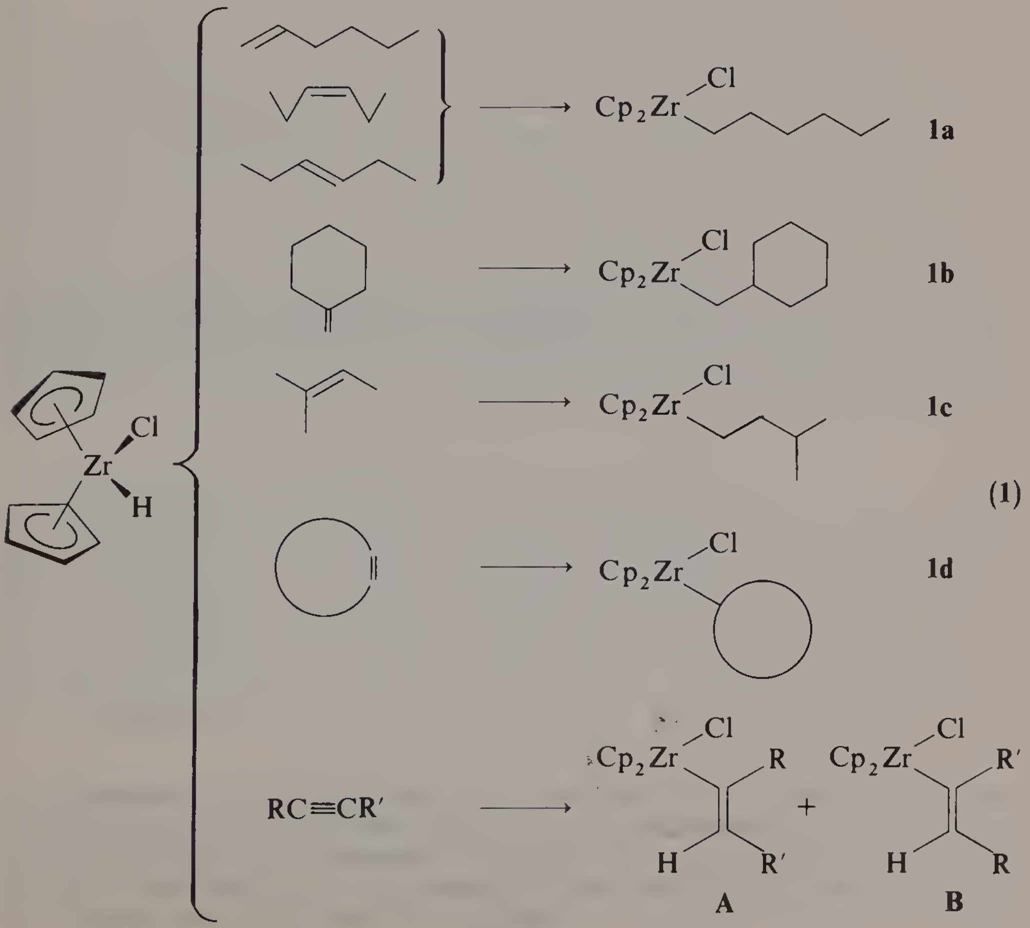
Organozirconium(IV) complexes (**1**) are readily prepared by hydrozirconation[1] of olefins or acetylenes by use of $Cp_2Zr(H)Cl$ ($Cp = \eta^5\text{-}C_5H_5$), as shown in reaction **1**. These organometallic species are valuable intermediates in organic synthesis; a variety of types of organic products can be obtained from them, with a high degree of specificity, by electrophilic cleavage of the C—Zr bond.[1-6] Electrophilic halogenation reagents (e.g., Br_2, I_2, *N*-bromo- or *N*-chlorosuccinimide) react with

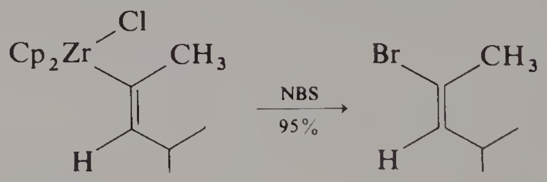


	Acetylene		Product Ratio (A : B)
1e,	R=H;	R′ = n—C_4H_9—	>98 : 2
1f,	R=CH_3;	R′ = CH_3CH_2—	89 : 11
1g,	R=CH_3;	R′ = $CH_3CH_2CH_2$—	91 : 9
1h,	R=CH_3;	R′ = $(CH_3)_2CHCH_2$—	>95 : <5
1i,	R=CH_3;	R′ = $(CH_3)_2CH$—	>98 : <2
1j,	R=CH_3;	R′ = $(CH_3)_3$—	>98 : <2

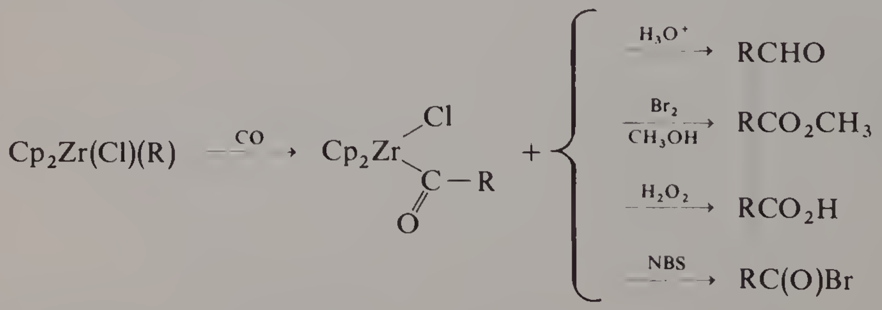
* Determined by nmr analysis.[3]

them to give the corresponding organic halides,[2–4] and, by use of *tert*-butyl, hydroperoxide alcohols are obtained[6] (reaction **2**). With few exceptions, however,

$$\mathrm{Cp_2Zr(Cl)(}n\text{-hexyl}) + \left\{\begin{array}{l} \mathrm{NBS} \xrightarrow{95\%} \mathrm{RBr} \\ \mathrm{NCS} \xrightarrow{67\%} \mathrm{RCl} \\ \mathrm{I_2} \xrightarrow{91\%} \mathrm{RI} \\ t\text{—}\mathrm{C_4H_9OOH} \xrightarrow{72\%} \mathrm{ROH} \end{array}\right. \qquad (\mathrm{R} = n\text{-hexyl}) \qquad \mathbf{(2)}$$



these organozirconium species have not yet been shown to be effective reagents in a general sense for routine formation of C—C bonds. For example, they do yield acyl derivatives by carbon monoxide insertion into C—Zr, followed by electrophilic cleavage[5] (reaction **3**);



(3)

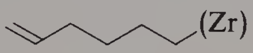
some of them can undergo acylation by acyl halides (but very slowly) and in good yield only if steric congestion is minimal.[2] None of them has been observed to add to the carbonyl group of aldehydes or ketones or to react with common alkylating agents, such as alkyl halides, sulfates, or fluorosulfonates.[7] Therefore, because C—C bond formation is of central importance in organic synthesis, we have begun to investigate the transfer of η^1-bound organic groups in **1** from zirconium(IV) to another metallic element whose chemistry is already well established with regard to C—C bond formation processes. Through the sequence of hydrozirconation, followed by transmetalation, it would be possible to take advantage of the ease and selectivity associated with hydrozirconation of olefins or acetylenes and the C—C bond-forming propensity of this other metallic element in a "one-pot" reaction. In this context, we have observed that transmetalation occurs from zirconium to several main group and transition metal elements. Our results locate these organocirconium complexes (**1**) in a transmetalation reactivity series for metal alkyls; this sequence can be used to *predict* transmetalation from **1** to other metals important in organic synthesis.

Studies[8] on the mechanism of electrophilic cleavage of the C—Zr bond suggest that transmetalation might be accomplished by treatment of **1** with a Lewis acidic metal halide, and we have found that simple mixing of **1** with the chlorides of aluminum,[9] zinc,[10] palladium,[11] copper,[11] or mercury[7]* yields the corresponding organometallic derivative (reaction **4**). Several such procedures are described below.

$$\mathrm{Cp_2Zr(Cl)(R)} + \left\{\begin{array}{ll} \xrightarrow{\mathrm{HgCl_2}} & \mathrm{RHgCl} \\ \xrightarrow{\mathrm{AlCl_3}} & \mathrm{RAlCl_2} \\ \xrightarrow{\mathrm{ZnCl_2}} & \mathrm{RZnCl} \\ \xrightarrow{\mathrm{CuCl}} & \mathrm{RCu} \quad (\mathrm{R} = \text{vinylic}) \\ \xrightarrow{\mathrm{PdCl_2}} & \mathrm{RPdCl}\ (\mathrm{R} = \text{vinylic}) \end{array}\right. \tag{4}$$

Transmetalation from zirconium to aluminum[9] by treatment of **1** with aluminum chloride (in CH_2Cl_2 at 0°C) can be conveniently monitored by nuclear magnetic resonance (nmr; in the case of alkylzirconium precursors, the nmr spectrum of the resultant compound is analogous to those observed for known alkylaluminum dichlorides). In this way, we have found in each case studied that transmetalation occurs nearly quantitatively and in less than 10 min at 0°C. Organoaluminum dichlorides in which a remote double bond is present can undergo intramolecular cyclization.† Thus, nmr analysis shows that **1k** gives (7-octenyl)aluminum chloride but that **1l** affords (cyclopentylmethyl)aluminum chloride‡; oxygenation of the latter species, followed by hydrolysis, gives the corresponding alcohols.

1k



1l

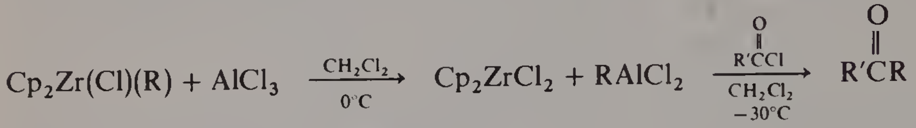
Organoaluminum dichlorides can act as mild alkylating agents; for example, several of them have been reported to be preferred precursors of ketones through acylation with acid chlorides.[14] To effect ketone synthesis, the reaction mixture that contains the organoaluminum dichloride is cooled to −30°C, and a small excess of acyl chloride is added slowly. Acylation of the organoaluminum compound is rapid and is usually complete in 15 min. This reaction can also be monitored conveniently by nmr; it gives aluminum chloride-coordinated ketone, from which

* Transmetalation has also been studied by Budnik and Kochi.[12]

† This reaction is closely analogous to the known cyclization of, for example, dialkyl(5-hexenyl)aluminum complexes.[13]

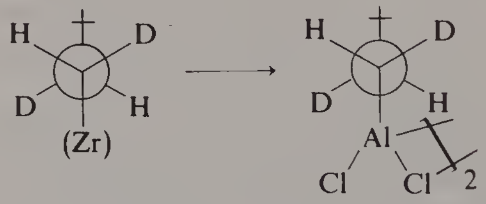
‡ $Cp_2Zr(Cl)$(3-pentenyl), on treatment with aluminum chloride, followed by acetyl chloride, yields 3-cyclopropyl-3-methylpropan-2-one (79%).

free ketone can be obtained simply by hydrolysis and extraction. Results for this procedure and for those with other organozirconium complexes are shown in reaction 5. Attempts to directly acylate vinylic organozirconium complexes failed; however, by transmetalation to the corresponding (alkenyl)aluminum dichlorides (which (themselves cannot be prepared directly from acetylenes), followed by acylation, a high yield of α,β-unsaturated ketones is obtained. Through this sequential use of two reactive organometallic species, ketone is formed stereospecifically by overall *cis* addition of acyl-α-H to an alkyne; regioselectivity in the ketone prepared is the same as that in its organozirconium precursor.[3]‡



$$Cp_2Zr(Cl)(R) + AlCl_3 \xrightarrow[0^\circ C]{CH_2Cl_2} Cp_2ZrCl_2 + RAlCl_2 \xrightarrow[CH_2Cl_2,\ -30^\circ C]{R'\overset{\overset{O}{\|}}{C}Cl} R'\overset{\overset{O}{\|}}{C}R \qquad (5)$$

The mechanism of transmetalation from zirconium to aluminum has been briefly investigated.[9,12] We have found that transmetalation occurs faster for vinylic substituents than for the alkyl ones. In addition, results that involve stereospecifically labeled dideuterio complex **2**[8] indicate that transmetalation from zirconium to aluminum proceeds predominantly with retention of configuration at carbon[15] § (as it does with vinylic substrates). These results suggest a mechanism for transmetalation that is, indeed, analogous to that reported[8] for electrophilic cleavage of alkylzirconium complexes; the transition state (or intermediate) for this reaction involves a transition metal—main group metal complex that contains a bridging alkyl (or vinylic) group. Such bridging alkyl or vinylic groups are well known in main group chemistry[14] and have been postulated to occur in intermediates[16,19] or also in isolable species[18,19] in transition metal chemistry. Shuttling of a σ-bonded substituent from one metal to another via such a bridged intermediate could be expected to proceed more rapidly for the bridging vinylic compared to the bridging alkyl case; it is well known in organoaluminum chemistry, for example, that vinylic bridges between two aluminum atoms are more stable than are alkyl ones.[20]¶ Preliminary results with mercury[7]* and zirconium dichlorides[10] suggest that analogous reactions occur with these metal salts.



2 **3**

Organoaluminum species, however, are of only limited utility in organic synthesis; transmetalation of alkenyl ligands from **1** (R = alkenyl) to Cu(I) can also be accomplished stereospecifically, in high yield and in straightforward fashion. Alkenylcopper(I) complexes are of demonstrated utility as synthetic intermediates in a variety of processes;[21–23] implementing currently available syntheses of these reagents, however, can be tedious,[22,24] and hydrozirconation-transmetalation to

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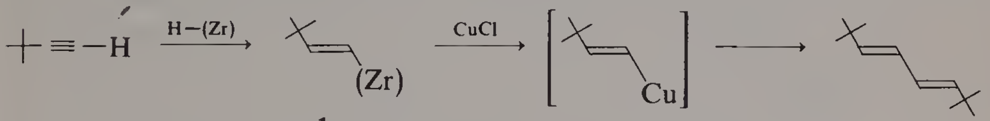
§ For *erythro*-**3**, $^{3}J_{HH} = 9$ Hz. We are unable, because of broadened lines in aluminum compound **4**, to determine, quantitatively, the percentage retention of configuration at carbon.

¶ Transmetalation of vinylic groups can proceed with a stoichiometry different from that observed for alkyl groups: with a Zr : Al ratio of 3 : 1, aluminum(alkenyl)$_3$ is formed.

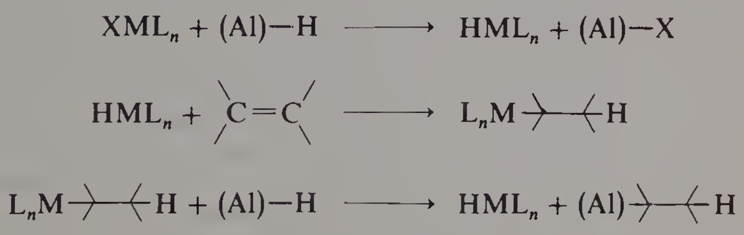
copper(I) provides an alternative, convenient route to them.[‖][**] Transmetalation from zirconium to copper(I) gives alkenylcopper(I) complexes in which the regio- and stereochemistries of the zirconium precursor[3] are maintained, and alkenylcopper(I) species prepared by transmetalation behave analogously to those prepared from vinyllithium reagents and cuprous halides.[24] Transmetalation to copper(I) is accomplished by stirring a suspension of cuprous chloride with an alkenylzirconium species (at 0°C) to give a yellow-green homogeneous solution. Because of the low thermal stability of alkenylcopper(I) compounds at 0°C,[24] the reaction mixture slowly decomposes to give a copper mirror and a nearly colorless solution of the 1,3-diene (reaction **6**). Where it was feasible to quantitatively assay for the stereospecificity of this coupling reaction, for example, for $Cp_2Zr(Cl)$-(*E*-1-propenyl), no loss of stereochemistry in the product diene was observable; only (*E*,*E*)-2,4-hexadiene, but no (*E*,*Z*)-isomer, was detected.[24] We find, too, that transmetalation from zirconium to copper with cuprous iodide proceeds well in sulfolane but poorly in THF; we have also observed that alkenylzirconium(IV) species react with palladium chloride in sulfolane to give the expected 1,3-diene and palladium metal.[††] Preliminary results indicate that alkenylcopper(I) complexes prepared by transmetalation at −20°C can be captured (at −20°C) as "ate" complexes and used subsequently in other C—C bond-forming reactions well known for these "species," such as alkylation[23] or conjugate addition to α,β-unsaturated ketones.[21]



1m

(6)

Stoichiometric transmetalation sequences, such as those described above, are of potential use in understanding catalytic processes that involve zirconium salts and main group metal reagents. It is known that several titanium(IV) or zirconium(IV) salts catalyze the terminal hydroalumination of acyclic internal olefins[28,29] or the reduction of alkynes and alkenes by aluminum lithium hydride.[30] These processes could be envisioned (reaction 7) to occur by initial formation of a discrete transition metal hydride by simple H for X ligand exchange, followed by addition of the transition metal hydride to the unsaturated organic unit. Ligand transfer of the resultant alkyl or alkenyl unit from zirconium (or titanium) to aluminum in exchange for H would then give the observed organoaluminum product and



(7)

M = Zr(IV) or Ti(IV)
L_n = nontransferred ligands
X = transferred ligand

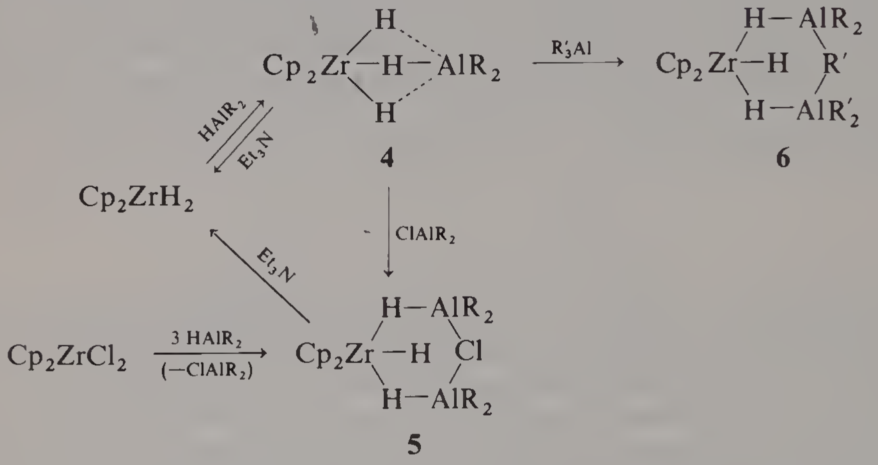
[‖] Reaction of acetylenes with alkylcopper(I) reagents gives alkenylcopper(I) species.[25]

[**] Vinylaluminum complexes can be used to prepare alkenylcopper(I) species.[26]

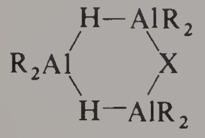
[††] Vinylmercurials react with palladium chloride to give dienes.[27]

regenerate the zirconium (or titanium) hydride. In an effort to elucidate actual mechanisms of such reactions, we studied model systems that involved the interaction of dialkylaluminum hydrides with several organozirconium complexes, Cp_2ZrX_2 ($Cp = \eta^5\text{-}C_5H_5$; X = H, Cl, alkyl).

We found, in contrast to reaction **7**, that reaction of dialkylaluminum hydride with Cp_2ZrX_2 proceeds not by simple ligand exchange but, rather, by aggregation to yield structurally related mixed Al—Zr trihydrido complexes that contain Al—H—Zr bridges (reaction **8**). Deep blue complex (**4**) is thermally unstable and decomposes at room temperature. Its structure is assigned on the basis of its ^1H nmr spectrum. Treatment of **4** with 1 equiv of *iso*-Bu_2AlCl immediately produces the thermally stable (at room temperature) pale violet complex **5**, whose formulation is consistent with its cryoscopic molecular weight determination in benzene. The ^1H nmr spectrum of **5** resembles the AB_2 pattern reported for Cp_2NbH_3[31] and Cp_2TaH_3.[32] For such trihydrides, coordination of triethylaluminum to the central hydride ligand results in an upfield shift of this ligand in the ^1H nmr spectrum of the resultant complex. Coordination of aluminum to the central hydride ligand in **4** and to the external hydride ligands in **5** is postulated by analogy to their reported niobium and tantalum counterparts.[33] Reaction of Cp_2ZrCl_2 with 3 equiv of *iso*-Bu_2AlH also gives **5** (plus 1 equiv of *iso*-Bu_2AlCl). Treatment of either **4** or **5** with Et_3N precipitates Cp_2ZrH_2 [identified by its quantitative reaction with acetone to give $Cp_2Zr(O{-}i{-}Pr)_2$]. Treatment of **4** with (1 equiv) trimethylaluminum also produces a complex that displays a high-field AB_2 pattern in its ^1H nmr spectrum. The structure of this complex (**6**) is assigned on the basis of these data and on cryoscopic molecular weight determination in benzene. These new Zr—H—Al complexes (**5**, **6**) are analogs of organoaluminum aggregates (**7**)[34,35] in which an H—Al—H unit is formally replaced by H—Zr(H)—H.

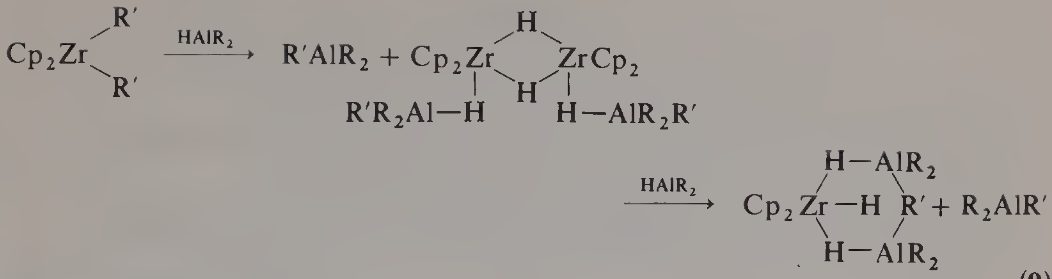


(8)

7 

R = *i*-butyl
R' = CH_3—
X = Cl—, *i*-butyl

Transmetalation of alkyl groups from zirconium to aluminum in exchange for H is a necessary step to regenerate mixed-metal hydrido complexes in *catalytic* sequences. It is therefore significant that Cp_2ZrR_2 reacts with excess *iso*-Bu_2AlH to give Zr—H—Al complexes and aluminum alkyls (reaction **9**).



(9)

R′ = *neo*-hexyl; R = *i*-butyl

Transmetalation results presented herein suggest that, in general, **1** should be able to alkylate metal salts in which the metal (with its complement of ligands) is more electronegative than is the Cp_2ZrCl moiety and that alkenyl complexes should be more reactive in this regard than alkyl ones. Our results for stoichiometric systems demonstrate that an easily prepared transition metal complex can serve as the convenient precursor of other reactive organometallic species. Those with bearing on catalytic systems show that zirconium-promoted reactions of alkylaluminum hydrides might not proceed by simple ligand exchange processes but, rather, could involve mixed-metal hydrido species. Taken together, then, these studies represent a point of departure for the rational development of new types of sequential organometallic reagent *systems*, be they stoichiometric or catalytic ones, in which the ability to transfer organic ligands readily from one metal to another provides a pathway to accomplish a synthetic transformation that is impossible (or at best tedious) for any one given type of organometallic species alone.

SUMMARY

Organozirconium(IV) complexes produced by hydrozirconation of olefins or acetylenes with $Cp_2Zr(H)Cl$ ($Cp = \eta^5\text{-}C_5H_5$) are useful as intermediates in organic synthesis for preparing a variety of C—X bonds; however, with few exceptions, these complexes have not yet been shown to be effective for routine synthesis of C—C bonds. They have been found, however, to serve as precursors of reactive organometallic complexes of metallic elements whose chemistry is well established with regard to C—C bond formation processes. By stoichiometric transmetalation, organic groups can be transferred stereospecifically from zirconium to aluminum, zinc, mercury, palladium(II) or copper(I) simply by treatment with the appropriate metal halide. By the sequence of hydrozirconation-transmetalation, it is possible to take advantage of the selectivity of hydrozirconation and the C—C bond-forming propensity of this other metallic element in a "one-pot" reaction. Synthetic and mechanistic aspects of this transmetalation procedure are reported.

Zirconium(IV) complexes also can serve as catalysts in organic synthesis. Studies that describe the interaction of zirconium(IV) complexes and dialkylaluminum hydrides are presented, and attention is drawn to the implications of these results for transition metal-catalyzed terminal addition of aluminum hydrides to internal olefins.

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CARBON—CARBON TRIPLE-BOND DICHOTOMY IN ALKYNES USING METAL CARBONYLS*

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Reactions of metal carbonyls with alkynes have long been known to proceed in one of the following two ways, depending on the particular metal carbonyl system[1,2]: formation of alkyne complexes, as exemplified by compounds of the general types (alkyne)$Co_2(CO)_6$, (alkyne)$Ni_2(C_5H_5)_2$, $C_5H_5V(CO)_2$(alkyne), $C_5H_5Mn(CO)_2$(alkyne), and (alkyne)$_3$WCO; cyclization of the alkyne either without incorporation of carbonyl groups to form cyclobutadiene, benzene, metallocyclopentadiene, or fulvene derivatives or with incorporation of one or two carbonyl groups to form cyclopentadienone, quinone, tropone, or metallocyclohexadienone derivatives. In all of these reactions, the carbons joined by the triple bond in the original alkyne remain bonded to each other in the resultant transition metal complex.

This paper considers the first examples of a third type of reactions of metal carbonyls with alkynes in which the C≡C of the original alkyne is completely broken in the transition metal complex obtained as the product. Such reactions have been called "alkyne dichotomy" reactions by Wilke *et al.*[3] The net effect of alkyne dichotomy reactions is the cleavage of the alkyne RC≡CR into two RC carbyne units. In principle, such carbyne (RC) units can bond to one, two, or three transition metals in the final products or may cyclize with two additional alkyne molecules to form pentaalkylcyclopentadienyl (R_5C_5) derivatives.

The earliest examples of alkyne dichotomy reactions consisted of the cyclization of the resultant carbyne unit with two additional alkyne units to form pentaalkylcyclopentadienyl derivatives. Hübel and Merényi[4] reported the first alkyne dichotomy reaction. They found that treatment of diphenylacetylene with hexacarbonylmolybdenum or diglymetricarbonylmolybdenum in benzene solution at 160 or 80°C, respectively, gave, in addition to other organomolybdenum products, a low yield (2–4%) of a brick red sparingly soluble solid identified as bis(pentaphenylcyclopentadienyl)molybdenum, $[(C_6H_5)_5C_5]_2Mo$ (**I**). This molybdenum complex was found to be paramagnetic, corresponding to two unpaired electrons ($\sim$3 B.M.), exactly analogous to the more familiar biscyclopentadienylchromium ["chromocene," $(C_5H_5)_2Cr$].

The first example of an alkyne dichotomy reaction that proceeds in high yield was reported considerably later by Wilke *et al.*[3] Reduction of a mixture of chromium(III) chloride and dimethylacetylene with an aluminum alkyl AlR_3 ($R = CH_3$, C_2H_5, or n-C_3H_7), followed by further reduction with lithium aluminum hydride or aqueous dithionite was found to give 60–70% yields of hexamethylbenzenepentamethylcyclopentadienylchromium, $(CH_3)_6C_6CrC_5(CH_3)_5$ (**II**). The formation of the same pentamethylcyclopentadienylchromium derivative, regardless of whether $Al(CH_3)_3$, $Al(C_2H_5)_3$, or $Al(n\text{-}C_3H_7)_3$ is used, indicates that

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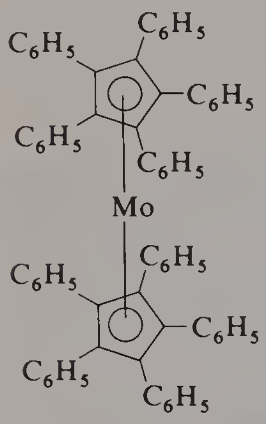
* Supported by Grant CA-12938 from the National Cancer Institute.

the $C-CH_3$ unit needed to cyclize with two dimethylacetylene units to form the pentamethylcyclopentadienyl ring arises from half of a dimethylacetylene molecule, rather than from the alkylaluminum.



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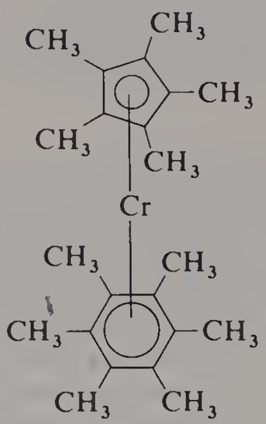
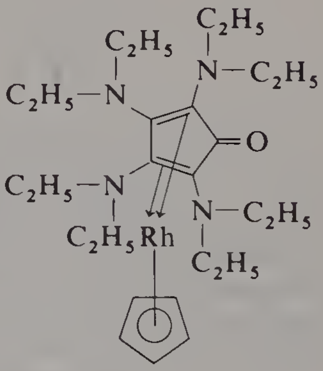


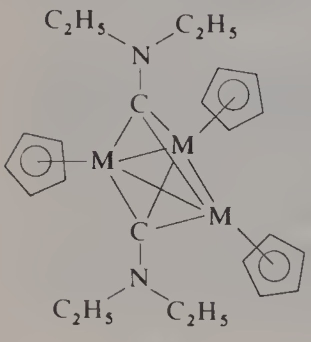
II



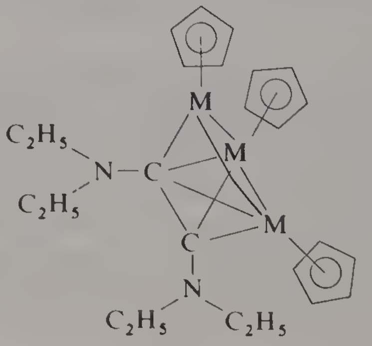
III

Our studies with alkyne dichotomy reactions have given the first products in which the carbyne RC formed by dichotomy of the alkyne $RC\equiv CR$ appears as a discrete ligand in the product without undergoing cyclizations with two additional alkyne units to form pentaalkylcyclopentadienyl derivatives, R_5C_5. We have used the rather unusual alkyne $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$ for our work.[5] The dialkylamino substituents in this alkyne appear to make its $C\equiv C$ unusually susceptible to dichotomy.

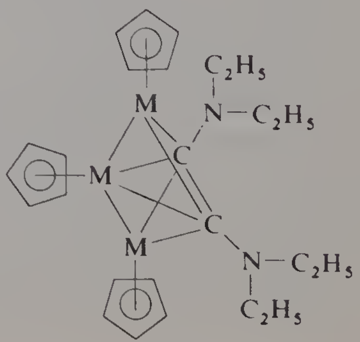
The first example of apparent dichotomy of the $C\equiv C$ in $(C_2H_5)_2NC\equiv CN(C_2H_5)_2$ was found in its reaction with $C_5H_5Rh(CO)_2$.[5] Two products were obtained from this reaction. The first product was an orange crystalline solid, melting point of 88–90°C, of the stoichiometry $[(C_2H_5)_2N]_4C_4CORhC_5H_5$, formulated as the cyclopentadienone complex **III**. The second product was a black crystalline solid, melting point of 150–153°C, of the stoichiometry $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$. The proton



IVa



IVb



IVc

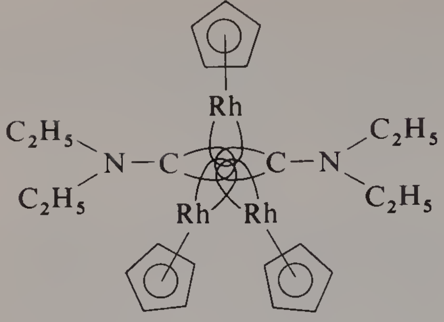
and C-13 nuclear magnetic resonance (nmr) spectra of this black rhodium complex exhibit the required resonances for the ethyl and cyclopentadienyl groups. However, in addition, the carbon atoms that participated in the alkyne triple bond in the $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ starting material appear as a single 1 : 3 : 3 : 1 triplet at $\delta 280.6$ in the C-13 nmr spectrum. This finding indicates that both carbon atoms are not only equivalent but also equivalently coupled to the three spin-1/2 rhodium atoms.

There are three possible structures (**IVa**, **IVb**, and **IVc**; M = Rh) for $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$ based on a trigonal bipyramid with rhodium atoms at three of the five vertices and the carbon atoms from the alkyne $C{\equiv}C$ at the remaining two of the five vertices. Only in structure **IVa** are both alkyne carbons equivalent and equivalently situated with respect to all three rhodium atoms, as required by the C-13 nmr data. In structure **IVa**, the two carbons from the $C{\equiv}C$ are at opposite apices of the trigonal bipyramid and not joined by an edge.

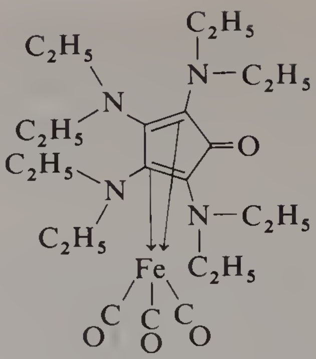
Initially, we were reluctant to believe that **IVa** (M = Rh) was the true structure for $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$, because the two carbons that participated in the $C{\equiv}C$ were located at opposite ends of the trigonal bipyramidal cluster. We could not exclude alternative explanations based on structures **IVb** and **IVc** with adjacent cluster carbon atoms but with fluxional properties,[6] making these carbon atoms both equivalent and equivalently situated with respect to the three rhodium atoms on the nmr time scale. However, x-ray crystallographic studies by Dahl and Broach[7] demonstrated unambiguously that **IVa** was the true structure for $(C_5H_5)_3Rh_3C_2[N(C_2H_5)_2]_2$, thereby excluding alternative formulations based on less symmetric structures, such as **IVb** and **IVc**, that exhibit fluxional properties.

The reaction of $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ with $C_5H_5Co(CO)_2$ gives a black crystalline complex of the analogous stoichiometry $(C_5H_5)_3Co_3C_2[N(C_2H_5)_2]_2$.[5] This complex apparently has structure **IVa** (M = Co), analogous to that of the trimetallic rhodium derivative discussed above. However, specific C-13 nmr information to confirm that this structure is the actual one for $(C_5H_5)_3Co_3C_2[N(C_2H_5)_2]_2$ is not available, because the spin 7/2 cobalt atom leads to a general broadening of the resonance from the cluster carbon atoms rather than to splitting it into a well-defined pattern, as was found for the rhodium analog. This broad resonance from the cluster carbon atoms in the cobalt complex $(C_5H_5)_3Co_3C_2[N(C_2H_5)_2]_2$ appears at $\delta 321$, which is at even a lower field than the $\delta 280.6$ resonance of the corresponding carbon atoms in the rhodium complex.

Initially, it was tempting to regard the cluster carbon atoms in the trimetallic clusters $(C_5H_5)_3M_3C_2[N(C_2H_5)_2]_2$ (**IVa**; M = Co or Rh) as not bonded to each other due to the fact that they occupy apical vertices of the trigonal bipyramid, which are the two vertices not connected by an edge. However, recent and rather successful theoretical treatments[8,9] of the bonding in closed triangulated polyhedral molecules, such as metal clusters and cage boranes, indicate that each vertex atom of the cluster polyhedron is bonded to every other vertex atom by overlap of their radial (unique internal) orbitals at the core of the polyhedron. This core bonding includes vertex atoms that are not connected by an edge of the polyhedron, such as the apical atoms in trigonal bipyramids. This information suggests that in the reactions of $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ with $C_5H_5M(CO)_2$ (M = Co or Rh), the $C{\equiv}C$ is not completely broken in $(C_5H_5)_3M_3C_2[N(C_2H_5)_2]_2$ (**IVa**, M = Co or Rh) but is merely lengthened by introduction of three bridging C_5H_5M units. The relevant core bonding of the radial orbitals of the vertex atoms in the $(C_5H_5)_3M_3C_2[N(C_2H_5)_2]_2$ (M = Co or Rh) clusters is more clearly depicted if structure **IVa** is redrawn as structure **V**. In this structure,



V



VI

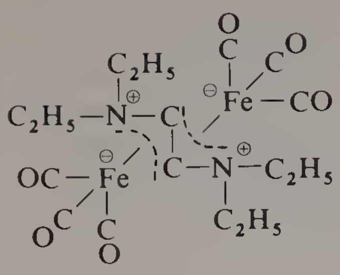
the "formal C—C bond order" of the two cluster carbon atoms is 2/5, because the electron pair in the five-centered core bond depicted in **V** is shared between five atoms and because there is no additional surface bonding between the apical carbon atoms that involves the tangential (twin internal) orbitals. Thus, the reaction of $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ with $C_5H_5M(CO)_2$ (M = Co or Rh) to form $(C_5H_5)_3M_3C_2[N(C_2H_5)_2]_2$ (**IVa** or **V**) results in a rather drastic reduction of the formal bond order of the alkyne carbons from 3 to 2/5, but the dichotomy of this bond is still incomplete.

We subsequently discovered an example of complete dichotomy of the C≡C in one of the products obtained from $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ and iron carbonyls. However, x-ray crystallographic work by Cash *et al.*[10] was required before this unprecedented example of complete alkyne dichotomy was recognized.

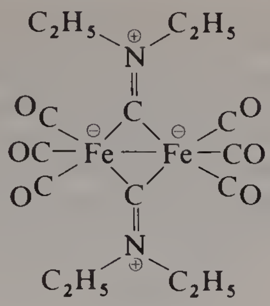
The reactions of $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ with iron carbonyls [$Fe(CO)_5$ or $Fe_3(CO)_{12}$] were found to give two products.[5] One of these products, an orange solid with a melting point of 119–121°C, was identified as the cyclopentadienone—iron tricarbonyl derivative $[(C_2H_5)_2N]_4C_4COFe(CO)_3$ (**VI**) of a type obtained from many reactions of alkynes with iron carbonyls.[1,2] The second product was a yellow solid, melting point of 103–105°C, of the stoichiometry $[(C_2H_5)_2NC]_2Fe_2(CO)_6$ and was clearly of a type not found in other reactions of alkynes with iron carbonyls.

We first attempted to elucidate the nature of $[(C_2H_5)_2NC]_2Fe_2(CO)_6$ by the usual spectroscopic techniques (infrared and nmr spectra). The infrared spectrum of this complex indicated only terminal carbonyl groups. The C-13 nmr spectrum of this complex exhibited only a single set of ethyl resonances (δ57.5 and δ13.7 for the CH_2 and CH_3 groups, respectively) and only a single resonance (δ257.6) for the two carbons that participated in the alkyne C≡C. This finding indicated that both of the $(C_2H_5)_2NC$ units that originate from both ends of the starting alkyne are equivalent in $[(C_2H_5)_2NC]_2Fe_2(CO)_6$. Because we had no basis for considering alkyne dichotomy in systems of this type at the time we interpreted these data, we postulated structure **VII** to account for the spectroscopic properties of $[(C_2H_5)_2NC]_2Fe_2(CO)_6$.

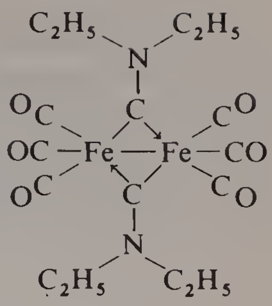
The subsequent x-ray crystallographic studies[10] clearly showed that structure **VII** was incorrect for $[(C_2H_5)_2NC]_2Fe_2(CO)_6$. Instead, the x-ray data indicated the unusual structure **VIII** for this complex. The distance between the carbons of the two bridging R_2NC units (i.e., those that arised from the triple bond in the original alkyne) was found to be 2.28 Å, clearly a nonbonding distance for carbon atoms. In contrast, the Fe—Fe distance in $[(C_2H_5)_2NC]_2Fe_2(CO)_6$ was 2.48 Å, clearly indicative of an Fe—Fe bond. Thus, the FeCFeC quadrilateral in $[(C_2H_5)_2NC]_2$-



VII



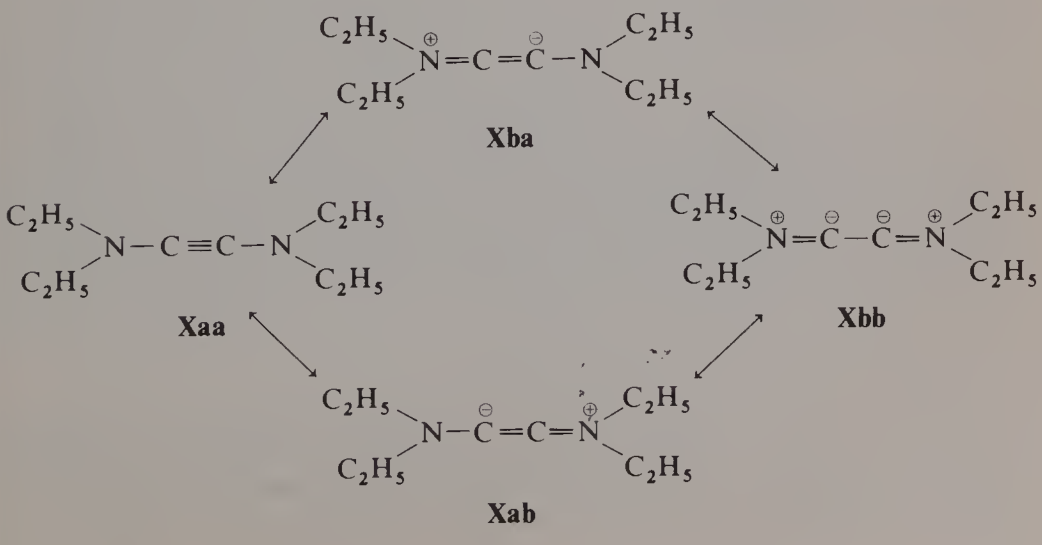
VIII



IX

$Fe_2(CO)_6$ (**VIII**) has a bond between the iron atoms but not between the carbon atoms.

Another very important feature of the observed structure (**VIII**) for $[(C_2H_5)_2NC]_2Fe_2(CO)_6$ is the 1.28 Å C—N bond length in the bridging $(C_2H_5)_2NC$ ligands, which corresponds to a double-bond, rather than a single-bond, distance. This finding indicates that the $(C_2H_5)_2NC$ ligands are the diethylimmoniocarbene units depicted in structure **VIII**, rather than the diethylaminocarbyne units depicted in structure **IX**. Furthermore, this finding suggests that the decrease of the alkyne C≡C bond order from three to zero in the formation of $[(C_2H_5)_2NC]_2Fe_2(CO)_6$ (**VIII**) from $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ is accompanied by an increase in the C—N bond orders from one to two. The dialkylamino substituents in $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ thus appear to be an essential feature of the dichotomy of its C≡C by iron carbonyls. The C≡C in $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ can be weakened by population of its antibonding orbitals with electron density from the nitrogen lone pairs, as represented by resonance structures **Xab**, **Xba**, and **Xbb** depicted below. One of these resonance structures (**Xbb**) has two negatively charged carbon atoms linked by a single bond. Such a situation should lead to easy dichotomy because of the repulsion of like charges.



Our work on the reactions of $(C_2H_5)_2NC{\equiv}CN(C_2H_5)_2$ with metal carbonyls clearly indicates that the $C{\equiv}C$ in this particular alkyne can undergo dichotomy on reaction with appropriate transition metal derivatives. Of particular interest will be whether reactions of transition metal compounds with alkynes that lack the special dialkylamino substituents can also be found that produce similar dichotomies. If such reactions can be found, alkyne dichotomy reactions with transition metal derivatives could have an interesting and useful place in organic synthesis.

ACKNOWLEDGMENTS

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REACTIVITY OF MONOOLEFINIC LIGANDS IN IRON—CARBONYL COMPLEXES*

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In contrast to complexes of olefins with transition metal cations, many reactions of which have been employed industrially, the chemistry of zero-valence metal complexes, including iron carbonyls, is still under investigation. At present, it would be premature to discuss industrial applications; nevertheless, the results obtained are worthy of the attention of synthetic and organic chemists.

Such synthetic possibilities primarily concern the olefinic π-acids. It is from such compounds that the comparatively stable iron carbonyl π-complexes were prepared. We previously demonstrated,[1] for β-substituted vinylketones (RCOCH=CHX), that stable π-complexes are formed only from olefinic ligands with certain optimal energies of the π^*-antibonding orbitals. A better evaluation of these synthetic possibilities in olefin chemistry can be obtained by comparing the changes in reactivities of coordinated versus free monoolefins. Considerable differences among the spectra of these complexes as compared to the corresponding free olefins indicate that such changes should be large. In brief, when the C=C is coordinated with the iron tetracarbonyl group, its absorption band in the infrared spectrum shifts by about 150–180 cm^{-1} to lower frequencies. The vinylic proton signals in the proton magnetic resonance (pmr) spectrum shift by 2.5–3 ppm upfield. Ultraviolet and nuclear magnetic resonance (nmr) data demonstrate that coordination of the conjugated C=C bond with the tetracarbonyliron group may essentially distort conjugation along the chain. All of these changes are consistent with the concept of substantial donation of electrons from the metal to the ligand and with the significant $SP^2 \rightarrow SP^3$ rehybridization of the olefinic carbon atoms. This mechanism was confirmed directly by x-ray data,[2–4] which will be discussed later.

These changes in the coordinated olefinic π-acids should lead first to an increase in electron density at the olefinic carbon atoms and at neighboring groups.† It should also be expected that the behavior of the coordinated olefin will be identical to that of the corresponding saturated compound.

Indeed, we have found that coordination of the iron tetracarbonyl group with the double bond of α,β-unsaturated ketones inhibits bimolecular nucleophilic reactions. Thus, the free β-chlorovinylketones display high reactivity toward trimethylamine and tiophenoxide ion, giving, almost quantitatively, the substitution products under very mild conditions.[6] Under the same conditions, however, the coordinated compounds do not react with these nucleophilic species. Under more drastic conditions, the complexes decompose.[1,7] It should be noted, however, that the tio-

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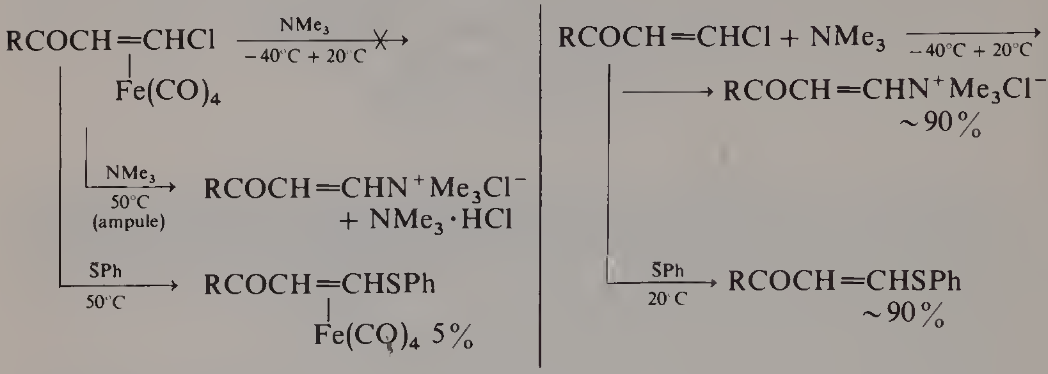
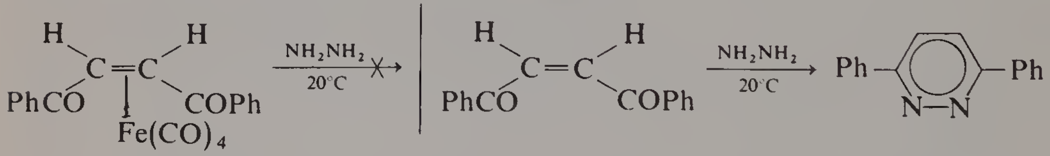
† This conclusion is also consistent with the determination of dissociation constants (H_2O, 25°C) for the free acrylic acid ($pK_a = 4.10$) and its iron tetracarbonyl complex ($pK_a = 5.16$).[5]

phenoxide ion gives the substitution product in 5% yield only on heating to 50°C. Its formation may be due to secondary processes, such as dissociation of the complex, or formation of the substitution product, followed by its coordination with the iron tetracarbonyl group (SCHEME 1).



SCHEME 1.

The coordinated α,β-unsaturated ketones do not react with hydrazine at the ketonic group. Cyclization of *cis*-dibenzoylethylene under the action of hydrazine with retention of metal coordination to the double bond was also unsuccessful. Free *cis*-dibenzoylethylene, however, readily yields 3,6-diphenylpyridazine. These results are consistent with a net donation of electrons from the metal to the ligand, and they illustrate how the unsaturated ketonic group in the polyfunctional compounds can be protected from attack by certain nucleophilic species.[8]

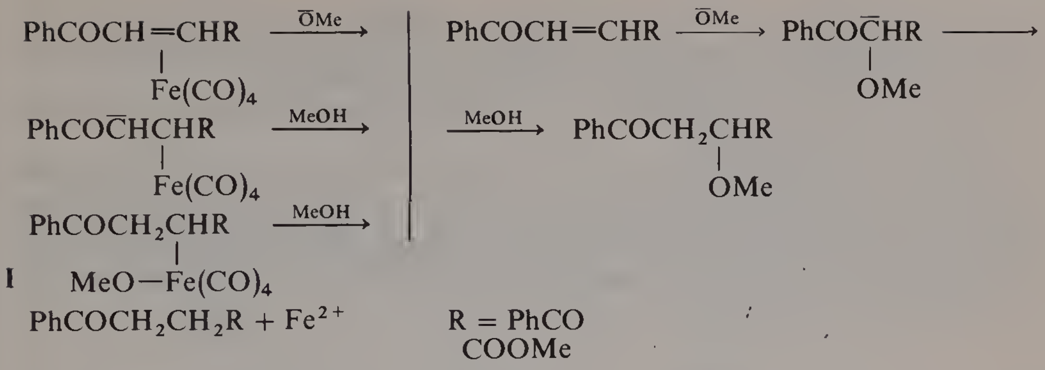


The coordinated and free ligands exhibit different properties in their reaction with methoxide ion in methanol.[9] Under the action of methoxide ion, the free α,β-unsaturated ketones yield the adducts of methanol to the double bond. Under the same conditions, the dibenzoylethylene and methyl benzoylacrylate iron tetracarbonyl complexes yield the products of double-bond reduction.

SCHEME 2 shows that in the former case, methoxide ion attacks the double bond at the β-carbon atom, whereas in the complexed state, the metal is subjected to nucleophilic attack. It may be assumed that the carbanion formed is protonated to give the unstable σ-complex (I). This complex splits into the saturated compound and bivalent iron derivative. In the last case, the ligand reacts with a proton. The net result is reductive protonation (SCHEME 2).

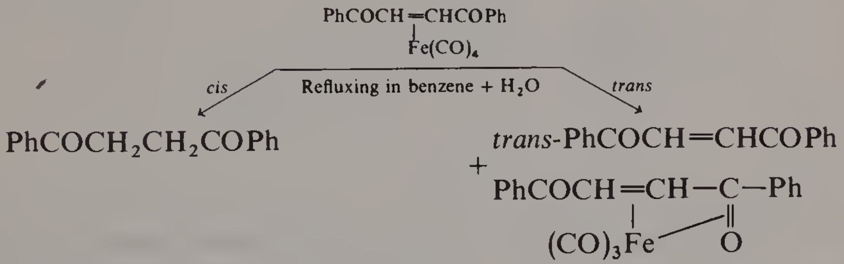
However, another possible hydrogenation mechanism, proposed by Noyori *et al.*,[10] which involves the hydride $[HFe_2(CO)_8]^-$ or $[HFe_3(CO)_{11}]^-$ as the intermediate formed from the iron tetracarbonyl fragment after decomposition of the σ-complexes, is not disproved. It is interesting that reduction of the complex with *cis*-dibenzoylethylene is easier than with the *trans* isomer, as we demonstrated on refluxing the complexes in wet benzene.

SCHEME 3 shows that reaction of the complex with the *cis* ligand gives, for the most part, a saturated compound, whereas under the same conditions, the isomeric complex with *trans*-dibenzoylethylene eliminates the starting ligand and yields some



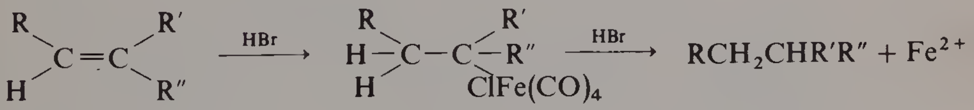
SCHEME 2.

iron tricarbonyl complex. The saturated product in this case has been isolated only in trace amounts.[11]



SCHEME 3.

Thus, the action of methoxide or hydroxide anion in a proton-containing medium on iron tetracarbonyl complexes may be utilized to effect double-bond reduction. It should be noted that the same result was obtained in the reaction of iron tetracarbonyl complexes with hydrohalogen acids[12,13]:

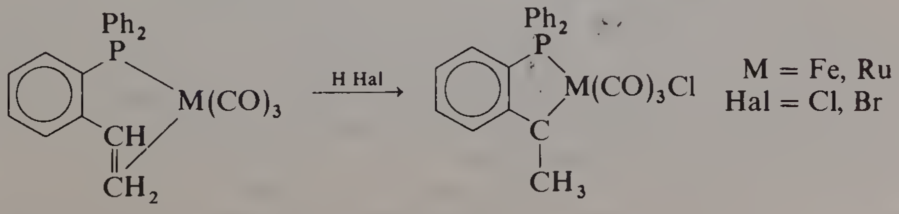


(a) $R + R' = -\underset{\overset{\|}{O}}{C}-O-\underset{\overset{\|}{O}}{C}-$, R = H

(b) R = H, R′ = Me, R″ = COOMe

It is assumed that in the reaction with hydrohalogen acids, the unstable σ-alkyl complexes formed as intermediates then decompose to give the saturated compound and bivalent iron derivative.

This mechanism was confirmed by isolation of the stable chelate σ-complex (**II**), the structure of which has been proven by x-ray analysis.[14]

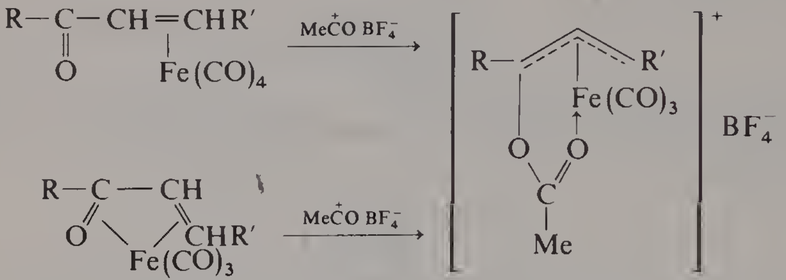


II

It is interesting to note that ultraviolet radiation stimulates this reaction, facilitating reduction of the olefinic ligand, even with acetic acid in benzene. In this case, the molecule is presumed to react in an excited state.[15]

The last examples demonstrate that coordination with the iron tetracarbonyl group facilitates protonation.

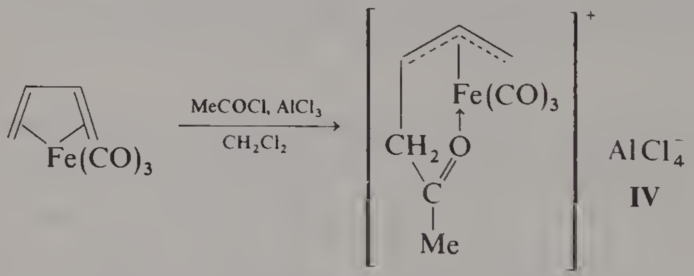
Acetylation of the iron tetra- and iron tricarbonyl complexes of α,β-unsaturated carbonyl-containing compounds is another example of electrophilic reactions. The complexes of methylvinylketone, chalcone, and cinnamic aldehyde are readily acetylated at the oxygen atom to form cationic complexes (III)[16] (SCHEME 4).



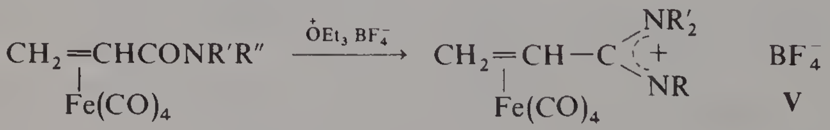
III

SCHEME 4.

In these compounds, the acetyl group is easily removed by alcohol to regenerate the initial iron tricarbonyl complex of the α,β-unsaturated ketone, thus proving *O*-acetylation. The structure of **III** was assigned on the basis of its infrared and pmr spectra. A similar cationic complex (**IV**) was an intermediate compound in acetylation of butadiene iron tricarbonyl, and its allylic structure was confirmed by x-ray analysis[17]:



We found that coordination with the iron tetracarbonyl group facilitates alkylation of the acrylic amides in complexes.[18,19]

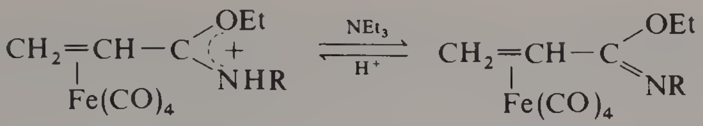


$$\underset{\mathrm{Fe(CO)_4}}{\mathrm{CH_2{=}CHCONR'R''}} \xrightarrow{\overset{+}{\mathrm{O}}\mathrm{Et_3\,BF_4^-}} \underset{\mathrm{Fe(CO)_4}}{\mathrm{CH_2{=}CH{-}C}}\overset{\mathrm{NR'_2}}{\underset{\mathrm{NR}}{\stackrel{+}{}}}\quad \mathrm{BF_4^-}$$

V

The carbenium ions (**V**) formed in high yield (70%) are more stable than the respective uncoordinated cations. They do not decompose in aqueous solutions and produce stable iminoester complexes (**VI**) under the action of NEt_3. It should be noted that the free unsaturated iminoesters could not be obtained. These compounds are stabilized by the donor iron tetracarbonyl group, which can hinder S_{N_2} solvolysis and inhibit polymerization.

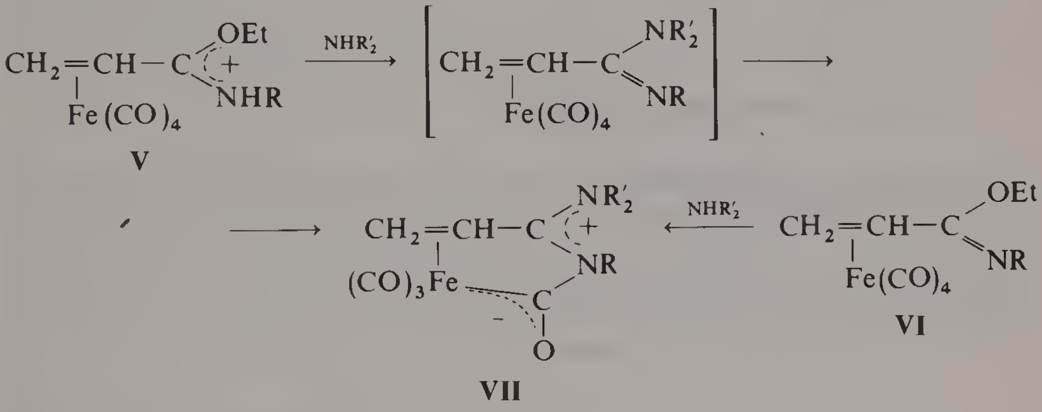
If ammonia or primary or secondary amines react with the carbenium ions (**V**), instead of the expected amidine complexes, the very stable zwitterion complexes



VI

R = H, Me

(**VII**) are formed.[19] These compounds can be also obtained from the iron tetracarbonyl complexes of iminoesters. Their formation may be due to a nucleophilic intramolecular attack of the imino group at the carbonyl ligand (SCHEME 5) in a manner analogous to the formation of Fischer's acylates in the synthesis of carbenic complexes.

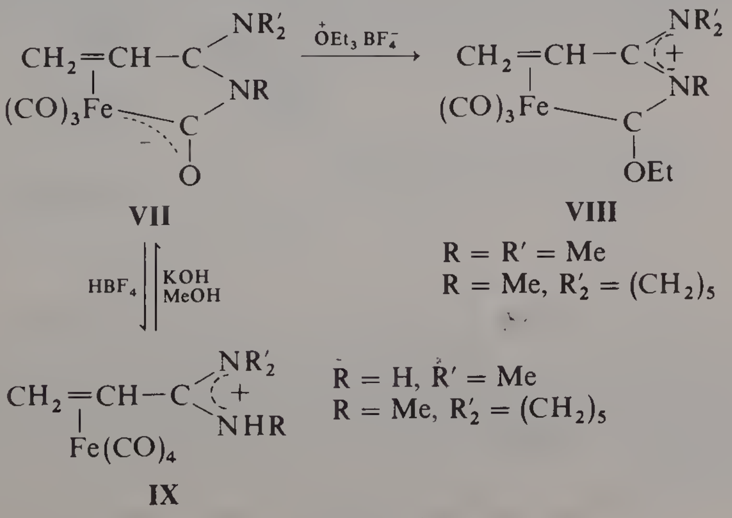


V **VII** **VI**

R = H, R′ = Me
R = R′ = Me
R = H, $R'_2 = (CH_2)_5$
R = Me, $R'_2 = (CH_2)_5$

SCHEME 5.

When reacted with Et_3OBF_4, these zwitterions (**VII**) yield iron carbonyl carbenic chelates (**VIII**) (SCHEME 6). The structures of **VII** and **VIII** were confirmed by x-ray analysis.[19] It should also be noted that the zwitterions (**VII**) by the action of fluoboric acid are transformed to the iron tetracarbonyl complexes of amidinium salts (**IX**), which are very unstable as the free compounds.



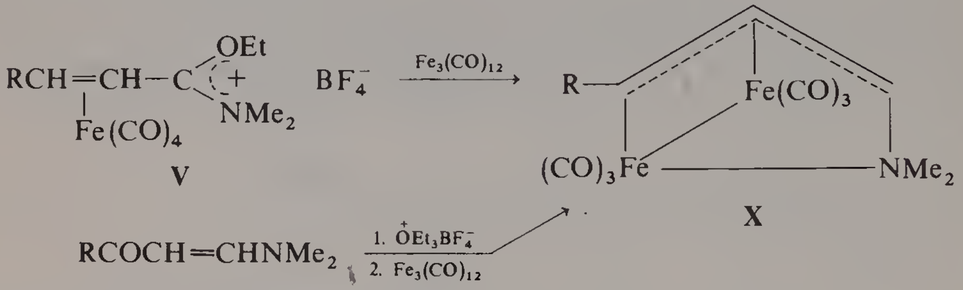
VII **VIII** **IX**

R = R′ = Me
R = Me, $R'_2 = (CH_2)_5$

R = H, R′ = Me
R = Me, $R'_2 = (CH_2)_5$

SCHEME 6.

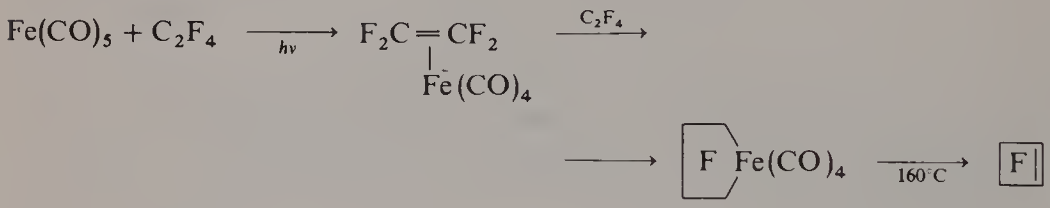
We also employed the starting carbenium ions (**V**) in organometallic synthesis. The new binuclear complexes (**X**) with the common aminoallyl ligand were obtained from them under the action of triiron dodecacarbonyl. It is interesting that such compounds could be prepared from β-aminovinylketones isomeric with α,β-unsaturated amides. The structure of complex **X** was confirmed by x-ray analysis.[20]



V

X

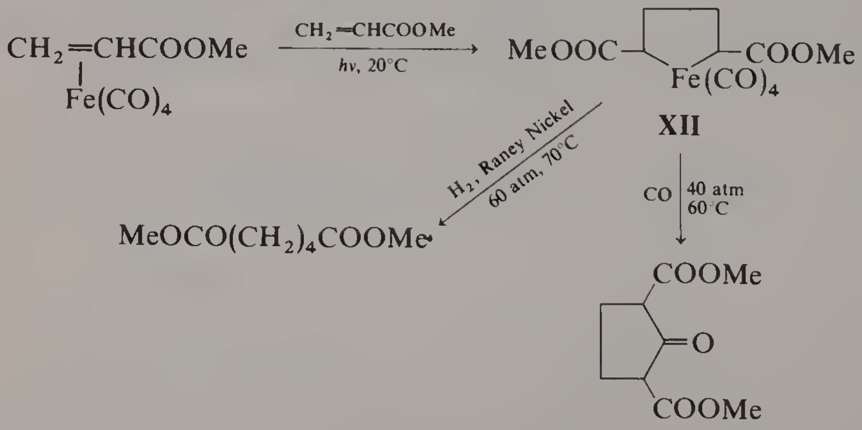
The formation of metallocycles (**XI**) is also one of the reactions of coordinated olefins with electrophilic species[21]:



XI

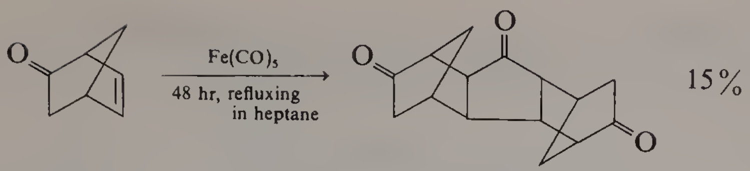
This reaction can be used for the synthesis of perfluorocyclobutene.[21a]

A similar ferracycle (**XII**) was obtained on the basis of methyl acrylate, as shown by Koerner von Gustorf *et al.*[22]:

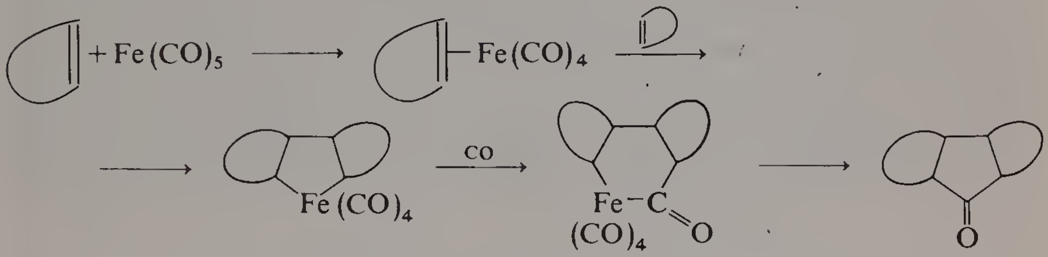


Its reduction on Raney Nickel® resulted in hydrodimerization product of methyl acrylate. This method is nonpreparative, but it shows clearly that such synthesis is possible. The action of carbon monoxide on ferracycle **XII** gives the cyclopentanone derivative.

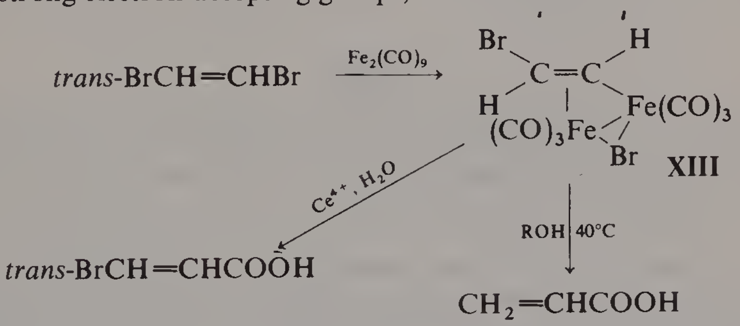
Various substituted cyclopentanones were prepared in one step in the following way[23,24]:

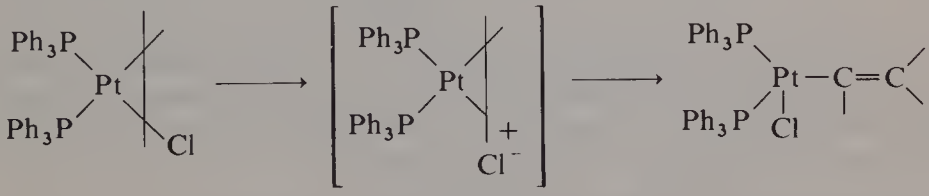


It is assumed that carbon monoxide inserts into the Fe—C bond of an intermediate ferracycle[25]:

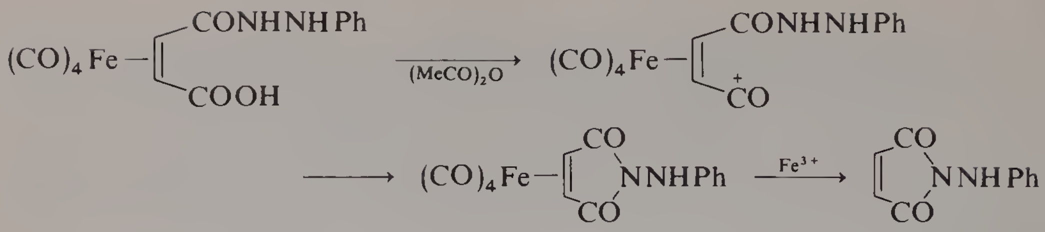


Koerner von Gustorf *et al.* have shown that when *trans*-HalCH=CHHal is reacted with diiron nonacarbonyl, one obtains binuclear compounds of type **XIII**, which can be transformed into bromoacrylic and acrylic acids.[26] The mechanism of formation of binuclear complex **XIII** has not yet been studied. A possible first step, however, is formation of iron tetracarbonyl complexes. These complexes do not contain strong electron-accepting groups, as do the above-mentioned complexes of β-chlorovinylketones. In this regard, it is possible that the iron tetracarbonyl group facilitates monomolecular nucleophilic substitution of the halogen atom. According to the literature data, such a mechanism has been found for the complexes of zero-valence platinum with halogen-substituted ethylenes.[27]

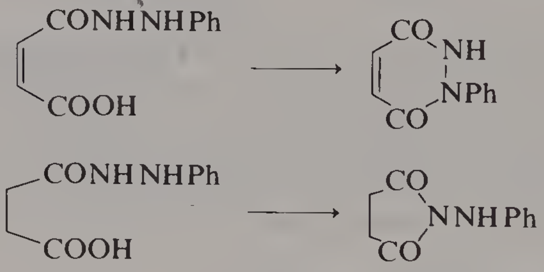




If the substantial electron donation from the metal to the ligand and considerable $sp^2 \rightarrow sp^3$ rehybridization of olefinic carbon atoms suggested above are apparent in for iron tetracarbonyl complexes, one may expect that these complexes undergo such reactions via intermediate carbenium ions with the positive charge α to the coordinated double bond. We obtained confirmation of this working hypothesis by performing intramolecular cyclization of the maleic acid *N*-phenylhydrazide complex under the action of acetic acid anhydride[28]:

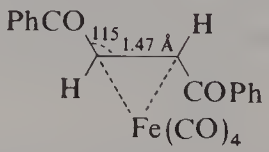


This reaction provides new synthetic possibilities, because the oxidative decomposition of the complex that results from the action of trivalent iron salt yields the imide of *N*-phenylaminomaleic acid. The latter cannot be obtained by cyclization of the free ligand, because under the same conditions, the free ligand gives a six-membered heterocycle (SCHEME 7). This result is firm evidence that the free and coordinated olefinic ligands exhibit different properties. Most interesting, however, the fact that the respective saturated compound cyclizes in the same way as does the coordinated olefin to give the five-membered heterocycle (SCHEME 7).

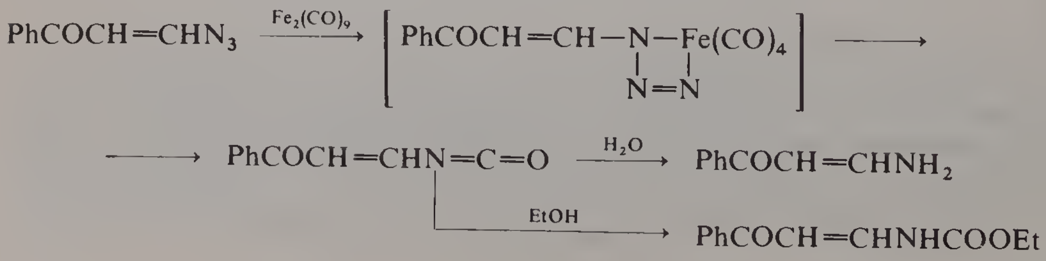


SCHEME 7.

This example is the first chemical evidence for significant $sp^2 \rightarrow sp^3$ rehybridization of the olefinic carbons on coordination of the olefinic π-acids with the iron tetracarbonyl complex, and it agrees with the x-ray data. X-ray investigation of the iron tetracarbonyl π-complex of α,β-dibenzoylethylene, performed by Strutchkov *et al.*,[2] gave a value of 1.47 Å for the length of the coordinated C=C bond. This value indicates a large increase in the double bond length on coordination, because a value of 1.33 Å was found for the free compound. The valence angles of the olefinic carbon atoms in this complex are 115–116°; the angles in the free compound are 120°.



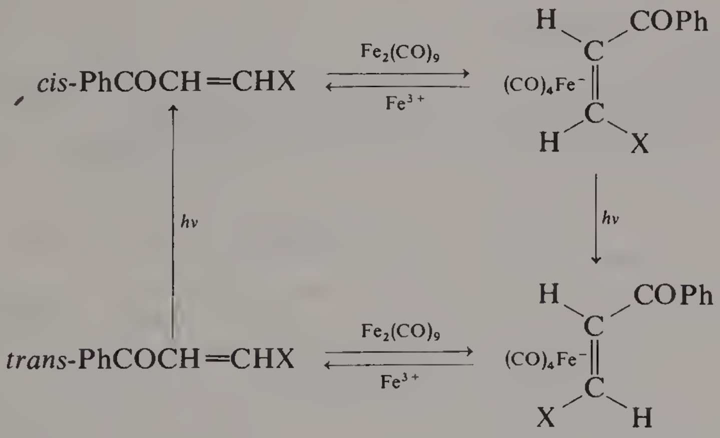
In the following reaction, the specificity of olefinic substituents becomes apparent. When phenyl β-azidovinylketone is reacted with diiron nonacarbonyl, it yields, rather than the iron tetracarbonyl complex, isocyanate, which is transformed into aminovinylketone and its respective carbamate[29]:



This action provides a method for transformation of some azides into isocyanates and their derivatives. We have obtained similar results with benzoyl azide‡:

$$\mathrm{PhCON_3} \xrightarrow{\mathrm{Fe_2(CO)_9}} \mathrm{PhCON{=}C{=}O} \xrightarrow{\mathrm{H_2O}} \mathrm{PhCONH_2}$$

In working with iron tetracarbonyl complexes of the olefinic π-acids, we studied the inverse *cis*→*trans* isomerization in the coordinated ligands versus the free olefins. It should be noted that coordination of the olefin itself with the iron tetracarbonyl group is practically stereospecific, as we have also observed for β-substituted vinylketones[1,11,31,32]; the same has been found for monoolefinic π-acids studied by other authors.[33,34] On ultraviolet irradiation, the complex prepared from the *cis*-olefin transformed into that with the *trans*-ligand, whereas *trans*→*cis* isomerization occurs when the free ligands are irradiated[11,15,32,33,35] (Scheme 8).



X = PhCO, COOMe, SO_2Ph

Scheme 8.

When it is considered that the olefinic ligand can be easily removed from the metal (for example, by oxidation with the trivalent iron), it may be seen that both methods supplement each other and that any starting isomer may readily produce its partner. It is interesting that for the less stable π-complexes (for example, the complex with stilbene), *cis*→*trans* isomerization has been performed in the presence of a catalytic amount of iron pentacarbonyl.[36]

We have discussed above the general transformations that olefinic π-acids undergo on coordination with the iron tetracarbonyl group.

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‡ It should be noted that the same transformation of benzoyl azide under the action of $\mathrm{ClIr(CO)(Ph_3P)_2}$ has been observed by Collman *et al.*[30]

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REDUCTION OF ORGANIC COMPOUNDS BY USE OF CARBON MONOXIDE AND WATER INSTEAD OF HYDROGEN*

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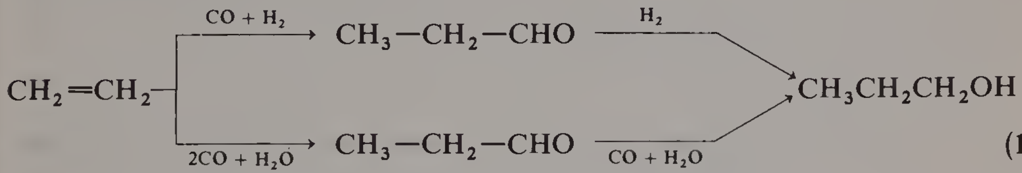
INTRODUCTION

In 1953, Reppe and Vetter reported an interesting variation of the hydroformylation reaction, or "OXO" process, in which they were able to catalytically effect the reductive addition of carbon monoxide to an olefin to yield a higher alcohol, not with the use of hydrogen, as is normally done, but through the use of an extra mole of carbon monoxide plus water.[1] The overall stoichiometries of the two reactions are shown in Equation **1**.



(1)

The Reppe catalyst system consists of iron pentacarbonyl in a basic aqueous medium (either Lewis bases, such as amines, or Brønsted bases, such as K_2CO_3), and it is of further interest to note that the conditions employed in this system, for the conversion of low-molecular-weight olefins, are much milder than those utilized in the normal hydroformylation reaction, namely, 100°C at 200 psi of carbon monoxide, as compared to 150–180°C at 3000 psi of carbon monoxide, respectively. At first glance, it might be surmised that the mechanism of the Reppe modification involves the *in situ* generation of hydrogen via a catalyzed water-gas shift reaction (Equation **2**) and that molecular hydrogen is, then, functioning as in the normal process. However, this idea is not tenable, because even under the more stringent conditions of the normal process, iron pentacarbonyl in conjunction

$$CO + H_2O \longrightarrow CO_2 + H_2 \qquad (2)$$

with molecular hydrogen is known to be a very poor catalyst system for the hydroformylation reaction.[2]

It appears, then, that in the Reppe modification of the hydroformylation reaction, we have a situation in which it is more effective to use the combination of carbon monoxide and water for reduction than it is to use molecular hydrogen itself. We were then interested in seeing if this concept could also be applied to other reductions in which hydrogen was normally used. In particular, we wished to

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investigate the possibility that methanol could be produced through the reduction of carbon monoxide, not with hydrogen, as is normally done (Equation **3**), but

$$CO + 2H_2 \longrightarrow CH_3OH \qquad (3)$$

$$3CO + 2H_2O \longrightarrow CH_3OH + 2CO_2 \qquad (4)$$

with carbon monoxide and water (Equation **4**). If successful, this reaction would, then, raise the possibility of preparing a liquid fuel (methanol) directly from carbon monoxide and water, and the reaction could conceivably play a role in the utilization of low-grade carbon sources, such as coal, lignite, and garbage.

In the following sections, we discuss our initial results with this type of reduction of organic compounds by use of carbon monoxide and water in place of hydrogen.

MECHANISM OF THE REPPE MODIFICATION OF HYDROFORMYLATION REACTIONS

As already stated, the Reppe modification of the hydroformylation reaction appeared to be a clear case in which carbon monoxide and water were functioning as a reducing system but without intermediate formation of molecular hydrogen; knowledge of how this catalyst system was functioning could be useful in considering other potential uses of carbon monoxide and water, which is why we have investigated this reaction further.

Early attempts to identify the catalytic species of the Reppe process were thwarted because the various metal carbonyl species produced on reaction of iron pentacarbonyl with a base were not fully characterized.[3,4] It is now established that two such species, namely, **1** and **2**, are produced on reaction of iron pentacarbonyl with aqueous base.[5]†

$$\overset{(-)}{HFe(CO)_4} \qquad \overset{(-)}{HFe_3(CO)_{11}} \qquad H_2Fe(CO)_4$$

1 **2** **3**

One proposed scheme for the mechanism of the Reppe process involved interaction of anion **2** with an olefin and carbon monoxide to form an acyl anion; this species would then be protonated to yield an aldehyde, which would be further reduced to product alcohol.[6] Another proposal invoked the protonated form of anion **2** as the catalyst, presumably in a mechanism similar to the normal reaction in which $HCo(CO)_4$ is the catalyst.[7] In light of the following results, neither of these proposals would seem to be acceptable.

We have found that formation of alcohols under Reppe conditions is strongly dependent on the pH of the solvent medium. When iron pentacarbonyl (10.0 g) is heated in aqueous potassium hydroxide (300 ml of a 3.3% solution) to 100°C in a liter autoclave under 200 psi of ethylene and 300 psi of carbon monoxide, the iron pentacarbonyl dissolves with formation of anion **1** according to Reaction **5**. The pH of the solution is initially 12.0,‡ and infrared analysis indicated that only

$$Fe(CO)_5 + OH^- \longrightarrow HFeCO_4{}^- + CO_2 \qquad (5)$$

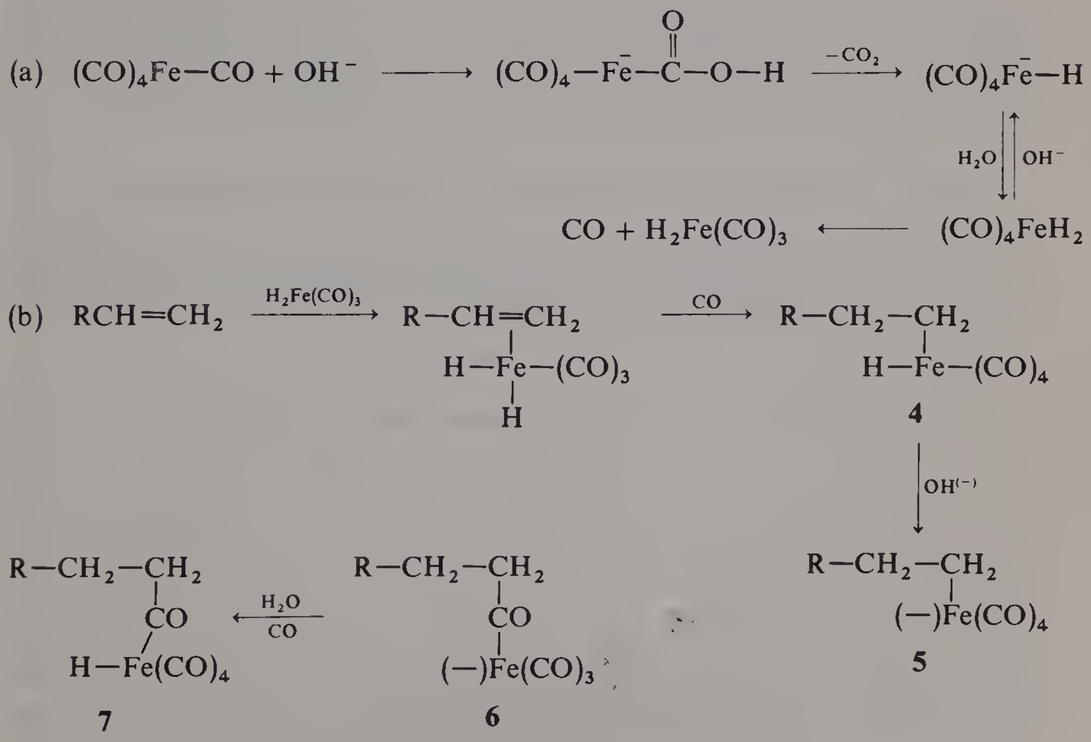
---

† Each of the two monoanions can lose a proton to give the corresponding dianion.

‡ The pH measurements were taken at room temperature on samples withdrawn from the autoclave.

anion **1** was present as the metal carbonyl species. As heating is continued, the pH of the solution decreases due to the reaction of carbon monoxide with hydroxide ion to yield formate ion. However, only when the pH drops to about 10.7 does absorption of ethylene and formation of propanol begin to occur; at this point, again, the principal metal carbonyl anion present is species **1**, although the solutions are frequently red in color, indicating the presence of some of the trinuclear anion (**2**). The formation of propanol continues until the pH finally falls to around 8.0.§ In an identical experiment, but with acetaldehyde added to the reaction mixture at pH 12.0, it is found that the acetaldehyde is immediately reduced to ethanol at the high pH, but, again, only when the pH drops to 10.7 does the ethylene react to form propanol.

These data indicate that whereas anion **1** is capable of reducing aldehydes, it is not capable of interacting with olefins. We conclude that at pH 10.7, the conjugate of acid of **1**, that is, species **3**, begins to be formed in significant concentration, and **3** is the species that is required to undergo initial reaction with the olefin. Consistent with this proposal, we find that when 1,5-cyclooctadiene is stirred with a solution of $KHFe(CO)_4$ in aqueous K_2CO_3 under an argon atmosphere at an initial pH of 12.0, and the pH is then lowered by addition of a stream of carbon dioxide, only when the pH is lowered to 10.7 does isomerization of 1,5- to 1,3-cyclooctadiene begin to occur. It is known that acid **3** is a powerful catalyst for double-bond isomerization reactions.[3] In a similar experiment in which the initial solution contained the $HFe_3(CO)_{11}$ anion **2**, no isomerization of 1,5-cyclooctadiene occurred in the pH range of 12.0–8.0. Although the trinuclear anion may be



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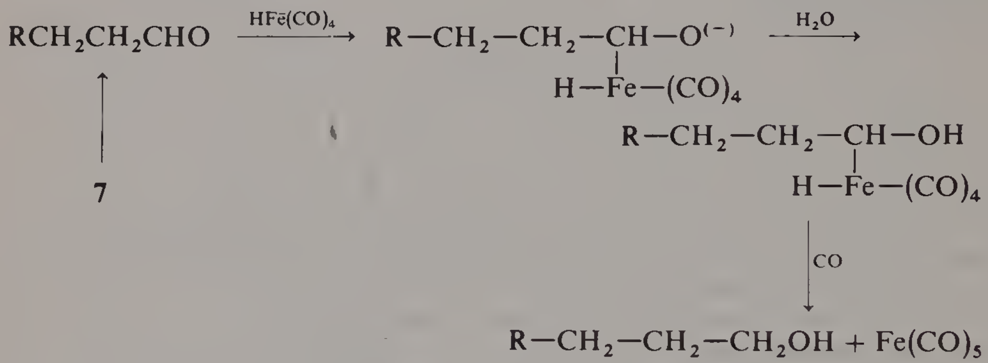
§ As the reaction proceeds, the pH drops due to the composition of the base, according to Reaction **2**.

observed in the Reppe modification, it is not a catalyst under the reaction conditions employed.[¶]

Also consistent is the fact that in the absence of olefins, basic solutions of anion **1** under a pressure of carbon monoxide begin to liberate molecular hydrogen when the pH is lowered to approximately 10.7. Species **3** is known to decompose readily with liberation of molecular hydrogen.[9] On the basis of these data, and by analogy with the mechanism of the normal reaction with $HCo(CO)_4$, as given by Heck and Breslow,[10] we propose the following mechanism for the Reppe modification. The principal steps would be generation of the catalyst,[‖] formation of aldehyde,[**] and reduction to alcohol:

(c)



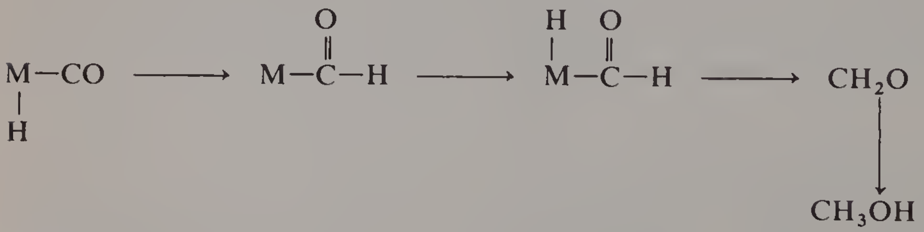
$$\mathrm{RCH_2CH_2CHO} \xrightarrow{\mathrm{H\overset{-}{Fe}(CO)_4}} \mathrm{R{-}CH_2{-}CH_2{-}\underset{\displaystyle H{-}Fe{-}(CO)_4}{\underset{|}{CH}}{-}O^{(-)}} \xrightarrow{\mathrm{H_2O}} \mathrm{R{-}CH_2{-}CH_2{-}\underset{\displaystyle H{-}Fe{-}(CO)_4}{\underset{|}{CH}}{-}OH} \xrightarrow{\mathrm{CO}} \mathrm{R{-}CH_2{-}CH_2{-}CH_2OH + Fe(CO)_5}$$

$$\mathbf{7} \longrightarrow \mathrm{RCH_2CH_2CHO}$$

We consider, then, that the normal hydroformylation reaction and the Reppe modification are mechanistically closely related. The essential point in the latter process is that it is easier to form species $H_2Fe(CO)_4$ from the reaction of iron pentacarbonyl and water plus a base than it is from iron pentacarbonyl and molecular hydrogen; for this reason, the combination of water and carbon monoxide provides a reducing system superior to molecular hydrogen in this instance.

DIRECT CONVERSION OF CARBON MONOXIDE AND WATER TO METHANOL

In our initial attempts to design a homogeneous catalyst for reduction of carbon monoxide to methanol, we considered that the following steps (Equation **5**) had to be accomplished by the catalyst system:



$$\mathrm{\underset{\displaystyle H}{\underset{|}{M}}{-}CO} \longrightarrow \mathrm{M{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H} \longrightarrow \mathrm{M{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H}\ (\mathrm{H\ on\ M}) \longrightarrow \mathrm{CH_2O} \longrightarrow \mathrm{CH_3OH} \qquad (5)$$

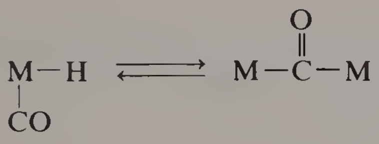
8 **9** **10**

[¶] We have found that under carbon monoxide pressure at 100°C, species **2** is converted to **1**, consistent with the observations of Wada and Matsuda.[8]

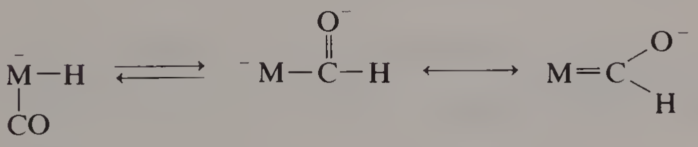
[‖] Proposed loss of a carbon monoxide ligand from species **3** is consistent with the pressure-product dependence studies of Wada and Matsuda.[11]

[**] Alkyl iron tetracarbonyl anions similar to **4** have been shown to readily undergo carbonyl insertion reactions,[12] and this reaction is indicated in our scheme; it would also seem that species **4** could be converted to **7** directly.

This scheme involves insertion of carbon monoxide into a metal hydride bond to generate a formyl complex (**8**→**9**), then formaldehyde, to finally yield methanol. Alternatively, complex **10** could be reduced to a hydroxymethyl complex with subsequent reductive elimination of methanol. The obvious difficulty in designing a practical system for such a conversion centered around the first step in this sequence: whereas there are numerous examples of insertion of a carbon monoxide ligand into a metal—alkyl bond to form a metal—acyl complex, there is no such analogous reaction that involves insertion of carbon monoxide into a metal—hydrogen bond. Only very recently have examples of metal—formyl complexes been formed, and in each case, their formation does not involve such an insertion reaction of carbon monoxide into a M—H bond.[13] It seems reasonable to assume that the absence of such an insertion reaction is associated with the relatively high bond strength of the M—H bond and the resultant unfavorable disposition of the equilibrium given by Equation **6**.



$$\underset{\displaystyle CO}{\underset{|}{M-H}} \rightleftharpoons M-\overset{\overset{\displaystyle O}{\|}}{C}-M \qquad (6)$$



$$\underset{\displaystyle CO}{\underset{|}{\overset{-}{M}-H}} \rightleftharpoons {}^{-}M-\overset{\overset{\displaystyle O^-}{\|}}{C}-H \longleftrightarrow M{=}C\genfrac{}{}{0pt}{}{\diagup O^-}{\diagdown H} \qquad (7)$$

We reasoned that if species **8** also carried a negative charge, the insertion reaction might, then, become more thermodynamically favorable due to the fact that in the formyl complex, the negative charge can be delocalized from the metal atom because of the resonance interaction indicated in Equation **7**. A potential candidate for a methanol or formaldehyde catalyst system would, then, be a metal carbonyl hydride that bears a negative charge. The reaction of aqueous base with iron pentacarbonyl produces such a species, and, accordingly, this reaction was studied as a possible homogeneous catalytic system for methanol synthesis. (In work conducted in conjunction with the mechanism of the Reppe reaction, we had shown that an aqueous solution of the $HFe(CO)_4$ anion reduced formaldehyde to methanol.)

The reaction of excess aqueous potassium carbonate with iron pentacarbonyl in a stirred autoclave at 100°C under a carbon monoxide pressure of 300 psi indeed produced methanol, together with larger amounts of hydrogen and formate ion. It was found that formation of these three products is strongly dependent on the pH of the reaction solution. At the beginning of the reaction (pH 12.0), the iron pentacarbonyl dissolves to form $KHFe(CO)_4$; then, as the reaction proceeds, the pH drops due to the formation of carbon monoxide and formic acid, finally reaching a value of approximately 8.5, at which point all of the iron is recovered as iron pentacarbonyl. Based on the amount of iron pentacarbonyl added initially, 10% MeOH, 150% H_2, and 700% $HCOO^-$ anion are produced. Formate ion is produced in two distinct stages: formation first at the initial high-pH range (~ 12.0), followed by a low-production phase, which rapidly increases again when the pH nears 10.7. The formation of hydrogen and methanol only begins when the pH has dropped to about 10.7; the formation of all three products then continues during the drop in pH from 10.7 to 8.5.

Although methanol was produced in this reaction, all attempts to confirm our initial speculation that an insertion reaction of carbon monoxide into an M—H bond was to be involved in its formation were completely unsuccessful; we conclude now that such a step is probably not involved. The best reasoning for this conclusion is the fact that under no conditions of temperature, solvent, and pressures of carbon monoxide up to 300 psi could we observe evidence for the formation of the known formyl anionic complex **11** (Equation **8**):

$$\mathrm{HFe(C\bar{O})_4 + CO \longrightarrow (CO)_3F\bar{e}CHO \xrightarrow{CO} \underset{\mathbf{11}}{(CO)_4F\bar{e}CHO}} \qquad (8)$$

With the data available at present, we consider that the following mechanistic scheme satisfactorily accounts for the formation of the three products and the dependence of their formation on the pH of the medium:

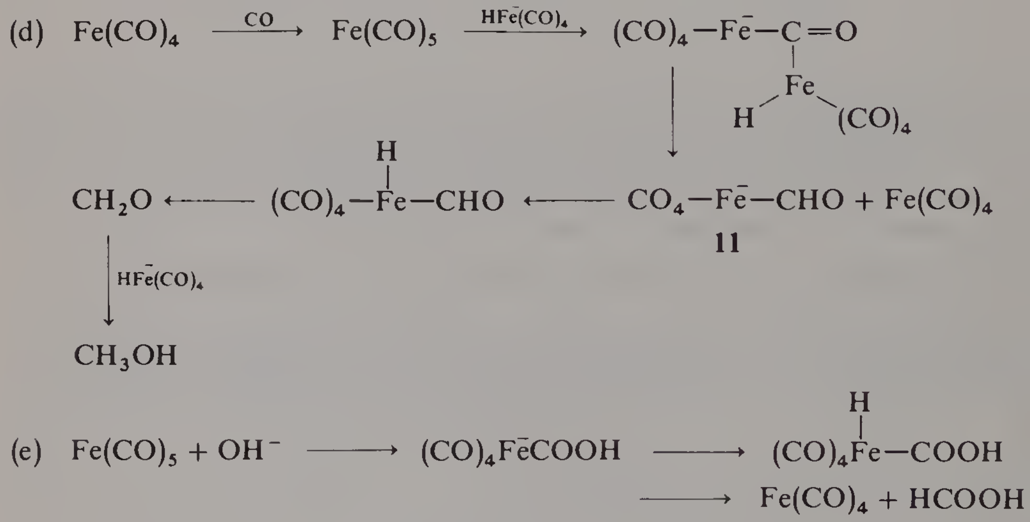
At pH 10.8

(a) $\mathrm{CO + OH^- \longrightarrow HCOO^-}$

(b) $\mathrm{Fe(CO)_5 + OH^- \xrightarrow{CO} HF\bar{e}(CO)_4 + CO_2}$

At pH 10.8

(c) $\mathrm{HF\bar{e}(CO)_4 \xrightarrow{H^+} H_2Fe(CO)_4 \longrightarrow Fe(CO)_4 + H_2}$



(d) $\mathrm{Fe(CO)_4 \xrightarrow{CO} Fe(CO)_5 \xrightarrow{HF\bar{e}(CO)_4} (CO)_4{-}F\bar{e}{-}\underset{\underset{H\quad (CO)_4}{Fe}}{C}{=}O}$

$$\mathrm{\downarrow}$$

$$\mathrm{CH_2O \longleftarrow (CO)_4{-}\overset{H}{Fe}{-}CHO \longleftarrow \underset{\mathbf{11}}{CO_4{-}F\bar{e}{-}CHO} + Fe(CO)_4}$$

$$\mathrm{CH_2O \xrightarrow{HF\bar{e}(CO)_4} CH_3OH}$$

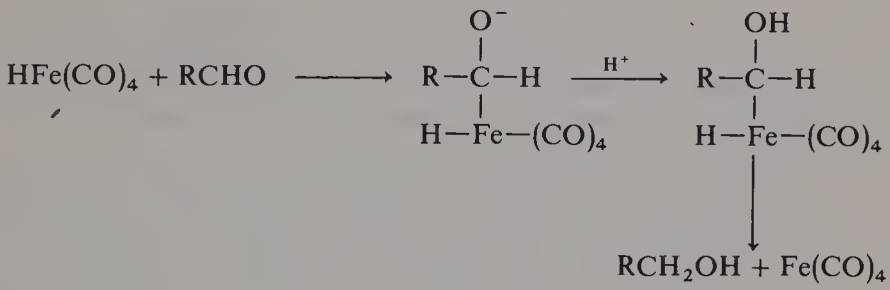
(e) $\mathrm{Fe(CO)_5 + OH^- \longrightarrow (CO)_4F\bar{e}COOH \longrightarrow (CO)_4\overset{H}{Fe}{-}COOH \longrightarrow Fe(CO)_4 + HCOOH}$

We propose, then, that formyl complex **11** is involved in the formation of methanol but that it is produced via nucleophilic attack of the $\mathrm{HFe(CO)_4^-}$ anion on iron pentacarbonyl, followed by reductive elimination, as shown, rather than by an intramolecular insertion reaction of carbon monoxide into an Fe—H bond, as speculated initially. An attractive feature of this proposed mode of formation is that the formyl—metal bond would be produced in a complex in which the full effective atomic number of the metal is not lost (i.e., in **11**), whereas in a scheme that involves intramolecular insertion, this is not the case (Equation **8**).

For iron pentacarbonyl, formation of hydrogen, methanol, and formate ion is a catalytic reaction in each case. However, with respect to the former two, which are obviously the most important products, production of formate ion would render the overall sytem noncatalytic in the sense that it consumes base. If conditions can be found to eliminate (or at least minimize) the production of formate ion, the system would seem to offer promise as a homogeneous catalyst for the conversion of carbon monoxide and water to methanol and also for conducting the water-gas shift reaction under very mild conditions.

REDUCTION OF ACID CHLORIDES TO ALDEHYDES

As mentioned in the second solution, the $HFe(CO)_4^-$ anion in protic solvents is capable of reducing aldehydes to alcohols. Presumably, the mechanism of this reduction involves nucleophilic attack of the anion on the carbonyl group, followed by protonation and reductive elimination, as indicated in Equation **9**.



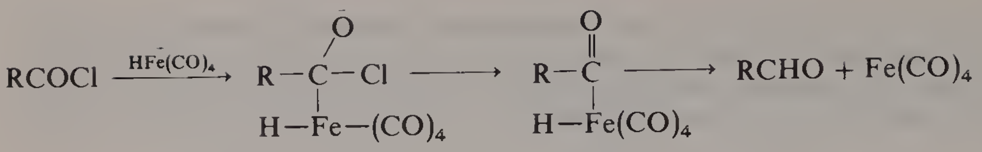
$$HFe(CO)_4 + RCHO \longrightarrow R-\overset{\overset{\displaystyle O^-}{|}}{\underset{\underset{\displaystyle H-Fe-(CO)_4}{|}}{C}}-H \xrightarrow{H^+} R-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H-Fe-(CO)_4}{|}}{C}}-H \longrightarrow RCH_2OH + Fe(CO)_4 \qquad (9)$$

Prompted by these considerations, we have studied the reaction of the $HFe(CO)_4^-$ anion with acid chlorides in an aprotic medium and have found that acid chlorides are converted to aldehydes in excellent yields. The results of the reaction of the tetramethylammonium salt of the $HFe(CO)_4^-$ anion with several acid chlorides in anhydrous methylene chloride at 25°C are listed in TABLE 1. Except for the unsaturated chlorides and those that contain an aromatic nitro group, the method offers promise as an excellent means for converting acid chlorides to aldehydes, and the reagent promises to be of synthetic utility.

Again, we presume that the mechanism of the reaction involves initial nucleophilic attack at the carbonyl group, followed by displacement of chloride and reductive elimination of the aldehyde from complex **12** (Equation **10**).

TABLE 1

Acid Chloride	Reaction Time (hr)	Percentage Aldehyde Yield
Benzoyl chloride	1.25	91*
2-Furoyl chloride	4.0	90*
Hexanoyl chloride	1.25	99*
Cyclohexanoyl chloride	2.75	95*
p-Bromobenzoyl chloride	1.0	80,* 75†
Cinnamoyl chloride	1.75	22*
Isobutyryl chloride	1.75	99,* 82†
Pivaloyl chloride	1.5	80‡
Acetyl chloride	3.0	100*
p-Nitrobenzoyl chloride	0–1	0§



$$\mathrm{RCOCl} \xrightarrow{\mathrm{H\bar{F}e(CO)_4}} \mathrm{R{-}\underset{H-Fe-(CO)_4}{\overset{O}{C}}{-}Cl} \longrightarrow \mathrm{R{-}\underset{H-Fe(CO)_4}{\overset{O}{\overset{\|}{C}}}} \longrightarrow \mathrm{RCHO + Fe(CO)_4} \quad (10)$$

12

The iron tetracarbonyl species, which is produced simultaneously with the aldehyde, apparently reacts with $N(CH_3)_4HFe(CO)_4$ to generate the trinuclear anion (**13**), which is relatively inert to further reaction (Equation **11**). Consequently, the best yields of aldehyde are obtained when the acid chloride—hydride complex is used in a 2 : 3 molar ratio, and this ratio was used for the data given in Table 1.

$$(CH_3)_4\overset{+}{N}\,H\overset{-}{Fe}(CO)_4 + 2Fe(CO)_4 \longrightarrow (CH_3)_4\overset{+}{N}\,H\overset{-}{Fe}_3(CO)_{11} + CO \quad (11)$$

This method of conversion of acid chlorides to aldehydes is similar to that reported by Watanabe *et al.* in which they react acid chlorides with the iron tetracarbonyl dianion and, through the addition of acid, protonate the resultant acyl iron tetracarbonyl monoanion to generate the same acyl complex (**12**), which yields the aldehyde.[14] The yields in both processes are similar.

Because acid chlorides are, of course, incompatible with water, direct catalytic reduction of acid chlorides to aldehydes by carbon monoxide and water does not appear to be a plausible scheme. However, since the trinuclear anion (**13**) is converted back to the mononuclear anionic species in the presence of base, water, and carbon monoxide pressure, through external regeneration of the $HFe(CO)_4^-$ anion, the overall reaction is thus the reduction of acid chlorides to aldehydes with water and carbon monoxide without any net consumption of iron pentacarbonyl.

CONCLUSIONS

The above results indicate that utilization of carbon monoxide and water, rather than hydrogen, for reducing organic compounds might well have fairly broad utility. The basic reason for this expectation is that hydrogen itself does not readily add to any organic species; only in the presence of a metal does reduction with hydrogen occur, and, presumably, some form of metal hydride is the active species. Metal hydride species can also be obtained from carbon monoxide and water, sometimes more readily than with hydrogen, and this combination should also be an effective reducing system. The extension of this concept to metals other than iron and with ligands other than carbon monoxide exclusively is under investigation.

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REACTIONS OF COORDINATED OLEFINS AND ACETYLENES*

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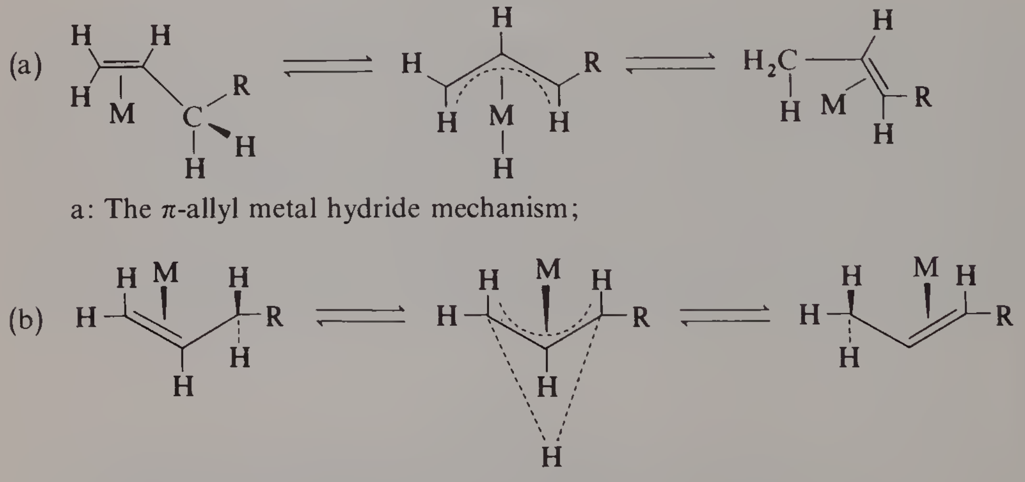
The level of sophistication that has been achieved in modern synthetic organic chemistry can be attributed to a large extent to our understanding of mechanism and stereochemistry. It is clear that if organometallic chemistry is to be successfully developed in the direction of the synthesis of organic molecules, a similar detailed understanding of mechanism must be obtained. This is by no means an easy task because of the involvement of transition metals with their attendant d orbitals. In this paper, I will describe our efforts to understand reactions that involve hydrogen shift processes and carbon—carbon bond formation.

The transition metal-promoted isomerization of olefins is one of the fundamentally important reactions of organometallic chemistry.[1] Two major mechanistic pathways are normally considered for such isomerizations: a metal hydride addition-elimination mechanism, which in effect constitutes a 1,2-hydrogen shift,[2,3] and the so-called π-allyl metal hydride mechanism, which involves a 1,3-hydrogen shift.[4] The latter mechanism has been the less well defined, although elegant studies by Casey and Cyr,[4] and by Whitesides and Neilan,[5] have indicated that such a mechanistic pathway must exist. In particular, studies of the isomerization of 3-ethylpent-2-ene and its 3-deutero analog to give 3-ethylpent-2-ene, catalyzed by $Fe_3(CO)_{12}$, have required π-allyl metal hydride intermediates to be invoked.[6] The π-allyl metal hydride mechanism is representatively depicted in SCHEME 1(a).



a: The π-allyl metal hydride mechanism;

b: metal-promoted sigmatropic 1,3-suprafacial hydrogen shift.

SCHEME 1.

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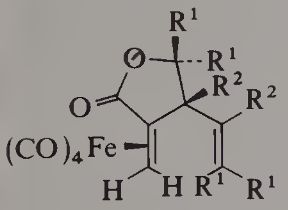
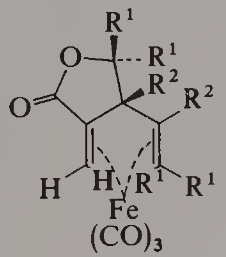
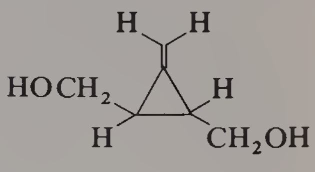
An alternative[6,7] to the π-allyl metal hydride mechanism involves a sigmatropic 1,3-suprafacial hydrogen shift, as depicted in SCHEME 1(b). Notably, the migrating hydrogen is never involved in bonding to the metal and migrates across the face of the olefinic ligand opposite to that on which the metal is bonded.[6,7] Although this process is thermally "forbidden" by orbital symmetry considerations in the free olefin, it has been proposed that coordination of the olefin to a transition metal can lift this symmetry-imposed restriction and make a metal-promoted 1,3-suprafacial hydrogen shift an energetically viable alternative to the π-allyl metal hydride mechanism.[6,7]

It must be noted, however, that because the net effect of both mechanisms is the same, in that a 1,3-hydrogen shift is effected, it is remarkably difficult to design a practical experiment to differentiate between the two possibilities. However, observations by Whitesides and Neilan,[5] based on the anticipated differences in isotope effects between the two mechanistic pathways, have indicated that the suprafacial shift mechanism may not be operating to a significant extent in the isomerizations of phenyl-substituted tricarbonyl(cyclohexa-1,3-diene)iron complexes.†



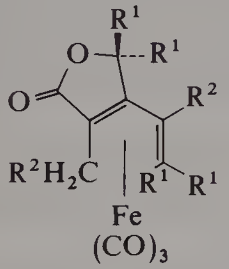




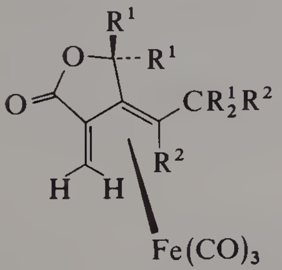
3

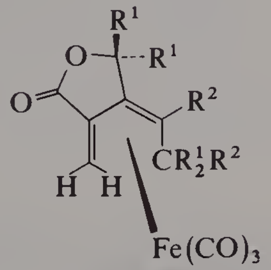
(**1a.** $R^1 = R^2 = H$;
1b. $R^1 = D, R^2 = H$;
1c. $R^1 = H, R^2 = D$)

(**2a.** $R^1 = R^2 = H$;
2b. $R^1 = D, R^2 = H$;
2c. $R^1 = H, R^2 = D$)



(**4a.** $R^1 = R^2 = H$;
4b. $R^1 = D, R^2 = H$;
4c. $R^1 = H, R^2 = D$)





(**5a.** $R^1 = R^2 = H$;
5b. $R^1 = D, R^2 = H$;
5c. $R^1 = H, R^2 = H$)

(**6a.** $R^1 = R^2 = H$;
6b. $R^1 = D, R^2 = H$;
6c. $R^1 = H, R^2 = D$)

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† Whitesides and Neilan consider the possibility of a sigmatropic 1,5-suprafacial hydrogen shift. This possibility may be equally well represented by two consecutive 1,3-suprafacial hydrogen shifts.

We have previously[8] described the preparation, properties, and both spectroscopic and crystallographic characterizations of complexes **1a** and **2a** and the preparation of the deuterium-labeled analogs **1b**, **1c** and **2b**, **2c**. (These complexes are hereafter referred to as *rac*-**1a**, *rac*-**2a**, and so on.) The proposed mechanism of formation of these complexes from *trans*- or *cis*-2,3-bis(hydroxymethyl)-methylenecyclopropanes and $Fe_2(CO)_9$ required[9] that the integrity of configuration at one of the two tetrahedral cyclopropane carbon atoms be retained. Thus, reaction of partially resolved (−)-*trans*-2(R),3(R)-bis(hydroxymethyl)methylenecyclopropane (**3**) (absolute configuration as drawn) with $Fe_2(CO)_9$ afforded optically active (+)-**1a** and (+)-**2a**, which must have the absolute configurations as drawn. Circular dichroism data for all optically active complexes are listed in TABLE 1.

Prolonged reflux of a solution of the tetracarbonyl complex *rac*-**1a** in diethyl ether afforded a single tricarbonyl complex, *rac*-**4a**. Similarly, the tetradeutero and dideutero complexes *rac*-**1b** and *rac*-**1c**, on refluxing in diethyl ether, afforded the analogous complexes *rac*-**4b** and *rac*-**4c**, respectively.

The rearrangement of (+)-**1a** was performed under identical conditions and afforded a sample of **4a** that exhibited no detectable specific rotation at the D line. The circular dichroism spectrum of this sample (TABLE 1), however, gave weak absorptions. Apparently, therefore, while the rearrangement of (+)-**1a** had occurred with extensive racemization, this racemization was not complete.

Similarly, rearrangement of a solution of *rac*-**2a** in refluxing diethyl ether proceded to completion more quickly than did that of *rac*-**4a** (4 hr under identical conditions of concentration) to yield a mixture of two tricarbonyliron complexes, both isomeric with *rac*-**4a**. The two products could not be separated by column chromatography but formed visually different crystalline species on crystallization from hexane. These forms could be physically separated by hand. The two complexes were characterized as the *syn* and *anti* isomers *rac*-**5a** and *rac*-**6a**. The ratio of *rac*-**5a**/*rac*-**6a**, determined by integration of the ^1H nuclear magnetic resonance (nmr) spectrum of the crude reaction mixture, was 1/2.3. When the rearrangement of *rac*-**2a** was performed in refluxing hexane, instead of diethyl ether, the same ratio of *rac*-**5a**/*rac*-**6a** was obtained.

No interconversion between isomers was observed when solutions of *rac*-**4a**, *rac*-**5a** or *rac*-**6a** in heptane were refluxed for 16 hr. Similarly, no traces of *rac*-**4a** were observed in the rearrangement of *rac*-**2a**, and no traces of either *rac*-**5a** or *rac*-**6a** were observed during the rearrangement of *rac*-**1a**.

The tetradeutero complex *rac*-**2b** similarly rearranged to a 1/2.3 mixture of *rac*-**5b**/*rac*-**6b** on refluxing in either diethyl ether or hexane. Similarly, the dideutero complex *rac*-**2c** rearranged in refluxing diethyl ether or hexane to afford a 1/2.3 mixture of *rac*-**5c**/*rac*-**6c**. No scrambling of deuterium between sites was

TABLE 1
Circular Dichroism Spectral Data for Complexes (+)-**1a**, (+)-**2a**, (+)-**4a**, (+)-**5a**, and (+)-**6a** (CH_3OH solution)

Complex	(+)-**1a**	(+)-**2a**	(+)-**4a**	(+)-**5a**	(+)-**6a**
λ_{max}(nm); $\Delta\varepsilon$	340; +0.27	421; −0.13	410; +0.007	391; +5.05	390; +4.60
	287; −1.82	312; +0.73	320; −0.148	339; −5.54	339; −6.50
	221; +2.44	245; −0.14	232; +0.89	299; −3.92	277; −4.40
		214; +1.50	203; +1.78	263; −3.06	240; +3.83
				225; +10.00	210; −7.65

observed, within the limits of ^{1}H nmr spectral integration, after refluxing the deuterated products in heptane.

The rearrangement of (+)-**2a** was performed under identical conditions in either refluxing diethyl ether or hexane and afforded a 1/2.3 mixture of (+)-**5a**/(+)-**6a**. Both isomers exhibited strong circular dichroism in their absorption spectra (Table 1). Furthermore, no loss of optical activity was observed on refluxing solutions of either (+)-**5a** or (+)-**6a** in heptane.

Thus, the tetracarbonyliron complexes (**1**) and the tricarbonyliron complexes (**2**) undergo remarkably regiospecific thermal rearrangements, under mild conditions, to yield different products. The use of the deuterium-labeled complexes **1** and **2** unambiguously defines the rearrangement of each as proceeding via a pure 1,3-hydrogen (or deuterium) shift, and observation of first-order kinetics for the rearrangement of complexes *rac*-**2a** and *rac*-**2c** confirms the unimolecularity of this rearrangement.

To assess the significance of the results of the rearrangements of the optically active complexes (+)-**1a** and (+)-**2a**, it is necessary to assign the absolute configurations of the reactants and products. Based on the knowledge of the absolute configuration of the organic starting material, (−)-*trans*-2(R),3(R)-bis(hydroxymethyl)methylenecyclopropane (**3**), the absolute configuration o the resultant 3-methylene-4(R)-vinyldihydrofuran-2(3H)-one ligand in both (+)-**1a** and (+)-**2a** must be as drawn. The positions of the Fe(CO)$_4$ moiety in (+)-**1a** and the Fe(CO)$_3$ moiety in (+)-**2a** are known from the molecular structures of their racemic analogs.[9] The absolute configurations of (+)-**1a** and (+)-**2a** must therefore be as drawn, with the iron atoms bounded to opposite faces of the lactone ring system.

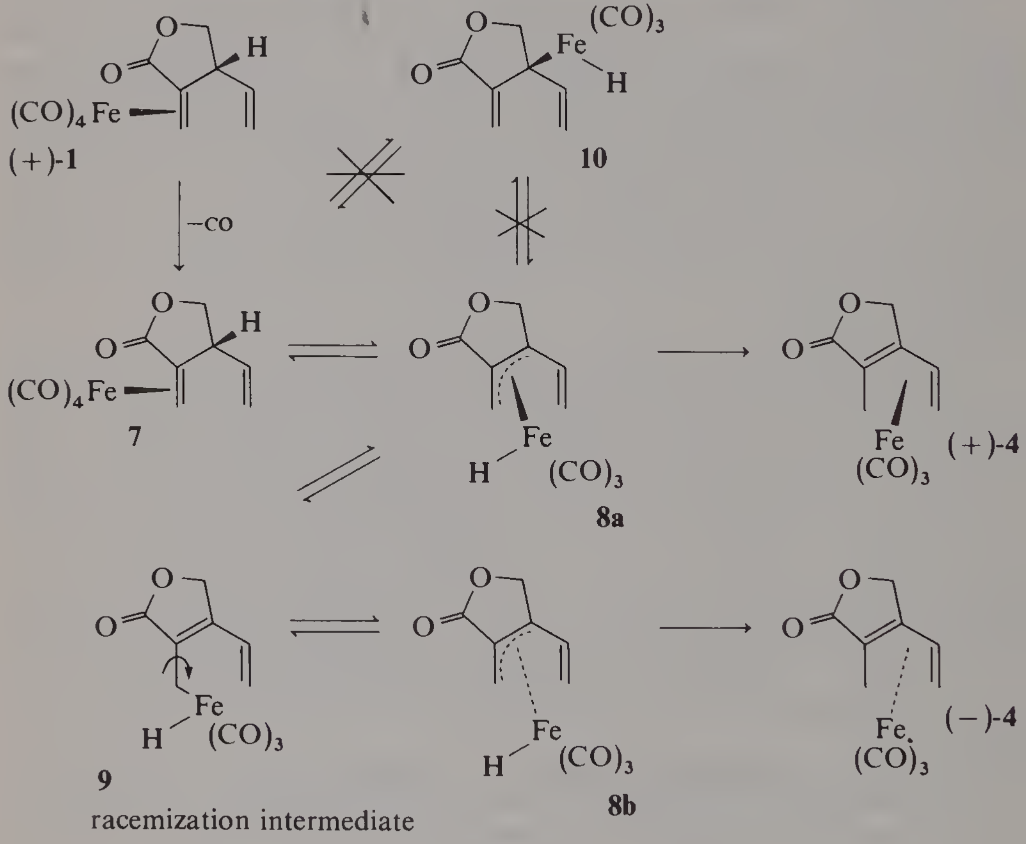
It has previously been established that for a variety of chiral transition metal complexes, the sign of the circular dichroism (CD) observed for d-d transitions can be related to the absolute configuration of the complex concerned.[10,11] In particular, the absolute configurations of tricarbonyliron complexes of prochiral 1,3-dienes, and tetracarbonyliron complexes of prochiral olefins, have been successfully related to the sign of the CD of the lowest-energy d-d transition.[10] It must be noted that the signs of the CD for d-d transitions must relate to the absolute configuration at the metal center in the case of prochiral ligands. It is not surprising, therefore, that the signs of the CD for the lowest-energy d-d transitions (Table 1) of (+)-**1a** (340 nm, positive) and (+)-**2a** (421 nm, negative) are opposite, even though the ligand has the same absolute configuration at its chiral carbon center in both cases, because the metal atoms are situated on opposite faces of the ligand.‡

Similarly, the complexes (+)-**5a** and (+)-**6a**, derived from the rearrangement of (+)-**2a**, must have the same absolute configuration as one another,[10] because both exhibit strongly positive CD for their lowest-energy d-d transitions. Observation of strongly positive CD places the Fe(CO)$_3$ moieties in both complexes (+)-**5a** and (+)-**6a** on the same face of the lactone ligand as the Fe(CO)$_4$ group in (+)-**1a** and, consequently, on the opposite face of the lactone ligand to the Fe(CO)$_3$ moiety in the precursor complex (+)-**2a**. Thus, the transformation of (+)-**2a** into either (+)-**5a** or (+)-**6a** involves a migration of the iron atom from one face of the ligand to the other; that is, the rearrangement proceeds with inversion of absolute configuration at the metal center.

‡ This requires that the major source of dissymmetric perturbation at the metal center is due to the prochiral lactone ring system rather than to the single chiral carbon atom in (+)-**1a** and (+)-**2a**.

The sample of (+)-**4a**, obtained by rearrangement of (+)-**1a**, exhibits only very weak CD for the d-d transitions. The CD for the lowest-energy band at 410 nm is particularly weak, by a factor of about 10^{-3}, compared to the CD for the corresponding bands in (+)-**5a** and (+)-**6a**. Because the three complexes are so similar structurally, we have concluded that extensive racemization occurs during the rearrangement of (+)-**1a** to (+)-**4a**. However, the CD of the 410-nm band of (+)-**4a**, though very weak, is positive in sign, placing the $Fe(CO)_3$ moiety in the dominant enantiomer on the same face of the lactone ring as the $Fe(CO)_4$ moiety in the precursor (+)-**1a**. Rearrangement of (+)-**1a** therefore occurs with extensive, though not complete, racemization and with slight retention of absolute configuration.

The mechanism that best fits the observations for the rearrangement of complexes **1** to complexes **4** is depicted in SCHEME 2, with the rearrangement of



SCHEME 2

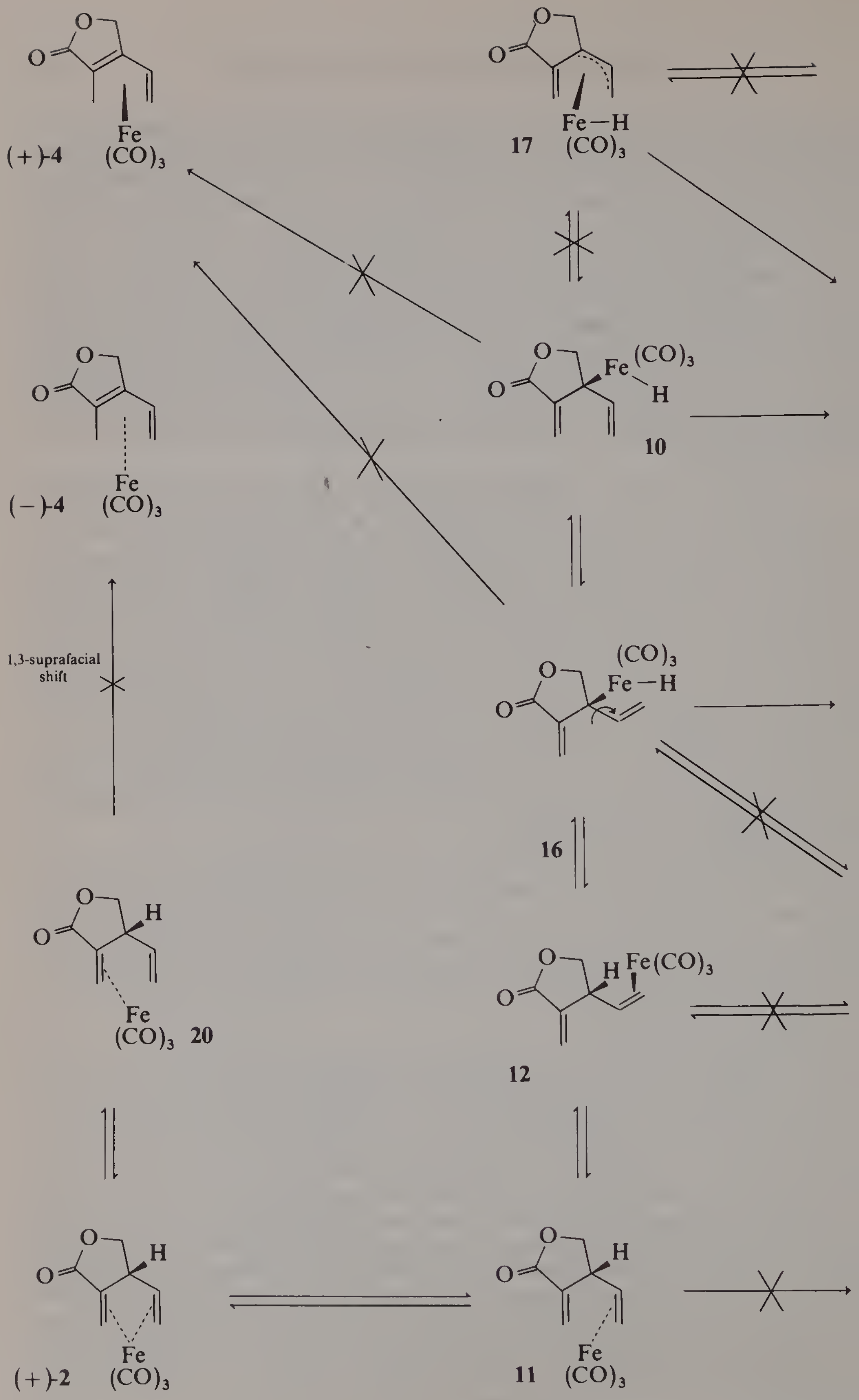
(+)-**1a** used as an example. The first, and presumably rate-determining, step involves loss of a carbonyl ligand to generate the coordinatively unsaturated species (**7**), which can then undergo an oxidative addition reaction to produce the π-allylic iron hydride (**8a**).[4] Intermediate **8a** has two available options, apart from regenerating **7**: it may directly undergo reductive elimination to afford (+)-**4a** or it may undergo a $\pi \rightarrow \sigma$ rearrangement to yield a short-lived terminal σ-allylic species (**9**). Rotation during the lifetime of **9**, as shown, followed by reformation of a π-allylic iron hydride (**8b**) generates the immediate precursor to (−)-**4a**. Intermediate **9** therefore represents a racemization intermediate. Because **9** can only be formed via the intermediacy of a π-allylic iron hydride, the observation of racemization in this system implies that the π-allylic iron hydride (**8a**) must have a sufficiently long lifetime for the rate of $\pi \rightarrow \sigma \rightarrow \pi$ formation, and consequently racemization, to compete effectively with the rate of reductive elimination to give the final product.

An alternative internal σ-allylic species (**10**) could also be conceivably formed by a $\pi \rightarrow \sigma$ transformation of **8a**. However, it has been previously well established that the free energy of activation for formation of a σ-allylic species from a π-allylic precursor increases with the number of substituents present on the carbon atom that becomes σ-bonded to the metal.[12,13] Consequently, formation of the primary carbon—metal σ-bond in **9** from **8a** must constitute a much lower energy process than the formation of a tertiary carbon—metal bond in **10** from **8a**. Species **10** must therefore be regarded as a relatively high-energy species to be formed via a π-allylic precursor.

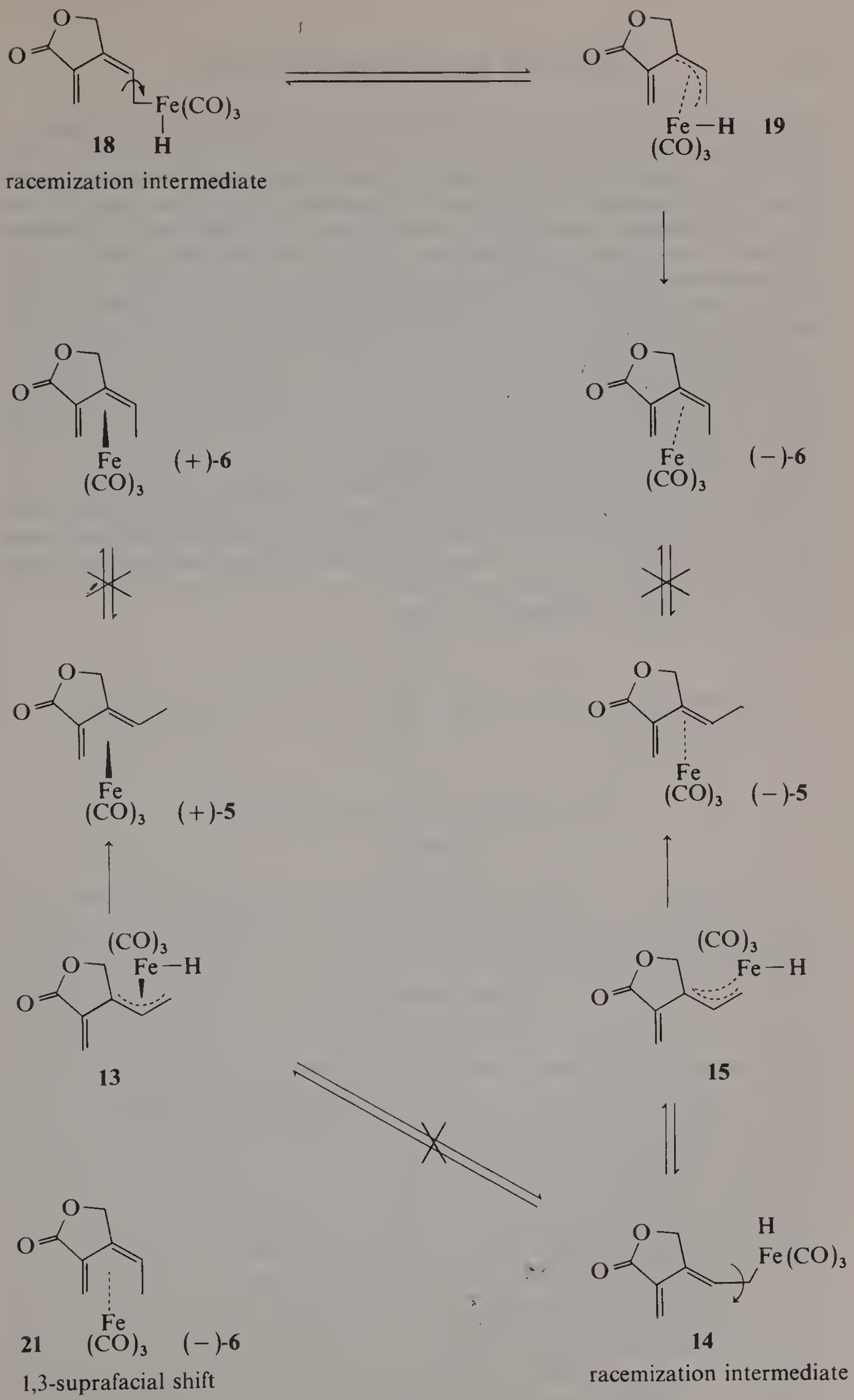
The various equilibria possible as mechanistic pathways for the rearrangement of complexes **2** into a 1 : 2.3 mixture of **5** and **6** are depicted in SCHEME 3, with the rearrangement of (+)-**2a** given as an example. Migration of the iron atom from one face of the organic ligand to the other is required to bring it into proximity with the hydrogen atom that is to undergo the eventual 1,3-shift, and also to explain the absolute configurations of the products obtained. This migration can be achieved by dissociation of the η^4-bonded ligand in (+)-**2a** to an η^2-bonded form, as in **11**; rotation around a carbon—carbon single bond is now possible, transferring the $Fe(CO)_3$ moiety from one face of the ligand to the other and generating **12**. Analogous processes have been proposed to explain the isomerizations of phenyl-substituted (cyclohexa-1,3-diene)iron tricarbonyl complexes[5] and the rearrangements of hexatriene iron tricarbonyl complexes.[14,15] Furthermore, because the rearrangements of *rac*-**2a** and *rac*-**2c** show no significant kinetic isotope effect, paralleling the results of Whitesides and Neilan,[5] this initial dissociation-rotation step is probably rate determining.

Transformation of **12** into a π-allylic iron hydride (**13**) seems, at first sight, the logical step immediately prior to the formation of (+)-**5**, as shown (SCHEME 3). Two problems arise: first, (+)-**6**, the major product, cannot be formed directly from **13**, nor can it be formed via (+)-**5**, because the isomers are noninterconvertible; second, formation of a π-allylic species, such as **13**, must lead to the possibility of a low-energy $\pi \rightarrow \sigma \rightarrow \pi$ transformation via the terminal σ-allylic species (**14**), with consequent racemization.

The only reaction pathway that can lead to the formation of both (+)-**5a** and (+)-**6a**, which have the same absolute configurations, must proceed via the internal σ-allylic intermediate (**16**), in which rotation of the vinyl group can lead to the conformer (**10**). As discussed previously, intermediate **16** cannot be formed via the intermediacy of a π-allylic species, such as **13**, because any $\pi \rightarrow \sigma \rightarrow \pi$ transformation of **13** would favor formation of (**14**) rather than **16** and would consequently lead to racemization. Intermediate **16** must therefore form directly from the olefinic complex **12** by a direct insertion of the $Fe(CO)_3$ moiety into the carbon—hydrogen bond. Similarly, it must be extremely unlikely that collapse of **16** into (+)-**5** occurs via the intermediate formation of **13**, because any significant lifetime for **13** should lead to racemization via **14**. It seems probable therefore that formation of (+)-**5a** from **16** and of (+)-**6a** from **10** occurs via a direct hydrogen migration from the metal to the terminal vinyl carbon atom. The preference for formation of (+)-**6** rather than (+)-**5** must reflect some difference in thermodynamic stability associated with the rotational form of the vinylic olefin in 10 compared to that in **16**.


(+)-4
Fe
(CO)$_3$
17
Fe—H
(CO)$_3$
(CO)$_3$
Fe
H
10
(−)-4
Fe
(CO)$_3$
1,3-suprafacial shift
(CO)$_3$
Fe—H
16
H
Fe(CO)$_3$
12
H
Fe
(CO)$_3$
20
H
Fe
(CO)$_3$
(+)-2
H
Fe
11
(CO)$_3$

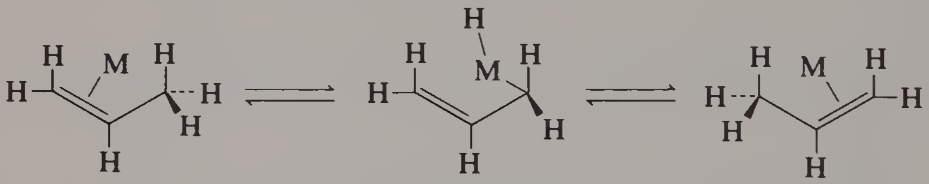
SCHEME 3



Scheme 3, *continued*

Notably, intermediates **10** and **16** exhibit no propensity toward collapse to (+)-**4**, nor can either **10** or **16** be formed directly from species **7** (SCHEME 2), because the products from one system are never observed in the other. Molecular models of intermediates **7**, **12**, **10**, and **16** demonstrate quite unambiguously that the rational flexibility of the vinylic olefin, compared to the rigidly constrained vinylidene olefin, enables the iron atom in **12** to approach much closer to the internal carbon—hydrogen bond than can the corresponding iron atom in **7**. The activation energy for insertion of the metal atom into the carbon—hydrogen bond in **12** to give **16** must be considerably lower than that for the corresponding transformation of **7**. Similarly, the free rotating vinylic olefin in intermediates **10** and **16** enables the terminal vinylic carbon atom to approach the iron—hydrogen bond much more closely than is possible for the terminal carbon of the constrained vinylidene olefin. Collapse of **10** or **16** to (+)-**6** or (+)-**5** must therefore be greatly facilitated compared to collapse to (+)-**4**.

These results imply that in cases where sufficient flexibility exists, direct insertion of a metal into an allylic carbon—hydrogen bond to give a σ-allylic species, and collapse of such a species via a direct hydrogen transfer from the metal to an olefinic carbon, can proceed as a low-energy olefinic isomerization pathway without requiring the intermediacy of a π-allylic metal bond. The proposed "σ-allyl metal hydride" mechanism is depicted in SCHEME 4.



The "σ-allyl metal hydride" mechanism.

SCHEME 4

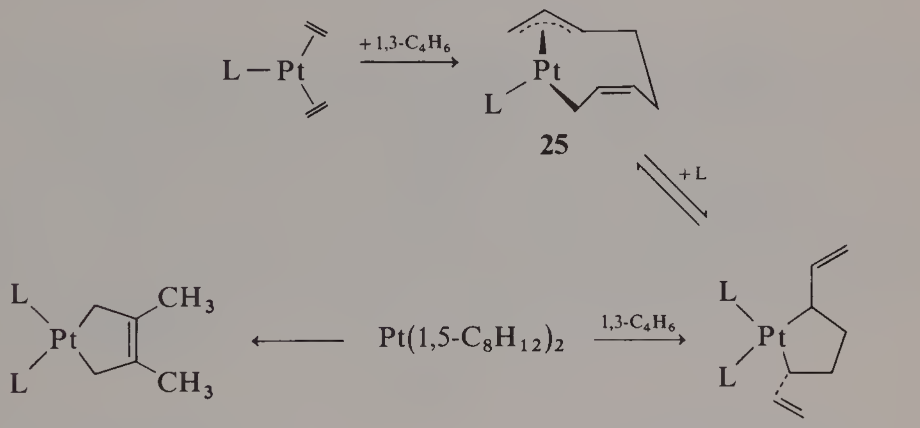
The possibility of a metal-promoted sigmatropic 1,3-suprafacial hydrogen shift mechanism has not yet been considered. Of the several possible intermediates available for the rearrangement of (+)-**2a** in SCHEME 3, two such species, **11** and **20**, comprise a coordinatively unsaturated metal fragment bonded in the theoretically ideal situation[6,7] for such a metal-promoted shift to occur. Furthermore, both **11** and **20** are generated by simple $\eta^4 \rightarrow \eta^2$ coordination changes in the organic ligand and as such are the first formed intermediates in any reaction of (+)-**2a**. A 1,3-suprafacial hydrogen shift is indeed the only pathway available to species **20**; however, no traces of complex (+)-**4**, the only possible product, are ever observed in this reaction system. A 1,3-suprafacial hydrogen shift in **11** can only lead to (−)-**6a**; this mechanism cannot be rationalized with the observed absolute configurations of both of the reaction products.

These results allow us to make the definite conclusion that any metal-promoted sigmatropic 1,3-suprafacial hydrogen shift in these systems is certainly not of sufficiently low energy to effectively compete with the σ-allylic metal hydride or the π-allylic metal hydride mechanisms for olefinic isomerization.

The discovery and development of the nickel(0)-catalyzed cyclodimerization and cyclotrimerization reactions of 1,3-dienes rank as one of the major achievements of organometallic chemistry.[16] Although considerable progress has been made toward understanding the mechanisms of these reactions, certain aspects still require clarification. The development[17] of a technique for synthesis of bis(cycloocta-1,5-diene)platinum allowed a study of the reaction with 1,3-dienes.

Treatment of [Pt(1,5-C_8H_{12})$_2$] with an excess of 2,3-dimethylbuta-1,3-diene afforded the platinum(II) complex (**22**), which, on reaction with *t*-butylisocyanide, led to displacement of 1,5-C_8H_{12} and formation of **23**. This interesting reaction probably involves the displacement of one cycloocta-1,5-diene to form (cycloocta-1,5-diene)(2,3-dimethylbuta-1,3-diene)platinum(0). Transfer of electrons from the metal to the π-system of the 1,3-diene then leads to the formation of carbon—platinum σ-bonds. Previously, it has been suggested that bis-olefinic complexes do undergo a related transformation, with the formation of a metallocyclopentane.[19,20]

In contrast, an excess of buta-1,3-diene reacts with [Pt(1,5-C_8H_{12})$_2$] to yield complex **24**, which was shown by x-ray crystallography to be a *trans*-2,5-divinylplatinacyclopentane. An insight into the mode of formation of this ring system was obtained from a study of the reaction of bis(ethylene)trimethylphosphineplatinum[17] with buta-1,3-diene. This reaction led to the formation of **25**, which was identified by ^1H and ^{13}C nmr spectroscopy as 1-η^1-6,7,8-η^3-*cis*-2-*trans*-6-octadienediyl(trimethylphosphine)platinum. The same complex was also obtained by reaction of **23** with one molar equivalent of trimethylphosphine. Interestingly, treatment of **24** with trimethylphosphine gave **26**, the analog of **23**. These transformations are summarized in SCHEME 5.



(**22**. L_2 = 1,5-C_8H_{12})
(**23**. L = Bu^{t}NC)

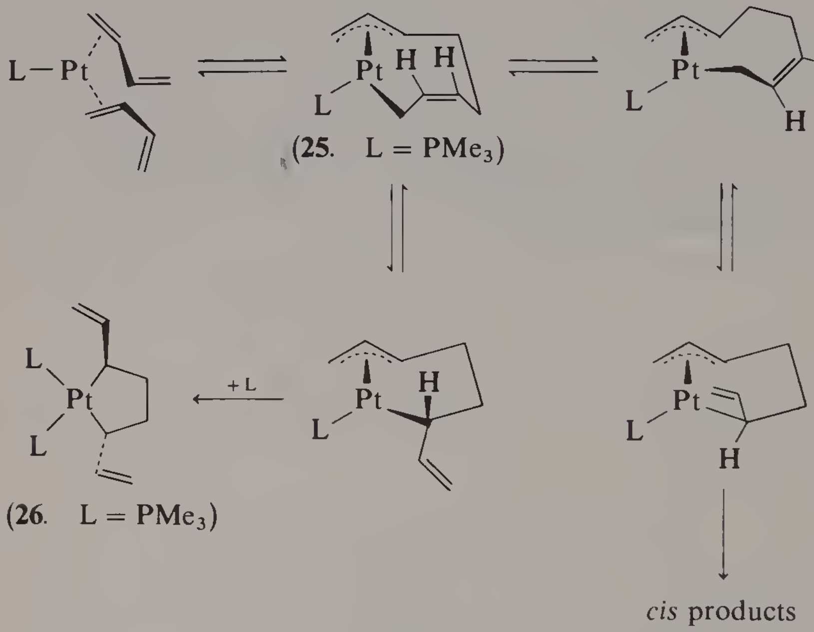
(**26**. L = PMe$_3$)
(**24**. L = 1,5-C_8H_{12})

SCHEME 5

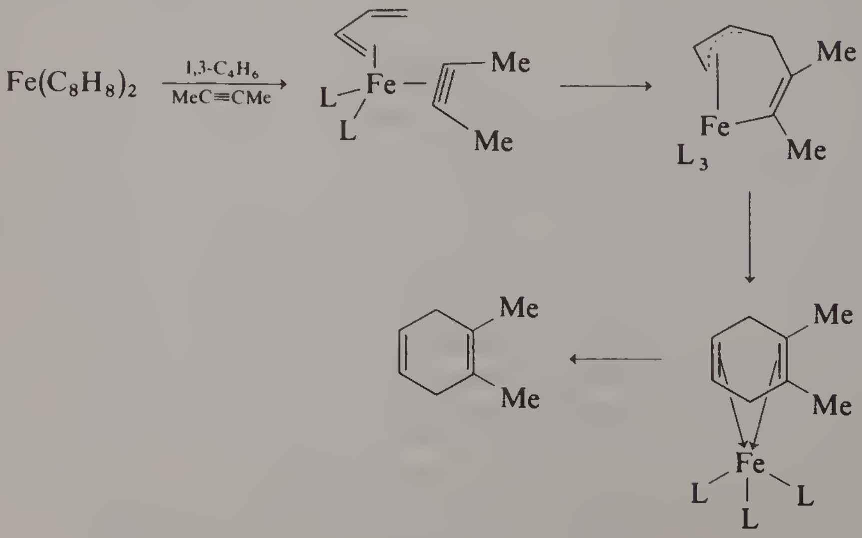
The formation of 2,5-divinylplatinacyclopentanes, in which the two vinyl groups have a relative *trans* stereochemistry, is unexpected in view of the suggestion[16] that a *cis*-2,5-divinylnickelacyclopentane is the precursor of *cis*-divinylcyclobutane in the Ni(0)-catalyzed dimerization of buta-1,3-diene. We believe that this proposal is essentially correct but that we must also take into account the different conformation that the η^3-allyl-C_8 chain can adopt. This idea is illustrated in SCHEME 6, where it is assumed that the precursor of **25** is a trigonal planar Pt(0) complex that contains *cis*- and *trans*-buta-1,3-diene molecules bonded in the 1,2-η mode. Examination of molecular models suggests that effective overlap between the π-orbitals of the two uncoordinated parts of the 1,3-dienes can easily occur. However, the question as to whether donation of electron density from the platinum to the diene π-systems with carbon—carbon bond formation is a concerted process is still unresolved.

The third type of reaction to be discussed is shown in SCHEME 7. Carbonaro *et al.*[21] have found that bis(cyclooctatetraene)iron is a catalyst for the metal-promoted cyclo-addition of buta-1,3-diene to but-2-yne. A plausible mechanism for this interesting reaction involves an oxidative bridging of the iron and one end of the 1,3-diene by the acetylene. The cyclization reaction is then completed by a reductive reaction. Direct evidence for such a suggestion was obtained from a study of the photochemical reaction of tricarbonyl(1,3-diene)iron complexes with hexafluorobut-2-yne.[22]

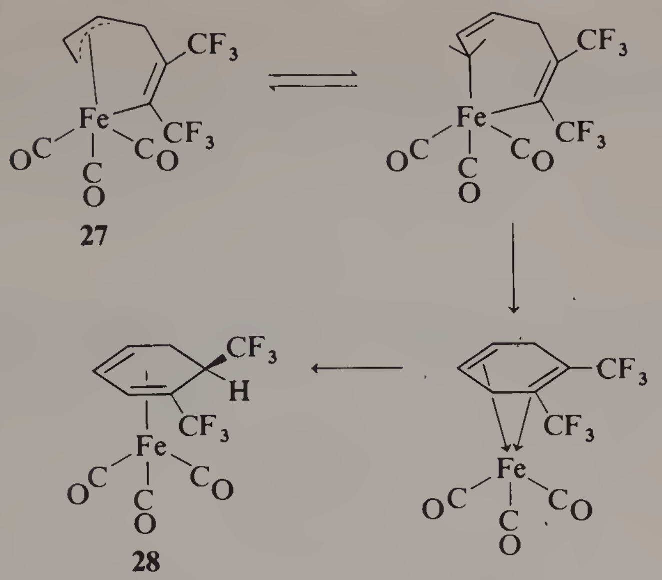
The product (**27**) of the reaction with the buta-1,3-diene complex was structurally characterized by nmr spectroscopy. Interestingly, in refluxing hexane, cyclization of the initial adduct occurred (SCHEME 8) to afford the substituted cyclohexa-1,3-diene



SCHEME 6



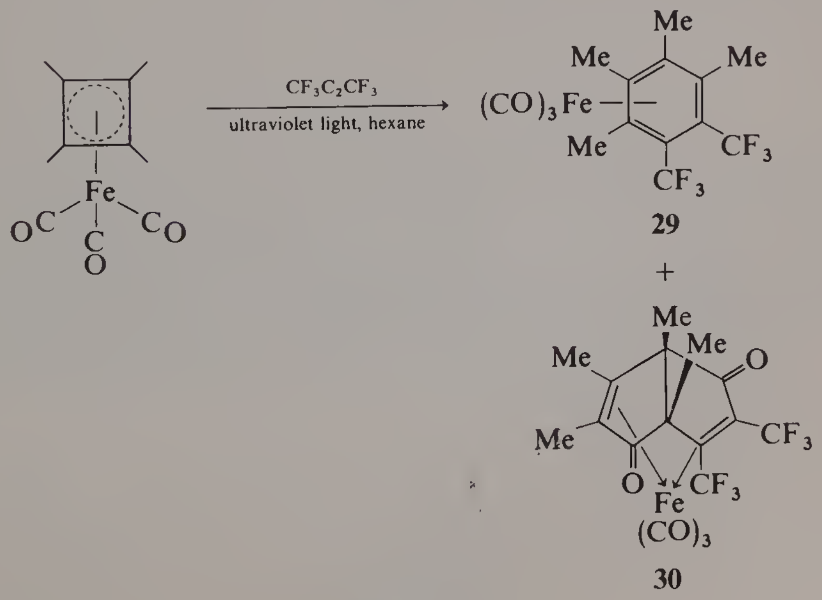
SCHEME 7



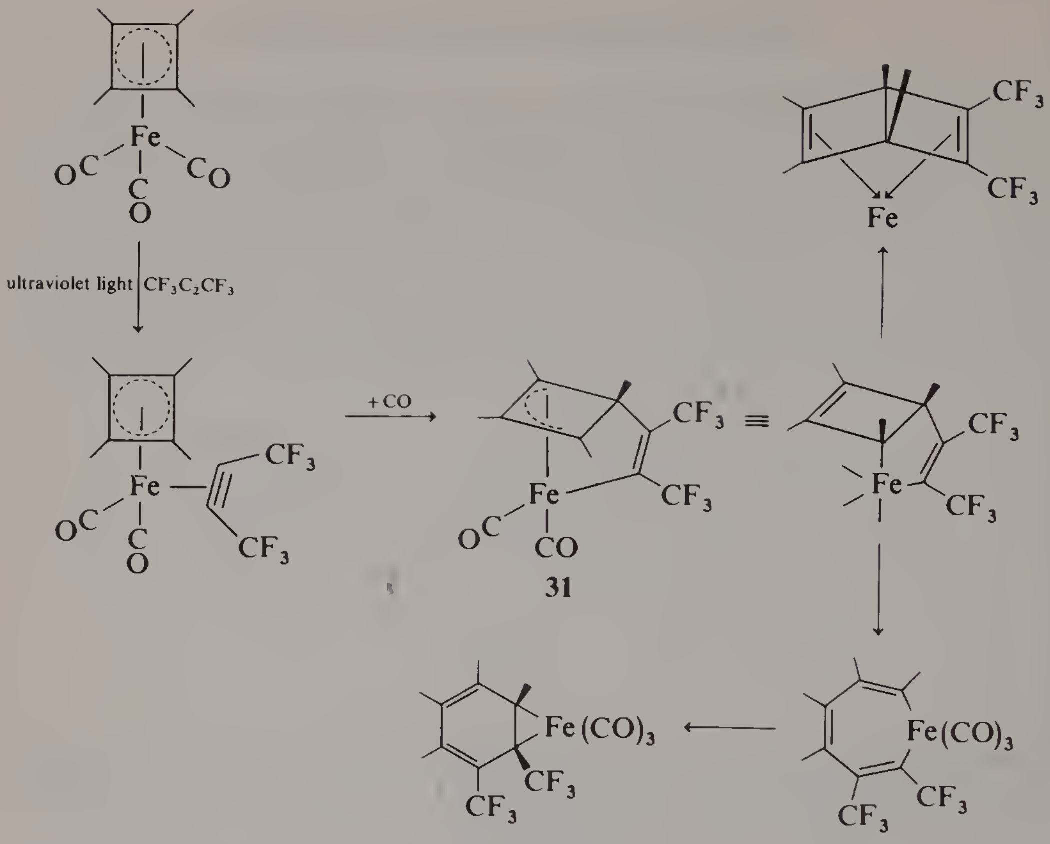
SCHEME 8

complex (**28**). A reasonable assumption is that the initial product of the carbon—carbon bond forming reductive reaction [Fe(II) → Fe(0)] undergoes a 1,3-hydrogen shift of the type discussed previously.

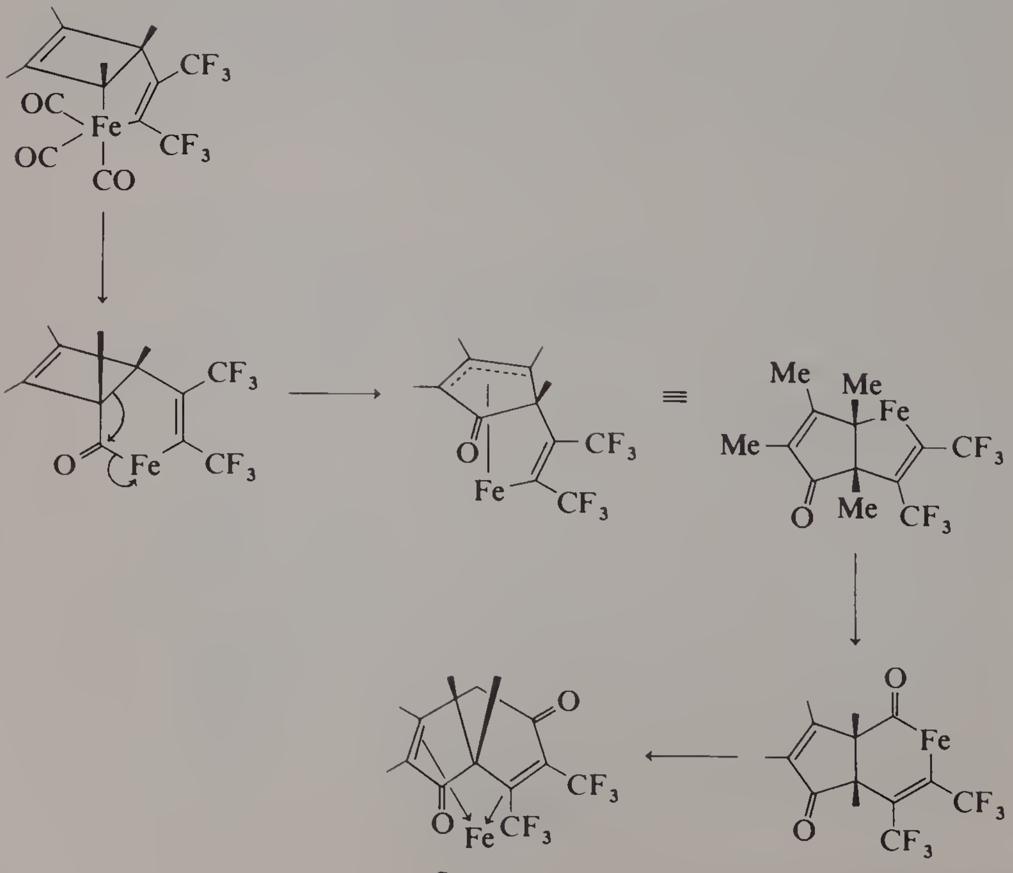
An attempt to extend these photochemical processes to the reaction of hexafluorobut-2-yne with tricarbonyl(tetramethylcyclobutadiene)iron led to the formation (SCHEME 9) of two interesting products, a tricarbonyliron benzene complex (**29**) and a bicyclic system (**30**).[23] The formation of both of these complexes can be rationalized in terms of competitive reactions that involve intermediate **31** (SCHEME 10). The benzene complex can be then formed either via a



SCHEME 9



Scheme 10



Scheme 11

photochemical disrotatory ring-opening reaction to give a metallocycloheptatriene or by a reductive carbon—carbon bond-forming reaction to give a Dewar benzene complex that rearranges to **29**. As shown in SCHEME 11, the diketone (**30**) can be produced via a sequence of carbonyl insertion reactions.

ACKNOWLEDGMENTS

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"TITANOCENE"-CATALYZED REACTIONS OF OLEFINS

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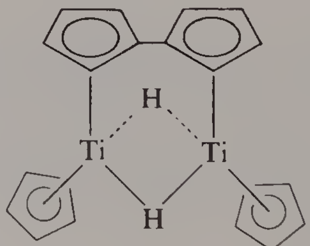
INTRODUCTION

Titanocene, or dicyclopentadienyl titanium, $(\eta\text{-}C_5H_5)_2Ti$, has long been a subject of controversy. Fischer and Wilkinson[1] first reported the preparation of a dark green air-sensitive $(C_5H_5)_2Ti$ material from the reaction of titanium dichloride with cyclopentadienyl sodium. However, later workers[2] were not able to duplicate this synthesis. The reduction of titanocene dichloride, $(C_5H_5)_2TiCl_2$, with sodium naphthalene[3] or sodium sand[4] and the thermolysis[5] or hydrogenation[6] of $(\eta\text{-}C_5H_5)_2Ti(CH_3)_2$ were reported to yield dark green or black materials claimed to have the composition $(C_5H_5)_2Ti$ or $[(C_5H_5)_2Ti]_2$. Brintzinger and Bercaw[7] realized, in 1969, that these materials exhibited infrared spectra that were far too complex to result from simple metallocenes. From a combination of chemical and mass spectral studies, they concluded that the chief product of many of the syntheses cited above is the light green hydride $[(C_5H_5)(C_5H_4)TiH]_2$, which is now known[7-9] to have the structure:



I

Mixtures of $(C_5H_5)_2TiCl_2$ with various reducing agents are known to reduce molecular nitrogen under ambient conditions[10-12] and to act as catalysts for the hydrogenation of olefins.[11] Compound **I**, although prepared by the same reduction of $(\eta\text{-}C_5H_5)_2TiCl_2$, does not possess these properties.* We sought, in 1970, to prepare a reduced form of $(C_5H_5)_2TiCl_2$ that would be reactive toward nitrogen. We believed that the hypothetic metal—metal bonded titanocene dimer $(\eta\text{-}C_5H_5)_2Ti{=}Ti(\eta\text{-}C_5H_5)_2$ could be prepared by reducing $(C_5H_5)_2TiCl_2$ with 2 mol of potassium naphthalene, at low temperatures, in an aprotic solvent. This reaction, in fact, yielded $\mu\text{-}(\eta^1:\eta^5)$-cyclopentadienyl)tris($\eta$-cyclopentadienyl) dititanium-(Ti—Ti), $\mu\text{-}(\eta^1:\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)_3Ti_2$ (**II**). The compound has been characterized from a combination of chemical studies and from a single-crystal x-ray structural determination of its bis-tetrahydrofuran (THF) derivative $\mu\text{-}(\eta^1:\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)_3\text{-}Ti_2(C_4H_8O)\cdot C_4H_8O$ (**III**).[13] In this paper, we will discuss the synthesis and structure of compounds **II** and **III** and their catalytic behavior in reactions with olefins.

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* However, the hydride (**I**) can function as a catalyst for the hydrogenation of some dienes (see TABLE 3).

SYNTHESIS OF $(C_5H_4)(C_5H_5)_3Ti_2$ (II) AND $(C_5H_4)(C_5H_5)_3Ti_2(C_4H_8O)\cdot C_4H_8O$ (III)[13]

This synthesis depends on the reaction of $(C_5H_5)_2TiCl_2$ with 2 mol of potassium naphthalene, at −80°C to room temperature, in tetrahydrofuran. A special apparatus that permits stirring of solutions at low temperatures for long periods of time was employed (see FIGURE 1). Potassium naphthalene in THF is prepared by mixing the reagents in the lower 1-liter bulb reactor, at room temperature. To this solution, frozen by cooling to −196°C, is added finely powdered solid $(C_5H_5)_2TiCl_2$. The mixture is then allowed to warm to −80°C and stirred rapidly at this temperature for several days. Slow warming to 23°C produces a dark green solution. Solvent and naphthalene are removed by evaporation under vacuum. Extraction of the residue with cold (−80°C) toluene, followed by several washings with *n*-octane and isopentane, yields crude $(C_5H_4)(C_5H_5)_3Ti_2$ (II) as a gray-black powder [yield based on $(C_5H_5)_2TiCl_2$ is from 45 to 60%]. Solutions of **II** in THF on slow evaporation yield crystals of $(C_5H_4)(C_5H_5)_3Ti_2(C_4H_8O)\cdot C_4H_8O$ (III). We have grown single x-ray-quality crystals of **III** by the slow diffusion of isopentane into solutions of **II** in THF at 5°C. The THF molecules in **III** may be removed by treatment of the crystalline compound with *n*-octane. This procedure yields very pure samples of $(C_5H_4)(C_5H_5)_3Ti_2$ (II).

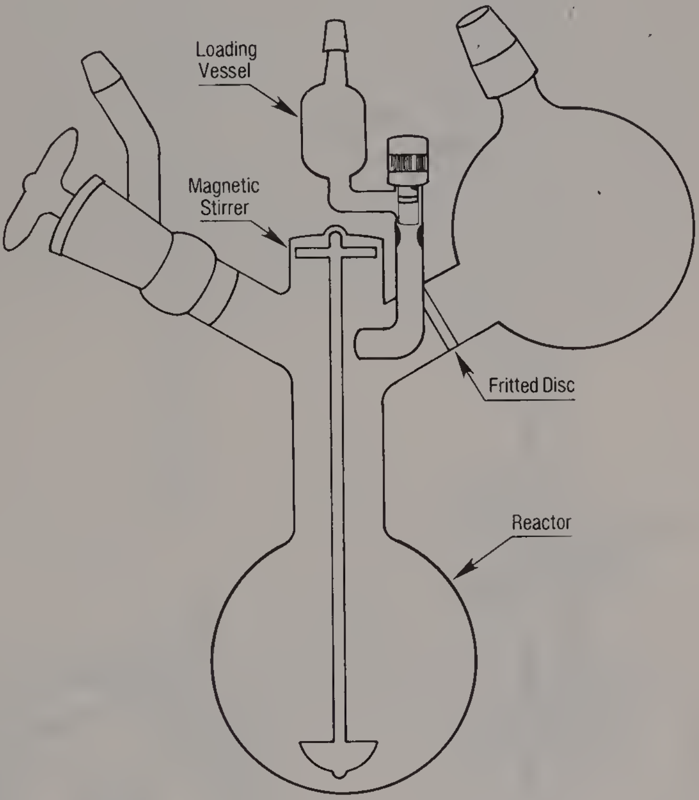


FIGURE 1. Apparatus for the low-temperature reduction of $(C_5H_5)_2TiCl_2$.[13]

STRUCTURE OF $(C_5H_4)(C_5H_5)_3Ti_2(C_4H_8O)\cdot(C_4H_8O)$ (III)[13]

Analysis of III by single-crystal x-ray diffraction methods gave the molecular structure shown in FIGURE 2. A selection of bond distances and angles is shown in TABLES 1 and 2. The molecule is seen to be a metal—metal-bonded dimer, which contains three η-bound C_5H_5 ligands and one bridging, $\eta^1:\eta^5$-bound C_5H_4 ligand. A molecule of THF is coordinated onto the formally divalent titanium atom: the second molecule of THF (not shown in FIGURE 2) occupies a diffuse position in the crystal lattice. Most of the internuclear distances in the molecule are not unlike those of related metallocenes. The Ti—Ti bond length of 3.336(4) Å is longer than the bond length of 2.895 Å for Ti—metal (α form) but is less than the 3.943(2) Å separation between titanium atoms in $[(\eta\text{-}C_5H_5)_2TiCl]_2$.[14] The striking feature of the molecule is the large degree of openness, or structural unsaturation, that is seen in the region bounded by atoms O-1, Ti-1, C-11, C-18, Ti-2, and C-20 (see FIGURE 2). This openness results from the effect of bridging only one side of the Ti—Ti bond with a ($\eta^1:\eta^5$-C_5H_4) ligand. The effective atomic number (Z_{eff}) around the Ti_2 unit is 31, as compared with the expected "count" of 34 electrons for a saturated metal—metal-bonded dimer. Thus, III possesses an unusual degree of electron unsaturation, and the effect is even more marked in II

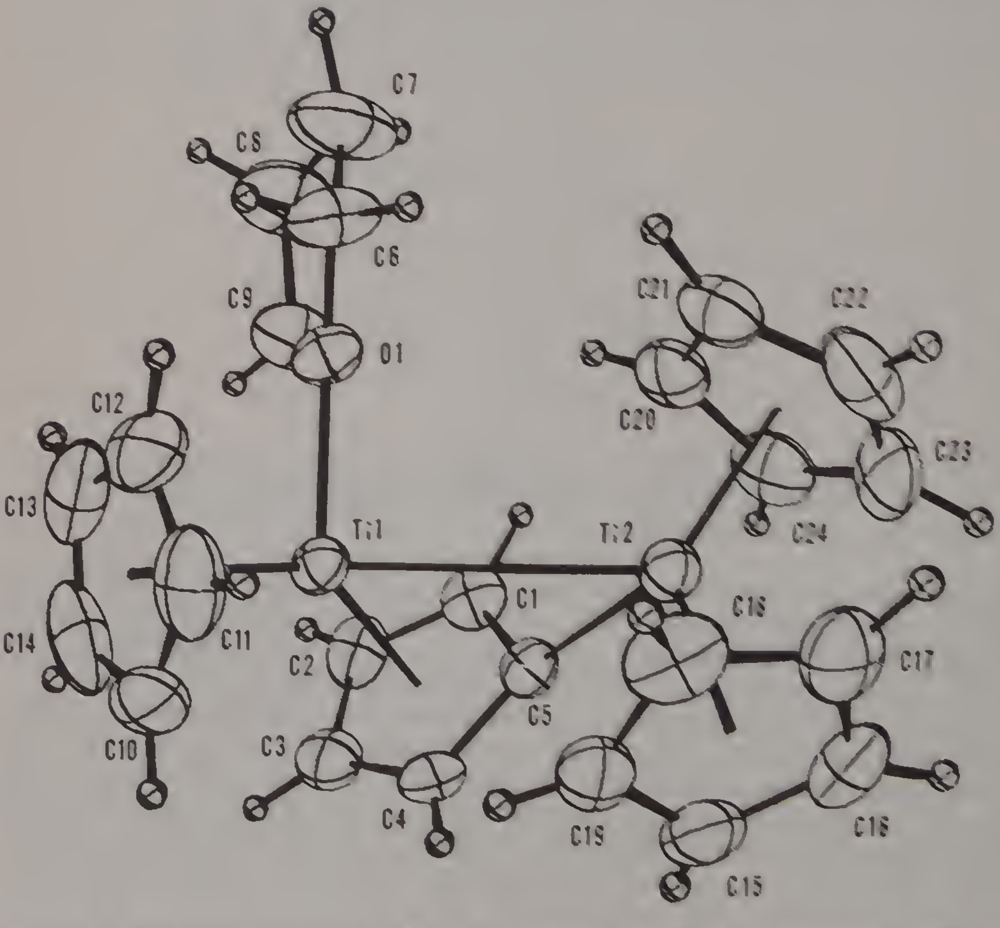


FIGURE 2. Molecular structure of $(\eta^1:\eta^5\text{-}C_5H_4)(\eta\text{-}C_5H_5)_3Ti_2(C_4H_8O)\cdot C_4H_8O$ (III) (the mole of C_4H_8O in the crystal lattice is not shown in this diagram).[13]

TABLE 1[13]

SELECTED BOND DISTANCES (Å) FOR $(C_5H_4)(C_5H_5)_3Ti_2(C_4H_8O)\cdot C_4H_8O$ (III)

Ti-1–Ti-2	3.336(4)	Ti-2–C-5	2.19(2)
Ti-1–O-1	2.26(1)	Ti-2–C-15	2.39(2)
Ti-1–C-1	2.34(2)	Ti-2–C-16	2.40(2)
Ti-1–C-2	2.37(2)	Ti-2–C-17	2.41(2)
Ti-1–C-3	2.37(2)	Ti-2–C-18	2.39(2)
Ti-1–C-4	2.32(2)	Ti-2–C-19	2.38(2)
Ti-1–C-5	2.32(2)	Ti-2–C-20	2.37(2)
Ti-1–C-10	2.38(2)	Ti-2–C-21	2.39(2)
Ti-1–C-11	2.38(2)	Ti-2–C-22	2.42(2)
Ti-1–C-12	2.37(2)	Ti-2–C-23	2.40(2)
Ti-1–C-13	2.40(2)	Ti-2–C-24	2.39(2)
Ti-1–C-14	2.39(2)	C-1–C-2	1.41(2)
O-1–C-6	1.46(2)	C-2–C-3	1.39(3)
O-1–C-9	1.45(2)	C-3–C-4	1.41(2)
C-6–C-7	1.48(4)	C-4–C-5	1.44(2)
C-7–C-8	1.46(4)	C-5–C-1	1.43(2)
C-8–C-9	1.47(3)	C-15–C-16	1.39(3)
C-10–C-11	1.36(3)	C-16–C-17	1.41(3)
C-11–C-12	1.36(3)	C-17–C-18	1.39(3)
C-12–C-13	1.34(3)	C-18–C-19	1.40(3)
C-13–C-14	1.37(3)	C-19–C-15	1.37(3)
C-14–C-10	1.39(3)	O-2–C-25	1.35(3)
C-20–C-21	1.40(3)	C-25–C-26	1.39(5)
C-21–C-22	1.39(3)	C-26–C-26′	1.65(9)
C-22–C-23	1.39(3)		
C-23–C-24	1.40(3)		
C-24–C-20	1.40(3)		

TABLE 2[13]

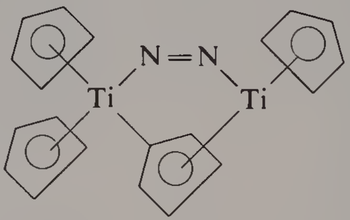
SELECTED BOND ANGLES (DEGREES) FOR $(C_5H_4)(C_5H_5)_3Ti_2(C_4H_8O)\cdot C_4H_8O$ (III)

Ti-1–Ti-2–C-5	43.8(4)	C-19–C-15–C-16	108.5(17)
Ti-2–Ti-1–C-5	40.9(4)	C-15–C-16–C-17	107.8(18)
Ti-2–Ti-1–O-1	96.1(3)	C-16–C-17–C-18	107.5(18)
Ti-1–O-1–C-6	125.4(11)	C-17–C-18–C-19	107.5(17)
Ti-1–O-1–C-9	124.5(11)	C-18–C-19–C-15	108.7(17)
Ti-1–C-5–Ti-2	95.3(6)	C-24–C-20–C-21	107.8(19)
Ti-2–C-5–C-1	125.6(12)	C-20–C-21–C-22	108.0(19)
Ti-2–C-5–C-4	124.2(13)	C-21–C-22–C-23	108.1(20)
O-6–O-1–C-9	108.2(14)	C-22–C-23–C-24	108.6(19)
O-1–C-6–C-7	105.1(19)	C-23–C-24–C-20	107.4(19)
C-6–C-7–C-8	106.3(22)	C-25–O-2–C-25′	114.4(41)
C-7–C-8–C-9	105.7(20)	O-2–C-25–C-26	109.7(34)
C-8–C-9–O-1	107.7(18)	C-25–C-26–C-26′	102.6(24)
C-5–C-1–C-2	110.9(17)		
C-1–C-2–C-3	107.9(16)		
C-2–C-3–C-4	107.6(17)		
C-3–C-4–C-5	110.7(16)		
C-4–C-5–C-1	102.9(14)		
C-14–C-10–C-11	106.7(20)		
C-10–C-11–C-12	109.0(21)		
C-11–C-12–C-13	108.3(22)		
C-12–C-13–C-14	108.5(21)		
C-13–C-14–C-10	107.4(21)		

($Z_{eff} = 29$), which does not contain any tetrahydrofuran. Because of this combined steric and coordinative unsaturation, we would expect **II** and **III** to be highly reactive toward small unsaturated molecules, namely, molecular nitrogen and hydrogen and olefins.

REACTIONS OF $(C_5H_4)(C_5H_5)_3Ti_2$ (II) WITH NITROGEN

Deep green solutions of **II** in toluene turn bright blue on exposure to nitrogen. The absorption of molecular nitrogen is reversible and yields an adduct of composition $[(C_5H_4)(C_5H_5)_3Ti_2]_2 \cdot N_2$ (**IV**).[18] This affinity of **II** for nitrogen is indeed remarkable; concentrated toluene solutions of **II** turn blue when contacted with as little as 3 Torr of N_2 pressure at −80°C! The nitrogen ligand in **IV** can be reduced by treatment with potassium naphthalene, followed by acid hydrolysis, to ammonia. Solutions of **II** in THF also react with molecular nitrogen (at 10 atm pressure) to give a cherry-red complex of probable structure:



V

This complex gives medium-intensity infrared absorption at 1296 cm^{-1}, which is shifted to 1252 cm^{-1} when it is prepared with $^{15}N_2$. The absorption is thus assigned to an N—N stretching vibration. Compound **V** is illustrative of the remarkable degree of molecular nitrogen reduction, or "activation," that can be achieved by reaction of molecular nitrogen with our "titanocene" compound **II**. We are presently involved in elucidating the structure of the complex by x-ray crystallography. Other molecular nitrogen derivatives of **II** can also be prepared.[15] On treatment of **IV** with hydrogen, all of the complexed molecular nitrogen is evolved, but, unfortunately, a catalytic reduction of molecular nitrogen to ammonia does not occur! Work is in progress on a study of the reactivity of **V** with hydrogen. Our $(C_5H_4)(C_5H_5)_3Ti_2$ (**II**)† displays both an extensive coordination chemistry with molecular nitrogen and an interesting catalytic chemistry with olefins.

CATALYTIC HYDROGENATION OF OLEFINS[18]

Solutions of **II** and **III** are very effective catalysts for the hydrogenation of olefins and diolefins to yield alkanes. We have performed some preliminary studies on the kinetics of hydrogenation of cyclohexene, cyclohexadiene, and cyclooctadiene

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† Several dinitrogen-reactive "titanocenes" have been described in the literature: preparation of a "metastable titanocene," $[(C_5H_5)_2Ti]_2$ via hydrogenolysis of $(C_5H_5)_2Ti(CH_3)_2$, that reacts reversibly with nitrogen to give a blue complex of formula $[(C_5H_5)_2Ti_2]N_2$[16]; reduction of $(C_5H_5)_2TiCl_2$ with sodium to yield a "highly unstable titanocene," $[(C_5H_5)_2Ti]_{n=1 \text{ or } 2}$[12]; a "black titanocene," $[(C_5H_5)_2Ti]_n$, said to result from photolysis of $(C_5H_5)_2Ti(CH_3)_2$.[17] Our compounds **II** and **III** are the only well-characterized dinitrogen-reactive "titanocenes" that have been reported thus far.

Table 3[18]

HYDROGENATION OF OLEFINS CATALYZED BY TITANIUM METALLOCENES

Catalyst	[Catalyst × 10^3] (M)	Temperature (°C)	Substrate	[Olefin] (M)	$P_o(H_2)$ (Torr)	$k \times 10^4$ (sec^{-1})	Initial Rate (cm^3 H_2/min/ mEquiv of Ti)	$t_{1/2}$ (min)	Product
$(C_5H_5)_3(C_5H_4)Ti_2$* (II)	8.51	20.8	cyclohexene	9.87	550	3.81	34.2	30.3	cyclohexane
$(C_5H_5)_3(C_5H_5)Ti_2$* (II)	2.71	20.4	cyclohexene	9.87	810	4.39	134.0	26.3	cyclohexane
$(C_5H_5)_3(C_5H_5)Ti_2$* (II)	1.15	20.6	cyclohexene	9.87	770	1.05	51.8	110	cyclohexane
$(C_5H_5)_3(C_5H_4)Ti_2$† (II)	2.68	21.4	cyclohexene	9.87	775	2.04	73.5	56.6	cyclohexane
$(C_5H_5)_3(C_5H_4)Ti_2$* (II)	2.94	20.1	cyclohexene in tetrahydrofuran	5.62	670	0.487		237	cyclohexane
Polymer-attached “$(C_5H_5)_2Ti$”[20]	—	RT‡	cyclohexene in cyclohexane	1.16	(760)§	—	88.7		cyclohexane
$(C_5H_5)_2Ti \cdot C_4H_4$-$(CH_3) + H_2)$[21]	8.6	RT‡	cyclohexene in cyclohexane	1.76	(760)§	—		6	cyclohexane
$(C_5H_5)_3(C_5H_4)Ti_2$† (II)	9.52	23.5	cycloocta-1,5-diene	8.15	700	6.75		17.1	cyclooctane
$(C_5H_5)_2(C_{10}H_8)$-Ti_2H_2 (I)¶	24.6	25.0	cyclohexa-1,4-diene	10.57	800	0.082		1410	cyclohexene
$(C_5H_5)_2(C_{10}H_8)$-Ti_2H_2	11.2	22.0	cycloocta-1,5-diene	8.15	781	0.067		1729	cyclooctane

* Prepared from crystalline $(C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O) \cdot (C_4H_8O)$ (III)

† Crude product of $(C_5H_5)_2TiCl_2 + 2KC_{10}H_8$ reaction.

‡ Room temperature; exact temperature not specified.

§ Assumed to be 760 torr.

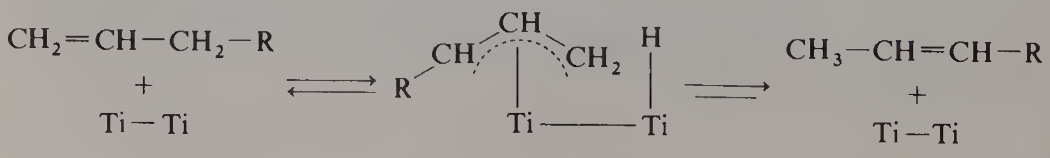
¶ Prepared from $(C_5H_5)_3(C_5H_4)Ti_2$.[18]

by **I**, **II**, and **III**. The hydrogenations were studied experimentally by following the drop in hydrogen pressure over a solution that contained olefin and dissolved catalyst, in a closed system approximately 500 cm^3 in total volume. An initial hydrogen pressure of approximately 1 atm was used. When this pressure had dropped to about 0.2 atm, fresh hydrogen was introduced, and in this manner, the reactions were followed over several hundred catalyst cycles. Our kinetic data are summarized in TABLE 3, which shows that pure $(C_5H_4)(C_5H_5)_3Ti_2$ (**II**) is an excellent catalyst for the hydrogenation of cyclohexene to cyclohexane. With **II** at a 0.00851 M concentration in cyclohexene, the reaction went over 430 catalyst turnovers without any apparent loss in activity. When crystalline $(C_5H_4)(C_5H_5)_3Ti_2(C_4H_8O)\cdot C_4H_8O$ (**III**) was used in THF, the cyclohexene hydrogenation rate was markedly less, and the catalyst was also found to be considerably deactivated with time. Apparently, coordination of titanium in **III** by THF inhibits, but does not quench, the capacity of $(C_5H_4)(C_5H_5)_3Ti_2$ (**II**) to catalyze the hydrogenation of cyclohexene. Compound **II** slowly decomposes in THF at room temperature, thus accounting for the slow decrease in hydrogenation rate in this solvent. It is interesting to note that the hydride, μ-H_2-μ-$(\eta^5:\eta^5$-$C_{10}H_8)(\eta^5$-$C_5H_5)_2Ti_2$ (**I**), is also a hydrogenation catalyst but only for diolefins (see TABLE 3).

Several organometallic mixtures that contain low-valence titanium species are known to function as olefinic hydrogenation catalysts.[12,19] A polystyrene-supported "$(C_5H_5)_2Ti$" catalyst (prepared by reducing polymer-attached $(C_5H_5)_2TiCl_2$ with *n*-butyl-lithium)[20] is comparable in activity to $(C_5H_4)(C_5H_5)_3Ti_2$ (**II**) for the hydrogenation of cyclohexene. A catalyst solution prepared by treating 1-methyl-η-allylbiscyclopentadienyltitanium with hydrogen[21] appears to be about one order of magnitude more active than **II**. Unfortunately, it is not possible to more definitively compare the performance of these various catalyst systems because of the different experimental conditions employed and the lack of comprehensive kinetic data. In any event, compounds **II** and **III** are the only well-characterized titanium species that are very active as catalysts for the hydrogenation of olefins.

Isomerization of Olefins by $(C_5H_4)(C_5H_5)_3Ti_2$ (II)

In the presence of $(C_5H_4)(C_5H_5)_3Ti_2$ (**II**), terminal olefins are readily converted into the more thermodynamically stable internal olefins. For example, a solution of 1-heptene, 0.028 M in catalyst, isomerizes at 30°C, with a half-life of 6.6 min, to yield mainly *trans*-2-heptene. Experimentally, the isomerization kinetics were studied by loading a nuclear magnetic resonance tube with the catalyst dissolved in the substrate and following the rise in the specific resonances of the products. A particularly interesting reaction is the isomerization of cycloocta-1,5-diene to cycloocta-1,3-diene (see FIGURE 3). This isomerization seems to proceed via intermediate formation of the 1,4 isomer. These isomerization reactions over $(C_5H_4)(C_5H_5)_3Ti_2$ (**II**) probably occur via formation of an intermediate η-allyl metal hydride:



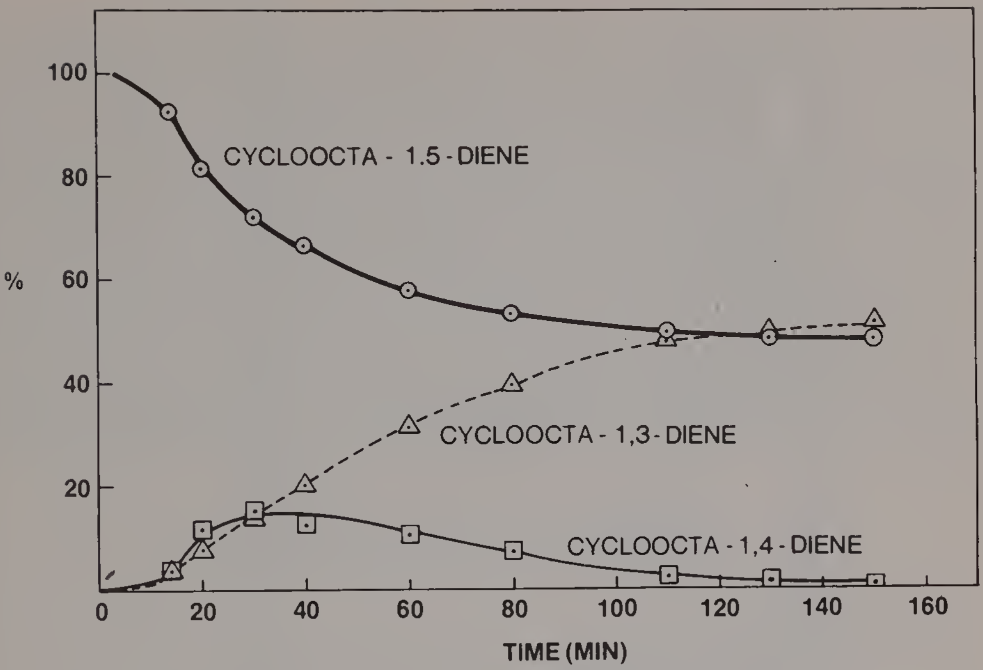


FIGURE 3. Isomerization of cycloocta-1,5-diene catalyzed by $(C_5H_4)(C_5H_5)_3Ti_2$ (**II**). Concentration of **II**, 2.8×10^{-2} M in C_8H_{12}; T, 30°C.[18]

DISPROPORTIONATION OF ETHYLENE

We have found that the "titanocenes" **II** and **III** catalyze the disproportionation of ethylene into ethane and 1,3-butadiene:

$$3C_2H_4 \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + C_2H_6.$$

As written, this is a novel chemical reaction, although other instances of the disproportionation of olefins into dienes and alkanes are known.‡ Ethane and 1,3-butadiene are formed when very pure ethylene at more than 8 atm pressure is contacted with either dry powdered $(C_5H_4)(C_5H_5)_3Ti_2$ (**II**) or with solutions of $(C_5H_4)(C_5H_5)_3Ti_2$ (**II**) in toluene, THF, or other aprotic solvents. An accompanying reaction is the formation of 1-butene, which can occur by simple dimerization of ethylene or by hydrogen transfer from ethylene to product 1,3-butadiene. Trace quantities of *n*-butane and 2-butenes are also formed. Specific conditions for the reaction are given in TABLE 4. Unfortunately, the reaction to yield 1,3-butadiene is very slow, but it is definitely catalytic. The highest turnover number obtained (i.e., moles of diene per mole of catalyst) is seven. This result is for the reaction of C_2H_4 (59 atm) over $(C_5H_4)(C_5H_5)_3Ti_2$ (**II**) for 9–11 days at 23°C in THF (runs 3 and 5, TABLE 4). It is interesting that the use of diethylamine greatly

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‡ A mixture of ethylene and benzene, when heated over Re_2O_7, MoO_3, and WO_3 catalysts at 200°C, is said to yield 1,3-butadiene.[22] The complexes $Ir(PPh_3)_2H_5$ and $Ir(P\text{-}i\text{-}Pr_3)_2H_5$ are reported to catalyze the disproportionation of 1-hexene into hexane and a mixture of hexadienes.[23]

TABLE 4
DISPROPORTIONATION OF ETHYLENE OVER "TITANOCENE" CATALYSTS

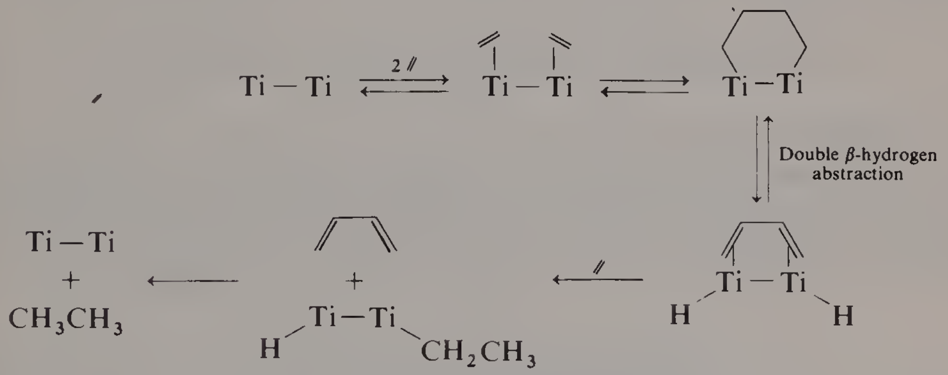
Run	Catalyst	Catalyst Concentration (M × 10^2)	Temperature (°C)	Time (days)	Ethylene Pressure (atm)	Solvent	Products (moles of product/mole of catalyst)		
							Ethane	1-Butene	1,3-Butadiene
1	$(C_5H_4)(C_5H_5)_3Ti_2$ **(II)***	4.33	23 ± 2	9	66	toluene	2.3	3.2	1.9
2	$(C_5H_4)(C_5H_5)_3Ti_2$ **(II)**	4.69	23 ± 2	10	12	THF	4.3	0.4	2.5
3	$(C_5H_4)(C_5H_5)_3Ti_2$ **(II)**	4.70	23 ± 2	9	59	THF	7.6	2.7	7.4
4	$(C_5H_4)(C_5H_5)_2Ti_2$ **(II)**	4.70	23 ± 2	9	59	THF	5.2	3.1	5.1
5	$(C_5H_4)(C_5H_5)_3Ti_2(C_4H_8O)$ $\cdot C_4H_8O$ **(III)**†	3.33	23 ± 2	11	59	THF	11.3	3.8	7.3
6	$(C_5H_4)(C_5H_5)_3Ti_2(C_4H_8O)$ $\cdot C_4H_8O$ **(III)**†	3.33	23 ± 2	6	12	THF	—	0.45	1.3
7	Dried catalyst residue from run 6	3.33	90 ± 2	0.7	11	THF	4.2	0.02	1.8
8	$(C_5H_4)(C_5H_5)_3Ti_2(C_4H_8O)$ $\cdot C_4H_8O$ **(III)**†	3.33	90 ± 2	0.87	39	THF	5.8	1.0	1.6
9	$(C_5H_4)(C_5H_5)_3Ti_2$* (1 mole + added $P(C_6H_5)_3$ (4 mol)	4.70	23 ± 2	10	9	toluene	—	1.7	0.83
10	$(C_5H_4)(C_5H_5)_3Ti_2$ **(II)***	4.33	23 ± 2	5	12	diethylamine	2.0	0.15	0.92

* Crude $(C_5H_4)(C_5H_5)_3Ti_2$ **(II)** as obtained directly from the reduction of $(C_5H_5)_2TiCl_2$.

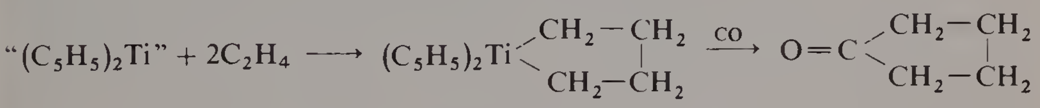
† Pure, crystalline $(C_5H_4)(C_5H_5)_3Ti_2(C_4H_8O)\cdot C_4H_8O$ **(III)**.

reduces the relative amount of by-product 1-butene. This result led us to use several different coordinating ligands in an attempt to improve the overall selectivity and (by heating) the rate of the reaction. We found that on addition of triphenylphosphine to normally green solutions of "titanocene," a deep violet color appears. On addition of ethylene, the green violet disappears, and the reaction still gives 1,3-butadiene but in lower yields. Triphenylphosphite and 2,2′-dipyridyl (BIPY) totally quench the reaction, presumably by tightly binding onto the metal sites.§ We hoped to accelerate the reaction by heating to 90°C (see runs 7 and 8, TABLE 4). However, the yield of 1,3-butadiene was not markedly improved. In these runs, the disproportionate amounts of ethane produced suggests that on heating, there is some loss of diene product, probably as nonvolatile oligomers.

This rather unique ethylene disproportionation reaction, although too slow for synthetic purposes, is, nevertheless, interesting from a mechanistic point of view. A possible mechanism¶ involves the formation of a dititanium heterocycle, as follows:



McDermott and Whitesides[25] were able to obtain cyclopentanone by contacting toluene solutions of $[(C_5H_5)_2Ti]_2$[16] at less than −30°C with C_2H_4 and carbon monoxide. They ascribe the formation of cyclopentanone to the reaction of carbon monoxide with a titanium metallocycle:



$$\text{“}(C_5H_5)_2Ti\text{”} + 2C_2H_4 \longrightarrow (C_5H_5)_2Ti\left\langle\begin{matrix} CH_2-CH_2 \\ | \\ CH_2-CH_2 \end{matrix}\right. \xrightarrow{CO} O{=}C\left\langle\begin{matrix} CH_2-CH_2 \\ | \\ CH_2-CH_2 \end{matrix}\right.$$

In view of this report, we took a toluene solution of compound **II** that had been in contact with C_2H_4 (10 atm) for 3 days, cooled it to −35°C, and added carbon monoxide. We did not detect any free cyclopentanone in the reaction products, only 1,3-butadiene that had presumably formed prior to the addition of carbon monoxide. It may be that a different mechanism is operating in the reaction system of McDermott and Whitesides. In any event, as noted earlier,† the identity of the $[(C_5H_5)_2Ti]_2N_2$ complex that they used as their source of "titanocene" has not been well established, so it is difficult to make a more detailed comparison between the two systems.

Much has been said recently[26] of the possibility of using metal cluster compounds to catalyze new chemical reactions; in fact, very few "cluster-catalyzed" transforma-

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§ 2,2′-Dipyridyldicyclopentadienyltitanium, $(\eta\text{-}C_5H_5)_2$Ti-BIPY, is a stable well-characterized compound.[24]

¶ I am indebted to Dr. R. A. Grey (Allied Chemical Corporation) for valuable thoughts and discussions regarding this mechanism.

tions are known. We have discovered three reactions of olefins that are catalyzed by the well-defined μ-($\eta^1:\eta^5$-cyclopentadienyl)tris(η-cyclopentadienyl)dititanium (Ti—Ti) compound (**II**). Although many "molecular" olefin hydrogenation and isomerization catalysts are known, compounds **II** and **III** appear to be unique catalysts for the disproportionation of ethylene into ethane and 1,3-butadiene. This finding is encouraging, because it suggests that other novel catalytic reactions might be shown to occur over coordinatively unsaturated, polymetallic complexes.

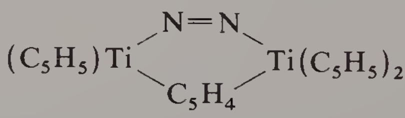
SUMMARY

Reduction of $(\eta\text{-}C_5H_5)_2TiCl_2$ at low temperatures with potassium naphthalene yields $(C_5H_4)(C_5H_5)_3Ti_2$ (**II**). The compound has been characterized by chemical methods and by an x-ray single-crystal structure determination of its bistetrahydrofuran adduct:

$$(\eta\text{-}C_5H_5)_2\overline{Ti\text{-}\mu\text{-}(\eta^1:\eta^5\text{-}C_5H_4)\text{-}Ti}(\eta\text{-}C_5H_5)(C_4H_8O)\cdot C_4H_8O$$

III

A key structural feature in these "titanocenes" is the presence of a geometrically exposed and chemically unsaturated Ti—Ti linkage. Solutions of $(C_5H_4)(C_5H_5)_3Ti_2$ in toluene reversibly bind molecular nitrogen to give a deep blue complex of composition $[(C_5H_4)(C_5H_5)_3Ti_2]_2N_2$. In THF, molecular nitrogen binds irreversibly to yield what we believe to be the "azo" bridging dinitrogen complex:



V

which exhibits an exceptionally low N—N stretching vibration at 1296 cm^{-1}. Both **II** and **III** are homogeneous catalysts for the hydrogenation of olefins and diolefins to yield alkanes. The $(C_5H_4)(C_5H_5)_3Ti_2$ compound (**II**) catalyzes the isomerization of terminal olefins to yield mixtures of *cis*- and *trans*-2-alkenes. Cycloocta-1,5-diene, in the presence of **II**, rearranges into cycloocta-1,3-diene. Compounds **II** and **III** are unique catalysts for the disproportionation of ethylene into ethane and 1,3-butadiene.

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STEREOSELECTIVE FORMATION AND REACTIONS OF CATIONIC η^4-DIENE AND η^3-ALLYL COMPLEXES OF MOLYBDENUM*

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The utility of transition metal-based reagents in organic synthesis derives from the activation afforded the ligating organic moiety by complexation.[1] The increased reactivity is often augmented by differences in the steric and electronic nature of the metal, which induce high stereoselectivity in reactions that involve coordinated ligands. This report reviews our research on the activation and accompanying stereospecific transformations of group-VI η^3-allyl and η^4-diene complexes.

The extensive chemistry associated with η^3-allyl palladium complexes has been used to advantage in organic syntheses, and we anticipate an even greater utility of the molybdenum derivatives. We have elucidated the detailed rearrangement mechanisms[2,3] and preferred configurations of substituted allylic complexes.[4] These studies provide the basis for determining the factors that influence the regioselectivity observed in allylic alkylations. The use of chiral phosphines in reactions that involve nucleophilic additions provides a route to asymmetric induction in chiral organic products.[5] Employment of bulky phosphines directs alkylation to the more hindered carbon of olefinic intermediates.[6] These reactions occur by overall *trans* addition,[7] exhibit a strong preference for axial approach,[6] and provide a technique through which stereoselective prenylation of acyclic terpenes may be achieved.[8] In contrast to the inversion of configuration attained in stoichiometric allylic alkylations by use of palladium moieties, catalytic alkylation proceeds with net retention of configuration.[9] The control of stereochemistry possible in the molybdenum systems suggests the possibility of reagents with even greater stereoselectivity.

Although the chemistry of diene complexes of group VIII, particularly those of the iron subgroup, has been explored in depth,[10] that of the corresponding group-VI complexes has received comparatively little attention.[11] Reactive η^4-diene complexes of molybdenum(II) have been prepared as shown in SCHEME 1.

Hydride abstraction from the anticrotyl complex, **1**,[12] or its methyl homologs **2** and **3** affords the η^4-diene cation **4**, the homologous isoprene **5**, and piperylene **6** cations. These cations exist as equilibrating conformational isomers, designated *exo* and *endo*, with the *endo* conformer predominating at equilibrium. Thus, for **4** at -50° C, $K_{exo/endo} = 0.24$ and $\Delta G^*_{10} = 14.1$ kcal/mol.

Stereospecific reduction ($NaBH_3CN$, THF, -78° C) of these cations has been observed. Cation **4** cleanly reforms **1** under these conditions, and **5** provides **2**. In the latter case, conformational destabilization of alternative product **7** appears to account for the high selectivity (SCHEME 2).

Piperylene cation **6** exists as both *cis* and *trans* isomers, **6a** and **6b**. Reduction of **6b** proceeds normally, reforming **3**. However, reduction of isomeric **6a** provides

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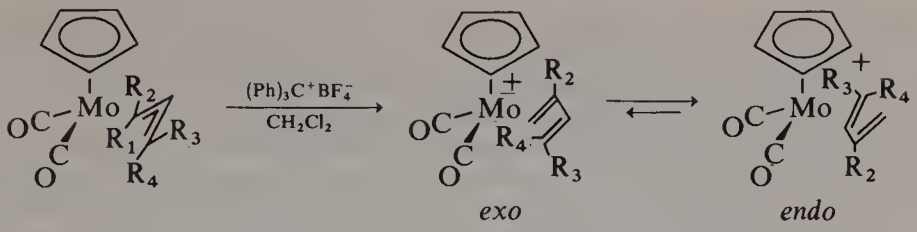
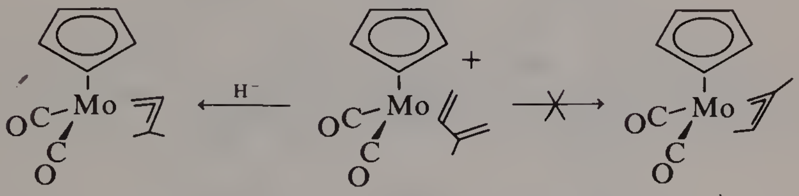
* Supported in part by National Science Foundation Grant CHE76-10762.



	R1	R2	R3	R4
1	Me	H	H	H
2	Me	Me	H	H
3	Me	H	Me	H

	R2	R3	R4
4	H	H	H
5	Me	H	H
6a	H	H	Me
6b	H	Me	H

SCHEME 1



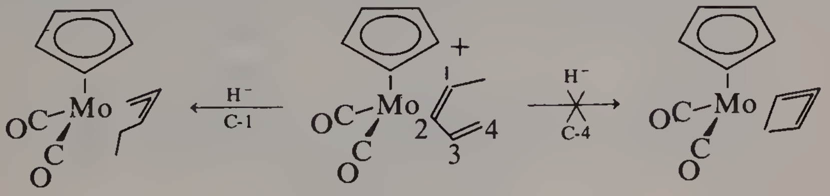
2 **5** **7**

SCHEME 2

8 (SCHEME 3), because the alternative product derived from attack at C-4 would be severely destabilized by the presence of an antianti-1,3-dimethyl configuration.[12]

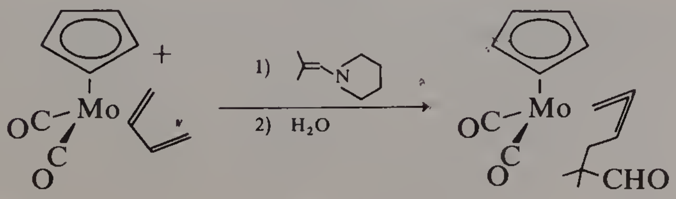
Thus, under *predictable* conditions, this technique may be utilized to isomerize substituted η^3-allyl complexes from the internal to the external mode while maintaining the less stable anti configuration.

The coordinated butadiene cation **4** functions as a useful electrophilic acceptor in condensations with organic nucleophiles. Thus, enamine alkylation of **4** provides the configurationally specific functionalized anticrotyl complex **9** (SCHEME 4).



8 **6a**

SCHEME 3

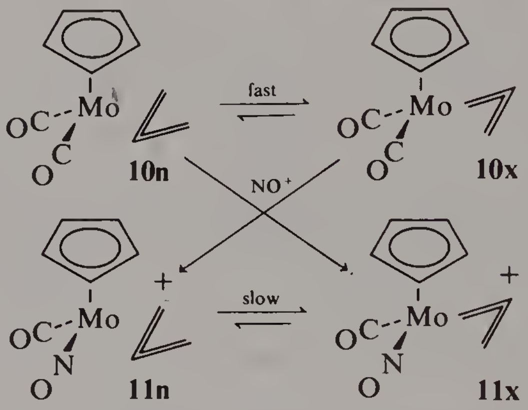


4 **9**

SCHEME 4

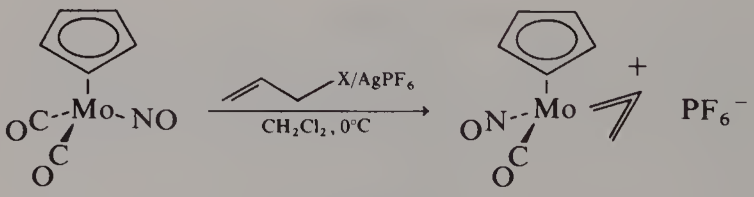
Trihaptoallyl complexes have been found to be useful as stoichiometric reactants in a variety of contexts. They may be employed as reagents for *trans* to *cis* isomerization of olefins,[13,14] as electrophiles in allylic alkylation sequences,[6] or as electron-rich components in radical coupling reactions.[15]

The availability of a series of methylated[16] and potentially functionally substituted η^3-allyl complexes of the type described above prompted an evaluation of the use of these materials as synthons in allylic alkylation reactions. Although neutral η^3-allyl complexes of type **10** are unreactive in addition reactions, activation of these species by nitrosonium displacement of carbonyl is effected by $NOPF_6$ in near quantitative yield[17] (SCHEME 5). The resultant cation, **11**, exists as *endo* and *exo* conformers, analogous to the starting complex.[18]



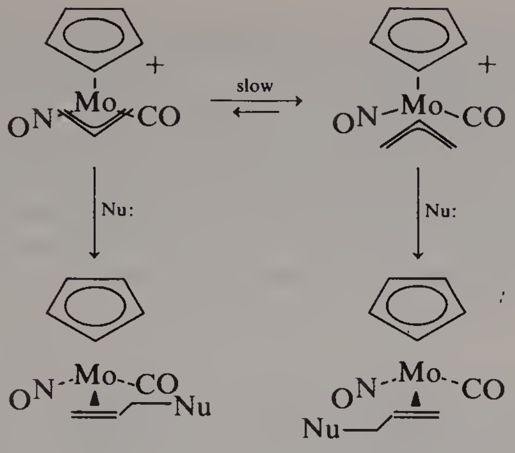
SCHEME 5

In SCHEME 5, the least stable *endo* conformer is produced on electrophilic replacement of CO by NO in *exo*-**10**. This conformational interconversion in the formation of cations is also observed in the 2-methallyl analog, for which the neutral *endo*-dicarbonyl allyl substrate kinetically affords the less stable *exo* conformer of the cation. While cation **11** may also be prepared by trapping of allyl carbonium ion (allyl halide, $AgPF_6$, CH_2Cl_2, 0° C) with η^5-$C_5H_5Mo(CO)_2NO$, this reaction provides the thermodynamically preferred *exo* cation **11x** (SCHEME 6).



SCHEME 6

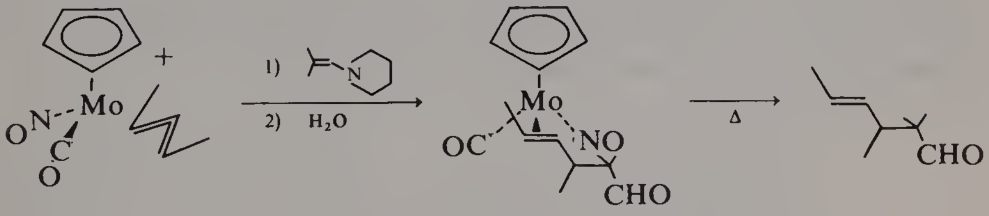
The reactivities of isomeric cations **11n** and **11x** have been investigated by use of a range of nucleophiles. Stereoselectivity has been observed in the addition of alcohols, thiols, phosphines, hydride, enolates, and enamines. Both **11n** and **11x** may be employed to generate only one of the two possible diastereomers of adduct **12** (SCHEME 7). Furthermore, these two conformers provide the *same* diastereomer in addition reactions of weak hydride donors ($NaBH_3CN$, THF, −78° C) or the pyrrolidine enamine of isobutyraldehyde. Thus, the high stereoselectivity observed is conformer dependent, and the site of attack on the allyl is controlled by the ability of the NO ligand to produce and stabilize a charge asymmetry.



12 **12**

Scheme 7

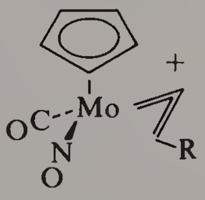
An isomeric mixture of *endo* and *exo* conformers of substituted cation **13** is alkylated in high yield to provide a single diastereomeric η^2-olefin complex, **14** (Scheme 8). Thermal decomplexation liberates *trans*-2,2-dimethyl-3-methyl-4-hexenal.



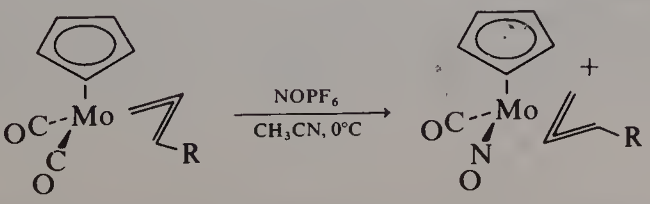
13 **14**

Scheme 8

Cations of type **15** may exist as eight isomers wherein the stereoisomerism may be expressed conformationally (*endo-exo*), geometrically (*cis-trans*), and configurationally (*syn-anti*). Within the *syn* manifold, four stereoisomers may be produced in the displacement of CO by NO. The reaction shown in Scheme 9 has been found to



15



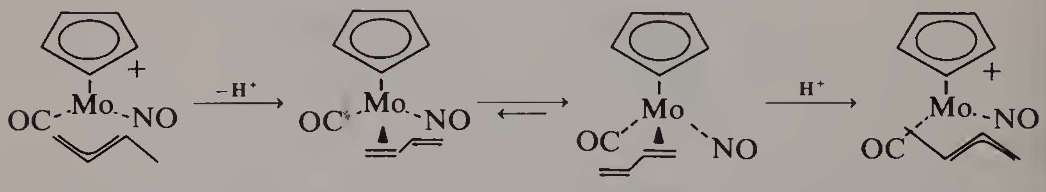
16

Scheme 9

occur with greater than 85% stereoselectivity for formation of a specific *endo* cation.

The crotyl cation of inverted stereochemistry may be conveniently produced by the sequence shown in SCHEME 10.

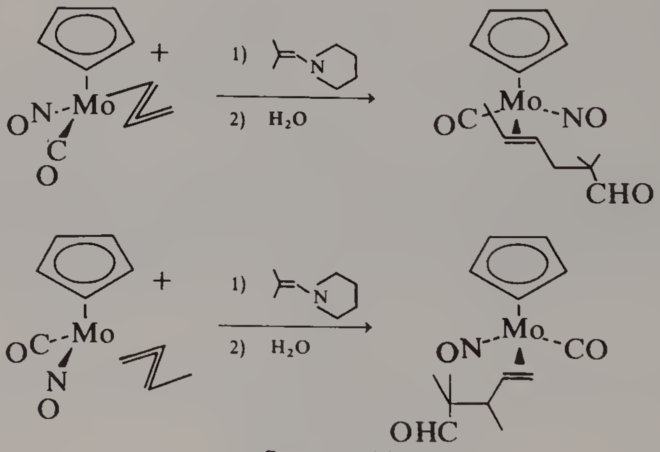
Deprotonation of kinetically generated **16** [$(C_6H_{11})_2NCH_2CH_3$, CH_2Cl_2, 0° C] cleanly provides the η^2-butadiene complex, **17**. This compound displays a temperature-dependent proton magnetic resonance spectrum consistent with restricted rotational motion around the metal-olefinic axis. This rapid rotation accommodates *cis-trans* geometric isomerization. Subsequent protonation (HPF_6, Ac_2O, Et_2O, 0° C) efficiently provides *exo* cation **18** of inverted geometric stereochemistry.



16 **17** **18**

SCHEME 10

Comparison of the reactivity associated with isomeric cations **16** and **18** illustrates the importance of charge stabilization in determination of reaction regioselectivity. Whereas cation **16** is alkylated at the least hindered carbon, isomeric compound **18** reacts at the more substituted carbon.†



SCHEME 11

As expected, use of the anticrotyl cation, which may be prepared with greater than 75% stereospecificity from the precursor anticrotyl dicarbonyl allyl complex, in the addition sequences illustrated in SCHEME 11, provides the *cis*-olefin complexes. Because the anticrotyl precursors are prepared from the homoallylic 4-butenyl halide, this series of reactions results in double bond migration, with production of *cis* geometry.

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† The relative configuration at the metal and crotyl ligand is uncertain; that is, we have not yet determined whether the methyl group is *cis* or *trans* to NO in **16**.

The results reported herein demonstrate that conformational effects may be strongly influential in the control of the reaction pathways available to coordinated ligands. Because the ability to control and alter reaction regiochemistry is of great importance in the design of synthetic strategy, molecules of the type discussed here and the concept of conformational control of site selection in alkylation reactions should prove extremely valuable.

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HYDROGENATION OF AROMATIC LIGANDS DURING EXCHANGE REACTIONS BETWEEN FERROCENE AND ARENES IN THE PRESENCE OF ALUMINUM CHLORIDE*

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INTRODUCTION

In 1963, Nesmeyanov *et al.*[1,2] first reported that η^6-arene-η^5-cyclopentadienyl cations could be prepared by the reaction of arenes with ferrocene and aluminum chloride. Much interesting chemistry developed when it was shown that halogen could be readily displaced from both the arene and the cyclopentadienyl ring of such complexes under mild conditions, reminiscent of the reactions of 1-halo-2,4-dinitrobenzenes.[3,4] Among the more intriguing early observations was that syntheses of complexes of chloro- and bromobenzene were complicated by the loss of halogen to give the benzene complex and, in some instances, biphenyl complexes.[5,6] Apart from complexes of naphthalene and fluorene,[6] early studies tended to neglect the reactions of polynuclear hydrocarbon with ferrocene. Our work in this area commenced with a successful attempt to prepare cations by an intramolecular ligand exchange process whereby bis-indenyl iron (**1**) was converted to the bright red cation (**2**) by boron trifluoride etherate,[7] a transformation that has since been confirmed by other workers.[8] This result ultimately led to the preparation of dications derived from such substrates as biphenyl, diphenylmethane, and fluorene (SCHEME 1) in which the two (cyclopentadienyl)iron moieties were shown to be *trans* to each other (**3**).[9]

While further studies were in progress in our laboratory, Hendrickson *et al.*[10] extended our observations to other polycyclic systems and subsequently reported extensively on the electron properties of these dications.[11] All of the early work in this area has recently been comprehensively reviewed.[12]

DISCUSSION

Our more recent work has consisted of a careful study of the reactions of polycyclic aromatics with ferrocene and aluminum chloride in the presence of aluminum.

Naphthalene

Naphthalene had been reported by both Nesmeyanov *et al.*[6] and Hendrickson *et al.*[10] under somewhat different conditions to yield complex **4**. However, a more careful study[13] has shown that this reaction is temperature dependant. High

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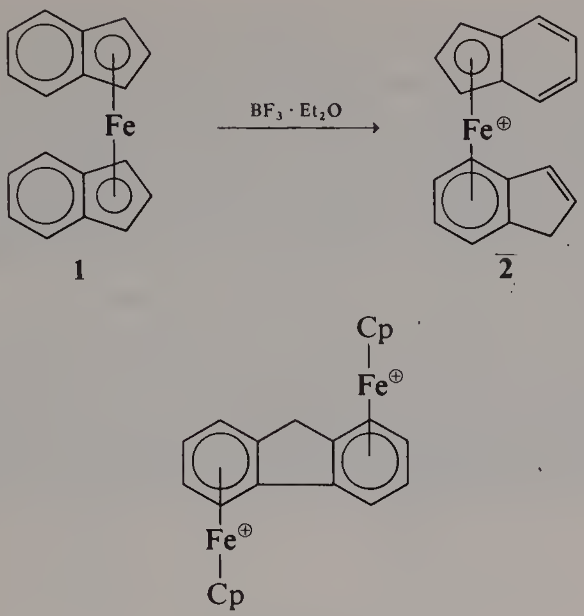
* Supported by the National Research Council of Canada and the Presidents Research Fund of the University of Saskatchewan.



1 **2** **3**

SCHEME 1

temperatures give rise to the tetralin complex (**5**), intermediate temperatures give mixtures of **5** and **4**, and low temperatures result in pure **4**. These results were obtained by use of reactant ratios of arene/ferrocene/$AlCl_3$/Al of 1 : 1 : 2 : 1 in inert solvents, such as cyclohexane or, more usually, Decalin®. The reaction was then subjected to more detailed scrutiny, where the reactant ratios were varied systematically. Some of the results are given in TABLE 1.

TABLE 1
VARIATION IN THE EXTENT OF HYDROGENATION WHEN REACTANT RATIOS ARE ALTERED

Variable Reactant	Reactant Ratio*	Percentage of **5**	Percentage Yield
Naphthalene	1 : 1 : 2 : 1	8	21
	2 : 1 : 2 : 1	46	14
	5 : 1 : 2 : 1	30	30
	10 : 1 : 2 : 1	22	19
Ferrocene	1 : 1 : 2 : 1	8	21
	1 : 2 : 2 : 1	4	29
	1 : 5 : 2 : 1	2	22
	1 : 10 : 2 : 1	1	30
Aluminum	1 : 1 : 2 : 1	8	21
	1 : 1 : 2 : 0.75	8	18
	1 : 1 : 2 : 0.5	9	23
	1 : 1 : 2 : 0.25	13	25
	1 : 1 : 2 : 0	19	20
Aluminum chloride	1 : 1 : 2 : 1	8	21
	1 : 1 : 4 : 1	21	31
	1 : 1 : 10 : 1	100	32
	1 : 1 : 20 : 1	100	28

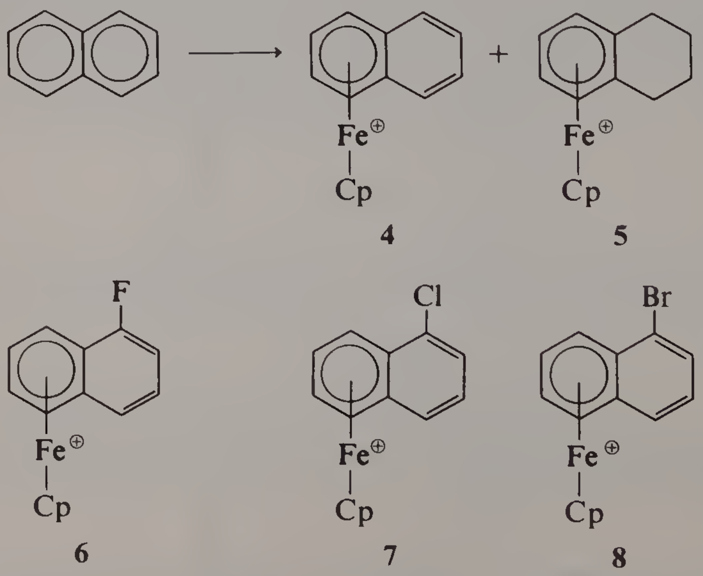
* Arene/ferrocene/$AlCl_3$/Al.

The reactions were performed under standard conditions, where the reactants in the ratio 1 : 1 : 2 : 1 were heated in 50 ml of Decalin for 4 hr at 140°C. The results clearly show that aluminum chloride plays a major role in determining the extent of hydrogenation; increasing the quantity of ferrocene decreases the amount of hydrogenated product, probably due to aluminum chloride being complexed to the metallocene via the iron atom. One possible source of error in the results was contamination of Decalin by Tetralin®, but blank runs showed that such contamination was not occurring. Refluxing nonane was also used as the solvent (155°C) with reactant ratios 1 : 1 : 2 : 1 and 1 : 1 : 5.6 : 1, in which case Tetralin complex yields of 7 and 12%, respectively, were obtained.

Early attempts to obtain mechanistic information involved workup of the reaction mixture with deuterium oxide, which showed that the additional hydrogens were added during the ligand exchange reaction and not during workup. Moreover, the use of perdeuteronaphthalene under conditions when the Tetralin complex (**5**) was obtained almost exclusively demonstrated the extensive exchange and scrambling of the label and did not allow any further information to be deduced.

1-Halonaphthalenes[14]

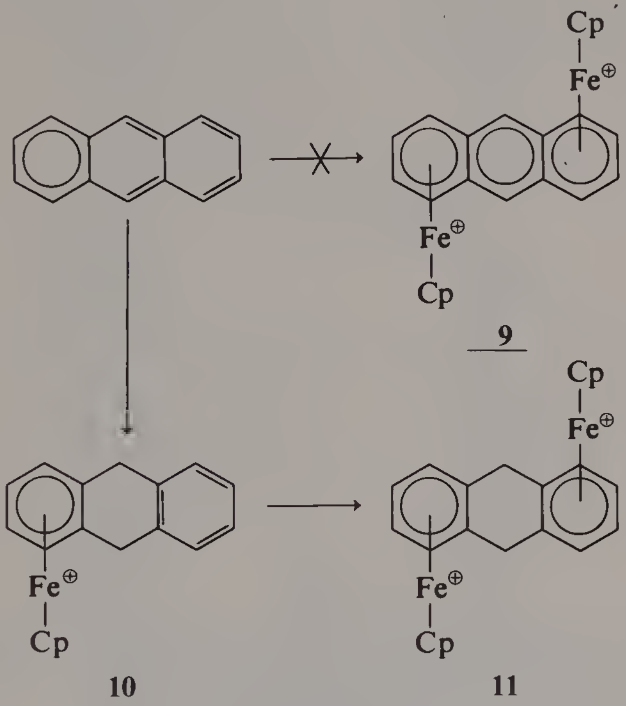
1-Fluoronaphthalene gave the expected complex (**6**) in refluxing cyclohexane, as did 1-chloronaphthalene at 80° C, but refluxing Decalin gave **4** and **5** instead of **7**; that is, the complex had been both dehalogenated and hydrogenated. With 1-bromonaphthalene, the dehalogenated cation (**4**) and the dehalogenated/hydrogenated cation (**5**) were obtained, as was **8**, at the low temperature of 80° C. A typical reaction time of 6 hr gave a ratio of 15 : 65 : 20 for **8**/**4**/**5**. The addition of either iodine or diphenylpicrylhydrazyl (DPPH) as radical scavengers suppressed the hydrogenation reaction; only **8** and **4** were isolated from such a reaction (Scheme 2).



Scheme 2

Anthracene[13]

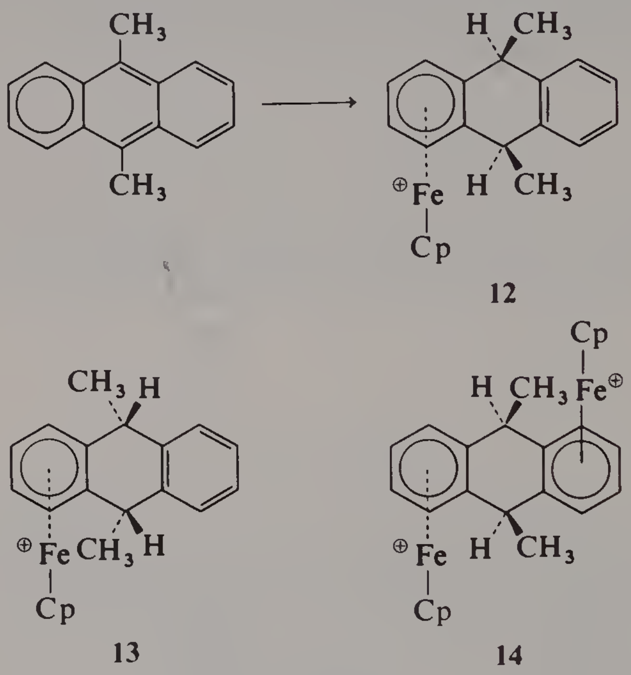
Anthracene is a 14 π-electron system and as such would not be expected to form a dication, because each coordinated ring is required to donate six electrons to the CP-Fe moiety, and this donation would necessitate the localization of odd electrons on the 9,10-positions. Hendrickson *et al.*[10] had previously reported such a complex (**9**) from the reaction of ferrocene and anthracene in the presence of aluminum chloride/aluminum, a result that was contrary to our findings. Their erroneous formulation was probably due to incorrect nuclear magnetic resonance (nmr) assignments. In our hands, this reaction gave the same product (SCHEME 3) as that obtained from 9,10-dihydroanthracene; by suitably varying the conditions, both mono- and dications (**10**) and (**11**) were obtained. Final proof of the nature of the ligand was obtained by photolysis experiments whereby the hydrogenated ligand was released from the metal complex and identified by comparison with authentic samples.



SCHEME 3

9,10-Dimethylanthracene[15]

9,10-Dimethylanthracene can readily be prepared in a one-step reaction from vinyl acetate, aluminum chloride, and benzene in good yield.[16] It was considered that this substrate would be very suitable for mechanistic and stereochemical studies, because, if hydrogenation occurred, the hydrogen would have to add to a ring that cannot be involved in complexation. 9,10-Dimethylanthracene did not react with ferrocene and aluminum chloride/aluminum in the ratio 1 : 1 : 2 : 1 at temperatures below 135° C, which was found to be the minimum temperature required for reaction. Above this temperature, only one product was obtained, and the cation formed was shown to be derived from a dihydroanthracene. The cation was shown to have the stereochemistry of compound **12**; that is, the hydrogen adds from the sterically hindered Cp-Fe side of the molecule. The free ligand could be obtained either by photolysis or pyrolytic sublimation (Scheme 4), and it was shown to be identical with an authentic sample of *cis*-9,10-dihydro-9,10-dimethylanthracene. When this hydrocarbon was used as a substrate in the ligand exchange reaction, the Cp-Fe group could add to either face of the molecule, and complex **13** was obtained in addition to **12**.



Scheme 4

The chemical shifts of **12** and **13** are given in Table 2. If we consider the methyl absorptions, the methyl resonance for **13** is found at 1.97 ppm, that is, a steric downfield shift relative to the proton absorption of **12**. This result is confirmed by the ^{13}C nmr data, in which the methyl resonance of **13** is shifted upfield to 11.9 ppm relative to the methyl carbon of **12** at 27.2 ppm.

The corresponding dication (**14**) was also prepared and shown to have *trans* stereochemistry, and the spectroscopic data obtained from this system further confirmed that the initial hydrogenation process was *endo* with respect to the Cp-Fe moiety.

Mechanism of the Hydrogenation Reaction

This ligand exchange reaction is a difficult one to handle experimentally; it is a heterogeneous reaction and as such is sensitive to minor variation in reaction conditions.

Our first major finding was that deuterium oxide is not incorporated and that the hydrogenation did occur during the ligand exchange process. The sensitivity of the reaction to the concentration of aluminum chloride, together with the scrambling

TABLE 2

^{13}C AND ^{1}H CHEMICAL SHIFTS FOR η-*Cis*-(*endo*-9,10-DIHYDRO)-9,10-DIMETHYLANTHRACENE-η-CYCLOPENTADIENYLIRON CATION (**12**) AND η-*Cis*-(*exo*-9,10-DIHYDRO)-9,10-DIMETHYLANTHRACENE-η-CYCLOPENTADIENYLIRON CATION (**13**)

	δ, ppm from TMS*									
	CH_3		CH		Cp		Complexed Aromatic		Uncomplexed Aromatic	
Ion	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H
12	27.2	1.59 (d) $J = 7.4$ Hz	39.2	4.13 (q) $J = 7.4$ Hz	76.4	4.59 (s)	86.2 86.4 105.8†	6.27 (s)	127.2 127.8 137.4†	7.42 (s)
13	11.9	1.97 (d) $J = 6.8$ Hz	34.4	3.66 (q) $J = 6.8$ Hz	75.0	4.21 (s)	83.4 84.4 108.9†	6.37 (m)	123.1 126.7 140.5†	7.52 (bs)

* The ^{13}C and ^{1}H nmr spectra were obtained in CD_3CN and CD_2Cl_2, respectively.

† Quaternary carbons.

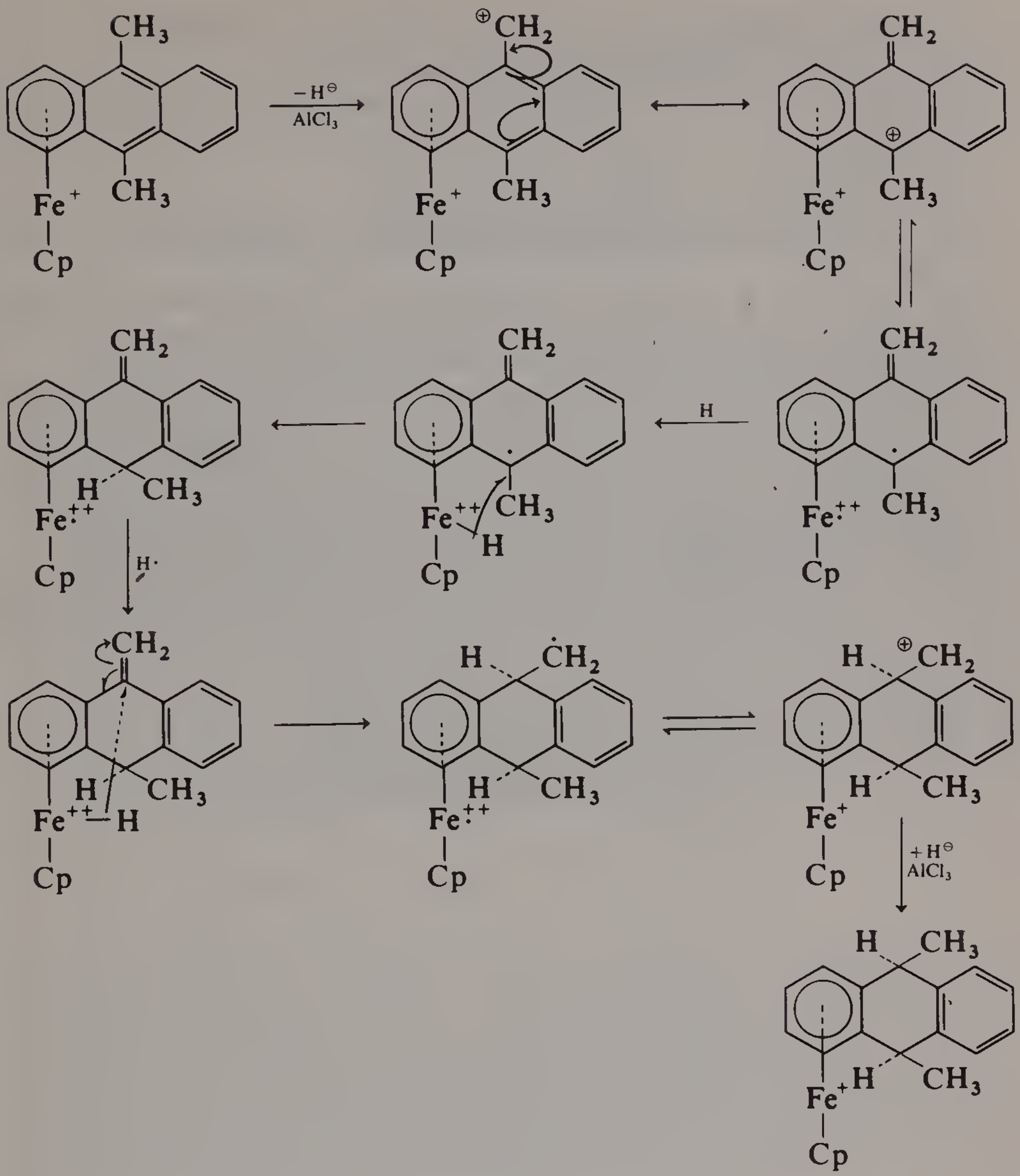
of the label in perdeuteronaphthalene, suggested that hydride abstraction by aluminum chloride in the form $HAlCl_3^-$ played an important role. The increase in the extent of hydrogenation when the concentration of aluminum was decreased suggested the involvement of a radical species, and the isolation of a ferricinium cation from a low-temperature reaction demonstrated that aluminum could not entirely suppress the formation of radical species. Our work with 1-halonaphthalenes supports the concept of a radical mechanism. The dehalogenation step in which X (Cl, Br) is lost as $XAlCl_3^-$ implies a ready abstraction reaction by aluminum chloride, followed by reduction of the naphthalene ligand. The relative ease of halogen removal (Br > Cl) indicates that the ease of loss of X^- has a direct effect on the ease of hydrogenation. The effect of radical scavengers in suppressing the hydrogenation but not the dehalogenation process indicates that at least two steps are involved: abstraction of X^- (H, Cl, or Br) and a subsequent radical reduction.

The solvent Decalin was shown to be the hydrogen source. Loss of six hydrogens would reduce Decalin to Tetralin, which could then form an arene complex. It was shown that Decalin was not converted to Tetralin in the absence of arene; in reactions with phenanthrene, the Tetralin complex (**5**) was isolated. The use of such solvents as nonane, which is a poorer hydrogen donor, led to a significant reduction in the hydrogenation of naphthalene and confirmed that Decalin was the major hydrogen source.

The determination of the stereochemistry of the addition of hydrogen to 9,10-dimethylanthracene was a major step in elucidating the reaction mechanism. Anthracene is hydrogenated at 80°C, whereas the 9,10-dimethyl derivative requires a temperature of 135°C; that is, the dimethyl complex has no easily abstractable hydrogen: a primary hydrogen has to be abstracted to initiate the hydrogenation. This abstraction is an energetically unfavorable process, and so there is an increased barrier to the reduction of this ligand. That the two hydrogens are added to the ligand with complete stereospecificity *cis* and *endo* to the complexed iron is of considerable importance. It shows that the iron must have been complexed to the ligand before hydrogenation and that an iron hydride intermediate is likely involved; such a stereospecific transfer of hydrogen has previously been observed in the fragmentation of (cyclohexadienylcyclopentadienyl)iron compounds.[17] The complete mechanism for hydrogenation of 9,10-dimethylanthracene is shown in SCHEME 5, and it can be readily modified to account for the formation of the Tetralin complex from **4**. Among the key steps in the mechanism is the intramolecular oxidation/reduction in which an electron is transferred from Fe(II) to give Fe(III), while a carbonium ion center is reduced to a free radical. This reaction has a ready analogy in the recent work of Cais *et al.*,[18] who found that a tertiary amine could transfer an electron to an α-ferrocenyl carbonium ion to give a radical that subsequently abstracts hydrogen to form product.

SYNTHETIC APPLICATIONS

The ready reduction of 9,10-dimethylanthracene to give the complex of *cis*-9,10-dihydro-9,10-dimethylanthracene and the simple vacuum pyrolysis to give the free ligand represent the best synthetic route to this hydrocarbon, because reduction of 9,10-dimethylanthracene usually yields mixtures of the *cis* and *trans* isomers.[19–21] The synthesis of the pure *cis* isomer requires a sequence of stereospecific reactions.[22,23] Preliminary studies with other 9,10-dialkylanthracenes indicate that the reaction is quite general.[24] Other related work with polycyclic aromatics, such as phenan-



SCHEME 5

threne, acenaphthene, chrysene, and pyrene, has shown that the reduction occurs readily to give partially reduced polycyclics, which can then be obtained in a pure form by chromatography of the complexes, followed either by photolysis or by vacuum pyrolysis to give the free ligand; for example, both 4,5-dihydropyrene and 4,5,9,10-tetrahydropyrene can be obtained in this manner from pyrene.

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CATALYTIC APPLICATIONS OF PALLADIUM IN ORGANIC SYNTHESES*

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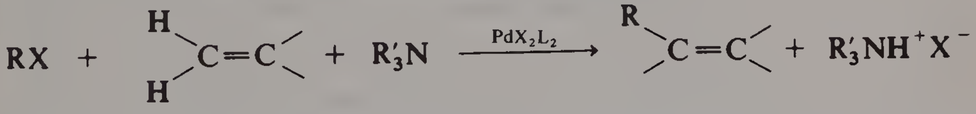
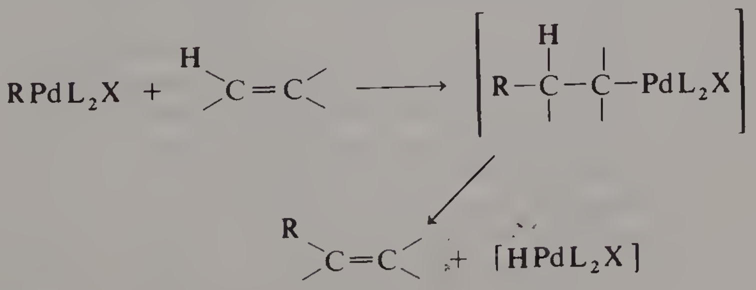
Several reactions of organopalladium compounds with potential applications in organic syntheses have been reported in recent years; however, very few of these reactions have ever actually been used to solve synthetic problems. This lack of interest is probably due to two factors: a lack of information on the reaction and a reluctance of the synthetic chemist to attempt reactions with unfamiliar reagents. Although many organometallic reactions require specialized techniques, such as very pure inert atmospheres, careful purification of reagents, precise concentration measurements, precausions for spontaneously inflammable or highly toxic reagents, and high-pressure apparatus, some palladium-catalyzed reactions do not require any of these techniques. In this paper, I will describe and summarize the available information on one of these reactions and indicate why I think it is a useful synthetic reaction. I believe the simplicity, convenience, and advantages of the reaction compared with other methods in many instances will become clear later on.

The reaction is the palladium-catalyzed vinylic hydrogen substitution reaction with organic halides. The basic reaction is the following:



$$\mathrm{RX} + \mathrm{H_2C{=}C\!<} + \mathrm{R'_3N} \xrightarrow{\mathrm{PdX_2L_2}} \mathrm{RHC{=}C\!<} + \mathrm{R'_3NH^+X^-}$$

The steps believed to be involved are shown in Scheme 1. The palladium catalyst added, usually palladium acetate with two equivalents of triphenylphosphine, is believed to be reduced initially to a palladium(0)-phosphine complex, which then oxidatively adds the organic halide to form a halobisphosphineorganopalladium species. The last complex then likely adds to the double bond of the alkene, and the adduct decomposes by eliminating hydridohalobisphosphinepalladium, forming the substituted alkene. The metal hydride finally loses hydrogen halide to the



Scheme 1

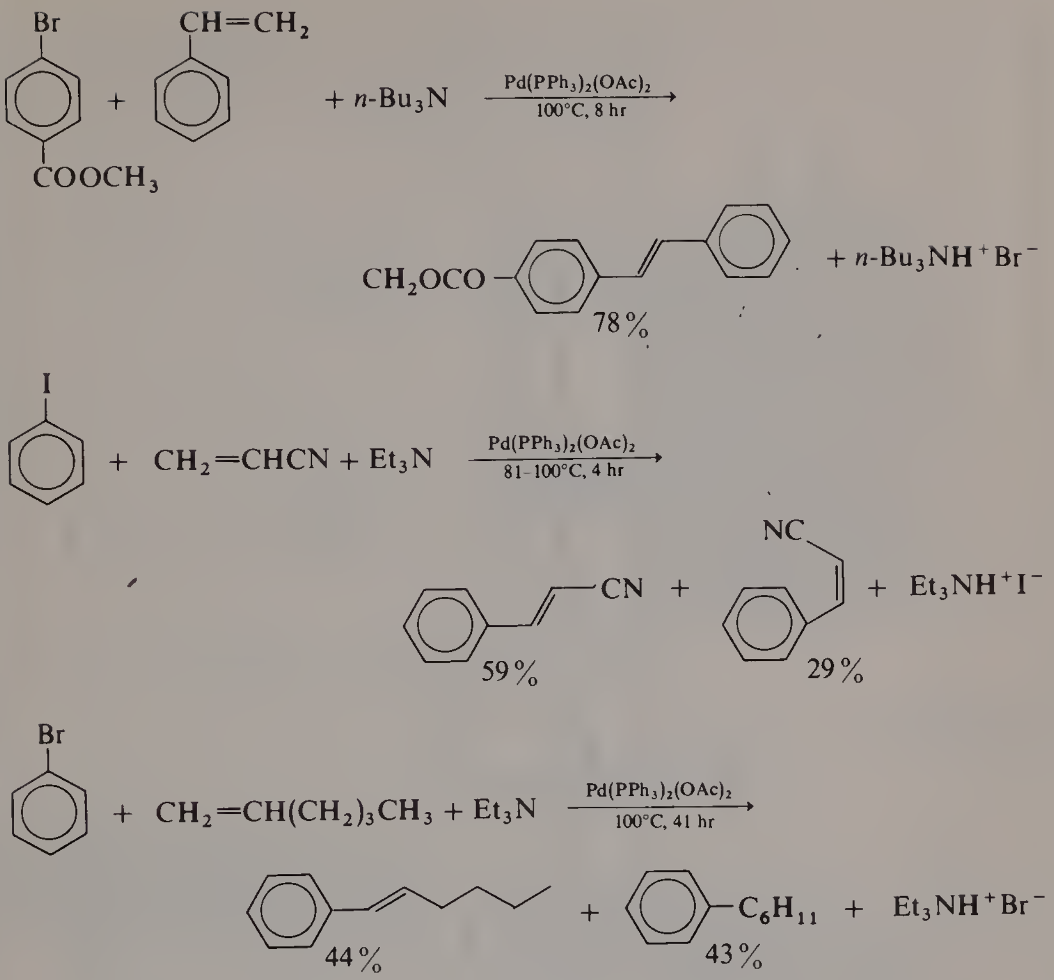
* Supported by National Science Foundation Grant CHE-74-13401.

tertiary amine present and reforms the palladium(0)-phosphine complex, and the cycle begins again. We do not yet know the actual identity and number of nonreacting ligands present in the intermediates in the above sequence, and the structures shown are only reasonable guesses. At least one phosphine group must be present in these complexes, however, because changing the phosphine generally influences the rate and course of the reaction.

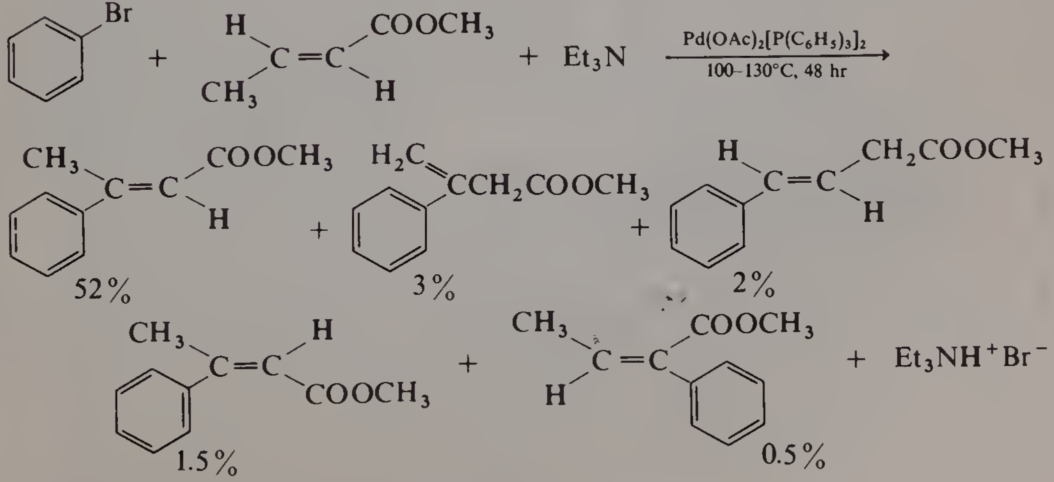
A serious limitation of the reaction is that organic halides with readily eliminatable β hydrogens, such as alkyl halides with two or more carbons, do not undergo the substitution but merely form alkenes. Fortunately, however, a wide variety of aryl, heterocyclic, and vinylic halides do react normally. Another limitation is that organic chlorides normally give much poorer yields of products than do the corresponding bromides or iodides. On the positive side, the reaction is tolerant of a surprising variety of functional groups. TABLE 1 shows examples of the arylation of methyl acrylate with various aryl halides. Chloro, cyano, alkoxyl, carboalkoxyl, nitro, and aryl groups are all inert under the reaction conditions, and the reactions proceed in good yields. In all cases, the organic group is added to the least substituted end of the double bond. The phenolic hydroxyl group and the amino group do interfere with the reaction under these conditions. These groups are tolerated, however, when certain triarylphosphines other than triphenylphosphine are employed, as will be explained later. 1-Bromonaphthalene reacted normally with methyl acrylate, although rather slowly. The reaction temperature was arbitrarily chosen as 100°C for convenience, and more rapid rates can be obtained at higher temperatures. Normally, 1 mol% of the catalyst is employed based on the organic halide, and, of course, rates could also be increased with more catalyst.

SCHEME 2 illustrates the reaction with three other alkenes: styrene, acrylonitrile, and 1-hexene. Thus, "activated" double bonds are not required for the reaction. Reactions with di- and trisubstituted alkenes also proceed well in many cases, although reaction rates are generally lower and yields may be smaller. The reaction is subject to steric inhibition by large groups near the olefinic double bond. An example that employs an alkene with a disubstituted double bond is shown in SCHEME 3. The alkene used was *trans*-methyl crotonate. In this reaction with bromobenzene, one major and four very minor products were identified. The major product, *E*-methyl 3-methyl cinnamate was present in 52% yield. The other four products, present in a total of 7% yield, were formed as a result of various double-bond isomerizations in the starting ester and the products or, in one instance, because of a reversed direction of addition of the palladium compound. With simpler alkenes, a single product is often obtained. The stereochemistry of the major product suggests that the reaction is stereospecific and a result of *syn* addition of the organopalladium compound to the *trans*-methyl crotonate, followed by a *syn* elimination of the hydridopalladium group. The other possible mechanism of *trans* addition and *trans* elimination appears to be unlikely, because in that case, phenyl radicals, or ions, would need to be involved. Because the reactions proceed in solvents reactive to these species, the former mechanism appears to be more probable. The proposed mechanism is shown in SCHEME 4. The same stereochemistry is observed in phenylation of *cis*- and *trans*-1-phenyl-1-propene, as shown in TABLE 2, confirming the predominant stereospecificity of the reaction. For comparison purposes, the stoichiometric reactions of phenylmercuric acetate, palladium acetate, and two alkenes are also shown. The mercurial and palladium acetate presumably form phenylpalladium acetate under the reaction conditions. Higher specificity is observed in these reactions, probably primarily because of the lower reaction temperatures employed (0–25° vs 100°C).

The reason why *p*-bromophenol gives poor yields in the vinylic substitution



SCHEME 2



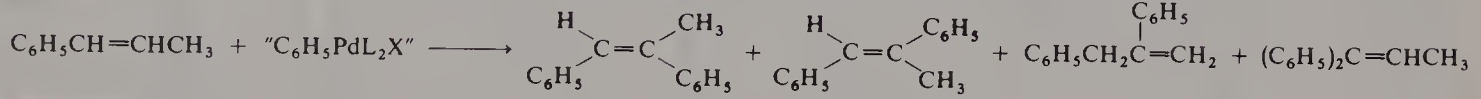
SCHEME 3

Table 1 Reactions of Various Aryl Bromides with Methyl Acrylate

$$ArBr + CH_2{=}CHR + R'_3N \xrightarrow[100\ C]{(PPh_3)_2Pd(OAc)_2} ArCH{=}CHR + R'_3NH^+Br^-$$

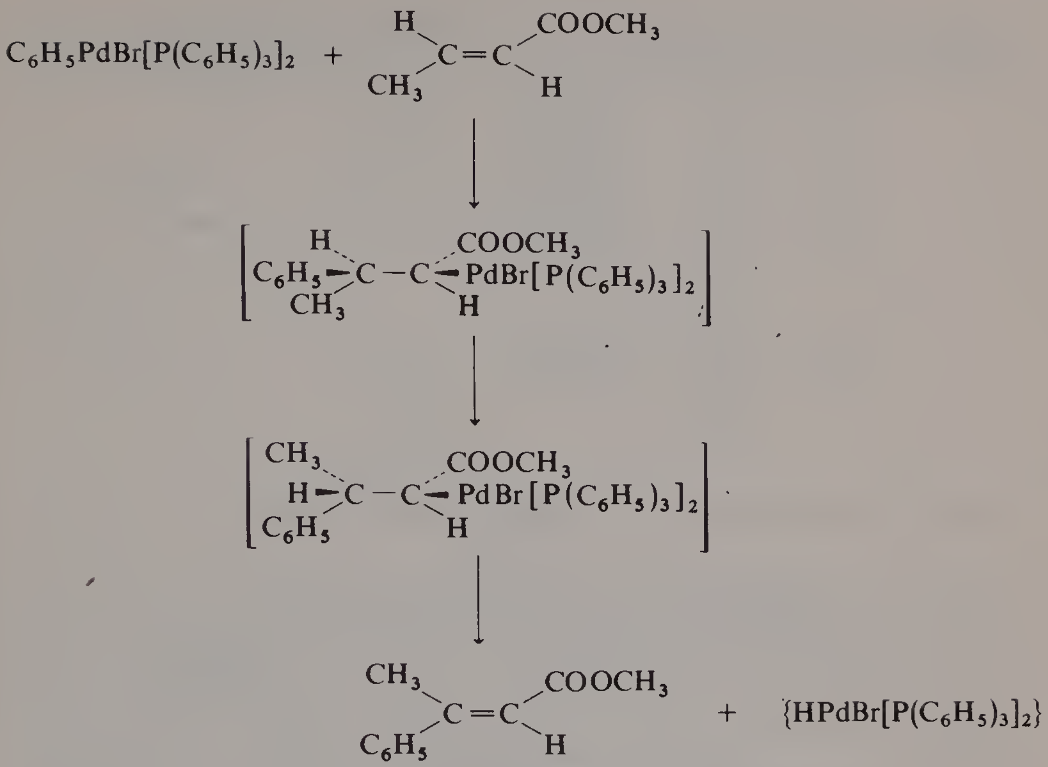
ArBr	Olefin	Reaction Time (hr)	Isolated Yield
C_6H_5Br	$CH_2{=}CHCOOCH_3$	68	E-$C_6H_5CH{=}CHCOOCH_3$ (88%)
4-ClC_6H_4Br	$CH_2{=}CHCOOCH_3$	12	E^4-$ClC_6H_4CH{=}CHCOOCH_3$ (54%)
4-NCC_6H_4Br	$CH_2{=}CHCOOCH_3$	2	E^4-$NCC_6H_4CH{=}CHCOOCH_3$ (80%)
4-$CH_3OC_6H_4Br$	$CH_2{=}CHCOOCH_3$	65	E^4-—$CH_3OC_6H_4CH{=}CHCOOCH_3$ (95%)
4-$CH_3OCOC_6H_4Br$	$CH_2{=}CHCOOCH_3$	7	E^4-$CH_3OCOC_6H_4CH{=}CHCOOCH_3$ (81%)
4-$NO_2C_6H_4Br$	$CH_2{=}CHCOOCH_3$	7	E^4-$NO_2C_6H_4CH{=}CHCOOCH_3$ (73%)
4-$(CH_3)_2NC_6H_4Br$	$CH_2{=}CHCOOCH_3$	21	E^4-$(CH_3)_2NC_6H_4CH{=}CHCOOCH_3$ (~40%)
4-HOC_6H_4Br	$CH_2{=}CHCOOCH_3$	48 (75°C)	E^4-$HOC_6H_5CH{=}CHCOOCH_3$ (3%)
2-$C_6H_5C_6H_4Br$	$CH_2{=}CHCOOCH_3$	65 (135°C)	E^2-$C_6H_5C_6H_4CH{=}CHCOOH$ (37%)
4-$H_2NC_6H_4Br$	$CH_2{=}CHCOOCH_3$	3	E^4-$H_2NC_6H_4CH{=}CHCOOCH_3$ (~1%)
2-$C_{10}H_7Br$	$CH_2{=}CHCOOCH_3$	7 days	E^1-$C_{10}H_7CH{=}CHCOOCH_3$ (62%)

Table 2 Stereochemistry of the Vinylic Substitution Reaction



$$C_6H_5CH{=}CHCH_3 + \text{"}C_6H_5PdL_2X\text{"} \longrightarrow (H)(C_6H_5)C{=}C(CH_3)(C_6H_5) + (H)(C_6H_5)C{=}C(C_6H_5)(CH_3) + C_6H_5CH_2\overset{C_6H_5}{\overset{|}{C}}{=}CH_2 + (C_6H_5)_2C{=}CHCH_3$$

							Total Yield (%)
Cis	+ C_6H_5HgOAc + $Pd(OAc)_2$	$\xrightarrow[30°C,\ 2\ hr]{CH_3CN}$	88.5	4	7.5	0	99
Trans	+ C_6H_5HgOAc + $Pd(OAc)_2$	$\xrightarrow[30°C,\ 2\ hr]{CH_3CN}$	0	99.5	0.5	0	86
Cis	+ C_6H_5I + Et_3N	$\xrightarrow[100°C,\ 34\ hr]{Pd(OAc)_2}$	13.5	57.0	22.6	6.9	85
Trans	+ C_6H_5I + Et_3N	$\xrightarrow[100°C,\ 34\ hr]{Pd(OAc)_2}$	2.0	52.7	13.6	31.7	83
Cis	+ C_6H_5I + Et_3N	$\xrightarrow[100°C,\ 34\ hr]{Pd(OAc)_2\cdot 2P\phi_3}$	75.8	15.2	1.7	7.3	93
Trans	+ C_6H_5I + Et_3N	$\xrightarrow[100°C,\ 34\ hr]{Pd(OAc)_2\cdot 2P\phi_3}$	0	71.0	0	29.0	99
Cis	+ C_6H_5Br + Et_3N	$\xrightarrow[100°C,\ 82\ hr]{Pd(OAc)_2\cdot 2P\phi_3}$	73.4	19.2	0	7.4	92
Trans	+ C_6H_5Br + Et_3N	$\xrightarrow[100°C,\ 43\ hr]{Pd(OAc)_2\cdot 2P\phi_3}$	0		0	21.5	72



SCHEME 4

reaction is that there is a competing side reaction that uses the required triphenylphosphine in the catalyst. Once the phosphine is gone, the palladium precipitates and the reaction stops. The side reaction is the formation of phosphonium salt from the organic halide and the phosphine. Because this reaction only occurs in the presence of the palladium, a mechanism that involves reductive elimination of the organic group on palladium with the phosphine appears to be likely. This reaction competes with the addition of the same complex to the alkene, possibly as shown in SCHEME 5. Thus, if the phosphonium salt formation is unusually favorable or if the olefin is relatively unreactive, phosphonium salt is formed, and the desired reaction does not go to completion. Some relative rates of phosphonium salt formation are shown in TABLE 3. It can be seen that iodobenzene is more reactive than bromobenzene and that bromobenzene reacts faster than chlorobenzene. More interesting is the fact that *p*-bromophenol is about 50 times more reactive than bromobenzene.

The obvious solution to the problem of phosphonium salt formation was to find a phosphine that does not quaternize but still functions as a ligand in the vinylic substitution reaction. A study of a variety of phosphines in the reaction revealed that *o*-alkyl-substituted triarylphosphines were substantially less reactive in the quaternization but, yet, were at least as useful as triphenylphosphine in the substitution. A comparison of various phosphines in the reaction of 4-bromophenol with methyl acrylate is shown in TABLE 4. Tri-*o*-tolylphosphine and tri-*o*-ethylphenylphosphine were good catalysts and were further improved by the addition of four more equivalents in excess of the amount needed to form the diphosphine-palladium salt complex. The excess undoubtedly replaced the small amounts that were quaternized, even with these phosphines. It is clear from the

TABLE 3 RELATIVE RATES OF PHOSPHONIUM SALT FORMATION

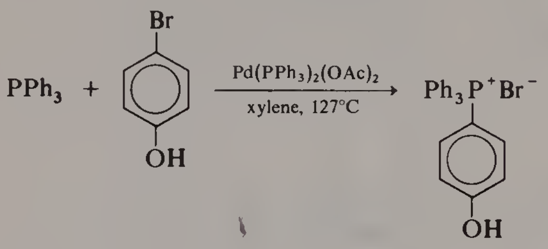
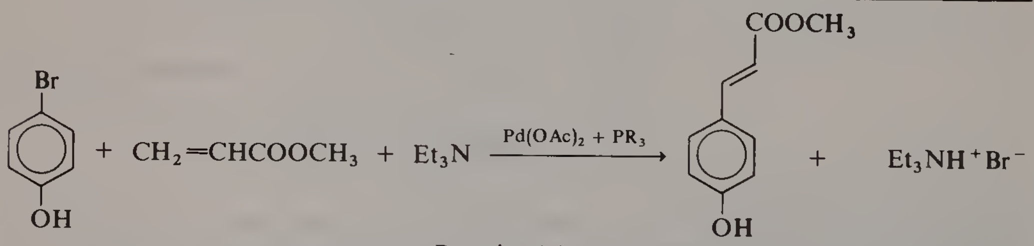
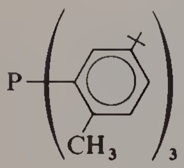
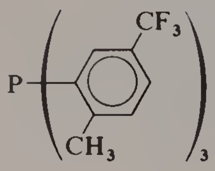
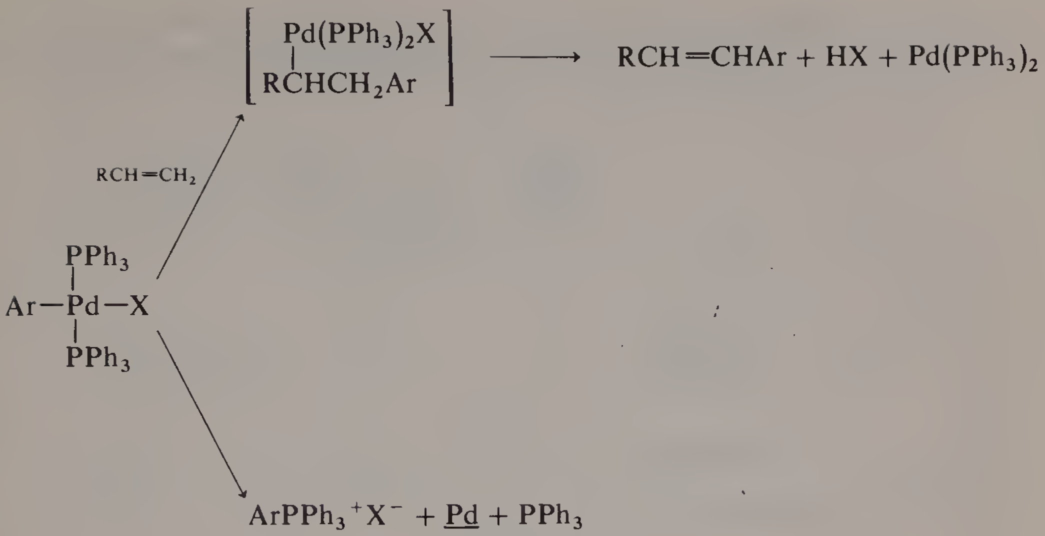
	$t_{1/2}$ (min)
$PPh_3 + C_6H_5I \xrightarrow[\text{xylene, 127°C}]{Pd(PPh_3)_2(OAc)_2} Ph_4P^+I^-$	71
$PPh_3 + C_6H_5Br \xrightarrow[\text{xylene, 127°C}]{Pd(PPh_3)_2(OAc)_2} Ph_4P^+Br^-$	570
$PPh_3 + C_6H_5Cl \xrightarrow[\text{mesitylene, 127°C}]{Pd(PPh_3)_2(OAc)_2} Ph_4P^+Cl^-$	<3000
	12

TABLE 4 INFLUENCE OF VARIOUS PR_3 DERIVATIVES



PR_3	P : Pd	Reaction Time (hr)	Temperature (°C)	Percentage Yield (glc)
PPh_3	2 : 1	48	75	3
	6 : 1	100	75	5
$P(2\text{-}CH_3C_6H_4)_3$	2 : 1	38	75	>95
	6 : 1	48	75	>95
$P(2\text{-}C_2H_5C_6H_4)_3$	2 : 1	51	75	58
	6 : 1	50	75	>95
$P(2,5\text{-}i\text{-}Pr_2C_6H_3)_3$	2 : 1	53	75	26
	6 : 1	50	75	68
	2 : 1	51	75	87
	6 : 1	48	75	>95
	2 : 1	34	75	29
	6 : 1	48	75	>95

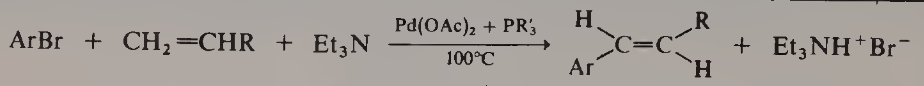


SCHEME 5

data that nearly quantitative yields of products can be obtained from *p*-bromophenol and methyl acrylate with the new phosphines. We are still investigating the effects of changing substituents in the arylphosphine groups, but we have observed that tri-*o*-tolylphosphine gives improved yields and faster reaction rates than does triphenylphosphine in many different vinylic substitution reactions. TABLE 5 shows some examples with other phenolic halides and haloanilines.

The conditions for the substitution reaction are relatively mild, so that a wide variety of olefinic compounds can be reacted. There is one group of olefinic compounds that is apparently largely polymerized under the weakly basic reaction conditions, however. This group is the α,β-unsaturated aldehydes and ketones. We have found, as would be expected, that the acetals and ketals of these compounds do react readily. An unexpected complication occurs in the aldehyde acetal reactions, however, which limits their synthetic utility. The adducts of the organopalladium species and the acetal not only undergo elimination to form the expected substituted acetal but also some elimination of the hydrogen on the acetal carbon occurs, producing a ketene acetal. Under our usual conditions, the ketene acetal is partially or completely converted into saturated ester, probably by reaction with the tertiary amine salt formed in the reaction. Thus, as shown in TABLE 6, bromobenzene and acrolein dimethyl acetal react to form a mixture of cinnamaldehyde dimethyl acetal and methyl 3-phenylpropionate. The suggested mechanism of this substitution reaction is shown in SCHEME 6; additional examples are illustrated in SCHEME 7. Crotonaldehyde diethyl acetal forms *E*-methylcinnamaldehyde diethyl acetal, ethyl 3-methyl-3-phenylpropionate, and some of the ketene acetal. Addition of water and warming cause conversion of the ketene acetal into the ester. The tendency for the palladium to abstract the more hydridic hydrogen in the elimination is observed on addition of *p*-bromonitrobenzene to acrolein dimethyl acetal, in which case only the ester product appears to be formed. Unsaturated ketals, of course, can only eliminate in one direction, and, as expected and shown in SCHEME 8, 3-buten-2-one ethylene ketal and bromobenzene reacted to form a single product, the benzalacetone ethylene ketal. For comparison again, the diphenylmercury-palladium acetate reaction with acrolein dimethyl acetal was performed. The reaction was much more selective than the bromobenzene reaction and formed only the cinnamaldehyde acetal, presumably mainly because of the low reaction temperatures employed, 0–25°C.

TABLE 5 VINYLIC SUBSTITUTIONS WITH HIGHLY ACTIVATED ARYL BROMIDES



$$ArBr + CH_2{=}CHR + Et_3N \xrightarrow[100^{\circ}C]{Pd(OAc)_2 + PR'_3} \overset{H}{\underset{Ar}{C}}{=}\overset{R}{\underset{H}{C}} + Et_3NH^+Br^-$$

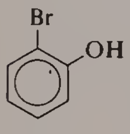
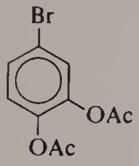
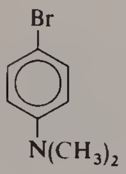
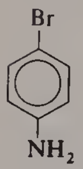
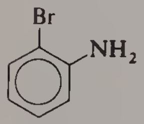
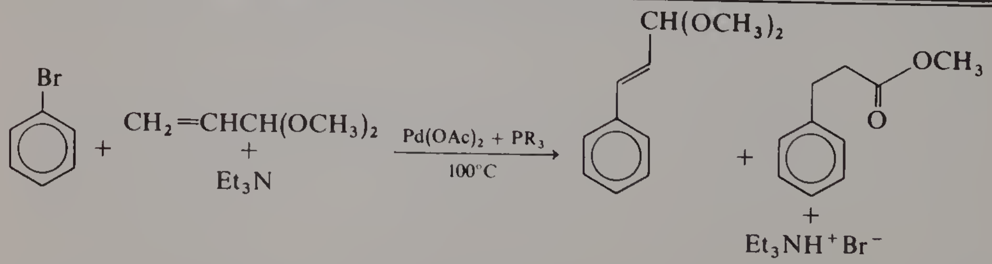
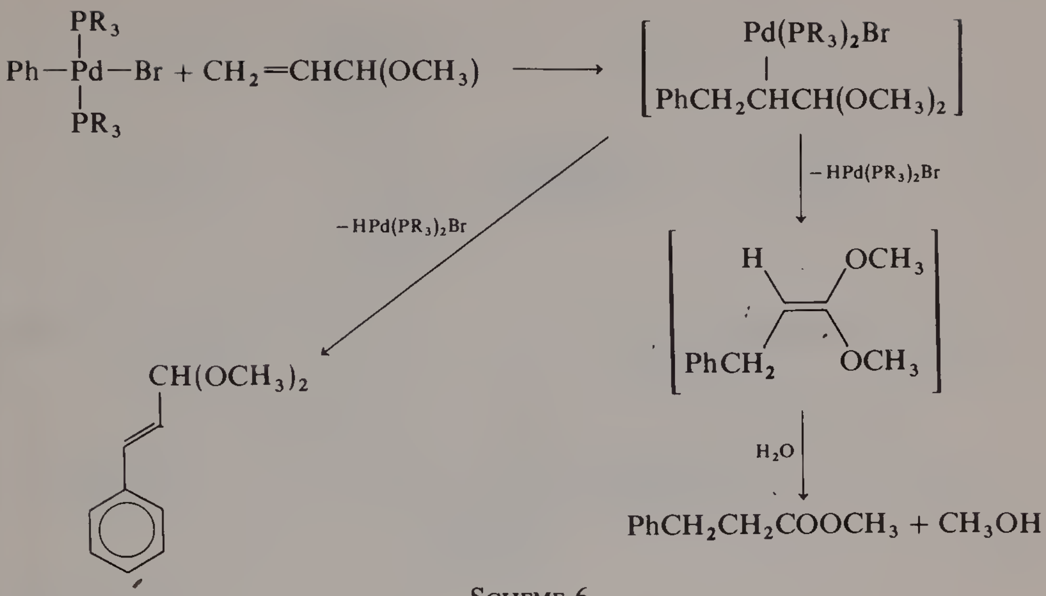
ArBr	R	Reaction Time (hr)	Product Yield (%)	
			Pd(OAc)$_2$:PPh$_3$	Pd(OAc)$_2$:Po-tol$_3$
	$-COOCH_3$	50	(1:6) 9	(1:6) 17
	$-COOCH_3$	7	(1:6) 2	(1:6) 73
	$-COOCH_3$	24	(1:8) 40	(1:8) 80
	$-COOCH_3$	2.5	(1:8) 4	(1:8) 73
	$-C_6H_5$	2	—	(1:4) 57
	$-C_6H_5$	2	—	(1:6) 70

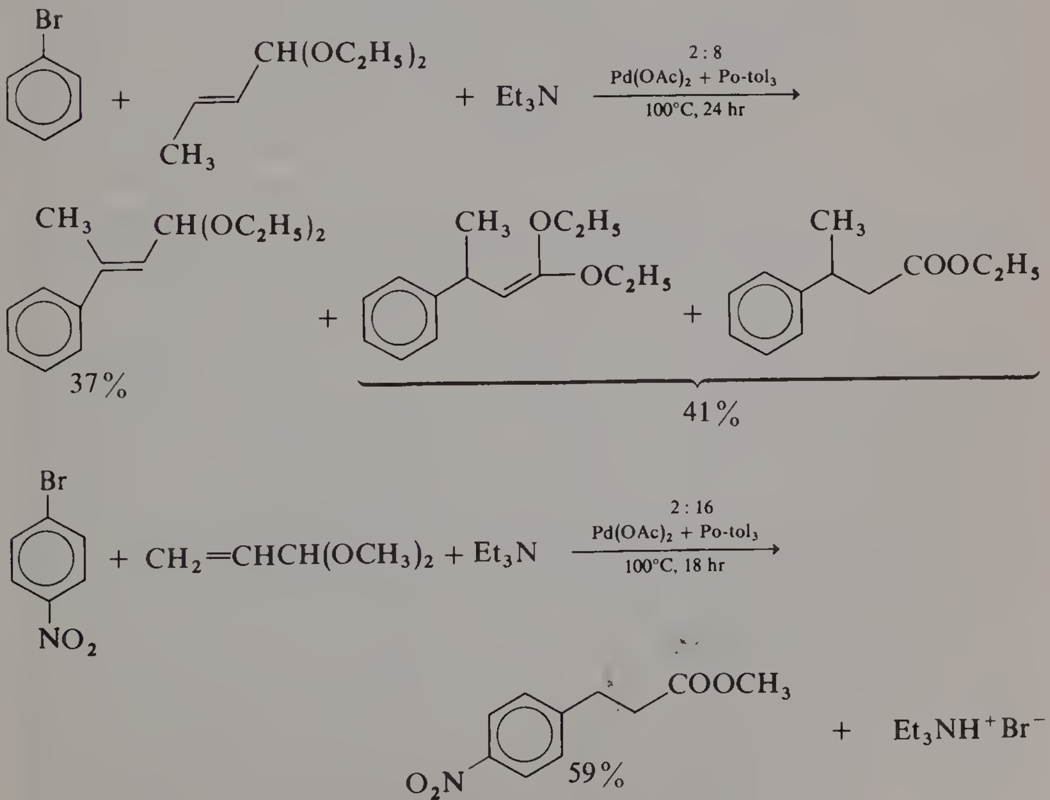
TABLE 6 PHENYLATION OF ACROLEIN DIMETHYL ACETAL



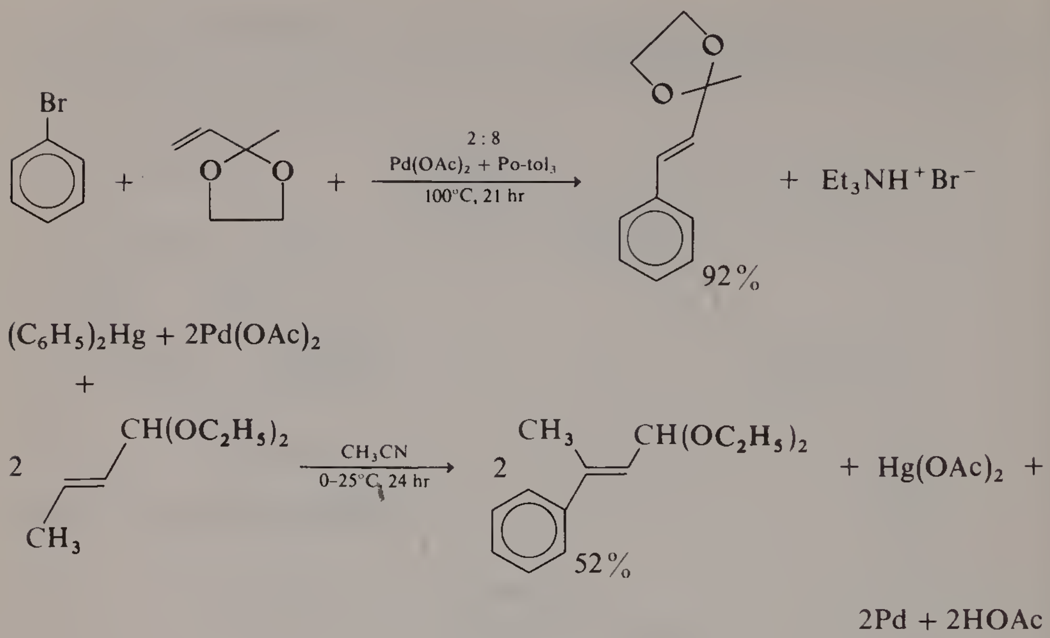
PR$_3$	P:Pd	Reaction Time (hr)	Product Yield (%)	
PPh$_3$	4:2	24	11	38
Po-tol$_3$	4:2	24	32	44
Po-tol$_3$	8:2	22	39	56



Scheme 6



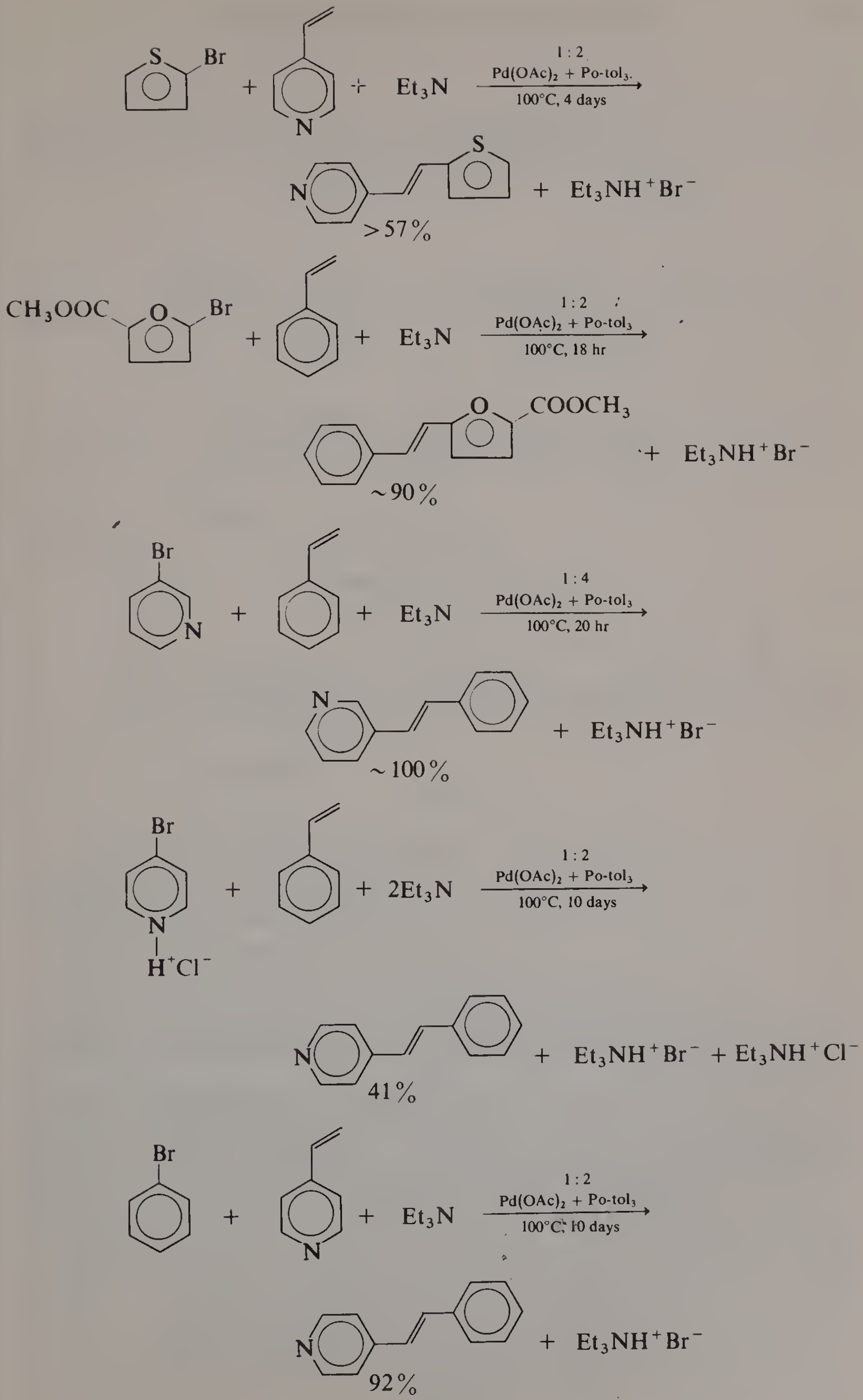
Scheme 7



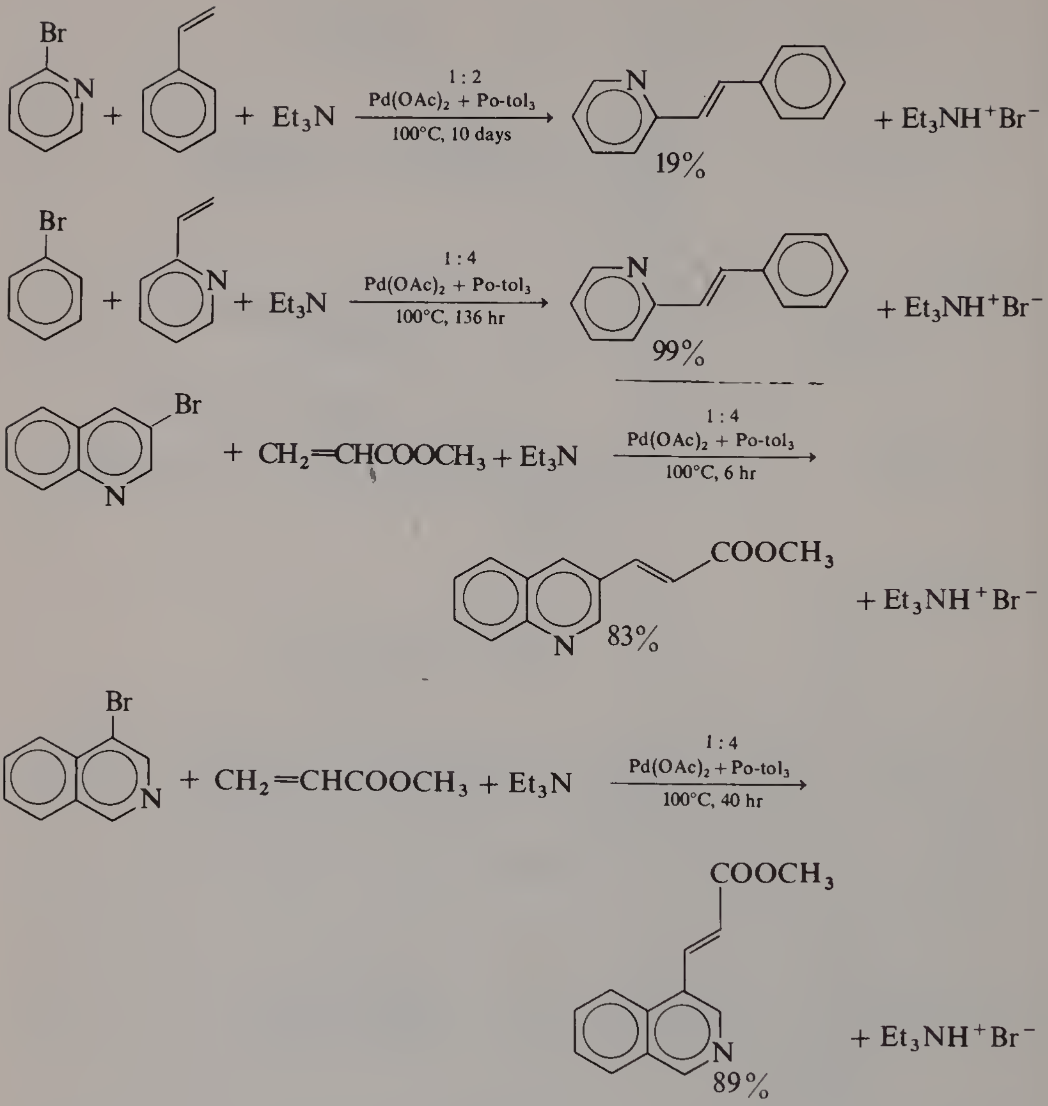
SCHEME 8

Several heterocyclic halides have also been successfully used in the vinylic substitution reaction. Examples are shown in SCHEMES 9–11. Useful reactions were found with 2-bromothiophene, methyl 2-bromofuran-5-carboxylate, 3-bromopyridine, 4-bromopyridine, 3-bromoquinoline, and 4-bromoisoquinoline. 2-Bromopyridine does not react well, probably because of chelation in the intermediate, forming unreactive complexes. Identical adducts can be made from reaction of the appropriate halides with 2-vinylpyridine, however. A very high yield was obtained in the reaction with bromobenzene, for example, as shown in SCHEME 10. 2-Iodoquinoline also reacted poorly. SCHEME 11 illustrates a new approach to the synthesis of nornicotine by means of the substitution reaction of 3-bromopyridine with *N*-butenylphthalimide. Hydrolysis, cyclization with mercuric acetate, and reduction of the product with sodium borohydride produce nornicotine.

Application of vinylic halides in the olefinic substitution reaction produces conjugated dienes. SCHEME 12 shows the reactions of *cis*- and *trans*-1-halo-1-hexenes with methyl acrylate. Under the usual conditions, considerable isomerization of the *cis*-1-hexene group to the *trans* isomer occurs. This isomerization can be minimized by using the vinylic bromide rather than the iodide, by adding more triphenylphosphine than the normal two equivalents per palladium, and by using a large excess of methyl acrylate. The hydridobromopalladium-π-alkene complex formed initially in the elimination reaction apparently dissociates more easily than does the iodo complex, and, consequently, there is less time for readdition of the hydride and isomerization. It is believed that the excess phosphine and ester improve the stereochemistry of the compound by displacing the diene product from the intermediate π-complex with the palladium hydride. If displacement is not rapid, readdition and isomerization occurs, with loss of stereochemistry. Again, generating the reacting the organopalladium compound at low temperatures produces a highly stereospecific reaction, as can be seen in the last two reactions of SCHEME 12. In these cases, the organopalladium species was formed from the 1-hexenylboronic acids and palladium acetate.


S
Br
N
Et3N
1:2
Pd(OAc)2 + Po-tol3
100°C, 4 days
>57%
Et3NH+Br−
CH3OOC
O
1:2
100°C, 18 hr
COOCH3
~90%
1:4
100°C, 20 hr
~100%
2Et3N
H+Cl−
100°C, 10 days
41%
Et3NH+Cl−
92%

SCHEME 9

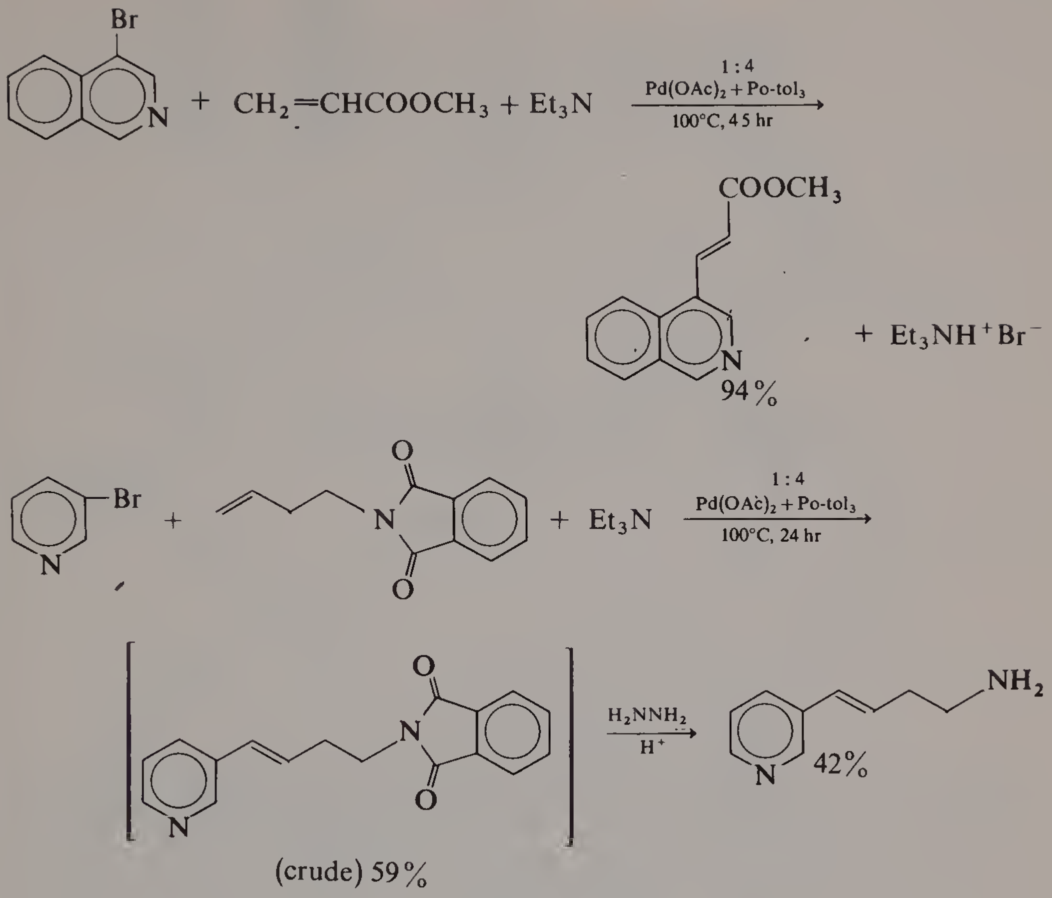


SCHEME 10

An application of the vinylic halide reagents is shown in SCHEME 13, where new and more convenient syntheses of the esters of chrysanthemum mono- and dicarboxylic acids are given.

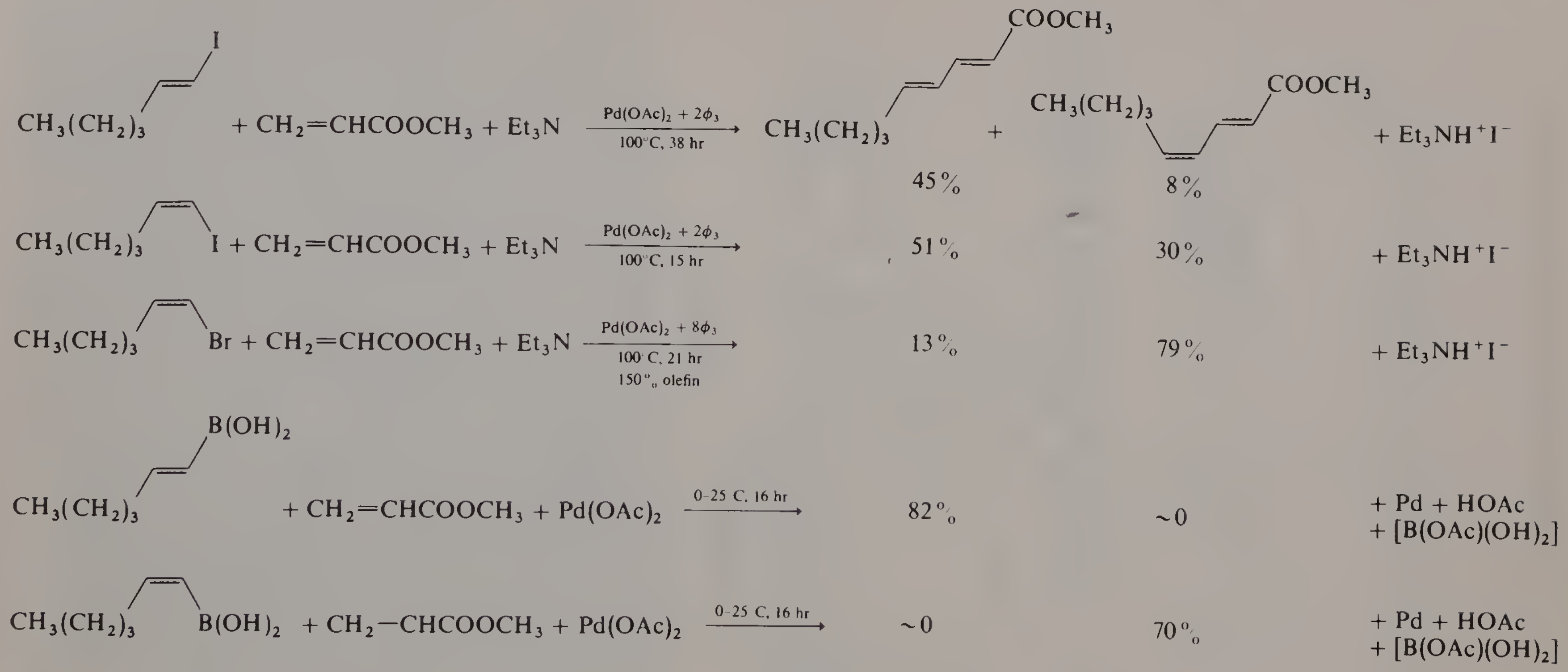
The synthesis of conjugated dienes by the above route is complicated in certain instances by competing Diels-Alder reactions. This complication appears when the olefin being reacted is a good dienophile and the diene being formed is not highly substituted at the double-bond carbons. For example, SCHEME 14 shows the reactions of vinyl iodide and of 2-bromopropene with methyl acrylate. In both instances, only Diels-Alder adducts of the expected conjugated dienes and methyl acrylate are found as products (even with a deficiency of methyl acrylate). If a better dienophile than methyl acrylate is also added, the intermediate diene can be "trapped" with it, as shown in the example where diethyl maleate is added. Maleate esters are very unreactive in the vinylic substitution reaction.

In another example, shown in SCHEME 15, the diene formed is unstable under the reaction conditions required, but it can be "trapped" also by the addition of dimethyl maleate, as a Diels-Alder adduct.

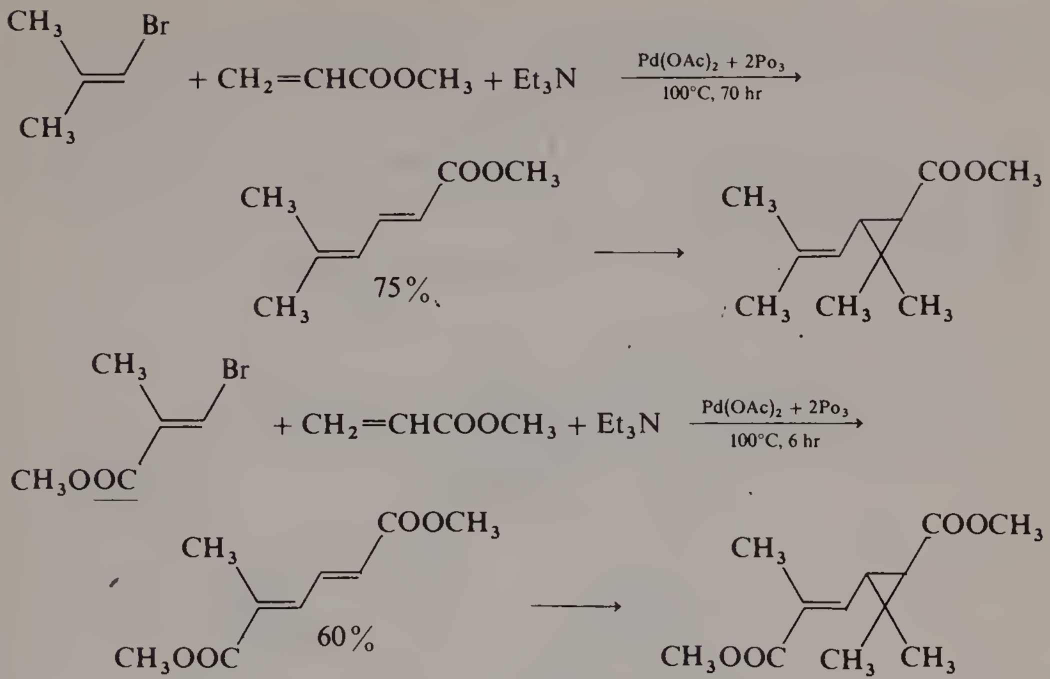


SCHEME 11

A useful variation of the olefinic substitution reaction occurs when allylic alcohols are used as the olefins. Tertiary allylic alcohols react normally, as can be seen from the reaction of iodobenzene with 2-methyl-3-buten-2-ol, shown in SCHEME 16. Primary and secondary allylic alcohols, on the other hand, produce largely or exclusively carbonyl-containing products under the same conditions. For example, in SCHEME 17, allyl alcohol and iodobenzene, in just 30 min at 100°C, form a mixture of 60 % 3-phenylpropionaldehyde and 11 % 2-phenylpropionaldehyde with palladium acetate used as the catalyst. The second product apparently arises from addition of the organic group to the more substituted carbon of the double bond. The same reaction with diacetatobistriphenylphosphinepalladium as the catalyst gave approximately the same yields of products but at about one tenth of the rate observed without the phosphine. Iodobenzene rather than bromobenzene was used in these reactions because iodobenzene reacted (without addition of the phosphine) at a faster rate, giving higher yields of products in many instances. In at least some of these cases, the aldol condensation of the aldehyde products was a competing reaction, and it was less serious with the shorter reaction times. The mechanism by which the carbonyl products are presumed to be formed is shown in SCHEME 18. An initial addition of the organopalladium species in both possible directions to the allylic double bond occurs, and this step is followed by the usual palladium hydride elimination to the alkene-hydride π-complex. In the "normal" adduct, elimination toward the CH group bearing the hydroxyl substituent would form the enol of the major product aldehyde. A simple dissociation or, more

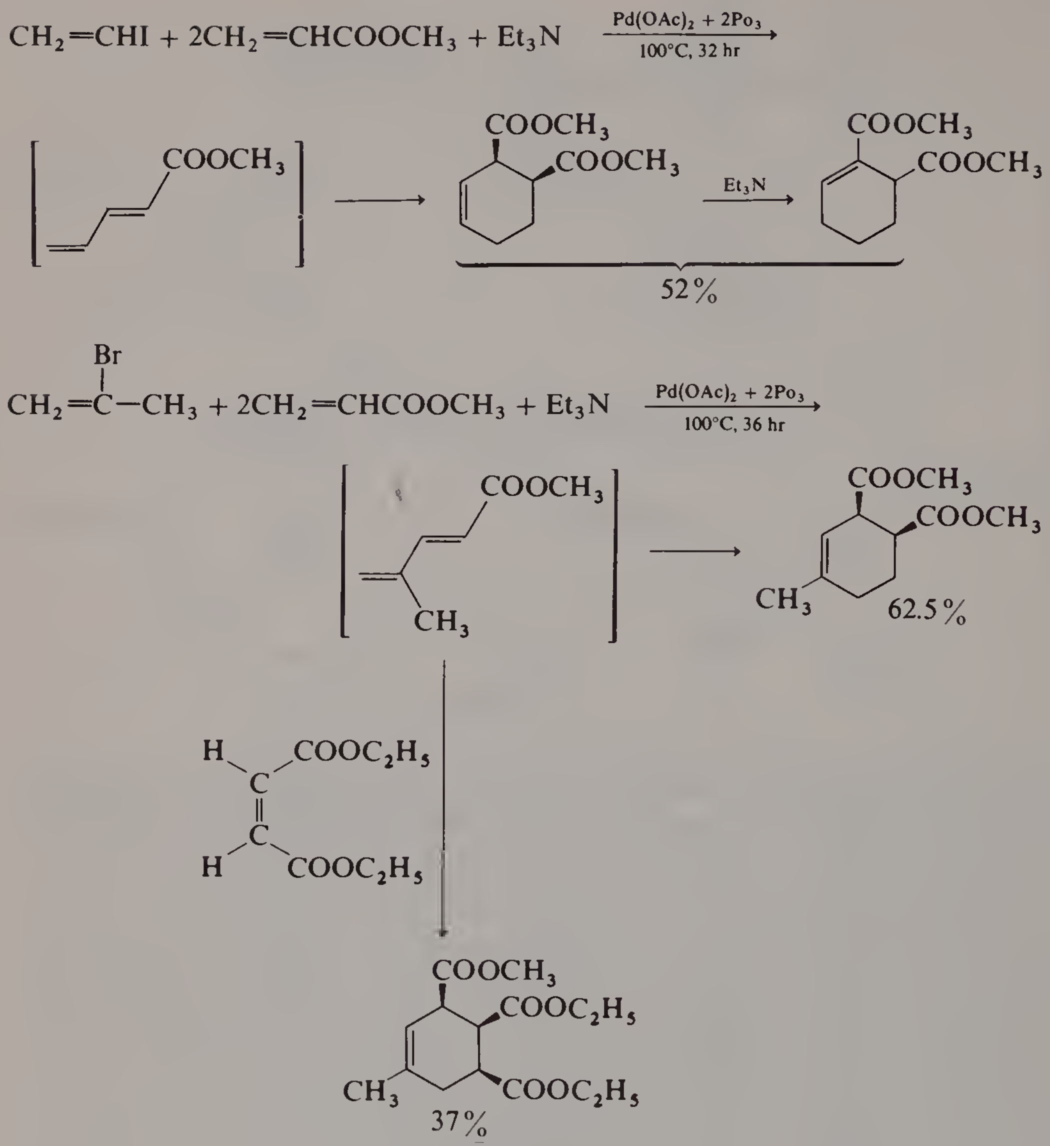

CH3(CH2)3
I
+ CH2=CHCOOCH3 + Et3N
Pd(OAc)2 + 2φ3
100°C, 38 hr
CH3(CH2)3
COOCH3
+
CH3(CH2)3
COOCH3
+ Et3NH+I−
45%
8%
Br
51%
30%
Pd(OAc)2 + 8φ3
100°C, 21 hr
150% olefin
13%
79%
B(OH)2
+ CH2=CHCOOCH3 + Pd(OAc)2
0–25 C, 16 hr
82%
~0
+ Pd + HOAc
+ [B(OAc)(OH)2]
+ CH2—CHCOOCH3 + Pd(OAc)2
~0
70%

SCHEME 12



SCHEME 13

probably, a reverse hydride readdition with β elimination of the hydroxyl hydrogen, followed by dissociation, would produce the 3-arylaldehyde. The 2-arylaldehyde must be formed by a sequence of palladium hydride eliminations and additions, ultimately ending up with the thermodynamically favored carbonyl compound. An alternative mechanism for formation of the 2-arylaldehyde involves the formation of a cyclic palladium alkoxide, as shown in SCHEME 18. The alkoxide could then eliminate the β-hydrogen on the hydroxyl carbon and transfer the hydrogen to the alkyl group. The use of 2-deuterio-3-buten-2-ol in the reaction with iodobenzene revealed deuterium shifts in the minor reaction product, 3-phenyl-2-butanone, consistent with the β elimination-readdition mechanism. On the other hand, if the central carbon of the allylic alcohol group is substituted with a methyl group, as in methallyl alcohol, reaction with iodobenzene still produces a minor amount of rearranged aldehyde, 4% 2-methyl-2-phenylpropionaldehyde, along with 91% of the "normal" product, 2-methyl-3-phenylpropionaldehyde, as shown in SCHEME 19. Clearly, the β-elimination-readdition mechanism cannot operate here. The use of 1,1-dideuterio methallyl alcohol in the reaction revealed the occurrence of a 1,3-deuterium shift, indicating that the cyclic alkoxide mechanism can also occur if the β-elimination route is blocked. The reaction of the secondary alcohol, 3-buten-2-ol, with iodobenzene gave an 88% yield of 4-phenyl-2-butanone and 8% of the 3-phenyl compound. These products are readily separated by fractionation, and this reaction is preparatively useful. The last example in SCHEME 19 shows an application of the substitution reaction to a homoallylic alcohol, 4-penten-2-ol. As expected, some isomerization to 4- and 5-phenyl-2-pentanones occurred, although both phenylated homoallylic alcohols were also produced. The yields of the various products depended significantly on reactants and reaction conditions. The use of bromobenzene instead of iodobenzene and, necessarily, the diacetatobistriphenylphosphine catalyst under the same conditions produced proportionately much more of the arylated homoallylic alcohols (75 vs 45%). Two factors are believed to be responsible for this difference: the hydridobromopalladium species does not add as

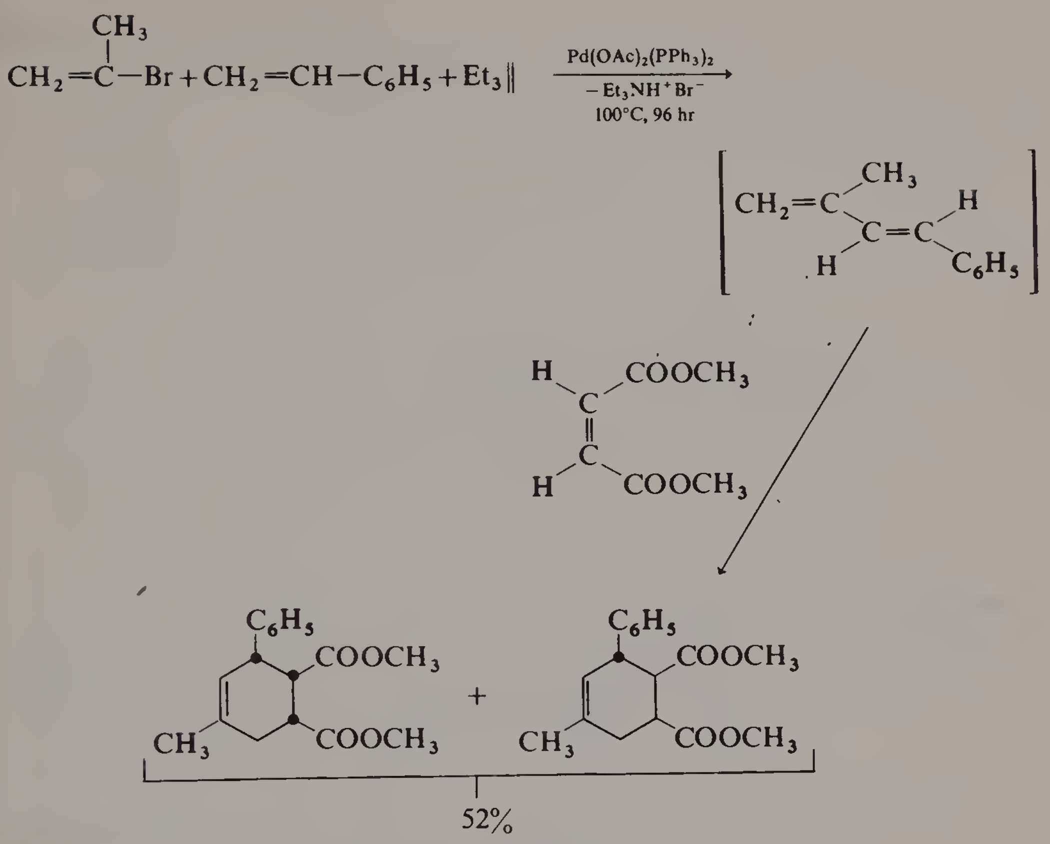


SCHEME 14

easily to double bonds as does the iodo complex (at least when both are triphenylphosphine complexes), and the presence of triphenylphosphine in the catalyst promotes dissociation of the hydrido-π-complex, compared with the simple solvated complex, and less rearrangement occurs.

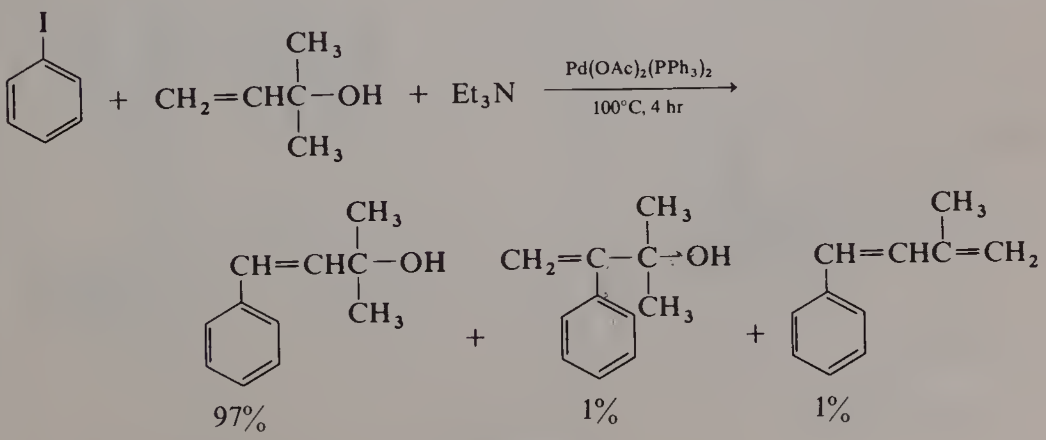
The influence of methyl substitution at the double bond of allyl alcohol can be seen in SCHEME 20. The change from allyl to crotyl to 3-methyl-3-butenyl alcohols causes a marked increase in the amount of substitution of phenyl in the β relative to the γ positions in the products. The ratio of γ/β changed from 5.3 for allyl to 2.8 for crotyl to 1.4 for the 3-methyl-2-butenyl alcohol. Yields were low in the last example because a major product, 3-methyl-2-phenyl-3-butenol, is a more reactive olefin in the substitution reaction than is the starting allylic alcohol.

SCHEME 21 again illustrates the influence that triphenylphosphine can exert on the substitution reaction. The phenylation of 3-buten-2-ol with bromobenzene and

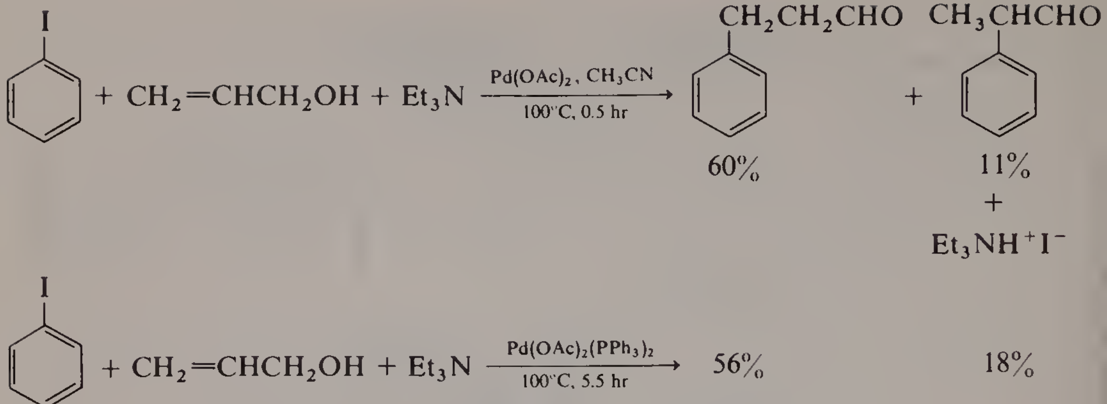


SCHEME 15

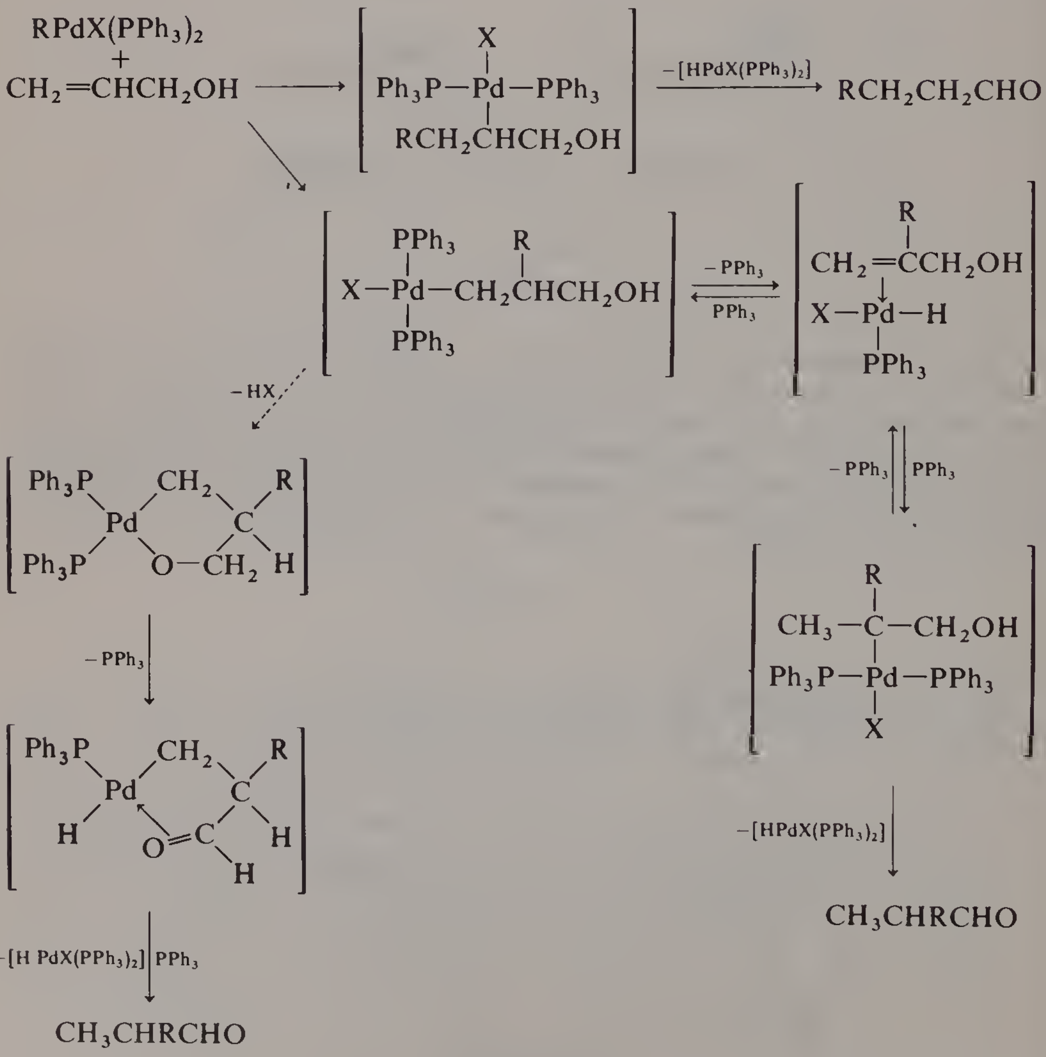
18 equiv of triphenylphosphine with 1 equiv of palladium acetate (1 mol% based on the bromobenzene) produced 53% of the two expected phenylated allylic alcohols and 21% of the two related phenylated ketones. The remainder of the product was tetraphenylphosphonium bromide, formed from the excess phosphine. These results contrast with the phenylation with iodobenzene and palladium acetate as the catalyst, where only the two carbonyl products were formed in near quantitative yield.



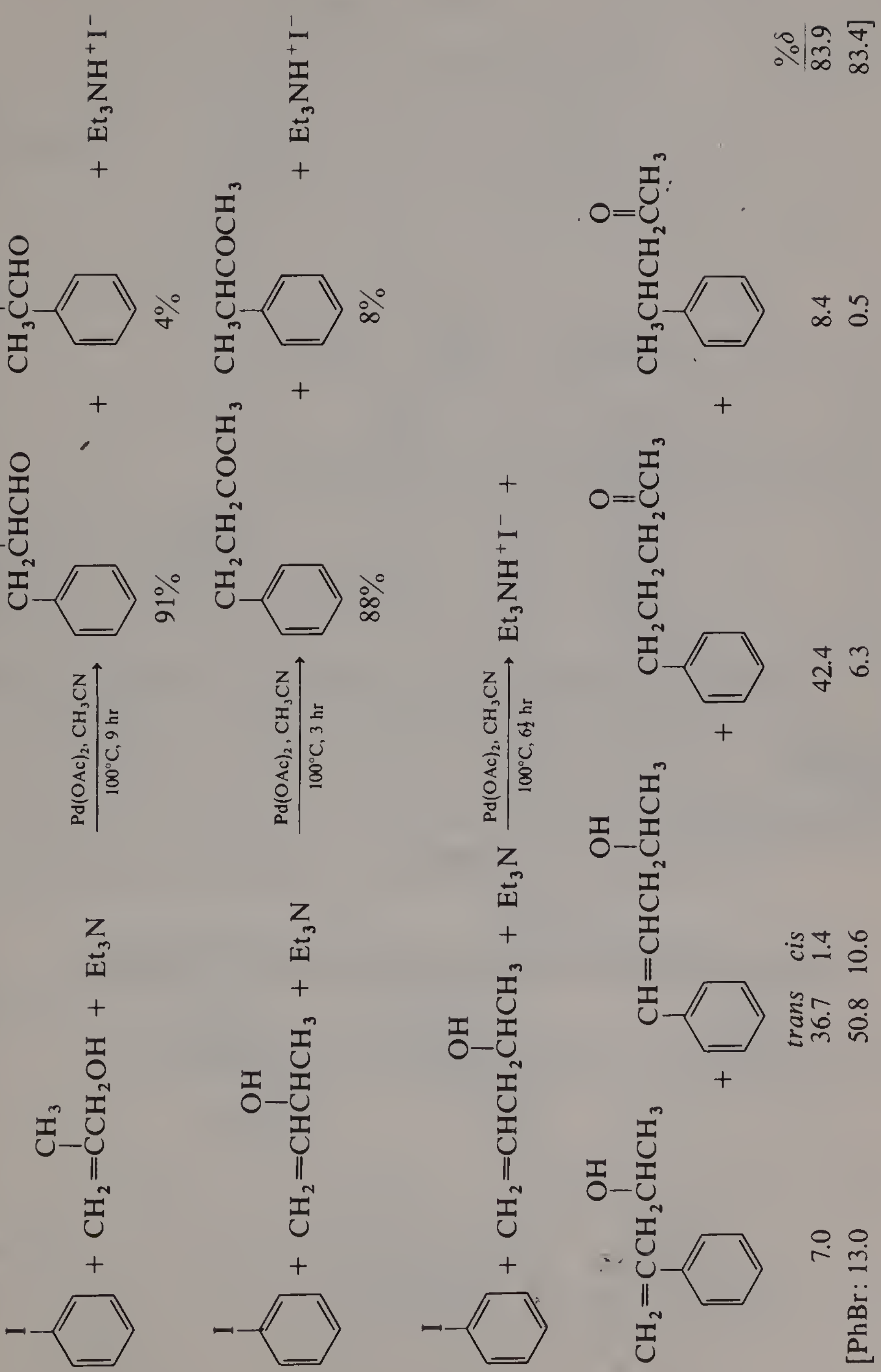
SCHEME 16



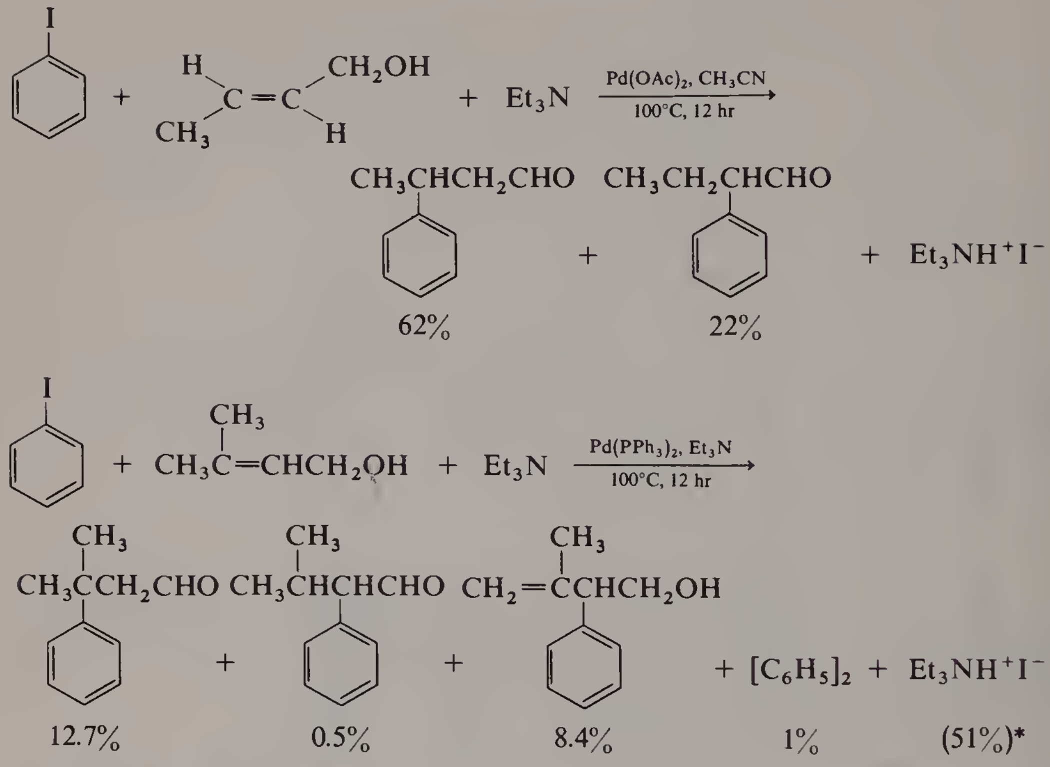
SCHEME 17



SCHEME 18


I
CH3
+ CH2=CCH2OH + Et3N
Pd(OAc)2, CH3CN
100°C, 9 hr
CH3
CH2CHCHO
91%
+
CH3
CH3CCHO
4%
+ Et3NH+I−
I
OH
+ CH2=CHCHCH3 + Et3N
Pd(OAc)2, CH3CN
100°C, 3 hr
CH2CH2COCH3
88%
+
CH3CHCOCH3
8%
+ Et3NH+I−
I
OH
+ CH2=CHCH2CHCH3 + Et3N
Pd(OAc)2, CH3CN
100°C, 6½ hr
Et3NH+I− +
OH
CH2=CCH2CHCH3
+
OH
CH=CHCH2CHCH3
+
O
CH2CH2CH2CCH3
+
O
CH3CHCH2CCH3
7.0
trans cis
36.7 1.4
42.4
8.4
%δ
83.9
[PhBr: 13.0
50.8 10.6
6.3
0.5
83.4]

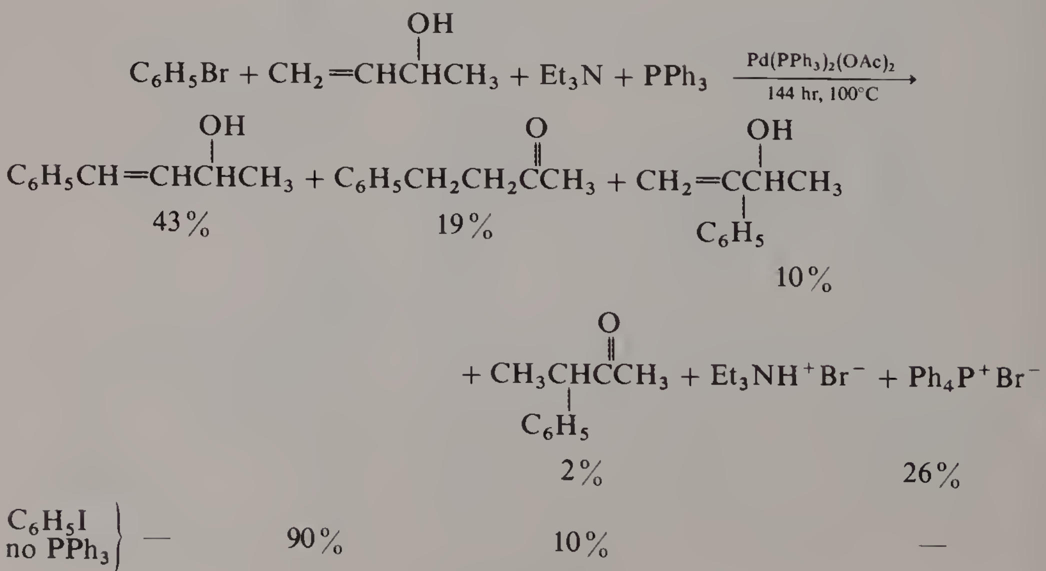
SCHEME 19



	$CH_2{=}CHCH_2OH$	$CH_3CH{=}CHCH_2OH$	$(CH_3)_2C{=}CHCH_2OH$
γ-phenylation/ β-phenylation	5.3	2.8	<1.4

*Total yield after 96 hr

SCHEME 20



$$C_6H_5Br + CH_2{=}CH\overset{OH}{\overset{|}{C}}HCH_3 + Et_3N + PPh_3 \xrightarrow[144\text{ hr, }100^\circ C]{Pd(PPh_3)_2(OAc)_2}$$

$$\underset{43\%}{C_6H_5CH{=}CH\overset{OH}{\overset{|}{C}}HCH_3} + \underset{19\%}{C_6H_5CH_2CH_2\overset{O}{\overset{\|}{C}}CH_3} + \underset{10\%}{CH_2{=}\underset{C_6H_5}{\underset{|}{\overset{OH}{\overset{|}{C}}}}HCH_3}$$

$$+ \underset{2\%}{CH_3\underset{C_6H_5}{\underset{|}{C}}H\overset{O}{\overset{\|}{C}}CH_3} + Et_3NH^+Br^- + \underset{26\%}{Ph_4P^+Br^-}$$

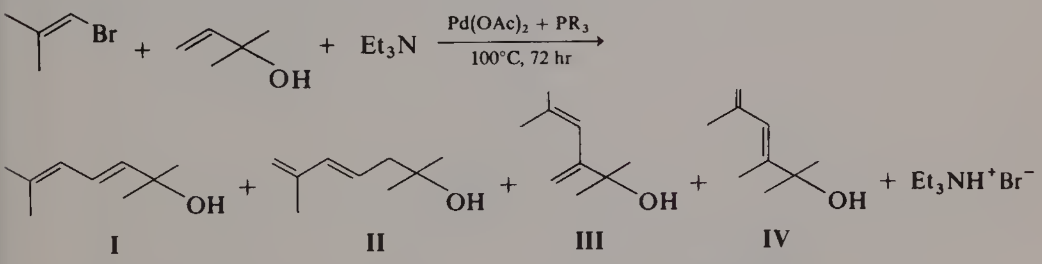
C_6H_5I no PPh_3 — 90% 10% —

SCHEME 21

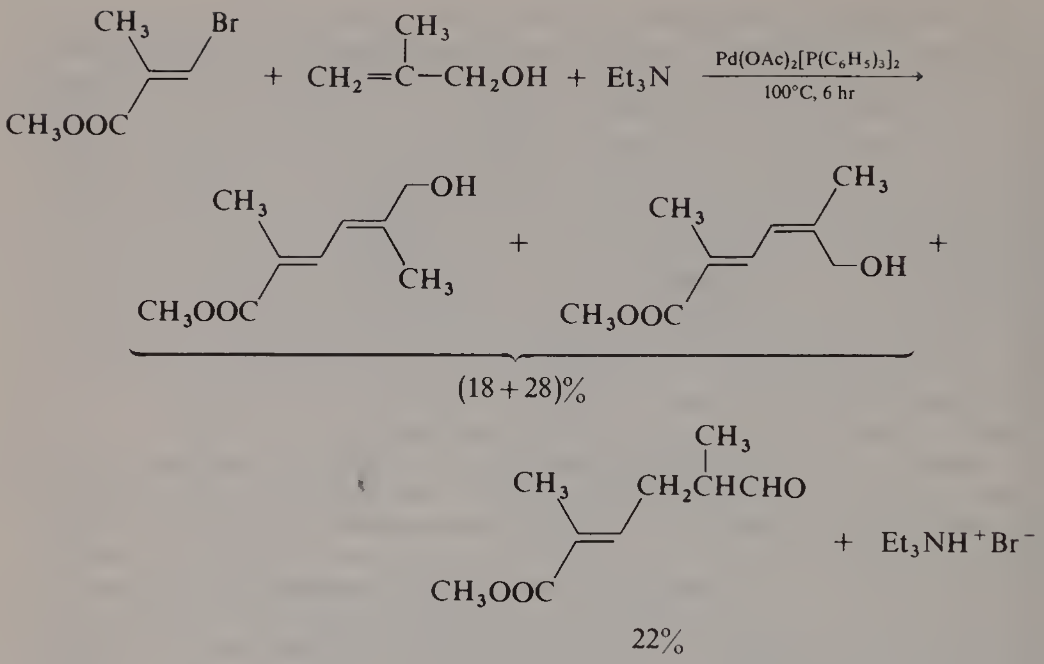
The reactions of vinylic halides with allylic alcohols have not yet been thoroughly investigated. It is apparent, however, that the *ortho*-substituted triarylphosphines are much better catalysts than is triphenylphosphine, as can be seen in TABLE 7. Here, 1-bromo-2-methyl-1-propene was reacted with 2-methyl-3-buten-2-ol with various phosphines used in the catalyst. The best yields of the terminal addition products were obtained with the triarylphosphine that had *o*-isopropyl groups. Four products were found. On hydrogenation, two saturated alcohols were formed. Nuclear magnetic resonance evidence suggests that the products were two double-bond isomers each of the terminal addition and internal addition products. The isomeric distribution in the products formed can be significantly influenced by the phosphine used in this example. One other example of this reaction is shown in SCHEME 22. With triphenylphosphine in the catalyst, a mixture of three major products, two dienols and an aldehyde, was obtained. Clearly, much work remains to be performed to attempt to make these reactions more selective.

Another group of olefins that appears to be of appreciable potential synthetic interest when used in the vinylic substitution reaction is the *N*-vinyl amides. Preliminary experiments appear promising. Bromobenzene and *N*-vinylpyrrolidone react, as shown in SCHEME 23, to form a 60:40 mixture of *N*-1-styryl- and *N*-1-styrylpyrrolidones. The strongly electron-supplying nitrogen group causes the unusually large amount of addition of the phenyl group to the more substituted carbon of the double bond. We do not yet know how much we can change the isomeric composition of the products by varying the phosphine used. A selective reaction was found in the arylation of *N*-vinylphthalimide. SCHEMES 23 and 24 illustrate the reactions between bromobenzene and *p*-bromophenyl acetate with *N*-vinylphthalimide that form the *trans*, terminally substituted products in good yields. Free bromophenol cannot be used in this instance, because the phenolic group apparently reacts with the vinyl amide function. These styrylphthalimide products appear to be potentially useful intermediates, and a few reactions have been performed with them. They catalytically hydrogenate easily and clearly to the *N*-phenethylphthalimides, and they can be expoxidized. The epoxides are catalytically reducible to *N*-2-hydroxy-2-phenethylphthalimides. A potential application in the synthesis of dopamine and its derivatives is shown in SCHEME 25. Several related reactions of *N*-vinylamine derivatives are currently under study.

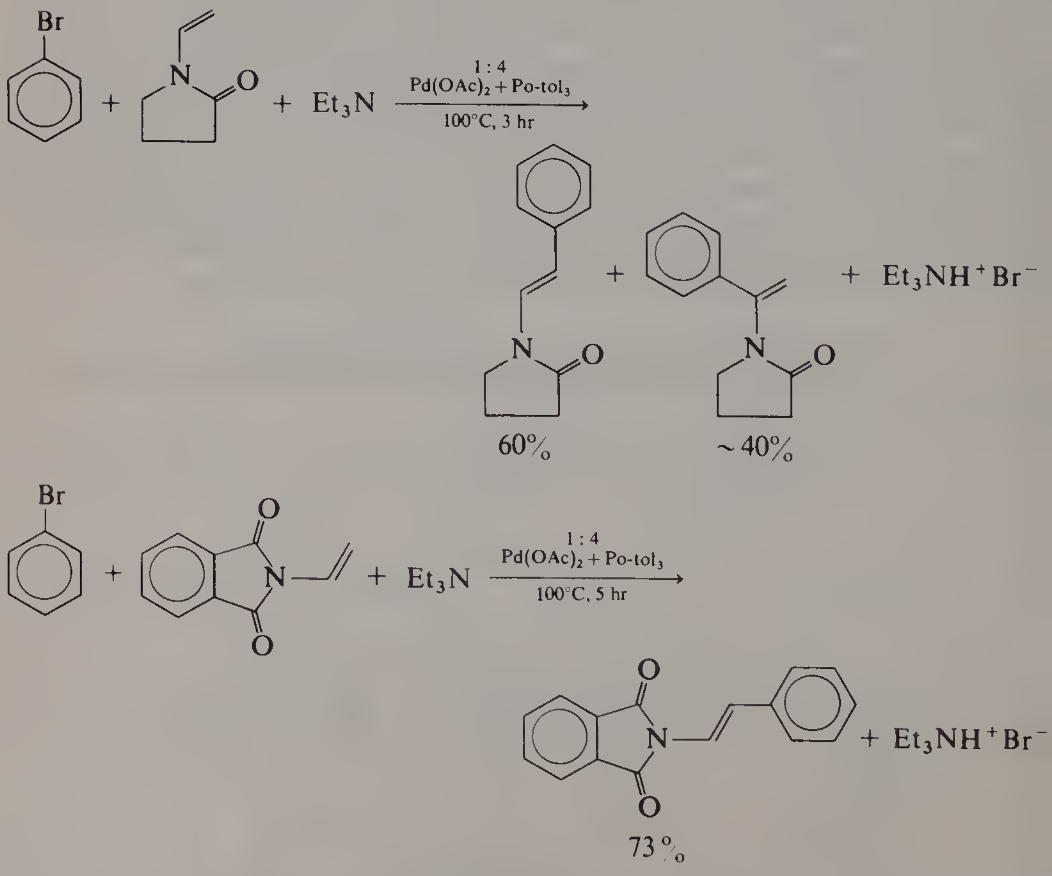
TABLE 7 PHOSPHINE EFFECTS IN VINYLIC SUBSTITUTION



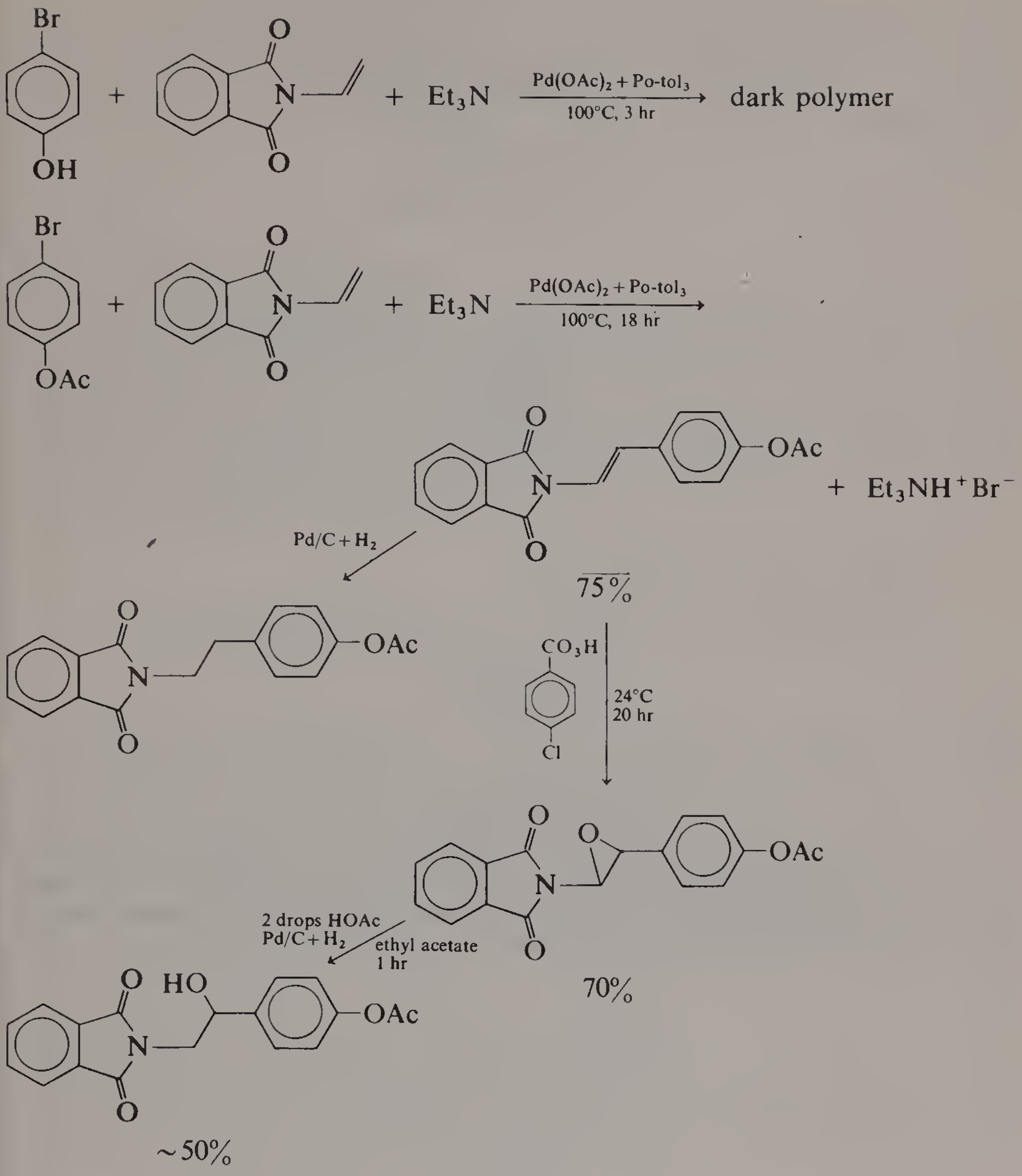
PR$_3$	P:Pd	Total	Product Yields (%)			
			I	II	III	IV
PPh$_3$	2:4	15	56	12	20	12
Po-tol$_3$	2:4	64	63	11	19	7
Po-tol$_3$	2:12	74	63	9	21	7
Po-EtPh$_3$	2:4	65	68	10	16	6
P(2,5-i-Pr$_2$Ph)$_3$	2:4	94	77	12	8	3



SCHEME 22

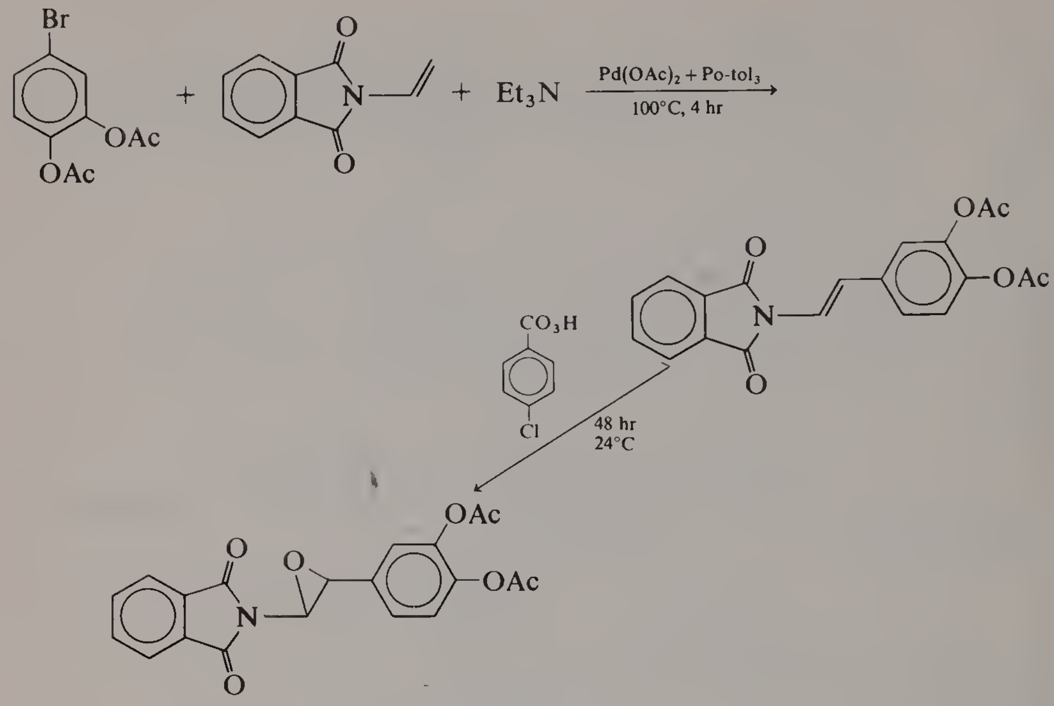


SCHEME 23



SCHEME 24

The above examples amply demonstrate the broad utility of the vinylic substitution reaction. Further study is necessary to find the best conditions for many of the reactions, and there is much to learn about how the catalyst ligands influence the reactions. Some control over reaction products has been achieved by varying ligands, and hopefully more selective catalysts will be found. Even at its present stage of development, this reaction offers the synthetic chemist a convenient and probably, in many instances, a superior route over more conventional methods to a wide variety of olefinic products.



SCHEME 25

ACKNOWLEDGMENTS

This work could not have been done without the able assistance of several coworkers, including Dr. Harold Dieck, Dr. John Melpolder, Carl Ziegler, Walter Frank, Dr. Babu Patel, and Tom Zebovitz.

IRON CARBONYLS IN ORGANIC SYNTHESIS

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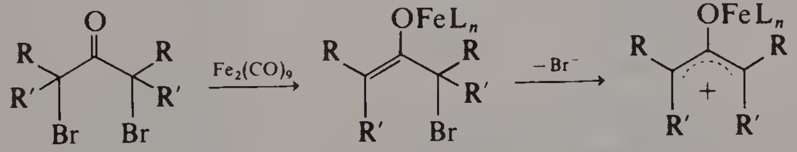
Metal carbonyls, among various transition metal complexes, occupy the most important position in organic synthesis and have been used widely both as stoichiometric reagents and as catalysts in a variety of carbon—carbon bond-forming processes. In this paper, we will describe the reaction of iron carbonyls and polybrominated ketones in the presence of various unsaturated substrates. The reactive C_3 intermediates serve as highly versatile building blocks in constructing odd-numbered carbon frameworks.

MECHANISTIC ASPECTS OF THE REACTION OF α,α′-DIMBROMOKETONES AND IRON CARBONYLS

α-Bromoketones are readily reduced by iron carbonyls. Reaction of *endo*-α-bromocamphor with $Fe_2(CO)_9$ in *N*,*N*-dimethylformamide (DMF) that contains 5% of deuterium oxide affords *exo*-α-deuteriocamphor. Certain dibromoketones undergo facile skeletal change on exposure to $Fe_2(CO)_9$. Thus, treatment of 1,3-dibromo-1,3-diphenylpropan-2-one with $Fe_2(CO)_9$ in benzene produces 1-phenyl-2-indanone. Reductive rearrangement of 2,4-dibromo-6,6-diphenylbicyclo[3.1.0]-hexan-3-one affords 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one. Reaction of 3,5-dibromo-2,2,6,6-tetramethylheptan-4-one gives a cyclization product, 2-*tert*-butyl-3,3,4-trimethylcyclobutanone. Reduction of 2,6-dibromo-2,6-di-*tert*-butylcyclohexanone in benzene gives a mixture of 5-*tert*-butyl-1,7,7-trimethylbicyclo[3.2.0]-heptan-6-one, 2-*tert*-butyl-6-isopropyl-6-methylcyclohex-2-enone, and 2,6-di-*tert*-butylcyclohex-2-enone. These findings indicate that the reaction of dibromoketone **1** with iron carbonyls produces first the enolate intermediate **2** and subsequently the reactive 2-oxyallyl—Fe(II) species **3**[1] (SCHEME 1). The cationic species also can be trapped with nucleophilic reagents. For instance, reaction of 2,4-dibromo-2,4-dimethylpentan-3-one (**4**) in the presence of sodium acetate gives 2-acetoxy-2,4-dimethylpentan-3-one and 2,4-dimethylpent-1-en-3-one. 2,6-Dibromo-2,6-diisopropylcyclohexanone, on reaction with $Fe_2(CO)_9$ in methanol, gives 2-methoxy-2,6-diisopropylcyclohexanone and 2,6-diisopropylcyclohex-2-enone. Thus,



1 **2** **3**, L = Br, CO, solvent

SCHEME 1

the oxyallyl intermediates, depending on the structures and reaction conditions, undergo various cationic rearrangements, nucleophilic trapping, and prototropy, forming α,β-unsaturated ketones. The negative charge on oxygen in the dipolar ion is masked by complexing with iron ion, and, consequently, the reactive species can behave as a typical allylic cation that bears an oxygen function at the central sp^2 carbon.

REACTION OF POLYBROMOKETONES AND 1,3-DIENES. NEW 3 + 4 → 7 CYCLOCOUPLING REACTION

2-Oxyallyl species generated from α,α'-dibromoketones and $Fe_2(CO)_9$ cycloadd to 1,3-dienes in a $3 + 4 \rightarrow 7$ manner, giving 4-cycloheptenones in fair to good yields (SCHEME 2 & TABLE 1).[2] The dienes with the high equilibrium concentration of the s-*cis* conformer serve as an efficient receptor of the reactive C_3 unit. 1,3-Diene—$Fe(CO)_3$ complexes are less reactive toward dibromoketones than is $Fe_2(CO)_9$, but use of such π-complexes increases the product yield to a considerable extent. Cyclopentadiene and furan derivatives are extremely good trapping agents of the oxyallyls (TABLE 2).[3] Pyrrole derivatives that have an electron-withdrawing group at the nitrogen atom give the $3 + 4$ cyclocoupling adducts,[4] while *N*-methylpyrrole or thiophene produces the electrophilic substitution products. Although reaction of 1,3-dienes and α,α'-dibromoacetone, unlike dibromides that possess long alkyl side chains, has failed to afford the cycloheptenone adduct, the reaction with $\alpha,\alpha,\alpha',\alpha'$-tetrabromoacetone proceeds smoothly.[5] Thus, the iron carbonyl-promoted reaction of tetrabromoacetone and 1,3-dienes, followed by zinc/copper couple reduction, formally corresponds to a $3 + 4$ cyclocoupling of dibromoacetone and dienes. This modification has considerable applicability and can also be used for the reaction of other methyl ketone polybromides (TABLE 3). Thus, we can now generate 2-oxyallyls with all kinds of substitution patterns, in the formal sense.

TABLE 1
REACTION OF α,α'-DIBROMOKETONES WITH OPEN-CHAIN 1,3-DIENES*

Dibromide	1,3-Diene	Yield of Cycloadduct (%)
4	2,3-Dimethyl-1,3-butadiene	71, 100†
4	1,3-Butadiene	33, 90†
4	Isoprene	47, 70†
5	2,3-Dimethyl-1,3-butadiene	46
5	1,3-Butadiene	30, 40†
5	Isoprene	36,‡ 51†
5	1,2-Dimethylenecyclohexane	80
6	2,3-Dimethyl-1,3-butadiene	36, 55†
6	1,3-Butadiene	44, 77†
6	Isoprene	31‡

* Unless otherwise stated, a mixture of dibromide, $Fe_2(CO)_9$ (1.0 : 1.0–1.2 molar ratio), and the diene (excess) in benzene was stirred at 60–90°C.

† In place of free 1,3-diene and $Fe_2(CO)_9$, the diene—$Fe(CO)_3$ complex was used.

‡ Reaction with irradiation of > 350-nm light.

TABLE 2

REACTION OF α,α′-DIBROMOKETONES WITH CYCLIC 1,3-DIENES*

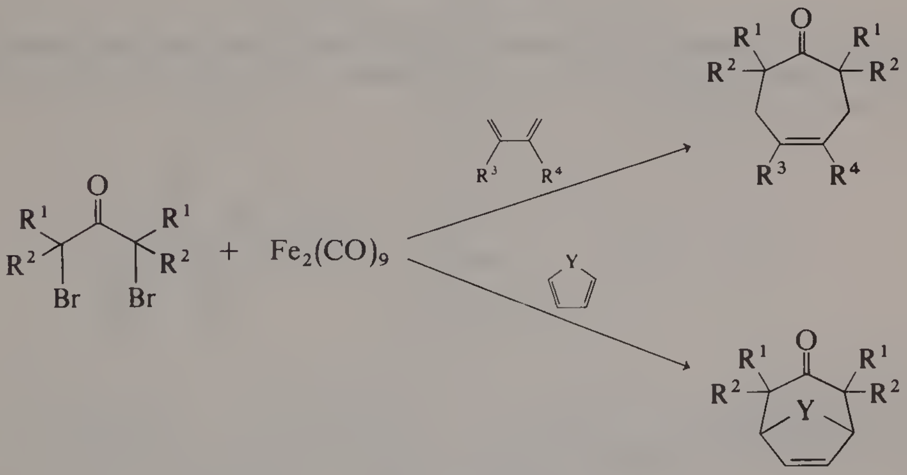
Dibromide	Diene	Yield of Cycloadduct (%)
4	Cyclopentadiene	82
5	Cyclopentadiene	86
6	Cyclopentadiene	93
4	Furan	96
5	Furan	90
6	Furan	97
7	Furan	90
8	Furan	35†
9	Furan	61†
10	Furan	60†
11	Furan	52†
5	2,5-Dimethylfuran	73
4	*N*-Acetylpyrrole	70‡
5	*N*-Carbomethoxypyrrole	60§

* Unless otherwise stated, the reaction was performed with the dibromide and $Fe_2(CO)_9$ (a 1:1.2 molar ratio) in the presence of excess diene substrate at 40–90°C.

† 2-(2-Furyl)cycloalkanone was formed as a by-product.

‡ Reaction with the dibromide and $Fe_2(CO)_9$ of a molar ratio of 1:0.5.

§ Reaction at 25°C with irradiation of > 350-nm light.



4, $R^1 = R^2 = CH_3$
5, $R^1 = CH_3$; $R^2 = H$
6, $R^1 = CH(CH_3)_2$; $R^2 = H$
7, $R^1 = C_6H_5$; $R^2 = H$
8, $R^1\text{—}R^1 = (CH_2)_3$; $R^2 = H$
9, $R^1\text{—}R^1 = (CH_2)_4$; $R^2 = H$
10, $R^1\text{—}R^1 = (CH_2)_5$; $R^2 = H$
11, $R^1\text{—}R^1 = (CH_2)_9$; $R^2 = H$

$Y = CH_2$, O, $NCOCH_3$, $NCOOCH_3$

SCHEME 2

TABLE 3

CYCLOCOUPLING REACTION OF TRI- AND TETRABROMOKETONES AND CYCLIC DIENES*

Bromide	Diene	Yield of Adduct (%)†
α,α,α′,α′-Tetrabromoacetone‡	cyclopentadiene	60
α,α,α′,α′-Tetrabromoacetone	furan	63
α,α,α′,α′-Tetrabromoacetone	2-isopropylfuran	47
α,α,α′,α′-Tetrabromoacetone	3-isopropylfuran	71
α,α,α′,α′-Tetrabromoacetone	*N*-carbomethoxypyrrole	70
1,1,3,3-Tetrabromobutan-2-one	furan	63
1,1,3-Ttribromo-4-methylpentan-3-one	furan	35
1,1,3-Tribromo-3-methylbutan-2-one	cyclopentadiene	83
1,1,3-Tribromo-3-methylbutan-2-one	furan	93

* Usually, polybromoketone and $Fe_2(CO)_9$ were used in a molar ratio of 1:1.2.

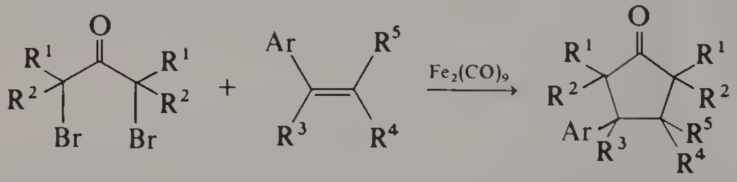
† Value obtained after zinc/copper reduction in methanol.

‡ $Fe(CO)_5$ was used as the reducing agent.

REACTION OF α,α′-DIBROMOKETONES AND OLEFINIC SUBSTRATES. NOVEL 3 + 2 → 5 CYCLOCOUPLING REACTIONS

Reaction with Aromatic Olefins

Reaction of secondary or tertiary α,α′-dibromoketones and aryl-substituted olefins (SCHEME 3) produces the 3 + 2 cycloadducts, the 3-arylcyclopentanones, in fair to good yields (TABLE 4).[6]



4, $R^1 = R^2 = CH_3$
5, $R^1 = CH_3$; $R^2 = H$
6, $R^1 = CH(CH_3)_2$; $R^2 = H$

SCHEME 3

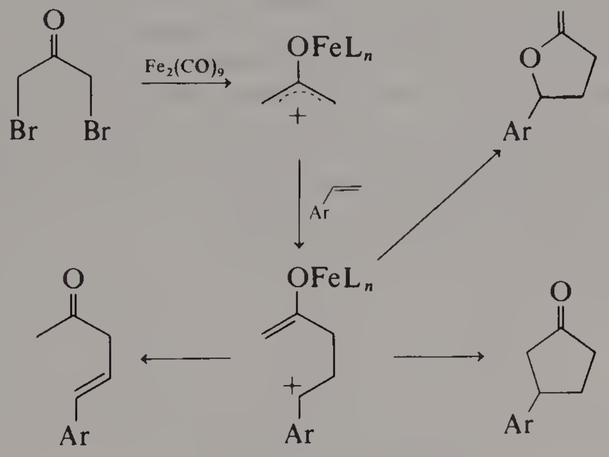
Apparently, the reactive oxyallyl—Fe(II) species **3** is involved. As by-products, open-chain olefinic ketones are formed via electrophilic olefinic substitution reactions. In certain cases, 2-alkylidenetetrahydrofurans are also produced. Introduction of a carbocation-stabilizing group at the arylated olefinic carbon or in the aromatic nucleus appears to facilitate the reaction. Intermolecular competition experiments have revealed that the relative reactivities decrease in the order of α-methylstyrene > styrene > β-methylstyrene, which suggests that both electronic and steric factors are controlling the ease with which the cycloaddition occurs. The reaction is best accommodated by the stepwise mechanism outlined in SCHEME 4. The reaction of

TABLE 4

IRON CARBONYL-PROMOTED REACTION OF α,α′-DIBROMOKETONES AND AROMATIC OLEFINS*

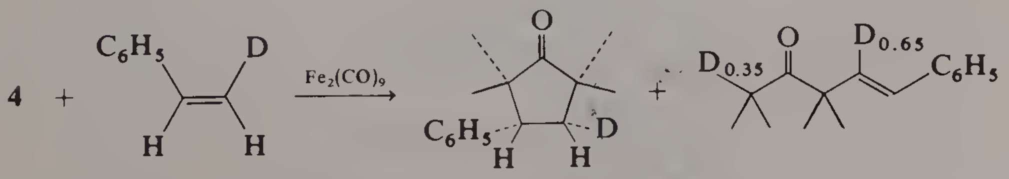
Dibromide	Aromatic Olefin	Yield of Cycloadduct (%)
4	Styrene	23
4	*trans*-Anethole	55
5	Styrene	65
5	α-Methylstyrene	70
5	α-Cyclopropylstyrene	95
5	1,1-Diphenylethylene	70
5	Ferrocenylethylene	30
5	*trans*-β-Methylstyrene	20
5	*trans*-Stilbene	30
5	Indene	45
6	1,1-Diphenylethylene	44

* Reaction was performed in benzene at 50–60°C with dibromide, olefin, and $Fe_2(CO)_9$ in a 1 : 2–4 : 1.2 molar ratio.



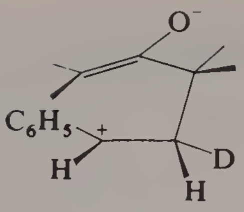
SCHEME 4

dibromoketone **4** and *cis*-β-deuteriostyrene gives rise to the 1 : 1 adducts **12** and **13**. The stereospecific 3 + 2 cycloaddition, which produces **12**, is considered to proceed via the rigid, U-shaped zwitterion **14U** (SCHEME 5), while the nonstereospecificity of the electrophilic substitution reaction that yields **13** is accounted for in terms of the flexible Z-shaped intermediate **14Z**.[7]

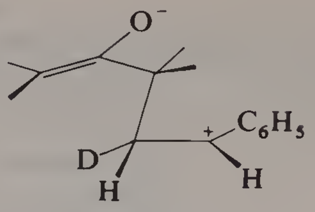


12 **13**

SCHEME 5



14U



14Z

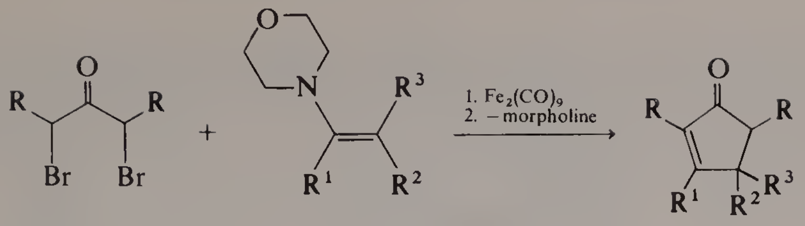
Reaction with Enamines

Heteroatom-substituted olefins, such as enamines, can also couple with dibromoketones in the presence of iron carbonyls.[8] For example, the reaction of **4** and 1-morpholinocyclohexene produces 1-morpholino-7,7,9,9-tetramethylbicyclo[4.3.0]-nonan-8-one. The cyclopentanone adducts derived from secondary dibromoketones and the enamines eliminate morpholine facilely, giving 2-cyclopentenones. This coupling reaction provides a new, single-flask procedure for the preparation of five-membered ketones (SCHEME 6 & TABLE 5). The 3 + 2 cyclocoupling reaction proceeds generally in high yield and finds wide applicability; the reaction with cyclic ketone enamines leads to bicyclo[*n*.3.0]alkenones, whereas the annelation reaction that employs enamines of cycloalkanecarboxaldehydes gives rise to a spiro[*n*.4]-alkenone system. The 7/5-fused bicyclic ketones obtained from 1-morpholinocycloheptene serve as a potential intermediate for azulenoid synthesis. The iron carbonyl-promoted reaction in a mixture of a morpholinoenamine and furan produces morpholinocyclopentanone and 8-oxabicyclo[3.2.1]oct-6-en-3-one derivatives, which indicates that both the 3 + 2 and 3 + 4 cyclocoupling reactions are going through a common oxyallyl intermediate.

TABLE 5
IRON CARBONYL-PROMOTED CYCLOPENTENONE SYNTHESIS
FROM α,α'-DIBROMOKETONES AND ENAMINES*

Dibromide	Parent Carbonyl Compound of Morpholinoenamine	Yield of Cyclopentenone (%)
5	Isobutylaldehyde	79
5	Acetophenone	91
5	3-Pentanone	73
5	Cyclopentanone	74
5	Cyclohexanone	100
5	Cycloheptanone	100
5	Cyclododecanone	90
5	Cyclohexanecarboxaldehyde	71
5	Cyclododecanecarboxaldehyde	65
6	Acetophenone	72
6	Cyclohexanone	73
7	Cyclopentanone	66
15	Acetophenone	64
15	3-Pentanone	70

* Reaction was performed in benzene at 25–30°C with dibromide, enamine, and Fe$_2$(CO)$_9$ in a molar ratio of 1 : 2.5–3.0 : 1.2.

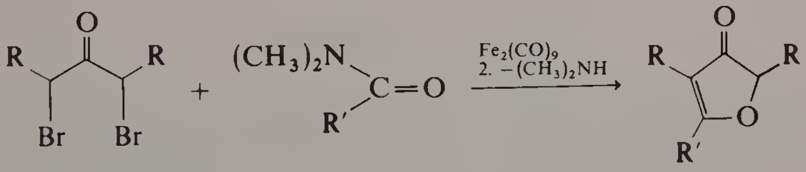


5, $R = CH_3$
6, $R = CH(CH_3)_2$
7, $R = C_6H_5$
15, $R = C_2H_5$

SCHEME 6

IRON CARBONYL-AIDED REACTION OF α,α′-DIBROMOKETONES AND CARBOXAMIDES. SYNTHESIS OF 3(2*H*)-FURANONES

This reaction can construct a carbon—oxygen bridge between the α and α′ positions of the parent dialkyl ketones.[9] Thus, treatment of secondary dibromoketones with $Fe_2(CO)_9$ in DMF at room temperature affords the corresponding 3(2*H*)-furanone derivative (SCHEME 7 & TABLE 6). In place of DMF, *N*,*N*-dimethylacetamide or *N*,*N*-dimethylbenzamide can be used. Apparently, the formation of the furanones proceeds by way of the thermally labile amino intermediates, and, in certain cases, the stable compounds can be isolated. Thus, reaction of 3,5-dibromo-2,2,6,6-tetramethylheptan-4-one and DMF with the aid of $Fe(CO)_9$ gives rise to the stable dimethylamino adduct 2,4-di-*tert*-butyl-5-dimethylaminodihydro-3(2*H*)-furanone. Reduction of **4** in DMF gives a mixture of 5-dimethylaminodihydro-2,2,4,4-tetramethyl-3(2*H*)-furanone and 2,4-dimethylpent-1-en-3-one. The reaction of **6** and *N*-methylpyrrolidone proceeds through an unstable spiro-fused dihydrofuranone to give, ultimately, 5-(3-methylaminopropyl)-2,4-diisopropyl-3(2*H*)-furanone. The furanones derived from secondary dibromoketones are an important class of compounds in connection with muscarine alkaloids.



5, $R = CH_3$
6, $R = CH(CH_3)_2$
15, $R = C_2H_5$

SCHEME 7

REGIOSELECTIVITY OF THE REACTIONS OF 2-OXYALLYL—Fe(II) SPECIES

Nucleophilic Trapping

Reaction of the unsymmetrically substituted dibromide **16** and $Fe_2(CO)_9$ in methanol gives regioisomeric methoxy ketones **18** and **19** in a ratio of 90 : 10 (SCHEME 8). The reaction in the presence of a fivefold excess of sodium acetate

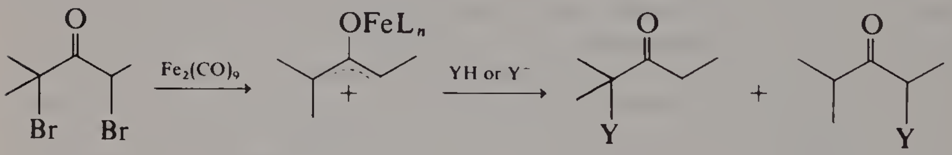
TABLE 6

IRON CARBONYL FURANONE SYNTHESIS FROM α,α'-DIBROMOKETONES AND CARBOXAMIDES*

Dibromide	Amide	Yield of Furanone (%)
5	DMF	53
6	DMF	90
6	*N,N*-Dimethylacetamide	87
6	*N,N*-Dimethylbenzamide	83
15	DMF	78
15	*N,N*-Dimethylacetamide	51
15	*N,N*-Dimethylbenzamide	42

* Reaction was performed at 20–25°C with dibromide and $Fe_2(CO)_9$ in a molar ratio of 1 : 1.2. DMF and dimethylacetamide were used as solvents. Dimethylbenzamide (20 equiv to dibromide) was used as the benzene solution.

affords a 69 : 31 mixture of **20** and **21**. The preferential attack of the nucleophiles at the more substituted sp^2 terminus of the oxyallyl intermediate **17** is reasonable in view of the stronger cationic character compared with the less substituted terminus.



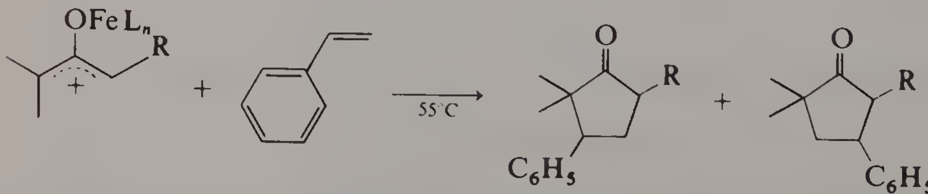
16 **17**

18, $Y = OCH_3$ **19**, $Y = OCH_3$
20, $Y = OCOCH_3$ **21**, $Y = OCOCH_3$

SCHEME 8

3 + 2 → 5 Cycloadditions

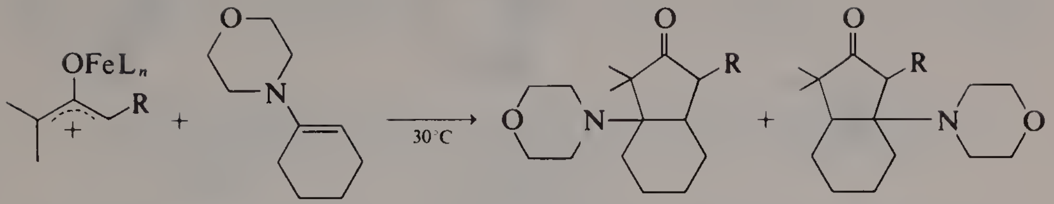
The unsymmetrically substituted oxyallyl intermediate **16** or **22**, generated from the corresponding dibromoketone, is trapped with styrene to give a mixture of regioisomeric 3-phenylcyclopentanones. The result is summarized in SCHEME 9. Apparently, the preferred orientation of the cationic 3 + 2 cycloaddition is the one that affords the maximal stabilization of the zwitterionic intermediates (cf. SCHEME 4). The same trend has been observed in a reaction that employs the enamine substrate 1-morpholinocyclohexene, as shown in SCHEME 10.



16, $R = CH_3$
22, $R = C_6H_5$

23, $R = CH_3$ **24**, $R = CH_3$ **23**/**24** = 94 : 6
25, $R = C_6H_5$ **26**, $R = C_6H_5$ **25**/**26** = 0 : 100

SCHEME 9

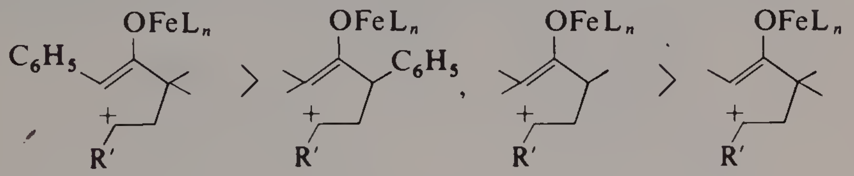


16, R = CH$_3$
22, R = C$_6$H$_5$

27, R = CH$_3$ **28**, R = CH$_3$ **27/28** = 59 : 41
29, R = C$_6$H$_5$ **30**, R = C$_6$H$_5$ **29/30** = 25 : 75

SCHEME 10

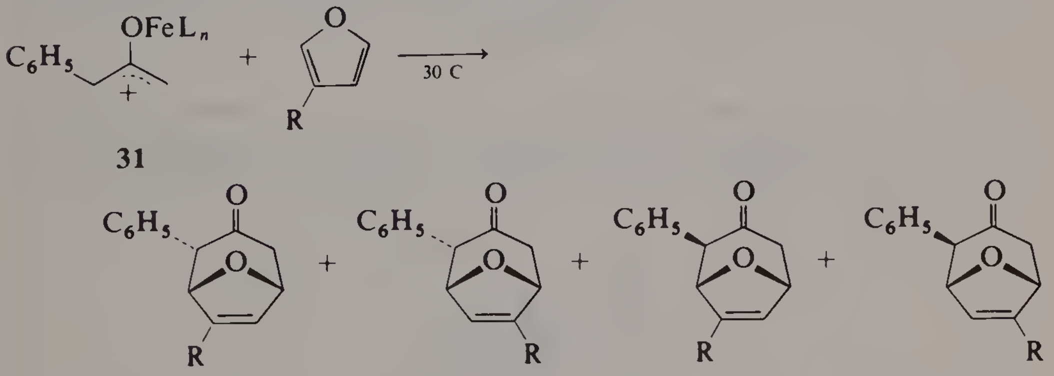
The following stability sequence is fully compatible with these findings:



R′ = C$_6$H$_5$ or N(CH$_2$CH$_2$)$_2$O

3 + 4 → 7 *Cycloaddition*

The cycloaddition between 2-oxyallyls and 1,3-dienes is classified as a symmetry-allowed [$\pi^2 + \pi^4$] process and indeed proceeds in a concerted manner. The reaction of 1-phenyl-2-oxyallyl (**31**) and 3-methylfuran leads to a mixture of **32**–**35**, in which the ratio of both **32**/**33** and **34**/**35** is 56 : 44 (SCHEME 11). The addition of **31** and ethyl 3-furoate affords a 55 : 45 mixture of **36** and **37**. The observed regioselectivity is best accounted for by considering the prime control of the frontier MOs of each cycloaddend, namely, LUMO of the electron-accepting oxyallyl and HOMO of electron-donating furan substrates. Thus, the transition state formed through dominant interaction between the reaction termini with the larger MO coefficient (primary MO interaction) results in the production of the major isomer. Interesting is the behavior displayed by 2-furoates that have com-



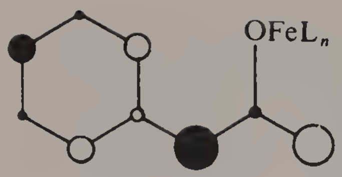
32, R = CH$_3$
36, R = COOC$_2$H$_5$

33, R = CH$_3$
37, R = COOC$_2$H$_5$

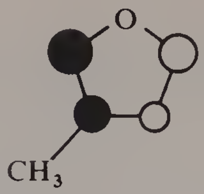
34, R = CH$_3$

35, R = CH$_3$

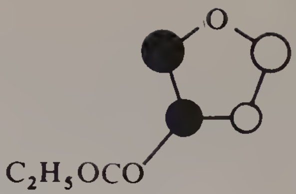
SCHEME 11



LUMO of **31**

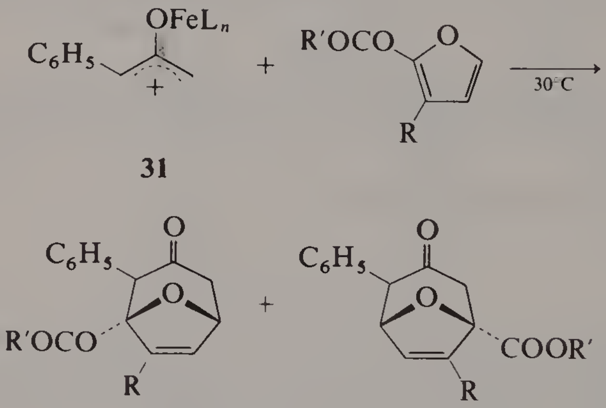


HOMO of
3-methylfuran



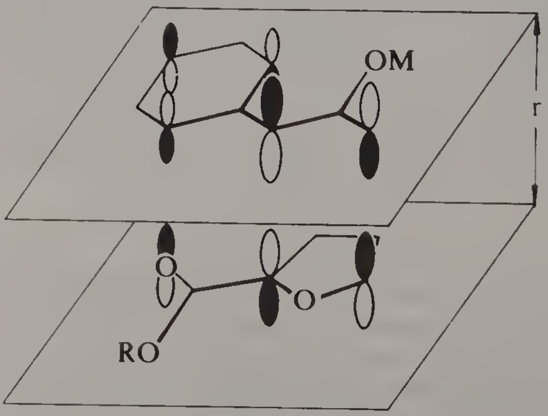
HOMO of ethyl
3-furoate

parable MO coefficients at the two reaction sites, C_2 and C_5; the bias toward the production of the major regioisomer is far greater than that expected from the degree of MO inclination (SCHEME 12). This bias is presumably due to the presence of the secondary MO interactions between the substituents, as featured by transition state **42**. There exists only a narrow energy gap between the frontier MOs of the cationic oxyallyl and furans; therefore, the two cycloaddends can achieve pericyclic



38, $R = H; R' = C_2H_5$ **39**, $R = H; R' = C_2H_5$ **38**/**39** = 90 : 10
40, $R = R' = CH_3$ **41**, $R = R' = CH_3$ **40**/**41** = 92 : 8

SCHEME 12



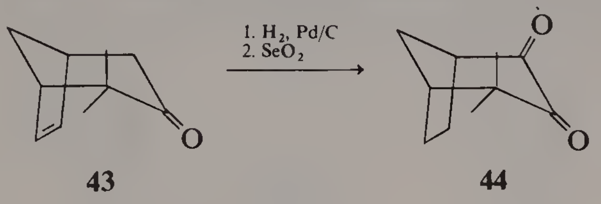
42

interaction, even at a long distance. Consequently, such secondary MO interactions become much more significant than in the ordinary nonpolar $[\pi^2 + \pi^4]$ process, such as Diels-Alder reactions.

SYNTHETIC APPLICATIONS OF THE 3 + 4 CYCLOCOUPLING REACTION

Carbocamphenilone and Camphenic Acid

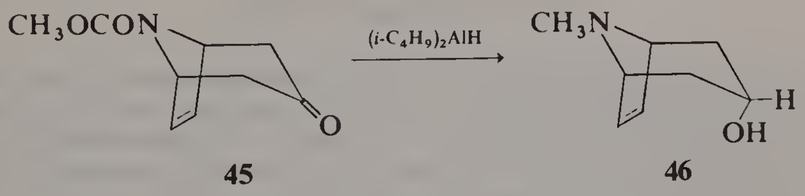
The bicyclic ketone (**43**) obtained by the 3 + 4 cyclocoupling reaction (TABLE 3) is readily converted to carbocamphenilone (**44**, SCHEME 13), a terpenic α-diketone, by catalytic hydrogenation, followed by selenium oxide oxidation.[10] Permanganate oxidation of **44** leads to camphenic acid.



SCHEME 13

Tropane Alkaloids

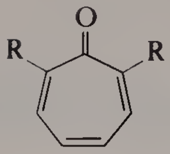
The aza bicyclic ketone, **45**, formed from tetrabromoacetone and *N*-carbomethoxypyrrole, is reduced stereoselectively[11] to 6,7-dehydrotropine (**46**) by treatment with diisobutylaluminum hydride (SCHEME 14). This product is a common intermediate for the synthesis of all naturally occurring tropane derivatives, and this method therefore marks the realization of a new, general synthesis of the alkaloid family.[12]



SCHEME 14

Alkylated Tropones and γ-Tropolones

2,7-Dialkylated 4-cycloheptenones, listed in TABLE 1, are synthetic intermediates of various troponoid compounds. The alkylated tropones (**47**) and γ-tropolones (**48**) have been prepared through a bromination-dehydrobromination procedure.[2] 8-Oxabicyclo[3.2.1]oct-6-en-3-ones, produced by the reaction of dibromoketones and furan, also serve as precursors of troponoid compounds.[13] 2,6-Nonamethylenetropone (**49**), a bridged tropone, or troponophane, has been prepared from the adduct of 2,12-dibromocyclododecanone and furan.



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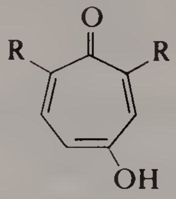

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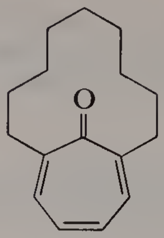
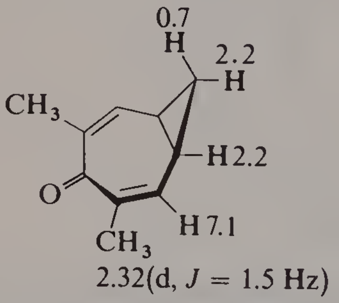


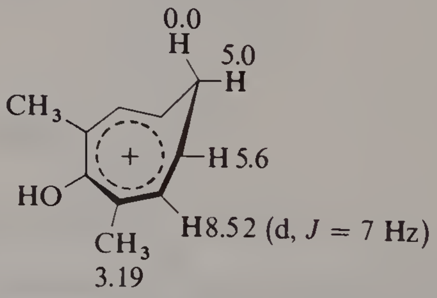
49

4,5-Homotropones

Cyclopropanation of 2,7-dimethyl-4-cycloheptenone with diazomethane—Cu(II) catalyst, followed by bromination-dehydrobromination, yields the 4,5-homotropone, **50**, which, in sulfuric acid, exists as the homoaromatic hydroxyhomotropylium ion **51**.[14]



nuclear magnetic resonance (nmr) of **50** in carbon tetrachloride, δ from tetramethylsilane as the external standard



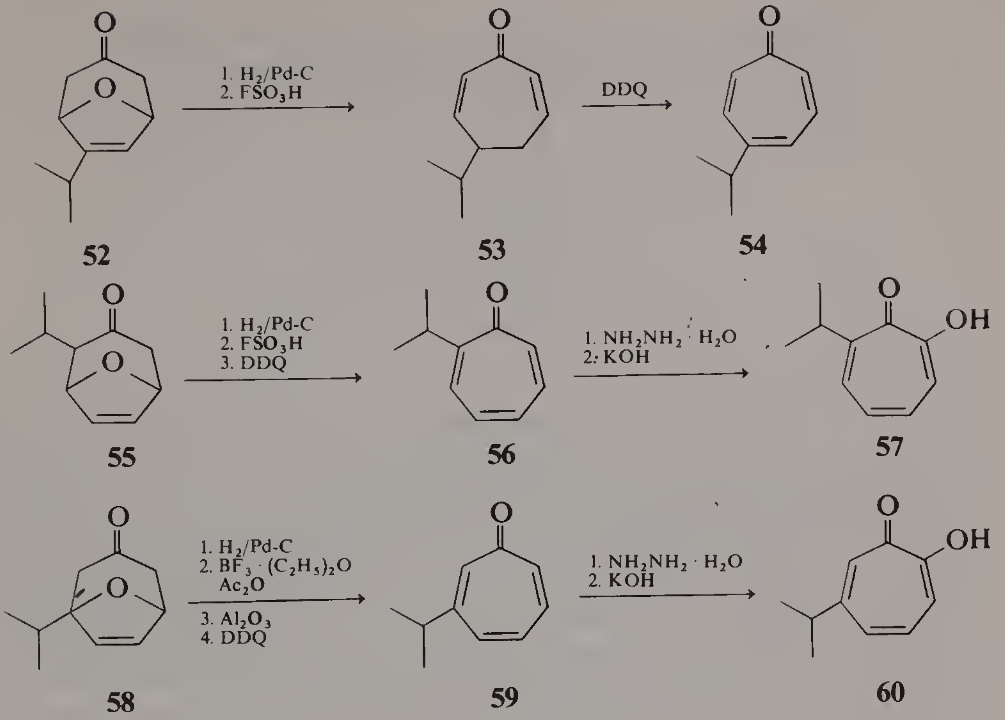
nmr of **51** in 96% H_2SO_4, δ from tetramethylsilane as the external standard

Natural Troponoid Compounds

The iron carbonyl-aided reaction of polybromoketones and furan derivatives (TABLE 3) is useful in the synthesis of naturally occurring troponoid compounds. Hydrogenation of ketone **52**, followed by treatment with fluorosulfuric acid affords the cross-conjugated dienone, **53** (SCHEME 15). Subsequent aromatization with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone gives nezukone (**54**).[15] In a similar fashion, bicyclic ketone **55** is converted to tropone **56**, hydroxylation of which gives rise to α-thujaplicin (**57**).[5] Ketone **5** is also transformed to β-thujaplicin (**60**) via tropone **59**.[5]

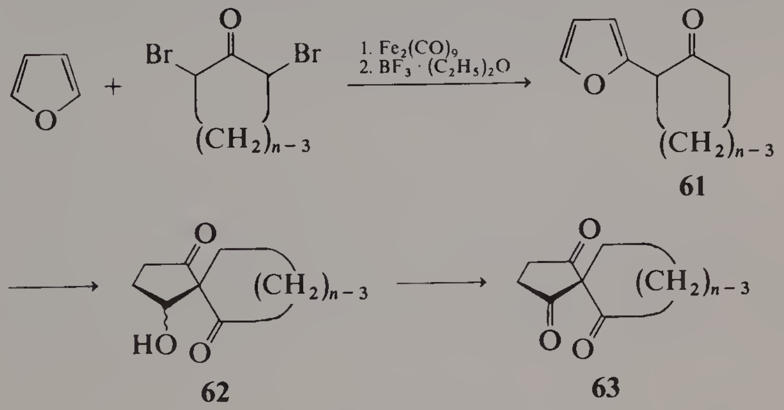
Spiro-Fused β,β′-Triketones

The reaction of furan and α,α′-dibromocycloalkanones with the aid of $Fe_2(CO)_9$, followed by treatment with borontrifluoro etherate affords the 1 : 1 adduct, **61** (SCHEME 16). The furan derivative can be transformed into the hydroxy spiro β-diketone, **62**, by sequential treatment with Br_2—CH_3OH, hydrogen—Rh/Al_2O_3, aqueous hydrochloric acid, and sodium bicarbonate. Finally, chromic oxidation of



SCHEME 15

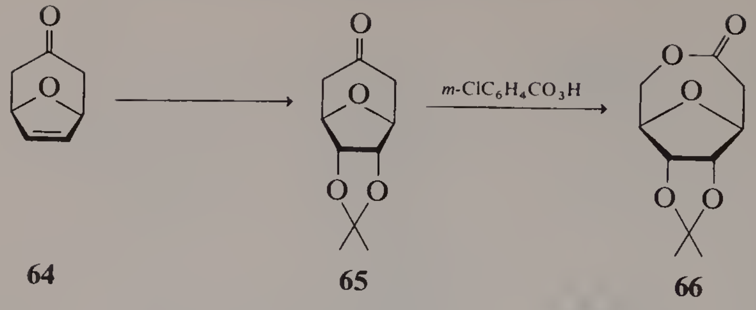
62 gives rise to the spiro-fused β,β'-triketone, **63**. Ultraviolet spectra of such triketones exhibit n-π^* bands with an unusually large extinction coefficient that arises from the unique arrangement of three carbonyl groups. For example, **63** ($n = 5$) shows a band at 291 nm, with $\varepsilon = 301$ ($CHCl_3$).



SCHEME 16

C-Nucleosides

The unsaturated ketone, **64**, is converted with perfect stereoselectivity to glycol acetonide **65** (SCHEME 17) by reaction with H_2O_2/OsO_4, followed by treatment with acetone/$HClO_4$. Its Baeyer-Villiger oxidation yields lactone **66**, which is an intermediate for the general synthesis of C-nucleosides. Apparently, the efficiency of this direct approach is based on the ready availability of oxa bicyclic ketone **64** through the cyclocoupling reaction of tetrabromoacetone and furan.



SCHEME 17

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INDUSTRIAL ORGANIC CHEMICALS THROUGH UTILIZATION OF SYNTHESIS GAS

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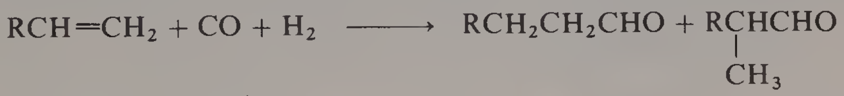
This paper will emphasize two areas of homogeneous transition metal catalysis. These areas concern the present or potential commercial synthesis of two large-volume organic chemicals, aldehydes produced by hydroformylation, or the oxo reaction, and ethylene glycol. The aldehydes are used to make monohydric alcohols for plasticizers, esters, or detergents; the principal uses of ethylene glycol are as an antifreeze agent or for polyester fabrics. Both products are produced in billion-pound quantities each year.

Synthesis gas, that is, a mixture of hydrogen and carbon monoxide, is an important raw material for industrial organic chemicals and is expected to increase in importance during the next decade. It can be produced from a variety of carbonaceous sources, ranging from coal to garbage. In the hydroformylation processes, the part that it contributes to the aldehyde product varies from 51% of propionaldehyde to 14% of a detergent range product and is 42% of butyraldehyde, the major single product. However, the potential ethylene glycol process would utilize 100% of a 3:2 hydrogen/carbon monoxide mixture. Presently, synthesis gas is the sole raw material for the latest technology in methanol and acetic acid manufacture.

The hydroformylation of olefins to produce aldehydes, and ultimately alcohols or acids, is conducted in practically every major industrial country. Until the last year, every announced plant has used cobalt as a catalyst. The general reaction is depicted in SCHEME 1.

The mechanism for this reaction was proposed by Heck and Breslow in 1960[2] and is shown in SCHEME 2.

The cobalt-catalyzed hydroformylation depicted in SCHEME 1 is beset with several difficulties. The linear isomer is of higher value than is the branched isomer, and only little control can be exercised over the reaction. Cobalt hydrocarbonyl is a volatile, unstable complex that is difficult to separate from the products and recycle into the system. The high temperatures usually employed promote the

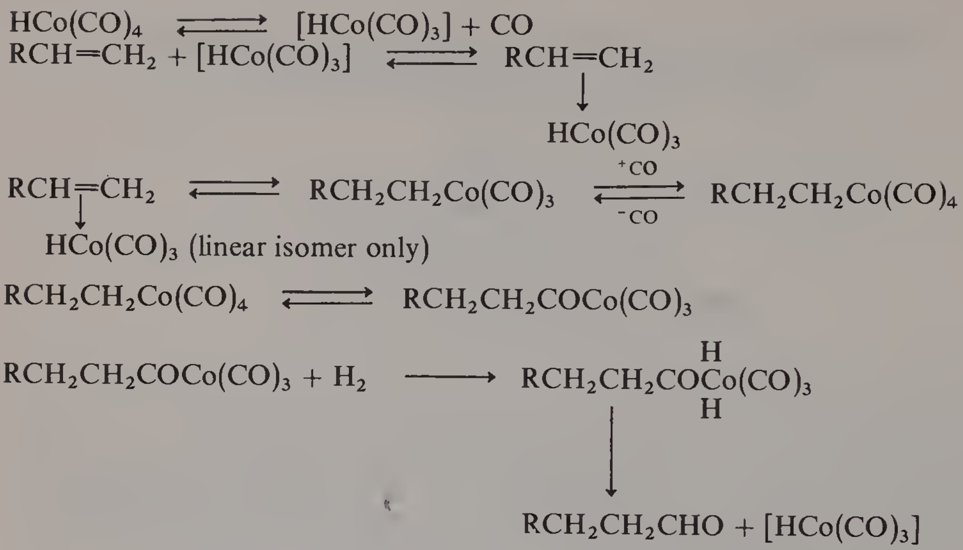


$$RCH{=}CH_2 + CO + H_2 \longrightarrow RCH_2CH_2CHO + \underset{\displaystyle CH_3}{\underset{|}{RCHCHO}}$$

Catalyst: $HCo(CO)_4$
Conditions: 150–180°C, 3000–6000 psi
By-products: alkane, alcohols, aldol condensation products
(catalyzed by Co^{2+}), ketone

Kinetics[1]: $-\mathrm{d}\,\dfrac{[\text{olefin}]}{\mathrm{d}t} = k[\text{olefin}][\text{Co}][H_2][\text{CO}]^{-1}$

SCHEME 1. Cobalt-catalyzed hydroformylation.



$$HCo(CO)_4 \rightleftharpoons [HCo(CO)_3] + CO$$

$$RCH{=}CH_2 + [HCo(CO)_3] \rightleftharpoons \underset{\overset{\downarrow}{HCo(CO)_3}}{RCH{=}CH_2}$$

$$\underset{\overset{\downarrow}{HCo(CO)_3\ \text{(linear isomer only)}}}{RCH{=}CH_2} \rightleftharpoons RCH_2CH_2Co(CO)_3 \underset{-CO}{\overset{+CO}{\rightleftharpoons}} RCH_2CH_2Co(CO)_4$$

$$RCH_2CH_2Co(CO)_4 \rightleftharpoons RCH_2CH_2COCo(CO)_3$$

$$RCH_2CH_2COCo(CO)_3 + H_2 \longrightarrow RCH_2CH_2CO\overset{H}{\underset{H}{Co}}(CO)_3 \longrightarrow RCH_2CH_2CHO + [HCo(CO)_3]$$

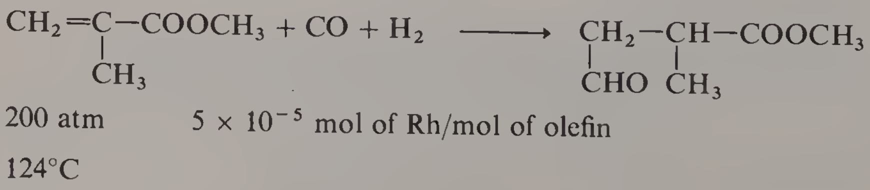
SCHEME 2. Mechanism of the hydroformylation reaction.

formation of by-products, such as alcohols and aldol condensation products. The alcohols form acetals with the aldehydes and complicate the separation schemes. Some alkane is usually formed by hydrogenolysis of the alkyl cobalt carbonyl intermediate, and ketone is produced by the bimolecular reaction of alkyl and acyl cobalt carbonyl.

All of these deficiencies have been accounted for by the use of rhodium as a catalyst, with excess triphenylphosphine used as the ligand modifier. In addition, the reaction proceeds at low pressure. Union Carbide has successfully commercialized this catalyst system in two large plants. Efficiencies to the desired aldehyde are high, and by-product formation is very low.

Rhodium is an extremely active metal in hydroformylations, as shown in SCHEME 3. Other metals of group VIII will effect the reaction but are much less active. Iridium gave lower yields, with significant hydrogenation being noted. Ruthenium has only slight activity.[3]

The most effective conditions for obtaining high ratios of linear aldehyde are hydroformylation at 90–110°C, use of a high phosphorus/rhodium ratio, such as 50 : 1 or 100 : 1, and a low partial pressure of carbon monoxide. The principal factor that determines the amount of linear isomer obtained is believed to be steric, with multiple substitution of phosphorus ligand on the rhodium substrate. High phosphorus/rhodium ratios and a low partial pressure of carbon monoxide favor this type of complex in the substitution equilibrium depicted in SCHEME 4.

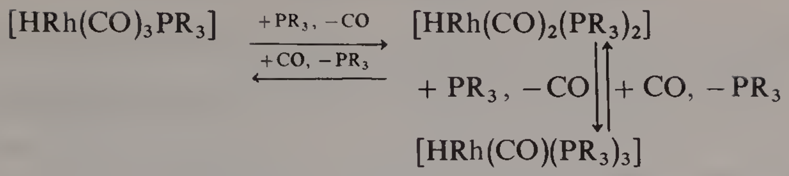


$$CH_2{=}\underset{\overset{|}{CH_3}}{C}{-}COOCH_3 + CO + H_2 \longrightarrow \underset{\overset{|}{CHO}}{CH_2}{-}\underset{\overset{|}{CH_3}}{CH}{-}COOCH_3$$

200 atm $\quad 5 \times 10^{-5}$ mol of Rh/mol of olefin

124°C

SCHEME 3. Activity of rhodium as a catalyst.



$$\begin{tikzcd}[HRh(CO)_3PR_3] \arrow[r, shift left, "+PR_3,\ -CO"] & {[HRh(CO)_2(PR_3)_2]} \arrow[l, shift left, "+CO,\ -PR_3"] \arrow[d, shift right, "+PR_3,\ -CO"'] \\ & {[HRh(CO)(PR_3)_3]} \arrow[u, shift right, "+CO,\ -PR_3"'] \end{tikzcd}$$

SCHEME 4. Catalyst equilibria.

It was found that these equilibria, as reflected by isomer ratio, also depend on the type of PR_3 ligand. More basic phosphines, such as trialkylphosphines, which have strong donor and poor acceptor properties, give relatively poor isomer ratios. Multiple substitution of phosphine is not favored under these conditions. The best ligands for high isomer ratios are phosphites or triarylphosphines. A further constraint is the fact that triarylphosphines or phosphites substituted in the *ortho* position are much less desirable, as shown in TABLE 1.

These results demonstrate that increasing ligand size is also an important factor for multiple substitution, and ultimately, aldehyde isomer ratio. Tolman *et al.*[4] have shown similar size effects on multiple substitution and bond strengths in the formation of $Ni(PR_3)_x$ complexes.

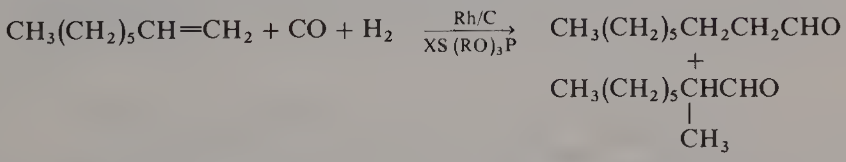
A summary of the relative activity and performance of cobalt and rhodium for the hydroformylation of a linear hydrocarbon α-olefin, oct-1-ene, is given in SCHEME 5. It must be recognized that differences in isomer ratios above about 10 : 1 have relatively little meaning. A change in the isomer ratio of from 2 : 1 to 4 : 1 reflects a difference in composition of 13 %, whereas a change of from 15 : 1 to 20 : 1 represents only a 1.4 % change in composition.

Olefins substituted with groups other than alkyl have provided interesting results. Ethyl acrylate was hydroformylated with rhodium and without phosphine ligand. The reaction proceeded almost exclusively to the terminal carbon, forming ethyl β-formylpropionate. However, addition of tributylphosphine resulted in almost exclusive (98 %) formation of the α-substituted ester.[5] It is concluded that the electronic effects due to the presence of the carboethoxy group are more controlling than are steric effects for this type of olefin.

The hydroformylation of styrene with cobalt gives much more hydrogenation than hydroformylation. Yields of ethylbenzene as high as 70 % have been noted.[1] With rhodium catalysts, the yields of ethylbenzene are insignificant; the reaction proceeds smoothly to give mixtures of α-phenyl α-methylacetaldehyde and β-phenylpropionaldehyde.

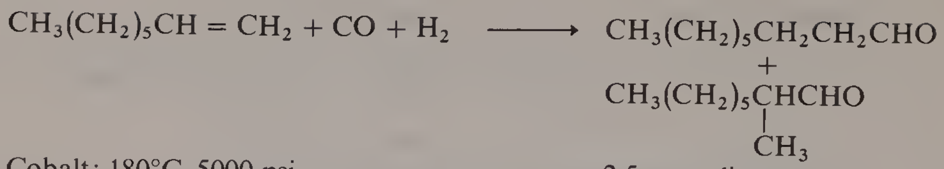
TABLE 1

COMPARISON OF PHOSPHORUS LIGANDS



$$CH_3(CH_2)_5CH{=}CH_2 + CO + H_2 \xrightarrow[XS\ (RO)_3P]{Rh/C} CH_3(CH_2)_5CH_2CH_2CHO + CH_3(CH_2)_5\underset{\displaystyle CH_3}{\underset{|}{C}}HCHO$$

R in $(RO)_3P$	Straight-Chain Aldehyde (%)
Phenyl	82
p-Diphenyl	85
o-Diphenyl	52
o-Methylphenyl	78
o,o-Dimethylphenyl	47



$$CH_3(CH_2)_5CH=CH_2 + CO + H_2 \longrightarrow CH_3(CH_2)_5CH_2CH_2CHO + CH_3(CH_2)_5\underset{\displaystyle CH_3}{\underset{|}{C}}HCHO$$

Cobalt: 180°C, 5000 psi	2.5 parts linear 1.0 part branched
Rhodium: 130°C, 200 psi	3.0 parts linear 7.0 parts branched
Rh + XS PPh_3: 110°C, 100 psi	15 parts linear 1 part branched

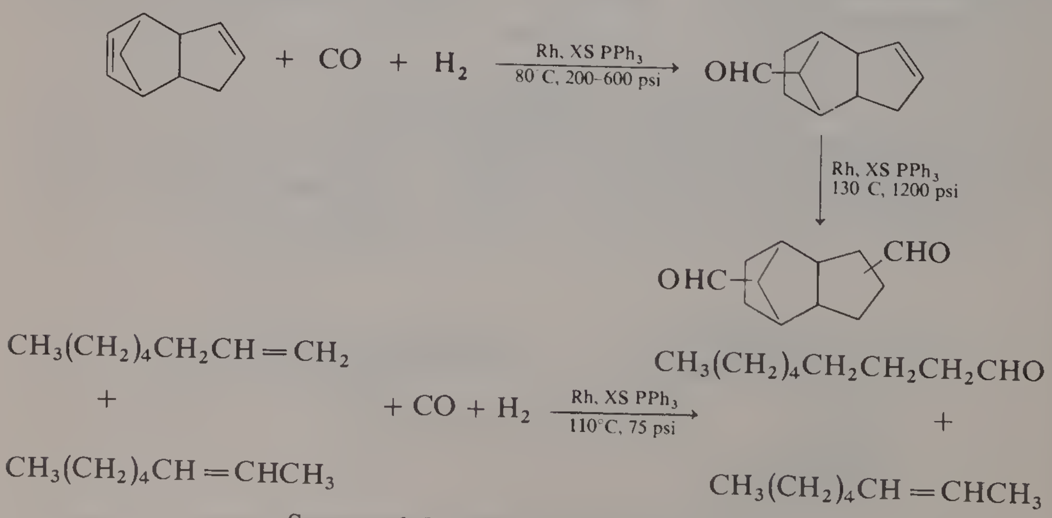
SCHEME 5. Comparison of cobalt and rhodium.

Tetrasubstituted alkenes are not hydroformylated with cobalt catalysts. Direct hydroformylation does not occur with rhodium either. However, isomerization of tetramethylethylene to α-olefin, followed by selective hydroformylation to 3,4-dimethylpentaldehyde proceeded smoothly.

Hydroformylation of dicyclopentadiene with rhodium catalysts has revealed differences in reactivity between strained-ring double bonds and unstrained C_5 olefinic bonds. The strained-ring olefin is hydroformylated easily, and the monoaldehyde can be isolated in good yields. Application of more forcing conditions (130°C, 1200 psi of synthesis gas) caused the free cyclopentene ring to enter into the reaction, and good yields of the dihydroformylated product have also been obtained. This dialdehyde has been hydrogenated to a diol and also reductively aminated to a diamine.

The selectivity of the rhodium catalyst—triphenylphosphine system was also demonstrated by hydroformylation of a mixture of oct-1-ene and oct-2-ene under mild conditions. Good yields of the linear isomer were again obtained from the α-olefin, whereas oct-2-ene did not react under the cited conditions. This result, in addition to results obtained with dicyclopentadiene, are illustrated in SCHEME 6.

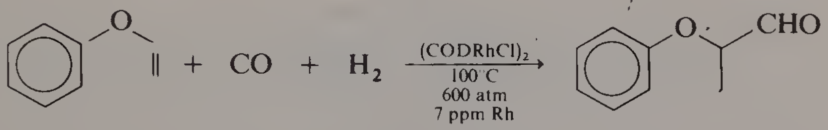
Aside from the very important issue of maximum efficiency to linear aldehyde, the commercial processes for hydroformylation have been deeply concerned with catalyst-product separation and catalyst recycling. Many schemes have been devised for this purpose with cobalt, including such methods as thermal decomposition to



SCHEME 6. Influence of olefinic type.

cobalt metal, extraction as cobalt formate followed by regeneration of the hydrocarbonyl, or extraction under pressure. Catalyst conservation is certainly of importance for the expensive metal rhodium, and several methods of conservation and recycling have been proposed.

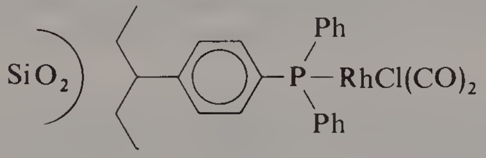
One method is an absolute minimum usage of rhodium in the system to minimize losses. Recovery and recycling can then be effected by normal chemical extractive means. Workers at BASF[6] have shown that as little as 7 ppm of rhodium may be sufficient for the chemical reaction shown in SCHEME 7.



SCHEME 7

Pruett and Smith[7] have discussed the effectiveness of a method in which the reaction is conducted in a high-boiling solvent, including condensation products of the product, followed by removal of the product by direct distillation, and recycling the complete residue to the reaction zone with no loss of catalyst.

Effective means of attaching the rhodium to a solid surface have received much attention. One such catalyst, employed for the production of propionaldehyde, has been described[8] and is illustrated in SCHEME 8.

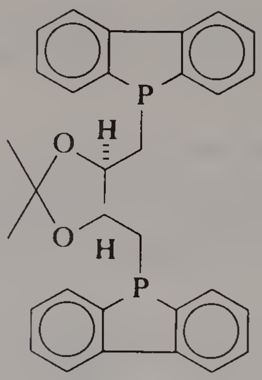


$CH_2{=}CH_2 + CO + H_2 \longrightarrow CH_3CH_2CHO$
Vapor phase, 100°C, 1 atm
$r = k[H_2][C_2H_4][CO]^{-0.5}$

SCHEME 8. Heterogeneous catalysts.

A most interesting method of catalyst retention was devised by Bayer and Schurig.[9] A polymer of styrene, with an average molecular weight of 100,000 and still soluble, was treated by chloromethylation, followed by $KPPh_2$, to give phosphine groups attached to the polymer. Digestion with $HRh(CO)(PPh_3)_3$ then gave a soluble catalyst of large molecular weight. After hydroformylation was complete, the product was removed with catalyst retention by a semipermeable membrane.

Many interesting variations on the hydroformylation theme have been published recently that are outside any area of our work. Whyman[10] has studied the infrared patterns for each step in the hydroformylation sequence by use of iridium as the catalyst and ethylene as the olefinic substrate (iridium gives a more stable intermediate). Chini *et al.*[11] have reported on a stoichiometric reaction of olefin, hydrogen, and $Rh_4(CO)_{12}$ to form aldehyde and $Rh_6(CO)_{16}$. Strohmeier and Kuhn[12] have studied rhodium turnover numbers as a function of reaction parameters. Finally, various workers have studied asymmetric hydroformylations by use of optically active phosphine ligands; the results obtained with styrene as the olefin and phosphine compound **1** as the ligand[13] are of special interest.



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The second portion of this paper will describe the results we have obtained in the direct synthesis of ethylene glycol from carbon monoxide and hydrogen, catalyzed by rhodium carbonyl species. This product is one of many that can be considered with these raw materials as the sole reactants. A partial list is given in TABLE 2; this Table is given to exemplify two types of products and the thermodynamics of their formation at 500°K.

It can be seen that formation of the ultimate hydrogenation products, alkane and water, is the favored reaction. The reaction to form methanol is unfavorable at the temperatures normally employed in commercial practice. Pressure is therefore required for formation of significant quantities in the gaseous mixture, and conversions of less than 50% are normally realized. The equilibrium constant is highly temperature dependent; the constant increases to greater than unity below about 130°C.

Direct condensation to other oxygenated products, without loss of water, becomes even less favorable as the carbon chain grows in length. However, because the number of moles of gas required to produce 1 mol of product also increases, and therefore the effect of pressure will increase logarithmically, the application of moderate pressure will be sufficient to yield significant quantities of a product like ethylene glycol. In fact, the compound erythritol, which requires the condensation of 4 mol of CO with 5 mol of H_2 for its synthesis, has been identified in minor quantities as a reaction product.

It has been found that rhodium, particularly in combination with promoters, such as 2-hydroxypridine, *o*-phenanthroline, pyridine, and cesium acetate, catalyzes the formation of ethylene glycol at temperatures of 210–250°C. At pressures of 18,000–25,000 psi, the reaction rates are very high. Rhodium may be added in any convenient form, such as dicarbonylacetylacetonatorhodium(I), hexarhodium hexadecacarbonyl, or tetrarhodium dodecacarbonyl. Other products formed to varying degrees are methanol, glycerin, ethanol, propylene glycol, and erythritol.

TABLE 2

SOME REACTIONS OF SYNTHESIS GAS

Reaction	ΔG_{500} 14	Log K_p
$CO + 3H_2 \longrightarrow CH_4 + H_2O$	-23.02	10.065
$CO + H_2 \longrightarrow CH_2O$	$+12.11$	$-$ 5.293
$CO + 2H_2 \longrightarrow CH_3OH$	$+$ 5.08	$-$ 2.222
$2CO + 3H_2 \longrightarrow HOCH_2CH_2OH$	$+15.77$	$-$ 6.891
$3CO + 4H_2 \longrightarrow HOCH_2CH(OH)CH_2OH$	$\sim +26$?	

Only methanol and glycerin are formed to a significant degree; the amounts of these coproducts and of the more minor components differed as the reaction parameters, such as the promoters, were varied. Efficiencies in the range of 75% have been obtained for the most desirable product, ethylene glycol. No methane formation was observed with these systems.

Other metals of group VIII were tested for activity under similar conditions, including cobalt, ruthenium, copper, manganese, iridium, and platinum. Only cobalt was found to have slight activity.[15a,b] Our results qualitatively agreed with those of Ziesecke.[15b]

Some of the experimental results obtained with rhodium at 18,000–20,000 psi, with and without amine promoters, are listed in TABLE 3. These data were obtained from experiments that were not optimized for maximum glycol rates; the data were chosen to illustrate the effects of some reaction variables and the product distribution obtained. Experiment 2 shows a typical product distribution. Experiments 1 and 4 demonstrate that tetraglyme is a preferred solvent over tetrahydrofuran (THF) and monoglyme. In experiment 1, a 10°C higher temperature was required to produce the same quantity of glycol as that obtained in experiment 2. The amount of methanol produced was greater, whereas the rate of glycerin formation was reduced. Experiment 3 shows the effect of omitting the promoter; the rate of glycol formation was reduced dramatically. Experiment 5 indicates that methanol is not an intermediate in glycol formation.

Infrared studies have been made of solutions that contained catalysts under pressures of 8000–15,000 psi and temperatures from ambient to above 200°C. A typical spectrum at 180°C has revealed strong terminal carbonyl absorption in the range of 2000–2050 cm^{-1} (complicated by solvent overtones and carbon mono-

TABLE 3

EXPERIMENTAL CONDITIONS AND PRODUCTS

Conditions*	Products (g)
1. $Rh(CO)_2(acac)$, 0.04 mol/liter; THF, 75 ml; 2-HP, 1.1 g; 1 : 1 H_2/CO; 230°C; 20,000 psi; 3 hr	glycol, 18.6 methanol, 7.9 glycerin, 1.7
2. $Rh(CO)_2(acac)$, 0.04 mol/liter; Tg, 75, ml; 2-HP, 1.1 g; 1 : 1 H_2/CO; 220°C; 20,000 psi; 3 hr	glycol, 16.1 methanol, 3.9 glycerin, 2.7 propylene glycol, 1.2
3. $Rh(CO)_2(acac)$, 0.03 mol/liter; Tg, 75 ml; 1.5 : 1 H_2/CO; 220°C; 18,000 psi; 4 hr	glycol, 1.2 methanol, 2.6 glycerin, 0
4. $Rh(CO)_2(acac)$; 0.04 mol/liter; glyme, 75 ml; 2-HP, 1.1 g; 1 : 1 H_2/CO; 220°C, 20,000 psi; 3 hr	glycol, 9.6 methanol, 3.0 glycerin, 1.9
5. $Rh(CO)_2(acac)$; 0.04 mol/liter; methanol, 75 ml; 2-HP, 1.1 g; 1 : 1 H_2/CO; 220°C; 20,000 psi; 3 hr	glycol, 8.9 methanol, not measured glycerin, not measured

* Abbreviations: acac, acetylacetonate; THF, tetrahydrofuran; 2-HP, 2-hydroxypyridine; Tg, tetraglyme or tetraethyleneglycol dimethyl ether.

TABLE 4
EFFECTS OF ALKALI METAL CATIONS

Salt Added	Glycol (g)	Methanol (g)
—	1.0	2.1
LiOAc	1.65	1.72
NaOAc	2.57	1.34
KOAc	2.15	0.89
CsOAc	3.90	1.58
$Ba(OAc)_2$	0.65	0.70

xide absorption) and a three-band pattern at 1869, 1838, and 1785 cm^{-1}, bridging carbonyl region, medium absorption. This spectrum matches that reported by Martinengo and Chini[16] for the anionic species $[Rh_{12}(CO)_{\sim 34}]^{2-}$.

The hypothesis that anionic species play an important role in the catalytic sequence, as suggested by infrared data, was reinforced by studies with added cations. Addition of the acetate salts of alkali metals caused increased rates of formation of ethylene glycol, as shown in TABLE 4. All of the experiments listed in this Table were conducted under the following conditions: 8000 psi of 1 : 1 H_2/CO synthesis gas, 220°C, 75 ml of tetraglyme as the solvent, 3 mmol of rhodium, 10 mmol of 2-hydroxypyridine, and 0.50 mmol of the salt; the reaction time was 4 hr.

The first experiment listed contained no added alkali metal cation. The succeeding results demonstrate the effect of increasing cation size. The amount of ethylene glycol increased from 1.65 g with lithium to 3.90 g with cesium acetate, whereas the amount of by-product methanol obtained did not change in any distinct manner. The effect of a large divalent cation was shown by the use of barium acetate.

In addition to the size of the alkali metal cation, the quantity added to the reaction mixture had a significant effect on the amount of glycol produced during the standard 4-hr experiment; these results are summarized in TABLE 5. The reaction conditions were as follows: 8000 psi of 1 : 1 synthesis gas, 220°C, 75 ml of tetraglyme as the solvent, 3 mmol of rhodium, and 10 mmol of 2-hydroxypyridine.

From the above data, it can be seen that the quantity of alkali metal is very important. The rate of glycol formation increased with increasing amounts of cesium formate up to a point, then decreased with further addition of salt. At higher levels of cesium formate, the amount of glycol was suppressed below the amount produced with no salt. The optimum amount of glycol was produced with a cesium/rhodium ratio of about 1 : 6. This finding agrees with the ratio in the compound

TABLE 5
EFFECTS OF VARYING CATION/RHODIUM RATIO

HCOOCs (mmol)	Glycol (g)	Methanol (g)
0	1.00	2.00
0.25	2.35	2.39
0.33	3.25	1.88
0.50	4.25	1.66
0.75	1.15	4.30
1.0	0.55	5.92
2.0	0.25	6.41
3.0	0.10	0.86

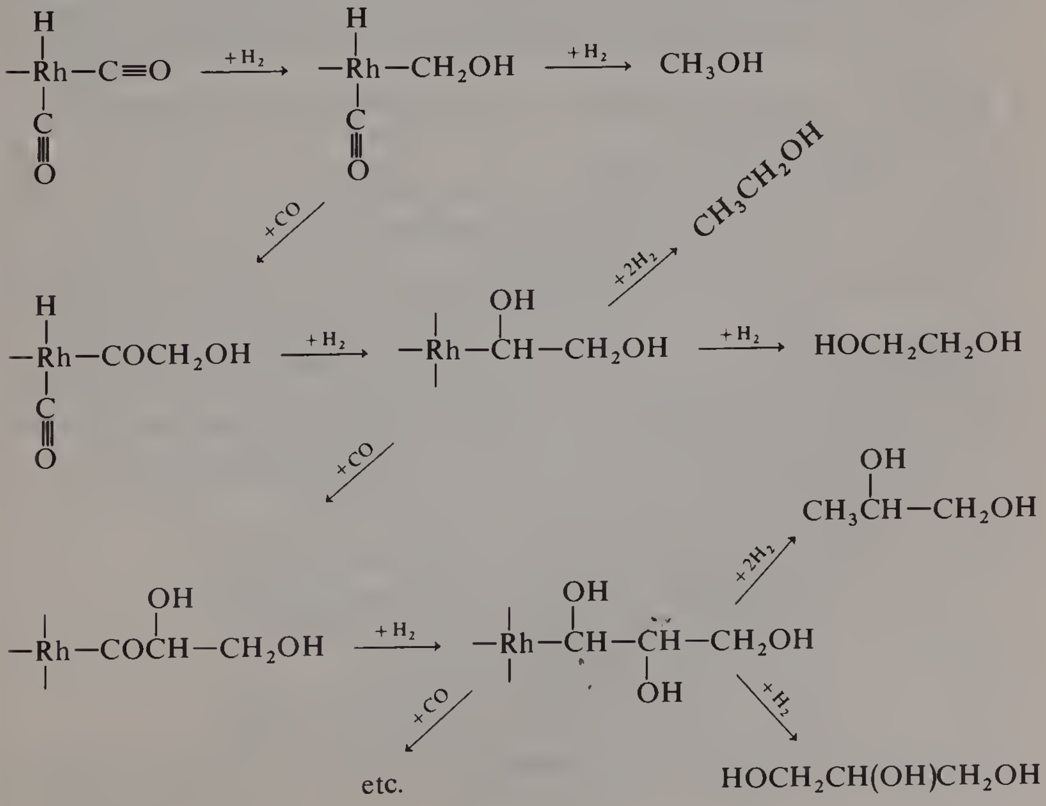
TABLE 6
BIS(TRIPHENYLPHOSPHINE)IMINIUM CATION

P_2N^+ (mmol)	Glycol (g)	Methanol (g)
0.5	3.6	1.8
0.625	4.95	1.4
0.75	4.80	1.5
0.875	4.20	1.8

$Cs_2[Rh_{12}(CO)_{\sim 34}]\cdot$solvate, which was seen in the infrared spectrum of a solution under elevated conditions of temperature and pressure. However, the methanol rate continued to increase far beyond the 1 : 6 ratio, suggesting that this type of species is less important for methanol formation.

Similar behavior was observed with utilization of a large cation, bis(triphenylphosphine)iminium, which was added as the acetate; these data are summarized in TABLE 6. These experiments were conducted under the same conditions of temperature and pressure as those in TABLES 1 and 2, except that 1.25 mmol of pyridine were used as the promoter. In this case also, the optimum amount was approximately correct for a cation/rhodium ratio of 1 : 6. The principal product ratio of 78% glycol and 22% methanol should also be noted.

The mechanism by which ethylene glycol is formed is not known. The product distribution of methanol, ethylene glycol, ethanol, glycerin, propylene glycol, and erythritol suggests a hydroxymethylene growth reaction, as outlined in SCHEME 9, but definite proof is not yet available.



SCHEME 9.

The hydroxymethyl—metal type of intermediate essential to this mechanism has not been experimentally demonstrated but has been suggested by Wilkinson *et al.*[3] and by Henrici-Olive and Olive.[17] In both of these reports, the metal used was ruthenium. Henrici-Olive and Olive[17] discussed the Fischer-Tropsch reaction as a methylene growth reaction, in which the product distribution was typified as similar to the polymeric growth distribution. The mechanism depicted was similar to the one proposed in this paper, up to the point of formation of the hydroxymethylene intermediate. This intermediate could either cleave to give alcohol (e.g., methanol) or *dehydrate* to give a methylene—metal bond, which then would be subjected to hydrogenation, carbon monoxide insertion, and hydrogenation to generate the next carbon chain length.

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NEW ORGANOCOPPER SYNTHETIC METHODS. α,β-DIALKYLATION OF α,β-ETHYLENIC KETONES: SYNTHESIS OF SESQUITERPENES*

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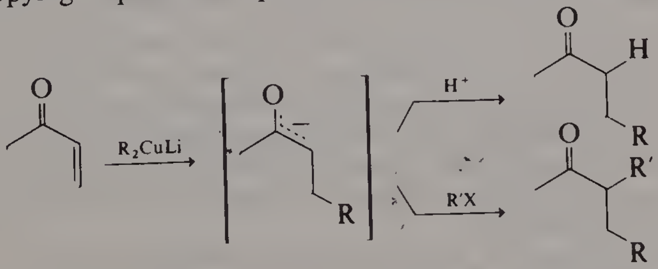
The place of organocopper reagents in organic synthesis is now well established.[1] The widespread use of these relatively new reagents is based largely on their ease of preparation and on their ability to effect transformations that are difficult or impossible to accomplish with any other reagents. The organocopper reagents often react in a highly selective fashion: stereoselectively, regioselectively, and chemoselectively. These characteristics are important, especially in the construction of complex organic molecules. Perhaps the most noteworthy example of the use of organocopper reagents in complex organic synthesis involves preparation of the E series of prostaglandins.[2] Although they have been used effectively and broadly during the past 10 years, organocopper reagents still pose structural and mechanistic problems; their thermal and air instability preclude their easy isolation, and their aggregation and ability to exist as mixed-valence clusters complicates mechanistic investigations.

Ketones are central to organic chemistry, because they can be converted to many other functional groups and because they can be used for attachment of other carbon units. Due to this key role of ketones, organocopper reagents have been applied to synthesis of ketones from carboxylic acid chlorides,[3] α-haloketones,[4] and α,β-unsaturated ketones.[1] Addition of organocopper reagents to α,β-ethylenic ketones leads regiospecifically to intermediates that can react with some electrophiles (R′X) to form α,β-disubstituted ketones[5] (Scheme 1). Some examples of natural products that are α,β-dialkyl ketones are shown in Scheme 2.

Synthesis of the valerane class of sesquiterpenes is difficult because of presence of two quaternary carbon centers at the ring fusion positions and because of the stereochemical relationship between the angular methyl groups and the pendant isopropyl group. Several possible organocopper β-addition/α-alkylation



Scheme 1. Organocopper β-addition/α-alkylation (α,β-ethylenic ketones → α,β-dialkyl ketones).

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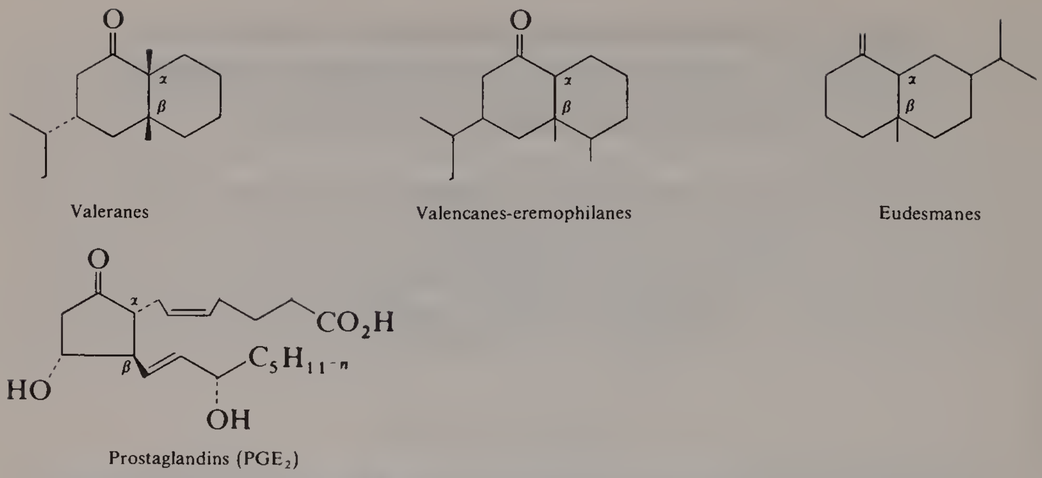
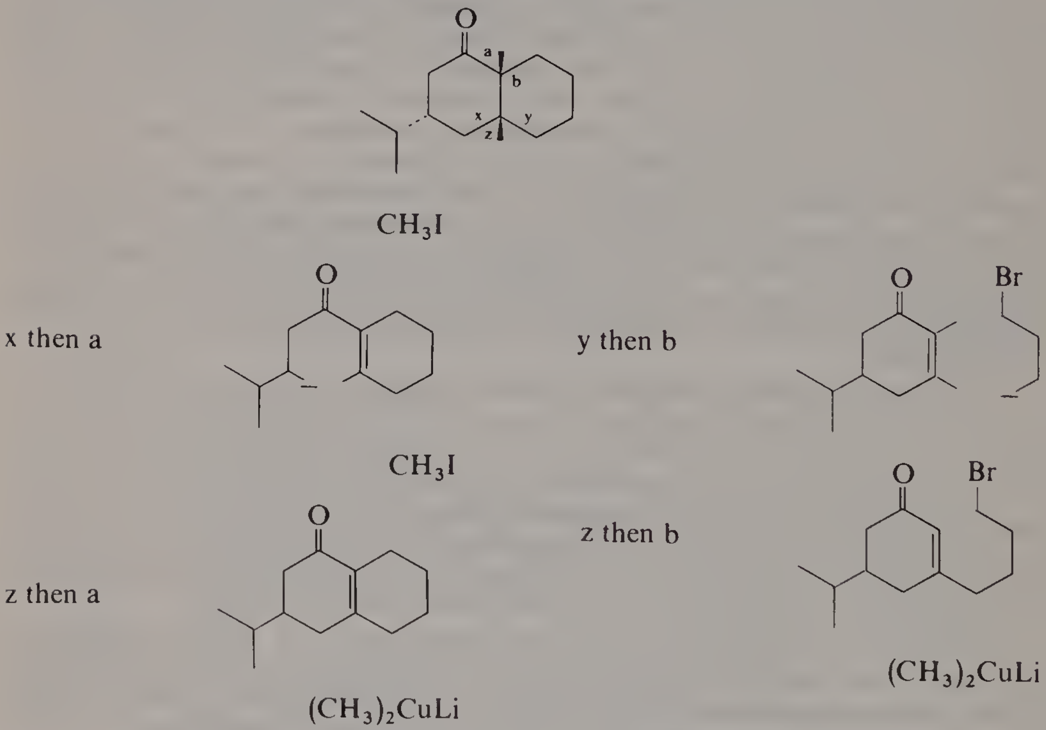
* Supported by National Science Foundation Grants GP-33667 and GP-43419X.



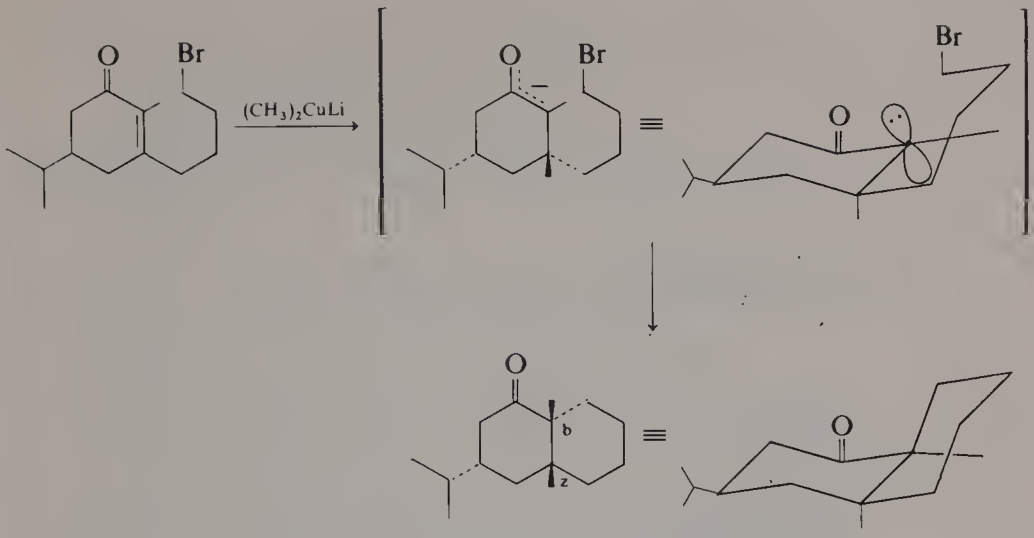
SCHEME 2. Some examples of α,β-dialkyl ketones: decalin sesquiterpenes.



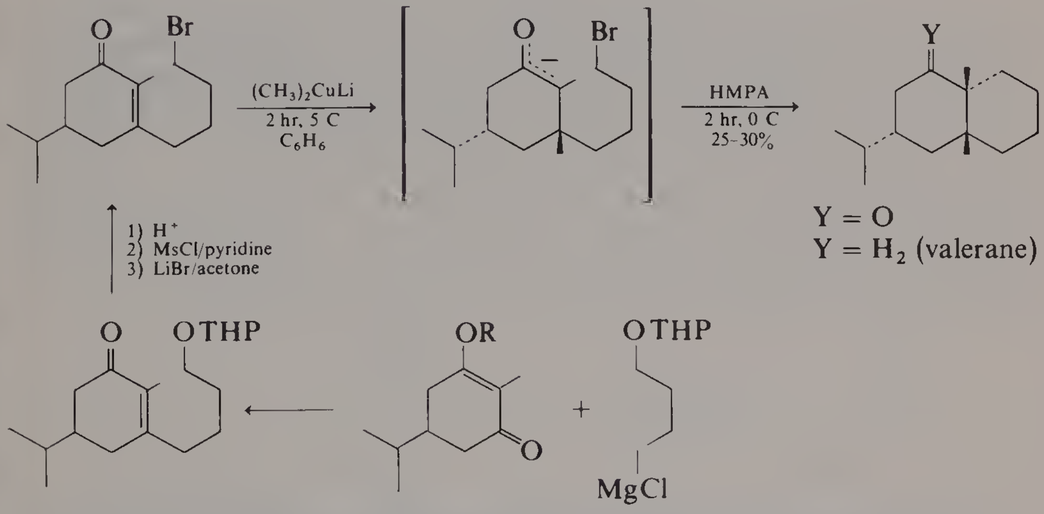
SCHEME 3. Some possible β-addition/α-alkylation sequences.

approaches can be envisioned for construction of the valerane skeleton (SCHEME 3), but only the last sequence seems promising. Lithium dimethylcuprate β-addition to the bromoenone (SCHEME 3), followed by intramolecular cyclization of the resultant intermediate was expected (based on previous analogies) to give the desired *trans*-1,3 relationship between (axial) methyl and (equatorial) isopropyl and the desired *cis*-decalin ring system (cf. SCHEME 4). Indeed, valerane was produced stereospecifically, as shown in SCHEME 5.[5f]

We are now applying this organocopper β-addition/cyclization approach to rapid construction of the pseudoguaiane sesquiterpene skeletal system, as shown in SCHEME 6.[6] This can be an effective new annelation procedure that should find use in construction of other types of α,β-disubstituted hydroazulenones.

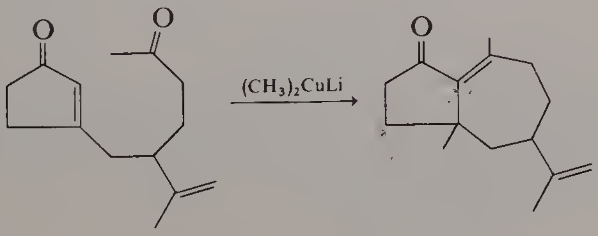


SCHEME 4. Stereochemical considerations.



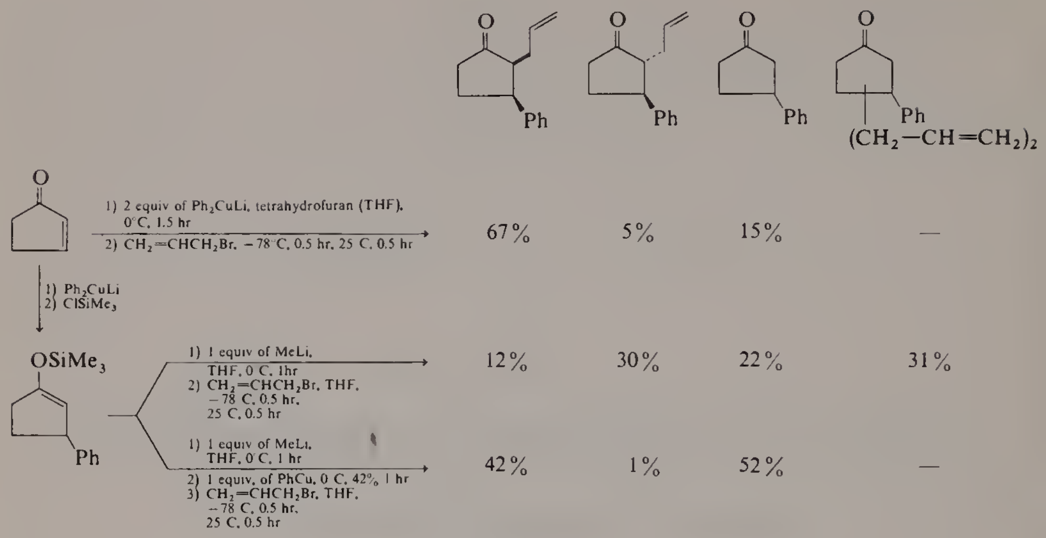
Y = O
Y = H_2 (valerane)

SCHEME 5. Conjugate addition-cycloalkylation: total synthesis of valerane.



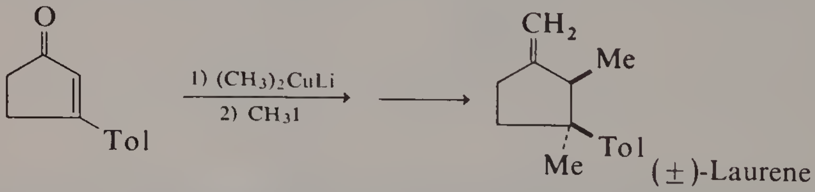
(pseudoguaiane)

SCHEME 6



Scheme 7

Recent chemical evidence indicates that the initial intermediate formed from organocopper addition to an α,β-ethylenic ketone is *not* a simple lithium enolate; the organocopper-generated intermediate is alkylated at a different rate and often with different stereochemistry than is the corresponding lithium enolate (Scheme 7).[7]* Furthermore, at least in the example shown in Scheme 7 for the 3-phenyl cyclopentanone series, an authentic lithium enolate (generated from an enol silyl ether and methyllithium) can react with phenylcopper to give a copper-containing intermediate. The high stereoselectivity with which the copper-containing intermediate can be alkylated on the α-carbon atom has allowed us to prepare sesquiterpene hydrocarbon (±)-laurene in a short, high-yield synthesis.[7]



Thus, organocopper regiospecific and stereoselective α,β-dialkylation of α,β-ethylenic ketones is a new and efficient synthetic method for construction of simple and complex organic molecules.

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CHEMISTRY OF DIENE AND ENONE IRON TRICARBONYL COMPLEXES*

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INTRODUCTION

The way in which the stabilities and reactivities of polyolefins are modified by coordination to transition metals has received considerable attention in recent years. Preparations of stable transition metal complexes of exceedingly reactive polyolefins, which are not normally isolable at ambient temperatures, represent some of the most intriguing and synthetically useful applications to emerge from this area. For example, the iron tricarbonyl moiety has been used successfully to stabilize and render isolable as iron complexes such highly reactive polyolefins as cyclopentadienone,[1] cyclobutadiene,[2] 7-norbornadienone,[3] and trimethylenemethane.[4] As demonstrated by the classic work of Pettit on cyclobutadieneiron tricarbonyl, such complexes can not only be used to "store" the ligand but, through oxidative cleavage of the complex, can also serve as a convenient source of the free polyolefin for use in synthesis.[2]

One particular aspect of this area of chemistry that has occupied our attention over the last few years has been the modification, through binding to transition metals, of the thermal chemistry of cyclic polyolefins capable of undergoing electrocyclic ring-opening and ring-closing reactions. We have observed that binding a metal to polyolefinic systems capable of such valence tautomerism can have substantial effects on both the rates of interconversion of the valence isomers and on the position of the tautomeric equilibrium. The first example of such an observed ring closure was our observation[5] that protonation of cyclooctatetraeneiron tricarbonyl at low temperatures led to the cyclooctatrienyliron tricarbonyl cation, **1**, which undergoes ring closure at $-60°C$ ($\Delta G^{\neq} = 15.7$ kcal/mol) to yield the previously observed bicyclo[5.1.0]octadienyliron tricarbonyl cation, **2** (see SCHEME 1). In this particular case, a meaningful comparison with the free ligand system is difficult to make, because protonation of free cyclooctatetraene leads to the homotropylium ion.[6] A more direct comparison can be made in the case of *cis*^{4}-cyclononatetraene (see SCHEME 1). Whereas *cis*^{4}-cyclononatetraeneiron tricarbonyl (**3**) is stable at room temperature and undergoes ring closure to *cis*-dihydroindeneiron tricarbonyl (**4**) at 100°C ($\Delta G^{\neq} = 28.4$ kcal/mol),[7] free cyclononatetraene undergoes ring closure to *cis*-dihydroindene rapidly at room temperature ($\Delta G^{\neq} \sim 23$ kcal/mol).[8] Thus, the effect of binding iron to the 1,3-diene unit is to raise the free energy of activation for ring closure by about 5 kcal/mol.

A system for which more quantitative data is available involves the equilibrium between 1,3,5-cyclooctatriene (**5**) and bicyclo[4.2.0]octadiene (**6**), established via electrocyclic ring-opening and ring-closing reactions (see SCHEME 1). Huisgen *et al.*

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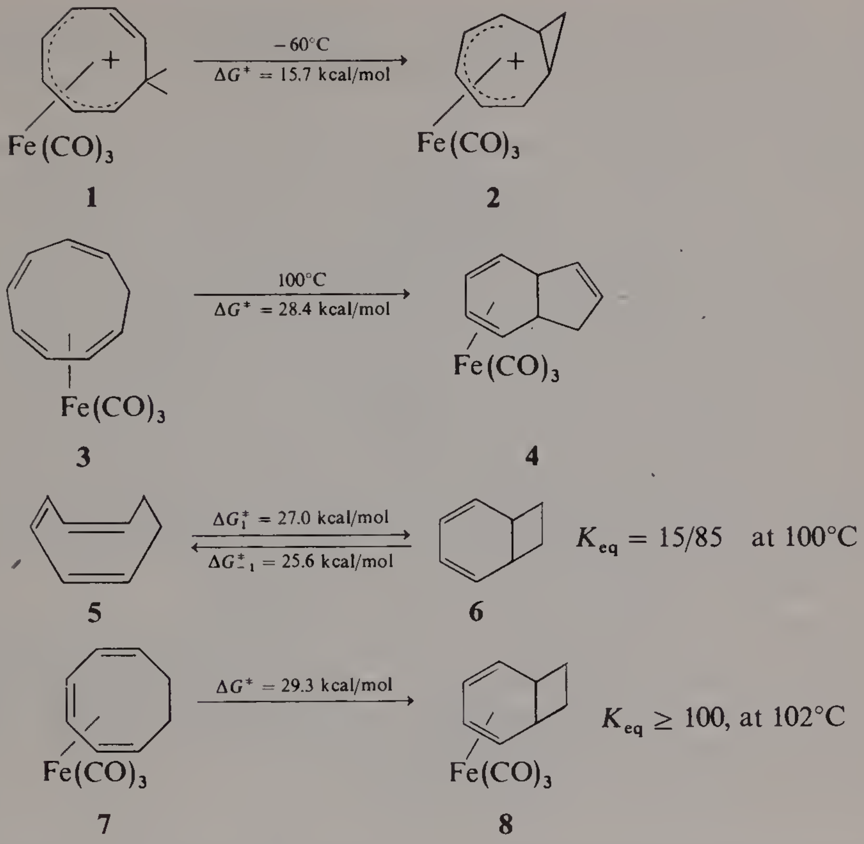
* Supported by National Science Foundation Grant MPS75-01239.



SCHEME 1. Electrocyclic ring closures of polyolefin iron tricarbonyl complexes.

have shown that the triene is favored over the diene by a ratio of 85 : 15 at 100°C, with the free energies of activation for the ring-closing and ring-opening reactions being 27.0 and 25.6 kcal/mol, respectively.[9] We have observed that cyclooctatrieneiron tricarbonyl (**7**) undergoes ring closure to bicyclo[4.2.0]octadieneiron tricarbonyl (**8**) at 102°C ($\Delta G^{\neq} = 29.3$ kcal/mol), with an equilibrium ratio of diene complex/triene complex of greater than 100 at 102°C (SCHEME 1).[10] Comparison of these systems thus allows a determination of the effects of the metal on the rate of ring closure and on the position of the tautomeric equilibrium. Similar to the cyclononatetraene case, the free energy of activation for ring closure of triene **5** has been found to be somewhat increased on binding iron to the diene unit, whereas the equilibrium has been very substantially shifted in favor of the diene isomer in the complexed systems. We ascribed this shift in equilibrium toward the diene isomer as arising from induced ring strain in triene complex **7** due to the distortion of the tub conformation of **5** into an energetically unfavorable conformation in triene complex **7**, in which the four carbons of the bound diene unit must be approximately coplanar.[10]

This specific example has demonstrated that such valence tautomeric equilibria may be significantly displaced by binding such systems to transition metals. If the equilibrium is displaced toward the thermodynamically unfavorable isomer, and if the metal can be readily removed, a synthetically convenient route to the higher-energy isomers results. For example, in cyclooctatriene systems where the triene isomer is highly favored at equilibrium, a convenient synthetic route to the higher-energy diene isomer may be through synthesis of the iron tricarbonyl complex, followed by oxidative cleavage. The feasibility of preparing such dienes as stable complexes has been demonstrated by Cotton and Deganello[11] through the isolation of tricyclo[4.4.0.0^{2,5}]deca-7,9-dieneiron tricarbonyl formed in low yields from the reaction of $Fe_2(CO)_9$ with bicyclo[6.2.0]decatriene, which exists predominantly as the triene isomer in solution.

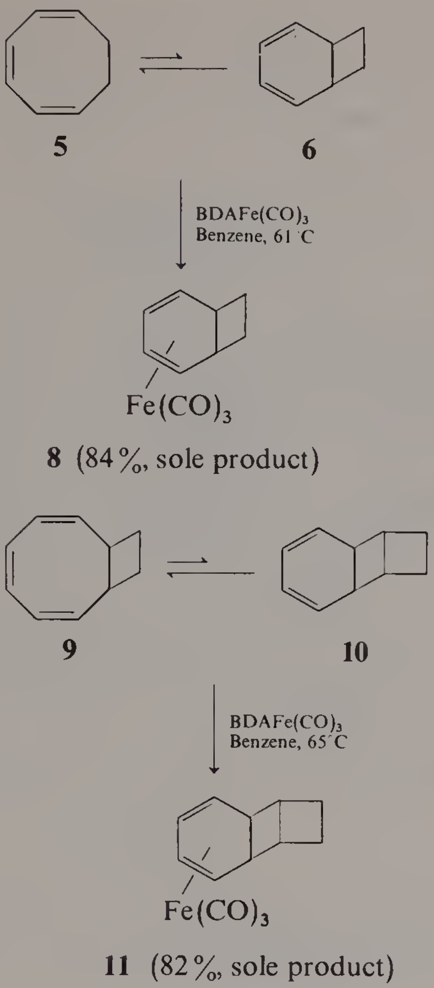
Because of the difficulties involved in preparing and isolating in good yields mononuclear trieneiron tricarbonyl complexes of substituted cyclooctatriene systems[11,12] and the further complications of the existence of isomeric triene complexes,[7a,12] we thought that maximum synthetic efficiency would result if triene complexes could be bypassed as intermediates and iron carbonyl precursors could be developed that would selectively trap the diene isomers present in low equilibrium concentrations, thus leading directly to the desired diene complexes. A survey of the known reactions of cyclooctatrienes with conventional iron carbonyl reagents, such as $Fe(CO)_5$ (thermally and photochemically) and $Fe_2(CO)_9$, reveals that these reagents do not display any special selectivity for the diene isomer.[10,13,14] However, we have discovered that benzylideneacetoneiron tricarbonyl [$BDAFe(CO)_3$] is a remarkably discriminatory reagent and leads to the selectivity desired.[15] $BDAFe(CO)_3$ was first synthetically used by Lewis *et al.*,[16] who demonstrated that the bound enone undergoes thermal exchange under mild conditions with heptafulvene derivatives to yield dieneiron tricarbonyl complexes.

The remainder of this paper is devoted to examining the reactions of $BDAFe(CO)_3$ with cyclooctatriene derivatives and other polyolefinic systems that illustrate the unusual selectivity and synthetic utility of this reagent. In addition, kinetic studies will be described that clarify the mechanism of product formation and that allow some tentative conclusions regarding the reasons for the high selectivity of the enoneiron tricarbonyl reagents.

Reactions of Benzylideneacetoneiron Tricarbonyl with Cyclooctatrienes

The reactions of $BDAFe(CO)_3$ with cyclooctatriene and its derivatives are summarized in Schemes 2–4. As noted under Introduction, 1,3,5-cyclooctatriene (**5**) is favored over its valence tautomer bicyclo[4.2.0]octa-2,4-diene (**6**) by an 85 : 15 ratio at 100°C. Reaction of this equilibrating pair of isomers with iron carbonyl reagents at high temperatures yields only diene complex **8**, whereas reaction with iron carbonyl reagents at more moderate temperatures leads to mixtures of diene complex **8** and triene complex **7**.[10,13,14] In contrast, reaction of cyclooctatriene with $BDAFe(CO)_3$ under mild conditions (61°C, benzene) leads to exclusive trapping of the diene isomer and formation of only diene complex **8**, in an 84% isolated yield[17] (see Scheme 2).

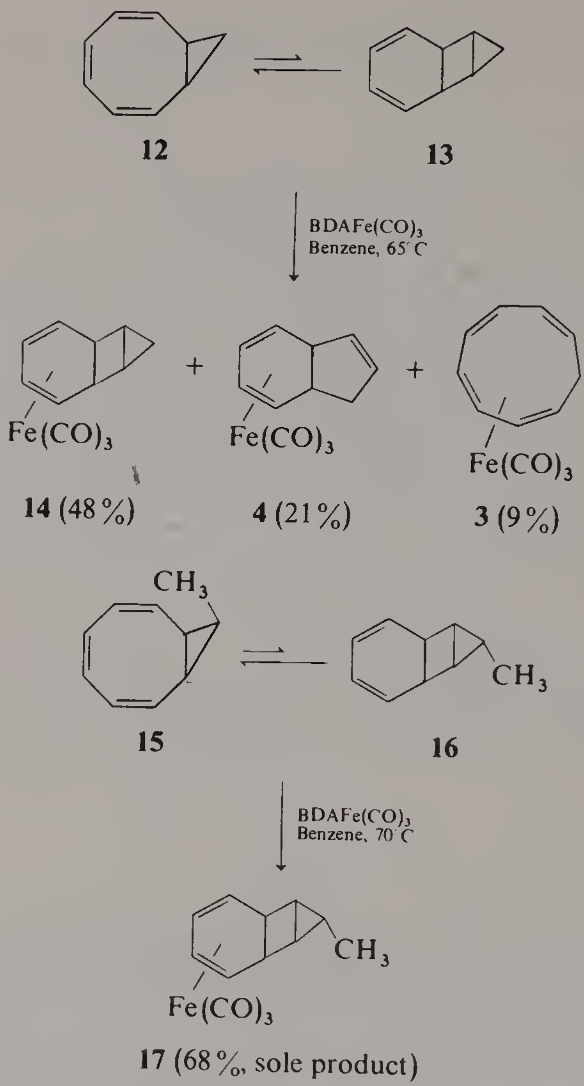
The high selectivity of $BDAFe(CO)_3$ is more dramatically illustrated in its reactions with cyclooctatriene derivatives in which the equilibrium is more substantially shifted in favor of the triene isomer. For example, in the ^1H nuclear magnetic resonance (nmr) spectrum of bicyclo[6.2.0]decatriene (**9**), no signals for the diene isomer (**10**) are apparent; thus, the equilibrium very substantially favors the triene isomer. However, reaction of triene **9** with $BDAFe(CO)_3$ in benzene at 65°C leads to selective trapping of only the diene valence tautomer and formation exclusively of tricyclo[4.4.0.0^{2,5}]deca-7,9-dieneiron tricarbonyl (**11**), in 82% isolated yield (see Scheme 2). This complex proved identical to that earlier isolated by Cotton and Deganello.[11] A crystal structure by Cotton and Troup[18] indicated that the stereochemistry about the central cyclobutane ring is *anti*, as shown in Scheme 2. Detailed analysis of the ^1H nmr spectrum also suggests *anti* stereochemistry.[17]



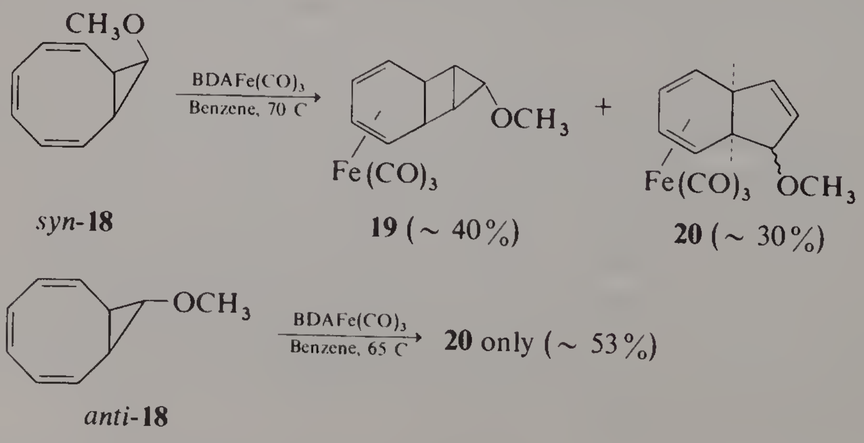
SCHEME 2. Reactions of cyclooctatriene and bicyclo[6.2.0]decatriene with BDAFe(CO)$_3$.

Further examples of the high selectivity of BDAFe(CO)$_3$ are derived from reactions with bicyclo[6.1.0]nonatriene derivatives.[17] For these systems, it might be expected that the equilibrium ratio of the triene/diene valence tautomers is even higher than that of the **9** : **10** ratio. For the unsubstituted system, no direct observation of the diene isomer (**13**) has been made (it cannot be detected by ^{1}H FT-nmr in equilibrium with **12**); however, it has been suggested as an intermediate in the Diels-Alder cycloaddition reactions of **12** with dienophiles.[19] Reaction of bicyclo[6.1.0]nonatriene (**12**) with BDAFe(CO)$_3$ in benzene at 65°C gives, as the major product in 48% isolated yield, tricyclo[4.3.0.0^{7,9}]nona-2,4-dieneiron tricarbonyl (**14**), from trapping of diene valence tautomer **13**. Its structure and stereochemistry were unambiguously established by ^{1}H and ^{13}C nmr analysis and by cerium cleavage to the free diene (see below).[15,17] The unsubstituted triene (**12**) is known to undergo thermal isomerization ($\Delta G^{\neq} = 28$ kcal/mol) to predominantly *cis*-dihydroindene via *cis*^{4}-cyclononatetraene[20]; thus, clearly, the complexes isolated in minor amounts result from trapping by BDAFe(CO)$_3$ of the thermal rearrangement products of the triene.

To avoid the complication of thermal rearrangements of the triene, we have examined the reaction of *syn*-9-methylbicyclo[6.1.0]nonatriene (**15**) with



SCHEME 3. Reactions of bicyclo[6.1.0]nonatriene and *syn*-9-methylbicyclo[6.1.0]-nonatriene with BDAFe(CO)$_3$.

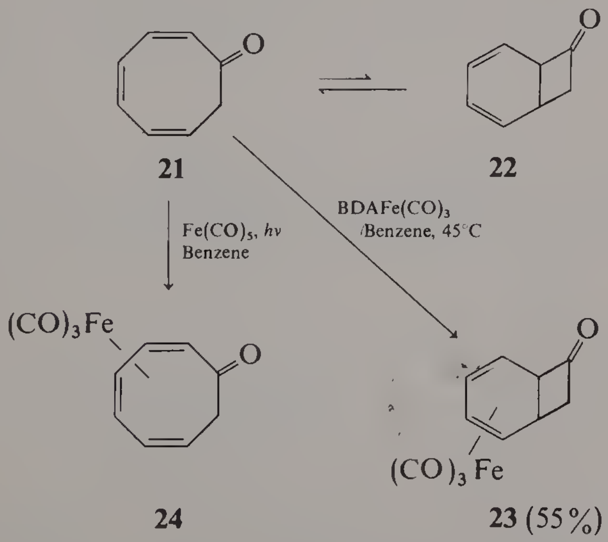


SCHEME 4. Reactions of *syn*- and *anti*-9-methoxy[bicyclo]nonatriene with BDAFe(CO)$_3$.

BDAFe$(CO)_3$. Due to the *syn*-methyl substituent, the triene (**15**) undergoes skeletal isomerization at much slower rates ($\Delta G^{\neq} = 31$ kcal/mol) than the unsubstituted triene (**12**)[21]; however, the *syn*-methyl substituent would be expected to have little effect on the rates of interconversion of the diene and triene valence tautomers. Thus, the major thermal reaction of triene **15** at 70°C would be equilibration with the energetically disfavored tricyclic diene (**16**). Indeed, reaction of *syn*-methyl triene (**15**) with BDAFe$(CO)_3$ in benzene at 70°C gives *syn*-8-methyltricyclo[4.3.0.$0^{7,9}$]nona-2,4-dieneiron tricarbonyl (**17**) as the sole detectable product (68% yield) from trapping of diene isomer **16**.[17]

The delicate balance in the bicyclo[6.1.0]nonatriene systems between the rate of thermal isomerization of the triene and the rate of ring closure to the diene isomer and the consequent effects on the BDAFe$(CO)_3$ trapping reaction are illustrated by the *syn*- and *anti*-9-methoxybicyclo[6.1.0]nonatrienes (**18**). The *syn*-OCH_3 triene (**18**) undergoes epimerization to *anti*-**18**, with a free energy of activation of about 26.0 kcal/mol,[22] and ring closure to the *syn*-OCH_3 tricyclic diene at a competitive rate with a $\Delta G^{\neq}$ of about 26.3 kcal/mol (see below), which is faster than the ring closure for the unsubstituted system ($\Delta G^{\neq} \sim 27.5$ kcal/mol; see below). The *anti*-OCH_3 triene (**18**) undergoes skeletal isomerization to the *cis*-dihydroindene system, with $\Delta G^{\neq} = 26.4$ kcal/mol,[23] which is faster than the analogous transformation of the unsubstituted triene (**12**). The rate of ring closure of the *anti*-OCH_3 triene is unknown but is apparently uncompetitive with skeletal isomerization (see below). Thus, when *syn*-**18** is treated with BDAFe$(CO)_3$, substantial amounts of both the *syn*-OCH_3 tricyclic diene complex (**19**, ~40%) and the methoxydihydroindene complex (**20**, ~30%) are formed (see SCHEME 4).[24] However, treatment of the *anti*-**18** methyl ether with BDAFe$(CO)_3$ results in no *anti*-OCH_3 tricyclic diene complex and only the dihydroindene complex (**20**; see SCHEME 4).[24]

The last cyclooctatriene derivative to be considered is cyclooctatrienone. Here, again, the triene isomer (**21**) is highly favored over the diene isomer (**22**); the equilibrium ratio at 25°C is about 140 : 1 (see below). Reaction of **21** ⇌ **22** with BDAFe$(CO)_3$ leads, again, to selective trapping of the diene isomer and formation

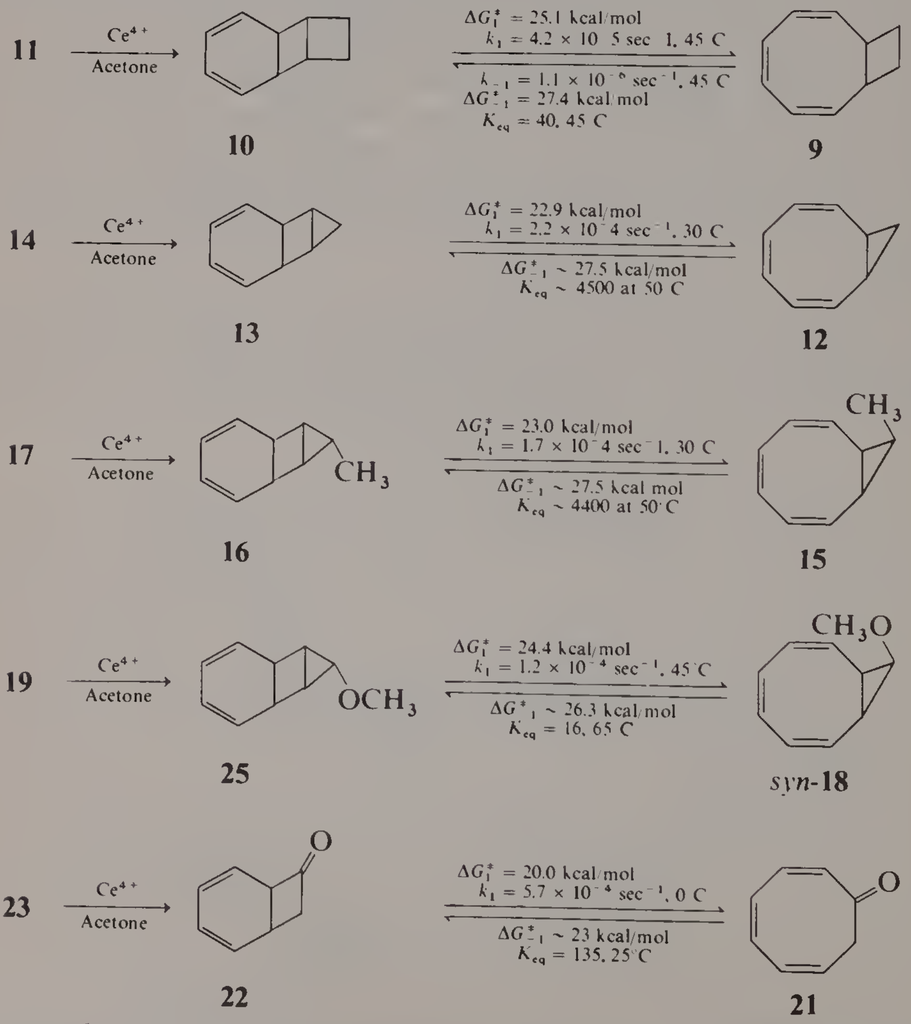


SCHEME 5. Reactions of cyclooctatrienone with iron pentacarbonyl and BDAFe$(CO)_3$.

of bicyclo[4.2.0]octa-2,4-dien-7-oneiron tricarbonyl (**23**, 55% yield; see SCHEME 5).[25] In contrast, photolysis of iron pentacarbonyl in the presence of trienone **21** leads exclusively to the cyclooctatrienoneiron tricarbonyl complex, **24**.

GENERATION OF THE FREE DIENE ISOMERS

As illustrated in the previous section, the reactions of BDAFe(CO)$_3$ with cyclooctatriene derivatives result in trapping of the high-energy diene isomers as iron tricarbonyl complexes. Low-temperature oxidative cleavage of these complexes serves as a convenient synthetic route to the free unstable diene isomers. At higher temperatures, the rates of electrocyclic ring openings of the dienes may be measured, and by comparing these values with the rates for ring closure, the value of the equilibrium ratio of the diene/triene isomers may be estimated. Thus, the use of BDAFe(CO)$_3$ as a trapping reagent not only allows isolation of the unstable diene isomers but also yields quantitative data regarding the relative stabilities of the diene and triene isomers. The cleavage experiments and the kinetic and thermodynamic data for the interconversion of the diene and triene isomers are summarized in SCHEME 6. Specific examples are discussed below.



SCHEME 6. Rate and equilibrium data for interconversion of the diene and triene valence tautomers of various cyclooctatriene derivatives.

Tricyclic diene complex **11** was cleaved at $-30°C$ in acetone by treatment with ceric ammonium nitrate to yield tricyclo[4.4.0.0^{2,5}]deca-7,9-diene, (**10**, 84% isolated yield).[17] On warming to 45°C, diene **10** undergoes clean first-order thermal electrocyclic ring opening to triene **9** ($k_1 = 4.2 \times 10^{-5}$ sec^{-1}; $\Delta G_1{}^{\neq} = 25.1$ kcal/mol). By ^{13}C nmr analysis, the equilibrium ratio of **9** : **10** could be estimated as 40 ($\Delta G_{rxn} = -2.3$ kcal/mol), and from this K_{eq}, k_{-1} could be estimated as 1.1×10^{-6} sec^{-1} ($\Delta G^{\neq} = 27.4$ kcal/mol) at 45°C.

In a similar manner, cleavage of tricyclic diene complexes **14** and **17** at $-30°C$ in acetone with cerium(IV) resulted in isolation of pure samples of the free tricyclic dienes, **13** and **16**.[17] These diene isomers are considerably more labile than is tricyclic diene **10**. On warming to 30°C, the unsubstituted diene (**13**) undergoes rapid first-order ring opening to bicyclo[6.1.0]nonatriene (**12**, $k_1 = 2.2 \times 10^{-4}$ sec^{-1}; $\Delta G^{\neq} = 22.9$ kcal/mol). The *syn*-methyl diene (**16**) behaves very similarly, opening to the *syn*-methyl triene at 30°C, with a first-order constant (k_1) corresponding to 1.7×10^{-4} sec^{-1} ($\Delta G^{\neq} = 23.0$ kcal/mol).

The rate of ring closure of bicyclo[6.1.0]nonatriene (**12**) cannot be easily measured; however, it can be estimated with a reasonable degree of accuracy based on the following information. First, triene **12** undergoes isomerization to 8,9-dihydroindenes with a free energy of activation of 28 kcal/mol.[20] Reaction of **12** with maleic anhydride gives Diels-Alder adducts of *cis*-8,9-dihydroindene and tricyclic diene **13**.[19] This finding implies that ring closure must be competitive with the irreversible isomerization to dihydroindene and sets an upper limit of about 28 kcal/mol on the free energy of activation of ring closure of **12** to **13**. Second, it is important to note that known free energies of activation for the closure of cyclooctatriene derivatives are remarkably similar, for example, unsubstituted 1,3,5-cyclooctatriene[9] (26.9 kcal/mol, 45°C), bicyclo[6.2.0]decatriene (27.4 kcal/mol, 45°C; see above), and cyclooctatetraene[9] (27.7 kcal/mol, 45°C). Based on this information, it is reasonable to expect that $\Delta G^{\neq}$ for closure of **12** should exceed that of cyclooctatriene and probably lies between the value of 27.4 kcal/mol for **9** and 27.7 kcal/mol for cyclooctatetraene, at approximately 27.5 kcal/mol. By use of this estimated $\Delta G_{-1}{}^{\neq}$ for closure of **12** and the measured $\Delta G_1{}^{\neq}$ for opening of **13** of 22.9 kcal/mol, a ΔG for the equilibrium can be estimated as 4.6 kcal/mol, indicating an equilibrium ratio of **12** : **13** of about 4500 at 50°C. These data demonstrate the remarkable selectivity of BDAFe(CO)$_3$, in that unstable tautomer **13** is efficiently trapped, even though it is present in only a 0.02% concentration relative to triene **12**. A similar equilibrium ratio no doubt applies to the *syn*-methyl isomers **15** and **16**.

Oxidative cleavage of tricyclic *syn*-OCH$_3$ complex **19** yields the free *syn*-OCH$_3$ tricyclic diene, **25**; however, this diene is considerably more stable than either of the tricyclic dienes, **13** or **16**.[24] To effect a convenient rate of ring opening, the *syn*-OCH$_3$ diene (**25**) was warmed to 45°C, at which temperature **25** opens to *syn*-triene **18**, with a rate corresponding to $k_1 = 1.2 \times 10^{-4}$ sec^{-1} ($\Delta G^{\neq} = 24.4$ kcal/mol). This represents an increase in activation energy for the opening of *syn*-OCH$_3$ diene **25** relative to unsubstituted diene **13** of about 1.5 kcal/mol. An ^1H FT-nmr experiment revealed detectable amounts of tricyclic isomer **25** in the equilibrated system, and the equilibrium ratio of *syn*-**18** : **25** could be estimated as 16 at 65°C ($\Delta G_{rxn} \sim -1.9$ kcal/mol). This value of K_{eq} leads to a calculated value of $\Delta G_{-1}{}^{\neq}$ of 26.3 kcal/mol, somewhat lower than that estimated for the unsubstituted system (27.5 kcal/mol). From the data, it is clear that, relative to the unsubstituted system **13** $\rightleftharpoons$ **12**, substitution of the *syn*-OCH$_3$ group decreases the energy difference between the diene and triene isomers by about 2.7 kcal/mol. The precise reasons for this effect are unclear, although a strictly steric explanation is unlikely, because the *syn*-CH_3 system **16**$\rightleftharpoons$**15** behaves almost identically to that of the unsubstituted system.

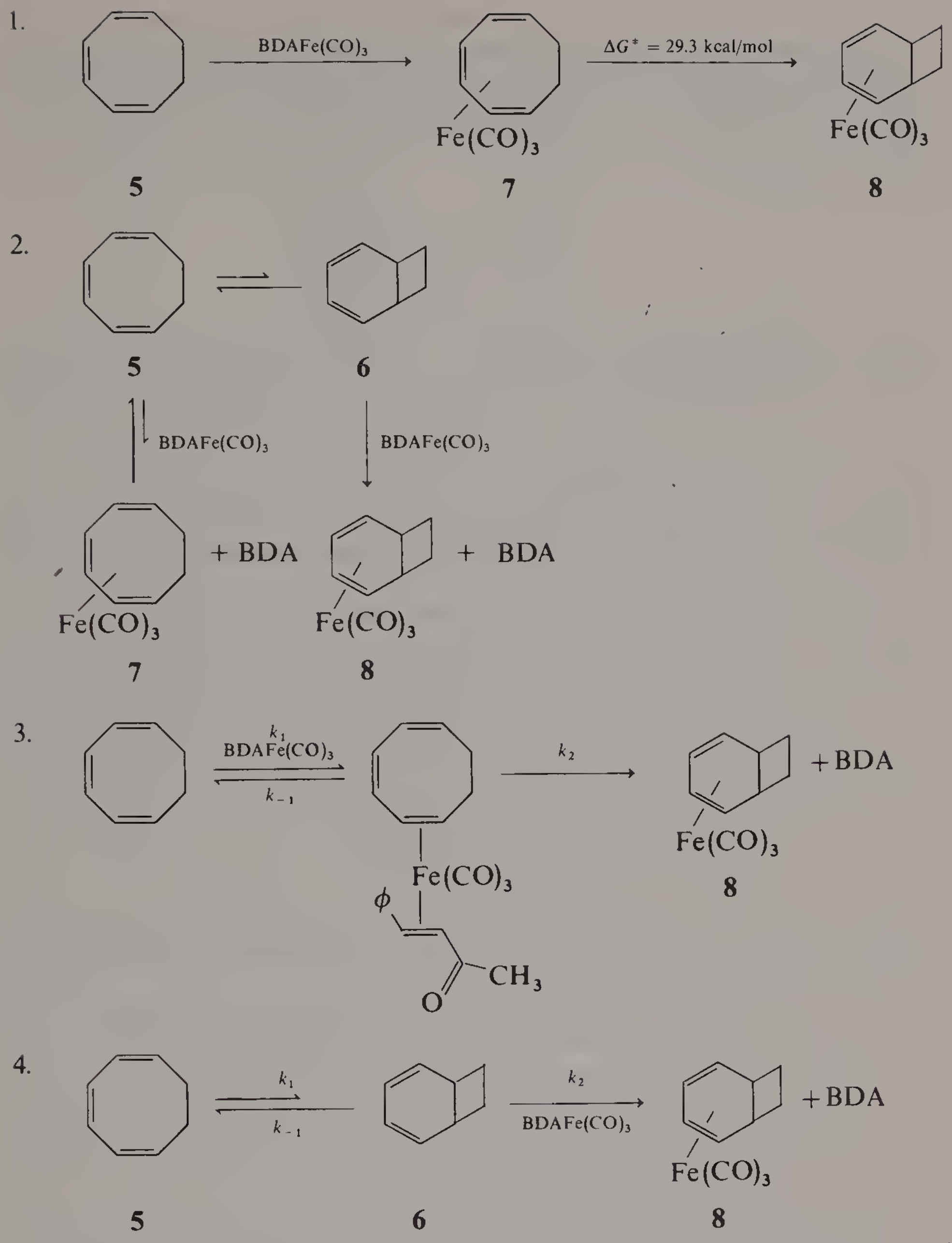
The last example to be discussed is the bicyclo[4.2.0]octadienoneiron tricarbonyl complex (**23**). Cleavage of this complex at −30°C with ceric ammonium nitrate leads to the free bicyclic ketone, **22**.[25,26] This bicyclic ketone undergoes ring opening at 0°C with a first-order rate constant $k_1 = 5.7 \times 10^{-4}$ sec^{-1} ($\Delta G^{\neq} =$ 20.0 kcal/mol; see SCHEME 6). Extrapolation of Huisgen *et al.*s' values[9] for k_{-1} to 0°C yields an estimated k_{-1} of 2.0×10^{-6} sec^{-1} and thus an estimated K_{eq} of 285 ($\Delta G_{rxn} = -3.1$ kcal/mol). This value of K_{eq} is substantially higher than the value of 20 (25°C) estimated previously by Huisgen *et al.* from provisional ^1H nmr data.[9] Reexamination of the equilibrium ratio of isomers at 25°C by use of ^1H FT-nmr techniques yields a value for K_{eq} of about 140 ($\Delta G_{rxn} = -2.9$ kcal/mol). These values are in accord with those estimated from the kinetic data and thus represent a substantially more accurate determination of K_{eq} than previously reported.

Kinetic and Mechanistic Studies

Kinetic studies were undertaken in an attempt to determine the mechanism of the reaction of $BDAFe(CO)_3$ with dienes and trienes and to understand the remarkable selectivity of the $BDAFe(CO)_3$ reagent. Qualitative data regarding the variation in product yields as a function of time and temperature suggested that the mechanism of reaction of $BDAFe(CO)_3$ with cyclooctatrienes involved very efficient trapping of the ring-closed diene isomer by $BDAFe(CO)_3$, which is a kinetic selectivity of $BDAFe(CO)_3$ for the diene isomer relative to the triene isomer. No firm proof of this mechanism was available; therefore, to clarify the details of this mechanism, a kinetic study of the reaction of cyclooctatriene **5** with $BDAFe(CO)_3$ to form bicyclo[4.2.0]octadieneiron tricarbonyl (**8**) was undertaken. Four possible mechanisms for this reaction were considered and are illustrated in SCHEME 7 and listed below:

1. $BDAFe(CO)_3$ reacts with triene **5** to form triene-$Fe(CO)_3$ complex **7**, which is followed by ring closure of **7** to diene complex **8**.
2. $BDAFe(CO)_3$ reacts with the triene to form triene complex **7** but is thermodynamically unstable with respect to $BDAFe(CO)_3$ and therefore reacts rapidly with the free benzylideneacetone to return to $BDAFe(CO)_3$. Thus, the triene complex never exists in any appreciable concentration. $BDAFe(CO)_3$ then eventually reacts with free bicyclic diene **6** as it is formed from triene to give diene complex **8** as the stable product. (Such a mechanism involves a *thermodynamic*, not a kinetic, selectivity of $BDAFe(CO)_3$ for the diene relative to the triene tautomer.)
3. $BDAFe(CO)_3$ reacts with the triene to form intermediate complex **26**, which involves both BDA and triene (dihapto coordinated),[15] followed by a metal-assisted ring closure of the bound triene and loss of BDA to give the product diene complex **8**.
4. Triene undergoes ring closure to the diene isomer, which is trapped by $BDAFe(CO)_3$ to yield diene complex **8**. (This mechanism suggests that the triene does not react with $BDAFe(CO)_3$ but that the selectivity is a kinetic selectivity of $BDAFe(CO)_3$ for the diene relative to the triene.)

The first two of the possibilities, mechanisms 1 and 2, can be readily eliminated. We have previously measured the rate of ring closure of triene complex **7** to diene complex **8** and find, at 102°C, that $k = 7 \times 10^{-5}$ sec^{-1} and $\Delta G^{\neq} = 29.3$ kcal/mol.[10]



SCHEME 7. Possible mechanisms of reaction of cyclooctatriene with $BDAFe(CO)_3$.

Extrapolation of this rate to 60°C yields a value for the rate constant of about 5×10^{-7} sec^{-1} ($t_{1/2} \sim 385$ hr), which is far too small to account for a half-life of product formation of about 10 hr at 60°C (see below), as required by mechanism 1. The second mechanism requires that the triene complex react rapidly with free BDA under the reaction conditions to yield $BDAFe(CO)_3$; this reaction is not found to occur. Treatment of cyclooctatrieneiron tricarbonyl with one equivalent of BDA at 60°C for 3.3 hr results in no reaction of triene complex and production of no $BDAFe(CO)_3$ (<2%).

To distinguish between mechanisms 3 and 4, a kinetic study must be performed. For mechanism 3, the rate of product formation should clearly depend on BDAFe(CO)$_3$ concentration, regardless of whether the formation of **26** or the conversion of **26** to product is rate determining. For mechanism 4, various kinetic expressions may apply, depending on the relative magnitudes of k_1, k_{-1}, and k_2. Applying the steady-state approximation to diene **6**, the reaction should obey the following rate law:

$$\text{rate} = \frac{k_1 k_2[\text{BDAFe(CO)}_3][\text{triene}]}{k_{-1} + k_2[\text{BDAFe(CO)}_3]}. \qquad (1)$$

If, as we suspected on the basis of earlier qualitative data, the trapping of the diene is efficient relative to ring opening, at high BDAFe(CO)$_3$ concentrations, $k_2[\text{BDAFe(CO)}_3]$ should be greater than k_{-1}, and Equation 1 simplifies such that rate = k_1[triene]; that is, the rate-determining step is ring closure of the triene, and the rate of formation of product will be independent of the concentration of BDAFe(CO)$_3$ (in contrast to mechanism 3). To test this possibility, we investigated the kinetics of the reaction between triene **5** and BDAFe(CO)$_3$ under conditions that employed a large excess of BDAFe(CO)$_3$ relative to triene **5**. The results are summarized in TABLE 1.

The results show that under conditions of excess BDAFe(CO)$_3$, the rate of the reaction has a first-order dependence on triene and has no dependence on BDAFe(CO)$_3$, because doubling the BDAFe(CO)$_3$ concentration has no effect on the rate. Furthermore, the average first-order rate constant measured for the reaction ($k_{\text{obs}} = 1.95 \times 10^{-5}$ sec^{-1}, 60°C; $\Delta G^{\neq} = 26.8$ kcal/mol) matches very closely that for the ring closure of triene **5** to diene **6** ($k_1 \sim 1.6 \times 10^{-5}$ sec^{-1}, 60°C; $\Delta G^{\neq} = 26.9$ kcal/mol) estimated from the data of Huisgen *et al.*[9] These results are in clear agreement with the diene-trapping reaction, mechanism 4. The fact that the rate is independent of BDAFe(CO)$_3$ rules out mechanism 3, while the identity of the measured rate constant to that of the known k_1 for ring closure of the triene confirms mechanism 4. Thus, under conditions of excess BDAFe(CO)$_3$, diene trapping is rapid, and the rate-determining step is ring closure of the triene to the diene tautomer.

To better understand the reaction between the bicyclic and tricyclic dienes and BDAFe(CO)$_3$, we have performed kinetic studies of the reaction of BDAFe(CO)$_3$ with 1,3-cyclohexadiene, which serves as a model for the diene tautomers. The 1,3-cyclohexadiene reacts with BDAFe(CO)$_3$ to give cyclohexadieneiron tricarbonyl (**27**) in quantitative yield. The rate of this reaction is, in general, substantially faster than those of BDAFe(CO)$_3$ with cyclooctatrienes due to lack of the requirement of ring closure, which is rate limiting in the case of the trienes. Kinetic measurements were performed under conditions of both excess cyclohexadiene and excess BDAFe(CO)$_3$. The results are summarized in TABLE 2.

TABLE 1
KINETICS OF REACTION OF BDAFe(CO)$_3$ WITH 1,3,5-CYCLOOCTATRIENE IN BENZENE AT 60.0°C

[BDAFe(CO)$_3$]/[Triene] (molar ratio)	[BDAFe(CO)$_3$] (M)	First-Order Rate Constant ($k_{\text{obs}} \times 10^5$ sec^{-1})
22.4 : 1.0	0.101	1.9 ± 0.2
44.8 : 1.0	0.202	2.0 ± 0.1

TABLE 2

KINETICS OF REACTION OF BDAFe(CO)$_3$ WITH 1,3-CYCLOHEXADIENE IN BENZENE

[BDAFe(CO)$_3$]/[Diene] (molar ratio)	[BDAFe(CO)$_3$] (M)	Temperature (°C)	First-Order Rate Constant ($k_{obs} \times 10^4$ sec^{-1})
1 : 10.9	0.0139	50.0	6.8 ± 0.4*
1 : 20.5	0.0144	50.0	6.6 ± 0.5*
1 : 22.0	0.0144	50.0	7.0 ± 0.4*
1 : 39.7	0.0134	50.0	6.1 ± 0.4*
20.6 : 3	0.0857	30.0	5.6 ± 0.7†
19.1 : 1	0.0834	30.0	3.3 ± 0.4†
40.9 : 1	0.171	30.0	8.1 ± 0.7†

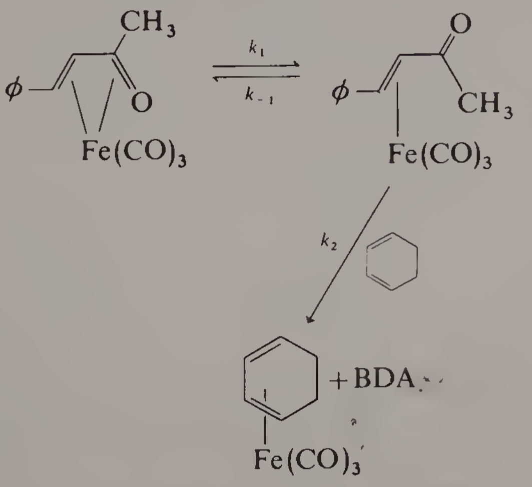
* First order in BDAFe(CO)$_3$.

† First order in 1,3-cyclohexadiene.

As shown by the results in TABLE 2, under conditions of excess diene, the reaction is first order only in BDAFe(CO)$_3$ and zero order in diene, whereas under conditions of excess BDAFe(CO)$_3$, the reaction is first order in both BDAFe(CO)$_3$ and diene. The simplest and most reasonable mechanism that accounts for these results is illustrated in SCHEME 8. The first-order dependence on only BDAFe(CO)$_3$ at high diene concentrations, yet overall second-order kinetics at low diene concentrations, suggests that an intermediate is formed reversibly that may be trapped by diene. The most reasonable structure we can envision for the intermediate is the 16-electron unsaturated intermediate **28**, which is formed by dechelation of the carbonyl group from BDAFe(CO)$_3$. Applying the steady-state approximation to **28**, the following rate law is obtained:

$$\text{rate} = \frac{k_1 k_2[\text{BDAFe(CO)}_3][\text{diene}]}{k_{-1} + k_2[\text{diene}]}. \qquad (2)$$

At high diene concentrations, $k_2[\text{diene}] > k_{-1}$, and Equation 2 reduces to rate $= k_1[\text{BDAFe(CO)}_3]$, where the rate-determining step is dechelation and formation of **28**. This finding is in agreement with the experimental results obtained at high



28

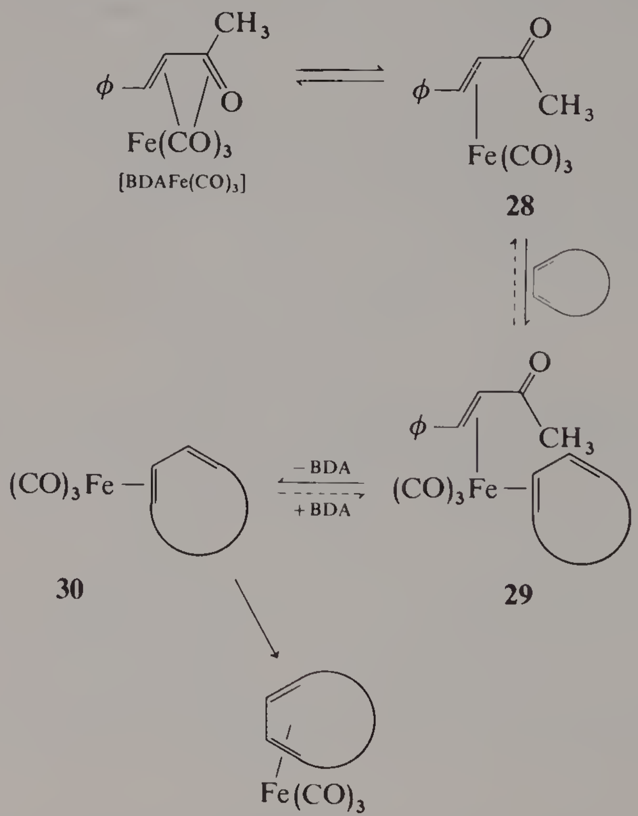
27

SCHEME 8. Kinetic description of the reaction of 1,3-cyclohexadiene with BDAFe(CO)$_3$.

diene concentrations, where $k_{obs} = k_1 = 6.6 \times 10^{-4}$ sec^{-1} at 50°C. At low diene concentrations, return to BDAFe(CO)$_3$ is rapid ($k_{-1} > k_2$[diene]), and the rate expression reduces to (k_1k_2/k_{-1}) [BDAFe(CO)$_3$][diene], where the observed pseudo first-order rate constant is (k_1k_2/k_{-1}) [BDAFe(CO)$_3$] (entries 5–7 in TABLE 2).

Several previous reports support the proposition that the carbonyl group of the bound enone initially dechelates in preference to the C=C. Dixneuf and Vessieres[27] and Cardaci *et al.*[28] have observed that reactions of substituted enoneiron tricarbonyl complexes with various donor ligands (L), such as P(OR)$_3$, PR$_3$, AS(C$_6$H$_5$)$_3$, and Sb(C$_6$H$_5$)$_3$, give complexes of the general structure (enone)-Fe(CO)$_3$L, where the enone is π bound to iron through the C=C. Formation of such complexes indicates that the carbonyl group of the bound enone is more weakly coordinated than is the C=C.

For the reaction of cyclohexadiene with BDAFe(CO)$_3$, the second step, trapping of the unsaturated intermediate, appears to be irreversible; to simplify kinetic arguments, we have therefore represented it as a single step in SCHEME 8. It seems likely, however, that a series of steps must be involved, and the complete mechanistic picture for a generalized diene is outlined in SCHEME 9. Unsaturated enone intermediate **28** is generated from BDAFe(CO)$_3$ by carbonyl dechelation, and this intermediate is then trapped by the diene to yield saturated intermediate **29**. To proceed to product, BDA must dissociate from **29** to yield the 16-electron dihapto-bound diene complex (**30**), which then must chelate with the second double bond of the diene to give product. Intermediate **29** and this general mechanistic scheme are analogous to those suggested by Cais and Maoz[29] for exchange of dieneiron tricarbonyl derivatives with free dienes.



SCHEME 9. Mechanism of reaction of a diene with BDAFe(CO)$_3$.

By use of this mechanistic model, an explanation can be offered to explain the selectivity of BDAFe$(CO)_3$. We believe that the high selectivity is a result of the varying rates for conversion of saturated intermediate **29** to product. For the planar diene unit of cyclohexadiene, which is geometrically ideal for chelation, the dissociation of BDA and the chelation of the second double bond may approach a synchronous process, or if such an intermediate as **30** is generated, it must collapse very rapidly to product. However, for the tub-shaped cyclooctatriene derivatives, a significant energy barrier for the conversion of **30** to product exists, because the dihapto-bound tub-shaped triene must very substantially distort to chelate the second double bond. Thus, in this case, the reaction is reversible by reaction of free BDA with **30** to return to **29**, which then may return to BDAFe$(CO)_3$ and free triene. We feel that the reversible nature of the **29**-**30** conversion and the overall higher free energy of activation for the conversion of **29** to product in the case of conjugated dienes that are twisted out of a planar configuration play the major role in governing the high selectivity of BDAFe$(CO)_3$.

Qualitative confirmation of this idea has been obtained by examining the reaction of cycloheptatriene with BDAFe$(CO)_3$. Due to its tub conformation, cycloheptatriene reacts slowly with BDAFe$(CO)_3$ (see below) but does yield the cycloheptatrieneiron tricarbonyl complex. Interestingly, the rate of product formation can be suppressed to varying degrees by adding incremental amounts of free BDA to the reaction mixture. That excess BDA retards the rate of product formation is consistent with the idea that the reaction of intermediate **30** with BDA to return to starting materials is competitive with product formation, namely, chelation, of the second double bond of the tub-shaped cycloheptatriene.

Reactions of BDAFe$(CO)_3$ with Other Dienes

The reactions of BDAFe$(CO)_3$ with several other dienes have been surveyed. The results are given in TABLE 3; yields quoted represent isolated yields of diene complexes. Several interesting features can be noted. As illustrated by the first four entries, reactions of BDAFe$(CO)_3$ with acyclic dienes lead to moderate to very

TABLE 3
REACTION OF BDAFe$(CO)_3$ WITH DIENES*

Diene	[Diene]/[BDAFe$(CO)_3$] (molar ratio)	Isolated Yield of Diene Complex† (%)
trans,trans-2,4-Hexadiene	1 : 1	54
trans-1,3-Pentadiene	5 : 1	84
2,3-Dimethylbutadiene	2 : 1	72
trans,trans-2,4-Hexadienal	1 : 1	96
1,3-Cyclohexadiene	1 : 1	> 95
1,4-Cyclohexadiene	4 : 1	0
Norbornadiene	3 : 1	9
1,3-Cyclooctadiene	1.2 : 1	0
1,5-Cyclooctadiene	1.3 : 1	0
Cycloheptatriene	1 : 1	50
Cyclooctatetraene	1.1 : 1	74

* All reactions performed in benzene at 55–60°C for 24–72 hr.
† Based on BDAFe$(CO)_3$.

good yields of the corresponding diene complexes. As noted earlier, 1,3-cyclohexadiene reacts rapidly with BDAFe(CO)$_3$ to give the diene complex in essentially quantitative yield. In contrast, the 1,4-cyclohexadiene is completely unreactive and gives no dieneiron complex. In this case, comparison of the reactivity of the BDAFe(CO)$_3$ reagent is interesting, in that reaction of 1,4-cyclohexadiene with pure iron carbonyl reagents [Fe$_2$(CO)$_9$ thermally or Fe(CO)$_5$ photochemically] results in 1,3 hydrogen migration, no doubt through a metal hydride intermediate, to give good yields of the 1,3-cyclohexadieneiron tricarbonyl complex.[30] Reaction of norbornadiene, a 1,4-diene, leads to a very low yield of diene complex. In this case, the diene unit is constrained in a somewhat better geometry for chelation, and, of course, norbornadieneiron tricarbonyl is known to be a stable diene complex.[31]

Further supporting the notion that the conformation of the diene is critical in terms of reactivity toward BDAFe(CO)$_3$ are the observations that tub-shaped 1,3-cyclooctadiene and the 1,5-cyclooctadiene are unreactive toward BDAFe(CO)$_3$. Cycloheptatriene (CHT) and cyclooctatetraene (COT) both react with BDAFe(CO)$_3$ to give the CHTFe(CO)$_3$ and COTFe(CO)$_3$ complexes, respectively, in moderate yields; additional data concerning their reactivity are discussed below.

To gain further insight into the selectivity of the BDAFe(CO)$_3$ reagent, we conducted competition studies in which mixtures of cyclohexadiene and a second diene were allowed to compete for small amounts of BDAFe(CO)$_3$. By analyzing the ratios of the two diene complexes produced, a reasonable estimate of the relative reactivities of the dienes could be made. The results are summarized in TABLE 4. A considerable range in relative reactivities is noted. None of the dienes studied was more reactive than the reference diene, 1,3-cyclohexadiene. The difference of about 35 in the relative reactivities of 2,3-dimethylbutadiene and *trans,trans*-2,4-hexadiene may be due to the fact that the hexadiene prefers the planar s-*trans* configuration, whereas the ground-state conformation of the 2,3-dimethylbutadiene is likely to be twisted and closer to the required planar s-*cis* geometry required for binding to iron.

TABLE 4

COMPETITION REACTIONS OF VARIOUS DIENES WITH 1,3-CYCLOHEXADIENE (CHD)

Diene	[Diene]/[CHD]/[BDAFe(CO)$_3$] (molar ratios)	Temperature (°C)	Reactivity Ratio CHD/Diene*
2,3-Dimethylbutadiene	20 6 1	60	4
trans,trans-2,4-Hexadiene	40 6 1	59	138
trans,trans-2,4-Hexadienal	40 6 1 12 6 1	56 60	7.4 7.5
Cyclooctatetraene (COT)	40 6 1 40 6 1	58 57	18 14
Cycloheptatriene (CHT)	CHT : COT : BDAFe(CO)$_3$ 12 6 1	60	~330†

* Corrected for the difference in initial ratios of Diene/CHD.

† Corrected assuming a CHD/COT reactivity ratio of 16 : 1.

The quite slow rate of reaction of cycloheptatriene can be understood in terms of conformational arguments presented earlier, but the relatively high reactivity of COT was surprising. Just as in the case of the cyclooctatrienes and cyclooctadiene, COT exists in a tub conformation. Preliminary qualitative data indicate that formation of the COTFe$(CO)_3$ complex from COT and BDAFe$(CO)_3$ is faster than COT ring closure to the bicyclo[4.2.0]octatriene isomer; therefore, no bicyclic diene complex is obtained. Although COT possesses several unique structural features in comparison with CHT or cyclooctatriene, the precise reason for its high reactivity relative to these systems cannot be specified at this time.

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APPLICATIONS OF OLEFIN METATHESIS TO ORGANIC SYNTHESIS

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INTRODUCTION

Olefin metathesis is a versatile and novel technique for the preparation of alkenes and alkynes, and it illustrates the remarkable transformations of organic molecules that can occur under the aegis of a transition metal. It is quite appropriate that this reaction be included in a conference on the place of transition metals in organic synthesis. Moreover, investigations into the mechanism of the metathesis reaction have resulted in new insights with both theoretical and synthetic implications for organometallic chemistry in general.

It is our purpose here to survey eclectically rather than comprehensively the transformations that can be effected by olefin metathesis with the hope that the examples chosen will illustrate its usefulness as a synthetic method and stimulate the creative application of metathesis to as yet unexplored areas. We will not deal, except incidentally, with the broad topics of the mechanism of the reaction or the nature of the catalytic species.

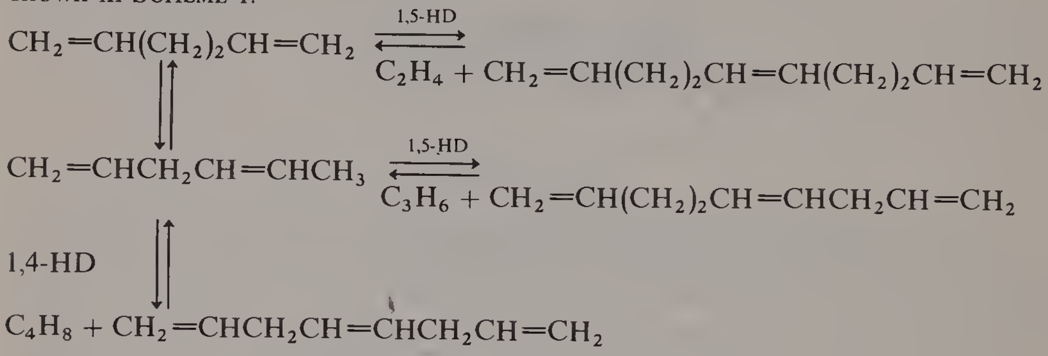
GENERAL COMMENTS

Some general comments that relate to the practical aspects of performing the metathesis reaction will serve appropriately as background material for our discussion of its application to organic synthesis.

Although the metathesis reaction can be quite selective, the experimentalist should be aware that side reactions are frequently encountered. These side reactions are of three general types: double-bond isomerization, oligomerization/polymerization, and alkylation of aromatic solvents. Some of the strategies that may be pursued to minimize these parasitic reactions include the proper choice of catalyst, temperature, reaction time, solvent, and selective poisoning, as the following discussion illustrates.

In our early work with homogeneous catalysts derived from $MoCl_2(NO)_2L_2$ [$L = (C_6H_5)_3P$, $(C_6H_5)_3PO$, pyridine, and so on] and organoaluminum reagents, we demonstrated that double-bond isomerization in acyclic olefinic substrates could be greatly reduced by lower reaction temperatures and short reaction times.[1] For example, metathesis of 1-octene at 25°C for 16 hr with an $MoCl_2(NO)_2$ $(pyridine)_2/C_2H_5AlCl_2$ catalyst gave a mixture of olefins that ranged from C_2 to C_{15}, with the expected product, 7-tetradecene, constituting only 12 wt% of the total. In contrast, the same catalyst system after 1 hr at 0–5°C gave essentially only ethylene and 7-tetradecene as products. The cocatalyst was also important. Thus, under the same conditions (50°C, 25 min), $(CH_3)_3Al_2Cl_3$ yielded 60% 7-tetradecene with only traces of other olefins, whereas $C_2H_5AlCl_2$ gave 64% 7-tetradecene along with 11% other olefins.[1]

Double-bond isomerization can also be reduced in certain catalyst systems by poisoning the species responsible for this side reaction without simultaneously destroying metathesis activity. Dall'Asta has reported that in the presence of $WCl_6/(ClCH_2)_2CHOH/(C_2H_5)_3Al_2Cl_3$, 1,5-hexadiene yields propylene and 2-butene, in addition to the expected ethylene due to double-bond isomerization, as shown in SCHEME 1.[2]



SCHEME 1. HD = hexadiene.

If 1 equiv of triphenylphosphine is added to the catalyst mixture, double-bond isomerization is curtailed, and only ethylene is observed. The selectivity to 7-tetradecene in the metathesis of 1-octene by a $WCl_6/(n - C_4H_6)_4Sn$ catalyst increases from 6% with no additive to 100% in the presence of 4 equiv of CH_3CN.[3]

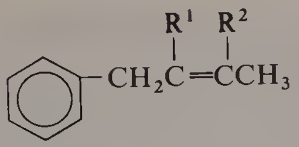
In similar fashion, treatment of heterogeneous catalysts, such as tungsten oxide on silica, with alkali metal ions greatly reduces olefinic isomerization.[4]

Selective inhibition is also effective in reducing the alkylation side reaction. Pyridine and triphenylphosphine prevent solvent benzene alkylation without impairing the metathesis activity of a $WCl_6/C_2H_5AlCl_2$ catalyst.[5] Chlorobenzene is an excellent solvent for numerous homogeneous catalysts and is much less susceptible to alkylation.

A large number of catalysts, both homogeneous and silica or alumina supported, are at the disposal of the experimentalist. Among the several factors that influence the choice of catalyst, the nature of the olefinic substrate is one of the most important. Although all homogeneous catalysts are effective for the metathesis of internal acyclic olefins, not all systems are capable of metathesizing terminal alkenes. For example, we have found that the catalyst $MoCl_2(NO)_2$-(pyridine)$_2/(CH_3)_3Al_2Cl_3$ gives a 22% conversion of 1-pentene to 4-octene and ethylene in 2 min at room temperature at an olefin/molybdenum ratio of 633 : 1.[6] In contrast, the catalyst derived from $WCl_6/C_2H_5OH/C_2H_5AlCl_2$ yields only trace amounts of 4-octene in 10 min at an olefin/tungsten ratio of 16 : 1.[7] Recent work has shown that the apparent low activity of the tungsten catalyst is not the result of an inherent inability to metathesize α-olefins but, rather, to its propensity to promote degenerate metathesis with this type of substrate. Thus, in the same 10-min period, a 1-pentene/1-pentene-d_{10} mixture gave 70% of the theoretical scrambling calculated according to Equation 1.[7]

$$C_3H_7CH{=}CH_2 + C_3D_7CD{=}CD_2 \rightleftharpoons C_3H_7CH{=}CD_2 + C_3D_7CD{=}CH_2 \tag{1}$$

The degree of substitution of a double bond influences its reactivity. Descotes *et al.* studied the metathesis of a series of aryl olefins of type **1** by use of an $MoCl_2(NO)_2[(C_6H_5)_3P]_2/C_2H_5AlCl_2$ catalyst.[8] When $R^1 = R^2 = CH_3$, no meta-



$C_6H_5CH_2C(R^1){=}C(R^2)CH_3$

1

thesis is observed; when $R^1 = R^2 = H$, a 23% conversion to 2-butene and 1,4-diphenyl-2-butene is obtained; and when $R^1 = H$ and $R^2 = CH_3$, intramolecular alkylation occurs. These studies and others have shown that in general, the rate of metathesis decreases in the order $CH_2{=} > RCH_2CH{=} > R_2CHCH{=} > R_2C{=}$.

Olefin metathesis is a reversible equilibrium-controlled reaction. For simple acyclic alkenes, the heat of reaction is essentially zero, and the equilibrium concentrations are dictated by entropy factors. Thus, in the metathesis of 2-pentene, a 50% conversion to 2-butene and 3-hexene is the maximum attainable and corresponds to a statistical distribution of alkylidene moieties. For substrates in which electronic or steric factors may be important, the equilibrium distribution will not be statistical. For example, isobutene cannot yield more than 1.4% of 2,3-dimethyl-2-butene at room temperature.[9] Potential reaction yields can be calculated from thermochemical data.

Most of the reactions cited in the following discussion were not studied from a synthetic standpoint; consequently, the quoted yields do not necessarily represent the maximum attainable.

ACYCLIC ALKENES

Virtually all types of acyclic alkenes undergo metathesis with the proper catalyst and subject to the thermodynamic constraints mentioned above. Metathesis of terminal alkenes may be used to prepare symmetric internal olefins. For example, 1-dodecene in the presence of a homogeneous $MoCl_2(NO)_2[OP(C_6H_5)_3]_2/(CH_3)_3Al_2Cl_3$ catalyst in chlorobenzene yielded 53.8 wt% of 11-docosene in 5.5 hr at room temperature (Equation **2**).[6]

$$2\ CH_2(CH_2)_9CH{=}CH_2 \rightleftharpoons C_2H_4 + CH_3(CH_2)_9CH{=}CH(CH_2)_9CH_3 \tag{2}$$

Removal of the volatile ethylene coproduct in the metathesis of 1-alkenes shifts the equilibrium to the right, increasing the yield. Thus, the yield of 7-tetradecene from 1-octene by use of a $WCl_6/CH_3CO_2CH_2CH_2CH_3/(n-C_4H_9)_4Sn$ catalyst increased from 43 to 59 mol% when ethylene was removed from the system.[3]

Terminal olefins can be synthesized by the reverse of reactions of the type shown in Equation **2** or by ethylene cleavage of an unsymmetric internal alkene. For example, 1-hexene was prepared by metathesis of 2-heptene and ethylene with a homogeneous molybdenum catalyst (Equation **3**).[1]

$$CH_3(CH_2)_3CH{=}CHCH_3 + C_2H_4 \rightleftharpoons CH_3CH{=}CH_2 + CH_2{=}CH(CH_2)_3CH_3 \tag{3}$$

Reaction **3** also serves to illustrate an important point pertaining to the metathesis of simple acyclic alkenes, which is that all double bonds in a metathesis system are potential reactants. Thus, in the above case, 2-heptene can undergo self-metathesis to produce 2-butene and 5-decene (Equation **4**).

$$2\ CH_3(CH_2)_3CH{=}CHCH_3 \rightleftharpoons CH_3CH{=}CHCH_3 + CH_3(CH_2)_3CH{=}CH(CH_2)_3CH_3 \tag{4}$$

These products can, in turn, react with ethylene to yield the same products as in Equation **3** (Equations **5** & **6**).

$$CH_3CH{=}CHCH_3 + C_2H_4 \rightleftharpoons 2\,CH_3CH{=}CH_2 \qquad \mathbf{(5)}$$

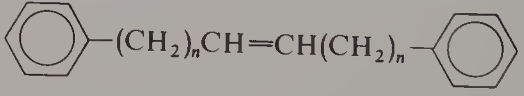
$$CH_3(CH_2)_3CH{=}CH(CH_2)_3CH_3 + C_2H_4 \rightleftharpoons 2\,CH_2{=}CH(CH_2)_3CH_3 \qquad \mathbf{(6)}$$

Under our reaction conditions (constant ethylene pressure of 1.35 atm), the yields of the various olefins after 3 hr at room temperature were (in weight percent) C_3H_6(6), C_4H_8(5), C_6H_{12}(19), C_7H_{14}(55), and $C_{10}H_{20}$(15). Presumably, higher ethylene pressures would increase the yield of 1-hexene.

In a metathesis system in which a terminal and an internal alkene are the reactants, not only is the cross-metathesis of the two olefins possible but each olefin may also react with itself. Recent work has revealed certain reactivity preferences in this type of system. Kelly and Calderon studied the metathesis of 1-pentene with *cis*-2-pentene by use of a $WCl_6/2ClCH_2CH_2OH/(C_2H_5)_2AlCl$ catalyst.[7] At the point where 25% of the original 2-pentene had been consumed, the following relative concentrations (in weight percent) of light olefinic products were observed: C_2H_4(1), $2{-}C_4H_8$(2) (symmetric products), C_3H_6(4), and $1{-}C_4H_8$(12) (unsymmetric products). Self-metathesis of either olefin will yield symmetric products, whereas cross-metathesis will produce unsymmetric products. The observed distribution of the products indicates that the preferred order of reactivity is 1-alkene + 2-alkene > 2-alkene + 2-alkene > 1-alkene + 1-alkene (excluding any degenerate reactions). The data also suggest that the affinity of 2-pentene to cross-metathesize with 1-pentene is eight times greater than its affinity to self-metathesize.

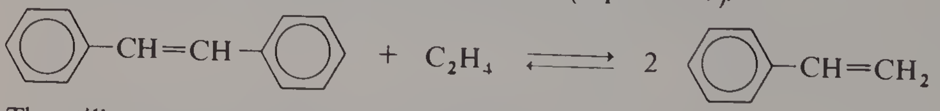
Aryl-substituted olefins may be prepared by metathesis. In a study of the metathesis of a series of alkenyl benzenes of the type

by use of an $MoCl_2(NO)_2[P(C_6H_5)_3]_2/C_2H_5AlCl_2$ catalyst, it was found that when $n = 0$, polymerization occurred.[8] Metathesis to ethylene and olefins of the type

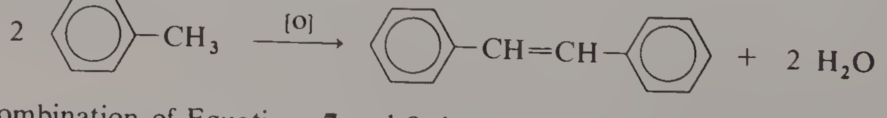


occurred when $n = 1$–6, with the fastest rate and highest conversion for $n = 2$. In all cases, the above molybdenum catalyst was more active than a $W(CO)_5P(C_6H_5)_3/C_2H_5AlCl_2/O_2$ catalyst.

An interesting example of the cometathesis of a phenyl-substituted olefin and ethylene is the conversion of stilbene to styrene (Equation 7).[10]


(7)

The stilbene was prepared by the oxidative coupling of toluene (Equation **8**).

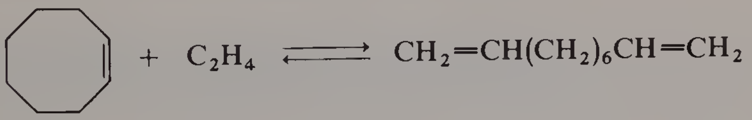

(8)

Combination of Equations **7** and **8** thus provides a route for the synthesis of styrene from toluene.[10]

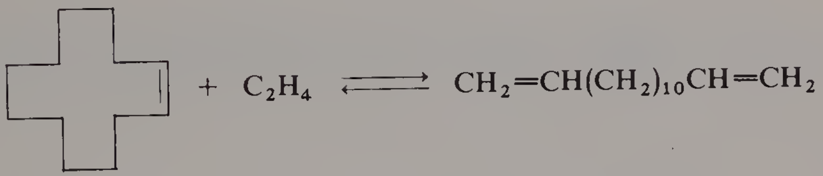
Metathesis of acyclic dienes can yield either cycloalkenes (intramolecular metathesis) or acyclic polyenes (intermolecular metathesis). We have studied the reaction of 1,5-hexadiene and of 1,7-octadiene by use of an $MoCl_2(NO)_2[P(C_6H_5)_3]_2/(CH_3)_3Al_2Cl_3$ catalyst in chlorobenzene at room temperature.[1] With the former substrate, the product mixture contained (by weight) 66% of 1,5-hexadiene, 25% of 1,5,9-decatriene, 7% of 1,5,9,13-tetradecatetraene, 3% of 1,5,9,13,17-octadecapentaene, and no cyclobutene. The latter substrate yielded (by weight) 91% of cyclohexene, 6% of 1,7-octadiene, and 3% of 1,7,13-tetradecatriene.

CYCLIC AND ACYCLIC ALKENES

The cross-metathesis of an acyclic and cyclic alkene provides a convenient route to multiple unsaturated derivatives. With ethylene as the acyclic reactant, α,ω-dienes are formed. For example, we have prepared 1,9-decadiene and 1,13-tetradecadiene from cyclooctene and cyclododecene, respectively, by use of a homogeneous molybdenum catalyst (Equations **9** & **10**).[1]



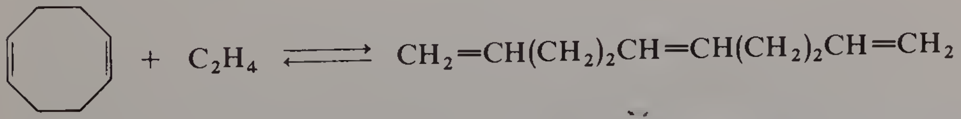
$$+ \ C_2H_4 \rightleftharpoons CH_2{=}CH(CH_2)_6CH{=}CH_2 \qquad (9)$$



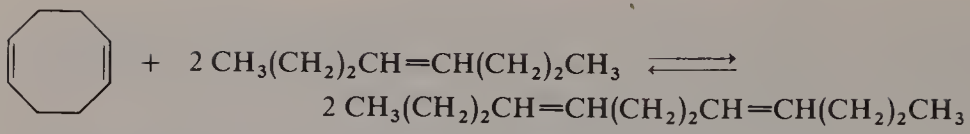
$$+ \ C_2H_4 \rightleftharpoons CH_2{=}CH(CH_2)_{10}CH{=}CH_2 \qquad (10)$$

Reaction **10** was studied in more detail utilizing a $WO_3(SiO_2)$ catalyst.[6] The yield of 1,13-tetradecadiene is enhanced by high pressures, high $C_2H_4/C_{12}H_{22}$ ratios, high space velocities, and temperatures in the range 350–370°C. In a 12-hr laboratory run at 600 psig, 370°C, and a 17 : 1 $C_2H_4/C_{12}H_{22}$ ratio, conversion declined from 94 to 75%, while selectivity increased from 51 to 78%; the average diene yield was 61%. Metathesis of cyclododecene with itself and double-bond isomerization account for the diminished selectivity. A distilled sample of the tetradecadiene was shown, however, to be more than 98% of the α,ω isomer.

The symmetric triene, 1,5,9,-decatriene, was obtained in 18% yield in 2 hr at 0°C by the metathesis of ethylene with 1,5-cyclooctadiene (Equation **11**).[1] The product triene can react with an additional mole of ethylene to yield 1,5-hexadiene. Indeed, the metathesis of cyclic dienes with acyclic alkenes is a preparatively useful method for synthesizing open-chain dienes. The position of the double bonds can be controlled to some extent by proper choice of reactants. Pinazzi and Reyx have obtained 4,8-dodecadiene by reacting 1,5-cyclooctadiene with 4-octene in the presence of $WCl_6/C_2H_5OH/C_2H_5AlCl_2$ (Equation **12**).[11] Diene yields of 70% (based on 1,5-cyclooctadiene) were obtained at a 4-octene/1,5-cyclooctadiene ratio of 2.5.

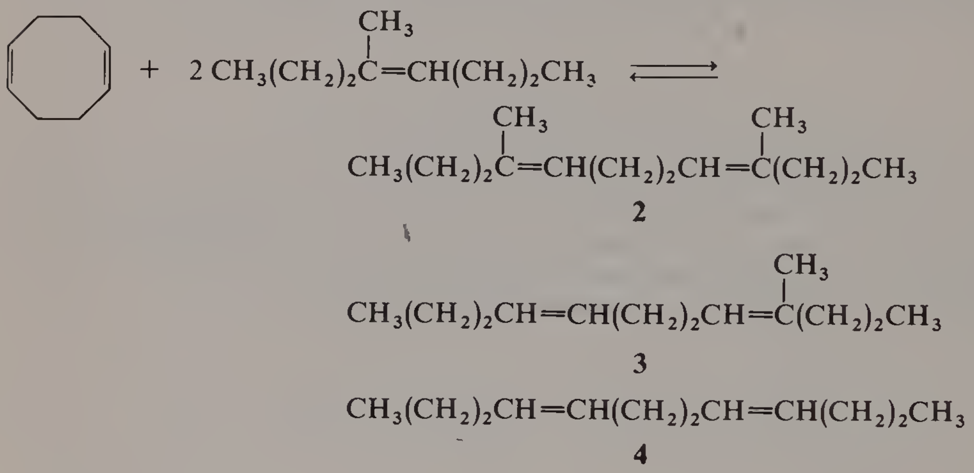


$$+ \ C_2H_4 \rightleftharpoons CH_2{=}CH(CH_2)_2CH{=}CH(CH_2)_2CH{=}CH_2 \qquad (11)$$



$$+\ 2\,\mathrm{CH_3(CH_2)_2CH{=}CH(CH_2)_2CH_3} \rightleftharpoons 2\,\mathrm{CH_3(CH_2)_2CH{=}CH(CH_2)_2CH{=}CH(CH_2)_2CH_3} \quad (12)$$

In an extension of this work, dienes **2–4** were obtained in 22, 31, and 15% yields, respectively, from the metathesis of 1,5-cyclooctadiene with 4-methyl-4-octene at a 2.14 : 1 ratio of alkene/cyclic (Equation **13**).[12]



$$+\ 2\,\mathrm{CH_3(CH_2)_2\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH(CH_2)_2CH_3} \rightleftharpoons$$

$$\mathrm{CH_3(CH_2)_2\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH(CH_2)_2CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}(CH_2)_2CH_3}$$

2

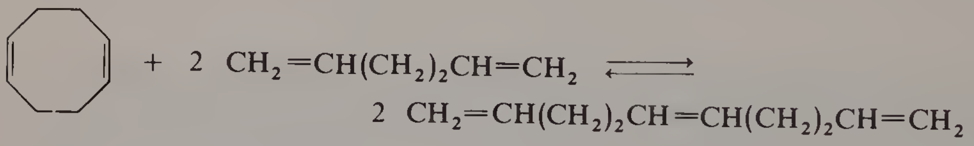
$$\mathrm{CH_3(CH_2)_2CH{=}CH(CH_2)_2CH{=}\overset{\displaystyle CH_3}{\overset{|}{C}}(CH_2)_2CH_3} \quad (13)$$

3

$$\mathrm{CH_3(CH_2)_2CH{=}CH(CH_2)_2CH{=}CH(CH_2)_2CH_3}$$

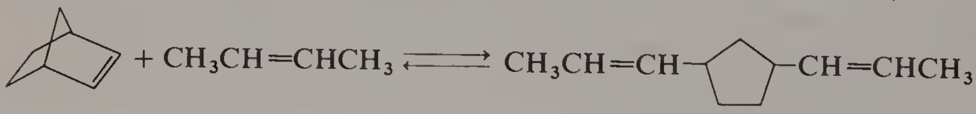
4

The cross-metathesis of a cyclic diene and an acyclic diene can be used to prepare trienes. For example, reaction of 1,5-cyclooctadiene with 1,5-hexadiene gave a 65% yield of 1,5,9-decatriene at a 2.5 : 1 ratio of hexadiene/cyclooctadiene (Equation **14**).[13]



$$+\ 2\ \mathrm{CH_2{=}CH(CH_2)_2CH{=}CH_2} \rightleftharpoons 2\ \mathrm{CH_2{=}CH(CH_2)_2CH{=}CH(CH_2)_2CH{=}CH_2} \quad (14)$$

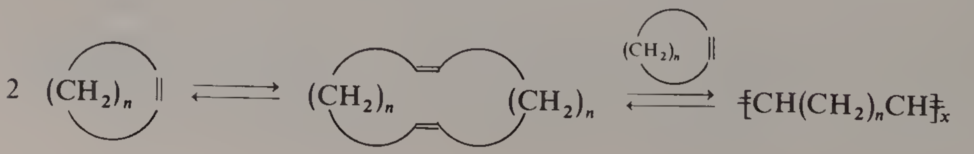
Bis(alkenyl)cycloalkanes may be prepared by metathesis of a bicyclic with an acyclic alkene. In the presence of $[\mathrm{IrCl(cyclooctene)_2}]_2$, norborene reacted with 2-butene to yield 11% of 1,3-bis(1-propenyl)cyclopentane (Reaction **15**).[14]



$$+\ \mathrm{CH_3CH{=}CHCH_3} \rightleftharpoons \mathrm{CH_3CH{=}CH}\text{–}\ \ \text{–}\mathrm{CH{=}CHCH_3} \quad (15)$$

CYCLOALKENES

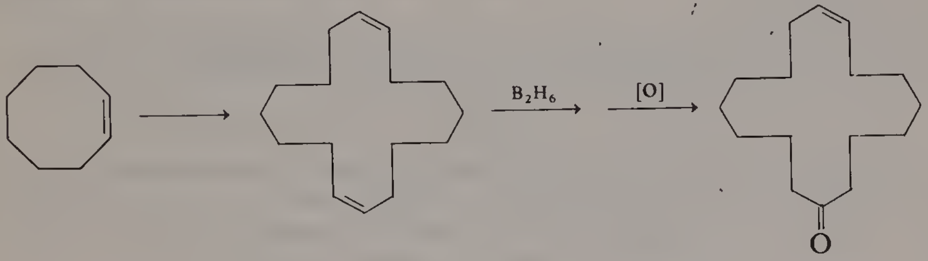
The metathesis of cycloalkenes offers synthetic possibilities in two areas: preparation of macrocyclic polyenes and of unsaturated polymers. Careful adjustment of experimental conditions is necessary to achieve reasonable yields of the former, because the product macrocycles may undergo further metathesis to high-molecular-weight polyalkeneamers (Equation **16**).



$$2\ (\mathrm{CH_2})_n \rightleftharpoons (\mathrm{CH_2})_n \quad (\mathrm{CH_2})_n \xrightleftharpoons{(\mathrm{CH_2})_n} \left[\mathrm{CH(CH_2)_nCH}\right]_x \quad (16)$$

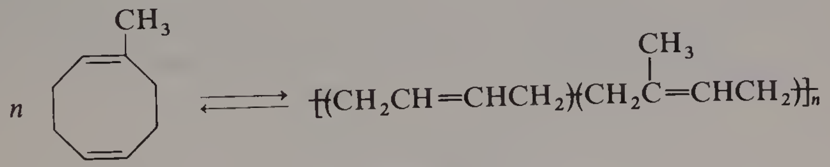
Oligomerization of a 0.5 wt% solution of cyclooctadiene in heptane with a heterogeneous $Re_2O_7(Al_2O_3)$ catalyst at 40°C yields 43% of C_{12}, 10% of C_{16}, and 11% of C_{20} macrocycles, along with 28% polymer at 100% conversion.[15] As might be expected, increasing the cyclooctadiene concentration to 5 wt% increases the yield of polymer to 46%. The sesquioligomers, C_{12} and C_{20}, result from intramolecular metathesis of the growing macrocycles.

The dimer of cyclooctene, 1,9-cyclohexadecadiene, was prepared in 20% yield and subsequently converted in 44% yield by the sequence of reactions in Equation **17** to the musklike ketone **5**.[16]



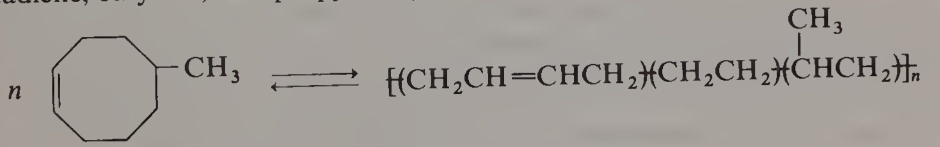
5

The preparation of polyalkeneamers by metathesis has been the subject of a large body of experimental work that is beyond the scope of this survey. The interested reader is referred to recent comprehensive summaries of this area of olefin metathesis.[17,18] One aspect of this work, however, merits special mention, because it exemplifies how synthetic objectives not attainable by any other technique can be achieved by metathesis. This is the synthesis of perfectly alternating interpolymers. By use of conventional methods, the copolymerization of butadiene and isoprene yields polymers that contain random sequences of $-CH_2CH{=}CHCH_2-$ and $-CH_2C(CH_3){=}CHCH_2-$ units. In contrast, metathesis of 1-methyl-1,5-cyclooctadiene yields a polymer in which these units are more than 97% perfectly alternating (Equation **18**).[19]



$$n\ \text{(ring)} \rightleftharpoons \left[(CH_2CH{=}CHCH_2)(CH_2\overset{\overset{CH_3}{|}}{C}{=}CHCH_2)\right]_n \qquad (18)$$

Metathesis of 5-methylcyclooctene gives the perfectly alternating terpolymer of butadiene, ethylene, and propylene (Equation **19**).[20]



$$n\ \text{(ring)}{-}CH_3 \rightleftharpoons \left[(CH_2CH{=}CHCH_2)(CH_2CH_2)(\overset{\overset{CH_3}{|}}{C}HCH_2)\right]_n \qquad (19)$$

Functional Alkenes

Metathesis of alkenes that bear functional groups would greatly extend the synthetic utility of the reaction. While many metathesis catalysts are deactivated in the presence of nonhydrocarbon olefins, limited success has been realized. Boelhouwer *et al.* were able to metathesize long-chain fatty acid esters by use of a $WCl_6/(CH_3)_4Sn$ catalyst.[21] Both internal and terminal esters were suitable substrates (Equations **20** & **21**).

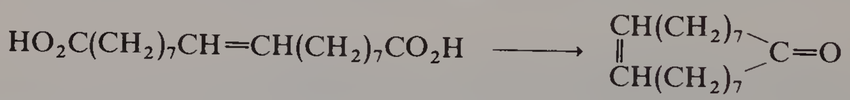
$$2\ CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3 \rightleftharpoons CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3 + CH_3O_2C(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3 \qquad (20)$$

$$2\ CH_2{=}CH(CH_2)_8CO_2CH_3 \rightleftharpoons C_2H_4 + CH_3O_2C(CH_2)_8CH{=}CH(CH_2)_8CO_2CH_3 \qquad (21)$$

The cross-metathesis of an unsaturated ester and 3-hexene was also demonstrated (Equation **22**).

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2CH_3 + CH_3CH_2CH{=}CHCH_2CH_3 \rightleftharpoons CH_3(CH_2)_7CH{=}CHCH_2CH_3 + CH_3CH_2CH{=}CH(CH_2)_7CO_2CH_3 \qquad (22)$$

The difunctional alkenes produced by these reactions are useful starting materials for other syntheses. For example, conversion of the 9-octadecene dimethylester from Equation **20** to the corresponding diacid provides starting material for the preparation of civetone, a valuable perfume component (Equation **23**)



$$HO_2C(CH_2)_7CH{=}CH(CH_2)_7CO_2H \longrightarrow \begin{array}{l} CH(CH_2)_7 \diagdown \\ \| \qquad\qquad\quad C{=}O \\ CH(CH_2)_7 \diagup \end{array} \qquad (23)$$

and for the preparation of unsaturated, vulcanizable polyesters.

Very recently, Nakamura *et al.* have reported the metathesis of functional olefins other than esters.[22] The unsaturated nitrile, 9-octadecenenitrile, was converted in 9% yield to the dinitrile by a $WCl_6/(CH_3)_3Al_2Cl_3$ catalyst (Equation **24**).

$$2\ CH_3(CH_2)_7CH{=}CH(CH_2)_7CN \rightleftharpoons CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3 + NC(CH_2)_7CH{=}CH(CH_2)_7CN \qquad (24)$$

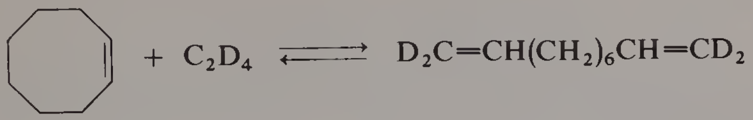
Interestingly, only trace amounts of product were obtained when $(C_2H_5)_3Al_2Cl_3$ was substituted for $(CH_3)_3Al_2Cl_3$. A combination of $MoCl_3(OC_2H_5)_2$ and $(CH_3)_3Al_2Cl_3$ was also effective. Metathesis of unsaturated ethers and ketones gave 2–10% yields, while amides gave trace yields of the corresponding difunctional alkenes. Amines, alcohols, and acids were unreactive.

ALKYNES

Most metathesis studies have centered on alkenes, and the usefulness of the analogous reaction of alkynes has received scant attention. The conversion of the internal alkyne, 2-pentyne, into 2-butyne and 3-hexyne over a $WO_3(SiO_2)$ catalyst occurs in 23% yield.[23] The metathesis of terminal acetylenes is less useful, because cyclotrimerization to benzene derivatives becomes the major reaction, at least with the catalyst systems investigated to date.[24] Like their olefinic counterparts, cycloalkynes undergo ring-opening metathesis; the conversion of cyclodecyne to a series of oligomers, $(C_{10}H_{16})_n$, up to the hexamer ($n = 6$) has been demonstrated.[25]

SYNTHESIS OF ISOTOPICALLY LABELED ALKENES

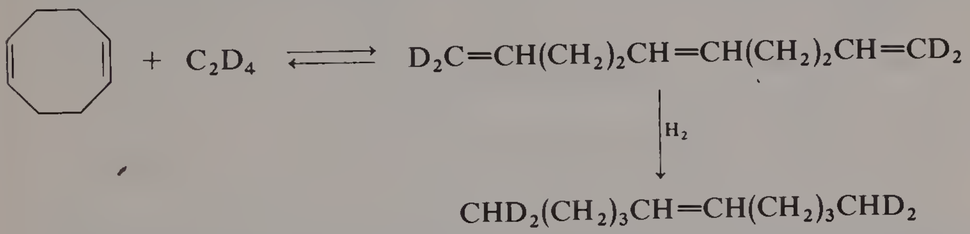
A potentially useful but heretofore unexploited application of metathesis is the synthesis of isotopically labeled olefins. For example, the cometathesis of readily available tetradeuteroethylene with cycloalkenes or symmetric internal alkenes would yield terminally deuterated α,ω-dienes and α-olefins, respectively (Equations **25** & **26**).



(25)

$$CH_3CH_2CH{=}CHCH_2CH_3 + C_2D_4 \rightleftharpoons 2\, CH_3CH_2CH{=}CD_2 \quad (26)$$

An internal olefin labeled at the terminal methyl groups would be available by the combination of metathesis and selective hydrogenation outlined in Equation **27**.



(27)

Model studies with deuterated butenes indicate that no hydrogen-deuterium scrambling occurs during metathesis.[26] The corresponding ^{14}C-labeled olefins would be available by the same types of reactions, starting with $^{14}CH_2{=}^{14}CH_2$.

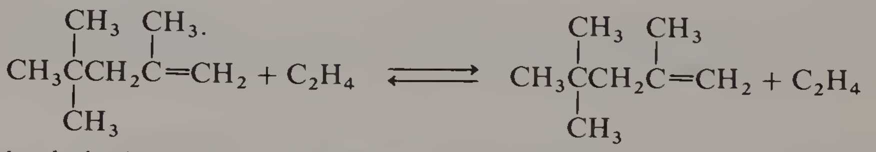
STEREOSELECTIVE SYNTHESES

In all cases of metathesis, except when ethylene is a reactant, an internal double bond is formed that may be either *cis* or *trans*. The ability to synthesize double bonds of specific configuration is highly desirable. Our early work on the stereochemistry of metathesis with a homogeneous molybdenum catalyst and 2-pentene as the substrate indicated some degree of stereoselectivity, with the products being predominantly of the same configuration as the starting material, namely, *cis*-2-pentene → *cis*-2-butene + *cis*-3-hexene.[27] The degree of selectivity was a function of the starting 2-pentene. *Trans*-2-pentene yielded 86% of the *trans* isomer in the 2-butene and 93% of the *trans* isomer in the 3-hexene at a conversion of 42% (50% conversion at equilibrium). On the other hand, *cis*-2-pentene gave 73% *cis*-2-butene and 67% *cis*-3-hexene at 26% conversion. The percentages of the *cis* isomer decreased with higher conversions. Both 2-pentene isomers show reduced selectivity at longer reaction times because of the fact that *cis*/*trans* isomerization accompanies metathesis, with the result that the product isomer distribution approaches the thermodynamic value.[27]

Recent work of Dall'Asta indicates that enhanced selectivity can be achieved by suitable modification of the catalyst. Metathesis of *cis*/*trans*-2-pentene with a $WCl_6/(ClCH_2)_2CHOH/(C_2H_5)_3Al_2Cl_3$ catalyst to which 1 equiv of triphenylphosphine has been added yields 3-hexene that is more than 90% *trans* at a 2-pentene conversion of 26%.[2] Selectivity in the product 2-butene is lower. As it stands, this system does not offer a route to *cis*-3-hexene, but it does offer reason to believe that with the proper catalyst system, either *cis* or *trans* double bonds of high configurational purity may be attainable by olefin metathesis.

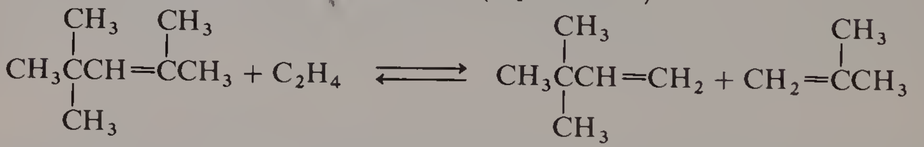
COMBINATION PROCESSES

Worthwhile synthetic manipulations may result from the combination of a metathesis catalyst with compatible catalysts for other reactions. Such an application has been made by Phillips Petroleum in the semiworks-scale manufacture of neohexene. The process is based on the cross-metathesis of ethylene and diisobutylene (2,4,4-trimethylpentene). The commercial diisobutylene feedstock is a mixture of the 1 and 2 isomers. Ethylene cleavage of the former regenerates the starting materials (Equation **28**), while the latter



$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\overset{CH_3}{C}{=}CH_2 + C_2H_4 \rightleftarrows CH_3\overset{CH_3}{\underset{CH_3}{C}}CH_2\overset{CH_3}{C}{=}CH_2 + C_2H_4} \qquad \textbf{(28)}$$

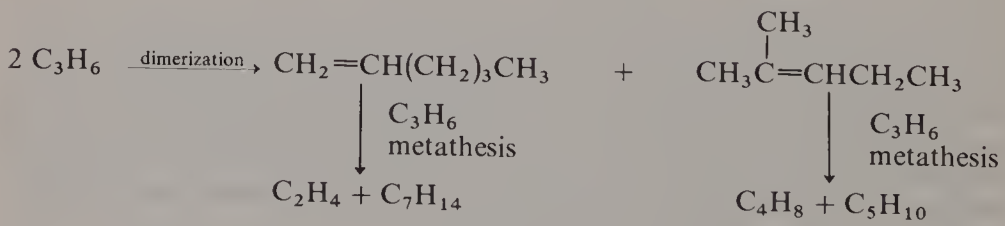
yields the desired product and isobutylene (Equation **29**).



$$\mathrm{CH_3\overset{CH_3}{\underset{CH_3}{C}}CH{=}\overset{CH_3}{C}CH_3 + C_2H_4 \rightleftarrows CH_3\overset{CH_3}{\underset{CH_3}{C}}CH{=}CH_2 + CH_2{=}\overset{CH_3}{C}CH_3} \qquad \textbf{(29)}$$

The neohexene yield is thus limited by the 2 isomer content of the diisobutylene. The inclusion of a catalyst capable of isomerizing the 1 isomer to the 2 isomer with a metathesis catalyst would enhance the yield of neohexene. Moreover, in the presence of excess ethylene the double-bond isomerization equilibrium will be constantly shifted toward the 2 isomer, which is being consumed in the metathesis step. A suitable catalyst combination for this process consists of $WO_3(SiO_2)$ (metathesis) and MgO (isomerization).[28] The effectiveness of this technique is illustrated by the following data. At 400 psig, 4 : 1 C_2H_4/diisobutylene, and 370°C, $WO_3(SiO_2)$ alone gives 4% neohexene; under the same conditions, a 3 : 1 $MgO/WO_3(SiO_2)$ mixture yields 37% neohexene.[6]

Another combination process that involves olefin dimerization and metathesis has been demonstrated by Zuech by use of propylene as the substrate.[29] In the absence of a metathesis catalyst, dimerization of the propylene would be the predominant reaction. In the mixed catalyst system, the dimers undergo metathesis with propylene to yield, for example, pentenes and heptenes (SCHEME 2).



SCHEME 2

Metathesis of other combinations of olefins in the system can yield higher-molecular-weight products. One millimole of $MoCl_2(NO)_2[P(C_6H_5)_3]_2$ (for metathesis) and 0.12 mmol of $NiCl_2[P(C_6H_5)_3]_2$ (for dimerization) jointly activated with $C_2H_5AlCl_2$ gave 16.4 wt% of C_5, 13.6 wt% of C_7, and a trace of $C_{>8}$ olefins (excluding C_2 and C_3 olefins in these percentages). Doubling the quantity of $NiCl_2[P(C_6H_5)_3]_2$ broadens the range of product olefins. In this case, the product mixture contained 9.9 wt% of C_5, 18.4 wt% of C_7, and 17.1 wt% of $C_{>8}$. Olefins of a broad range of molecular weights can thus be obtained from a single low-molecular-weight alkene by this combination process.

PHEROMONE SYNTHESIS

An interesting and potentially important application of the cross-metathesis of two acyclic olefins is the synthesis of insect pheromones. Muscalure (*cis*-9-tricosene), the sex pheromone of the common housefly (*Musca domestica*), has been prepared by two routes: metathesis of 1-decene with 1-pentadecene by use of an $MoCl_2(NO)_2[P(C_6H_5)_3]_2/C_2H_5AlCl_2$ catalyst (Equation **30**)[30] and metathesis of 2-hexadecene with 9-octadecene by use of a $WCl_6/C_2H_5OH/C_2H_5AlCl_2$ catalyst (Equation **31**).[31]

$$CH_2{=}CH(CH_2)_7CH_3 + CH_2{=}CH(CH_2)_{12}CH_3 \rightleftharpoons CH_3(CH_2)_7CH{=}CH(CH_2)_{12}CH_3 + C_2H_4 \quad (30)$$

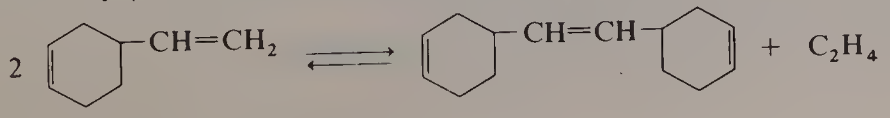
$$CH_3CH{=}CH(CH_2)_{12}CH_3 + CH_3(CH_2)_7CH{=}CH(CH_2)_7CH_3 \rightleftharpoons CH_3CH{=}CH(CH_2)_7CH_3 + CH_3(CH_2)_{12}CH{=}CH(CH_2)_7CH_3 \quad (31)$$

The 9-tricosene from Equation **31**, which constituted 9.1 wt% of the product mixture, was separated by fractional distillation as a *cis*/*trans* mixture. In similar fashion, *cis*-13-heptacosene, the pheromone of another species of fly (*Musca autumnalis*), was obtained in 10.2 wt% yield from 1-tetradecene and 2-hexadecene.[31]

The starting materials required in these syntheses are all available from α-olefin processes and, thus, ultimately from ethylene. The 2-alkenes can be obtained by selective isomerization of the α-olefin, and the 9-octadecene is available from the metathesis of 1-decene. Thus, metathesis makes possible the synthesis of these natural products from petrochemical raw materials. The low yields may be tolerable because of the extremely high physiologic activity of pheromones. In addition, separation of the (in these cases) active *cis* isomer from the inactive *trans* isomer is not essential, because the pheromones are generally used in high dilution and the *trans* isomer may be considered as an inert solvent.

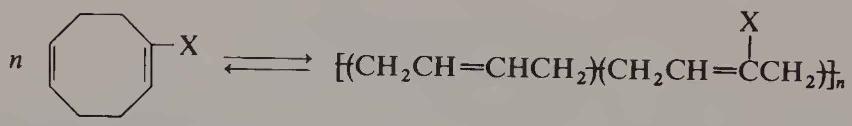
SELECTIVITY DIFFERENCES

Differing patterns of reactivity may be used advantageously in designing synthetic sequences that involve substrates that contain multiple double bonds. These reactivity differences may result from the nature of the double bond itself or from the particular catalyst employed and, in principle, offer the possibility that under the proper circumstances, certain double bonds can be metathesized, while others are left intact. Studies of the metathesis of polyenes in which the double bonds differ significantly in character are sparse; however, the few examples available will serve to illustrate our point. For example, metathesis of 4-vinylcyclohexene occurs only at the exocyclic bond because of the thermodynamic stability of the cyclohexene ring, thus allowing the preparation of 1,2-bis(cyclohexenyl)ethylene in high selectivity (Equation **32**).[32]



(32)

Ring-opening metathetic polymerization of 1,5-cyclooctadienes substituted on one of the double bonds occurs virtually exclusively at the unsubstituted double bond due to steric hindrance (Equation 33).[19]



$$n\ \text{C}_8\text{H}_{11}\text{X} \rightleftharpoons \left[(CH_2CH{=}CHCH_2)(CH_2CH{=}\overset{X}{\overset{|}{C}}CH_2)\right]_n \qquad (33)$$

$X = Cl, C_2H_5$

Recent work of Dall'Asta indicates that catalyst modification can lead to reactivity discrimination based on the configuration of the double bond. A 27.5% *cis*/72.5% *trans* mixture of 2-pentene was reacted with a $WCl_6/(ClCH_2)_2CHOH/$-$(C_2H_5)_3Al_2Cl_3$ catalyst modified by the addition of 1 equiv of triphenylphosphine. During the time that 80% of the *cis* isomer had undergone metathesis, only 4% of the *trans* isomer had reacted.[2]

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