# INSERTION AND THERMAL DECOMPOSITION REACTIONS OF CYCLOPENTADIENYLCOBALT(III) DIALKYL COMPLEXES

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## Abstract

$PMe_3$ replaces $PPh_3$ in $CpCo(PPh_3)(Me)_2$ (1, Cp = $\eta^5$-$C_5H_5$) in a dissociative substitution reaction to give $CpCo(PMe_3)(Me)_2$; the first order rate constant for $PPh_3$ loss from 1 is $4 \times 10^{-4}$ $sec^{-1}$ at 30°C in toluene-$d_8$. Dialkyl complex 1 doubly alkylates CO in an intramolecular process to give acetone in high yield; this proceeds via CO substitution in 1 to give the spectroscopically observed intermediate $CpCo(CO)(Me)_2$ (6), followed by migratory insertion, and reductive elimination from an acyl-alkyl complex. Heating and then carbonylating mixtures of 1-$d_0$ and 1-$d_6$ (deuterated methyl groups) in benzene revealed the presence of an intermolecular methyl exchange process in 1. We have reinvestigated the reaction of 1 with diphenylacetylene and, in addition to the organometallic products observed by previous workers, isolated two new organic products 2,3-diphenyl-1-butene (11) and Z-2,3-diphenyl-2-butene; these products account for >95% of the methyl groups in starting 1 and were formed in the ratio 14:1 in the absence of added $PPh_3$. Additional experiments designed to probe the mechanism of product formation led to the following conclusions: (1) high yield stereospecific double alkylation of diphenylacetylene is a feasible process; (2) reactions of 11 in this system involve two diastereomeric $\eta^2$-olefin complexes which

are interconvertible only by dissociation of the olefinic ligand from the metal; (3) hydrogen shifts involved in the $Cp(PPh_3)Co$-catalyzed isomerization of alkenes occur more rapidly than dissociation of the alkene from the metal center; and (4) interconversion of $\eta^3$-allyl complexes via rotation in $\eta^1$-allyl complexes is much slower than hydrogen transfer and product formation. Ethylene reacts with 1 to give methane, propene, and the new ethylene complex $CpCo(PPh_3)(C_2H_4)$ (14); this was independently generated by thermal $PPh_3$ or photochemical CO substitution in $CpCo(PPh_3)_2$ and $CpCo(CO)(PPh_3)$, respectively. The production of propene from ethylene and 1 is a model for the chain-growth step in the Ziegler-Natta polymerization of olefins. The products can be explained by a classical mechanism involving insertion of ethylene into a cobalt-carbon $\sigma$-bond or an alternative one involving ethylene addition to an intermediate metal-carbene complex formed by $\alpha$-elimination. Labeling experiments in this system have shown propene is formed by transfer of one intact methyl group to ethylene, in agreement with the classical view. Thermal decomposition of 1 is competitive with the alkylation of ethylene and gives mostly methane, abstracting the fourth methane hydrogen from the cyclopentadienyl ring. The decomposition has been monitored by $^1H$ NMR spectroscopy in the presence of added $PPh_3$ and ethylene (conditions where no propene is generated) and $Cp'Co(PPh_3)(C_2H_4)$ ($Cp' = \eta^5CH_3C_5H_4$)

and $Cp'Co(PPh_3)(Me)_2$ have been observed spectroscopically and identified as the primary and secondary products of the decomposition, respectively. Together, these reactions show reductive elimination in alkyl-acyl and alkyl-vinyl complexes is more favorable than alkyl-alkyl reductive elimination and this is attributed to the ability of the former systems to donate an additional pair of electrons to the metal center in the reductive elimination transition state.

$\eta^5$-Cyclopentadieny(triphenylphosphine)cobaltacyclopentane (18) has been prepared by reaction of $CpCo(PPh_3)I_2$ with 1,4-dilithiobutane at low temperature. This metallacycle is thermally more sensitive than its dimethyl analog 1 and decomposes to give 1-butene which is subsequently isomerized by the organometallic products to a mixture of 2-butenes. In this system, ethylene insertion cannot compete with thermal decomposition, but CO and diphenylacetylene insertion can. CO reacts with 18 to give cyclopentanone via the CO substituted analog of 18; this has been observed spectroscopically and builds up to a greater degree than the dimethyl analog observed during the reaction of 1 with CO. Diphenylacetylene reacts with 18 to give the expected products of double alkylation, 1,2-diphenylcyclohexene and 2,3-diphenylcyclohexene, and Z-1,2-diphenyl-1,5-hexadiene as well. The latter product is presumably derived from β-elimination in an intermediate metallacycloheptene which also generates the cyclohexenes via reductive elimination.

Table of Contents


| | | Page |
|---|---|---|
| I. | Reactions of $PMe_3$, CO, Diphenylacetylene, Ethylene, and Propene with $CpCo(PPh_3)(Me)_2$ and Some Features of its Thermal Decompositon | |
| | A. Introduction | 2 |
| | B. Results and Discussion | 5 |
| | C. Summary and Conclusions | 41 |
| | D. Experimental Section | 44 |
| | E. Figure 1 | 79 |
| II. | Preparation, Thermal Decomposition, and CO and Diphenylacetylene Insertion Reactions of Cyclopentadienyl(triphenylphosphine)cobalta-cyclopentane | |
| | A. Introduction | 82 |
| | B. Results and Discussion | 84 |
| | C. Summary and Conclusions | 108 |
| | D. Experimental Section | 110 |
| III. | Appendix I: the Reaction of $CpCo(PPh_3)(Me)_2$ with Styrene | 127 |
| IV. | References and Notes | 135 |

# Chapter I

## Reactions of $PMe_3$, CO, Diphenylacetylene, Ethylene, and Propene with $CpCo(PPh_3)(Me)_2$ and Some Features of its Thermal Decomposition

## Introduction

The overall insertion of an unsaturated molecule X into a transition metal-alkyl or hydride bond (equation 1) is one of the fundamental steps in organometallic reactions and often a primary process in reactions catalyzed by homogeneous solutions of transition metal complexes.[1] The insertion of CO,[2] an alkyne,[3] or an alkene[4] into a metal-alkyl bond is of particular interest because it generates a new C-C bond. If a complex bearing two alkyl groups reacts in this way, two new C-C bonds can be formed. Insertion followed by reductive elimination in the new acyl-alkyl (equation 2), vinyl-alkyl (equation 3) or dialkyl (equation 4) complex can generate a ketone, olefin, or alkane respectively.

There are several examples of the reaction of a dialkyl complex with CO to give the corresponding ketone.[5] The analogous dialkylation of alkynes is much less common[6] and the reaction of a well-characterized dialkyl complex with an alkyne to generate a new olefin[7] had not been reported before the completion of our work to the best of our knowledge. The double alkylation of an olefin by a transition metal dialkyl is an unknown process at present. In fact, despite the existence of a few isolated alkyl-olefin complexes,[8] the direct insertion of the coordinated olefin in such a complex into the metal-carbon bond to give the corresponding isolable alkyl complex has not been

Equation 1

$$M\text{-}R + X \rightarrow M - X - R \qquad R = H, \text{alkyl}$$

Equation 2

$$R_2M + CO \rightarrow R - \overset{\overset{O}{\|}}{M} - R \rightarrow M + \overset{\overset{O}{\|}}{R\quad R}$$

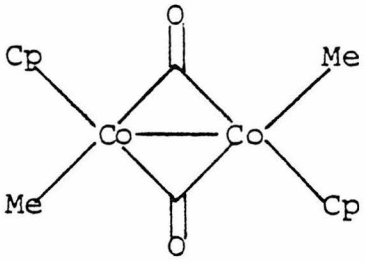
Equation 3

$$R_2M + R'\text{-}C{\equiv}C\text{-}R' \rightarrow R - \overset{R'\quad R'}{\underset{\|}{M}} - R \rightarrow M + \overset{R'\quad R'}{\underset{\|}{R\quad R}}$$

Equation 4

$$R_2M + R'_2C{=}CR'_2 \rightarrow R - M - CR'_2CR'_2R \rightarrow M + RR'_2C\text{-}CR'_2R$$

Equation 5




4

$\rightarrow [CpCo(CO)(Me_2)] \rightarrow CpCo(CO)_2$

6 5

$+ CH_3\overset{\overset{O}{\|}}{C}CH_3 +$ clusters

observed. This kind of an insertion has long been thought to provide the chain-growth step in the Ziegler-Natta catalyzed polymerization of olefins,[9] one of the most important homogeneous catalytic processes.

The mechanistic details of the insertion reaction are best understood for the case of CO insertion.[2] Here CO coordination to the metal center is followed by alkyl group migration to CO to give an acyl complex. Using this reaction to model other potential insertions and considering equations 2 - 4, one can generate a list of requirements a dialkyl complex must meet in order to successfully undergo the double alkylations outlined above: (1) a relatively low-energy pathway for the coordination of an unsaturated ligand must be available, (2) insertion must be competitive with other modes of reaction (including decomposition), and (3) some means of stabilizing the coordinatively unsaturated and formally reduced organometallic product of the final reductive elimination which generates the free organic product must be available. This often means the formal metal oxidation state two units lower than that in the starting dialkyl complex must be readily accessible.

We have found that the known[10] dimethyl complex, $\eta^5$-cyclopentadienyl(triphenylphosphine)dimethylcobalt(III) (1) satisfactorily meets these requirements and in this paper[11] we present details of the reaction of 1 with $PMe_3$, CO, diphenylacetylene, ethylene, and propene.

## Results and Discussion

Substitution reactions of 1 with $PMe_3$. The substitutional lability of the triphenylphosphine in 1 was demonstrated by the rapid, quantitative (NMR) reaction of 1 and trimethylphosphine. When a toluene-$d_8$ solution of 1 and a deficiency of trimethylphosphine were observed by $^1H$ NMR (180 MHz) the cyclopentadienyl (δ 4.44 ppm), methyl (δ 0.49 ppm, d, $J_{PH}$ = 6 Hz) and triphenylphosphine (δ 7.50 ppm, ortho-H) signals of 1 decreased in intensity as signals due to free triphenylphosphine (δ 7.32 ppm, ortho-H) and new cyclopentadienyl (δ 4.37 ppm) and methyl (δ 0.16 ppm, d, $J_{PH}$ = 6 Hz) absorptions grew in. The absorption for free trimethylphosphine (δ 0.76 ppm, d, $J_{PH}$ = 2.4 Hz) was replaced by a new doublet ($J_{PH}$ = 9 Hz) at δ 0.77 ppm as well. The appearance of free triphenylphosphine and disappearance of free trimethylphosphine are consistent with the substitution of one ligand for the other and the new cyclopentadienyl, methyl, and trimethylphosphine signals were assigned to $CpCo(PMe_3)(Me)_2$ (2), (Cp = $\eta^5$-$C_5H_5$).[12] The upfield shift of the cyclopentadienyl and methyl absorptions for 2 relative to those for 1 is consistent with the stronger σ-donating capabilities of trimethylphosphine over triphenylphosphine.[13]

There are two straightforward mechanistic alternatives for the substitution of triphenylphosphine in 1 by trimethylphosphine to give 2. An associative process involving direct attack of trimethylphosphine on 1 to displace triphenyl-

phosphine and a mechanism involving dissociation of triphenylphosphine to generate a coordinatively unsaturated 16-electron intermediate which is trapped by trimethylphosphine to give 2 need to be distinguished (Scheme I). The two alternatives were distinguished by measuring the rate of disappearance of starting material 1, $k_{obs}$, at two different trimethylphosphine concentrations. The rate law for path A, (Scheme I) predicts $k_{obs}$ will be first order in [1] and [$PMe_3$] whereas the rate law for path B predicts $k_{obs}$ will be first order in [1] and independent of [$PMe_3$], when $k_2[PMe_3]$ is large relative to $k_{-1}[PPh_3]$. A first order plot of the disappearance of 1 (NMR) in the presence of an initial five-fold excess of trimethylphosphine (0.51 M) in toluene-$d_8$ was linear over three half-lives and gave a rate constant $k_{obs}$ = (4.49 ± 0.05) x $10^{-4}$ $sec^{-1}$ at 30°C. The rate constant for the reaction with a ten-fold excess of trimethylphosphine (0.96 M) was (3.89 ± 0.05) x $10^{-4}$ $sec^{-1}$. The similarity[14] of these rate constants shows the rate is independent of trimethylphosphine concentration and establishes the dissociative nature of the substitution.

It is interesting to compare the rates of phosphine dissociation ($k_1$) in 1 and a related complex, $CpCoC(Me)C(Me)C(Me)C(Me)(PPh_3)$ (3). Metallacyclopentadiene 3 also undergoes dissociative substitution of triphenylphosphine but at a much lower rate ($k_1$ = 5.8 x $10^{-5}$ $sec^{-1}$, 74°C, benzene-$d_6$).[15] The slower rate of substitution in 3 presumably reflects the ability of the cyclic, conjugated

Scheme I

Path A:

$$CpCo(PPh_3)(Me)_2 + PMe_3 \xrightarrow{k} CpCo(PMe_3)(Me)_2 + PPh_3$$

$$\underset{\sim}{1} \qquad\qquad \underset{\sim}{2}$$

$$\frac{-d[\underset{\sim}{1}]}{dt} = k[\underset{\sim}{1}][PMe_3]$$

Path B:

$$\underset{\sim}{1} \underset{k_{-1}[PPh_3]}{\overset{k_1}{\rightleftharpoons}} CpCo(Me)_2 \xrightarrow{k_2[PMe_3]} \underset{\sim}{2}$$

A

$$\frac{-d[1]}{dt} = \frac{k_1 k_2 [PMe_3][\underset{\sim}{1}]}{k_{-1}[PPh_3] + k_2[PMe_3]}$$

dialkyl substituent to remove electron density from the metal center more effectively than the two methyl groups in 1, thereby raising the energy of the 16-electron intermediate and/or lowering the energy of the coordinatively saturated starting material in 3 relative to 1.

This rate difference emphasizes the ability of ligands to modify the apparent electronic properties of metal centers in the same formal oxidation state.

Carbonylation of 1. The dinuclear dimethyl complex 4 decomposes in an intermolecular process to give acetone, $CpCo(CO)_2$ (5) and additional $\eta^5$-cyclopentadienylcobaltcarbonyl clusters. The decomposition also proceeds under a CO atmosphere where acetone and 5 are the only products. Under either set of conditions, an intermediate is observed during the decomposition and was identified as $CpCo(CO)(Me)_2$ (6) on the basis of spectroscopic (NMR, IR) evidence (*vide infra*). This intermediate decomposes in an intramolecular process and is the major source of acetone under low CO pressures (equation 5).[16] These observations motivated our initial interest in 1, as successful substitution of triphenylphosphine by CO would constitute an independent synthesis of intermediate 6 and should therefore generate acetone via an intramolecular process as well.

Dimethyl complex 1 reacted cleanly with CO to give acetone (100% NMR) and 5 and $CoCo(CO)(PPh_3)$ (7) in varying relative amounts depending on the amount of CO available in

the system (5 was the major product under excess CO and 7 under a deficiency). The carbonylation was attempted in several different solvents and monitored by NMR to determine the best conditions for observing intermediate 6. Only very small absorptions consistent with the intermediacy of 6 were observed in benzene-$d_6$, even under high pressures (5 atm) of CO. Larger absorptions were observed in cyclohexane-$d_{12}$ but the best results were obtained in tetrahydrofuran (THF) where 1 is more soluble. After standing several hours at room temperature under ca. 1 atm of CO the cyclopentadienyl (δ 4.43 ppm) and methyl (δ 0.07 ppm, d, $J_{PH}$ = 6 Hz), absorptions of 1 were accompanied by small cyclopentadienyl signals due to 5 (δ 5.15 ppm) and 7 (δ 4.62 ppm, d, $J_{PH}$ = 1 Hz) as well as new singlets in the cyclopentadienyl (δ 4.96 ppm) and methyl (δ 0.37 ppm) region and a small singlet due to acetone (δ 2.03 ppm). The IR spectrum of a reaction mixture generated this way showed a new band at 1998 $cm^{-1}$ and bands characteristic of 5 (2017, 1960 $cm^{-1}$), 7 (1929 $cm^{-1}$), and acetone (1716 $cm^{-1}$) after the CO was removed. The new signals match those assigned to 6 during the decomposition of 4.[16] During the carbonylation of 1, 6 reached a maximum concentration of about 8% of the combined organometallic species present in the reaction mixture. In the absence of CO, the half life for disappearance of 6 was ca. 11 hr at room temperature.

The intramolecularity of acetone production from 1 was

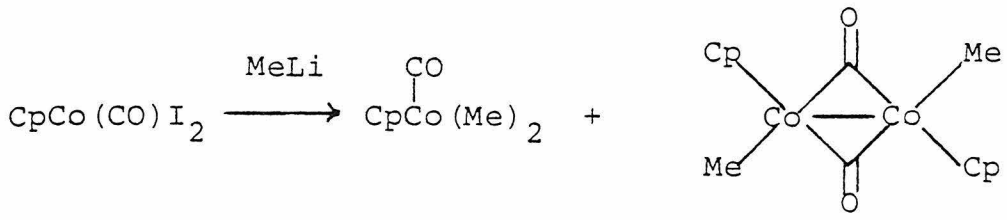
probed by carbonylating (8 atm, 60°C, ca. 18 hr, benzene) known mixtures of $\underset{\sim}{1}$-$d_0$ and $\underset{\sim}{1}$-$d_{21}$ (completely deuterated phosphine and methyl groups) and measuring mass spectroscopically the isotope distribution in the acetone product after isolation by preparative GC. Carbonylation of a 0.05 M solution of $\underset{\sim}{1}$ led to nominal (2%) crossover[17] in the product acetones, confirming the intramolecularity of the acetone production. However, a surprising concentration dependence on the intramolecularity of the reaction was discovered. Carbonylation of a 0.25 M solution of $\underset{\sim}{1}$ showed 12% crossover in the products and furthermore, heating a 0.24 M solution of $\underset{\sim}{1}$ for 42 hr at 60°C, followed by dilution to 0.05 M and subsequent carbonylation led to 100% crossover. These results demonstrate that although the carbonylation of $\underset{\sim}{1}$ to give acetone is intramolecular as expected on the basis of results obtained from the decomposition of $\underset{\sim}{4}$, a competing and normally degenerate process involving net exchange of intact methyl groups (insignificant amounts of acetone-$d_1$, $d_2$, $d_4$, and $d_5$ were observed) in starting $\underset{\sim}{1}$ exists. This process is also much faster than the rate of decomposition of $\underset{\sim}{1}$ (*vide infra*). Although a few examples of methyl group exchange between transition metal centers are known, the mechanistic details of such exchange are poorly understood at present.[18] For example, the question of whether or not the exchange proceeds through coordinatively unsaturated intermediates has not been addressed. These and other

mechanistic questions concerning the methyl exchange in 1 are currently being explored in our laboratory. The present preliminary results further emphasize the important role crossover experiments can play in elucidating mechanistic details of apparently straightforward, high-yield reactions.[19]

Because treatment of $CpCo(PPh_3)I_2$ with MeMgI gave 1, the possibility of independently generating 6 by a similar reaction with $CpCo(CO)I_2$ was explored. After treating a cold (-78°C) diethylether slurry of 8 with 0.6 equivalent (less than the theoretical 2 equivalents required to doubly alkylate 8) of 0.2 M MeLi, an IR spectrum (room temperature) of the resulting mixture showed the band due to 8 (2067 $cm^{-1}$) had completely disappeared and was replaced by a small band due to 6 (2001 $cm^{-1}$) as well as much larger bands (1860, 1828 $cm^{-1}$) consistent with the presence of 4. After 2 equivalents of MeLi were added, a roughly 1:1 mixture of 6 and 4 was obtained (eq 6). Similar treatment of 8 with a single aliquot (2 equivalents) of 1.8 M MeLi gave a mixture containing traces of 6 in the presence of 4. Although these reactions did generate solutions displaying the IR band characteristic of 6, it appears a competitive process involving reduction, dimerization, and finally alkylation to give 4 from 8 predominates under these conditions[20] and additional efforts to prepare 6 in this way were not pursued.

A mechanism for the formation of acetone from 1 and CO consistent with the above results is shown in Scheme II.

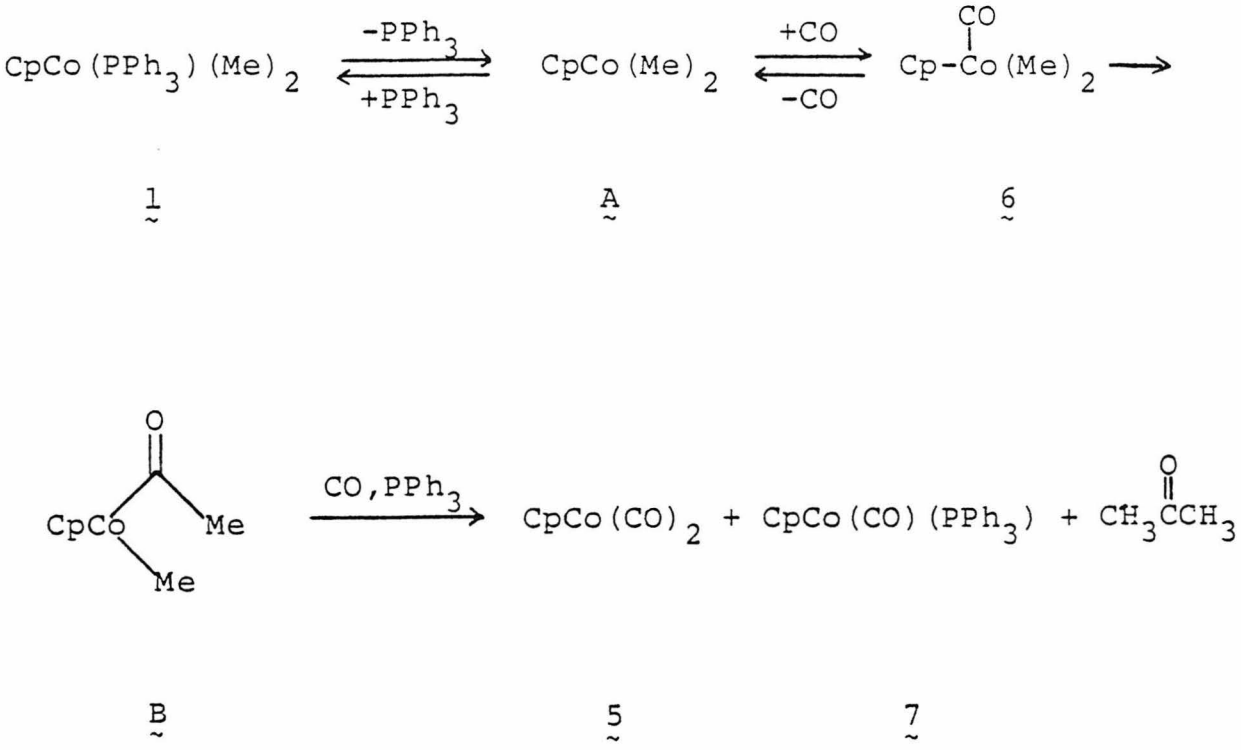
Equation 6




6 (minor)

4 (major)

Scheme II


CpCo(PPh3)(Me)2
-PPh3
+PPh3
CpCo(Me)2
+CO
-CO
CO
Cp-Co(Me)2
1
A
6
O
CpCo
Me
Me
CO,PPh3
CpCo(CO)2 + CpCo(CO)(PPh3) + CH3CCH3
O
B
5
7

In analogy to the trimethylphosphine case, CO substitution to give spectroscopically observed 6 is assumed to proceed through triphenylphosphine dissociation from 1 and CO trapping of the resulting 16-electron intermediate A. Methyl migration in 6, followed by reductive elimination in an acyl-methyl complex such as B, generates acetone and the resulting organometallic fragment is scavenged by the available ligands to give 5 and 7. In this case, we do not know whether reductive elimination occurs in 16-electron intermediate B or an 18-electron analog generated by ligand trapping. This question is approached in another system described below.

Reaction of 1 with diphenylacetylene. In their paper presenting the preparation of 1, Yamazaki and Hagihara also described the reaction of 1 with diphenylacetylene. They reported that heating a solution of 1 (0.07 M) and diphenylacetylene (0.19 M) for 4 hr in refluxing benzene gave the metallacyclopentadiene 9 (Scheme III) and $\eta^4$-tetraphenylcyclobutadiene($\eta^5$-cyclopentadienyl)cobalt(I) (10) in 49 and 13% isolated yields, respectively.[10a] Because this report did not account for the methyl groups originally bound to 1, and 1 reacts with CO by ligand substitution, migratory insertion, and reductive elimination to give acetone in high yield, we reinvestigated the reaction of 1 and diphenylacetylene. We monitored the reaction by $^1$H NMR spectroscopy (90 MHz) in sealed tubes so all the products could be

observed, including any volatile ones.

In a typical reaction, a solution of 1 (0.19 M) and diphenylacetylene (0.76 M) in benzene-$d_6$ was heated at 56°C for 30.5 hr, after which time 94% of the methyl signal from 1 had disappeared. Over the course of the reaction the cyclopentadienyl singlet (δ 4.46 ppm) and methyl doublet (δ 0.58 ppm, J = 6 Hz) due to 1 were replaced by a new singlet at δ 4.78 ppm and doublet (J = 7 Hz) at δ 1.36 ppm. Smaller absorptions were observed at δ 5.34 (broad s), 5.06 (m), 4.48 (s), 3.87 (q, J = 7 Hz), and 2.01 (s) ppm. When the reaction was complete, very small singlets at δ 4.68 and 2.45 ppm were also present. The components of this product mixture were separated by a combination of column and vapor phase chromatography and in this way the major organometallic product was shown to be 9, (95%; Cp, δ 4.78 ppm) in agreement with Yamazaki's earlier observation. Under our reaction conditions only small amounts of cyclobutadiene complex 10 were observed (3%; Cp, δ 4.48 ppm). Yamazaki's isolation of much larger quantities of 10 relative to 9 can be readily explained by the known [10a] facile thermal conversion of 9 to 10 which would be expected to take place more rapidly at the higher reaction temperatures (80° instead of 56°C) he used.

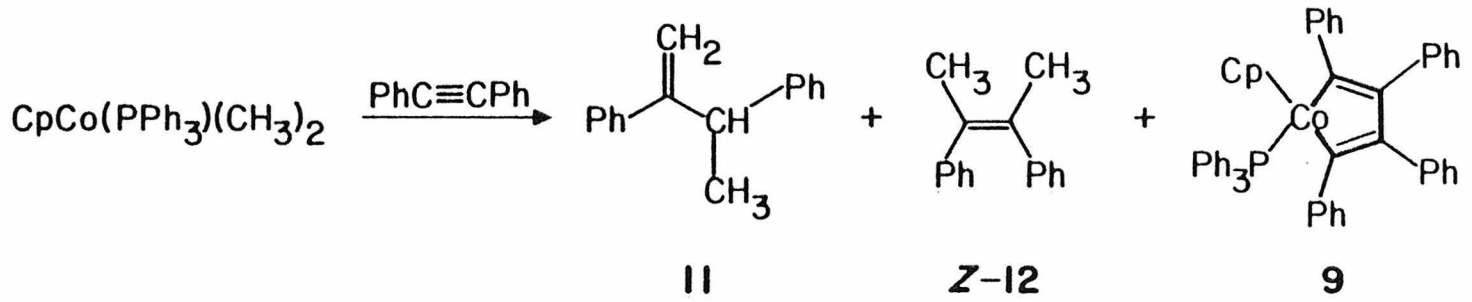
In addition to these organometallic products, we discovered two organic products in a ratio of 14:1 which jointly accounted for >95% of the methyl groups present in starting 1. The major product was 2,3-diphenyl-1-butene (11)

whose identity was confirmed by independent synthesis from 1,2-diphenyl-1-propanone and triphenylphosphonium methylide. This material accounts for the NMR absorptions at δ 1.36, 3.87, 5.06, and 5.34 ppm. The singlet at δ 2.01 ppm is due to Z-2,3-diphenyl-2-butene (Z-12), the minor organic product. This compound and its isomer, E-2,3-diphenyl-2-butene (E-12), were independently prepared by acid catalyzed rearrangement of 11 (*vide infra*). Significantly, no E-12 (<1%) was observed.

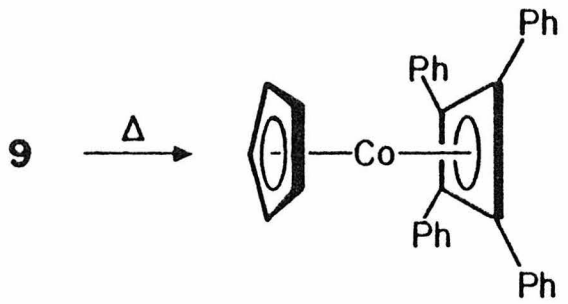
We were not able to isolate or identify the trace product or products responsible for the singlets at δ 4.68 and 2.45 ppm. The chemical shift of the low-field signal is consistent with a cyclopentadienyl absorption, and if this identification is correct, the unknown product accounts for 2% of the cyclopentadienyl-containing products. The signal at δ 2.45 ppm is derived from the methyl groups in starting 1 because it is absent in product mixtures generated from reactions of 1-$d_6$ (completely deuterated methyl groups) and diphenylacetylene. It accounts for the remainder of the starting methyl groups.

The results of this reaction are summarized in Scheme III. The production of Z-12 and the absence of E-12 demonstrate 1 is capable of doubly alkylating diphenylacetylene cleanly and stereospecifically. The other organic product 11 is probably derived from a complex containing Z-12 via a hydrogen shift; however its presence as the major reaction

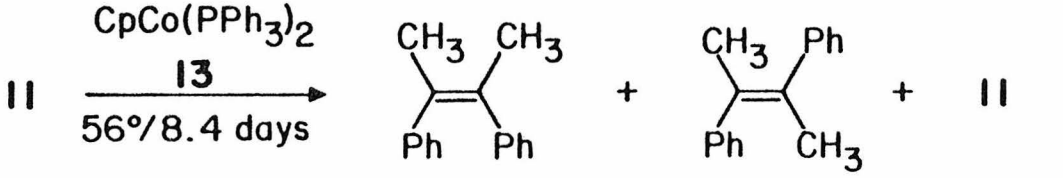
Scheme III




11 Z-12 9




10




Z-12 (7%) E-12 (89%) (4%)

product was surprising since it was expected to be less stable than Z-12 (or E-12) as the free olefin.[21]

We conducted several additional experiments to probe the mechanism governing the production of 11 and Z-12. The intramolecularity of the reaction was explored by heating benzene solutions of excess diphenylacetylene and known mixtures of 1-$d_0$ and 1-$d_6$ in benzene at 56°C until the reaction was >90% complete. After separating the organic products from 9 and 10 by column chromatography, the organic mixture was analyzed by GC-mass spectroscopy. The spectra of 11 and Z-12 obtained in this way displayed only peaks found in authentic samples of 11-$d_0$, 11-$d_6$, Z-12-$d_0$, and Z-12-$d_6$ prepared from separate reactions of 1-$d_0$ and 1-$d_6$ with diphenylacetylene. The relative peak intensities in the spectra of the products from the crossover reaction also matched those of the authentic samples, establishing that the transferred methyl groups came from the same molecule of 1 (<2% crossover) and hydrogen transfer was intramolecular as well (no $d_1$, $d_2$, $d_4$, or $d_5$, as well as $d_3$ olefins were detected). It is interesting to note the intermolecular methyl group transfer in 1 observed during the carbonylation reactions was no longer detectable in the diphenylacetylene reaction even though these crossover experiments were conducted at moderately high concentrations of 1 (for example: 1, 0.23 M; diphenylacetylene, 0.89 M). This observation is consistent with the possibility the transfer requires at least one coordinatively unsaturated metal center

and the high ligand (diphenylacetylene) concentration keeps the concentration of such centers so low, the transfer is no longer detectable.

We isomerized samples of the pure olefins with trifluoromethanesulfonic acid in wet ($H_2O$) benzene at 56°C to determine the true relative thermodynamic stabilities of all three olefin isomers in question: 1-1, Z-1-2, and E-1-2. Starting with either 1-1, Z-1-2, or E-1-2, the final product mixture contained these olefins in the ratio 2:33:65 at equilibrium.

In an effort to examine the ability of coordinatively unsaturated $\eta^5$-cyclopentadienyl(triphenylphosphine)cobalt fragments to isomerize olefins 1-1, Z-1-2, and E-1-2, we heated a benzene solution of 1-1 and $CpCo(PPh_3)_2$ (1-3) at 56°C. The terminal olefin was again isomerized, but this time a non-thermodynamic mixture of Z-1-2 and E-1-2 was generated, giving an 8:92 ratio of Z-1-2:E-1-2. Pure samples of Z-1-2 and E-1-2 were stable to isomerization under these conditions.

Contrary to our experience during the reaction of 1 and CO, we were unable to spectroscopically observe any intermediates in the reaction between 1 and diphenylacetylene. Observation ($^1H$ NMR, 90 MHz) of dilute solutions of 1 (ca. 0.055 M) in the presence of high concentrations of diphenylacetylene (ca. 0.9 M) in benzene-$d_6$ or THF-$d_8$ kept at room temperature for 5 hr did not reveal any transient absorptions. All the peaks observed could be assigned to 1 or known

products of the reaction.

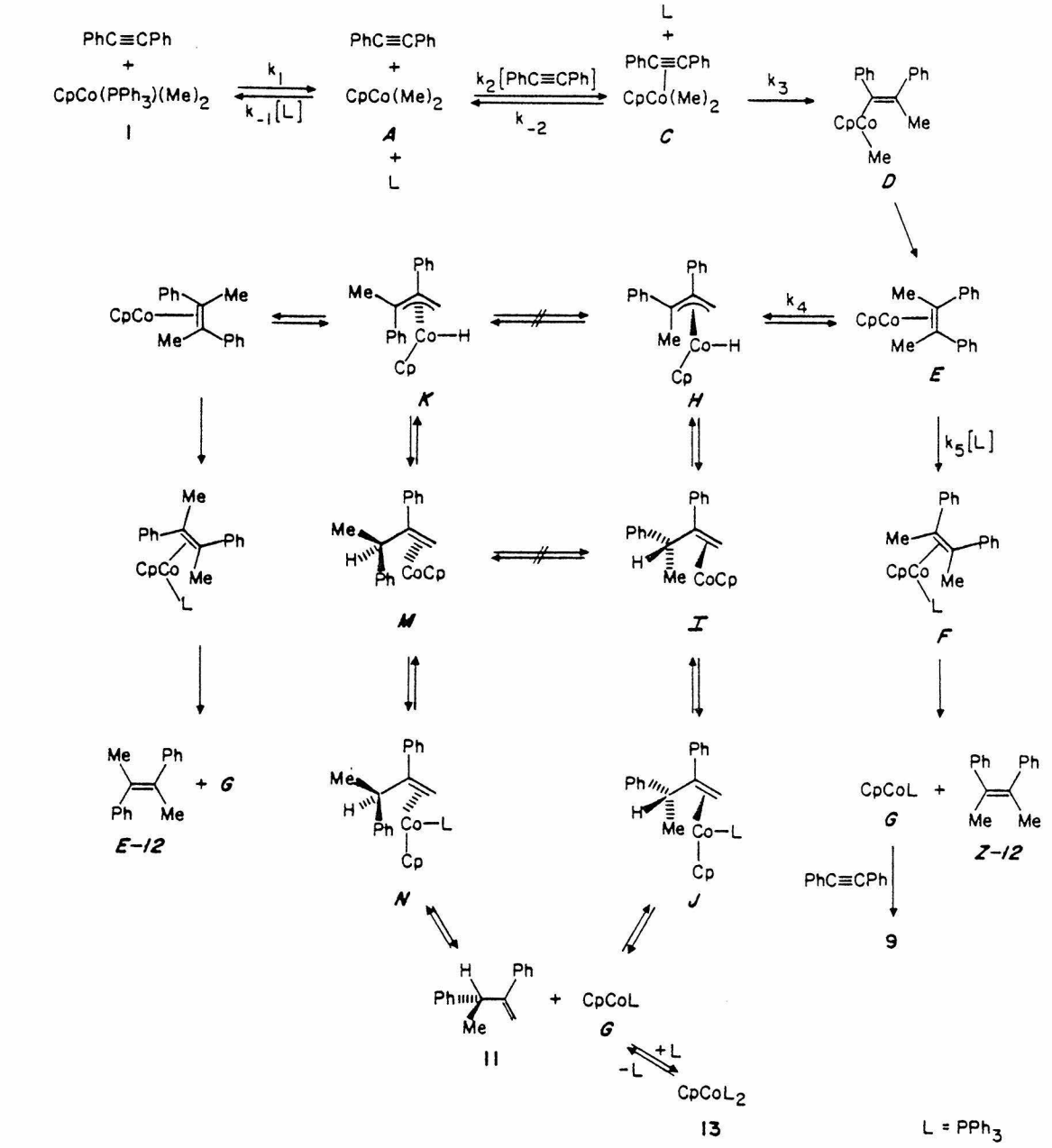
In the presence of more than a three-fold excess of diphenylacetylene, the disappearance of $\underset{\sim}{1}$ obeyed a first order rate law for at least one half-life.[22] By monitoring ($^1$H NMR) the rate of disappearance of $\underset{\sim}{1}$-$d_0$ and $\underset{\sim}{1}$-$d_6$ in a known mixture of these starting materials we were able to show the isotope effect on this disappearance was negligible: $k_{h6}/k_{d6}$=1.01±0.04. The rate of disappearance of $\underset{\sim}{1}$ is strongly inhibited by the presence of added triphenylphosphine in the reaction solution. Whereas at 56°C, $k_{obs}$= (88±13)x$10^{-6}$ $sec^{-1}$ in the absence of added triphenylphosphine (initially 0.19 M in $\underset{\sim}{1}$, 0.76 M in diphenylacetylene) $k_{obs}$ dropped to (3.6±0.3) x $10^{-6}$ $sec^{-1}$ when the triphenylphosphine concentration was raised to 0.90 M (initially 0.10 M in $\underset{\sim}{1}$, 0.90 M in diphenylacetylene). The addition of extra triphenylphosphine also dramatically affected the product ratio. The ratio of $\underset{\sim\sim}{11}$:Z-$\underset{\sim\sim}{12}$ decreased from 14:1 in the absence of added phosphine to 0.9:1 in the reaction described above with 0.9 M added ligand.

The reaction of $\underset{\sim}{1}$ with diphenylacetylene to give $\underset{\sim\sim}{11}$ and Z-$\underset{\sim\sim}{12}$ but not E-$\underset{\sim\sim}{12}$ is particularly interesting when compared to the favored production of E-$\underset{\sim\sim}{12}$ over Z-$\underset{\sim\sim}{12}$ when samples of $\underset{\sim\sim}{11}$ are isomerized by $\underset{\sim\sim}{13}$. The first results suggest a low-energy barrier connects $\underset{\sim\sim}{11}$ and Z-$\underset{\sim\sim}{12}$ and a higher one leads to E-$\underset{\sim\sim}{12}$. However, this appears to contradict the second observation which demonstrates a cyclopenatadienylcobalt-

induced pathway connects 11 and E-12 and is more accessible than the one connecting 11 and Z-12.

A mechanism which accommodates these and the other results described above is shown in Scheme IV. The rate inhibition by added phosphine suggests 1 is in equilibrium with the diphenylacetylene-substituted intermediate C (whose CO-substituted analog 6 we have observed directly) through a dissociative process involving coordinatively unsaturated intermediate A, in analogy to the trimethylphosphine and CO substitutions discussed earlier. Overall addition of a cobalt-methyl bond across one side of the coordinated alkyne in C gives the vinyl-alkyl intermediate D. Our inability to observe C spectroscopically is due to faster insertion or a less favorable equilibrium between 1 and C than in the CO case. Consistent with other recent reports of reductive elimination from coordinatively unsaturated metal centers,[23] we propose stereospecific reductive elimination occurs in D to give the unsaturated $\eta^2$-olefin-containing intermediate E. This is the partitioning point which explains the effect of added phosphine on the product ratio. Excess phosphine traps E generating saturated intermediate F. Facile olefin dissociation in F releases free olefin Z-12 to give the unsaturated intermediate G. Competitive with ligand trapping of E is cobalt insertion into an allyl C-H bond to give the saturated $\eta^3$-allyl intermediate H where hydrogen transfer and subsequent ligand trapping occur to generate the least substituted and probably most stable[24]

Scheme IV


PhC≡CPh
+
CpCo(PPh3)(Me)2
1
k1
k-1[L]
PhC≡CPh
+
CpCo(Me)2
A
+
L
k2[PhC≡CPh]
k-2
L
+
PhC≡CPh
CpCo(Me)2
C
k3
D
k4
E
k5[L]
F
K
H
M
I
N
J
E-12
+ G
G
CpCoL +
Z-12
PhC≡CPh
9
11
+ CpCoL
G
+L
-L
CpCoL2
13
L = PPh3

olefin complex J. Analogous to F, olefin dissociation generates the free organic product 11 and the unsaturated fragment G.[25] This intermediate must rapidly be scavenged by excess diphenylacetylene to generate the final organometallic product 9[26] or E-12 would be observed from cobalt-catalyzed isomerization of 11 (*vide infra*). The absence of E-12 also requires the syn $\eta^3$-allyl intermediate H to be the only $\eta^3$-allyl complex accessible from E and syn-anti conversion to K (presumably via an $\eta^1$-allyl complex) must be slow relative to the other processes which occur here.[27]

Central to this discussion is the realization 11 is a prochiral olefin and coordination to a metal center can generate one of two diasteriomeric olefin complexes (J or N) depending on which face is attached.[28] This explains the favored formation of E-12 when 11 and 13 are mixed. Starting from separate molecules 11 and 13,[29] cobalt coordination to either side of 11 is possible and both diasteriomers J and N are now accessible. Each of these complexes is related (via the corresponding $\eta^3$-allyl-hydride (H or K) as shown in the Scheme) to only one of the two possible internal olefins Z-12 and E-12. This is because the rate of direct interconversion of H and K, I and M, J and N is not competitive with that of product formation. Access to one side of the mechanism from the other requires the intermediacy of free 11 and a suitable coordinatively unsaturated cobalt fragment. In the reaction of 1 and diphenylacetylene, this fragment is rapidly trapped so no E-12 is observed.

In agreement with the prediction made by the mechanism in Scheme IV, we do not observe an appreciable deuterium isotope effect on the rate of disappearance of $\underset{\sim}{1}$ having completely deuterated methyl groups. However, an isotope effect on the relative ratios of products $\underset{\sim\sim}{11}$ and Z-$\underset{\sim\sim}{12}$ is expected since $\underset{\sim\sim}{11}$ is a product of C-H (or C-D) insertion and Z-$\underset{\sim\sim}{12}$ is not. From the mass spectra of the $\underset{\sim\sim}{11}$ and Z-$\underset{\sim\sim}{12}$ generated in reactions of known mixtures of $\underset{\sim}{1}$-$d_0$ and $\underset{\sim}{1}$-$d_6$ with diphenylacetylene in the absence of any added phosphine (the same data used to establish the intramolecularity of the reaction) we determined the ratios ($\underset{\sim\sim}{11}$-$d_0$)/($\underset{\sim\sim}{11}$-$d_6$), (Z-$\underset{\sim\sim}{12}$-$d_6$)/(Z-$\underset{\sim\sim}{12}$-$d_0$) and calculated the product of the two, R. Assuming (1) equilibration between intermediates E and I is slow relative to ligand trapping to give F and J, (2) ligand trapping is irreversible, and (3) there is no isotope effect on phosphine trapping of E to give F ($k_{5d_6}/k_{5d_0} = 1$), the ratio R represents the overall isotope effect on the production of $\underset{\sim\sim}{11}$ from E. If the first assumption is not applicable in the absence of added phosphine, the observed ratio R should rise to a limiting value[30] as the rate of ligand trapping is raised by increasing the phosphine concentration, and the assumption then becomes valid. We determined R for two separate runs with no added phosphine and obtained values of 1.6 and 1.7. When the reaction was repeated in the presence of 0.77 M added triphenylphosphine, R did not change appreciably, (R=1.5), suggesting E$\rightleftharpoons$I equilibration is slow. Considering the number of steps between E and J it is risky

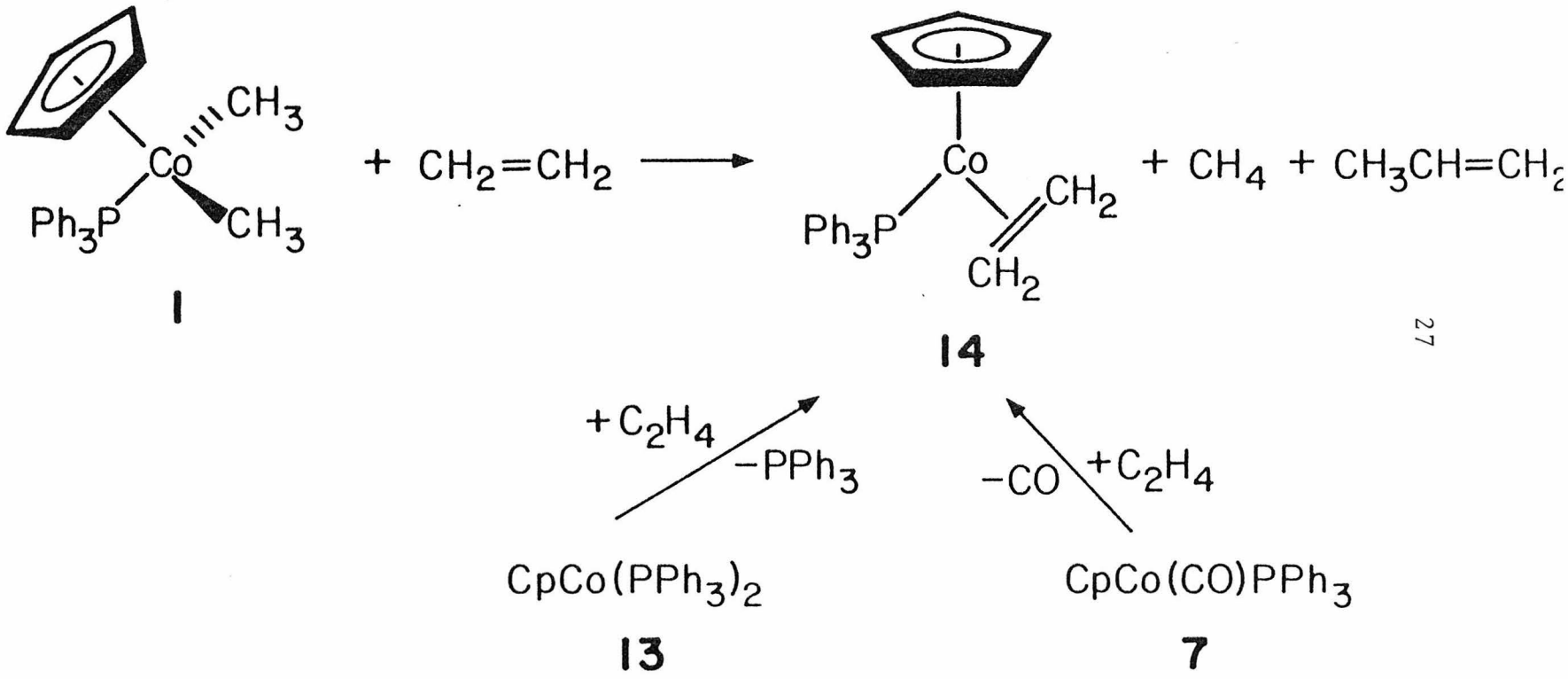
to assign any additional significance to the isotope effect we have measured here (1.6 ± 0.1), although under certain circumstances it would be the isotope effect for insertion into the allyl C-H bond of E.[31]

Our study of the reaction of 1 and diphenylacetylene leads to the following generalizations: (1) clean, high yield, stereospecific double alkylation of diphenylacetylene, and presumably other alkynes as well,[32] is a feasible process; (2) the hydrogen shifts involved in the $\eta^5$-cyclopentadienyl(triphenylphosphine)cobalt-catalyzed isomerization of alkenes occur more rapidly than dissociation of the alkene from the metal center;[33] and (3) interconversion of $\eta^3$-allyl complexes via rotation in $\eta^1$-allyl complexes is much slower than hydrogen transfer and product formation.

Reaction of 1 with ethylene and propene and some results of its thermal decomposition. Complex 1 reacts with ethylene. When a 0.13 M solution of 1 in benzene-$d_6$ was heated under ethylene (2.9 atm, 0.31 M) at 76°C for 30 hr in a sealed tube, observation by $^1$H NMR showed the absorptions characteristic of 1 and ethylene (δ 5.24 ppm) had decreased in intensity while absorptions due to methane (0.19) and propene (1.58, $CH_3$) grew in. A new cyclopentadienyl resonance (4.48) and two new multiplets at 1.07 and 2.48 ppm also appeared, in addition to several smaller absorptions: δ 0.48 (d, J = 5.5 Hz), 0.82 (s, ethane), and

1.43 (d, J = 2 Hz) ppm. A complex displaying the major new absorptions could be isolated free of starting 1 by several recrystallizations (benzene-mixed hexanes) from product mixtures generated under higher ethylene pressures and at lower temperatures (*vide infra*). This isolated product remained contaminated (ca. 10%) with the material showing the δ 1.43 ppm absorption, however, and decomposed slowly in solution at room temperature under $N_2$ with loss of ethylene. $^1H$ NMR absorptions identical to those observed in the new complex were generated by two independent routes: (1) photolysis of the carbonyl(triphenylphosphine)cobalt complex 7 under ethylene, and (2) thermal reaction of the bis(triphenylphosphine)cobalt complex 13 with ethylene which released one equivalent of triphenylphosphine while giving the new absorptions. The structure of the new product is assigned as the olefin complex 14 on the basis of these observations (Scheme V). Thermal substitution of one triphenylphosphine in 13 by ethylene is the most efficient way of generating clean solutions of 14 for observation by NMR. Isolation was precluded by the difficulty of removing the mole of free triphenylphosphine generated during the substitution. The free phosphine drives the equilibrium shown in equation 7 (alkene = ethylene) back to the left in the absence of ethylene. For ethylene, the equilibrium constant, K (equation 7) was estimated to be: 200 ± 100 (28°C). An alkyl substituent

Scheme V




1

14

13

7

Equation 7

$$CpCo(PPh_3)_2 + \text{alkene} \rightleftharpoons CpCo(\text{alkene})(PPh_3) + PPh_3$$

on the olefin decreased K substantially; e.g., K dropped to 0.22 ± 0.01 (25°C) for propene.[25]

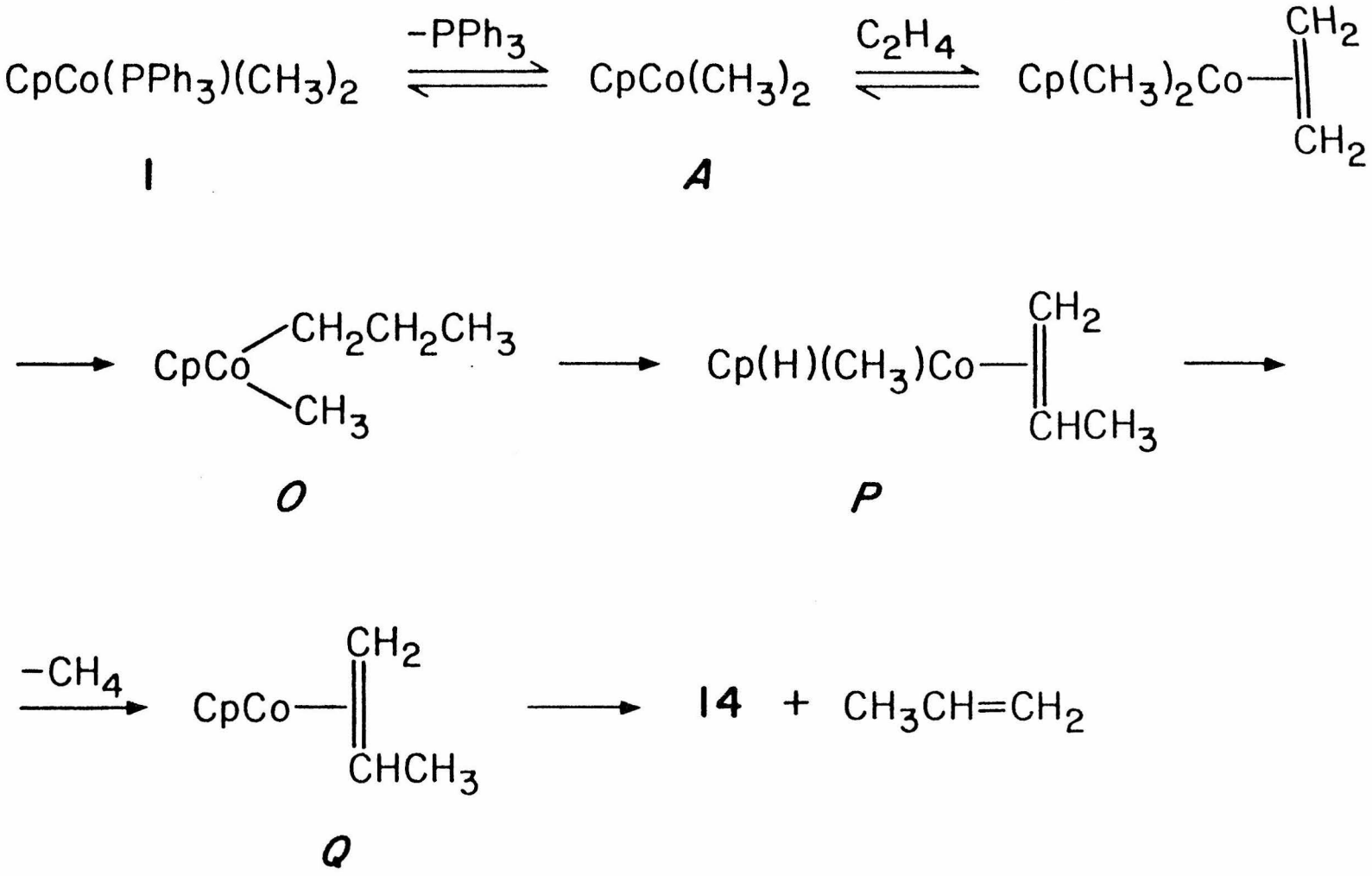
The two multiplets at δ 1.07 and 2.48 ppm form the AA'BB' portion of an AA'BB'X spectrum (the $^{1}H\{^{31}P\}$ spectrum reveals a totally symmetrical AA'BB' system) and were analyzed using a least squares simulation program to give the coupling constants used to generate the simulated spectrum shown in Figure 1. Apparently at room temperature ethylene rotation is still slow on the NMR time scale.[34] The presence of only one $^{13}C$ absorption (δ 25.0 ($J_{CH}$ = 143 Hz) ppm)[35] for the coordinated ethylene shows the ethylene is oriented perpendicular to the Cp-Co-$PPh_3$ plane in the molecule. This is the same orientation assumed by ethylene in the corresponding rhodium complex where the structure has been determined by X-ray diffraction techniques.[36] When the cyclopentadienyl ring is substituted with a methyl group the olefinic multiplets do not change detectably in appearance but their chemical shifts move to δ 1.19 and 2.14 ppm (*vide infra*). The protons pointing to the cyclopentadienyl ring are assigned to the downfield multiplet.

The formation of methane and propene (the organic products of the reaction of $\underset{\sim}{1}$ with ethylene) can be explained by either of two different mechanisms, both of which have important implications for the mechanism of the chain-growth step in the Ziegler-Natta catalyzed

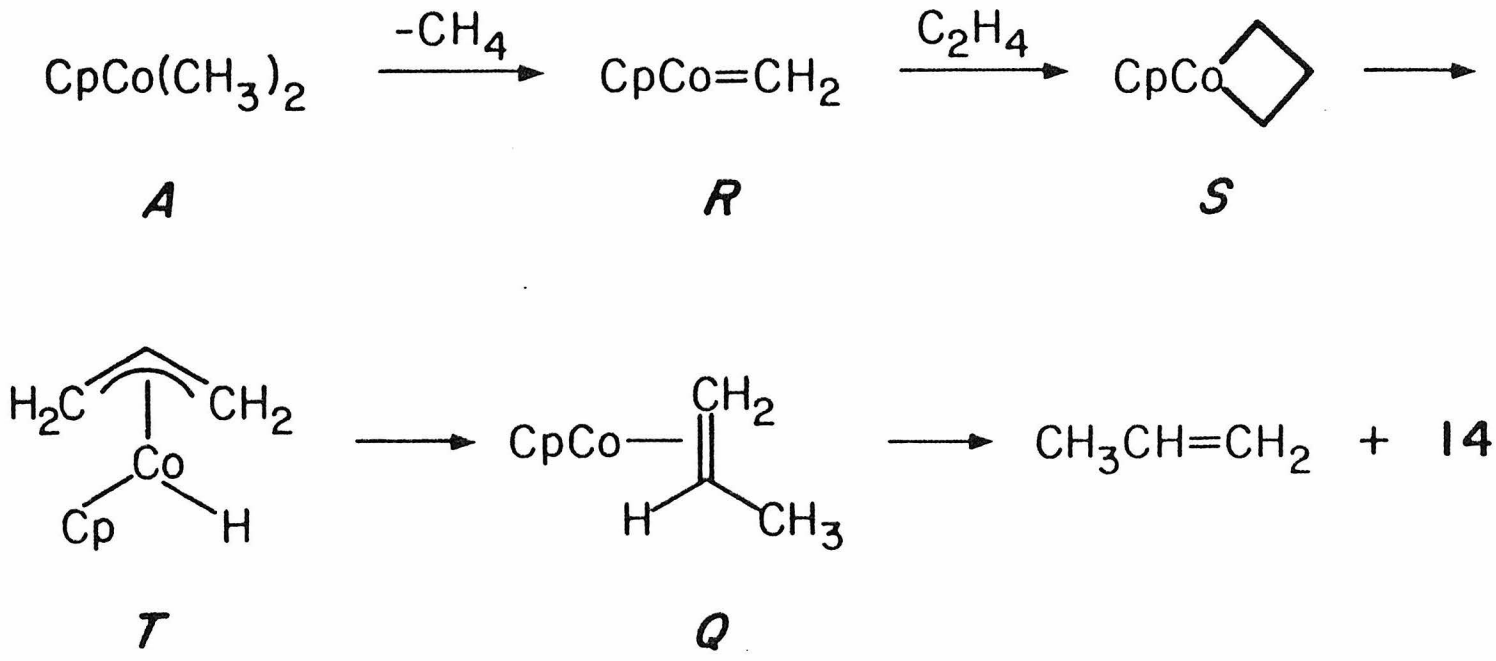
polymerization of olefins. This process has long been thought to proceed through olefin insertion into the metal-carbon bond of an intermediate metal-alkyl[9] and this mechanism, applied to the reaction of 1 and ethylene is outlined in Scheme VI. Here, ethylene coordination to the unsaturated intermediate A generated by phosphine dissociation, followed by migratory insertion gives the unsaturated propyl-methyl intermediate O. β-Hydrogen elimination in O generates the hydrido-methyl-olefin intermediate P. Reductive elimination of methane[37] gives the unsaturated propene complex Q which is scavenged by ethylene and triphenylphosphine to give 14 and propene.

The absence of a well-documented case in which an isolated alkyl-olefin complex has been shown to undergo this direct insertion reaction has prompted Green and his coworkers to suggest an alternative mechanism for apparent insertion reactions. This involves olefin addition to a transient carbene complex formed by α-elimination in the starting metal-alkyl.[8c,38] The formation of methane and propene in our reaction might also be explained by such a mechanism, as shown in Scheme VII. α-Elimination in the unsaturated intermediate A, followed by reductive elimination of methane gives the carbene complex R which adds ethylene to give the unsaturated metallacyclobutane S. β-Hydrogen elimination in S followed by reductive elimination in the intermediate $\eta^3$-allyl-hydride T gives Q

Scheme VI


CpCo(PPh3)(CH3)2
-PPh3
CpCo(CH3)2
C2H4
Cp(CH3)2Co
CH2
CH2
I
A
CpCo
CH2CH2CH3
CH3
O
Cp(H)(CH3)Co
CH2
CHCH3
P
-CH4
CpCo
CH2
CHCH3
Q
14 + CH3CH=CH2

Scheme VII


CpCo(CH3)2
-CH4
CpCo=CH2
C2H4
CpCo
A
R
S
H2C
CH2
Co
Cp
H
T
CpCo
CH2
H
CH3
Q
CH3CH=CH2 + 14

which generates 14 and propene as before.

In our system, these two alternatives can be distinguished by the appropriate labeling experiments. In the insertion pathway the product methane is generated from a cobalt-bound methyl group and one hydrogen from the ethylene. A complete methyl group is also transferred to the ethylene in the insertion process. In the α-elimination pathway, all the methane hydrogens are derived from cobalt-bound methyl groups since the methane is generated prior to ethylene coordination. Here, a methylene group is finally transferred to the ethylene.

Both mechanisms predict equal quantities of methane and propene should be produced in the reaction. However, an initial quantitative reaction conducted at 75°C under 4 atm of ethylene gave methane (80%)[39], propene (57%), and ethane (3%). These results suggested an independent process which also generates methane was competing with the reaction of 1 and ethylene. Confirming this suspicion, heating 1 under 1 atm of $N_2$ in place of ethylene gave both methane (58%) and ethane (10%). Because we planned to examine the isotopic composition of labeled methanes from the reaction of 1 and ethylene, we briefly examined some details of the thermal decomposition of 1 in benzene solution, and looked for ways to supress the unwanted thermal decomposition.

Heating a 0.13 M solution of 1 under $N_2$ for 17 hr 36 min

at 110°C gave methane (82.3 ± 1.2%), ethane (14.2 ± 0.2%), and no ethylene (<0.1%). When a solution 0.12 M in $\underset{\sim}{1}$ was pyrolyzed under similar conditions in the presence of added triphenylphosphine (0.62 M), the ratio of methane to ethane rose sharply: 107 ± 8% methane and only 0.4% ethane were observed. The phosphine inhibition of ethane production is consistent with the notion expressed earlier that reductive elimination in these cyclopentadienylcobalt systems proceeds from a coordinatively unsaturated intermediate.

In an effort to determine the source of the fourth hydrogen in the methane, we decomposed samples of $\underset{\sim}{1}$-$d_{21}$ with completely labeled methyl and phosphine groups and analyzed the isotope distribution in the product by mass spectroscopy. The methane from thermolysis of $\underset{\sim}{1}$-$d_{21}$ in benzene at 71°C was shown to be a mixture of $CD_3H$ (88%), $CD_4$ (9%), and other methanes (3%) in this way, demonstrating the labeled ligands were not a major source of hydrogen. When a similar thermolysis was conducted in benzene-$d_6$, essentially the same mixture was obtained: $CD_3H$(89±5%), $CD_4$(5±1%), and other methanes (6±5%). Therefore, the cyclopentadienyl ligand must be the major source of methane hydrogen[40] since it is the only unlabeled moiety in this thermolysis. We do not know if transfer of the cyclopentadienyl-hydrogen to the methyl group is intramolecular, and the crossover experiment needed to determine this (decomposition of a mixture of $\underset{\sim}{1}$-$d_0$ and $\underset{\sim}{1}$-$d_{11}$ with labeled methyl and Cp ligands) is precluded by the known ability of $\underset{\sim}{1}$ to exchange methyl

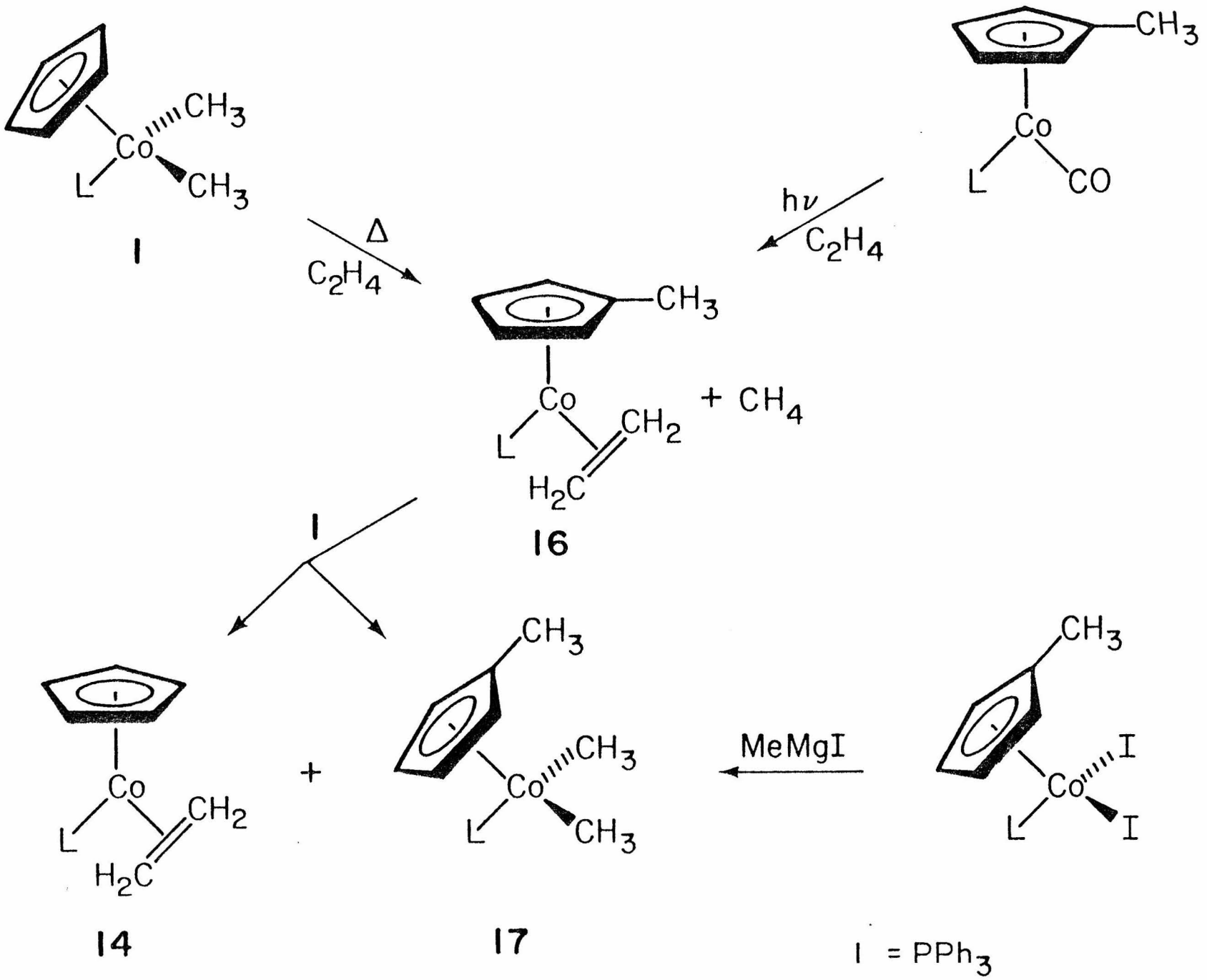
groups under milder conditions than those required for decomposition.

Thermal decomposition of 1 in the absence of triphenylphosphine gave a dark grey homogeneous solution from which we were unable to isolate any tractable ($^1$H NMR observable) organometallic products. However, decomposition of 1 in the presence of additional phosphine appeared to give a cleaner reaction. We were able to monitor the progress of the decomposition by $^1$H NMR when 1 was heated at relatively low temperatures for long periods of time in the presence of excess phosphine and under high ethylene pressures. Thus, when a 0.25 M solution of 1 in benzene-$d_6$ was heated at 58±2°C in the presence of triphenylphosphine (0.87 M) and ethylene (0.91 M, 17.9 atm) the first change in the $^1$H NMR spectrum was the appearance of an absorption due to methane (δ0.19 ppm), a smaller one for ethane (δ0.82 ppm) a new doublet (J = 2Hz) at 1.43 ppm, a broad cyclopentadienyl resonance at 4.50 ppm and two new multiplets at 1.19 and 2.14 ppm which looked exactly like the ethylene absorptions in 14 but appeared at different chemical shifts. Upon further heating absorptions due to 14 grew in along with more new ones: δ4.30 and 4.11 (broad m), 1.73 (d, J = 2 Hz), and 0.48 (d, J = 5.5 Hz) ppm. No propene was detected under these conditions. The initial absorptions (δ4.50,2.14,1.43, and 1.19 ppm), were identical to those observed upon photo1-

ysis of an authentic sample of $Cp'Co(CO)(PPh_3)$ (15, Cp' = $\eta^5$-$CH_3C_5H_4$) in benzene-$d_6$ under ethylene and are assigned to the new olefin complex $Cp'Co(C_2H_4)(PPh_3)$ (16) on the basis of this observation. The new absorptions which appeared later were identical to those displayed by an authentic sample of $Cp'Co(PPh_3)(Me)_2$ (17). These products from thermal decomposition of 1 are responsible for the small additional absorptions (δ1.43 and 0.48 ppm) observed during the original reaction of 1 and ethylene (*vide supra*). The general features of these results are summarized in Scheme VIII. A reasonable route to the observed products involves decomposition of 1 through methyl migration to the cyclopentadienyl ligand.[41] Elimination of a cyclopentadienyl-hydrogen and the remaining methyl group as methane yields an unsaturated intermediate which is ultimately trapped by ethylene to give 16. This is consistent with the observed stoichiometry of the methane decomposition (only one mole of methane is generated per mole of 1) and the labeling experiments which demonstrate the methane hydrogen is derived from the cyclopentadienyl ring. The regular olefin complex 14 and the methylcyclopentadienylsubstituted dimethyl complex 17 may be generated by subsequent methyl group exchange between 1 and 16, *via* a mechanism related to the intermolecular methyl exchange detected during carbonylation of 1.

Although we were not able to completely prevent thermal decomposition of 1 during the reaction with ethylene, we were

Scheme VIII


CH3
Co
L
CH3
CH3
Co
L
CO
1
Δ
C2H4
hν
C2H4
CH3
Co
CH2
L
H2C
+ CH4
16
1
CH3
Co
CH2
L
H2C
CH3
Co
CH3
L
CH3
MeMgI
CH3
Co
I
L
I
14
17
1 = PPh3

able to limit the decomposition to <10% of the reaction pathway by conducting the reaction at lower temperatures and under higher ethylene pressures. Thus, heating a 0.13 M solution of 1 in benzene under 11.1 atm of ethylene at 54±1°C for 121 hr 15 min gave: methane (86%), propene (79%), butane (0.2%), 14 (91%), and 16 (9%) after correcting for remaining 1. Small amounts of linear butenes were observed as well: 1-butene (4.9%), E-2-butene (2.7%), and Z-2-butene (0.5%).[42] No (<0.1%) propane and only a trace (<2%) of 17 were detected.

Having developed a better understanding of the thermal behavior of 1, we turned our attention again to its reaction with ethylene. The methane generated by heating a 0.14 M solution of 1-$d_{21}$ in benzene for 120 hr 35 min at 54±1°C under 11.1 atm of ethylene was analyzed by mass spectroscopy and shown to be identical to $CD_3H$ prepared by quenching ($H_2O$) a portion of the $CD_3MgI$ used to synthesize 1-$d_{21}$. The propene produced in this reaction was shown to be ≥96% propene-$d_3$ by similar analysis. In another experiment, reaction of 1-$d_{21}$ with ethylene-$d_4$ under similar conditions gave 95% $CD_4$. Together, these results establish the new methane hydrogen is derived from ethylene and from no other hydrogen source in the system (cyclopentadienyl ring, solvent, phosphine) and the elements of a complete methyl group are transferred to the ethylene.

An additional and important prediction made by the insertion mechanism is that the methyl group in 1 is trans-

ferred to the ethylene in one piece. If deuterated methyl groups are used in 1, the propene-$d_3$ should contain all the deuterium label in the methyl group. Careful monitoring by both $^1H$ and $^2D$ NMR of the reaction of 1-$d_{21}$ and ethylene-$d_0$ showed the initially formed propene carried all (>95%) of the deuterium label in the methyl group. The label eventually scrambled, presumably through the kind of mechanism outlined for the isomerization of 11 in Scheme IV, but at a rate slower than that of propene production. For example, after heating a 0.28 M solution of 1-$d_{21}$ under ethylene (12.4 atm, 0.68 M) for ca. 90 hr at 59±2°C, 50% of the starting material had reacted with ethylene to give propene while 87% of that propene was still $CH_2{=}{=}CHCD_3$.[43] This last result provides confirmatory evidence that insertion rather than α-elimination is the mechanism responsible for alkylation of ethylene by 1.

We are unsure of the source of the small but significant amounts of linear butenes generated during the reaction of 1 with ethylene. Reaction of product propene with starting 1 could generate butenes *via* processes analogous to those involved in the alkylation of ethylene to give propene. Another possibility involves catalytic dimerization of ethylene to linear butenes carried out by olefin complex 11 and proceeding through the corresponding metallacyclopentane. Several systems which convert unstrained olefins to

metallacyclopentanes are known[44] and the catalytic dimerization of olefins through intermediates of this kind has recently been described.[44b,45] We checked the first possibility by heating a 0.14 M solution of 1 under ca. 11 atm of propene at 53±2°C for 170 hr. Analysis of the product gases gave: methane (65.9%), ethane (2.0%), butane (0.2%), 1-butene (0.1%), 2-methylpropene (2.0%), E-2 butene (1.6%), Z-2-butene (0.9%), and a trace (<0.1%) of ethylene (yields relative to starting 1). Contrary to our experience in the ethylene reaction, the organometallic products of this reaction were not easily characterizable, the $^1$H NMR of the product mixture showing only severely broadened peaks. This observation combined with the high yield of methane shows that even under high pressures of propene the primary reaction pathway is thermal decomposition and the products are not successfully stabilized by propene as they are by ethylene. To the small extent insertion does occur, as measured by the production of butenes, addition of a methyl group to the 2-position of the propene accounts for 42% of the insertion pathway. This product, 2-methyl-propene, is not observed in the reaction of 1 with ethylene. These results exclude product propene as a source of the linear butenes observed in the ethylene reaction. We are currently exploring possibilities for olefin complex catalyzed dimerization of ethylene.

## Summary and Conclusions

Together, the results of the reaction of 1 with trimethylphosphine, CO, diphenylacetylene, and ethylene described here show 1 is well-suited to undergo most of the elementary processes summarized in equations 2 - 4. Although 1 is not itself coordinatively unsaturated, triphenylphosphine dissociation is extremely facile and the unsaturated intermediate formed by phosphine loss can be captured by several ligands. When the entering ligand is CO the new complex 6 can be observed spectroscopically before it reacts further via insertion. With CO and diphenylacetylene, phosphine replacement is followed smoothly by insertion and reductive elimination in the vinyl-alkyl or acyl-alkyl complex so produced to give a doubly alkylated organic product. Reaction with diphenylacetylene gives exclusively the Z-olefin, demonstrating the metal and alkyl group are added to the same side of the alkyne in the insertion step. The initial coordinatively unsaturated cobalt(I) fragment generated by each of these reductive eliminations is scavenged by ligands in the reaction mixture to give a stable isolable product. In the case of ethylene, the reaction is not so straightforward. Under conditions required to induce the insertion reaction, thermal decomposition via methyl group migration to, and hydrogen abstraction from, the cyclopentadienyl ring to give methane and

methylcyclopentadienyl products is competitive. However, insertion does occur and labeling studies showed this involves direct transfer of an intact methyl group to the ethylene instead of a process involving α-elimination and ethylene addition to a metal-carbene intermediate. In the new dialkyl complex generated by olefin insertion, carbon-carbon bond-forming reductive elimination does not compete successfully with β-hydrogen elimination. This prevents overall double alkylation of ethylene. However, the reaction is terminated by C-H bond-forming reductive elimination (in an alkyl-hydride intermediate) to give an unsaturated cobalt(I) fragment which is trapped to form the new olefin complex 14.

Within this series of reactions, potential reductive eliminations from a dimethyl complex to give ethane and from a propyl-methyl complex to give butane proceed with difficulty and are largely superseded by other reaction pathways. On the other hand, reductive elimination from acyl-alkyl or vinyl-alkyl complexes appears to be the lower energy reaction pathway. We believe the important difference between these two situations lies in the presence of an extra pair of π or non-bonding electrons in the acyl-alkyl and vinyl-alkyl complexes which may coordinate to the metal in the reductive elimination transition state and provide a low energy route for this process which is not present in the dialkyl complexes. This is particularly important if, as

our evidence seems to suggest, reductive elimination proceeds from a coordinatively unsaturated 16-electron intermediate. Reductive elimination in the acyl or vinyl-substituted complexes can still generate a 16-electron species as the initial product whereas similar elimination in an unsaturated dialkyl will generate a much less stable 14-electron intermediate.

## Experimental Section

General. All manipulations of oxygen or water sensitive materials were conducted under a pre-scrubbed recirculating atmosphere of $N_2$ in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train or using standard Schlenk or vacuum line techniques.[46]

Tetrahydrofuran (THF) and diethyl ether were distilled from dark purple solutions of sodium/benzophenone ketyl under vacuum. Benzene, toluene, mixed hexanes, and petroleum ether were distilled from dark purple solutions of sodium/benzophenone ketyl in tetraglyme under vacuum. Before distillation, petroleum ether ("analyzed reagent" grade hydrocarbon fraction, bp 30-60°C, J.T. Baker) was stirred for 24 hr each over two portions concentrated $H_2SO_4$ and two portions saturated $KMnO_4$ in 15% $H_2SO_4$, washed with two portions distilled water, one portion saturated $Na_2CO_3$, two additional portions distilled water, and dried over anhydrous $MgSO_4$. Methylene chloride was distilled from $CaH_2$ under $N_2$ prior to use.

$PMe_3$ (Strem); diphenylacetylene (1% E-1,2-diphenylethylene by GC), $D_2O$ (99.7 atom % D), and trifluoromethanesulfonic acid from Aldrich; $CH_3Li$, n-BuLi, and potassium t-butoxide (Alfa); methane and CO (CP grade, Matheson Gas Products); and ethylene-$d_4$ (mass spectrum by us (10 ev): 99.6 atom % D) from Merck Sharp and Dohme were used as received. The condensable (-196°C) gases (CP grade,

Matheson): ethane, ethylene, propene, cyclopropane, butane, 1-butene, E-2-butene, Z-2-butene, and 2-methylpropene were degassed with at least one freeze-pump-thaw cycle on a vacuum line prior to use. $PPh_3$ (Matheson, Coleman and Bell) was recrystallized twice from mixed hexanes and dried at room temperature under vacuum for 4 hr, $PCl_3$ (Matheson, Coleman and Bell) was distilled and stored under $N_2$, ferrocene (Aldrich) was sublimed (1 atm, 120°C), and $CD_3I$ (Merck or Aldrich) was dried over Linde 4Å molecular sieves and stored over a drop of Hg or coil of clean ($HNO_3$) Cu wire, prior to use. $CpCo(CO)_2$,[47] $CpCo(CO)(PPh_3)$,[10b] $CpCo(CO)I_2$,[10b,48] $CpCo(PPh_3)_2$,[26a,49] and 1,2-diphenyl-1-propanone[50] were prepared by previously published methods. $Cp'Co(CO)_2$ and $Cp'Co(PPh_3)(Me)_2$ (Cp' = $\eta^5$-$CH_3C_5H_4$) were prepared by the same methods used for the normal cyclopentadienyl analogs with methylcyclopentadiene substituted for cyclopentadiene.[51]

Infrared (IR) spectra were recorded on Perkin-Elmer 257 or Perkin-Elmer 283 grating spectrophotometers using solutions of samples in sodium chloride cells (0.10 mm path length).

Routine $^1H$ nuclear magnetic resonance (NMR) spectra were recorded on Varian A60-A or EM-390 spectrometers. High field $^1H$ (180.09 MHz), $^{13}C$ (45.29 MHz), $^{31}P$ (72.90 MHz), and $^2H$ (27.64 MHz) NMR spectra (Fourier transform) were recorded on an instrument equipped with a Bruker magnet, Nicolet

Technology Corp. model 1180 data system, and electronics assembled by Mr. Rudi Nunlist (U.C. Berkeley). Simulations of $^{1}H$ NMR spectra were conducted with Nicolet software (NTCFT-1180, NCTSIM, ITRCAL). $^{1}H$ NMR spectra are reported in units of $\delta$ (ppm downfield from tetramethylsilane) but were most often measured relative to the residual $^{1}H$ absorption in the deuterated solvent: benzene-$d_6$ (7.15), toluene-$d_8$ (2.09), THF-$d_8$ (1.73), acetone-$d_6$ (2.04), and cyclohexane-$d_{12}$ (1.38). $^{13}C$ NMR spectra were also measured relative to a solvent absorption, toluene-$d_8$ (20.4) and acetone-$d_6$ (29.8) and reported in units of $\delta$ (ppm downfield from tetramethylsilane). $^{31}P$ NMR spectra are reported and were measured in units of $\delta$ (ppm downfield from internal triphenylphosphine). Benzene-$d_6$, toluene-$d_8$, and THF-$d_8$ from Merck were distilled from sodium/benzophenone ketyl prior to use. Acetone-$d_6$ (Merck) was dried over Linde 4Å molecular sieves, degassed with three freeze-pump-thaw cycles on a vacuum line, and distilled under vacuum prior to use. Cyclohexane-$d_{12}$ (Norell Chemical) was opened under $N_2$ and used as received. The NMR absorptions of $^{31}P$ and $^{13}C$ ($\sigma$-bound) nuclei directly bound to Co were significantly broadened at room temperature by coupling with the Co quadrapole ($I = 7/2$). This interaction was successfully reduced by lowering the sample temperature.[52]

Preparative gas-liquid chromatography (GC) was conducted on a Varian Aerograph 90-P gas chromatograph. Analytical GC

analyses were performed using either Hewlett-Packard 5750, perkin-Elmer 3920, or Perkin-Elmer Sigma 3 gas chromatographs equipped with flame ionization detectors and interfaced with a Spectra Physics Autolab System 1 computing integrator. For each quantitative analysis the response factors of the components relative to an internal standard were determined with known mixtures, except in the case of 2,3-diphenyl-1-butene, Z-2,3-diphenyl-2-butene, and E-2,3-diphenyl-2-butene where each of the $C_{16}H_{16}$ hydrocarbons was assumed to have the same relative response factor. Gas samples were handled in a gas-tight Pressure Lok syringe from Precision Sampling Corporation and withdrawn through rubber septa backed up by a stopcock which was opened only during sampling. The columns used were (1) 5' x ¼" aluminum, 5% SE-30 on Chromosorb (Chrom) P, acid washed (AW), 60/80 mesh; (2) 12' x ¼"aluminum, 5% SE-30 on Chrom W, AW, 60/80; (3) 30 meter open tubular glass capillary, SP2100 (Supelco, Inc. cat. no. 2-3710); (4) 9' x ¼" aluminum packed with 53% by vol 20% SE-30 on Chrom P, non acid washed (NAW), 60/80; 44% by vol 25% SE-30 on Chrom P, 60/80; and 3% by vol 30% SE-30 on Chrom W, AW, DMCS, 60/80; (5) 7' x 1/8" stainless steel, 10% DEGS on Chrom P, NAW, 60/80; (6) 9' x 1/8" stainless steel, Poropak Q (Waters Assoc.), 100/120; (7) 23' x 1/8" stainless steel, 15% DBT on Chrom P, NAW, 100/150; and (8) 7' x ¼" stainless steel, Poropak Q, 80/100.

Mass spectroscopic (MS) analyses were conducted on an

AEI-MS12 mass spectrometer. GC-MS analyses were obtained using a Finnigan 4000 GC-mass spectrometer. Both systems were interfaced with Finnigan/INCOS data systems.

Sical Gel 60 (EM Reagents) was used for column chromatography. Prior to use in the dry box, it was heated at ca. 150°C under vacuum for 16 hr and backflushed with dry $N_2$. Melting points of air or water sensitive compounds were performed in sealed capillaries under $N_2$, those for air stable compounds were performed in open capillaries under air, on a Thomas Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by either the California Institute of Technology or U.C. Berkeley analytical facilities. Photolyses were conducted in pyrex NMR tubes immersed in a $H_2O$ bath (ca. 20°C) and irradiated with a Hanovia 977B-1 DC mercury-xenon lamp powered by an Oriel Corporation (model 6128) Universal Lamp Power Supply and mounted in an Oriel focused beam lamp housing. Kinetic data were analyzed using the "Regression" routine in the Statistical Package for the Social Sciences (SPSS) program[53] at the U.C. Berkeley Computer Center.

Reactions under positive pressures of CO, ethylene, and propene were conducted in sealed NMR tubes or heavy-walled glass tubes (25mm OD, 17mm ID) fused directly to a Kontes 4mm (K-826600) vacuum stopcock mounted so the tip of the Teflon stopcock plug was exposed to the reaction mixture. The heavy-walled reactors were soaked overnight in chromic

acid, rinsed with distilled $H_2O$, soaked overnight in a buffered solution of EDTA,[54] rinsed exhaustively (x 15) with distilled $H_2O$, then acetone (x 2), petroleum ether (x 2), and a 10% by volume solution of hexamethyldislazane in petroleum ether (x 2), and dried (130°C). A small Teflon-coated stir bar was dropped through the stopcock opening and reaction solutions were stirred magnetically.

Preparation of $CpCo(PPh_3)I_2$. This procedure represents a modification of King's initial preparation.[10b] A solution of triphenylphosphine (0.71 gm, 2.71 mmol) in 9 ml of $CH_2Cl_2$ was added dropwise over 5-10 min to a stirred, deoxygenated (10 min $N_2$ purge) solution of $CpCo(CO)I_2$ (1.02 gm, 2.51 mmol) in 30 ml of $CH_2Cl_2$ while vigorously purging the solution with $N_2$. The initial dark purple solution turned dark blue-green during the addition. The reaction mixture was stirred an additional 5 min after the addition was complete, the solution volume was reduced to ca. 8 ml, and the resulting green-black microcrystalline solid which precipitated was collected, washed with two portions of diethylether, and dried under vacuum to give 1.21 gm of $CpCo(PPh_3)I_2$ (75%): mp = 172-173°C dec. (lit.[10b] 176-178°C dec., lit.[10a] 169-172°C dec.). $^1H$ NMR ($CDCl_3$): $\delta$ 5.11 (s, Cp), 7.2-8.0 (m, $C_6H_5$) ppm (lit.[10a] $\delta$ 5.06, 7.2-8.0 ppm); (THF-$d_8$): $\delta$ 5.10, 7.2-8.0 ppm.

If CO is not purged from the solution as it is formed during the triphenylphosphine substitution or if the original solution of $CpCo(CO)I_2$ is too concentrated, several unwanted side products are formed. When a solution of triphenylphosphine (7.0 gm, 26.7 mmol) in 75 ml of $CH_2Cl_2$ was added to a stirred but unpurged solution of $CpCo(CO)I_2$ (10.03 gm, 24.7 mmol) in 75 ml of $CH_2Cl_2$ over 27 min, the IR spectrum of the resulting solution showed bands characteristic

of 5 (2020, 1959 $cm^{-1}$) and 7 (1923 $cm^{-1}$).

$CpCo(PPh_3)I_2$-$d_{15}$ was prepared in an analogous fashion from $CpCo(CO)I_2$ and $PPh_3$-$d_{15}$ (94:6, $PPh_3$-$d_{15}$:biphenyl-$d_{10}$ by weight, *vide infra*): 88%; mp = 171-173°C.

Preparation of $CpCo(PPh_3)(Me)_2$ (1). This procedure gives higher yields than either of those reported earlier.[10] A filtered solution of MeMgI prepared from Mg turnings, (0.61 gm, 25.1 mmol) and a solution of $CH_3I$ (3.75 gm, 26.4 mmol) in 25 ml of diethylether was added dropwise over 1 hr at room temperature to a stirred slurry of $CpCo(PPh_3)I_2$ (4.02 gm, 6.28 mmol) in 30 ml of benzene to give a homogeneous, dark orange-red solution which was stirred for 12 additional hr. This reaction mixture was transferred through a double-ended needle onto 35 ml of a rapidly stirred, saturated, aqueous solution of $NH_4Cl$ held at 0°C. The resulting mixture was shaken vigorously to ensure complete hydrolysis of the excess MeMgI, opened to the air, and washed with 100 ml of additional $H_2O$. The organic layer and a subsequent 150 ml diethylether wash of the aqueous phase were dried for 15 min over anhydrous $MgSO_4$ and the solvent was removed under reduced (ca. 20 mm) pressure to give a crude orange-brown solid. This solid was chromatographed (silica gel, 18 cm x 20 mm, benzene) under $N_2$ and the orange powder obtained from the major, bright orange band recrystallized (-30°C, benzene:mixed hexanes, 1:4 by vol.) to give dark orange-red cubes of 1 (1.60 gm, 61%). The mother liquors yielded 240 mg

(9%) of additional material. During the chromatography, the bright orange band of 1 was followed by a much smaller brown band which has been identified[10a] as the iodo-methyl complex, $CpCo(PPh_3)(Me)I$, but was not isolated here. Although solutions of 1 are moderately air-stable for short periods of time, it is important to hydrolyze the reaction mixture under $N_2$ as the mixture of 1 and excess MeMgI is very air-sensitive. $^1H$ NMR ($CDCl_3$): δ 0.08 (d, $J_{PH}$ = 6 Hz, Me), 4.47 (s, Cp), 7.35 (m, $C_6H_5$) ppm (lit.[10a] δ 0.06, 4.41, 7.3 ppm); (THF-$d_8$): δ 0.07, 4.43, 7.36 ppm; (cyclohexane-$d_{12}$): δ 0.09, 4.34, 7.19-7.69 ppm; (benzene-$d_6$): δ 0.58, 4.46, 7.04 (m, meta- and para-H in $C_6H_5$), 7.52 (m, ortho-H in $C_6H_5$) ppm; (toluene-$d_8$): δ 0.49, 4.44, 7.02, 7.50 ppm. $^{13}C$ NMR (acetone-$d_6$, -30°C, $^1H$ decoupled): δ -15.6 (d, $J_{PC}$ = 29 Hz, Me), 88.8 (s, Cp), 128.5 (d, $J_{PC}$ = 9 Hz, ortho- or meta-C in $C_6H_5$), 130.2 (s, para-C in $C_6H_5$), 134.3 (d, $J_{PC}$ = 9 Hz, ortho- or meta-C in $C_6H_5$), 135.4 (d, $J_{PC}$ = 38 Hz, ipso-C in $C_6H_5$) ppm. $^{31}P$ NMR (toluene-$d_8$, -65°C, $^1H$ decoupled): δ 76.6 (bs, $PPh_3$) ppm. mp = 142-143°C dec. (lit.[10a] 142-143°C dec., lit.[10b] 138-141°C dec.).

$CpCo(PPh_3)(Me)_2$-$d_6$ was prepared in an analogous fashion from $CpCo(PPh_3)I_2$ and MeMgI-$d_3$ generated from $CD_3I$. Likewise, $CpCo(PPh_3)(Me)_2$-$d_{21}$ was prepared from $CpCo(PPh_3)I_2$-$d_{15}$ and MeMgI-$d_3$. The 1-$d_{21}$ obtained in this way was ≥ 97.6 atom % D in the methyl groups and ≥ 98.4 atom % D in the triphenylphosphine ($^1H$ NMR in THF-$d_8$).

Preparation of $PPh_3$-$d_{15}$. Although our synthesis of $PPh_3$-$d_{15}$ was based on a tested and published procedure,[55] several features of this preparation are worth noting. In our hands, the addition of $PCl_3$ in diethylether to the $PhMgBr$-$d_5$ solution gave a pale yellow solid and creamy solution. When the reaction was conducted on a larger scale (61.4 instead of 10.3 gm of $PhBr$-$d_5$) than previously described, a magnetic stirrer was unable to stir the reaction mixture throughout the addition. Although efficient stirring was not absolutely crucial to the $PCl_3$ addition, it was vital to the hydrolysis of the reaction mixture as the precipitated solids reacted violently with $H_2O$ and a mechanical stirrer was used for this reason. Rather than distill the biphenyl impurity from the product mixture, we found direct sublimation of the crude product mixture gave a white solid which was a mixture of $PPh_3$-$d_{15}$ and biphenyl-$d_{10}$ (94:6 by weight, GC column 1) and suitable for our use.

The bulk of the reaction mixture was exhaustively extracted (Soxhlet, 36 hr) with mixed hexanes to give a crude product which was purified by an additional crystallization from mixed hexanes. mp = 74-77°C, (lit.[55] 76-77°C).

Reaction of 1 and $PMe_3$ to give $CpCo(PMe_3)(Me)_2$ (2). The facile substitution of $PPh_3$ in 1 by $PMe_3$ to give 2 was first observed in a benzene-$d_6$ solution of 1 (0.08 M), $PMe_3$ (0.17 M), and diphenylacetylene (0.88 M) where the

absorptions from 1 were completely replaced by new ones assigned to 2 in less than 5 min at 56°C. $^1$H NMR: δ 0.16 (d, $J_{PH}$ = 6 Hz, Me), 0.79 (d, $J_{PH}$ = 9 Hz, $PMe_3$), 4.37 (s, Cp) ppm; lit.[12] δ 0.36 (d, $J_{PH}$ = 5.8 Hz), 1.03 (d, $J_{PH}$ = 9.1 Hz), 4.60 (s) ppm.

The kinetics of the substitution were measured by observing the $^1$H NMR (180 MHz) spectra of toluene-$d_8$ solutions of 1 and $PMe_3$ over time. A stock solution of 1 (64 mg, 0.154 mmol) and ferrocene (7.3 mg, 0.039 mmol) was prepared by adding enough toluene-$d_8$ to the solids to give 1.45 ml of solution. Identical 0.43 ml aliquots of this solution were transferred (0.50 ml syringe) to each of 3 NMR tubes. The tubes were frozen in liquid $N_2$ and evacuated. $PMe_3$ was added, and the tubes were sealed under 280 mm of $N_2$. A trial tube containing 0.46 mmol of $PMe_3$ was used to set the spectrometer parameters and establish a convenient temperature for monitoring the reaction. The remaining tubes: (a) $PMe_3$ (0.23 mmol, 0.51 M), 1 (0.10 M) and (b) $PMe_3$ (0.45 mmol, 0.96 M), 1 (0.10 M) were removed from liquid $N_2$, shaken vigorously at room temperature until they no longer condensed water, inserted into the $^1$H NMR probe maintained at 30°C, and observed at regular intervals for more than three half-lives. The resulting spectra were integrated using the internal ferrocene as a standard and the data obtained by monitoring the cyclopentadienyl signals of 1 (ln $Cp_t$ vs. t) and 2 [ln ($Cp_\infty$-$Cp_t$) vs. t] and the

cobalt-bound methyl signal of 2 [ln ($Me_\infty$-$Me_t$) vs. t] for three half-lives were used to determine the rate constant $k_1$ (30°C) (reported here as $k_1 \times 10^4$ $sec^{-1}$) in Scheme I: tube (a): Cp-1, 4.49 ± 0.05; Cp-2, 4.44 ± 0.11; Me-2, 4.65 ± 0.12 and tube (b): Cp-1, 3.89 ± 0.05; Cp-2, 4.10 ± 0.11; Me-2, 4.42 ± 0.08.

Carbonylation of 1. (a) Spectroscopic observation of $CpCo(CO)(Me)_2$ (6). When a solution of 1 (25 mg, 0.060 mmol) in 0.37 ml of THF-$d_8$ under ca. 1 atm of CO was held for 3 hr at room temperature, $^1H$ NMR absorptions consistent with 5, 6, 7, and acetone were observed (see Results and Discussion for values). Another solution of 1 (16 mg, 0.038 mmol) in 0.56 ml of THF-$d_0$ (so the strong THF-$d_8$ IR band at 2000-2300 $cm^{-1}$ would not compete with the anticipated CO absorptions) under 1.3 atm of CO was kept at room temperature and monitored by $^1H$ NMR until the absorptions due to 6 reached their maximum intensity (15 hr 35 min, 8% of the combined organometallic species present). The tube was opened and the reaction solution monitored by IR and $^1H$ NMR spectroscopy in the absence of CO. The initial IR spectrum showed bands due to 5, 6, 7, and acetone (see Results and Discussion for values). After 44 hr 25 min at room temperature only a trace of 6 remained, the amount of 5 had decreased, and the amounts of 7 and acetone had increased (IR). These observations are consistent with the decomposition of 6 to give acetone and the simultaneous

thermal substitution reaction of $PPh_3$ with 5 to give 7. By integrating the NMR spectra of the solution just before the CO was removed and 1.75 and 41.50 hr after it was removed, and plotting ln (6) vs. time, it was possible to extract an approximate rate constant for the rate of disappearance of 6 in the absence of CO: $k_{obs}(23°C) = (1.7 \pm 0.5) \times 10^{-5}$ $sec^{-1}$, ($t_{\frac{1}{2}} \sim 11$ hr).

A solution of 1 (29 mg, 0.070 mmol) in 0.52 ml of benzene-$d_6$ was sealed under CO (0.525 mmol in 2.57 ml total volume, ca. 5 atm), stored at 4°C and monitored periodically by $^1H$ NMR. After 5 days new absorptions consistent with 6 (δ 0.58 (s, Me), 4.35 (s, Cp) ppm) reached their maximum intensity (5% of the total Cp signal) while absorptions characteristic of 5 (δ 4.42 (s, Cp) ppm), 7 (δ 4.59 (d, $J_{PH}$ = 1 Hz, Cp) ppm), and acetone (δ 1.60 ppm) continued to grow in.

A solution of 1 (10 mg, 0.024 mmol) in 0.69 ml of cyclohexane-$d_{12}$ was sealed under CO (0.1 mmol in 2.5 ml total volume, ca. 1 atm). After 4 hr at room temperature new absorptions consistent with 6 (δ 0.41 (s, Me), 4.79 (s, Cp) ppm) had reached their maximum intensity (ca. 13% of the total Cp signal) as peaks characteristic of 5 (δ 4.92 (s, Cp) ppm), 7 (δ 4.53 (d, $J_{PH}$ = 1 Hz, Cp) ppm) and acetone (δ 1.94 ppm) continued to grow in.

(b) Crossover experiments. $CpCo(PPh_3)(Me)_2$ (44 mg, 0.106 mmol) and 1-$d_{21}$ (47 mg, 0.107 mmol) were dissolved in

0.85 ml of benzene. A 0.40 ml aliquot of the resulting stock solution was removed, diluted with 1.60 ml of additional benzene, and sealed under CO (5.5 mmol in 17.4 ml total volume, 7.7 atm). The remaining stock solution was also sealed under CO (5.3 mmol in 16.0 ml total volume, 8.1 atm) and both samples were heated with stirring at 60°C for 17 hr 27 min. The CO was removed (one freeze-pump-thaw cycle) and the volatiles (benzene, acetone, and a small amount of $\underset{\sim}{5}$) were distilled from the reaction mixture under vacuum (10 mm Hg) while the reaction flask was cooled (15°C) to reduce the amount of $\underset{\sim}{5}$ which transferred. The resulting solution was capped under $N_2$ with a septum and the acetone isolated from it by preparative GC (column 2). During the time it took to isolate the acetone, the initial pale-orange solution darkened and a black precipitate formed due to slow, oxidative decomposition of $\underset{\sim}{5}$. The decomposition products did not catalyze H- or methyl-group exchange in the product acetone to a detectable (< 2% crossover) extent (*vide supra*). The acetone was analyzed by mass spectroscopy (12 ev). Under these conditions substantial fragmentation (methyl loss) still occurred; however, independent control experiments conducted in our laboratory[19a] have shown the deuterium isotope effect on the fragmentation is insignificant so only the intensities of the parent peaks are necessary to determine the ratios of labeled acetones. For each sample, three different scans were taken, the intensities

of the relevant peaks were manually averaged and corrected for background and $^{13}C$ contributions and these data were used to calculate the % crossover[17] in each sample. Values of 2 and 12% were obtained for the dilute (0.05 M) and concentrated (0.25 M) samples, respectively. To check whether the observed methyl-group scrambling was independent of the carbonylation, $\underset{\sim}{1}$-$d_0$ (21.3 mg, 0.051 mmol) and $\underset{\sim}{1}$-$d_{21}$ 24.4 mg, 0.056 mmol) were dissolved in 0.44 ml of benzene. A 0.40 ml portion of this solution was heated at 60° under $N_2$ for 42 hr. The solution was diluted with 1.60 ml of additional benzene, sealed under CO (5.5 mmol in 16.0 ml total volume, 8.4 atm) and heated at 60° for 18 hr 40 min. Analysis of the acetone produced showed 100% crossover.

Reaction of 1 with diphenylacetylene. (a) Product isolation, kinetics, crossover experiments, and isotope effects. In general, solutions of 1 (0.055 - 0.23 M) and diphenylacetylene (0.67 - 0.90 M) in benzene-$d_6$ were sealed in NMR tubes under vacuum or $N_2$, heated at 56°C, and monitored by $^1H$ NMR (90 MHz). The details of a reaction used to generate several different kinds of information are described below.

An NMR tube was charged with 1-$d_0$ (67 mg, 0.161 mmol), 1-$d_6$ (63 mg, 0.149 mmol), and diphenylacetylene (217 mg, 1.22 mmol). Tetramethylsilane (73 mm in 25.85 ml at 25°C, 0.101 mmol) and benzene-$d_6$ (enough to give 1.60 ml of solution) were distilled onto the solids under vacuum, the tube was sealed under ca. 0.8 atm of $N_2$, heated at 55 ± 1°C, and monitored periodically by $^1H$ NMR. During the reaction, the new peaks described in the Results and Discussion appeared and the absorptions due to TMS and the cyclopentadienyl and methyl groups were carefully integrated. After 30 hr 26 min at 55°C 94% of the starting material had disappeared and

integration of the entire spectrum gave the product yields reported in the Results and Discussion. The reaction mixture changed from orange to dark red brown during the reaction and a brown solid precipitated in the tube after standing at room temperature for several days.

The integrations of the methyl and cyclopentadienyl signals were normalized[56] using the internal TMS as a standard and because the methyl absorption at δ 0.58 ppm gave the amount of $\underset{\sim}{1}$-$d_0$ and the cyclopentadienyl absorption at δ 4.46 ppm gave the combined amounts of $\underset{\sim}{1}$-$d_0$ and $\underset{\sim}{1}$-$d_6$, we could follow the disappearance of both the labeled and unlabeled components of the reaction. A plot of ln (Me) vs. time over one half-life[22] gave a pseudo first order rate constant $k_{h6} = (8.8 \pm 1.3) \times 10^{-5}$ $sec^{-1}$ for the disappearance of $\underset{\sim}{1}$-$d_0$ where (Me) was the normalized intensity of the methyl absorption. The slope of a plot of ln [(1.2(Cp)/(Me)) - 1 ] vs. time gave a value for the difference between the pseudo first order rate constants for the disappearance of $\underset{\sim}{1}$-$d_0$ and $\underset{\sim}{1}$-$d_6$: $k_{h6} - k_{d6} = (0.08 \pm 0.31) \times 10^{-5}$ $sec^{-1}$ where (Cp) was the normalized intensity of the cyclopentadienyl absorption. The isotope effect on the disappearance of $\underset{\sim}{1}$, $k_{h6}/k_{d6}$ = 1.01 ± 0.04, was calculated from these data.

The products of the reaction were isolated by opening the tube, washing the contents out with benzene, and removing the solvent at reduced pressure to leave an oily brown slurry. This residue was washed with four 4 ml portions of mixed

hexanes to give a brown powder identified as metallacyclopentadiene 9 on the basis of its $^1$H NMR ($C_6D_6$):δ 4.78 (s, Cp) ppm; ($CDCl_3$):δ 4.69 ppm (lit.[10a] δ 4.82 ppm) and thermal conversion (refluxing toluene, 18 hr) to 10.[10a] The solvent was removed from the combined hexane washes to give a red brown oil and some solid. This mixture was triturated with ca. 0.5 ml of benzene:mixed hexanes, 1:9 by volume, and the soluble fraction chromatographed on silica gel (6.5 cm x 10 mm) in the same solvent to remove the last traces of organometallic material. The first 75 ml of clear eluent were collected and the solvent was removed to leave the organic products and remaining diphenylacetylene as a clear oil. A trace of yellow solid did not dissolve in the benzene:hexanes mixture used for the chromatography and was identified as tetraphenylcyclobutadiene complex 10 on the basis of its $^1$H NMR ($C_6D_6$):δ 4.48 (s, Cp) ppm; ($CDCl_3$):δ 4.58 ppm (lit.[47] δ 4.68 ppm) and mass spectrum (70 ev) m/e (rel intensity): 482(4.9), 481(28.6), 480(78.9), 303(14.4), 302 (68.1), 179(5.1), 178(30.0), 125(6.1), and 124 (100.0). In the initial reactions the organic products were isolated by preparative GC (column 1) and identified by comparison (GC coinjection, $^1$H NMR) with authentic samples of 11 and Z-12 (*vide infra*). For labeling experiments such as the one described in detail here, the mixture of organic products was analyzed by GC-mass spectroscopy (column 3).

GC-mass spectroscopic analysis of the organic products

of the crossover experiment, a mixture of pure $\underset{\sim\sim}{11}$-$d_6$ and Z-$\underset{\sim\sim}{12}$-$d_6$ prepared from the reaction of $\underset{\sim}{1}$-$d_6$ and diphenylacetylene, and a pure sample of $\underset{\sim\sim}{11}$-$d_0$ conducted under identical spectrometer conditions (16 ev) in one continuous session showed there was no detectable (<2% crossover) deuterium scrambling during the reaction. Given these results, it was then possible to determine the ratio $R = (\underset{\sim\sim}{11}\text{-}d_0)(Z\text{-}\underset{\sim\sim}{12}\text{-}d_6)/(\underset{\sim\sim}{11}\text{-}d_6)(Z\text{-}\underset{\sim\sim}{12}\text{-}d_0)$ by separately measuring the ratios $(\underset{\sim\sim}{11}\text{-}d_0)/(\underset{\sim\sim}{11}\text{-}d_6)$ and $(Z\text{-}\underset{\sim\sim}{12}\text{-}d_6)/(Z\text{-}\underset{\sim\sim}{12}\text{-}d_0)$ from the mass spectra of $\underset{\sim\sim}{11}$ and Z-$\underset{\sim\sim}{12}$. There was a noticeable isotope effect on the fragmentation of $\underset{\sim\sim}{11}$ (Z-$\underset{\sim\sim}{12}$ did not fragment under these conditions) so the intensities of the major fragments were summed to give the total amounts of $\underset{\sim\sim}{11}$-$d_0$ and $\underset{\sim\sim}{11}$-$d_6$. Using this consideration and the spectra of the known labeled compounds, the peaks at m/e: 210, 209, 208, 194, 193, 131, 130, and 129 were used for $\underset{\sim\sim}{11}$-$d_0$; 215, 214, 213, 197, 196, 137, 136, and 135 for $\underset{\sim\sim}{11}$-$d_6$; 215, 214, 211, 210, and 207 for Z-$\underset{\sim\sim}{12}$-$d_6$; and 209, 208, 206, and 204 for Z-$\underset{\sim\sim}{12}$-$d_0$. The value of R obtained in this way from these data was 1.6. The value obtained from the reaction of $\underset{\sim}{1}$-$d_0$ (38 mg, 0.091 mmol), $\underset{\sim}{1}$-$d_6$ (41 mg, 0.097 mmol), and diphenylacetylene (129 mg, 0.724 mmol) in 0.82 ml of solution was 1.7 and from $\underset{\sim}{1}$-$d_0$ (21 mg, 0.050 mmol), $\underset{\sim}{1}$-$d_{21}$ (27 mg, 0.062 mmol), diphenylacetylene (153 mg, 0.858 mmol), and excess $PPh_3$ (230 mg, 0.877 mmol) in 1.14 ml of solution was 1.5.

(b) Effect of added $PPh_3$. A solution of 1 (23 mg, 0.055 mmol), diphenylacetylene (87 mg, 0.488 mmol), $PPh_3$ (129 mg, 0.492 mmol), and TMS (32 mm in 25.36 ml at 25°C, 0.044 mmol) in 0.54 ml of solution was heated at 56°C and monitored at regular intervals by $^1H$ NMR. Integration of the cyclopentadienyl and methyl absorptions of 1 using the TMS as an internal standard followed by a first order treatment of these data (ln (Cp) vs. time, ln (Me) vs. time) over one half-life gave pseudo first order rate constants $K_{obs} = (3.6 \pm 0.3) \times 10^{-6}$ $sec^{-1}$ and $k_{obs} = (3.4 \pm 0.3) \times 10^{-6}$ $sec^{-1}$ for the disappearance of the cyclopentadienyl and methyl signals, respectively. In this reaction the ratio of 11:Z-12 was 0.9 as measured by integration of the signals at δ 2.01 and 1.36 ppm. In another reaction with 1 (24 mg, 0.058 mmol), diphenylacetylene (136 mg, 0.763 mmol), and $PPh_3$ (67 mg, 0.255 mmol) in 0.63 ml of solution, the ratio of 11:Z-12 was 2.0.

(c) Attempt to observe reaction intermediates by $^1H$ NMR. Dilute solutions of 1 in the presence of high concentrations of diphenylacetylene in benzene-$d_6$ (1 (10 mg, 0.024 mmol) and diphenylacetylene (66 mg, 0.370 mmol) in 0.44 ml) and THF-$d_8$ (1 (10 mg, 0.24 mmol) and diphenylacetylene (75 mg, 0.421 mmol) in 0.45 ml) were kept at room temperature and monitored periodically by NMR for 5 hr. Only absorptions due to the known starting materials and products were observed, (THF-$d_8$): δ 4.77 ppm (9), δ 1.44, 4.02, 5.09, 5.35

ppm (11), δ 2.15 ppm (Z-12), and δ 2.50 ppm (trace unknown methyl). The ratio of 11:Z-12 was 1.7 in the reaction conducted in THF-$d_8$ in the absence of any additional $PPh_3$.

2,3-diphenyl-1-butene (11). A solution of n-butyllithium (18 ml of 2.42 M solution, 43.6 mmol) in n-hexane was added dropwise to a stirred slurry of methyltriphenylphosphonium bromide (11.13 gm, 43.3 mmol) in 220 ml of diethyl ether at room temperature over 15 min to give an orange solution which was stirred an additional 3 hr 40 min. 1,2-Diphenyl-1-propanone (9.0 gm, 42.8 mmol) in 25 ml of diethyl ether was added dropwise to the stirred ylid solution over 15 min with precipitation of a sticky white solid. The resulting reaction mixture was held at reflux for 3 hr 10 min, cooled to room temperature, and poured into 150 ml of an ice/$H_2O$ slush to give a sticky yellow solid, cloudy white aqueous phase, and light yellow organic layer. The aqueous fraction was washed with 2 additional portions of ether. The ether fractions were combined, washed with three 100 ml portions of $H_2O$ and one 100 ml portion of saturated aqueous NaCl, and dried over anhydrous $MgSO_4$ overnight. Solvent removal gave a thick yellow brown oil containing mostly 11 and unreacted starting material from which 11 was isolated as a clear oil by preparative GC (column 2). $^1H$ NMR ($CCl_4$): δ 1.41 (d, J = 7 Hz, $CH_3$), 3.90 (q, J = 7 Hz, methine H), 5.07 (m, 1 H), 5.31 (br s, 1 H), 7.1 (br m, $C_6H_5$) ppm;

($C_6D_6$): see Results and Discussion.

Z and E-2,3-diphenyl-2-butene (Z and E-12). A 1 gm portion of the crude product mixture containing 11 prepared above was dissolved in 25 ml of dimethylsulfoxide (DMSO), combined with 280 mg (2.5 mmol) of potassium t-butoxide, and heated at 140°C for 35 hr 30 min. The resulting brown reaction mixture was treated with 70 ml of $H_2O$ to give an emulsion which was broken up with the addition of 20 ml of saturated aqueous NaCl. The aqueous phase was washed with four 50 ml portions of diethyl ether. The organic fractions were combined, washed with five 40 ml portions of $H_2O$ and one 40 ml portion of saturated aqueous NaCl, and dried over anhydrous $MgSO_4$. The solvent was removed and the crude product mixture was filtered through a column of silica gel (15 cm x 20 mm) with benzene to remove deeply colored impurities. Pure Z-12 and E-12 were isolated from the resulting mixture by preparative GC (column 4). Z-12: $^1H$ NMR ($CCl_4$):δ 2.12 (s, $CH_3$), 6.87 (m, $C_6H_5$) ppm (lit.[57] δ 2.16 ppm); ($C_6D_6$):δ 1.99 (s, $CH_3$) ppm. E-12: $^1H$ NMR ($CCl_4$):δ 1.83 (s, $CH_3$), 7.14 (m, $C_6H_5$) ppm (lit.[57] δ 1.88 ppm); ($C_6D_6$): δ 1.90 (s, $CH_3$) ppm.

Isomerization of 11, Z-12, and E-12. (a) Acid catalyzed. Pure samples (5-15 mg) of the olefin to be isomerized were dissolved in a mixture of benzene (1.0 ml) and $H_2O$ (0.3 ml) to which ca. 30 drops of trifluoromethanesulfonic acid were

then added. This two-phase mixture was stirred under Ar and heated at 56°C. Small aliquots (100 - 200 µl) of the mixture were withdrawn periodically and extracted with diethyl ether. The ether extract was dried over anhydrous $MgSO_4$ and analyzed by GC (column 5). In this way, the equilibrium mixture of olefins was shown to contain 1.9 ± 0.4% 1-1, 33 ± 3% Z-1-2, and 65 ± 3% E-1-2.

(b) Base catalyzed. Potassium t-butoxide (ca. 7 mg) was added to a solution of the olefin to be isomerized (5-15 mg) in 1.0 ml of DMSO and this mixture was stirred and heated at 56°C under Ar. Aliquots were withdrawn as before, diluted with $H_2O$, and extracted with ether. The ether extract was dried and analyzed as before. The equilibrium mixture obtained under these conditions contained 2 ± 0.5% 1-1, 31 ± 2% Z-1-2, and 67 ± 3% E-1-2.

(c) $CpCo(PPh_3)_2$ catalyzed. A solution of 1-1 (9 mg, 0.043 mmol) and 1-3 (33 mg, 0.051 mmol) in 0.37 ml of benzene-$d_6$ was filtered into an NMR tube, sealed under $N_2$, and heated at 56°C. After 8.4 days at this temperature only a trace of 1-1 was detectable by NMR and integration of the NMR spectrum showed the ratio E-1-2:Z-1-2 was 12.35 ± 0.25. The tube was opened in the air and the contents were filtered through a small (4 cm x 4 mm) column of fluorosil with petroleum ether to remove the oxidized metal-containing residue and analyzed by GC (column 5). The organic mixture contained 7% Z-1-2, 89% E-1-2, and 4% 1-1.

A solution of a mixture (8.0:1) of Z-12 and E-12 (10 mg, 0.048 mmol) and 13 (52 mg, 0.080 mmol) in 0.52 ml of benzene-$d_6$ was filtered into an NMR tube, TMS (18 mm in 25.85 ml at 25°C, 0.025 mmol) was added as an internal standard, sealed under $N_2$, and heated at 56°C for 86.0 days. After this time the ratio Z-12:E-12 had not changed detectably (NMR) and 92 ± 4% of the starting olefins remained.

Pure (>99.5%) E-12 (11.5 mg, 0.055 mmol) and 13 (61 mg, 0.094 mmol) were similarly combined in 0.58 ml of benzene-$d_6$ and heated at 56°C for 103.2 days. After this time traces of Z-12 (2%) and 11 (1%) were detectable (NMR).

During the course of these long reactions, the nature of the $CpCo(PPh_3)_2$ catalyst changed slightly as shown by the gradual appearance of a singlet in the cyclopentadienyl region at δ 4.41 ppm which grew in next to the signal due to 13 at δ 4.44 (t, $J_{PH}$ = 1 Hz) ppm along with smaller singlets at δ 4.36, 4.71, and 4.81 ppm. A multiplet at δ 7.4 ppm characteristic of free $PPh_3$ also appeared. Over 100 days, less than ca. 25% of the starting 13 appeared to be affected by this reaction and because the isomerization of 11 to Z-12 and E-12 was fast on this time scale and the mass balance was good throughout the longer reactions of Z-12 and E-12 we assume the Co-mediated isomerizations were independent of this slow reaction.

Thermal substitution of $PPh_3$ in $CpCo(PPh_3)_2$ (13) by olefins. (a) Ethylene. An NMR tube containing 13 (36 mg,

0.056 mmol) in 0.48 ml of benzene-$d_6$ was sealed under ethylene (0.114 mmol, 2.60 ml total tube vol.). $^1$H NMR (28°C): δ 1.07 (m, AA' of AA'BB'X for coordinated ethylene), 2.48 (m, BB' of AA'BB'X for coordinated ethylene), 4.48 (d, $J_{PH}$ = 0.5 Hz, Cp), 5.24 (s, free ethylene), 7.02 (br m, meta- and para-H of $C_6H_5$), 7.37 (br m, ortho-H of free $C_6H_5$), 7.65 (br m, ortho-H of coordinated $C_6H_5$) ppm. At high resolution (180 MHz) a tiny triplet (J = 1.4 Hz at δ 4.44 ppm due to 13 was detectable and integration of the signals corresponding to the two cyclopentadienyl absorptions of 14 and 13, free $PPh_3$, and free ethylene permitted the estimation of K (equation 7) as 200 ± 100. A tube containing 13 (123 mg, 0.190 mmol) in 2.9 ml of toluene-$d_8$ was sealed under ethylene (0.484 mmol, 12.7 ml total tube vol.). $^{13}$C NMR (-30°C, $^1$H gated decoupled): δ 25.0 (t, $^1J_{CH}$ = 143 Hz, coordinated ethylene), 83.0 (d of t, $^1J_{CH}$ = 171 Hz, $^2J_{CH}$ = 6 Hz, Cp) ppm.

(b) Propene. A tube containing 13 (31 mg, 0.048 mmol) and TMS (15 mm in 25.85 ml at 23°C, 0.021 mmol) in 0.53 ml of benzene-$d_6$ was sealed under propene (0.235 mmol, 2.61 ml total tube vol.) and examined by $^1$H NMR (180 MHz, 7°C). In this case, phosphine substitution to form the olefin complex is not as favorable and in addition to the absorptions due to 13, free propene, and free triphenylphosphine, a new cyclopentadienyl resonance (δ 4.49 (d, $J_{PH}$ = 0.5 Hz) ppm) and new signals at δ 2.23 (d of d, J's ca. 10 and 3 Hz, 1 H), 1.62 (d, J = 2 Hz, too close to the free propene methyl to

integrate) and 1.23 (t, J ca 6.9 Hz, 1 H) ppm were observed. The absorptions at δ 2.23 and 1.23 ppm were assigned to the terminal vinyl protons of the coordinated propene, each coupled to $^{31}P$ and the undetected H at the 2-position. The doublet at δ 1.62 ppm presumably is part of the coordinated propene methyl signal, the remainder of which is buried under the large free propene methyl signal. From integration of this spectrum the equilibrium constant (equation 7) was estimated to be 0.22 ± 0.01 (25°C).

Preparation of $(\eta^5\text{-}CH_3C_5H_4)Co(CO)(PPh_3)$ (15). A solution of $Cp'Co(CO)_2$ (1.40 gm, 7.21 mmol) and $PPh_3$ (2.51 gm, 9.57 mmol) in 10 ml of toluene was held at reflux for 16 hr, the solvent was removed under vacuum, and the resulting thick red brown oil was redissolved in THF and filtered. The solvent was removed, the thick oil dissolved in 30 ml of mixed hexanes, and cooled (-30°C) to give red brown crystals (1.63 gm, 53%) which were washed with three portions of cold hexanes and dried under vacuum. $^1H$ NMR (benzene-$d_6$): δ 1.89 (d, $J_{PH}$ = 1.4 Hz, $CH_3$), 4.13 (m, AA' of AA'BB'X for substituted Cp), 4.87 (m, BB' of AA'BB'X for substituted Cp), 7.03 (m, meta- and para-H in $C_6H_5$), 7.72 (m, ortho-H of $C_6H_5$) ppm; IR (benzene-$d_0$): $\nu_{CO}$ 1925 $cm^{-1}$. A portion of this material was recrystallized (toluene:mixed hexanes, 1:2.9 by vol, 93% recovery) to give an analytical sample. mp = 95-96.5°C. Anal. Calcd for $C_{25}H_{22}CoOP$: C, 70.09; H, 5.19. Found: C, 70.25; H, 5.37.

Photochemical substitution of CO in ($\eta^5$-$RC_5H_4$)Co(CO)($PPh_3$) by ethylene. (a) R = H. Photolysis of a solution of 7 (36 mg, 0.087 mmol) in 0.48 ml of benzene-$d_6$ under ethylene (0.443 mmol, 2.30 ml total tube vol.) for 1 hr generated $^1$H NMR absorptions identical to those observed during the reaction of 13 with ethylene (δ 1.07, 2.48, 4.48 ppm) and assigned to 14. A photostationary mixture combined of 51% 7, 37% 14, and 12% 5 was reached after 4 hr 24 min of photolysis.

(b) R = $CH_3$. Photolysis of a solution of 15 (27 mg, 0.063 mmol) in 0.50 ml of benzene-$d_6$ under ethylene (0.591 mmol, 2.61 ml total tube vol.) generated $^1$H NMR absorptions due to Cp'Co$(CO)_2$ (δ 1.50 (s, $CH_3$), 4.34 (m, AA' of AA'BB' for substituted Cp), 4.53 (m, BB' of AA'BB' for substituted Cp) ppm) and new absorptions assigned to the methyl (δ 1.43 ppm, d, $J_{PH}$ = 2 Hz), cyclopentadienyl (δ 4.50 ppm, br s, in theory AA'BB'X, very weakly coupled here) and ethylene (δ 1.19, 2.14 ppm, m, AA'BB' portion of AA'BB'X spectrum) moieties of the methylcyclopentadienyl ethylene complex Cp'Co$(C_2H_4)$(PPh) (16).

Preparation of $CD_4$ and $CD_3H$. Two 2 ml portions of a filtered solution of $CD_3MgI$ prepared from Mg turnings (0.76 gm, 31.3 mmol) and a solution of $CD_3I$ (4.5 gm, 31.0 mmol) in 32 ml of diethyl ether were transferred to separate flasks. The remainder was used to prepare 1-$d_{21}$. $CD_3H$ was prepared by rigorously degassing (4 freeze-pump-thaw cycles)

one of the Grignard solutions, distilling in 5 ml of $H_2O$ under vacuum, pulling the methane through two cold (-196°C) traps in series, and collecting the volatile product with a Toepler pump. $CD_4$ was prepared in an analogous manner using $D_2O$ and the other Grignard solution. In this case, the vacuum manifold was preconditioned by distilling ca. 10 ml of $D_2O$ into the manifold and letting it equilibrate overnight. This $D_2O$ was distilled back out of the manifold before fresh $D_2O$ was used to quench the Grignard solution.

Reaction of 1 with ethylene. (a) Initial observations. A solution of 1 (33 mg, 0.079 mmol) in 0.59 ml of benzene-$d_6$ was sealed under ethylene (0.40 mmol, 2.45 ml total tube vol.), heated initially at 64°C (20 hr 25 min) and then at 76°C, and monitored periodically by $^1H$ NMR. After 17 hr 37 min at 76°C, the spectral changes noted in the Results and Discussion were observed. GC analysis (columns 6 and 7) of the gas phase above this final reaction mixture confirmed the identity of the major products methane, propene, and ethane observed by NMR and detected trace amounts of 1-butene, Z, and E-2-butene.

(b) Quantitative product analysis. Because one of the products of the reaction, methane, was noncondensable we prepared product mixtures for analysis with a Toepler pump. The volatile components of the reaction were pulled through two -78°C traps connected in series until all the benzene had distilled from the reaction mixture into the first trap.

This trap was warmed to room temperature and pumping was continued until the benzene had completely sublimed into the second trap. A known amount of internal standard (cyclopropane) was added to the gases collected with the Toepler pump in this way and the resulting mixture was analyzed by GC, (columns 6 and 7). Separate GC analysis did not detect any $C_4$ or lighter hydrocarbons in the benzene solution generated by thawing the second trap.

A solution of 1 (98 mg, 0.235 mmol) in 2.0 ml of benzene was sealed under ethylene (2.73 mmol in 16.3 ml total vol., 4 atm) and heated at 75 ± 2°C for 33 hr 25 min. Removal of the volatile components left a thick red brown oil which displayed severely broadened $^1$H NMR absorptions. The volatile reaction mixture contained: methane (0.189 mmol), ethane (0.007 mmol), and propene (0.135 mmol), as well as traces of linear butenes.

A solution of 1 (106 mg, 0.255 mmol) in 2.0 ml of benzene was heated at 54 ± 1°C under ethylene (5.2 mmol in 11.5 ml total vol., 11 atm) for 121 hr 15 min. The volatile product mixture contained: methane (0.160 mmol), propene (0.147 mmol), butane (0.27 μmol), 1-butene (12.6 μmol), E-2-butene (6.9 μmol), and Z-2-butene (1.2 μmol). This time, the organometallic residue crystallized after the solvent was removed, was redissolved in benzene-$d_6$ with a known amount of ferrocene, and integration of the $^1$H NMR spectrum showed the presence of: 14 (0.169 mmol), 16

(0.017 mmol), starting 1 (0.069 mmol) and a trace of 17.

(c) Isolation of $CpCo(C_2H_4)(PPh_3)$ (14). A solution of 1 (600 mg, 1.44 mmol) in 6 ml of benzene was sealed under ethylene (8.0 mmol in 17.4 ml total vol.) and heated at 53 ± 2°C for 21 days. The reaction mixture was filtered and the solvent removed to give a purple red oil which crystallized on standing at room temperature. The residue was recrystallized (benzene:mixed hexanes, 1:6.5 by vol) to yield 416 mg (70%) of crude ($^1H$ NMR showed contamination by 1, 16, and 17) 14. An additional recrystallization (benzene:mixed hexanes, 1:5 by vol) reduced the contamination by 1 and 17 but left some 16 (ca. 10%) in the final product as indicated by the characteristic absorption at δ 1.43 ppm. $^1H$ and $^{13}C$ NMR (see reaction of 13 with ethylene described above); $^{31}P$ NMR (-65°C, toluene-$d_8$, $^1H$ decoupled): δ 78.0 (br s, $PPh_3$) ppm.

(d) Labeling studies. Methane samples were analyzed by mass spectroscopy at a beam voltage of 50 ev. Significant fragmentation could not be eliminated by using lower voltages and the observed fragmentations were also less reproducible under these conditions where fewer ions were generated. Known samples of $CD_3H$ and $CD_4$ were analyzed at the same time as unknowns under identical spectrometer conditions. In this way, the amounts of $CD_4$ and $CD_3H$ were determined and the remaining signal was assigned to other methanes. For each sample, three different scans were

taken and the intensities of the relevant peaks (m/e 20 - 14) were manually averaged and corrected for background (determined separately for each sample after the system was pumped down) and $^{13}C$ contributions.

A solution of 1-$d_{21}$ (127 mg, 0.290 mmol) in 2.0 ml of benzene was heated at 54 ± 1°C under ethylene (7.9 mmol in 17.4 ml total vol, 11 atm) for 120 hr 35 min. The reaction mixture was degassed with a Toepler pump into two -196°C traps connected in series. When the benzene started to distill, the first trap was warmed to -78°C to permit the ethylene and propene to transfer to the second trap. After the solvent had distilled, the methane which had been collected by the Toepler pump was analyzed by mass spectroscopy as described above and the propene was separated from the excess ethylene by preparative GC (column 8) and analyzed by mass spectroscopy (10.5 ev), m/e (relative intensity, corrected for background and $^{13}C$ contributions): 45 (100.00), 44 (3.84), 43 (1.01). These data show greater D incorporation than that predicted (45 (100.00), 44 (7.38), 43 (0.18)) on the basis of the observed limits of D incorporation in the methyl groups of starting 1-$d_{21}$ and represent complete methyl group transfer within the limits of our experiment. Methane from this reaction: 19 (100.0), 18 (39.5), 17 (43.5), 16 (3.9), 15 (2.1), 14 (1.9); methane from $H_2O$ quench of $CD_3MgI$: 19 (100.0), 18 (39.9), 17 (44.1), 16 (4.0), 15 (2.1), 14 (1.9).

A solution of $\underset{\sim}{1}$-$d_{21}$ (110 mg, 0.251 mmol) in 2.0 ml of benzene was heated at 52 ± 2°C under ethylene-$d_4$ (5.4 mmol in 11.6 ml total vol, 11 atm) for 118 hr 25 min. The methane from this reaction was 95% $CD_4$ and 5% $CD_3H$.

A medium-walled NMR tube (Wilmad 504-PP) containing $\underset{\sim}{1}$-$d_{21}$ (51 mg, 0.117 mmol) in 0.42 ml of benzene-$d_6$ was sealed under ethylene (0.977 mmol in 1.79 ml total vol, 0.68 M, 12.4 atm), heated at 59 ± 2°C, and the contents observed by $^1H$ NMR. Integration of the NMR spectrum after 90 hr showed 13%[58] of the propene carried $CH_2D$ methyl groups while 50% of the $\underset{\sim}{1}$-$d_{21}$ had reacted to give propene. After 188 hr, the corresponding figures were 29 and 64%, respectively.

A solution of $\underset{\sim}{1}$-$d_{21}$ (51 mg, 0.117 mmol) in 0.40 ml of benzene-$d_0$ was sealed under ethylene (0.533 mmol in 1.90 ml total vol, 0.51 M, 5.4 atm), heated at 59 ± 2°C, and monitored by $^2D$ NMR. After 40 hr 30 min, no terminal vinyl absorptions for propene were detectable, despite the presence of the propene methyl signal. After 188 hr, absorptions due to deuterium in the terminal vinyl positions had appeared; however, no deuterium was detectable in the 2-vinyl position.

Thermal decomposition of $\underset{\sim}{1}$. (a) Organic products. The volatile products from thermal decompositions of $\underset{\sim}{1}$ were isolated and analyzed in the same way described for the products of the reaction of $\underset{\sim}{1}$ and ethylene. A solution of

1 (110 mg, 0.264 mmol) in 2.0 ml of benzene was heated at 75 ± 2°C under 1 atm of $N_2$ for 33 hr 25 min. Methane (0.152 mmol) and ethane (0.027 mmol) were evolved.

A solution of 1 (111 mg, 0.267 mmol) in 2 ml of benzene was heated under 1 atm of $N_2$ for 17 hr 36 min at 110°C to give a dark grey solution. The volatile mixture contained methane (0.220 ± 0.003 mmol) and ethane (0.0377 ± 0.0006 mmol), no ethane was detected. The organometallic residue gave severely broadened NMR spectra even after chromatography (19 cm x 10 mm; 1:1, benzene:mixed hexanes by vol) on silica gel.

A solution of 1 (49 mg, 0.118 mmol) and $PPh_3$ (163 mg, 0.621 mmol) in 1 ml of benzene was heated for 18 hr at 110° C to give an orange brown solution. The volatile mixture contained methane (0.126 ± 0.009 mmol) and ethane (0.45 μmol).

(b) Organometallic products. A medium-walled NMR tube containing 1 (44 mg, 0.106 mmol) and $PPh_3$ (98 mg, 0.374 mmol) in 0.43 ml of benzene-$d_6$ was sealed under ethylene (1.46 mmol in 1.89 ml total vol, 0.91 M, 17.9 atm), heated at 58 ± 2°C, and the contents observed by $^1H$ NMR. The spectral changes described in the Results and Discussion were observed over the first 16 days of heating. Heating was discontinued after 33 days, by which time additional unassigned absorptions at δ 1.47 (d, J = 1.5 Hz) and 1.67 (br s) ppm had also appeared. No propene (δ 1.58 ppm, $CH_3$)

was detectable at this time. The tube was opened and 6 mg (0.014 mmol) of authentic $Cp'Co(PPh_3)(Me)_2$ were added to the reaction mixture. No new absorptions appeared and the ones at δ 4.30, 4.11, 1.73, 0.48 ppm grew in intensity.

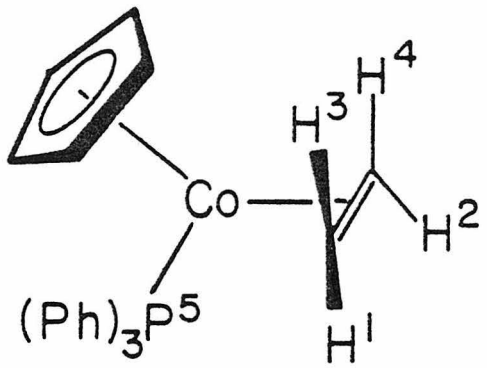
(c) Labeling studies. A solution of $\underset{\sim}{1}$-$d_{21}$ (96 mg, 0.219 mmol) in 2.0 ml of benzene was heated at 71 ± 1°C under 1 atm of $N_2$ for 83 hr 20 min and mass spectroscopic analysis of the methane produced showed it contained 88% $CD_3H$, 9% $CD_4$, and 3% other methanes.

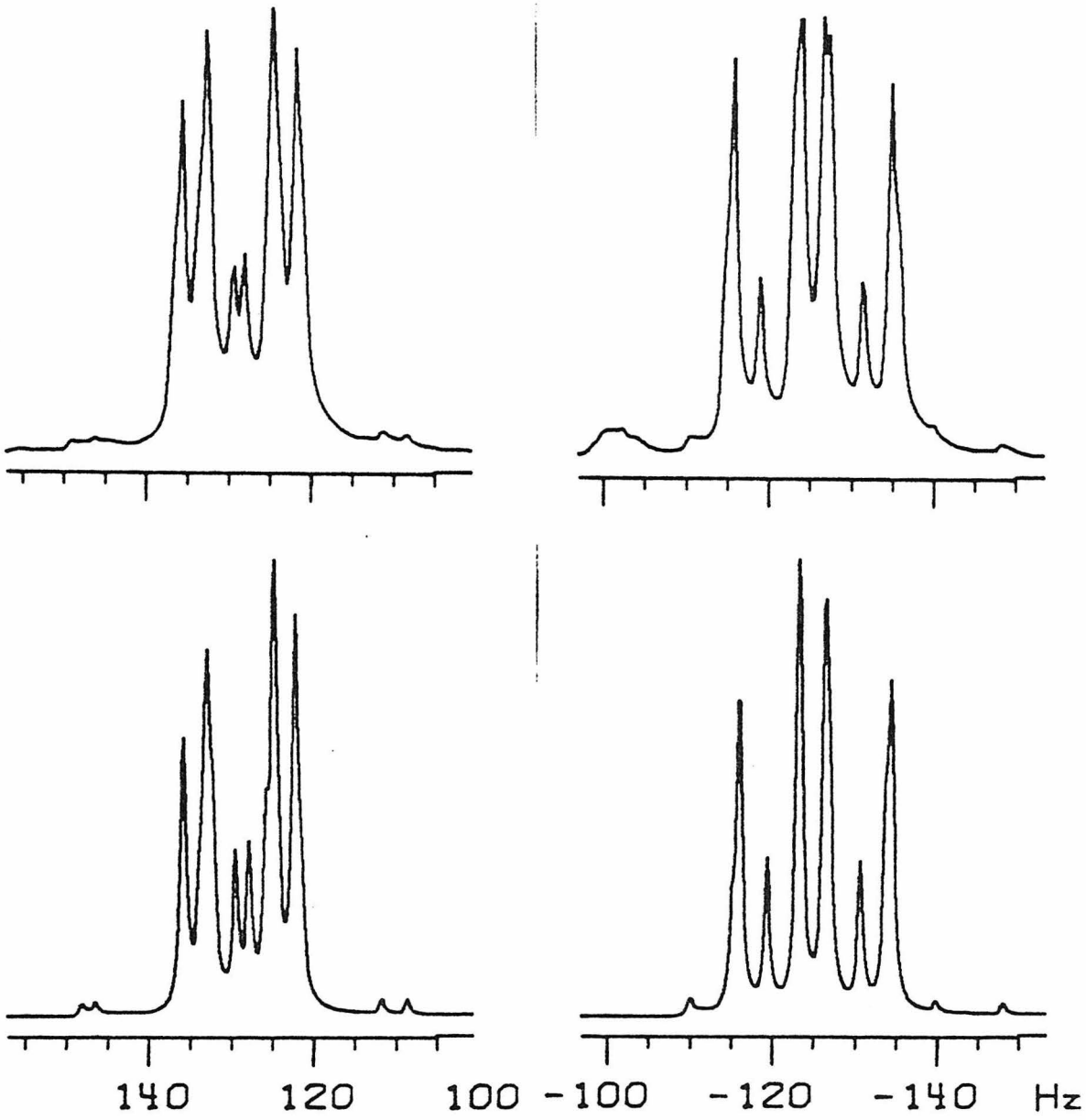
When a solution of $\underset{\sim}{1}$-$d_{21}$ (65 mg, 0.149 mmol) in 1.0 ml of benzene-$d_6$ was heated under the same conditions for 90 hr 16 min, 0.057 mmol of methane were produced and mass spectroscopic analysis showed it contained 89 ± 5% $CD_3H$, 5 ± 1% $CD_4$, and 6 ± 5% other methanes.

Reaction of $\underset{\sim}{1}$ with propene. A solution of $\underset{\sim}{1}$ (116 mg, 0.279 mmol) in 2.0 ml of benzene was heated at 53 ± 2°C under propene (5.4 mmol in 11.5 ml total vol) for 170 hr. The volatile product mixture contained (amounts in μmol): methane (184), ethylene (0.2), ethane (5.6), butane (0.7), 1-butene (0.4), 2-methylpropene (5.5), E-2-butene (4.6), Z-2-butene (2.6), and small amounts of several heavier hydrocarbons (one component coinjects with 1-hexene, column 7) which were not in the starting benzene. Solvent removal left a dark red brown oil which displayed a severely broadened $^1H$ NMR spectrum after dissolution in benzene-$d_6$ and filtration.

Acknowledgment. We are grateful to Mr. Rudi Nunlist, Ms. Vera Mainz, and Dr. William Jones for assistance in obtaining high-field NMR spectra; to Ms. Sherri Ogden, Mr. Paul Becker, and Dr. Arnold Falick for assistance in obtaining MS spectra; to Dr. Donald McAlister and Mr. Andrew Janowicz for supplying samples of $CpCo(PPh_3)_2$; and to Mr. Henry Bryndza for supplying samples of $Cp'Co(CO)_2$ and $Cp'Co(PPh_3)(Me)_2$. We are also grateful to the National Science Foundation (Grant No. CHE 78-08706) for financial support of this work.

Figure 1. (Top) Observed and (bottom) calculated $^1H$ NMR spectrum of coordinated ethylene in 14. Simulation parameters: $\nu(1) = \nu(2) = -125.51$ Hz; $\nu(3) = \nu(4) = 128.12$ Hz; $J(1,2) = 7.95$; $J(1,3) = J(2,4) = -.46$; $J(1,4) = J(2,3) = 11.07$; $J(1,5) = J(2,5) = 7.67$; $J(3,4) = 8.48$; $J(3,5) = J(4,5) = 2.71$ Hz.


H4
H3
Co
H2
(Ph)3P5
H1

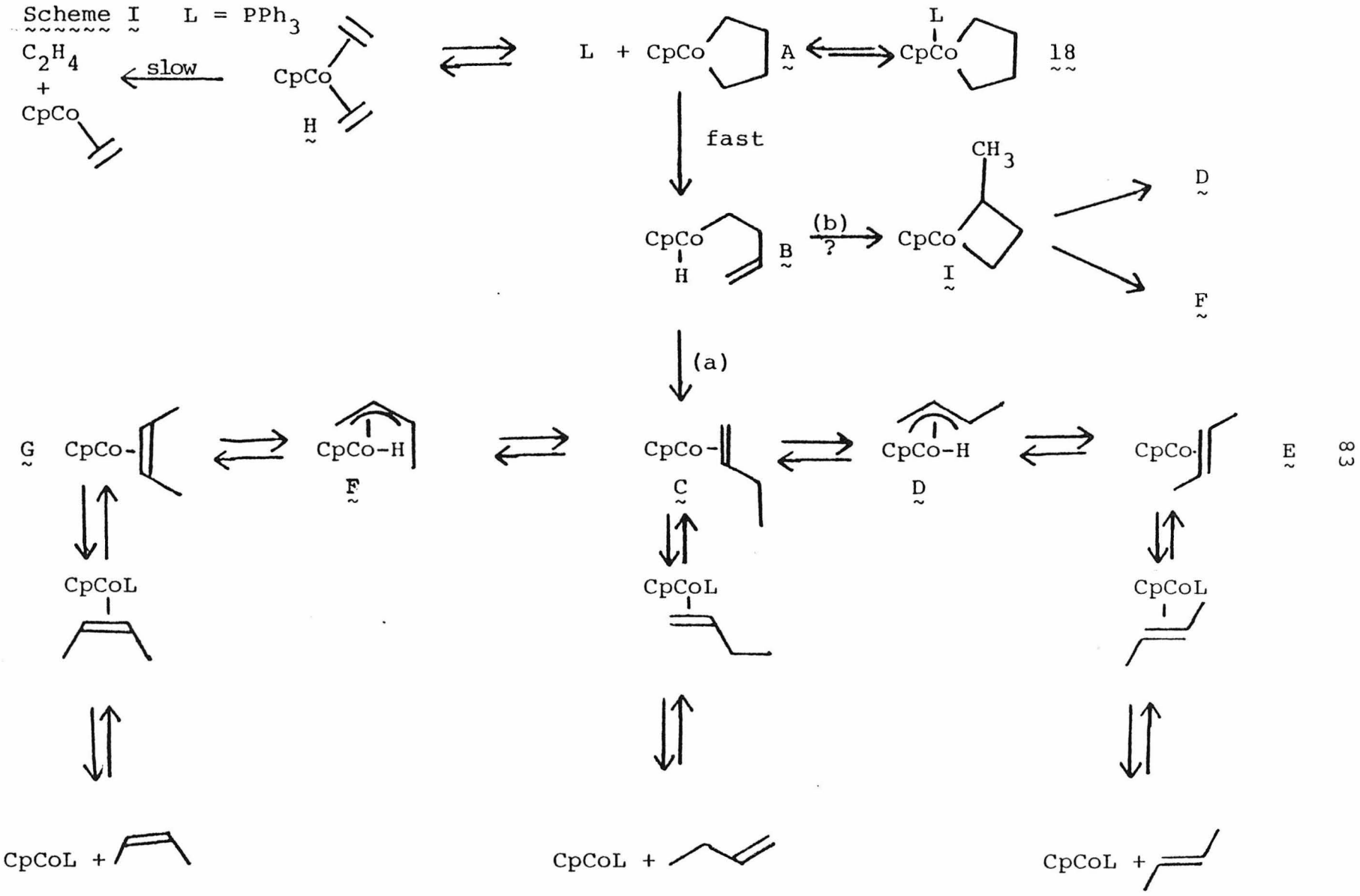

140
120
100
-100
-120
-140
Hz

# Chapter II

## Preparation, Thermal Decomposition, and CO and Diphenylacetylene Insertion Reactions of Cyclopentadienyl(triphenylphosphine)cobaltacyclopentane

## Introduction

Transition metal metallacyclopentanes have recently been implicated as intermediates in systems which catalytically dimerize simple unstrained terminal olefins.[44b,45] In addition, they are unusually (kinetically) stable relative to analogous linear dialkyl compounds.[59] Consistent with their involvement in olefin dimerization, some metallacyclopentanes have been prepared by the reaction of a suitable organometallic precursor with two moles of a terminal olefin.[44] Most tetramethylene metallacyclopentanes have been generated by the more common route involving treatment of a metal-dihalide with a 1,4-di-Grignard or 1,4-dilithiobutane reagent.[44a,c;59,60] $\eta^5$-cyclopentadienyl(triphenylphosphine)cobaltacyclopentane (18, Scheme I) was recently prepared in this way.[60a] We were particularly interested in this report because: (1) the production of small amounts of linear butenes during the reaction of 1 with ethylene to give propene and methane (Chapter I) was consistent with the presence of metallacyclopentanes, (2) there are very few known cobalt dialkyls analogous to 1 because β-hydrogen elimination is apparently very facile in this system, and (3) reaction of CO, diphenylacetylene, and ethylene with 18 would provide an excellent opportunity to further develop the comparative chemistry of dialkyl systems of this kind. This chapter describes our preparation of 18 and preliminary


Scheme I L = PPh3
C2H4
+
CpCo
slow
CpCo
H
L + CpCo
A
L
CpCo
18
fast
CpCo
H
B
(b)
?
CH3
CpCo
I
D
F
(a)
G
CpCo-
CpCo-H
F
CpCo-
CpCo-H
C
D
CpCo
E
CpCoL
CpCoL
CpCoL
CpCoL +
CpCoL +
CpCoL +

results of its thermal decomposition, reactions with CO, diphenylacetylene, and ethylene, and ability to catalyze the dimerization of ethylene to linear butenes.

## Results and Discussion

Preparation and characterization of 18. In their communication[60a] describing 18, Ingrosso, et al. reported that reaction of $CpCo(PPh_3)I_2$ with the di-Grignard of 1,4-dibromobutane in diethyl ether (1:3 molar ratio) at room temperature, followed by alumina chromatography and crystallization from cold pentane, gave 18 as orange-red crystals (15% yield) which they characterized by X-ray diffraction techniques.

In our hands, the di-Grignard approach to 18 proved unsuccessful. After numerous attempts based on the procedures described in the reported synthesis as well as those employed for our own successful preparation of 1, we were able to isolate only traces (<10%) of 18 and these samples were severely contaminated with excess $PPh_3$. We did discover, however, that the extra $PPh_3$ could be removed by recrystallization from benzene/acetronitrile, in which the $PPh_3$ is very soluble. The phosphine-free samples of 18 were, in turn, much more thermally sensitive in solution than their phosphine-contaminated counterparts. Ten minutes after dissolving solid 18 in benzene-$d_6$ at room temperature, the solution had darkened considerably and peaks in the $^1H$ NMR

spectrum were noticeably broadened. Standing at room temperature for longer times resulted in further decomposition, eventually leading to precipitation of solids and total deterioration of the $^1$H NMR spectrum. With these observations in mind, we treated $CpCo(PPh_3)I_2$ with a 5% excess of 1,4-dilithiobutane in diethyl ether at -45°C and were able to isolate phosphine-free 18 in 45% yield on the first attempt. One drawback of using the benzene/acetonitrile mixture for recrystallizing 18 was that some acetonitrile (mole ratio of 18:acetonitrile ca. 1.8:1) was apparently trapped in the crystalline 18. It was not removed by drying for more than 24 hr under high vacuum at room temperature. Initial reactions of 18 were carried out using samples prepared in this way. Later, we found we could avoid the acetonitrile co-crystallization by careful crystallization of 18 from a mixture of diethyl ether, benzene, and acetonitrile. In the future, use of a polar, but less coordinating, solvent such as acetone in the place of acetonitrile may more conveniently lead to pure samples of 18. The $^1$H NMR spectrum (benzene-$d_6$) of 18 displays triphenylphosphine (δ7.56 (m, ortho-H in $C_6H_5$), 7.04 (m, meta- and para-H in $C_6H_5$) ppm) and cyclopentadienyl (δ4.43 (s) ppm) absorptions analogous to dimethyl complex 1. The protons on the tetramethylene ring appear in two broad and indistinct multiplets (δ3.38 (2 H), 1.05-1.65 (6 H) ppm). The proton-decoupled $^{13}$C

spectrum of 18 displays signals at δ88.4 (s), 35.6 (s), and 9.6 (d, J = 28 Hz) ppm which were assigned to the cyclopentadienyl, and β and α-carbons of the metallacyclopentane ring, respectively. The α-carbon was assigned to the upfield doublet based on the observed methyl signal for 1 (δ-15.6 (d, $J_{PH}$ = 29 Hz) ppm).

Thermal decomposition of 18. The original report[60a] of 18 states that $C_4$-hydrocarbons were the only volatile products of thermal decomposition in mesitylene at 110°C but does not present any additional details. It is not clear whether the hydrocarbon products were all linear, or if any cyclobutane was produced in the decomposition.

Our early attempts to isolate 18 provided ample evidence of its thermal sensitivity and, like 1, the solid melts (99-100°C) with gas evolution. We conducted several other experiments to identify the products of this decomposition. Heat gun pyrolysis of solid 18 under vacuum generated a mixture of $C_2$-hydrocarbons (1.0%, ethane or ethylene), 1-butene (19.5%), E-2-butene (56.0%), Z-2-butene (20.2%), and traces (<0.5%) of methane and n-butane. No cyclobutane was detected. Heating a 0.07 M solution of 18 in benzene at 70°C for 1 hr under vacuum gave a solution containing 1-butene, E-2-butene, and Z-2-butene in a 0.25:1.00:0.45 ratio. The solution did not contain any methane, $C_2$-hydrocarbons, or butane.

Thermal decomposition apparently represents a much lower energy reaction pathway for 18 than for 1. As a result, 18 does not appear (NMR, *vide infra*) to react directly with ethylene even in the absence of added triphenylphosphine. Decomposition under ethylene, however, does stabilize the organometallic product and the reaction can be monitored by $^1$H NMR. Thus, when a 0.16 M solution of 18 in benzene-$d_6$ was sealed under ethylene (0.52 M, 3.2 atm), allowed to stand at room temperature, and observed periodically by $^1$H NMR, the absorptions due to 18 decreased in intensity while those due to ethylene complex 14 and 1-butene (δ0.89 (t, J = 7.5 Hz, $CH_3$), 1.93 (p of m, J = 7.5 Hz, allyl $CH_2$) ppm) grew in. On further standing after the starting material had disappeared, the signal due to 1-butene decreased as signals at δ1.55 ppm characteristic of the methyl groups in Z and E-2-butene increased in intensity. After the starting material had disappeared, integration of the spectrum showed the ratio of 14 to the sum of the butenes was 1:1. After heating a 0.08 M solution of 18 in benzene under 1.4 atm of ethylene at 45°C for 1 hr, GC analysis of the gas phase above the solution (1 ml solution in 88.9 ml total vol) showed 1-butene, E-2-butene, and Z-2-butene in a 21.0:1.0:0.0 ratio. After additional heating for 1 hr 45 min at 100°C, the butene ratio had changed to 0.13:1.00:0.27. These results show decomposition of 18 under ethylene gives 1-butene

as the initial organic product which is subsequently isomerized to a mixture of 2-butenes.

A mechanism for the decomposition of 18 consistent with the above results is shown in Scheme I (path a). Consistent with the observed phosphine inhibition of decomposition and in analogy with other studies[61] of β-hydrogen elimination, we propose phosphine dissociation from 18 generates a coordinatively unsaturated intermediate A, from which β-elimination can proceed to give butenyl-hydride B. Reductive elimination in B generates the unsaturated 1-butene complex C. This then enters a manifold similar to that described for the reaction of diphenylacetylene and 1 (Chapter I, Scheme III). This time, however, we enter the olefin-$\eta^3$-allyl-hydride manifold with the terminal olefin complex instead of an internal olefin complex, and ligand trapping and olefin dissociation to give free 1-butene is faster than hydride transfer to give the 2-butene complexes E and G. Because the reactive cyclopentadienylcobalt fragments are not quickly trapped (as they are in the reaction with diphenylacetylene), the 1-butene is slowly isomerized to a mixture of Z and E-2-butene just as 2,3-diphenyl-1-butene was isomerized by $CpCo(PPh_3)_2$. When 18 is decomposed under ethylene, the unsaturated cyclopentadienyl(triphenylphosphine)cobalt fragments are stabilized as the known ethylene complex 14.

The absence of significant amounts of ethylene from the thermal decomposition of 18 suggests either the equilibrium between unsaturated metallacyclopentane A and bis-olefin complex H strongly favors A or ethylene dissociation from H is slow relative to β-elimination in A. The nature of the possible equilibrium between A and H could be explored with a labeling experiment analogous to that conducted by Grubbs in a nickelacyclopentane system.[44c] Here partial decomposition of a 2,2,5,5-tetradeuteriometallacyclopentane, reisolation of starting material, and analysis of the label position in the $C_4$-carbon backbone will tell if A is in detectable equilibrium with H where the α and β carbons of the metallacyclopentane can exchange and the deuterium label will move in a pairwise fashion.

Although our results are consistent with the mechanism we have outlined, they do not rule out an alternative (path b) where reductive elimination in B is slow relative to olefin insertion into the cobalt-hydrogen bond to give metallacyclobutane I. β-Elimination in I would generate $\eta^3$-allyl-hydrides D and F directly and also give the observed products. In an elegant labeling study, McLain, Sancho, and Schrock have recently demonstrated that tantalacyclopentanes do decompose to give terminal olefins by this route.[45b] The presence of such a pathway could be

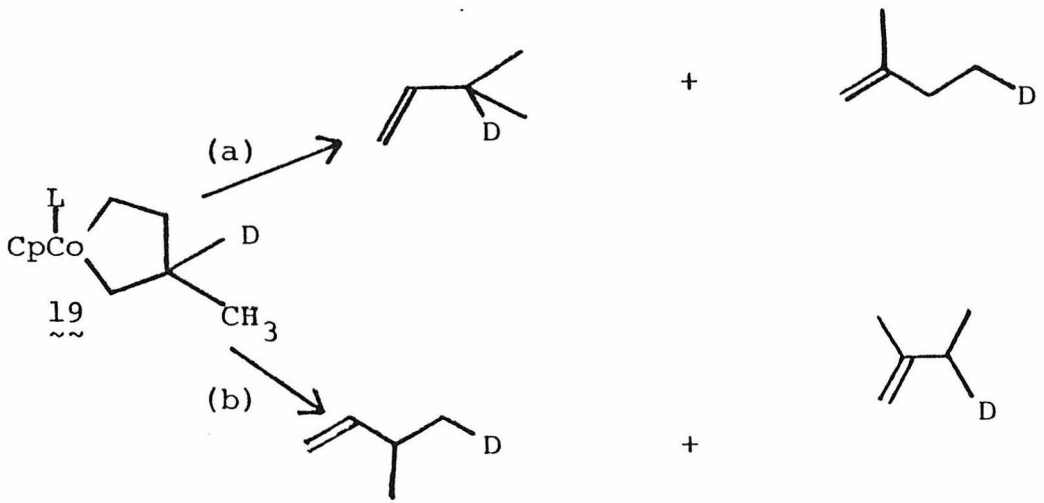
detected in our system by preparing the 3-deuterio-3-methylcobaltacyclopentane 19 (Scheme II) and analyzing the initial products of the decomposition. Decomposition via path (a) in Scheme I would give 3-deuterio-3-methyl-1-butene and 4-deuterio-2-methyl-1-butene whereas path (b) in Scheme I would generate 3-deuterio-2-methyl-1-butene and 4-deuterio-3-methyl-1-butene (Scheme II).

Carbonylation of 18. In analogy to dimethyl complex 1, metallacyclopentane 18 reacted with CO to give cyclopentanone and varying amounts of $CpCO(CO)_2$ (5) and $CpCO(CO)(PPh_3)$ (7). In this system, thermal decomposition was competitive with carbonylation and small amounts of 1-butene were observed as well. Thus, after heating a 0.16 M solution of 18 in benzene-$d_6$ under 6 atm of CO at 45°C for 36 hr the $^1H$ NMR signals due to 18 had been replaced by cyclopentadienyl signals due to 5 (δ4.42 ppm) and 7 (δ4.59 ppm), multiplets at δ1.71 and 1.31 ppm identical to those shown by authentic cyclopentanone, and a triplet (δ0.89 (J = 7.5 Hz) ppm) characteristic of 1-butene. Integration of the final spectrum showed the ratio of cyclopentanone to 1-butene was 4.3:1.0.

The most surprising feature of the carbonylation was the substantial accumulation of several new absorptions during the initial stages of the reaction. After ca. 17 hr at room temperature, the reaction mixture described above

Scheme II

L = $PPh_3$

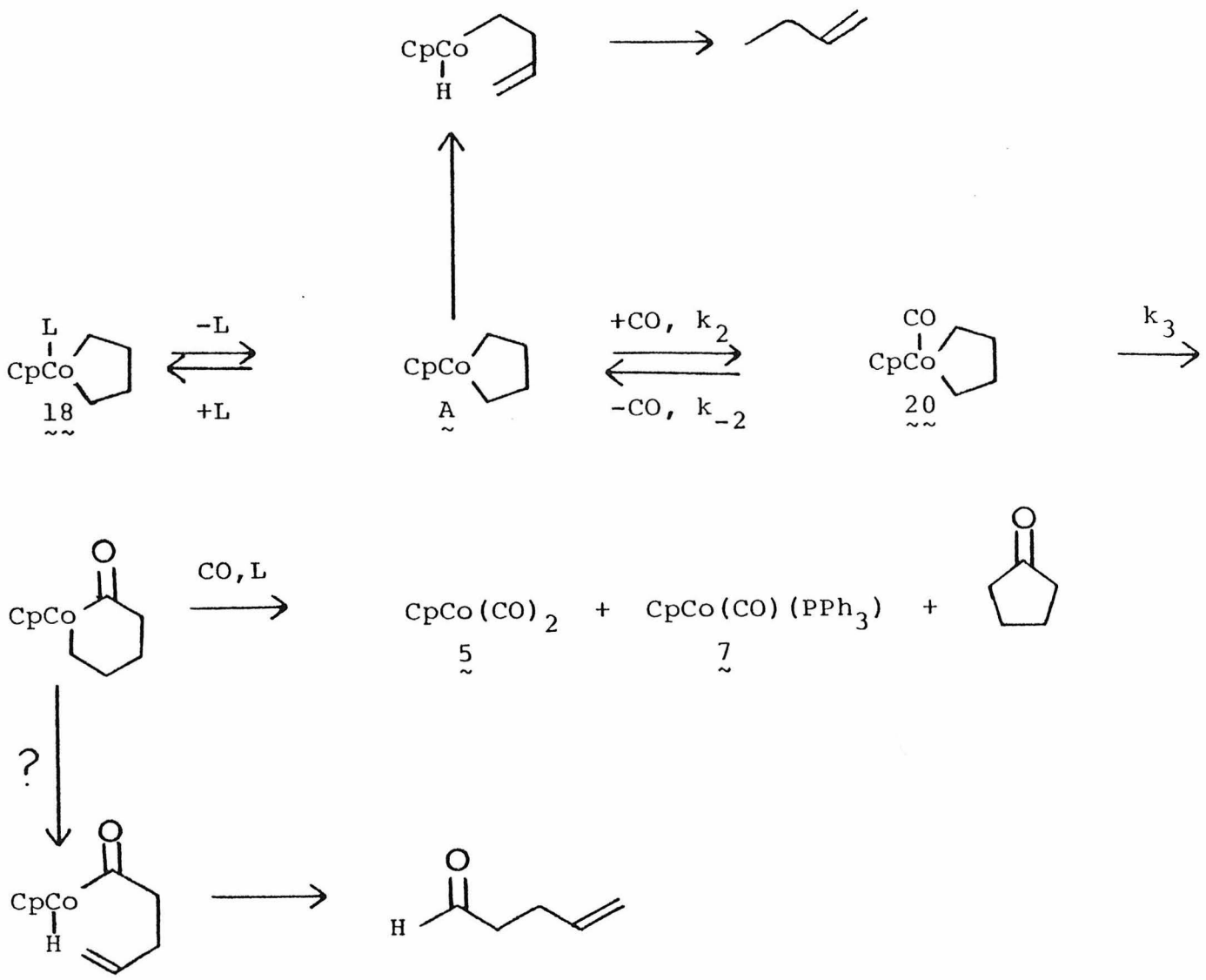


displayed new absorptions at δ4.37 (s), 2.87 (broad, featureless multiplet similar to that in 18 at 3.38 ppm), 1.84 (shoulder on the upfield multiplet of 18) ppm. Integration of the cyclopentadienyl region of the spectrum showed the new material accounted for 33% of the organometallic species present in solution. An IR spectrum of a similar reaction mixture was obtained by keeping a 0.11 M solution of 18 at 4°C until the absorption at δ4.37 ppm accounted for 25% of the organometallic components, opening the tube, and taking the IR spectrum. This showed bands characteristic of 5 (2019, 1961 $cm^{-1}$), 7 (1924 $cm^{-1}$), and cyclopentanone (1744 $cm^{-1}$) as well as a new band at 1990 $cm^{-1}$. On the basis of these spectral observations and in analogy with the known chemistry of 1, the new intermediate in the carbonylation was assigned as the CO-substituted metallacyclopentane 20 (Scheme III). This intermediate built up to much higher concentrations than the dimethyl analog generated by carbonylating 1, which never accounted for more than 5% of the reaction mixture in benzene-$d_6$. In the absence of CO, the rate of disappearance of 20 was ca. $5 \times 10^{-6}$ $sec^{-1}$, ($\tau_{1/2}$ = 38.5 hr).

A mechanism consistent with these results and analogous to that proposed for the carbonylation of 1 is shown in Scheme III. Phosphine dissociation gives unsaturated intermediate A which is trapped by CO to give the spectroscopic-

Scheme III

L = $PPh_3$



ally observed complex 20. CO insertion in 20, followed by reductive elimination in the resulting acyl-alkyl complex J, generates cyclopentanone; the organometallic fragment is scavenged by the available ligands to give 5 and 7. An interesting feature of this reaction is that β-elimination in A is competitive with bimolecular reaction of A with phosphine or CO to give 18 or 20. Coordinatively unsaturated intermediate J is also a potential candidate for β-elimination which would ultimately generate 4-penten-1-al. Although we did not check specifically for the unsaturated aldehyde in these initial experiments, future experiments should establish whether this is a reaction product, and in that way probe the extent to which β-elimination competes with another intramolecular process, reductive elimination, to give cyclopentanone. This competition has been observed in a cobaltacycloheptenyl system (*vide infra*).

Also of interest is the extent to which 20 builds up during this reaction relative to the dimethyl analog formed during the carbonylation of 1. This can be explained by either (1) slower CO insertion (assuming insertion and de-insertion are both slow relative to reductive elimination) or (2) a greater equilibrium concentration of the CO-substituted dialkyl in the metallacyclopentane system than the dimethyl system. It is hoped that future kinetic studies will resolve these questions.

Reaction of 18 with diphenylacetylene. We were particularly interested in the reaction between 18 and diphenylacetylene because double alkylation of diphenylacetylene by 18 would open a new area of metallacyclopentane chemistry,[62] and provide a second example of alkyne double alkylation by a transition metal dialkyl complex.

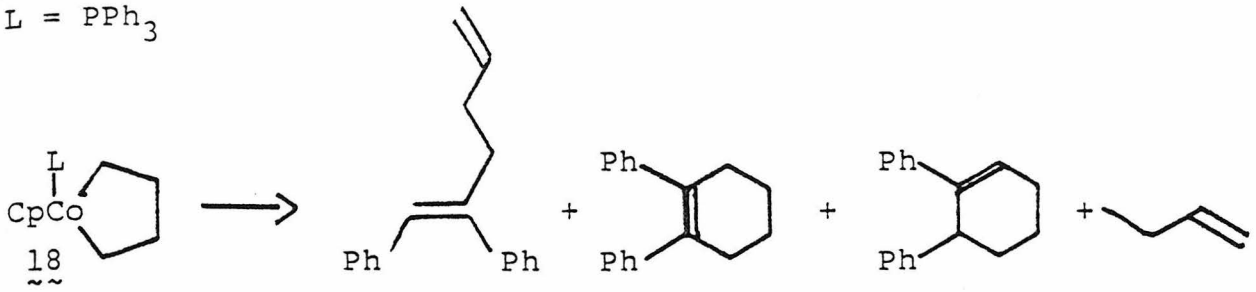
After heating a solution of 18 (0.13 M) and diphenylacetylene (0.66 M) in benzene-$d_6$ at 45°C for 7 hr, the $^1H$ NMR absorptions due to 18 had disappeared and the only distinctive features of the resulting spectrum were a singlet at δ4.78 ppm characteristic of tetraphenylcobaltacyclopentadiene 9 and a triplet (0.89 ppm), characterisitic of 1-butene, which was produced in 35-40% yield (NMR). The remainder of the spectrum displayed an overlapping series of multiplets in the alkyl and vinyl regions. Separation of the organic from the organometallic products by differential solubility and column chromatography, and GC (preparative column) analysis of the organic fraction showed three unidentified peaks, X, Y, and Z representing approximately 40, 5,and 55% of the mixture, respectively. GC-mass spectroscopic analysis of the same mixture showed peaks X and Z contained compounds with parent ions at m/e 234 consistent with a $C_{18}H_{18}$ hydrocarbon generated by adding diphenylacetylene to a tetramethylene moiety. In the same way, peak Y was shown to contain two compounds. The first

to elute had a parent ion at m/e 234, while the second had a parent ion at m/e 130 and was assigned the structure divinylbenzene by the GC-MS data system library (we believe this is an impurity in the diphenylacetylene). The compounds in X and Z were isolated by preparative GC and identified as Z-1,2-diphenyl-1,5-hexadiene (Z-21) and 2,3-diphenylcyclohexene (22), respectively, by comparison (NMR, IR, GC retention time) with independently prepared authentic samples (*vide infra*). The component of Y with a parent ion at m/e 234 was identified as 1,2-diphenylcyclohexene (23) by comparison of its GC retention time and mass spectrum with those of an authentic sample. Significantly, no E-1,2-diphenyl-1,5-hexadiene (E-21) was detected (Scheme IV).

The initial spectral data for peak X were consistent with a 1,2-diphenyl-1,5-hexadiene. Because neither structural isomer was known and we wanted to be sure of the stereochemistry of the reaction with diphenylacetylene, it was necessary to prepare both isomers and establish the stereochemistry of each. We decided to prepare a mixture of the two isomers, separate them, and determine their respective structural geometries on the basis of spectral data and comparison with a suitable model system instead of synthesis by separate stereospecific routes. The hexadienes were prepared by the route outlined in Scheme V, isolated by preparative GC and compared with E and Z-1,2-diphenyl-

Scheme IV

L = $PPh_3$

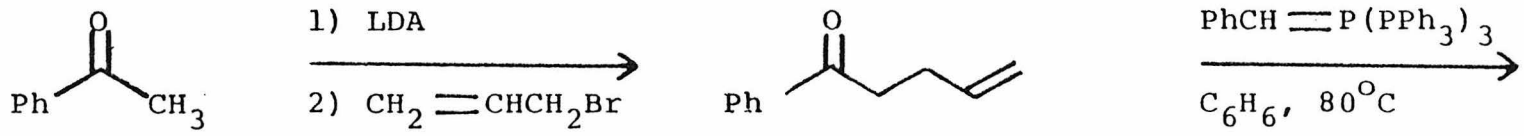


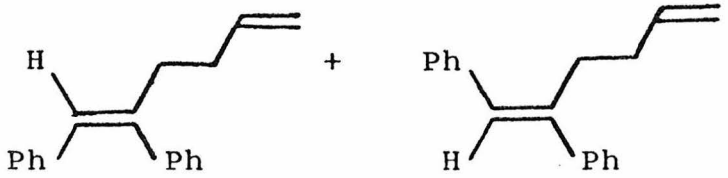

18 + PhC≡CPh → Z-21 + 23 + 22 + $CH_2$=$CHCH_2CH_3$

28.8 : 1.0 : 45.0

75% 11%

Scheme V



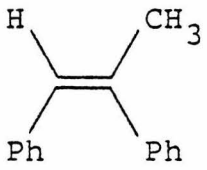
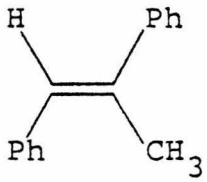
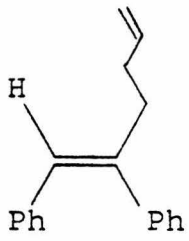
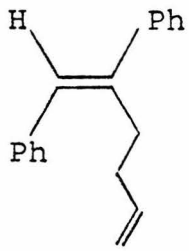

Z-21 E-21

propene (E and Z-24), the α-methylstilbenes. A summary of the relevant spectral data is presented in Table I. All three spectral parameters described are internally consistent and support the assigned structures. As in the parent system, stilbene,[63] the E isomers of 21 and 24 displayed a maximum in the UV absorption spectrum at a longer wavelength and with a higher extinction coefficient than the corresponding Z isomer. Consistent with observations in other olefinic systems,[64] the $^{13}C$ NMR resonance of the allylic carbon on the trisubstituted double bond appeared at higher field in the most sterically congested environment (cis to phenyl instead of H). The $^{1}H$ NMR absorptions of the stilbenyl-hydrogens were shifted downfield when located cis to the phenyl group.

In a quantitative reaction, an acetonitrile-free solution of 18 (0.07 M) and diphenylacetylene (0.74 M) in benzene-$d_6$ was kept at room temperature for 76 hr 40 min. After this time, a small amount of 1-butene (ca. 11%) had appeared and no starting material remained (NMR). The organic products were isolated as before, combined with a known amount of an internal standard, and analyzed by analytical GC. The mixture contained Z-21 (29%), 23 (1%), and 22 (45%), (yields based on starting 18).

Table I

Spectral parameters for 1,2-diphenyl-1,5-hexadienes and model compounds.

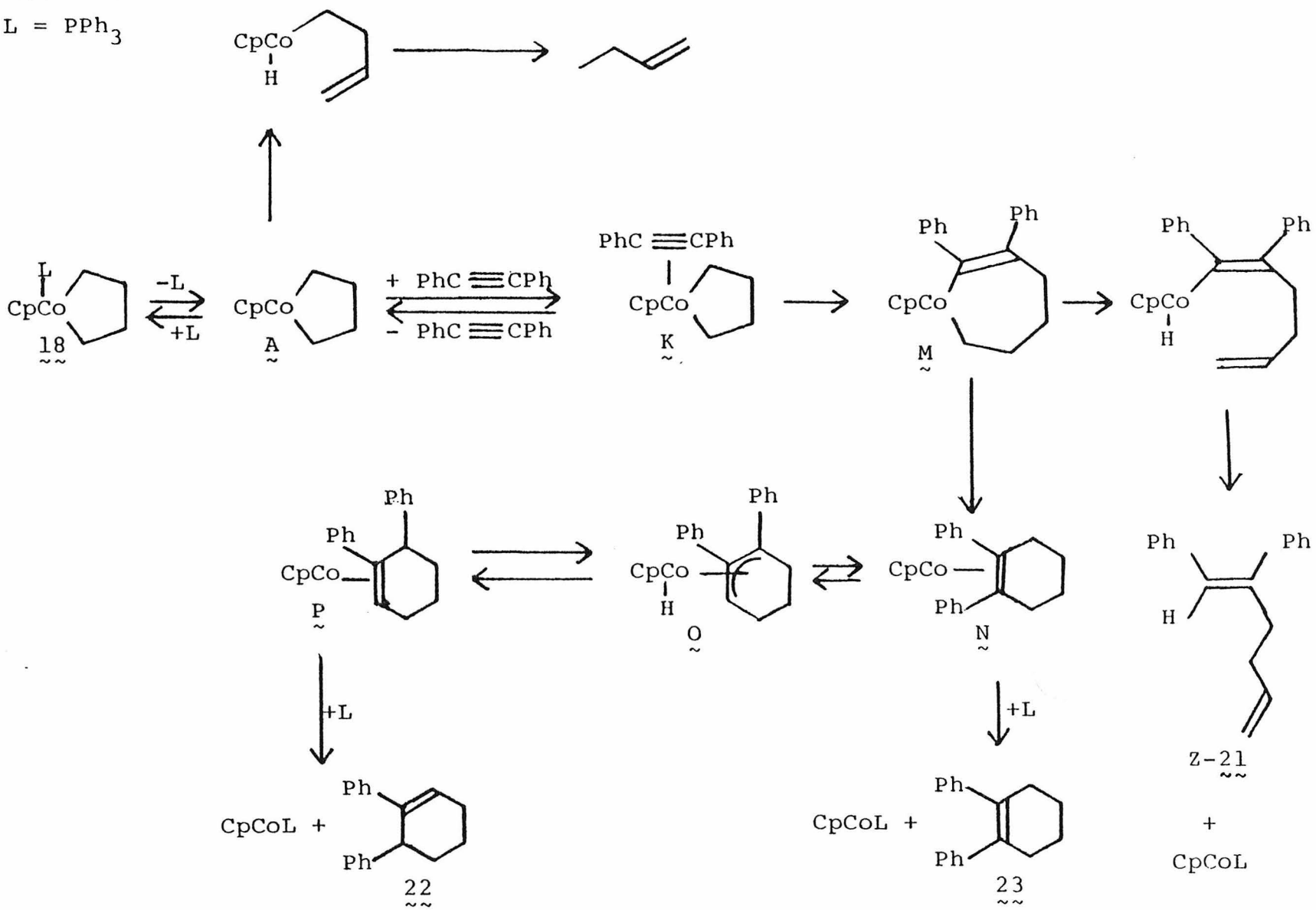
| Compounds | | UV[a] | $^{13}C$ NMR[b] | $^{1}H$ NMR[c] |
|---|---|---|---|---|
|  | Z-24 | 264 (11,550) | 27.0 | 6.36 |
|  | E-24 | 273 (22,640) | 17.4 | 6.72 |
|  | Z-21 | 258 (14,380) | 40.1 | 6.35 |
|  | E-21 | 268 (18,950) | 32.7 | 6.61 |

(a) $\lambda_{max}$ in nm, ($\varepsilon$) in l $mol^{-1}$ $cm^{-1}$, in heptane; (b) stilbenyl $CH_3$ or $CH_2$, ppm downfield of TMS in $CDCl_3$; (c) stilbenyl H, ppm downfield of TMS in $CCl_4$.

A mechanism consistent with the results of this reaction and applying the conclusions reached for the reaction of 1 and diphenylacetylene is shown in Scheme VI. In analogy with all our previous results, phosphine dissociation from 18 generates coordinatively unsaturated intermediate A, the first of three partitioning points along the reaction pathway. Intramolecular β-hydrogen abstraction in A (to give a butenyl-hydride which generates 1-butene by reductive elimination) occurs in competition with bimolecular phosphine or diphenylacetylene trapping to give 18 or K. Insertion of diphenylacetylene into a cobalt-carbon bond in K generates the unsaturated metallacycloheptene M, another partitioning point in the reaction. Here two intramolecular processes, β-elimination and reductive elimination, compete. β-Elimination followed by reductive elimination gives the observed 1,5-hexadiene Z-21. Reductive elimination in M generates the cyclohexene complex N which is the third partitioning point in the system. As in the reaction between 1 and diphenylacetylene, ligand trapping of N gives the internal olefin 1,2-diphenylcyclohexene. This is competitive with intramolecular allyl C-H insertion which generates the $\eta^3$-allylhydride O; this in turn gives the rearranged olefin 22 by reductive elimination and subsequent ligand loss. As before, the unsaturated cyclopentadienylcobalt fragments are quickly scavenged by diphenyl-

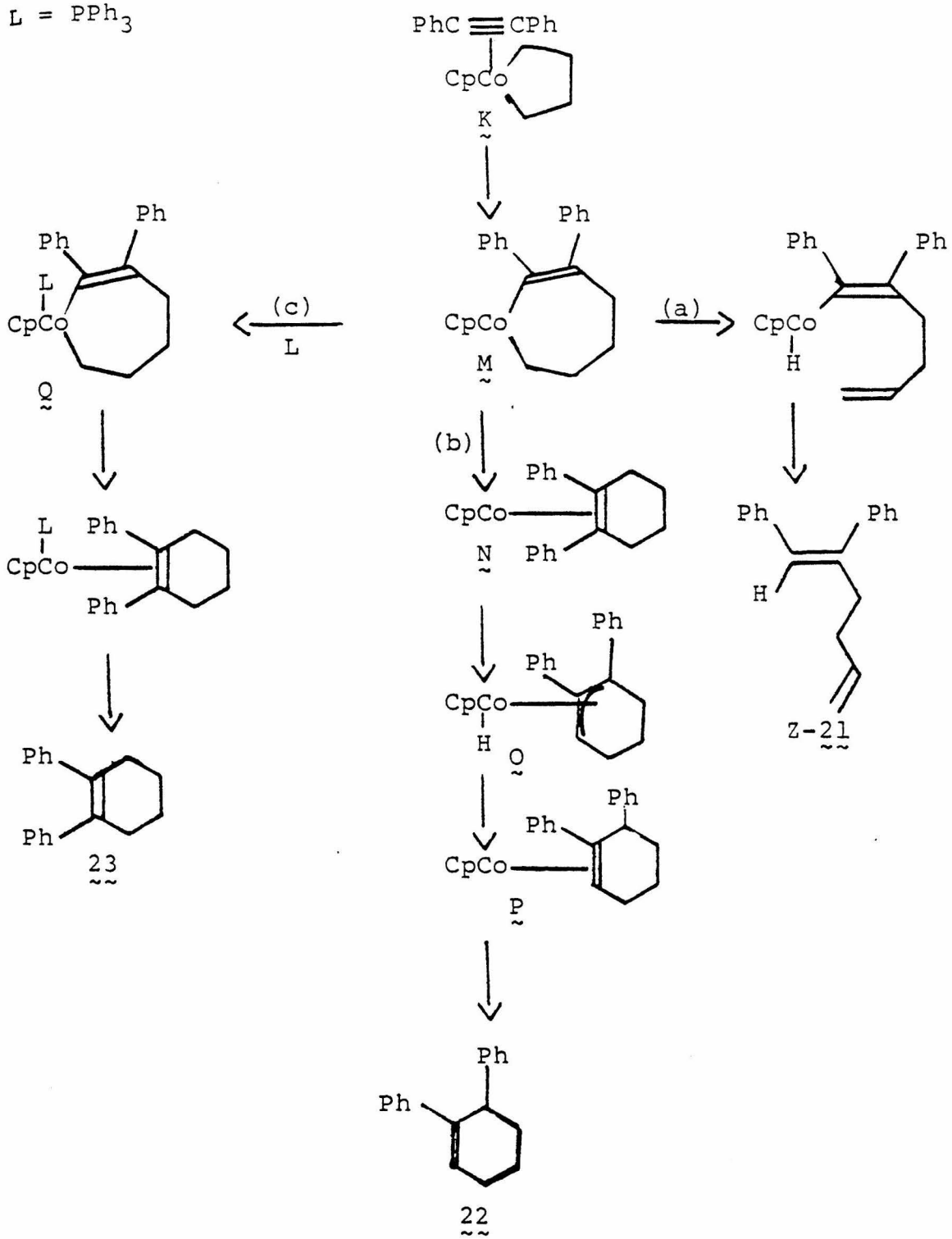
Scheme VI

L = $PPh_3$



Scheme VII

L = $PPh_3$



acetylene to give metallacyclopentadiene 9. The observed product ratios suggest reductive elimination in M occurs approximately 1.5 times more rapidly than β-elimination; C-H insertion in H competes more rapidly with ligand trapping than in the dimethyl case (rearranged:unrearranged olefin equals 45:1 instead of 14:1, in the absence of added triphenylphosphine).

An important feature of this mechanism is the assumption that reductive elimination proceeds from coordinatively unsaturated intermediates. As pointed out during our discussion of the reaction of 1 and diphenylacetylene,[25] the observed phosphine effect on the product ratio can also be explained by assuming the unrearranged product is generated by reductive elimination in a coordinatively saturated vinylalkyl intermediate. This alternative, applied to the reaction of 18 and diphenylacetylene, is outlined in Scheme VII. Here the unsaturated metallacycloheptene M is the partitioning point for three competing processes: (a) intramolecular β-elimination to generate Z-21, (b) intramolecular reductive elimination to give N where rapid H-migration generates the rearranged olefin complex P that releases 22, and (c) bimolecular ligand trapping to give the coordinatively saturated intermediate Q where reductive elimination followed by olefin dissociation gives the unrearranged olefin 23. In this metallacyclopentane system, the two alternatives out-

lined in Schemes VI and VII can be distinguished because an additional intramolecular process occurs in the vinyl-alkyl intermediate to generate a single product that is not generated in any other way. Thus, if the mechanism conforms to Scheme VI, the product ratio (22 + 23)/(Z-21) will not change in experiments conducted in the presence of added phosphine, while this ratio will increase if Scheme VII is obeyed.

Reaction of 18 with 2-butyne. Upon heating a solution of 18 (0.20 M) and 2-butyne (1.02 M) in benzene-$d_6$ at 45°C under vacuum, the $^1$H NMR absorptions due to 18 and 2-butyne (δ1.54 ppm) decreased in intensity while signals characteristic of tetramethylmetallacyclopentadiene 3[15] (δ4.73 (s, Cp), 2.24 and 1.59 (s, $CH_3$'s) ppm), 1-butene, and hexamethylbenzene (δ2.12 (s) ppm) grew in. Unidentified singlets in the methyl region (δ2.46, 1.86, 1.82, 1.57 ppm) and a small one in the cyclopentadienyl region (δ4.24 ppm) also appeared. The new cyclopentadienyl signal may be due to $\eta^4$-tetramethylcyclobutadiene($\eta^5$-cyclopentadienyl)cobalt(I), generated in small amounts during the reaction of 18 with 2-butyne in analogy with production of the tetraphenyl analog (δ4.48 (Cp) ppm) during the reactions of 1 or 18 with diphenylacetylene. It seems reasonable to expect the unidentified methyl singlets belong to new organic products derived from the combination of 2-butyne with the tetramethylene moiety.

Although we have not yet investigated this system further, these preliminary results are encouraging and permit a tentative conclusion concerning the relative reactivity of 18 and 1 toward alkynes. We have not yet measured the kinetics of the reaction of 18 with diphenylacetylene, but it is already clear the starting material disappears more rapidly during the reaction of diphenylacetylene with 18 than with 1. In a preliminary reaction between 1 and 2-butyne[32] (0.26 M 1, 0.84 M 2-butyne) only 20% of 1 had disappeared after 1 hr 20 min at 80°C. Together, these results suggest the metallacyclopentane 18 is more reactive toward alkynes than the dimethyl complex 1. The reasons for this reactivity difference are not yet clear.

Are ethylene complex 14 and metallacyclopentane 18 on a catalytic pathway connecting ethylene and 1-butene? Our initial interest in metallacyclopentane 18 was generated, in part, by the possibility it might be an intermediate (along with ethylene complex 14) on the pathway which generated linear butenes during the reaction between 1 and ethylene. This possibility was further supported by two initial experiments. After heating a 0.06 M solution of bisphosphine complex 13 under 5.2 equivalents (ca. 2 atm) of ethylene for 45 hr at 112°C, GC analysis of the gas phase above the solution showed the presence of butane, 1-butene, E-2-butene, and Z-2-butene in the approximate ratio

0.7:1.0:2.6:1.4. After a solution of 7 (0.016 M), 14 (0.027 M), and 13 (0.006 M) in toluene was heated at reflux under 710 mm of ethylene for 13.5 hr, the gas phase above it also contained small amounts (less than 1 equivalent) of linear butenes.

With isolated samples of 14 and 18 in hand, we sought to follow up on the earlier experiments. After a 0.056 M solution of ethylene complex 14 was heated at 70°C under 4 atm of ethylene for 144 hr, analysis of the gas phase above the reaction solution (1 ml solution in 88.9 ml total vol) did not reveal any butenes (>0.05 turnovers based on starting 14 could have been detected). The ethylene complex was recovered unchanged ($^1$H NMR) from this reaction. In a similar experiment, a 0.056 M solution of 14 was heated under 4 atm of ethylene for 16 hr 35 min at 100°C and no butenes were detected. After 5 additional hr at 125°C, small amounts of E and Z-2-butene (0.07 and 0.05 turnovers, respectively) were detected in the reaction solution. $^1$H NMR observation of the resulting organometallic mixture revealed several new cyclopentadienyl absorptions in addition to that from 14. Heating a 0.08 M solution of 18 under 1.4 atm of ethylene at 100°C for 18 hr generated no more than 1 equivalent of linear butenes in the gas phase above the solution (1 ml in 88.9 ml total vol).

These results suggest complexes 14 and 18 are not capable of dimerizing ethylene to linear butenes, although reaction mixtures generated by heating 14 above its decomposition point may be capable of doing so. This leaves the source of the linear butenes observed during the reaction of 1 with ethylene a mystery at the present time. The reaction conditions under which butenes were observed were much milder than any employed in our separate attempts to dimerize ethylene with 14 or 18.

## Summary and Conclusions

The observations presented here show metallacyclopentane 18 displays overall chemistry similar to the parent dimethyl complex 1, although thermal decomposition is much more facile here. Preliminary experiments suggest thermal decomposition to give 1-butene is much faster than reaction with ethylene to give insertion-derived products. Instead, ethylene traps the organometallic product of the decomposition to give the previously isolated ethylene complex 14, which slowly isomerizes 1-butene to a mixture of 2-butenes. Ligand substitution and insertion processes with CO and diphenylacetylene, however, are competitive with thermal decomposition. Reaction with CO forms cyclopentanone via a CO-substituted metallacyclopentane intermediate; this builds up to a much greater degree than the dimethyl analog in the

reaction between 1 and CO. The reasons for this difference are not yet clear. Reaction with diphenylacetylene gives the expected products of double alkylation, 1,2-diphenylcyclohexene and 2,3-diphenylcyclohexene, except that more of the rearranged olefin is generated in this system than during the reaction of 1 with diphenylacetylene. In addition, an unexpected product, Z-1,2-diphenyl-1,5-hexadiene, is formed by β-elimination in the intermediate metallacycloheptane formed by insertion of diphenylacetylene into one of the cobalt-carbon bonds of 18. In this intermediate, β-elimination is competitive with reductive elimination. In future experiments which monitor the ratio of the organic products as a function of added phosphine concentration, the presence of this competition will allow us to resolve a mechanistic ambiguity that remains in these reactions with diphenylacetylene: Is the unrearranged olefin formed by reductive elimination in a coordinatively unsaturated or saturated intermediate? The results so far suggest 18 is generally more reactive towards alkynes than 1 and the source of this reactivity should be explored to further extend the scope of the alkyne double alkylations we have observed here. Finally, preliminary experiments with isolated samples of 14 and 18 suggest these compounds are not important in the dimerization of ethylene to linear butenes observed during the reaction of 1 with ethylene. The source of these products in this reaction currently remains unknown.

## Experimental Section

General. The equipment and procedures described in the beginning of the Experimental Section in Chapter I were used here. New information pertinent to this chapter is summarized below.

Hexamethylbenzene and 2-phenylcyclohexanone were used as received from Aldrich. Acetophenone (Matheson, Coleman and Bell) was dried over Linde 4Å molecular sieves and 2-butyne (Farchan) was stored over sodium and distilled from sodium under vacuum immediately before use. 3-Bromopropene (Matheson, Coleman and Bell) was washed with equal volumes of sat. aq. $NaHCO_3$ (x 2), $H_2O$ (x 1), and sat. aq. NaCl (x 1), dried for 30 min over $MgSO_4$ and 5 hr over Linde 4Å molecular sieves, and filtered through a column (8 cm x 20 mm) of Woelm neutral alumina (activity I), before use. 1,4-Dilithiobutane was prepared[44a] and titrated[65] by previously published methods.

IR spectra of organic compounds were obtained from thin films of the neat liquid on NaCl plates. $^{13}C$ NMR spectra (Fourier transform) of organic compounds were recorded at 25.14 MHz on a Nicolet TT-23 spectrometer in $CDCl_3$ solution, are reported in units of δ (ppm downfield from tetramethylsilane), and were measured relative to the solvent absorption (δ 77.0 ppm).

Ultraviolet (UV) absorption spectra were obtained on a Varian Associates, Cary 118 UV/visible spectrophotometer

using heptane (Matheson, Coleman and Bell; spectrograde) solutions in 1 cm matched quartz cells. Additional columns used for GC analyses were: (9) 12' x 1/8" aluminum, 15% dimethylsulfolane on Chrom P, NAW and (10) 12' x 1/8" stainless steel, 9% SE-30 on Chrom G, NAW, hexamethyldislazane, 60/80.

Attempts to dimerize ethylene to linear butenes with benzene solutions of 14 or 18 were conducted in a glass bulb sealed to an "anti-chamber" made of two Kontes 4 mm vacuum stopcocks fused back to back. The reactor volume was 88.9 ml and the anti-chamber volume was 3.9 ml. The reactions were monitored by evacuating the anti-chamber, expanding the gas phase above the reaction mixture into it, closing the reaction mixture off from the antichamber, and analyzing the gas mixture isolated in this way by GC.

Preparation of $\eta^5$-cyclopentadienyl(triphenylphosphine) cobaltacyclopentane (18). A slurry of $CpCo(PPh_3)I_2$ (3.15 gm, 4.92 mmol) in 40 ml of diethylether was cooled to -40°C and treated dropwise over 1 hr with 7.8 ml of 0.66 M 1,4-dilithiobutane in ether (5.15 mmol) while maintaining the cooling bath between -40 and -50°C to give a homogeneous dark orange-brown solution. After 20 min of additional stirring and slight warming, the -30°C reaction mixture was transferred onto a rapidly stirred ice-cold aqueous solution of $NH_4Cl$ (3 ml of sat.(at room temperature) aq. $NH_4Cl$ and 40 ml of $H_2O$), the resulting mixture was shaken vigorously and opened to the air, and the ether layer was dried briefly (ca. 1 min) over

cold (-78°C) $MgSO_4$. The $MgSO_4$ was collected on a medium sintered glass frit and washed with ether until the filtrate was colorless to give a homogeneous orange-brown solution; this left an orange-brown oil after solvent removal under vacuum. The crude product mixture was taken into the dry box and triturated with 10 ml of benzene/mixed hexanes (20:80 by vol) to give a dark orange solution and orange granular solid. The soluble fraction was chromatographed on silica gel (23 cm x 15 mm) in benzene/mixed hexanes (20:80 by vol), the major red-orange fraction which ran between a faint orange band and an immobile black band was collected and the contents were recrystallized from benzene/acetonitrile (1:7 by vol, -30°C) to give 334 mg of 18 (15%) as orange needles contaminated with acetonitrile (ratio 18:acetonitrile ca. 1.5:1 by NMR). The orange solid that did not dissolve in the benzene/hexanes mixture was dissolved in benzene and filtered, the solvent was removed under vacuum until 8-10 ml of solution remained, and the solution was diluted with acetonitrile (40 ml) and cooled (-30°C) to give 640 mg of 18 (30%) as orange needles also contaminated with acetonitrile (18:acetonitrile ca. 1.7:1). An acetonitrile-free sample was prepared by dissolving 114 mg of contaminated material in a mixture of diethyl ether (2.4 ml) and benzene (15 drops), diluting this solution with acetonitrile (4 ml), and cooling the mixture to -35°C to give clean (NMR) crystals: mp = 99-100°C with gas evolution (crystals darkened at 95°C, prior to melting). Anal.

Calcd for $C_{24}H_{28}CoP$: C, 73.29; H, 6.39; Co, 13.32; P, 7.00. Found: C, 73.21; H, 6.52; Co, 13.3.

If too much benzene is used in the ether/benzene mixture, acetonitrile is trapped during the crystallization. For example: when a recrystallization was attempted on a larger scale and 552 mg of 18 were dissolved in a solution composed of 10 ml of 5% (by vol) benzene in ether + 5 ml of 10% benzene in ether + 40 drops of benzene, and diluted with 40 ml of acetonitrile, the resulting crystals still contained some acetonitrile (18:acetonitrile ca. 2.6:1).

NMR data for 18: $^1$H NMR (benzene-$d_6$, under ethylene, room temperature): δ1.05-1.65 (m, 6 H), 3.38 (m, 2 H), 4.43 (s, Cp), 7.04 (m, meta-and para-H of $C_6H_5$), 7.56 (m, ortho-H of $C_6H_5$) ppm; $^{13}$NMR (toluene-$d_8$, -30° C, $^1$H decoupled): δ9.6 (d, $J_{PH}$ = 28 Hz, α-C), 35.6 (s, β-C), 88.4 (s, Cp) ppm.

Thermal decomposition of 18. (a) As a solid. A 10 ml pear flask with a septum-covered side arm was charged with 28 mg (0.063 mmol) of 18, evacuated, charged with 2-methylpropane (0.043 mmol, internal standard), and heated with a heat gun until the molten mixture stopped bubbling. The gas mixture generated in this way contained: methane (trace) ethane and/or ethylene (0.6 μmol), butane (0.2 μmol), 1-butene (12.3 μmol), E-2-butene (35.3 μmol), and Z-2-butene (12.7 μmol), (GC analysis, column 7). No cyclobutane was detected. The identity of the major products, 1-butene and E and Z-2-butene, was confirmed by co-injection on another column (column 9) as well as $^1$H NMR (vide infra).

(b) In solution. A solution of 18 (15 mg, 0.034 mmol) in benzene was heated under vacuum, at 70°C for 1 hr, the volatile components of the thermolysis mixture were distilled into another flask under vacuum and GC analysis of the resulting solution showed the presence of 1-butene, E-2-butene, and Z-2-butene in the ratio 0.26:1.00:0.45.

(c) In solution under ethylene. A solution of 18 (37 mg, 0.084 mmol) in 0.52 ml of benzene-$d_6$ was sealed under ethylene (0.541 mmol, 2.56 ml total tube vol), kept at room temperature, and observed periodically by $^1$H NMR. The spectral changes described in the Results and Discussion were observed.

Carbonylation of 18. A solution of 18 (41 mg, 0.093 mmol) in 0.57 ml of benzene-$d_6$ was sealed under CO (0.595 mmol in 2.30 ml total tube vol), kept at room temperature for 46 hr, heated at 45°C for 36 hr, and monitored periodically over this time by $^1$H NMR. The spectral changes described in the Results and Discussion were observed.

Another solution of 18 (17 mg, 0.038 mmol) in 0.36 ml of benzene-$d_6$ was sealed under CO (0.507 mmol in 2.57 ml total tube vol) and kept at 4°C for 24.2 days after which the reaction mixture contained: 7 (3%), 18 (58%), 5 (14%), and 20 (25%). The tube was opened and the reaction solution monitored by IR and $^1$H NMR spectroscopy in the absence of CO. The initial IR spectrum showed bands due to 5, 20, 7, and cyclopentanone (see Results and Discussion for values). After 70 hr at room temperature the band due to 20 had

disappeared, the amount of 5 had decreased, and the amount of 7 had increased (IR). By integrating the NMR spectra of the solution just before the CO was removed and 28.75 and 69.58 hr after it was removed, and plotting ln (20) vs. time, it was possible to extract an approximate rate constant for the rate of disappearance of 20 in the absence of CO: $k_{obs}(23°C) = (5 \pm 1) \times 10^{-6}$ $sec^{-1}$, ($t_{½}$ ca. 38.5 hr).

Reaction of 18 with diphenylacetylene. A solution of 18 (70 mg, 0.158 mmol, ratio of 18:$CH_3CN$ = 1.5) and diphenylacetylene (141 mg, 0.791 mmol) in 1.20 ml of benzene-$d_6$ was sealed in an NMR tube under vacuum, heated at 45°C, and observed periodically by $^1H$ NMR. After 7 hr, no starting material remained, the spectral changes noted in the Results and Discussion had taken place, and integration of the spectrum (using $CH_3CN$ as an internal standard) showed a 38% yield of 1-butene relative to the total initial cyclopentadienyl signal. The reaction products were washed from the tube in the air with benzene, the solvent was removed, and the resulting oily brown slurry was washed with mixed hexanes to leave 98 mg of 9 (82%) as a brown powder. The hexane-soluble fraction was chromatographed on silica gel (10 cm x 10 mm) with a mixed hexanes:benzene gradient (0 - 30% benzene by vol over ca. 250 ml of eluent) and the fractions containing new organic products (monitoring by GC, column 1) were combined to give a pale yellow oil after solvent removal. GC analysis (column 1) showed three un-

identified peaks, X, Y, and Z, (40, 5, and 55% of the mixture, respectively) the contents of which were isolated by preparative GC. The products in peaks X and Z were shown to be Z-1,2-diphenyl-1,5-hexadiene (Z-21) and 2,3-diphenylcyclohexene (22), respectively, by comparison ($^1$H NMR, IR, GC retention time (column 10)) with authentic samples. Peak Y was too small to be cleanly separable from X and GC-mass spectroscopic analysis (column 3) showed it in fact contained two compounds, the first to elute had a parent ion at m/e 234 and the second, one at 130. The first component was assigned the structure 1,2-diphenylcyclohexene (23) by comparison of its mass spectrum (50 ev; m/e (rel intensity): 235 (18), 234 (91), 206 (25), 205 (28), 191 (35), 178 (19), 165 (17), 156 (20), 143 (54), 130 (72), 129 (48), 128 (52), 117 (26), 115 (66), 91 (100), 77 (21)) and GC retention time (column 10) with those of an authentic sample. It is important to note that this minor product which we were unable to isolate is not E-1,2-diphenyl-1,5-hexadiene (E-21), the two compounds have very different mass spectra. The second component of peak Y was assigned the structure divinylbenzene by the GC-MS data system library. This may be a trace impurity in the starting diphenylacetylene.

In a quantitative reaction, a solution of 18 (22 mg, 0.050 mmol, $CH_3CN$-free analytical sample) and diphenylacetylene (93 mg, 0.522 mmol) in 0.71 ml of benzene-$d_6$ was kept at room temperature for 76 hr 40 min. After this time, the

starting material had disappeared and a small amount of 1-butene (ca. 11%) was visible (NMR). The mixture of hexanes-soluble products was isolated as before and chromatographed on silica gel (6 cm x 10 mm) in benzene:mixed hexanes (10:90 by vol). The first 100 ml of eluent were collected, the solvent was removed to leave a white crystalline solid, hexamethylbenzene was added as an internal standard, and the mixture was analyzed by GC (column 10). It contained: Z-21 (0.0144 mmol), 23 (0.0005 mmol), and 22 (0.0225 mmol).

Preparation of 1,2-diphenylcyclohexene (23) and 2,3-diphenylcyclohexene (22). This preparation was based on the reported[66] synthesis of 22 and 23 up through the dehydration step. The final isolation procedure was different. 2-Phenylcyclohexanone (10.05 gm, 57.7 mmol) was dissolved in 90 ml of diethyl ether and treated dropwise with 35 ml of 1.82 M PhMgBr (63.7 mmol) in diethyl ether at ice-bath temperature over 1 hr 50 min. The reaction mixture was heated at reflux for 11 hr, after which time monitoring by GC (column 1) showed a substantial amount of starting material remained. Additional PhMgBr (10 ml, 18.2 mmol) was added to the stirred reaction mixture and it was heated at reflux for another 2 hr 45 min. Monitoring at this point (quenching with acetone and looking for 2-phenyl-2-propanol) showed (1) the ratio of products to starting material remained unchanged and (2) there was ample active Grignard reagent remaining in the solution. The reaction mixture was quenched in 100 ml of ice-cold satd. aq. $NH_4Cl$ solution, the aqueous phase was washed with one 50 ml portion

of diethyl ether, the organic phases were washed one time each with $H_2O$, satd. aq. NaCl, and satd. aq. $Na_2SO_4$, and dried over $Na_2SO_4$, and the solvent was removed to give a thick oil. This crude product mixture was redissolved in methylene chloride (35 ml), mixed with 15 ml of dry pyridine, and treated dropwise with a solution of $SOCl_2$ (10 ml) in 10 ml of pyridine at 0°C. After the addition was complete, the reaction mixture was stirred for 35 min at room temperature. The resulting dark orange-brown mixture was poured slowly onto 200 gm of crushed ice, the aqueous layer was washed with methylene chloride (3 x 50 ml), the organic phases were combined, washed with $H_2O$ (3 x 75 ml), 1.2 N HCl (2 x 65 ml), and $H_2O$ (2 x 50 ml), and dried ($MgSO_4$), and the solvent was removed to leave a thick orange oil. This mixture was chromatographed on silica gel (51 cm x 30 mm) in benzene: mixed hexanes (2:98 by vol) to give three different fractions (6.25 gm, 46% from 2-phenylcyclohexanone) containing pure 22 and 23 and a mixture of the two. The solids obtained by cooling the pure fractions were recrystallized once from MeOH to give clean 22: mp = 51.5 - 53.5°C (lit.[66] 51 - 53°C); $^1H$ NMR ($CCl_4$): $\delta$ 7.07 (m, 10 H, $C_6H_5$), 6.27 (t, J = 4 Hz, 1 H, vinyl H), 3.90 (br m, 1 H, benzylic allylic H), 2.44 - 1.37 (series of three overlapping m, 6 H, three chemically different sets of methylene H) ppm; IR (neat film): 3082 (w), 3058 (m), 3022 (m), 2932 (s), 2862 (m), 2828 (w), 1599 (m), 1491 (m), 1450 (m), 1444 (m), 1428 (w), 1071 (w), 1025 (w), 889 (w), 786 (w), 763 (w), 751 (s), 742 (s), 691 (s) $cm^{-1}$, (lit.[66]

1635, 1077, 894, 793, 770 $cm^{-1}$); and 23: mp = 47 - 48.5°C (lit.[66] 48 - 48.5°C); $^1H$ NMR ($CCl_4$): δ 6.93 (m, 10 H, $C_6H_5$), 2.43 (m, 4 H, allyl methylene H), 1.82 (m, 4 H, methylene H) ppm; IR (neat film): 3082 (m), 3058 (m), 3022 (m), 2932 (s), 2854 (m), 2828 (m), 1599 (m), 1491 (m), 1441 (m), 1432 (m), 1354 (w), 1130 (w), 1065 (m), 1027 (w), 1000 (w), 902 (w), 747 (s), 691 (s) $cm^{-1}$, (lit.[66] 1132, 1068, 905 $cm^{-1}$); mass spectrum (50 ev; m/e (rel intensity): 235 (20), 234 (100), 206 (25), 205 (23), 193 (16), 191 (31), 178 (21), 165 (16), 156 (18), 143 (40), 142 (25), 130 (48), 129 (29), 128 (36), 115 (58), 107 (26), 91 (77), 89 (16), 79 (48), 78 (17), 77 (71), 51 (25).

Preparation of benzyltriphenylphosphonium chloride. A solution of triphenylphosphine (25.6 gm, 98 mmol) and benzyl chloride (11 gm, 87 mmol) in 150 ml of mixed xylenes was heated at reflux for 40 hr to give a clear solution and white precipitate. The solid was collected, washed with two portions of benzene, and dried for 6 hr under vacuum at room temperature to give 29.86 gm (88%) of product.

Preparation of E and Z-1,2-diphenylpropene (E and Z-24). Olefins E and Z-24 were prepared by a Wittig reaction to model the planned synthesis of the 1,2-diphenyl-1,5-hexadienes and to provide model compounds for spectral comparison. Benzyltriphenylphosphonium chloride (23.33 gm, 60 mmol) was slurried in 200 ml of diethyl ether and treated with 25.5 ml of 2.32 M n-BuLi (59 mmol, in hexane) at 0°C to give an orange solution and a yellow solid. Acetophenone (7.8 gm, 65 mmol, in 25 ml of diethyl ether) was added and the resulting

mixture heated at reflux for 20 hr. The mixture did not change detectably in appearance during this time, so the diethyl ether was removed by distillation and benzene was added until the solvent mixture boiled at 75° C. The solution turned darker orange in the new solvent. After 26.5 additional hr at reflux, the solution was lighter orange, additional acetophenone (3.14 gm, 26.1 mmol) was added and the solution was heated at reflux for 13 hr. The reaction mixture was poured into 210 ml of 0.6 M HCl, the aqueous phase was washed with 100 ml of diethyl ether, the organic layers were combined, and the solvent was removed to give a white crystalline solid and thick yellow oil. The solid was washed rigorously with 400 ml of diethyl ether and the ether washes were dried over $MgSO_4$. The ether was removed and the mixture of yellow oil and white solid which remained was washed with a total of 150 ml of mixed hexanes/diethyl ether (1:1 by vol). The components of this crude product mixture were separated and purified by a combination of fractional crystallization, column chromatography (silica gel in benzene/mixed hexanes, 2:98 by vol) and recrystallization from MeOH to give pure E-24 (3.68 gm), pure Z-24 (60 mg), and a mixture of the two (5.38 gm); total yield of 24: 78%. Data for E-24: mp = 80.5 -81.5° C (lit.[67] 81 - 82° C); $^1$H NMR ($CCl_4$): δ 7.22 (m, 10 H, $C_6H_5$), 6.72 (m, 1 H, vinyl H), 2.22 ( d, J = 1.4 Hz, 3 H, $CH_3$) ppm, (lit.[68] δ 7.24, 6.78, 2.24 (J = 1.36) ppm, in $CCl_4$); $^{13}$C NMR ($CDCl_3$): δ 17.4 (s, $CH_3$) ppm; UV ($\lambda_{max}$, (∈), in heptane): 273 nm (22,640) (lit.[67] 274 (19,500), in EtOH). Data for Z-24: mp = 46.5 -

48°C (lit.[67] 47 - 48°C); $^{1}$H NMR ($CCl_4$): δ 7.21 - 6.71 (m, 10 H, $C_6H_5$), 6.36 (m, 1H, vinyl H), 2.17 (d, J = 1.6 Hz) ppm; $^{13}$C NMR ($CDCl_3$): δ 27.0 (s, $CH_3$) ppm; UV ($\lambda_{max}$, (∈), in heptane): 224 nm (15,940), 264 nm (11,550), (lit.[67] 261 (11,480), in EtOH).

Preparation of 1-phenylpent-4-ene-1-one. Diisopropylamine (13.03 gm, 129 mmol) was dissolved in 300 ml of THF, cooled to -5°C, and treated dropwise with 54 ml of 2.32 M n-BuLi (125 mmol, in hexane) while maintaining the bath temperature between -10 and 0°C. Acetophenone (15.02 gm, 125 mmol) was added dropwise over 1 hr to the resulting light orange solution of lithium diisopropylamide (LDA) at -78°C. 3-Bromopropene (18,0 gm, 149 mmol) was added to this solution at -78°C, and the resulting mixture was allowed to warm up slowly and stirred for 22 hr at room temperature. The reaction mixture was hydrolyzed in a slurry of 140 gm of ice, 150 ml of $H_2O$, and 20 ml of conc. HCl, and diluted with 250 ml of additional ether. The aqueous phase was washed with ether (3 x 100 ml) and, the organic layers were combined, washed with one 300 ml portion of sat. aq. NaCl, and dried ($MgSO_4$) overnight at 4°C. GC analysis (column 1) of the golden-yellow oil (19.09 gm) remaining after solvent removal showed a fair amount of acetophenone as well as two major new products. These were tentatively identified as the ketones generated by single and double alkylation of acetophenone, based on their GC retention times relative to that of acetopheone. In an effort to reduce the extent of double alkylation, the reaction was repeated using the same general procedure, except

1 equivalent of TMEDA was added to the solution of acetophenone enolate and the enolate solution was added to excess 3-bromopropene (1.7 equivalents) at -40 to -30° C. This approach did not appreciably improve the product distribution, so the products from both reactions were combined (total 39.45 gm of crude material) and the desired product was isolated by tedious distillation (2 x on a 31 cm Ta wire, vacuum-jacketed column, at 1.3 mm Hg) to give 2.34 gm (6% yield) of reasonably pure (ca. 90%) product; bp = 69 - 74° C, 0.8 - 1.3 mm Hg (lit.[69] 75° C, 1 - 1.5 mm Hg); semicarbazone[70] mp = 159 - 160° C (lit.[69] 159 - 160° C); $^1$H NMR ($CCl_4$): δ 7.82 (m, 2 H, ortho-H in $C_6H_5$), 7.40 (m, 3 H, meta- and para-H in $C_6H_5$), 5.80 (m, 1 H, vinyl H on substituted carbon), 5.06, 4.94, 4.83 (m, 2 H, typical second order pattern for terminal vinyl H's on monosubstituted olefin), 2.95 (t, J = 7.5 Hz, 2 H, methylene α to carbonyl), 2.42 (q, J = 7.5 Hz with other smaller couplings superimposed, 2 H, allylic methylene) ppm, (lit.[71] δ 7.9 (2 H), 7.4 (3 H), 5.8 (1 H), 5.0 (2 H), 3.0 (2 H), 2.5 (2 H) ppm. IR (neat film): 1689 $cm^{-1}$, $\nu_{CO}$.

The $^1$H NMR ($CCl_4$) of the highest boiling component of the reaction mixture was consistent with the structure of the doubly alkylated ketone: δ 7.83 (m, 2 H, ortho-H in $C_6H_5$), 7.40 (m, 3 H, meta- and para-H in $C_6H_5$), 5.65 (m, 2 H, vinyl H on substituted carbon), 5.01, 4.94, 4.83 (m, 4 H, characteristic second order pattern for termianl vinyl H's on monosubstituted olefin), 3.43 (p, J = 6.5 Hz, 1 H, methine H α to carbonyl), 2.33 (m, 4 H, allylic H) ppm.

Preparation of E and Z-1,2-diphenyl-1,5-hexadiene (E and Z-21). Benzyltriphenylphosphonium chloride (7.78 gm, 20 mmol) was slurried in 80 ml of benzene and treated with 8.3 ml of 2.32 M n-BuLi (19.3 mmol, in hexane) at 5°C to give a bright orange solution and yellow solid. 1-Phenyl-pent-4-ene-1-one (2.34 gm, 14.6 mmol, in 10 ml of benzene) was added and the resulting mixture heated at reflux for 96 hr. The reaction mixture was poured into 110 ml of 1.1 M HCl and diluted with 100 ml of diethyl ether, the aqueous phase was washed with 50 ml of ether, and the organic layers were combined, washed with 100 ml of sat. aq. $Na_2CO_3$, and dried ($MgSO_4$). The solvent was removed to leave a yellow solid and light yellow oil; this mixture was washed exhaustively with benzene/mixed hexanes (2:98 by vol) and the soluble fraction was chromatographed on silica gel (44 cm x 22 mm) in the same solvent, to give 2.67 gm (78%) of 21. The first and last product-containing fractions were not substantially enriched in the pure E and Z isomers of 21, so these compounds were isolated by preparative GC (column 4) for spectral characterization.

Data for E-21: $^1$H NMR ($CCl_4$): δ 2.12 (m, 2 H, methylene at 4-position), 2.74 (m, methylene at 3-position), 4.78, 4.90, 4.96 (m, 2 H, terminal vinyl on monosubstituted olefin), 5.71 (m, 1 H, vinyl H), 6.61 br s, 1 H, stilbenyl H), 7.21 (m, 10 H, $C_6H_5$) ppm; $^{13}$C NMR ($CDCl_3$, $^1$H decoupled): δ 29.6 (C-4), 32.7 (C-3), 114.7 (C-6), 137.9 (C-5) ppm; IR (neat film): 1640 (m), 1598 (m), 1494 (m), 1441 (m), 1070 (w), 1021 (w), 988 (w), 909 (m), 858 (w), 749 (m), 734 (w), 691 (s) $cm^{-1}$;

UV ($\lambda_{max}$, ($\in$), in heptane): 268.5 (18,950); mass spectrum (50 ev; m/e (rel intensity): 234 (12), 193 (49), 178 (34), 165 (12), 143 (15), 142 (20), 130 (13), 115 (100), 107 (22), 91 (38), 89 (12), 79 (43), 77 (54), 65 (14), 57 (18), 55 (16), 51 (23). Anal. Calcd for $C_{18}H_{18}$: C, 92.24; H, 7.76. Found: C, 92.27; H, 7.79

Data for Z-21: $^1$H NMR ($CCl_4$): $\delta$ 2.11 (m, 2 H, methylene at 4-position), 2.55 (m, 2 H, methylene at 3-position), 4.83, 4.95, 5.01 (m, 2 H, terminal vinyl on monosubstituted olefin), 5.75 (m, 1 H, vinyl H), 6.35 (br s, 1 H, stilbenyl H), 6.70 - 7.30 (m, 10 H, $C_6H_5$) ppm; $^{13}$C NMR ($CDCl_3$, $^1$H decoupled): $\delta$ 32.2 (C-4), 40.1 (C-3), 114.8 (C-6), 138.1 (C-5) ppm; IR (neat film): 1639 (m), 1598 (m), 1492 (m), 1440 (m), 1073 (w), 1021 (w), 987 (w), 909 (m), 857 (w), 766 (m), 749 (m), 718 (w), 688 (s) $cm^{-1}$; UV ($\lambda_{max}$, ($\in$), in heptane): 258.5 (14,380). Anal. Calcd for $C_{18}H_{18}$: C, 92.24; H, 7.76. Found: C, 92.30; H, 7.81.

Reaction of 18 with 2-butyne. A mixture of 18 (82 mg, 0.185 mmol) and 2-butyne (670.5 mm in 25.85 ml at 23°C, 0.938 mmol) in enough benzene-$d_6$ to give 0.92 ml of solution was sealed under vacuum, kept at room temperature for 19 hr 30 min and then heated at 45°C for 31 hr 35 min, and observed periodically by $^1$H NMR. The spectral changes described in the Results and Discussion were observed. After standing at room temperature, 30% of the starting 18 had disappeared, and after heating at 45°C, all of 18 had been consumed. It is also interesting to note that the singlet due to the

acetonitrile ( $\delta$ 0.69 ppm) present in starting 18 also decreased in intensity over the course of this reaction. The acetonitrile may have been consumed by cotrimerization with 2-butyne.[72]

Ethylene dimerization to linear butenes. (a) Initial observations. An NMR tube containing 13 (40 mg, 0.062 mmol) in 0.42 ml of benzene-$d_6$ was sealed under ethylene (0.321 mmol, 2.52 ml total tube vol) and observation by $^1$H NMR showed signals characteristic of ethylene complex 14. The solution was heated for 2 hr 14 min at 58°C, 1 hr 23 min at 80°C, 15 hr 18 min at 92°C, 5 hr 56 min at 108°C, and 45 hr at 112°C. No substantial changes in the NMR spectrum occurred at 92°, but after heating at 112°C, several new absorptions appeared in the cyclopentadienyl, alkyl, and vinyl regions of the spectrum. GC analysis (column 7) of the gas phase above the solution at this point showed the presence of butane, 1-butene, E-2-butene, and Z-2-butene in the approximate ratio 0.7: 1.0:2.6:1.4.

A mixture of solid 7 (32 mol %), 14 (55 mol %) and 13 (12 mol %),(173 mg), was dissolved in 8 ml of toluene, the $N_2$ was removed on a vacuum line, 2-methylpropane (0.636 mmol) and ethylene (15 mmol) were added, and the resulting reaction solution was heated at reflux under 711 mm of total pressure for 13 hr 30 min. After this time the ratio of linear butenes: 2-methylpropane in the gas phase above the solution (8 ml solution, ca. 400 ml total vol) was 0.24:1.0.

(b) Additional reactions with isolated 14 and 18. A solution of ethylene complex 14 (24 mg, 0.056 mmol) in 1.0 ml

of benzene was sealed under 2-methylpropane (0.329 mmol, internal standard) and ethylene (14.7 mmol in 88.9 total vol, 4 atm) and heated at 70°C for 143 hr 38 min. After this time, no linear butenes were detected (GC column 7) in the gas phase above the solution. The solvent was removed, the remaining solid redissolved, in benzene-$d_6$, and the $^1$H NMR spectrum showed unchanged 14.

A solution of 14 (23 mg, 0.056 mmol) in 1.0 ml of benzene was sealed under 2-methylpropane (0.327 mmol) and ethylene (14.4 mmol in 88.9 ml total vol, 4 atm) and heated at 100°C for 16 hr 35 min. After this time, no linear butenes were detected (GC column 7) in the gas phase above the solution. The mixture was heated 5 hr 5 min at 125°C, and the ratio of 2-methylpropane:E-2-butene:Z-2-butene in the reaction solution was 81.8:1.0:0.8. An NMR spectrum of the nonvolatile residue in benzene-$d_6$ showed several new absorptions in the cyclopentadienyl and alkyl region of the spectrum in addition to those due to 14.

A solution of 18 (34 mg, 0.077 mmol) in 1.0 ml of benzene was sealed under 2-methylpropane (0.328 mmol) and ethylene (4.93 mmol in 88.9 ml total vol, 1.4 atm) and heated at 45°C for 1 hr. After this time the ratio of 2-methylpropane:1-butene:E-2-butene:Z-2-butene was 167:21.0:1.00:0.00. After 1 hr 46 min at 100°C this ratio changed to 7.3:0.13:1.00:0.27 and was 8.0:0.10:1.00:0.36 after 16 additional hr at 100°C.

# Appendix I

## The Reaction of $CpCo(PPh_3)(Me)_2$ with Styrene

Introduction

The successful insertion reaction of ethylene with 1 raised the possibility of using a suitably labeled alkene to examine the stereochemistry of the insertion and determine whether the cobalt and methyl-carbon atoms of 1 were added to the same (cis insertion) or opposite (trans insertion) sides of the alkene. Pd-aryl addition to olefins has been shown to proceed with cis stereochemistry (assuming, as we must here, that β-hydrogen elimination proceeds with cis stereochemistry as well).[4a] Because styrene inserts in other metal-methyl bonds[18c] and the cis and trans-β-deuteriostyrenes are well characterized,[73] we began approaching this problem by considering the reaction of 1 with styrene.

Our system must fulfill several requirements in order to successfully answer the question raised here. These requirements are: (1) styrene inserts in the cobalt-methyl bond of 1; (2) a significant fraction of the reaction pathway involves Co-addition to the phenyl-bearing carbon in styrene; and (3) the observed organic products are the true kinetic products of the reaction. The interpretation of the experimental results must be based on the assumption that β-elimination in the intermediate methyl-alkyl generated by olefin insertion proceeds with cis stereochemistry.[74] Because we can't observe the alkyl-methyl intermediate generated by alkene insertion directly, only the overall stereochemistry of the combined insertion and β-elimination

processes can actually be determined. Thus, cis-β-elimination in the alkyl-methyl intermediate A (Scheme I), generated by cis addition of the cobalt-methyl bond to trans-β-deuterio-styrene could give either E or Z-1-phenylpropene depending on which β-hydrogen (deuterium) was abstracted but all the deuterium label would be contained in the E isomer. If, on the other hand, trans insertion occurred, the Z isomer would contain the deuterium label and the E isomer would not. This appendix describes the preliminary reactions which have been carried out in an effort to develop this experiment and is intended to summarize the progress made to date for the benefit of any future workers on this problem.

## Results and Discussion

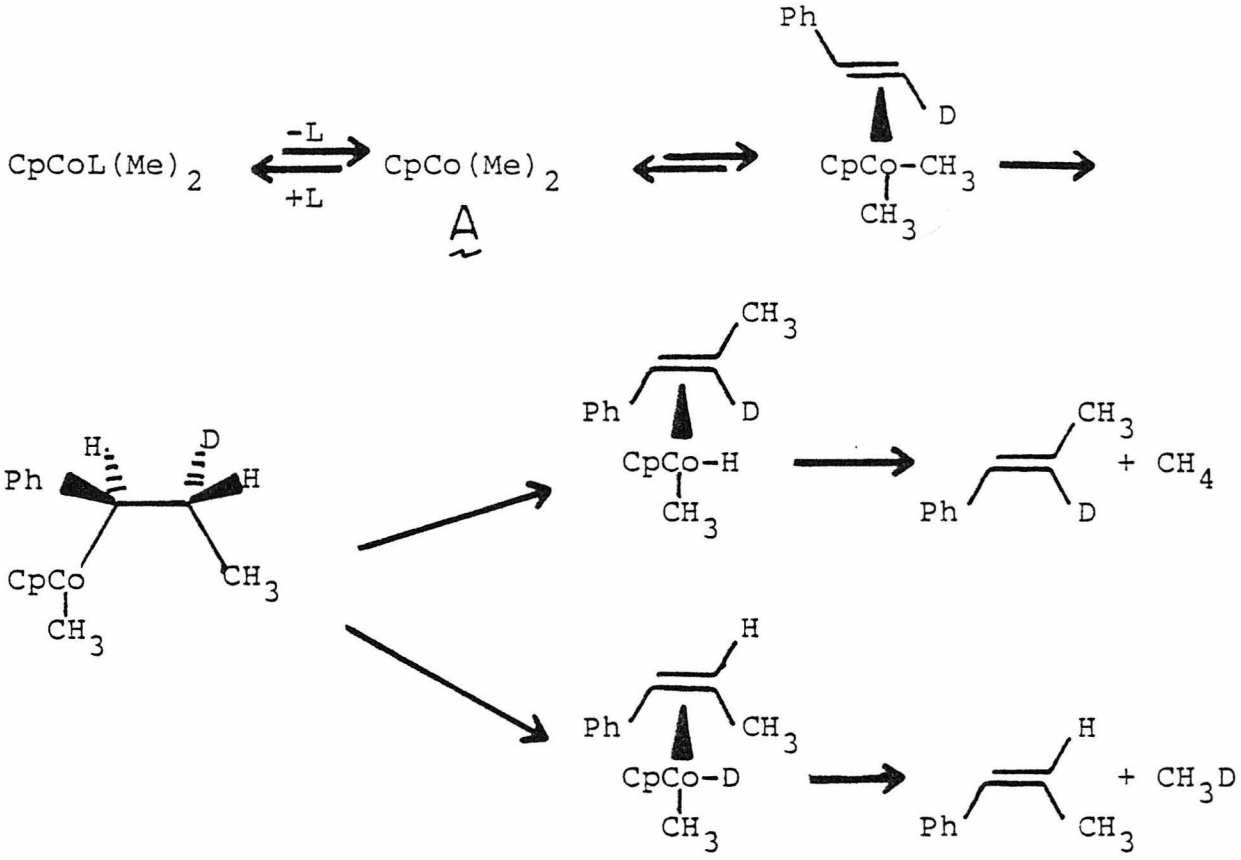
When a 0.15 M solution of $CpCo(PPh_3)_2$ (13) in benzene-$d_6$ was treated with styrene (enough to yield a 0.91 M solution) the absorptions due to 13 ( δ 4.44 (Cp) ppm) were completely (Varian T-60) replaced by a new cyclopentadienyl signal ( δ 4.24 (s) ppm) and multiplets at δ3.00 (2 H) and 1.20 1 H) ppm. The new signals were assigned to the styrene complex $CpCo(PPh_3)$(styrene) (25) in anology with the previously observed substitutions of phosphine in 13 by ethylene and propene to give the corresponding monoalkene complexes.

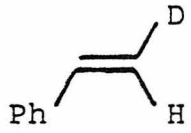
Absorptions characteristic of 25 were also observed after heating a solution of 1 (0.15 M) and styrene (0.82 M) for 16.5 hr at 77°C. These absorptions were accompanied by

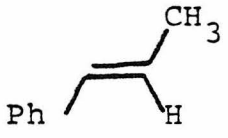
Scheme I

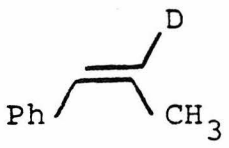
Cis insertion pathway

L = $PPh_3$




Products from trans insertion of  :



other unidentified absorptions (probably due to organic products of the reaction of 1 with styrene and products generated by styrene trapping of thermal decomposition products of 1) in the alkyl region. Subsequent reactions were conducted at lower temperatures in neat styrene and monitored by GC.

In a quantitative reaction, an initially 0.12 M solution of 1 in neat styrene was heated at 64°C for 232 hr after which time 95% of starting 1 had disappeared and the reaction mixture contained a 27:1 ratio of E-1-phenylpropene: Z-1-phenylpropene; no (>2%) 2-phenylpropene was detected. In another reaction, an initially 0.2 M solution of 1 in neat styrene was heated at 65°C for 165 hr, authentic Z-1-phenylpropene was added, and the resulting mixture was heated at 65°C for 56.5 additional hr. The amount of Z-1-phenylpropene in the reaction mixture did not change over this time.

These results show 1 reacts with styrene and the major organic product is generated by cobalt addition to the phenyl-bearing carbon in styrene, satisfying the first two requirements for using this system to determine the stereochemistry of the insertion reaction. Although the fact that added Z-1-phenylpropene is not isomerized by the reaction mixture is necessary evidence to establish that the observed product ratio is a kinetic one, it is not sufficient. It is still necessary to establish that the ratios of E and Z-1-phenylpropene observed during the reaction of 1 with styrene and by treating a styrene solution of 25 with 3-phenylpropene

are different. If the product ratios are the same, it is likely that the olefins produced in the reaction of 1 with styrene are generated by secondary isomerizations of olefins in initially formed π-complexes.

## Experimental Section

General. The equipment and procedures described in the Experimental Sections of Chapters I and II were used here. New information pertinent to this appendix is summarized below.

$^1$H NMR spectra were recorded on a Varian Associates T-60 instrument. 2-Phenylpropene and E and Z-1-phenylpropene were purchased from Chemical Samples, dried over Linde 4Å molecular sieves, and distilled under vacuum (< 1 μ Hg) prior to addition to reactions containing organometallic reagents. A 100 ml portion of styrene (Matheson, Coleman and Bell, inhibited) was washed with a total of 250 gm of 6% (by weight) aq. NaOH divided into three portions, $H_2O$ (2 x 100 ml), and sat. aq. NaCl (1 x 100 ml), dried over $MgSo_4$ at 4°C, distilled (20 mm Hg, 48 - 51°C) through a 30 cm tantalum wire column onto Linde 4Å molecular sieves, and distilled from the sieves under vacuum prior to use. Despite these efforts, the styrene was only 98.8% pure (GC) and contained several high-boiling impurities, two of which gave small peaks that coinjected with authentic 2-phenylpropene and Z-1-phenylpropene. This impurity problem should be solved before any additional work on product ratios is attempted.

The reaction mixtures were analyzed with GC column (11) 12' x 1/8" stainless steel, 10% SF-96 on Chrom P, AW, 100/150.

Thermal substitution of $PPh_3$ in $CpCo(PPh_3)_2$ (13) by styrene. Ferrocene (11 mg, 0.059 mmol) and 13 were dissolved in 0.48 mmol of benzene-$d_6$. The $^1H$ NMR spectrum of this solution displayed absorptions characteristic of ferrocene ($\delta$ 4.02 ppm) and 13 and integration showed the mole ratio of ferrocene:13 was 0.8:1.0. Styrene (50 µl, 0.435 mmol) was added to this solution and the new absorptions described in the Results and Discussion were observed.

Reaction of $CpCo(PPh_3)(Me)_2$ (1) with styrene. (a) Preliminary observation by $^1H$ NMR. A solution of 1 (33 mg, 0.079 mmol) and styrene (50 µl, 0.435 mmol) in 0.53 ml of benzene-$d_6$ was heated for 16 hr 57 min at 57°C, 2 hr 39 min at 67°C, and 16 hr 28 min at 77°C, and monitored periodically by $^1H$ NMR over this time. The spectrum of the final reaction solution displayed absorptions characteristic of styrene, 25, methane, and ethane and other unidentified signals in the alkyl region.

(b) In neat styrene. Samples of 1 were dissolved in styrene in the dry box, heated under $N_2$, and analyzed using GC column 11. The organometallic components of reaction solutions were not removed prior to GC analysis so the GC traces showed peaks generated by injector port pyrolysis of 1. The methane/ethane peak from this decomposition was used as an approximate internal standard. Benzene was also a product of the thermolysis.

A solution of 1 (95 mg, 0.228 mmol) in ca. 1.1 ml of styrene was heated at 65 ± 5°C for 165 hr 15 min after which time >80% of the starting material had disappeared (judging by the injector port pyrolysis peaks of 1). Z-1-phenylpropene (15 µl) was added to the reaction mixture and the amount of this material did not change after 56 hr 35 min of additional heating at 65°C.

A solution of 1 (99 mg, 0.238 mmol) and octane (10 µl, internal standard) in 2 ml of styrene was heated at 64°C for 231.8 hr and monitored periodically. At the end of this time 95 % of the starting 1 had disappeared, based on the size of the pyrolysis products peaks. The ratio of E-1-phenylpropene: Z-1-phenylpropene was 27:1 and no 2-phenylpropene was detected.

Two features of these reactions are worth noting. The organic products, E and Z-1-phenylpropene have only been identified by GC coinjection to date, they have not yet been isolated by preparative GC and characterized spectroscopically. After the reaction mixtures were heated for more than 100 hr, peaks at much longer retention times than the substituted styrenes began to appear during the GC analyses; the nature of these products has not been explored.

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(16) (a) Schore, N. E.; Ilenda, C.; Bergman, R. G. J. Am. Chem. Soc. 1976, 98, 7436;

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(17) The fraction of the acetone which is present as an equilibrium mixture of $d_0$, $d_3$, and $d_6$-acetone (assuming only methyl scrambling) gives the percent crossover when multiplied by 100. A 1:2:1 ratio of $d_0$:$d_3$:$d_6$-acetone generated from an initial 50:50 mixture of 1-$d_0$:1-$d_{21}$ shows 100% crossover. For the more general case where y is the initial ratio 1-$d_0$/1-$d_{21}$ and (58), (61), and (64) are the intensities of the $d_0$, $d_3$, and $d_6$-acetone parent ions in the mass spectrum, the fraction of the acetone which is composed of an equilibrium mixture (assuming no isotope effects) is given by the expression: (61)(y/2 + 1 + 1/2y)/[(58) + (61) + (64)].

(18) For several examples of methyl exchange in transition metal systems, see

(a) Johnson, A.; Puddephatt, R. J. J. Organomet. Chem. 1975, 85, 115;

(b) Puddephatt, R. J.; Thompson, P. J. J. Chem. Soc., Dalton 1977, 1219;

(c) Visser, J. P.; Jager, W. W.; Masters, C. Rec. Trav. Chim. 1975, 94, 70;

(d) Puddephatt, R. J.; Thompson, P. J. J. Chem. Soc., Dalton 1975, 1810-1814.

(19) (a) Bryndza, H. B.; Bergman, R. G. J. Am. Chem. Soc. 1979, 101, 4766-4768;

(b) Bergman, R. G. Accounts Chem. Res., in press.

(20) For another case where reduction of $CpCo(CO)I_2$ leads to Co-Co dimers, see Lee, W.-S.; Brintzinger, H. H. J. Organomet. Chem. 1977, 127, 87-92 and 93-103.

(21) Benson, S. W. "Thermochemical Kinetics," Second ed.; John Wiley and Sons: New York, N.Y., 1976.

(22) Because of the stoichiometry of the reaction (every mole of 1 reacts with 3 moles of diphenylacetylene) the assumption the diphenylacetylene concentration does not change which must hold for the disappearance of 1 to obey a first order rate law, breaks down relatively rapidly. See Scheme III where

$$k_{obs} = \frac{k_1 k_2 k_3 [\text{diphenylacetylene}]}{k_2 k_3 [\text{diphenylacetylene}] + k_{-1}[PPh_3](k_3 + k_{-2})},$$

assuming the rate determining step occurs at or before the conversion of C to D and this conversion is irreversible. The solubility of diphenylacetylene and the amount of 1 needed to give easily integrated $^1H$ NMR signals restricted the range of concentrations available to work in.

(23) (a) Komiya, S.; Allright, T. A.; Hoffman, R.; Kochi, J. K. J. Am. Chem. Soc. 1976, 98, 7255-7265;

(b) Brown, M. P.; Puddephatt, R. J.; Upton, C. E. E. J. Chem. Soc., Dalton 1974, 2457-2465.

(24) Although internal olefins are more stable than the terminal isomer, as the free olefin, steric interactions are generally strong enough to reverse this order when the olefins are coordinated to a transition metal, for example

(a) Cramer, R. J. Am. Chem. Soc. 1967, 89, 4621;

(b) Hartley, F. R. Chem. Rev. 1973, 73, 163-190.

(25) Any mechanism where Z-12 is derived from phosphine trapping of an intermediate which also can react in a phosphine independent step to generate a precursor to 11 will explain the observed phosphine effect on the product ratio. An alternative mechanism which preserves this feature and is consistent with the other results described above involves competition between ligand trapping of D to give a coordinatively saturated vinyl-alkyl complex and reductive elimination in D to give the coordinatively unsaturated olefin complex E. In this case, reductive elimination in the saturated vinyl-alkyl complex generates a saturated olefin complex which gives free Z-12 by olefin dissociation and cannot generate 11 because C-H insertion is blocked by the coordinated phosphine. Reductive elimination in E, followed by rapid C-H insertion in the unsaturated olefin complex produced gives 11 via the $\eta^3$-allyl-hydride H. Because the competing steps which give Z-12 and 11 involve reductive elimination in a vinyl-alkyl and ligand trapping, respectively, this mechanism predicts a very small (secondary) deuterium isotope effect on the overall formation of 11. This is contrary to our observation (vide infra) and therefore we favor the mechanism shown where all the reductive elimination occurs in coordinatively unsaturated intermediate E.

(26) Coordinatively unsaturated cyclopentadienylcobalt(I) fragments react quickly with two equivalents of alkyne to give the corresponding metallacyclopentadiene

(a) Yamagaki, H.; Wakatsuki, Y. J. Organomet. Chem. 1977, 139, 157;

(b) Bushnell, L. P. M.; Evitt, E. R.; Bergman, R. G. ibid., 1978, 157, 445-456;

(c) Ref. 15.

(27) Normally $\eta^3 \rightleftarrows \eta^1$ rearrangement is quite a facile process. See, for example,

(a) Cruikshank, B. I.; Davies, N. R. Aust. J. Chem. 1973, 26, 1935;

(b) Fowles, G. W. A.; Pu, L. S.; Rice, D. A. J. Organomet. Chem. 1973, 54, C17;

(c) Rakowski, M. C.; Hirsekorn, F. J.; Stuhl, L. S.; Muetterties, E. L. Inorg. Chem. 1976, 15, 2379;

(d) Tolman, C. A. J. Amer. Chem. Soc. 1970, 92, 6785;

(e) Faller, J. W.; Rosan, A. M. ibid. 1976, 98, 3388;

(f) Green, M.; Hughes, R. P.; J. Chem. Soc., Chem. Commun. 1975, 619;

(g) Faller, J. W.; Chen, C. C.; Mattina, M. J.; Jakubowski, A. J. Organomet. Chem. 1973, 52, 361;

(h) Graham, C. R.; Stephenson, L. M. J. Amer. Chem. Soc. 1977, 99, 7098.

For a system in which $\eta^3 \rightleftarrows \eta^1$ rearrangement seems to be slow, see

(i) Whitesides, T. H.; Arhart, R. W.; Slaven, R. W. J. Amer. Chem. Soc. 1973, 95, 5792.

(28) For a case in which prochiral olefin $\eta^2$-complex diastereomers have been isolated in the Cp-molybdenum series, see Faller, J. W.; Johnson, B. V.; Schaeffer, C. D., Jr. J. Am. Chem. Soc. 1976, 98, 1395.

(29) Reactions of 11 in Scheme III are illustrated for only one enantiomer of this olefin.

(30) If E⇄I equilibration was fast a very small to negligible isotope effect would be expected because the equilibrium isotope effect on E⇄I and the kinetic isotope effects on the conversions of E→F and I→J are all probably very small.

(31) If C-H insertion in E to give H was the slowest forward step and the back reactions connecting E and J were slower than this, the measured isotope effect could be interpreted in this way.

(32) Although we have not yet explored the scope of this reaction, recent studies in other systems[3b,c] suggest conditions do exist where alkynes other than the commonly used[3] hexafluoro-2-butyne and acetylenedimethyldicarboxylate will give insertion-derived products, and our results show dialkylation is feasible as well. Acetylenedimethyldicarboxylate reacts with 1 at room temperature to consume more than 3 equivalents per mole of 1 whereas 1 reacts significantly

slower with 2-butyne than diphenylacetylene. The products of these preliminary experiments have not yet been characterized.

(33) A similar conclusion has been reached in the $Fe_3(CO)_{12}$ catalyzed isomerization of olefins, Casey, C. P.; Cyr, C. R. J. Am. Chem. Soc. 1973, 95, 2248-2253.

(34) We did not determine the barrier to ethylene rotation in 14 but did notice the $^1H$ NMR spectrum (180 MHz) did not change up to 55°C, (the highest temperature where we observed it). In way of comparison, the $E_a$ for ethylene rotation in $CpRh(C_2H_4)_2$ is 15 kcal/mole: Cramer, R.; Kline, J. B.; Roberts, J. D. J. Am. Chem. Soc. 1969, 91, 2519-2524. For barriers in other complexes, see Faller, J. W. Adv. Organomet. Chem. 1977, 16, 211-239, and references cited therein.

(35) For comparison, consider: $(PPh_3)_2Pt(C_2H_4)$, 39.6;[35a] $(\eta^5\text{-}C_5H_5)Rh(C_2H_4)_2$, 60.2;[35b] $(acac)Rh(C_2H_4)_2$, 36.3;[35b] $NbH(C_2H_4)_2(dmpe)_2$, 32 and 35;[35c] $(\eta^5\text{-}C_5H_5)_2Ta(C_2H_4)(CH_3)$, 20.9 and 20.2[8b] $(\eta^5\text{-}C_5H_5)_2Nb(C_2H_4)(CH_2CH_3)$, 27.6 and 29.4;[8a] and $(\eta^5\text{-}C_5(CH_3)_5)TaCl_2(C_2H_4)$, 69.4.[35d]

(a) Chisholm, M. H.; Godleski, S. Prog. Inorg. Chem. 1976, 20, 299;

(b) Bodner, G. M.; Storhoff, B. N.; Doddrell, D.; Todd, L. J. J. Chem. Soc., Chem. Commun. 1970, 1530;

(c) Schrock, R. R. J. Organomet. Chem. 1976, 122, 121, 373;

(d) McLain, S. J.; Wood, C. D.; Schrock, R. R. J. Am. Chem. Soc. 1979, 101, 4558-4570.

(36) Porgio, W.; Zorchi, M. J. Am. Chem. Soc. 1978, 100, 2048.

(37) For a discussion of reductive elimination in hydridoalkyl-complexes, see: Norton, J. R. Accounts Chem. Res. 1979, 12, 139-145.

(38) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. J. Chem. Soc., Chem. Commun. 1978, 604-606;

(39) Throughout this discussion, the yield of methane is based on a theoretical yield of one mole of methane per mole of 1, consistent with predictions from mechanisms for the reaction of 1 with ethylene and the known (vide infra) stoichiometry of the thermal decomposition of 1.

(40) For two examples of well-characterized systems where thermal decomposition of a metal-alkyl proceeds via H abstraction from an $\eta^5$-$C_5H_5$ ligand, see

(a) Marks, T. J.; Wachter, W. A. J. Am. Chem. Soc. 1976, 98, 703-710;

(b) Marks, T. J.; Seyam, A. M.; Kolb, J. R. ibid., 1973, 95, 5529.

(41) For some other examples of alkyl group migration to an $\eta^5$-cyclopentadienyl ligand, see

(a) Fachinetti, G.; Del Neso, S.; Floriani, C. J. Chem. Soc., Dalton 1976, 203;

(b) McCleverty, J. A.; Wilkinson, G. J. Chem. Soc. 1963, 4096-4099;

(c) Nesmeyanov, A. N.; Makarova, L. G.; Ustynyuk, N. A.; Bogatyreva, L. V. J. Organomet. Chem. 1972, 46, 105-108;

(d) Pittman, C. U. Jr., Felis, R. F. ibid. 1974, 72, 399-413.

The reverse of this reaction, alkyl group migration from an $\eta^4$-5,5-dialkylcyclopenta-1,3-dienyl ligand to a transition metal center has also been observed, for a review see

(e) Eilbracht, P. "Metallinduzierte C-C-Bindungsspaltung 1,1-Dialkylsubstituierter Cyclopentadiene," Habilitationsschrift, Technischen Hochschule Darmstadt, 1978.

(42) The yields of butenes are not corrected for remaining 1 but determined relative to the total amount of starting material to aid comparison with results from the reaction of 1 and propene, (vide infra).

(43) We are grateful to M. L. H. Green for suggesting a mechanism for the reaction of 1 and ethylene which involves an α-elimination step, proceeds through olefin addition to a metal-carbene intermediate, and does not give $CD_4$ and propene-$d_2$ but $CD_3H$ and propene-$d_3$ as observed in our labeling studies. This prompted us to pursue a more rigorous search for the initial position of the deuterium label in the product propene. An early experiment designed to explore this question had indicated label scrambling was competitive with the rate of propene production.

(44) (a) McDermott, J. X.; Wilson, M. E.; Whitesides, G. M. J. Am. Chem. Soc. 1976, 98, 6529-6536;

(b) Grubbs, R. H.; Miyashita, A. ibid. 1978, 100, 7416-7418;

(c) Grubbs, R. H.; Miyashita, A. ibid. 1978, 100, 1300-1302;

(d) Manriquez, J. M.; McAlister, D. R.; Sanner, R. D.; Bercaw, J. E. ibid. 1978, 100,2716-2724;

(e) McLain, S. J.; Wood, C. D.; Schrock, R. R. ibid. 1979, 101, 4558-4570.

(45) (a) McLain, S. J.; Schrock, R. R. J. Am. Chem. Soc. 1978, 100, 1315-1317;

(b) McLain, S. J.; Sancho, J.; Schrock, R. R. ibid. 1979, 101, 5451-5453.

(46) (a) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, N.Y. 1969;

(b) Brown, H. C. "Organic Syntheses via Boranes"; John Wiley and Sons: New York, N.Y., 1975, pp 191 ff.

(47) Rausch, M. D.; Genetti, R. A. J. Org. Chem. 1970, 35, 3888-3897.

(48) Heck, R. F. Inorg. Chem. 1965, 4, 855-857.

(49) Rinze, P. V.; Lorberth, J.; Noth, H.; Stutle, B. J. Organomet. Chem. 1969, 19, 399-403.

(50) Sawaki, Y.; Ogata, Y. J. Am. Chem. Soc. 1975, 97, 6983-6989.

(51) Satisfactory spectral and elemental analyses were obtained, details of these preparations will be reported elsewhere; Bryndza, H. and Bergman, R. G.

(52) Todd, L. J.; Wilkinson, J. R. J. Organomet. Chem. 1974, 80, C31-C34.

(53) Nie, N. H.; Hull, C. H.; Jenkins, J. G.; Steinbrenner, K.; Bent, D. H. "SPSS-Statistical Package for the Social Sciences", Second edition; McGraw-Hill: New York, N.Y., 1975; pp 320-367.

(54) Ammonium nitrate (36 gm), disodium (ethylenedinitrilo)-tetraacetate dihydrate (EDTA·$2H_2O$, 37 gm), and 200 ml of aqueous ammonia solution (ammonia, solution strong, N.F. 27%, Mallinckrodt) were diluted with enough $H_2O$ to give 500 ml of solution.

(55) Bianco, V. D.; Doronzo, S. Inorg. Syn. 1976, 16, 164-166.

(56) For each spectrum the observed intensities of the cyclopentadienyl and methyl signals were divided by the intensity of the TMS signal, no correction was made for the absolute number of protons in each moiety at this point.

(57) Umbert, M. A.; White, E. H. J. Org. Chem. 1976, 41, 479.

(58) This figure assumes the label scrambling generates only $CH_2D$ methyl groups which would be the initial product of cyclopentadienyl cobalt-catalyzed ($\eta^3$-allyl-hydride intermediate) isomerization of $CH_2CHCD_3$ as well as the product (along with $CH_2CHCD_3$) of alternative mechanisms[43] for the reaction of 1 and ethylene. If, however, only $CHD_2$ methyl groups were generated, 26% of the propene would have been isomerized. These figures are the lower and upper limits, respectively, for the amounts of isomerized propene present at this time.

59. (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. J. Am. Chem. Soc. 1976, 98, 6521;

(b) Young, G. B.; Whitesides, G. M. ibid. 1978, 100, 5808-5815.

60. (a) Diversi, P.; Ingrosso, G.; Lucherni, A.; Porzio, W.; Zocchi, M. J. Chem. Soc., Chem. Commun. 1977, 811;

(b) Diversi, P.; Ingrosso, G.; Lucherni, A.; Martinelli, P.; Benetti, M.; Pucci, S. J. Organomet. Chem. 1979, 165, 253;

(c) Diversi, P.; Ingrosso, G.; Lucherni, A.; J. Chem. Soc., Chem. Commun. 1978, 735;

(d) Doyl, M. J.; McMeeking, J.; Binger, P. ibid. 1976, 376;

(e) Grubbs, R. H.; Miyashita, A.; Liu, M.; Burk, P. J. Am. Chem. Soc. 1978, 100, 2418-2425.

61. See, for example

(a) Whitesides, G. M.; Gaasch, J. F.; Stedronsky, E. R. J. Am. Chem. Soc. 1972, 94, 5258-5270;

(b) Reger, D. L.; Culbertson, E. C. ibid. 1976, 98, 2789-2794.

62. Several reactions between CO and a metallacyclopentane to give the corresponding cyclopentanone have been described, see for example: refs 44a, 60e, and

McLain, S. J.; Wood, C. D.; Schrock, R. R. J. Am. Chem. Soc. 1977, 99, 3519-3520.

In contrast, no reports of reactions between metallacyclopentanes and alkynes have appeared, to the best of our knowledge.

63. Beale, R. N.; Roe, E. M. F. J. Chem. Soc. 1953, 2755-2763.

64. de Haan, J. W.; van de Ven, L. J. M. Org. Magnetic Resonance 1973, 5, 147-153.

65. Whitesides, G. M.; Casey, C. P.; Krieger, J. K. J. Am. Chem. Soc. 1971, 93, 1379.

66. Tomboulian, P. J. Org. Chem. 1961, 26, 2652-2656.

67. Cram, D. J.; Elhafez, F. A. A. J. Am. Chem. Soc. 1952, 74, 5828-5835.

68. Rottendorf, H.; Sternhell, S.; Wilmshurst, J. R. Aust. J. Chem. 1965, 18, 1759-1773.

69. Roberts, R. M.; Landolt, R. G.; Greene, R. N.; Heyer, E. W. J. Am. Chem. Soc. 1967, 89, 1404-1411.

70. Pasto, D. J.; Johnson, C. R. "Organic Structure Determination;" Prentice Hall: Englewood Cliffs, NJ; p 390.

71. Suga, K.; Watanabe, S.; Yamaguchi, Y.; Tokyama, M. Synthesis 1970, 189-90.

72. Wakatsuki, Y.; Yamazake, H. J. Chem. Soc., Chem. Commun. 1973, 280.

73. For stereospecific syntheses of E and Z-1-deuterio-2 phenylethylene see:

(a) Yoshino, T.; Manabe, Y.; Kikuchi, Y. J. Am. Chem. Soc. 1964, 86, 4670-4673.

(b) Buza, M.; Snyder, E. I. ibid. 1966, 88, 1161-1165.

(c) Cornforth, J. W.; Redmond, J. W. Eur. J. Biochem. 1970, 14, 1-13;

(d) Casey, C. P.; Scheck, D. M.; Shusterman, A. J. J. Am. Chem. Soc. 1979, 101, 4233-4236.

74. Although the stereochemistry of β-hydrogen elimination has not been proven, the reverse process, alkene insertion into a metal-hydrogen bond, does proceed by metal and hydrogen addition to the same side of the alkene:

(a) Labinger, J. A.; Hart, D. W.; Seibert, W. E. III; Schwartz, J. J. Am. Chem. Soc. 1975, 97, 3851-3852.

Details of some metal-catalyzed isomerizations of strained ring systems cannot be explained without invoking syn elimination in metallacyle intermediates. See, for example:

(b) Salomon, R. G.; Salomon, M. F.; Kachinski, J. L. C. ibid. 1977, 99, 1043;

(c) Sohn, M.; Blum, J.; Halpern, J. ibid. 1979, 101, 2694-2698.