

perature (23 °C). The tube was then placed in the probe at 23 °C, and the change in the ratio of the Cp proton resonances [δ 5.79 for **10a**, δ 5.92 for $\text{Pd}(\text{C}_5\text{H}_5)(\text{PR}_3)(\text{CH}_2\text{CH}_2\text{OMe})$] was followed at appropriate intervals. Plots of $\log [10\text{a}]$, against time gave straight lines over 3 half-lives. From the pseudo-first-order rate constants, 4.0×10^{-3} , 6.8×10^{-3} , and $11.6 \times 10^{-3} \text{ s}^{-1}$ at $[\text{PR}_3] = 5.7 \times 10^{-2}$, 10.9×10^{-2} , and $15.3 \times 10^{-2} \text{ M}$, respectively, $k_5 = (6.9 \pm 0.7) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ was calculated. The equilibrium constant of eq 5 was found to be 3.8 ± 0.2 from equilibrium mixtures employing comparable concentrations of **10a** and PR_3 .

Spectra. ^1H NMR spectra were measured on a JEOL PS-100 spectrometer equipped with a JNM-VT-3B variable-temperature controller, and ^{13}C NMR spectra on a JEOL FX-60 spectrometer, both with tetramethylsilane as internal reference. Except as specified, the spectra

were taken at 23 °C. The spectra of the deuterio analogues of **9** and **10** were also taken at -50 °C to minimize the quadrupole-broadening effect of deuterium. To maintain temperature stability during the equilibrium measurements, we made little adjustments in gas-flow and spinning rates. The probe temperature was checked before and after each measurement by using the chemical shift of methanol on the basis of the calibration chart supplied from JEOL. Temperature stability was believed to be ± 0.5 °C, and accuracy would be ± 1 °C. IR spectra were obtained on a Hitachi 225 spectrophotometer.

Acknowledgment. Thanks are due to Professor N. Kasai and Mr. K. Miki of the same department for kindly informing us of the X-ray crystallographic results prior to publication.

Substitution, Alkyl-Transfer, and Thermal-Decomposition Reactions of η^5 -Cyclopentadienyl(triphenylphosphine)dimethylcobalt(III)

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Abstract: Reactions of $\text{CpCo}(\text{PPh}_3)(\text{CH}_3)_2$ (**1**, $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) with PMe_3 , CO, $\text{PhC}\equiv\text{CPh}$ and ethylene have been investigated in detail. PMe_3 replaces PPh_3 in **1** in a dissociative substitution reaction to give $\text{CpCo}(\text{PMe}_3)(\text{Me})_2$; the first-order rate constant for PPh_3 loss from **1** is $4 \times 10^{-4} \text{ s}^{-1}$ 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 $\text{CpCo}(\text{CO})(\text{Me})_2$ (**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 η^2 -olefin complexes which are interconvertible only by dissociation of the olefinic ligand from the metal; (3) hydrogen shifts involved in the $\text{Cp}(\text{PPh}_3)\text{Co}$ -catalyzed isomerization of alkenes occur more rapidly than dissociation of the alkene from the metal center; and (4) interconversion of η^3 -allyl complexes via rotation in σ^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 $\text{CpCo}(\text{PPh}_3)(\text{C}_2\text{H}_4)$ (**14**); this was independently generated by thermal PPh_3 or photochemical CO substitution in $\text{CpCo}(\text{PPh}_3)_2$ and $\text{CpCo}(\text{CO})(\text{PPh}_3)$, respectively. The production of propene from ethylene and **1** is a model for the chain-growth step in the Ziegler-Natta polymerization of olefins. Labeling experiments have shown propene is formed by transfer of one intact methyl group to ethylene, in agreement with a classical mechanism involving insertion of ethylene into a cobalt-carbon σ bond, rather than ethylene addition to an intermediate metal-carbene complex formed by β -elimination. 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 $\text{Cp}'\text{Co}(\text{PPh}_3)(\text{C}_2\text{H}_4)$ ($\text{Cp}' = \eta^5\text{-CH}_3\text{C}_5\text{H}_4$) and $\text{Cp}'\text{Co}(\text{PPh}_3)(\text{Me})_2$ 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.

Introduction

The overall insertion of an unsaturated molecule into a transition metal-alkyl or hydride bond 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 alkene⁴ into a metal-alkyl bond is of particular interest because it generates a

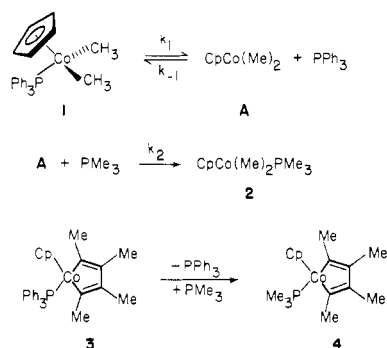
new C-C bond. If a complex bearing two alkyl groups reacts in this way, two new C-C bonds can be formed. Insertion followed

(1) For reviews, see: (a) Parshall, G. W. *J. Mol. Catal.* **1978**, *4*, 243-270; (b) Khan, M. M. T.; Martell, A. E. "Homogeneous Catalysis by Metal Complexes"; Academic Press: New York, 1964; Vols. I and III; (c) Heck, R. F. "Organotransition Metal Chemistry, A Mechanistic Approach"; Academic Press: New York, 1974; (d) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1979.

(2) For reviews, see: (a) Wojcicki, A. *Adv. Organomet. Chem.* **1973**, *11*, 87-145; (b) Calderazzo, F. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 299-311.

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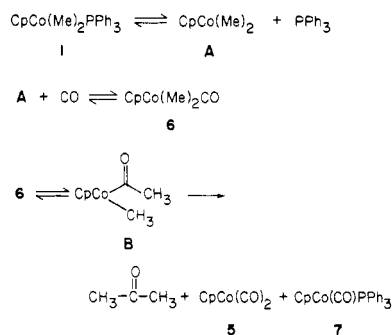
Scheme I



by reductive elimination in the new acyl-alkyl, vinyl-alkyl, or dialkyl complex can generate a ketone, olefin, or alkane, respectively.

There are several examples of the reaction of dialkyl complexes 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 olefin⁷ had not been reported, before the completion of this

Scheme II



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 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.

We have found that the known¹⁰ dimethyl complex, η^5 -cyclopentadienyl(triphenylphosphine)dimethylcobalt(III) (1) undergoes insertion reactions with CO and some alkynes and alkenes. In this paper¹¹ we present details of our studies of the reactions of 1 with PMe_3 , CO, diphenylacetylene, and ethylene. We have tried to duplicate as little as possible of the material presented earlier in communication form; reactions not discussed earlier are treated here in more detail. Sufficient experimental detail has been included to ensure our work will be easily repeatable, but a substantial portion of this information is contained in the supplementary material.

Results and Discussion

Substitution Reactions of 1 with PMe_3 . The substitutional lability of the triphenylphosphine in 1 was demonstrated by the rapid, quantitative reaction of 1 in toluene- d_8 with trimethylphosphine to give 2. Upfield shifts of the cyclopentadienyl and methyl absorptions for 2 relative to those for 1 are consistent with the stronger σ -donating capabilities of trimethylphosphine over triphenylphosphine.¹²

A first-order plot of the disappearance of 1 (NMR) in the presence of an initial fivefold excess of trimethylphosphine (0.51 M) in toluene- d_8 was linear over 3 half-lives and gave a rate constant $k_{\text{obsd}} = (4.49 \pm 0.05) \times 10^{-4} \text{ s}^{-1}$. The rate constant for the reaction with a tenfold excess of trimethylphosphine (0.96 M) was $(3.89 \pm 0.05) \times 10^{-4} \text{ s}^{-1}$. The similarity¹³ of these rate

(3) For examples of apparent alkyne insertion into metal-alkyl bonds, see: (a) Bruce, M. I.; Gardner, R. C. F.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1979**, 906; (b) Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 4410; (c) Tremont, S. J.; Bergman, R. G. *J. Organomet. Chem.* **1977**, *140*, C12; (d) Chandhury, N.; Kekre, M. G.; Puddephatt, R. J. *Ibid.* **1974**, *73*, C17-C19; (e) Rausch, M. D.; Boon, W. H.; Alt, H. G. *Ibid.* **1977**, *141*, 299-312; (f) Boon, W. H.; Rausch, M. D. *J. Chem. Soc., Chem. Commun.* **1977**, 397-398; (g) Chisholm, M. H.; Clark, H. C. *Acc. Chem. Res.* **1973**, *6*, 202-209; (h) Appleton, T. G.; Chisholm, M. H.; Clark, H. C.; Yasafuka, K. *J. Am. Chem. Soc.* **1974**, *96*, 6600; (i) Appleton, T. G.; Chisholm, M. H.; Clark, H. C. *Ibid.* **1972**, *94*, 8912-8914; (j) Clark, H. C.; Werner, K. von *J. Organomet. Chem.* **1975**, *101*, 347-358. When complexes containing CO and alkyl groups are treated with alkynes, CO insertion often precedes alkyne insertion. For examples of reactions involving apparent alkyne insertion into metal-acyl bonds, see: (k) Watson, P. L.; Bergman, R. G. *J. Am. Chem. Soc.* **1979**, *101*, 2055-2062; (l) Heck, R. F. *Ibid.* **1964**, *86*, 2819-2824; (m) Davidson, J. L.; Green, M.; Nyathi, J. Z.; Scott, C.; Stone, F. G. A.; Welch, A. J.; Woodward, P. J. *J. Chem. Soc., Chem. Commun.* **1976**, 714-715; (n) Booth, B. L.; Hargreaves, R. G. *J. Chem. Soc., Dalton Trans.* **1979**, 820-825; (p) Alt, H. G. *J. Organomet. Chem.* **1977**, *127*, 349.

(4) For a review of olefin insertion into metal-aryl bonds, see: (a) Heck, R. F. *Acc. Chem. Res.* **1979**, *12*, 146-151. For examples of apparent olefin insertion into metal-alkyl bonds, see: (b) Chiusoli, G. P. *Acc. Chem. Res.* **1973**, *6*, 422-427; (c) Chiusoli, G. P.; Salerno, G.; Dallatomasina, F. *J. Chem. Soc., Chem. Commun.* **1977**, 793. For examples of olefin insertion into metal-acyl bonds, see: (d) James, D. E.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1810-1823; (e) Cooke, M. P., Jr.; Parلمان, R. M. *Ibid.* **1975**, *97*, 6863; **1977**, *99*, 5222; (f) Booth, B. L.; Gardner, M.; Haszeldine, R. N. *J. Chem. Soc., Dalton Trans.* **1975**, 1856. A detailed theoretical study of the olefin insertion reaction has recently appeared: (g) Thorn, D. L.; Hoffman, R. J. *Am. Chem. Soc.* **1978**, *100*, 2079.

(5) For example: (a) Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421-5422; (b) Yamamoto, T.; Kohara, T.; Yamamoto, A. *Chem. Lett.* **1976**, 1217-1220; (c) Fachinetti, G.; Floriani, C. *J. Chem. Soc., Chem. Commun.* **1972**, 654-655; (d) Masai, H.; Sonogashira, K.; Hagihara, N. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 750-751; (e) Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1978**, 1139-1143; (f) Klein, H.-F.; Karsch, H. H. *Chem. Ber.* **1976**, *109*, 1453-1464; (g) Ikariya, T.; Yamamoto, A. *J. Organomet. Chem.* **1976**, *116*, 239-250; (h) Ikariya, T.; Yamamoto, A. *Ibid.* **1976**, *118*, 65-78; (i) Ito, T.; Tsuchiya, H.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1319-1327.

(6) Surprisingly few examples of alkyne double alkylation are known. Double alkylation of diphenylacetylene by mixtures of methyl Grignard and various transition-metal halides is seriously complicated by side reactions: (a) Michman, M.; Steinberger, B.; Gershoni, S. *J. Organomet. Chem.* **1976**, *113*, 292; (b) Michman, M.; Balog, M. *Ibid.* **1971**, *31*, 395-402; (c) Light, J. R. C.; Zeiss, H. H. *Ibid.* **1970**, *21*, 517-528. Bis(η^3 -allyl)nickel and related systems have been shown to react with some alkynes to give the corresponding disubstituted olefin in moderate yields: (d) Eisch, J. J.; Damasavitz, G. A. *Ibid.* **1975**, *96*, C19-C22; (e) Baker, R.; Bevan, P.; Cookson, R. C. *J. Chem. Soc., Chem. Commun.* **1975**, 752; (f) Bussemeier, B.; Jolly, P. W.; Wilke, G. *J. Am. Chem. Soc.* **1974**, *96*, 4726-4727.

(7) For two systems where a dimethyl complex reacts with an alkyne to give a methyl-vinyl complex which does not reductively eliminate to give the corresponding olefin, see ref 3d,e,f. In one case, a dimethyl complex reacts with 2 equiv of alkyne to give a divinyl complex: Johnson, A.; Puddephatt, R. J.; Jarvis, J. A. *J. Chem. Soc., Chem. Commun.* **1973**, 373.

(8) For example: (a) Guggenberger, L. J.; Meakin, P.; Tebbe, F. N. *J. Am. Chem. Soc.* **1974**, *96*, 5420; (b) Schrock, R. R.; Sharp, P. R. *Ibid.* **1978**, *100*, 2389-2399; (c) Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Dalton Trans.* **1979**, 262-265; (d) Werner, H.; Werner, R. *J. Organomet. Chem.* **1979**, *174*, C63-C66; (e) Cooper, N. J.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1974**, 761-762.

(9) For reviews, see: (a) Boor, J. "Ziegler-Natta Catalysts and Polymerizations"; Academic Press: New York, 1978; (b) Chien, J. C. W. "Coordination Polymerization"; Academic Press: New York, 1975. For theoretical investigations of the insertion mechanism applied to Ziegler-Natta model systems, see: (c) Cossee, P. *J. Catal.* **1964**, *3*, 80; (d) Armstrong, D. R.; Perkins, P. G.; Stewart, J. J. P. *J. Chem. Soc., Dalton Trans.* **1972**, 1972; (e) Cassoux, P.; Crasnier, F.; Labarre, J.-F. *J. Organomet. Chem.* **1979**, *163*, 303.

(10) (a) Yamazaki, H.; Hagihara, N. *J. Organomet. Chem.* **1970**, *21*, 431-443; (b) King, R. B. *Inorg. Chem.* **1966**, *5*, 82-87.

(11) For preliminary reports of this work, see: (a) Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.*, **1978**, *100*, 3237-3239; (b) Evitt, E. R.; Bergman, R. G. *Ibid.* **1979**, *101*, 3973-3974.

(12) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313-348.

(13) The small (15%) difference in the rate constants determined by observing the disappearance of the cyclopentadienyl signal in 1 may be due to a small solvent effect (0.51 M vs. 0.96 M PMe_3) but is probably insignificant considering the spread of rate constants obtained by observing other integrable absorptions during the reaction (see Experimental Section).

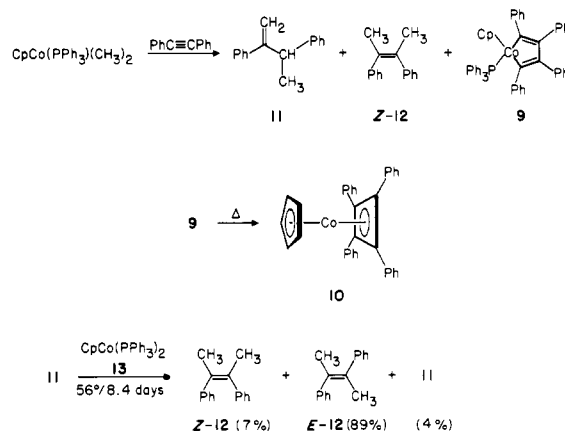
constants shows the rate is independent of trimethylphosphine concentration and establishes the dissociative nature of the substitution (Scheme I). $k_{\text{obsd}} = k_1$, the rate of PPh_3 dissociation, under these conditions.

It is interesting to compare the rates of phosphine dissociation (k_1) in **1** and the related complex **3** (Scheme I). Metallacyclopentadiene **3** also undergoes dissociative substitution of triphenylphosphine to give **4**, but at a much lower rate ($k_1 = 5.8 \times 10^{-5} \text{ s}^{-1}$, 74°C , benzene- d_6).¹⁴ The slower rate of substitution in **3** presumably reflects the ability of the cyclic, conjugated "dialkenyl" 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. Dimethyl complex **1** reacted cleanly with CO (Scheme II) to give acetone (100% by NMR), $\text{CpCo}(\text{CO})_2$ (**5**) and $\text{CpCo}(\text{CO})(\text{PPh}_3)$ (**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 in order to determine whether presumed intermediate **6** (Scheme II) might be observed. 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 the solution stood several hours at room temperature under ca. 1 atm of CO, the cyclopentadienyl (δ 4.43) and methyl (δ 0.07 (d, $J_{\text{PH}} = 6 \text{ Hz}$)) absorptions of **1** were accompanied by small cyclopentadienyl signals due to **5** (δ 5.15) and **7** (δ 4.62 (d, $J_{\text{PH}} = 1 \text{ Hz}$)) as well as new singlets in the cyclopentadienyl (δ 4.96) and methyl (δ 0.37) regions and a small singlet due to acetone (δ 2.03). The IR spectrum of a reaction mixture generated this way showed a new band at 1998 cm^{-1} and bands characteristic of **5** ($2017, 1960 \text{ cm}^{-1}$), **7** (1929 cm^{-1}), and acetone (1716 cm^{-1}) after the CO was removed. The new signals match those assigned to **6** and observed previously during the decomposition of the binuclear dimethyl complex $[\text{CpCoMe}(\text{CO})]_2$.¹⁵ 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 h at room temperature.

The intramolecularity of acetone production from **1** was probed by carbonylating (8 atm, 60°C , ca. 18 h, benzene) known mixtures of **1-*d*₀** and **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 **1** led to nominal (2%) crossover¹⁶ 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 **1** showed 12% crossover in the products, and furthermore, heating a 0.24 M solution of **1** for 42 h 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 **1** to give acetone

Scheme III



is intramolecular, 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 **1** is present. This process is also much faster than the rate of decomposition of **1** (vide infra).

Because treatment of $\text{CpCo}(\text{PPh}_3)_2$ with MeMgI gave **1**, the possibility of independently generating **6** by a similar reaction with $\text{CpCo}(\text{CO})\text{I}_2$ (**8**) was explored. After a cold (-78°C) diethyl ether slurry of **8** was treated with 0.6 equiv (less than the theoretical 2 equiv 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 assigned to **6** (2001 cm^{-1}) and larger bands from the dimethyl dimer $[\text{CpCo}(\text{Me})\text{CO}]_2$.¹⁵ After 2 equiv of MeLi were added, a roughly 1:1 mixture of **6** and the dimer was obtained. Similar treatment of **8** with a single aliquot (2 equiv) of 1.8 M MeLi gave a mixture containing traces of **6** in the presence of the dimer. 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 dimethyl dimer from **8** predominates under these conditions¹⁷ and additional efforts to prepare **6** in this way were not pursued.

In analogy to the trimethylphosphine case, CO substitution to give spectroscopically observed **6** is assumed to proceed as shown in Scheme II, via initial 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 analogue generated by ligand trapping. This question is approached in another system described below. At relatively high concentration, we suggest that intermediate A can react with **1** to give a bridging-methyl complex, which is responsible for the methyl-interchange process uncovered by the isotope crossover experiments.¹⁸

Reaction of 1 with Diphenylacetylene. Yamazaki and Hagihara have reported that **1** reacts with diphenylacetylene to give metallacyclopentadiene **9** and η^4 -tetraphenylcyclobutadiene(η^5 -cyclopentadienyl)cobalt(I) (**10**) (Scheme III). Because this report did not account for the methyl groups originally bound to **1**, we reinvestigated this reaction. In agreement with the earlier report, we found the major (95%) organometallic product was **9**. Under our reaction conditions only small (3%) amounts of cyclobutadiene complex **10** were observed, presumably because of the milder reaction conditions we employed (**9** is converted to **10** thermally).

(17) For another case where reduction of $\text{CpCo}(\text{CO})\text{I}_2$ leads to Co-Co dimers, see: Lee, W.-S.; Brintzinger, H. H. *J. Organomet. Chem.* **1977**, *127*, 87-92 and 93-103.

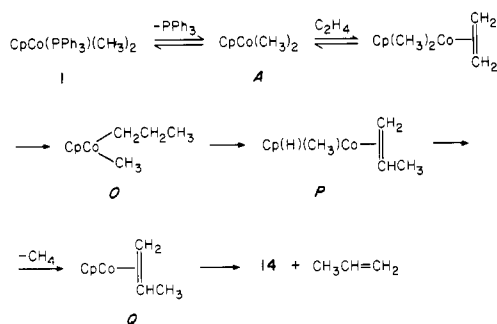
(18) The kinetics and chemical requirements of this methyl exchange reaction are presented in another report: Bryndza, H. E.; Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 4948-4951.

(14) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666-1668.

(15) (a) Schore, N. E.; Ilenda, C.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 7436; (b) White, M. A.; Bergman, R. G. *J. Chem. Soc., Chem. Commun.* **1979**, 1056; (c) Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113.

(16) The fraction of the acetone which is present as an equilibrium mixture of acetone- d_0 , $-d_3$, and $-d_6$ (assuming only methyl scrambling) gives the percent crossover when multiplied by 100. A 1:2:1 ratio of acetone- d_0 : d_3 : d_6 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 acetone- d_0 , $-d_3$, and $-d_6$ 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: $(61)(y/2 + 1 + 1/2y)/[(58) + (61) + (64)]$.

Scheme VI



(equilibrium) mixture of alkenes (**11**:**Z-12**:**(E)-12** = 2:33:(65), whereas reaction of **13** with **11** produced a nonthermodynamic mixture of the (*Z*)- and (*E*)-alkenes (8:92).

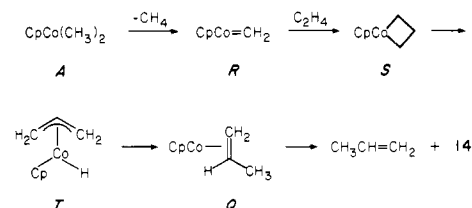
These results are most adequately accounted for by the mechanism outlined in Scheme IV. This set of pathways has been discussed in detail in our earlier note,^{11a} and so we summarize only its most important features here: (a) reductive elimination in alkyl-vinyl complex D must be rapid relative to elimination in dimethyl complex A (see discussion of this problem later); (b) reductive elimination from coordinatively unsaturated intermediate D to generate the unsaturated alkene complex E also explains the effect of added phosphine on the product ratio; and (c) diastereomeric (i.e., inherently chiral) η^2 -alkene and η^3 -allyl complexes, which are not interconvertible on the time scale required for the other transformations of the intermediates shown in Scheme IV, are required to explain why only **11** and (*Z*)-**12** are formed from **1**, but both stereoisomers of **12** can be reached starting from **13** and **11**.

Reaction of 1 with Ethylene and Some Results of Its Thermal Decomposition. Complex **1** reacts readily with 2.9 atm of ethylene at 76 °C in benzene-*d*₆. The major products of this reaction are propene, methane, and the new cobalt(I) complex **14** (Scheme V). The extreme substitution lability of this π complex precluded its isolation in pure form, but the same material could be generated by treatment of complexes **13** and **7** with ethylene (Scheme V). Studies on the equilibrium shown in eq 1 allowed us to estimate

the equilibrium constant for this process (alkene = ethylene) as 200 ± 100 at 28 °C. When the alkene is propene, *K* drops to a value of 0.22 ± 0.01 (25 °C). The $^1\text{H}\{^31\text{P}\}$ NMR spectrum of **14** shows a completely symmetrical AA'BB' system for the complexed ethylene. Apparently at room temperature ethylene rotation is still slow on the NMR time scale.²⁰ The presence of only one ^{13}C absorption (δ 25.0 ($J_{\text{CH}} = 143$ Hz))²¹ for the coordinated ethylene shows the alkene is oriented perpendicular to the Cp-Co-P plane in the molecule.²²

The conventional mechanism which might be written for the formation of methane and propene in the reaction of **1** with ethylene is outlined in Scheme VI. The critical step in this route involves insertion of the alkene into a metal-carbon bond; this

Scheme VII



is analogous to the insertion postulated as the chain-growth step in the Ziegler-Natta polymerization of ethylene.⁹ However, the absence of a well-documented case in which an isolated alkyl olefin complex has been directly observed to undergo such an insertion recently prompted Green, Rooney and their co-workers to suggest an alternative mechanism for the Ziegler-Natta chain-growth step which involves α -elimination and cycloaddition to the resulting metal-carbene complex.²³ Applied to the cobalt system under discussion here, the Green-Rooney alternative is outlined in Scheme VII. These two types of mechanisms may be distinguished easily in our reaction by using isotope-labeling techniques. Reaction of **1** containing CD_3 in place of CH_3 groups should lead to CD_3H and propene-*d*₃ by the insertion (Scheme VI) mechanism and to CD_4 and propene-*d*₂ by the Green-Rooney mechanism.

Unfortunately, we encountered a complication which might potentially have frustrated this experiment. Both mechanisms predict equal quantities of methane and propene should be produced. However, an initial quantitative reaction conducted at 75 °C under 4 atm of ethylene gave methane (80%),²⁴ 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 slowly 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 suppress the unwanted thermal decomposition.

Heating a 0.13 M solution of **1** under N_2 for 17.5 h at 110 °C gave methane ($82.3 \pm 1.2\%$) and ethane ($14.2 \pm 0.2\%$) and no ethylene ($<0.1\%$). When a solution 0.12 M in **1** was pyrolyzed under similar conditions in the presence of added triphenylphosphine (0.62 M), the ratio of methane to ethane rose sharply: $107 \pm 8\%$ 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 **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 **1-d**₂₁ in benzene-*d*₆ at 71 °C was shown to be a mixture of CD_3H ($89 \pm 5\%$), CD_4 ($5 \pm 1\%$), and other methanes ($6 \pm 5\%$). Therefore, the cyclopentadienyl ligand must be the major source of methane hydrogen²⁵ 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 **1-d**₀ and **1-d**₁₁ with labeled methyl and Cp ligands) is precluded by the known ability of **1** to exchange methyl groups under milder conditions than those required for decomposition.

(20) 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 $\text{CpRh}(\text{C}_2\text{H}_4)_2$ is 15 kcal/mol: 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.

(21) For comparison, consider: $(\text{PPh}_3)_2\text{Pt}(\text{C}_2\text{H}_4)$, 39.6;^{21a} $(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(\text{C}_2\text{H}_4)_2$, 60.2;^{21b} $(\text{acac})\text{Rh}(\text{C}_2\text{H}_4)_2$, 36.3;^{21b} $\text{NbH}(\text{C}_2\text{H}_4)_2(\text{dmpe})_2$, 32 and 35;^{21c} $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ta}(\text{C}_2\text{H}_4)(\text{CH}_3)$, 20.9 and 20.2;^{21b} $(\eta^5\text{-C}_5\text{H}_5)_2\text{Nb}(\text{C}_2\text{H}_4)(\text{CH}_2\text{CH}_3)$, 27.6 and 29.4;^{21a} and $(\eta^5\text{-C}_5(\text{CH}_3)_5)\text{TaCl}_3(\text{C}_2\text{H}_4)$, 69.4.^{21d} (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. Chem. Soc.* **1979**, *101*, 4558–4570.

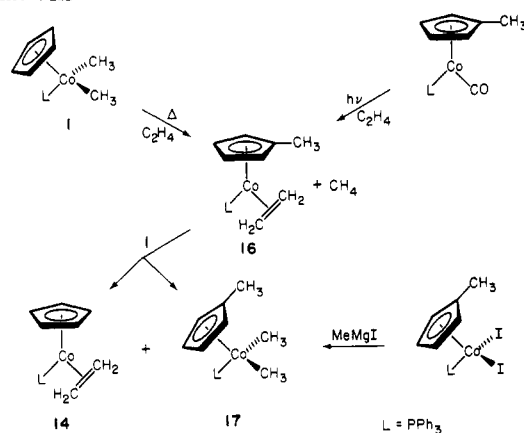
(22) This is the same orientation assumed by ethylene in the corresponding rhodium complex: Porgio, W.; Zorchi, M. *J. Am. Chem. Soc.* **1978**, *100*, 2048.

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

(24) Throughout this discussion, the yield of methane is based on a theoretical yield of 1 mol of methane/mol 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**.

(25) For two examples of well-characterized systems where thermal decomposition of a metal-alkyl proceeds via H abstraction from an $\eta^5\text{-C}_5\text{H}_5$ 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.

Scheme VIII



Thermal decomposition of **1** in the absence of triphenylphosphine gave a dark gray homogeneous solution from which we were unable to isolate any tractable 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 ¹H 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 °C in the presence of triphenylphosphine (0.87 M) and ethylene (0.91 M, 17.9 atm), the first change in the ¹H NMR spectrum was the appearance of an absorption due to methane, a smaller one for ethane, a new doublet (*J* = 2 Hz) 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 of the solution, absorptions due to **14** grew in along with more new ones: δ 4.30 and 4.11 (br 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 (δ 4.50, 2.14, 1.43, and 1.19) were identical with those observed upon photolysis of an authentic sample of Cp'Co(CO)(PPh₃)₂ (**15**, Cp' = η⁵-CH₃C₅H₄) in benzene-*d*₆ under ethylene and were assigned to the new olefin complex Cp'Co(C₂H₄)(PPh₃) (**16**) on the basis of this observation. The new absorptions which appeared later were identical with those displayed by an authentic sample of Cp'Co(PPh₃)(Me)₂ (**17**). 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.²⁶ Elimination of a cyclopentadienyl hydrogen and the remaining methyl group as methane (in a reaction step which is presumably *intermolecular*) 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 1 mol of methane/mol of **1** is generated) and the labeling experiments which demonstrate the methane hydrogen is derived from the cyclopentadienyl ring. The parent olefin complex **14** and the methylcyclopentadienyl-substituted 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

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 °C for 121 h and 15 min gave methane (86%), propene (79%), butane (0.2%), **14** (91%), and **16** (9%) after correcting for remaining **1**.²⁷ 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 120.5 h at 54 °C under 11.1 atm of ethylene was analyzed by mass spectroscopy and shown to be identical with CD₃H prepared by quenching (H₂O) a portion of the CD₃MgI 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% CD₄. Together, these results establish, as reported earlier,^{11b} that 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 transferred 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 ²H 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 h at 59 ± 2 °C, 50% of the starting material had reacted with ethylene to give propene while 87% of that propene was still CH₂=CHCD₃.³⁰ This last result provides confirmatory evidence that insertion rather than α-elimination is the mechanism responsible for alkylation of ethylene by **1**.

Summary and Conclusions

Complex **1** is clearly able to transfer methyl groups both to a range of organic molecules, as well as to other cobalt centers. Although **1** is not itself coordinatively unsaturated, triphenylphosphine dissociation is facile and the unsaturated intermediate formed by phosphine loss can be captured by other 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

(27) We are unsure of the source of small but significant amounts of linear butenes observed as well: 1-butene (4.9%), (*E*)-2-butene (2.7%), and (*Z*)-2-butene (0.5%) (yields uncorrected for remaining **1**). A control experiment with **1** and propene showed the butenes were not formed by reaction of product propene with remaining **1**. Several systems which convert unstrained olefins to metallacyclopentanes are known²⁸ and the catalytic dimerization of olefins through intermediates of this kind has recently been described.^{28b,29} We are currently exploring possibilities for olefin complex catalyzed dimerization of ethylene.

(28) (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) *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.

(29) (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.

(30) 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 CD₄ and propene-*d*₂ but CD₃H 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.

(26) For some other examples of alkyl group migration to an η⁵-cyclopentadienyl ligand, see: (a) Fachinetti, G.; Del Neso, S.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **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 η⁵-5,5-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.

(Z)-olefin, demonstrating the metal and alkyl groups 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)³¹ 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 is facile. These intermediates have an extra pair of π -bonding or nonbonding electrons which may coordinate to the metal in the reductive elimination transition state and provide a low-energy route for elimination 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 Data. All manipulations of oxygen or water-sensitive materials were conducted under a prescrubbed recirculating atmosphere of N_2 in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train or by using standard Schlenk or vacuum line techniques.³²

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 h over two portions of concentrated H_2SO_4 and for 24 h over two portions of saturated KMnO_4 in 15% H_2SO_4 , washed with two portions of distilled water, one portion of saturated Na_2CO_3 , and two additional portions of 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 *tert*-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 h. 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 4A molecular sieves and stored over a drop of Hg or coil of clean (HNO_3) Cu wire, prior to use. $\text{CpCo}(\text{CO})_2$,³³ $\text{CpCo}(\text{CO})(\text{PPh}_3)$,^{10b} $\text{CpCo}(\text{Co}(\text{CO})\text{I}_2)$,^{10b,34} $\text{CpCo}(\text{PPh}_3)_2$,³⁵ and 1,2-

diphenyl-1-propanone³⁶ were prepared by previously published methods. $\text{Cp}'\text{Co}(\text{CO})_2$ and $\text{Cp}'\text{Co}(\text{PPh}_3)(\text{Me})_2$ ($\text{Cp}' = \eta^5\text{-CH}_3\text{C}_5\text{H}_4$) were prepared by the same methods used for the normal cyclopentadienyl analogues with methylcyclopentadiene substituted for cyclopentadiene.³⁷

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

Routine ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Varian A60-A or an EM-390 spectrometer. 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 ^1H NMR spectra were conducted with Nicolet software (NTCFT-1180, NCTSIM, ITRCAL). ^1H NMR spectra are reported in units of δ (ppm downfield from tetramethylsilane) but were most often measured relative to the residual ^1H absorption in the deuterated solvents benzene- d_6 (δ 7.15), toluene- d_8 (δ 2.09), THF- d_6 (δ 1.73), acetone- d_6 (δ 2.04), and cyclohexane- d_{12} (δ 1.38). ^{13}C NMR spectra were also measured relative to a solvent absorption, toluene- d_8 (δ 20.4) and acetone- d_6 (δ 29.8) and reported in units of δ (ppm downfield from tetramethylsilane). ^{31}P NMR spectra are reported and were measured in units of δ (ppm downfield from internal triphenylphosphine). Benzene- d_6 , toluene- d_8 , and THF- d_6 from Merck were distilled from sodium-benzophenone ketyl prior to use. Acetone- d_6 (Merck) was dried over Linde 4A 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.

Preparative gas-liquid chromatography (GC) was conducted on a Varian Aerograph 90-P gas chromatograph. Analytical GC analyses were performed by using either a Hewlett-Packard 5750, Perkin-Elmer 3920, or Perkin-Elmer Sigma 3 gas chromatograph equipped with flame ionization detectors and interfaced with a Spectra Physics Autolab System 1 computing integrator. The columns used were (1) 5 ft \times $1/4$ in. aluminum, 5% SE-30 on Chromosorb (Chrom) P, acid washed (AW), 60/80 mesh, (2) 12 ft \times $1/4$ in. aluminum, 5% SE-30 on Chrom W, AW, 60/80; (3) 30-m open tubular glass capillary, SP2100 (Supelco, Inc. catalogue no. 2-3710), (4) 9 ft \times $1/4$ in. aluminum packed with 53% by volume 20% SE-30 on Chrom P, nonacid washed (NAW), 60/80; 44% by volume 25% SE-30 on Chrom P, 60/80; and 3% by volume 30% SE-30 on Chrom W, AW, DMCS, 60/80, (5) 7 ft \times $1/8$ in. stainless steel, 10% DEGS on Chrom P, NAW, 60/80, (6) 9 ft \times $1/8$ in. stainless steel, Poropak Q (Waters Assoc.), 100/120, (7) 23 ft \times $1/8$ in. stainless steel, 15% DBT on Chrom P, NAW, 100/150, and (8) 7 ft \times $1/4$ in. stainless steel, Poropak Q, 80/100.

Mass spectroscopic (MS) analyses were conducted on an AEI-MS12 mass spectrometer. GC-MS analyses were obtained by using a Finnigan 4000 GC-mass spectrometer. Both systems were interfaced with Finnigan/INCOS data systems.

Elemental analyses were performed by either the California Institute of Technology or U.C. Berkeley analytical facilities.

Preparation of $\text{CpCo}(\text{PPh}_3)(\text{Me})_2$ (1). This procedure gives higher yields than either of those reported earlier.¹⁰ A filtered solution of MeMgI prepared from Mg turnings (0.61 g, 25.1 mmol) and a solution of CH_3I (3.75 g, 26.4 mmol) in 25 mL of diethyl ether was added dropwise over 1 h at room temperature to a stirred slurry of $\text{CpCo}(\text{PPh}_3)_2$ (4.02 g, 6.28 mmol) in 30 mL of benzene to give a homogeneous, dark orange-red solution which was stirred for an additional 12 h. 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 diethyl ether wash of the aqueous phase were dried for 15 min over anhydrous MgSO_4 , and the solvent was removed under reduced (ca. 20 mmHg) pressure to give a crude orange-brown solid. This solid was chromatographed (silica gel, 18 cm \times 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 g 61%). The mother liquors yielded 240 mg (9%) of additional material. During the chromatography, the bright

(31) For a discussion of reductive elimination in hydridoalkyl complexes, see: Norton, J. R. *Acc. Chem. Res.* **1979**, *12*, 139–145.

(32) (a) Shriver, D. F. "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969; (b) Brown, H. C. "Organic Syntheses via Boranes"; Wiley: New York, 1975; pp 191ff.

(33) Rausch, M. D.; Genetti, R. A. *J. Org. Chem.* **1970**, *35*, 3888–3897.

(34) Heck, R. F. *Inorg. Chem.* **1965**, *4*, 855–857.

(35) (a) Yamazaki, H.; Wakatsuki, Y. *J. Organomet. Chem.* **1977**, *139*, 157. (b) Rinze, P. V.; Lorberth, J.; Noth, H.; Stutle, B. *Ibid.* **1969**, *19*, 399–403.

(36) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1975**, *97*, 6983–6989.

(37) Satisfactory spectral and elemental analyses were obtained; details of these preparations will be reported elsewhere.

(38) Aviles, T.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1979**, 1116–1120.

orange band of **1** was followed by a much smaller brown band which has been identified^{10a} as the iodo-methyl complex, $\text{CpCo}(\text{PPh}_3)(\text{Me})\text{I}$, 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, $J_{\text{PH}} = 6$ Hz, Me), 4.47 (s, Cp), 7.35 (m, C_6H_5) (lit.^{10a} δ 0.06, 4.41, 7.3). ^1H NMR ($\text{THF}-d_6$): δ 0.07, 4.43, 7.36. ^1H NMR ($\text{cyclohexane}-d_{12}$): δ 0.09, 4.34, 7.19–7.69. ^1H NMR ($\text{benzene}-d_6$): δ 0.58, 4.46, 7.04 (m, *m*- and *p*-H in C_6H_5), 7.52 (m, *o*-H in C_6H_5). ^1H NMR ($\text{toluene}-d_8$): δ 0.49, 4.44, 7.02, 7.50. ^{13}C NMR ($\text{acetone}-d_6$, -30°C , ^1H decoupled): δ -15.6 (d, $J_{\text{PC}} = 29$ Hz, Me), 88.8 (s, Cp), 128.5 (d, $J_{\text{PC}} = 9$ Hz, *o*- or *m*-C in C_6H_5), 130.2 (s, *p*-C in C_6H_5), 134.3 (d, $J_{\text{PC}} = 9$ Hz, *o*- or *m*-C in C_6H_5), 135.4 (d, $J_{\text{PC}} = 38$ Hz, *ipso*-C in C_6H_5). ^{31}P NMR ($\text{toluene}-d_8$, -65°C , ^1H decoupled): δ 76.6 (bs, PPh_3). Melting point: $142\text{--}143^\circ\text{C}$ dec (lit.^{10a} $142\text{--}143^\circ\text{C}$ dec, lit.^{10b} $138\text{--}141^\circ\text{C}$ dec).

$\text{CpCo}(\text{PPh}_3)(\text{Me})_2$ was prepared in an analogous fashion from $\text{CpCo}(\text{PPh}_3)_2$ and MeMgI - d_3 generated from CD_3I . Likewise, $\text{CpCo}(\text{PPh}_3)(\text{Me})_2$ - d_{21} was prepared from $\text{CpCo}(\text{PPh}_3)_2$ - 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 $\text{THF}-d_8$).

Reaction of 1 and PMe_3 to Give $\text{CpCo}(\text{PMe}_3)(\text{Me})_2$ (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 . ^1H NMR: δ 0.16 (d, $J_{\text{PH}} = 6$ Hz, Me), 0.79 (d, $J_{\text{PH}} = 9$ Hz, PMe_3), 4.37 (s, Cp) (lit.³⁸ δ 0.36 (d, $J_{\text{PH}} = 5.8$ Hz), 1.03 (d, $J_{\text{PH}} = 9.1$ Hz), 4.60 (s)).

The kinetics of the substitution was measured by observing the ^1H 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 three NMR tubes. The tubes were frozen in liquid N_2 and evacuated. PMe_3 was added, and the tubes were sealed under 280 mmHg 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. Absorptions assigned to **2** appeared at δ 0.16 (d, $J_{\text{PH}} = 6$ Hz, Me), 0.77 (d, $J_{\text{PH}} = 9$ Hz, PMe_3), 4.37 (s, Cp). The remaining tubes (a) PMe_3 (0.23 mmol, 0.51 M) and **1** (0.10 M) and (b) PMe_3 (0.45 mmol, 0.96 M) and **1** (0.10 M) were removed from liquid N_2 , shaken vigorously at room temperature until they no longer condensed water, inserted into the ^1H NMR probe maintained at 30°C , and observed at regular intervals for more than 3 half-lives. The resulting spectra were integrated by using the internal ferrocene as a standard and the data obtained by monitoring the cyclopentadienyl signals of **1** [$\ln \text{Cp}$, vs. t] and **2** [$\ln (\text{Cp}_w - \text{Cp}_t)$, vs. t] and the cobalt-bound methyl signal of **2** [$\ln (\text{Me}_w - \text{Me}_t)$, vs. t] for 3 half-lives were used to determine the rate constant k_1 (30°C) (reported here as $k_1 \times 10^4 \text{ s}^{-1}$) in Scheme 1. Tube a: Cp-1, 4.49 ± 0.05 ; Cp-2, 4.44 ± 0.11 ; Me-2, 4.65 ± 0.12 . 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 $\text{CpCo}(\text{CO})(\text{Me})_2$ (**6**).** When a solution of **1** (25 mg, 0.060 mmol) in 0.3 mL of $\text{THF}-d_6$ under ca. 1 atm of CO was held for 3 h at room temperature, ^1H NMR absorptions consistent with **5** (δ 5.15), **6** (δ 4.96, 0.37), **7** (δ 4.62 (d, $J_{\text{PH}} = 1$ Hz)), and acetone (δ 2.03) were observed. Another solution of **1** (16 mg, 0.038 mmol) in 0.56 mL of $\text{THF}-d_6$ (so the strong $\text{THF}-d_6$ IR band at $2000\text{--}2300 \text{ cm}^{-1}$ 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 h and 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** (2017, 1960 cm^{-1}), **6** (1998 cm^{-1}), **7** (1929 cm^{-1}), and acetone (1716 cm^{-1}). After 44 h and 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). By integrating the NMR spectra of the solution just before the CO was removed and 1.75 and 41.50 h after it was removed, and plotting \ln vs. time, it was possible to extract an approximate rate constant for the rate of disappearance of **6** in the absence of CO: $k_{\text{obsd}}(23^\circ\text{C}) = (1.7 \pm 0.5) \times 10^{-5}$, ($t_{1/2} \approx 11$ h).

(b) **Crossover Experiments.** $\text{CpCo}(\text{PPh}_3)(\text{Me})_2$ (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 h and 27 min. The

CO was removed (one freeze-pump-thaw cycle), and the volatiles (benzene, acetone, and a small amount of **5**) were distilled from the reaction mixture under vacuum (10 mmHg) while the reaction flask was cooled (15°C) to reduce the amount of **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 **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 laboratory³⁹ 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 percent crossover¹⁶ 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, we dissolved **1**- d_6 (21.3 mg, 0.051 mmol) and **1**- d_{21} (24.4 mg, 0.056 mmol) in 0.44 mL of benzene. A 0.40-mL portion of this solution was heated at 60°C under N_2 for 42 h. 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°C for 18 h and 40 min. Analysis of the acetone produced showed 100% crossover.

Thermal Substitution of PPh_3 in $\text{CpCo}(\text{PPh}_3)_2$ (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). ^1H 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, $J_{\text{PH}} = 0.5$ Hz, Cp), 5.24 (s, free ethylene), 7.02 (br m, *m*- and *p*-H of C_6H_5), 7.37 (br m, *o*-H of free C_6H_5), 7.65 (br m, *o*-H of coordinated C_6H_5). At high resolution (180 MHz) a tiny triplet ($J = 1.4$ Hz at δ 4.44) 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 (eq 1) 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 , ^1H gated decoupled): δ 25.0 (t, $^1J_{\text{CH}} = 143$ Hz, coordinated ethylene), 83.0 (d of t, $^1J_{\text{CH}} = 171$ Hz, $^2J_{\text{CH}} = 6$ Hz, Cp).

(b) **Propene.** A tube containing **13** (31 mg, 0.048 mmol) and Me_4Si (15 mmHg in 25.85 mL at 23°C , 0.21 mmol) in 0.53 mL of benzene- d_6 was sealed under propene (0.235 mmol, 2.61-mL total tube volume) and examined by ^1H 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, $J_{\text{PH}} = 0.5$ Hz)) 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) were observed. The absorption at δ 2.23 and 1.23 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 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 (eq 1) was estimated to be 0.22 ± 0.01 (25°C).

Preparation of $(\eta^5\text{-CH}_3\text{C}_5\text{H}_4)\text{Co}(\text{CO})(\text{PPh}_3)$ (15**).** A solution of $\text{Cp}^*\text{Co}(\text{CO})_2$ (1.40 g, 7.21 mmol) and PPh_3 (2.51 g, 9.57 mmol) in 10 mL of toluene was held at reflux for 16 h, 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 was dissolved in 30 mL of mixed hexanes, and the solution was cooled (-30°C) to give red brown crystals (1.63 g, 53%) which were washed with three portions of cold hexanes and dried under vacuum. ^1H NMR ($\text{benzene}-d_6$): δ 1.89 (d, $J_{\text{PH}} = 1.4$ 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, *m*- and *p*-H in C_6H_5), 7.72 (m, *o*-H of C_6H_5) ppm. IR ($\text{benzene}-d_6$): ν_{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. Melting point: $95\text{--}96.5^\circ\text{C}$. Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{CoOP}$: C, 70.09; H, 5.19. Found: C, 70.25; H, 5.37.

Photochemical Substitution of CO in $(\eta^5\text{-RC}_5\text{H}_4)\text{Co}(\text{CO})(\text{PPh}_3)$ 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

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tube volume) for 1 h generated ^1H NMR absorptions identical with those observed during the reaction of **13** with ethylene (δ 1.07, 2.48, 4.48) and assigned to **14**. A photostationary mixture made up of 51% **7**, 37% **14**, and 12% **5** was reached after 4 h and 24 min of photolysis.

(b) $\text{R} = \text{CH}_3$. 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 volume) generated ^1H NMR absorptions due to $\text{Cp}^*\text{Co}(\text{CO})_2$ (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) and new absorptions assigned to the methyl (δ 1.43 (d, $J_{\text{PH}} = 2$ Hz)), cyclopentadienyl (δ 4.50 (br s, in theory AA'BB'X, very weakly coupled here)), and ethylene (δ 1.19, 2.14 (m, AA'BB' portion of AA'BB'X spectrum)) moieties of the methylocyclopentadienyl ethylene complex $\text{Cp}^*\text{Co}(\text{C}_2\text{H}_4)(\text{PPh}_3)$ (**16**).

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 volume), heated initially at 64 °C (20 h and 25 min) and then at 76 °C, and monitored periodically by ^1H NMR. After 17 h and 37 min at 76 °C, observation by ^1H NMR showed the absorptions characteristic of **1** and ethylene (δ 5.24) had decreased in intensity while absorptions due to methane (δ 0.19) and propene (δ 1.58, CH_3) grew in. A new cyclopentadienyl resonance (δ 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. 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 and (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 volume, 4 atm) and heated at 75 ± 2 °C for 33 h and 25 min. Removal of the volatile components left a thick red brown oil which displayed severely broadened ^1H 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 volume, 11 atm) for 121 h and 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 and was redissolved in benzene- d_6 with a known amount of ferrocene, and integration of the ^1H 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 $\text{CpCo}(\text{C}_2\text{H}_4)(\text{PPh}_3)$ (**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 volume) 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 volume) 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 volume) 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. ^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).

(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 medium-walled NMR tube containing **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 volume, 0.68 M, 12.4 atm) and heated at 59 ± 2 °C, and the contents were observed by ^1H NMR. Integration of the NMR spectrum after 90 h showed 13%⁴⁰ of the propene carried CH_2D methyl groups while 50% of the **1**- d_{21} had reacted to give propene. After 188 h, the corresponding figures were 29 and 64%, respectively.

A solution of **1**- d_{21} (51 mg, 0.117 mmol) in 0.40 mL of benzene- d_6 was sealed under ethylene (0.533 mmol in 1.90 mL of total volume, 0.51 M, 5.4 atm), heated at 59 ± 2 °C, and monitored by ^2H NMR. After 40 h and 30 min, no terminal vinyl absorptions for propene were detectable, despite the presence of the propene methyl signal. After 188 h, absorptions due to deuterium in the terminal vinyl positions had appeared; however, no deuterium was detectable in the 2-vinyl position.

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Supplementary Material Available: Experimental details of procedures discussed in the text but not included in the primary journal experimental section including the following: preparation of CpCoI_2 , preparation of PPh_3 - d_{15} , carbonylation of **1** and spectroscopic observation of $\text{CpCo}(\text{CO})\text{Me}_2$ (**6**), reaction of **1** with diphenylacetylene ((a) product isolation, kinetics, crossover experiments, and isotope effects, (b) effect of added PPh_3), preparation of 2,3-diphenyl-1-butene (**11**), preparation of (Z)- and (E)-2,3-diphenyl-2-butene ((Z)- and (E)-**12**)), details of acid-, base-, and cobalt-catalyzed isomerization of **11**, (Z)-**12**, and (E)-**12**, preparation of CD_4 and CD_3H , and labeling studies on the reaction of **1** with ethylene (12 pages). Ordering information is given on any current masthead page.

(40) This figure assumes the label scrambling generates only CH_2D methyl groups which would be the initial product of cyclopentadienyl cobalt-catalyzed (η^3 -allyl-hydride intermediate) isomerization of CH_2CHCD_3 as well as the product (along with CH_2CHCD_3) of alternative mechanisms³⁰ for the reactions 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.

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(42) For each spectrum the observed intensities of the cyclopentadienyl and methyl signals were divided by the intensity of the Me_4Si signal; no correction was made for the absolute number of protons in each moiety at this point.

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