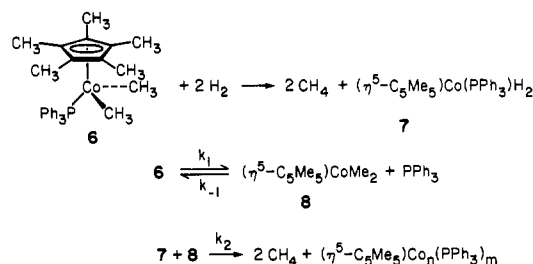


Figure 1. Concentration vs. time plots for the disappearance of complex **1** (0.10 M initial concentration of **1**; 3 atm H_2), in benzene- d_6 at 45 °C, with the following additives: (Δ) no additives, (\diamond) 0.025 M PPh_3 , (\square) 0.05 M PPh_3 , (\times) 0.10 M PPh_3 , (\circ) 0.10 M PPh_3 and 0.017 M **2**.

Scheme III



Complex **7** is one of the few mononuclear dihydridocobalt complexes which have been prepared. Although rapid H_2 loss has prevented us from isolating **7** as a pure solid, benzene solutions of the dihydride are stable for relatively long periods of time. This stability encouraged us to carry out a direct study of the interaction of dimethyl complex **6** with **7**. Dialkyl **6** and dihydride **7** reacted readily at 45 °C, as predicted by Scheme II, to give 2 mol of methane. We have not yet been able to characterize the organometallic products of this reaction, but in the presence of excess **7** and PPh_3 , the rate of disappearance of **6** (as determined by 1H NMR spectroscopy) showed good pseudo-first-order kinetics. Steady-state analysis of the mechanism shown in Scheme III gives a rate law which predicts that the reciprocal of the pseudo-first-order rate constant k_{obsd} should depend upon the dihydride and PPh_3 concentrations as shown in eq 3. The rate constant

$$1/k_{obsd} = (1/k_1) + [k_{-1}[PPh_3]/(k_1k_2[7])] \quad (3)$$

k_{obsd} was therefore determined at several different concentrations of PPh_3 and **7**, and plotted according to eq 3. As shown in Figure 2, the predicted linear behavior is observed. From the slope and intercept of the plot, we calculate $k_1 = 1.83 \times 10^{-4} s^{-1}$ and $k_{-1}/k_2 = 1.44$.

Scheme III and the corresponding rate law posit a specific level of unsaturation of each reacting partner in the rate-determining step associated with microscopic rate constant k_2 ; i.e., the dialkyl reactant is coordinatively unsaturated, whereas the hydride is saturated. The rate law itself rules out the possibility that both reactants are unsaturated; reversible dissociation of phosphine followed from both **7** and **6**, followed by reaction of the two unsaturated species so produced, would give an inverse squared dependence upon the concentration of phosphine, which is not observed. That it is the dialkyl complex, rather than the dihydride, which is unsaturated is suggested by the ease with which PMe_3 replaces PPh_3 in **6**. This result parallels that of **1** which undergoes PMe_3 substitution by a dissociative mechanism⁸ through intermediate **3**.

In summary, even though the inaccessibility of the formal Co(V) oxidation state prevents oxidative addition of H_2 to cyclopentadienylcobalt(III) derivatives, they still undergo facile hy-

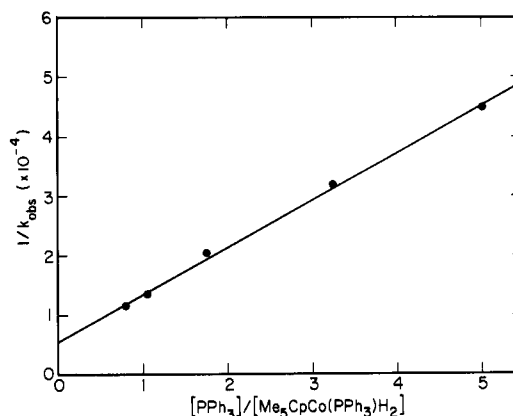


Figure 2. Dependence of the pseudo-first-order rate constant for reaction of complex **6** with dihydride **7** (measured in the presence of excess **7** and PPh_3) upon the ratio of PPh_3 to **7**.

drogenolysis, and this hydrogenolysis involves a metal alkyl/metal hydride reaction as a critical step. The lack of a stoichiometric amount of metal hydride reagent present at the beginning of the hydrogenolysis reaction leads to an autocatalytic mechanism; direct reaction between dialkyl and dihydride does not require autocatalysis. As in other reactions involving interaction of a metal hydride with a coordinatively unsaturated alkyl,⁶ we do not yet know the precise structure of the intermediate involved in the M-R/M-H step, but we assume interaction initially involves entry of the hydride end of the M-H bond into the metal coordination sphere of the dialkyl, forming a bridging hydride. The precise structure of this complex, and how reductive elimination occurs within it, is not yet clear.¹¹ It is interesting, however, that on the basis of the relative rate constant ratio k_2/k_{-1} measured in our kinetic study, PPh_3 reacts with the unsaturated intermediate **8** only slightly more rapidly than does the dihydride **7**.

Acknowledgment. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48.

(11) One possibility (also suggested by both referees) is that the unsaturated dialkyl and saturated dihydride first react to give $CpCo(PPh_3)(CH_3)(H)$ and $CpCo(CH_3)(H)$. These alkyl hydrides can then undergo rapid reductive elimination.

Synthesis and Reactions of a Binuclear Cobalt Bridging Methylene ($\mu-CH_2$) Complex. Conversion to $\mu-CH_2$ Rh/Co and Rh/Rh Complexes and Methylene Transfer to Ethylene Involving Activation by a Second Metal Complex

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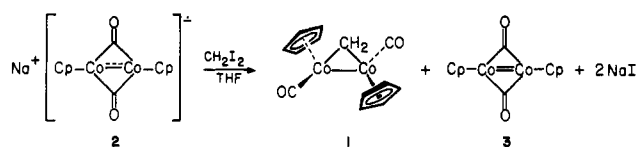
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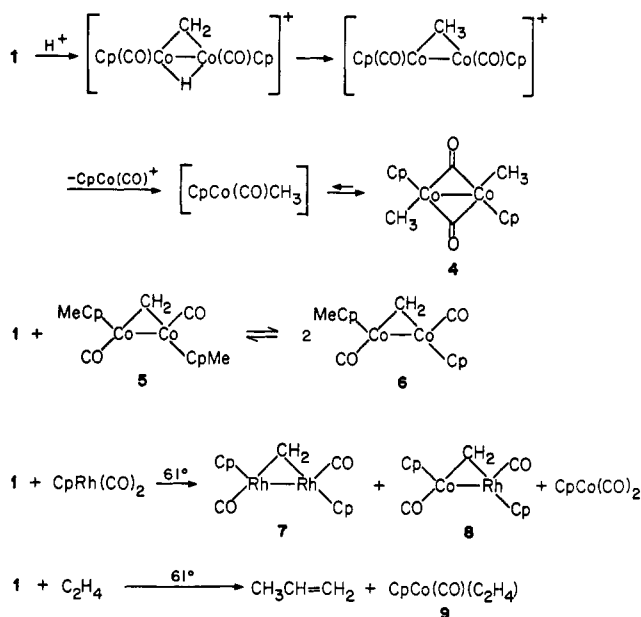
Bridging methylene complexes are among the most interesting binuclear metallacycles, both for structural reasons¹ and because

[†]Holder of an Ephraim Weiss Scholarship from the University of California, Berkeley, 1979-present.

Scheme I



Scheme II



of their possible relationship to organometallic species involved in processes such as methylene transfer, the Fischer-Tropsch reaction, and olefin metathesis.² Several such complexes have been prepared recently, and information about their descriptive chemistry is beginning to appear.³ However, only qualitative information about the mechanisms of these reactions has been obtained. In this note we wish to describe the synthesis, characterization, and chemical reactions of complex **1**, one of very few bridging methylene complexes yet known¹⁸ in the cobalt series. We have found that this material participates in several quite unusual transformations, and preliminary studies on the mechanism of one of its reactions reveals a type of complexity not obvious from superficial scrutiny of the reaction.

Addition of 1.5 equiv of diiodomethane to a suspension of binuclear cobalt radical anion⁴ **2** in THF resulted in an immediate color change from pale green to blue green (due to the formation⁵ of neutral dimer **3**; cf. Scheme I), and then to dark red. Evap-

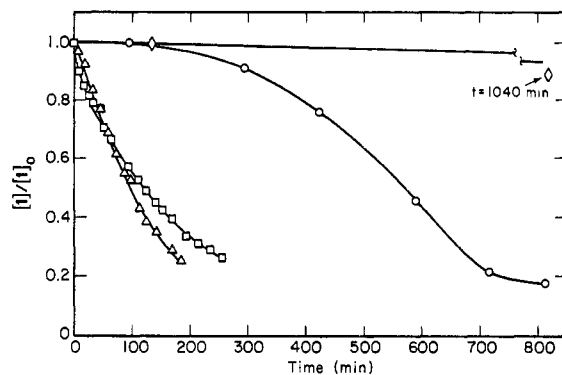
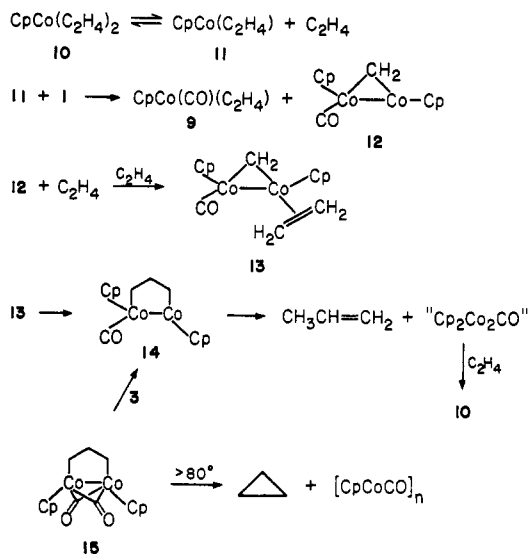


Figure 1. Concentration vs. time plots for reaction of 0.064 M $\mu\text{-CH}_2$ -complex **1** with 4.5 atm of C_2H_4 in C_6D_6 at 61°C : (O) no other additives, (Δ) 0.11 M $\text{CpCo(C}_2\text{H}_4)_2$ added, (□) 0.66 M unsaturated dimer **3** added, and (◇) 4 atm of C_2F_4 added.

Scheme III



oration of solvent and chromatography of the residue on alumina under air-free conditions, followed by recrystallization from hexane, afforded μ -methylene-bis(η^5 -cyclopentadienylcarbonyl-cobalt) (**1**) in 48% yield. Complex **1** forms dark-red plates which are stable in air as a solid but which oxidize slowly in solution. The spectroscopic data on this material are consistent with the presence of 95% of one stereoisomer (presumably trans) and 5% of the other.⁶

Complex **1** reacts readily with several reagents, but in most cases mild heating is required. For example, treatment with H_2 leads to methane, reaction with ethylene leads to propene, and treatment of **1** with strong acid (e.g., HBF_4) gives the earlier characterized^{4b,7} dimethyl complex **4** (Scheme II). Presumably this latter transformation occurs via cationic intermediates similar to those formed from the corresponding rhodium^{3b} and ruthenium^{1e} complexes (cf. Scheme I), followed by loss of $[\text{CpCo(CO)}]^+$ and dimerization of the 17-electron species CpCo(CO)CH_3 . Perhaps most interesting are reactions of **1** with related metal complexes. For example, when **1** was heated with its bis(methylcyclopentadienyl) analogue **5** at 63°C in benzene- d_6 for 2 days, a mixture of **1**, **5**, and the mixed dimer **6** (cf. Scheme II) was formed

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(6) Data for **1**: mp 68°C ; IR (THF) 1966 (w), 1957 (br s), 1924 (w) cm^{-1} ; ^1H NMR (benzene- d_6) δ 6.90 (s, 2 H), 4.64 (s, 10 H) (trans); δ 7.80 (s, 1 H), 6.22 (s, 1 H), 4.52 (s, 10 H) (cis); ^{13}C NMR (benzene- d_6) δ 207.8, 104.4, 86.5 (trans); δ 85.2 (cis); MS (15 eV), m/e 318 (M^+). Anal. Calcd for $\text{C}_{13}\text{H}_{12}\text{Co}_2\text{O}_2$: C, 49.09; H, 3.80; Co, 37.05; M_r 317.9501. Found: C, 48.86; H, 3.89; Co, 36.0; M_r 317.9492.

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in statistical (1:1:2) ratio.⁸ When **1** was heated with $\text{CpRh}(\text{CO})_2$, an even more interesting exchange reaction took place which led to a mixture of **1** and the two other possible Rh/Co μ -methylene dimers **7** and **8**. These three complexes were separated by column chromatography on alumina. The homonuclear rhodium complex had been obtained earlier in elegant work by Herrmann and his group,^{1c} and our sample of **7** was characterized by comparison of spectral data with those reported for Herrmann's complex. The new material **8** was characterized by conventional analytical and spectroscopic techniques and is apparently a very rare example of a heterobinuclear μ -methylene complex.⁹

Because it involves a relatively clear example of a binuclear methylene-transfer reaction, we examined the reaction of **1** with ethylene in somewhat more detail. When a solution of **1** in benzene- d_6 under 4.5 atm of C_2H_4 was heated to 61 °C for 20 h, NMR observation showed it had reacted completely, leading to propene in 65% yield along with a small amount (3%) of methane. The organometallic product of the reaction is a sensitive material which is stable in solution only under ethylene. On the basis of its IR and ^1H NMR spectra,¹⁰ we assign to it the carbonyl/ethylene complex structure **9**; it is formed in 95% yield (NMR). Support for this assignment is provided by examination of the reaction between neutral dimer **3** and ethylene. This leads rapidly to the known compounds $\text{CpCo}(\text{CO})_2$ and $\text{CpCo}(\text{C}_2\text{H}_4)_2$,¹¹ which then more slowly symproportionate to give **9**.

As reported for the corresponding reaction of $\mu\text{-CH}_2\text{Fe}_2(\text{CO})_8$ with ethylene,^{3c} the rate of conversion of **1** to propene is strongly inhibited by CO. Although this qualitative result alone might be taken as evidence for an initial step involving dissociative CO loss, two pieces of evidence suggest that the nature of the inhibition is more complicated. First, the rate does not obey good first- or second-order kinetics. Second, the reaction is also inhibited strongly by ligands other than CO (see, for example, the effect of C_2F_4 shown in Figure 1), but without the buildup of any detectable alkene complexes formed reversibly from **1**. The only way such an inhibition can be operating is if the inhibitor is scavenging some material (e.g., a reactant involved in the propagation step of a chain reaction or a catalyst for the reaction) which is involved in the activation of one of the starting materials. Some indication as to what this "hidden" partner might be was provided by carrying out the reaction of **1** with ethylene in the presence of dimer **3**. Monitoring by NMR showed the initial transformation of **3** to $\text{CpCo}(\text{C}_2\text{H}_4)_2$ (**10**), as described above, followed by rapid conversion of **1** to propene. Addition of independently prepared **10** to the reaction produced a similarly dramatic acceleration in rate (Figure 1).

It seems clear from these experiments that the reaction of **1** with ethylene is autocatalytic, and the catalyst is coordinatively unsaturated $\text{CpCo}(\text{C}_2\text{H}_4)$ (**11**). This material is generated rapidly by ethylene loss from $\text{CpCo}(\text{C}_2\text{H}_4)_2$. We propose the pathway summarized in Scheme III as a likely mechanism for the autocatalytic reaction. Dissociation of ethylene from **10** gives **11**, and this species is capable of abstracting CO, in a bimolecular step,¹² from **1**. This leads to unsaturated binuclear complex **12**, which reacts with ethylene to give propene. It seems likely that this occurs by π complexation followed by insertion to give **14**, a

coordinatively unsaturated relative¹³ of metallacyclopentane **15**, as suggested by Pettit and his co-workers for the related iron system.^{3c} The metal fragments are then scavenged by ethylene to regenerate **10** and a second molecule of **9**. Supporting evidence for this hypothesis is provided by additional experiments involving **15**. As reported earlier,¹³ thermolysis of **15** leads to propene and cyclopropane in about a 4:1 ratio. Thermolysis of **15** in the presence of **3** leads to a significant increase in this ratio (propene/cyclopropane = 9.0), presumably because **3** increases (as it does with **1**) the amount of reaction proceeding by initial CO removal to give **14** (Scheme III).

Further experiments will be required to determine whether this mechanism is correct in detail. However, it is clear from this work that the observation of qualitative inhibition of a reaction by the addition of excess ligand is not sufficient to establish a dissociative first step in its mechanism. In addition, it seems likely that other apparently straightforward insertion and group-transfer processes may involve intermolecular activation by a second metal complex.

Acknowledgment. We are grateful to Professor W. A. Herrmann for helpful discussions and several useful exchanges of information. Financial support for this work was provided by the National Science Foundation (Grant CHE 78-08706).

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Structure of Palytoxin

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Palytoxin, an extremely poisonous, water-soluble substance from marine coelenterates belonging to the genus *Palythoa*,¹ is cleaved into several compounds by sodium periodate. The structures of some of these degradation products have been recently described and indicate that partial structures **1a-f** are present in palytoxin (Scheme I).^{2,3} The presence of unit **1g** in palytoxin from *Okinawan P. tuberculosa* is suggested from the structure of another periodate oxidation product.⁴ This unit, however, appears to be slightly modified in the palytoxins from Hawaiian *P. toxica* and a *Palythoa* sp. from Tahiti.³ We report here the structures of additional periodate oxidation products which show that units **1h** and **1i** are present in palytoxin from a Tahitian *Palythoa* sp. Units **1a-f**, **1h**, and **1i** account for the eight carbon-carbon double bonds, seven methyl groups, and three quaternary carbons indicated by the ^{13}C NMR spectrum. Also reported are the structures of several ozonolysis products which allow us to sequence these units into a total gross structure **1a** for this toxin.

Oxidation of palytoxin, hexadecahydropalytoxin, or *N*-(*p*-bromobenzoyl)palytoxin with excess NaIO_4 in water at 0 °C for

(8) Data for **5**: mp 57.5–58.5 °C; IR (toluene) 1950 cm^{-1} (br s); ((KBr) 1978 (m), 1938 (br s) cm^{-1} ; ^1H NMR (benzene- d_6) δ 6.80 (s, 2 H), 4.58–4.57 (q, 8 H), 1.75 (s, 6 H); MS (15 eV), m/e 346 (M^+). Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{Co}_2\text{O}_2$: C, 52.05; H, 4.66; Co, 34.05. Found: C, 52.44; H, 4.81; Co, 33.2. The mixed dimer **6** was identified by ^1H NMR, MS and HRMS analysis of the mixture formed on heating dimers **1** and **5**. Data for **6**: ^1H NMR (benzene- d_6) δ 6.85 (s, 2 H), 4.66 (s, 5 H), 4.55 (m, 4 H), 1.73 (s, 3 H); HRMS. Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{Co}_2$: 331.9658. Found: 331.9659.

(9) Data for **8**: mp 67.5 °C, IR (toluene) 1977 (w), 1962 (br s) cm^{-1} ; ^1H NMR (acetone- d_6) δ 6.84 (s, 2 H), 5.37 (d, 5 H, $J_{\text{HRb}} = 0.62$ Hz), 5.07 (s, 5 H) (trans isomer); 7.70 (q, 1 H, $J_{\text{HRb}} = 3.24$ Hz, $J_{\text{HH}} = 0.34$ Hz), 6.17 (q, 1 H, $J_{\text{HRb}} = 1.13$ Hz), 5.52 (d, 5 H, $J_{\text{HRb}} = 0.52$ Hz), 5.14 (s, 5 H) (cis isomer); MS (15 eV), m/e 362 (M^+) HRMS. Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{O}_2\text{CORh}$: 43.12; H, 3.34; Co, 16.3; Rh, 391.9215. Found: C, 42.79; H, 3.35; Co, 16.0; Rh, 361.9227.

(10) ^1H NMR (C_6D_6) δ 2.15 (br s, 2 H), 2.55 (br s, 2 H), 4.40 (s, 5 H); IR 1974 cm^{-1} .

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