Synthesis and Reaction Chemistry of a New Class of μ-Alkylidene Dicobalt Complexes. Crystal and Molecular Structure of (μ-Methylene)bis[η^5-(methylcyclopentadienyl)carbonylcobalt]

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Abstract: Treatment of Na[CpCo(CO)]$_2$ with *gem*-diiodoalkanes ($RR'CI_2$, R = H, alkyl) leads to a class of dinuclear μ-alkylidene complexes containing two adjacent cobalt atoms. Cis and trans isomers were observed in certain of these materials, as well as bridging and terminal carbonyls, depending upon the substituents located at the alkylidene carbon. Complexes having two alkyl substituents attached to this carbon lose one CO ligand, leading to stable unsaturated μ-alkylidene complexes. The molecular structure of (μ-methylene)bis[η^5-(methylcyclopentadienyl)carbonylcobalt] (**11**) was determined by X-ray diffraction (R = 2.82%). The crystals were triclinic (space group $P\bar{1}$), with unit cell parameters a = 8.0529 Å, b = 9.5160 Å, c = 9.9330 Å, α = 69.678°, β = 74.769°, and γ = 83.704°. At elevated temperatures dimers **10** (M, M' = Co; R = H; R' = neopentyl) and **13** (M = Co; M' = Rh; R, R' = H) undergo cis-trans isomerization at a rate which is rapid on the NMR time scale. Treatment of **1** (M, M' = Co; R, R' = H) with **11** or CpRh(CO)$_2$ leads to metal-metal exchange reactions, resulting in the formation of heteronuclear (Co-Rh) μ-alkylidene complexes. **1** reacts with ethylene to give propene and CpCo(CO)(C_2H_4). Mechanistic studies have demonstrated that this process is autocatalytic, and addition of other ligands (e.g., CO, C_2F_4, propene) retards the rate of the reaction by scavenging the unsaturated cobalt complexes which function as the autocatalysts. Finally, thermolysis of "internal" or disubstituted alkylidene complexes **2**, **5**, and **7** causes a novel rearrangement in which the dicobalt moiety migrates to the end of the alkylidene carbon chain, generating terminal alkylidene complexes having the same number of carbon atoms. Labeling studies have demonstrated that both sequential 1,2 metal shift (leading to alkene π complexes) and allylic C-H activation (leading to π-allyl complexes) are involved as steps in this rearrangement.

Of the possible types of dinuclear metallacycles, μ-alkylidene complexes (bridging methylene complexes; dimetallacyclopropanes) are receiving especially intense investigation. Interest in these materials is due to their unique structural and chemical properties,[1] as well as their potential use as models for intermediates in the Fischer-Tropsch reaction.[2] A large number of μ-alkylidene complexes have now been prepared and characterized structurally. However, in-depth study of their chemical reactions has so far been relatively limited.[3]

As an extension of our earlier work on dinuclear cobalt-containing metallacycles,[4] we have now prepared a series of dicobaltacyclopropanes, complexes in which the dicobalt moiety is bridged by a μ-alkylidene ligand. The study of the chemistry of these materials has revealed a variety of new and interesting transformations. This paper reports the details of our research on these systems.[5]

Results and Discussion

Preparation of μ-Alkylidene Dimers. As described earlier, the dinuclear radical anion Na[CpCo(CO)]$_2$ can be doubly alkylated with a variety of 1,n-dihalides to afford dicobaltacycles of various ring sizes.[4] We have now used *gem*-diiodoalkanes in this reaction to prepare metallacycles in which the dicobalt moiety is bridged by alkylidene ligands. For example, when diiodomethane was added to a suspension of Na[CpCo(CO)]$_2$[6] in THF at room temperature, an immediate color change to an intense blue green indicated reaction. Over the course of ca. 10 min the color of the solution changed again, now to a dark red. At the same time the IR carbonyl stretching frequencies of the radical anion (at 1740, 1690, and 1660 cm^{-1}) were replaced by new absorptions at 2020 and 1960 cm^{-1}. The absorption at 1960 cm^{-1} was too strong to be assigned to the coincident absorption of CpCo(CO)$_2$ (2020 and 1955 cm^{-1}) and indicated a product with terminal carbonyl ligands. Column chromatography on alumina yielded a first fraction of yellow CpCo(CO)$_2$ followed by a dark red fraction of a new material. Analytical data and spectroscopic characterization of this material (see Experimental Section) are consistent with structure **1** (Scheme I), a cobalt dimer in which the two metal atoms are bridged by a methylene group. Complex **1** was isolated in 48% yield based on Na[CpCo(CO)]$_2$. The dark red plates of **1** are air stable, but solutions of it are moderately air sensitive. The ^{1}H NMR spectrum of **1** indicates the presence of 95% of the trans isomer and 5% of the cis isomer.

Similar results were obtained when one of the hydrogen atoms of diiodomethane was replaced by an alkyl group, as shown in Scheme I. As the alkyl group becomes sterically more demanding, the isolated yield of μ-alkylidene dimer decreases. The materials isolated from these reactions are all mixtures of trans and cis

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[1] For reviews, see: (a) Herrmann, W. A. *Angew. Chem.* **1982**, *94*, 118. (b) Herrmann, W. A. *Adv. Organomet. Chem.* **1982**, *20*, 159.

[2] (a) Brady, R. C., III; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 6181. (b) Osterloh, W. T.; Cornell, M. E.; Pettit, R. *J. Am. Chem. Soc.* **1982**, *104*, 3759.

[3] For some interesting recent observations on the reactions of di- and trinuclear μ-alkylidene complexes, as well as leading references to earlier structural and synthetic work, see: (a) Herrmann, W. A.; Huggins, J. M.; Bauer, C.; Smischek, M.; Pfisterer, H.; Ziegler, M. L. *J. Organomet. Chem.* **1982**, *226*, C59. (b) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134. (c) Levisalles, J.; Rose-Munch, F.; Rudler, H.; Daran, J.-C.; Jeanin, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 1057. (d) Shapley, J. R.; Sievert, A. C. *J. Am. Chem. Soc.* **1981**, *103*, 6975. (e) Clauss, A. D.; Shapley, J. R.; Wilson, S. R. *Ibid.* **1981**, *103*, 7387. (f) Dawkins, G. M.; Green, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 41. (g) Herrmann, W. A.; Plank, J.; Riedel, D.; Ziegler, M. L.; Weidenhammer, K.; Guggolz, E.; Balbach, B. *J. Am. Chem. Soc.* **1981**, *103*, 63. (h) Messerle, L.; Curtis, M. D. *Ibid.* **1980**, *102*, 7791.

[4] (a) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5694. (b) Theopold, K. H.; Bergman, R. G. *Organometallics* **1982**, 1, 1571.

[5] Some of the results reported here were described earlier in preliminary form: (a) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 2489. (b) Theopold, K. H.; Bergman, R. G. *Organometallics* **1982**, *1*, 219.

[6] (a) Schore, N. E.; Ilenda, C. S.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *103*, 7436; **1977**, *99*, 1781. (b) The material used throughout this study was the crude product of the reduction of CpCo(CO)$_2$ with sodium amalgam. The actual concentration of Na[CpCo(CO)]$_2$ in this material is ca. 70% by weight.

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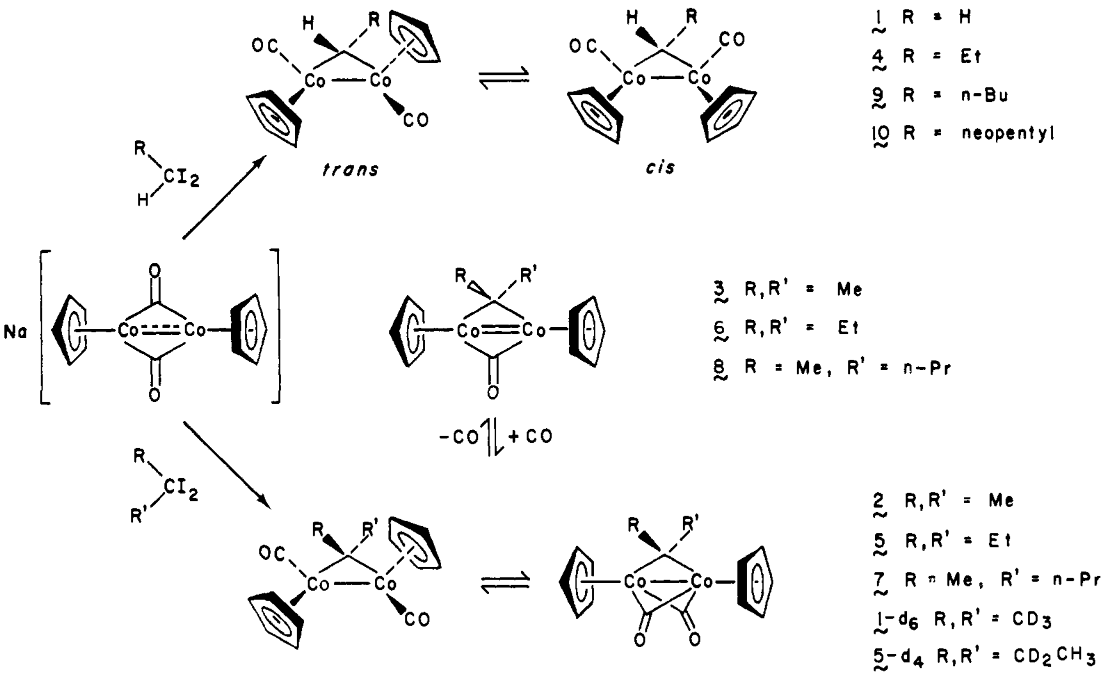
Scheme I



isomers and in all but the neopentyl-substituted complex **10** the minor isomer (presumably cis) is present to the extent of ca. 5%. The neopentyl group of **10** is apparently bulky enough to shift this equilibrium to a cis content of 20%. The IR spectra of these compounds exhibit carbonyl stretching frequencies consistent with terminal CO ligands only.

Substitution of both hydrogens of CH_2I_2 with alkyl groups leads to a change in this pattern. For example, when 2,2-diiodopropane was added to a suspension of $Na[CpCo(CO)]_2$ the color of the solution changed first from pale green to bluegreen, then to an intense purple and finally (after ca. 15 min) to dark brown. Chromatographic separation of this mixture yielded two new materials. The major product forms black air-stable crystals, and its spectral and analytical properties are consistent with structure **2** (Scheme I). The ^1H NMR spectrum of **2** consists of 2 singlets (δ 4.54 and 2.18) indicating the presence of one isomer (presumably trans) only. Solutions of **2** exhibit carbonyl stretching frequencies (1937, 1853, and 1813 cm^{-1}) consistent with a mixture of CO-terminal and CO-bridging structures which are presumably interchanging rapidly on the NMR time scale.

The second product isolated from this reaction, albeit in only 2% yield, forms dark purple needles which are very air sensitive. On the basis of spectral and analytical properties, its structure can be assigned as **3**, which on the basis of convenience and the 18-electron rule we have drawn with a cobalt–cobalt double bond (Scheme I). This doubly bonded complex is derived from **2** by loss of one CO ligand. Accordingly in solution **3** reacts immediately and quantitatively with CO to form the corresponding saturated dimer **2**. Analogous doubly bonded complexes **3**, **6**, and **8** can also be generated by irradiation of solutions of saturated complexes **2**, **5**, and **7**, respectively, under vacuum, or simply by heating solutions of the saturated dimers. Alternatively they may be isolated in ca. 50% yield from the reaction of the saturated dimers with $CpCo(C_2H_4)_2$,[7a] which is a ready source of coordinatively unsaturated cobalt.

However, these methods are not suitable for the preparation of these materials on a large scale, and their study has therefore been deferred until a more convenient synthesis becomes available.[7b]

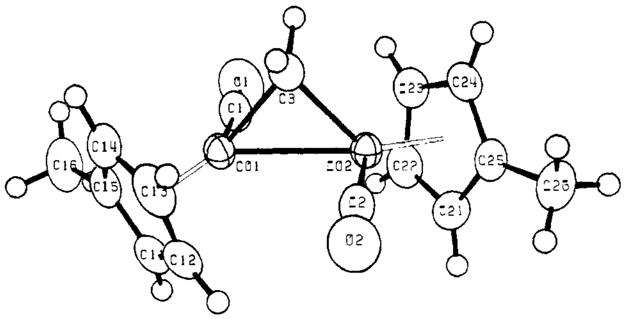


Figure 1. ORTEP drawing of one molecule of $Co_2(CO)_2(CH_2)(CH_3C_5H_4)_2$ (**11**), showing the atomic labeling scheme. Thermal ellipsoids are scaled to represent the 50% probability surface.

X-ray Structure Determination. μ-Alkylidene dimers are a small but rapidly growing class of novel organometallic compounds and have attracted considerable theoretical interest.[8] A complete structural characterization therefore seemed appropriate. Despite numerous attempts, parent compound **1** did not yield crystals suitable for an X-ray crystallographic study. However, its MeCp analogue **11** gave crystals amenable to such a study upon slow sublimation at 40 °C under high vacuum. A total of 1796 reflections were measured and the structure was refined to an R value of 2.8%. **11** crystallizes in space group $P\bar{1}$ with the cell dimensions a = 8.0529 (23) Å, b = 9.5160 (28) Å, c = 9.9330 (45) Å, α = 69.678 (31)°, β = 74.769 (30)°, and γ = 83.704 (23)°. The crystal consists of well-separated molecules of **11**. There are no unusually short intermolecular contacts. Figure 1 shows an ORTEP drawing of the molecule with the atom numbering scheme. Selected distances and angles are compiled in Table I.

Each molecule has strong noncrystallographic 2-fold symmetry with the molecular axis passing through C3 and bisecting the Co1–Co2 bond. Figure 2 shows a view down this axis. The agreement between bond lengths related by this 2-fold axis is excellent, extending even to the "slippage" of the MeCp rings away from the bridging methylene group. Bond distances and angles in the molecule all appear normal. The hydrogen atoms of the bridging methylene group were refined, showing the μ-CH_2 plane

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(7) (a) Jonas, K.; Krueger, C. *Angew. Chem.* **1980**, *92*, 513. (b) For an earlier example of this type of unsaturated cobalt μ-alkylidene complex, see: Halbert, T. R.; Leonowicz, M. E.; Maydonovitch, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 5102.

(8) (a) Hofmann, P. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 554. (b) Pinhas, A. R.; Albright, T. A.; Hofmann, P.; Hoffmann, R. *Helv. Chim. Acta* **1980**, *63*, 29.

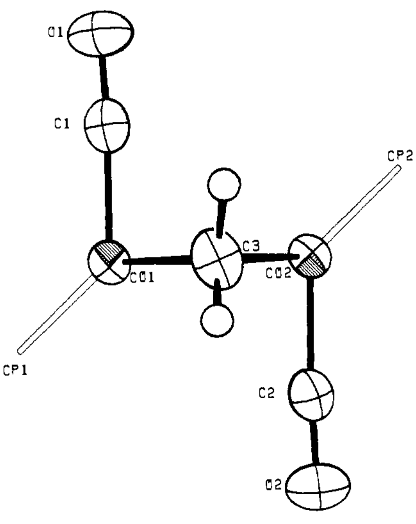

Figure 2. ORTEP drawing showing a view of **11** normal to the Co1–Co2 bond, in the Co1–C3–Co2 plane. Only the connections to the centroids of the methylcyclopentadienyl rings are shown for clarity.

to be twisted from the perpendicular position with respect to the Co1–Co2–Co3 plane by 4.3° (Figure 2). It is unlikely that this is more than marginally significant, but the magnitude and direction of the distortion resemble those observed[9] in the related μ-$CH_2[CpRh(CO)]_2$ by neutron diffraction at 15 K.

The Co–Co distance of 2.497 Å indicates a metal–metal single bond, consistent with the EAN rule and the description of this class of compounds as dimetallacyclopropanes. Combined with the short but normal Co–C distances of 1.920 and 1.925 Å, **11** exhibits the smallest μ-CH_2–M_2 ring characterized to date. Both the M–C–M (81.0°) and μ-CH_2 H–C–H (108.1°) angles are similar to those in other known compounds of this type.

DNMR Studies. Recently Knox and co-workers reported and proposed a mechanism for the cis–trans isomerization of (μ-CMe_2)(μ-CO)$[CpRu(CO)]_2$ which occurs on the NMR time scale.[10] Ziegler[11] and Casey[12] have independently prepared (μ-CH_2)(μ-CO)$[CpFe(CO)]_2$ and found the cis and trans isomer interconverting readily at room temperature. When a solution of neohexylidene complex **10** in acetone-d_6 was heated in the probe of an NMR spectrometer, the resonances of *cis*- and *trans*-**10** broadened and coalescence was observed at ca. 55 °C. At 70 °C the single Cp resonance began to sharpen again, but onset of the thermal decomposition of **10** at higher temperatures prevented further examination of this phenomenon. These reversible changes in the spectrum are consistent with a rapid cis–trans isomerization occurring on the NMR time scale. The coalescence temperature of 55 °C provides estimated free energies of activation for this isomerization: $\Delta G_{\text{cis}\to\text{trans}}^{*} = 17.0$ kcal/mol and $\Delta G_{\text{trans}\to\text{cis}}^{*} = 18.2$ kcal/mol. These values are in good agreement with the aforementioned observations.

Complete dissociation of these dimers apparently is much less facile, albeit possible. When an equimolar mixture of the parent μ-CH_2 complex **1** and its MeCp analogue **11** in benzene-d_6 was heated to 63 °C for 2 days, a mixture of **1**, **11**, and the mixed dimer **12** was formed in statistical ratio (Scheme II). The mixed dimer **12** was identified by ^1H NMR, MS, and high-resolution MS analysis of the mixture formed on heating dimers **1** and **11**. Evidence against mere exchange of cyclopentadienyl ligands as a pathway for this reaction was provided by observation of a similar exchange reaction with $CpRh(CO)_2$. When a solution of **1** and $CpRh(CO)_2$ in benzene was heated to 63 °C, a mixture of **1** and the two other possible Rh/Co μ-methylene dimers **13** and **14** was obtained. These three complexes were separated by column chromatography on alumina. The homonuclear rhodium complex had been prepared earlier by Herrmann and co-workers,[14] and our sample of **14** was characterized by comparison of spectral data with those reported for Herrmann's complex. However, in our hands this compound appears to be a mixture of cis and trans isomers (ca. 13% cis isomer), the resonances of the major trans isomer having the previously reported chemical shifts. The new material **13** was characterized by conventional analytical and spectroscopic techniques and is apparently a rare example of a heterobinuclear μ-methylene complex. Similar to its two homologues it is a mixture of the two stereoisomers (ca. 12% cis), as indicated by the room-temperature ^1H NMR spectrum in ace-

Table I. Selected Distances (Å) and Angles (deg)[a] for 11

Co1–Co2	2.497 (1)	Co2–Co1–C1	89.26 (7)
Co1–C1	1.707 (3)	Co2–Co1–C3	49.40 (7)
Co2–C2	1.720 (2)	Co2–Co1–CP1[b]	135.1
Co1–C3	1.925 (2)	C1–Co1–C3	92.02 (11)
Co2–C3	1.920 (2)	C1–Co1–CP1	130.3
Co1–C11	2.117 (2)	C3–Co1–CP1	131.4
Co1–C12	2.115 (2)	Co1–Co2–C2	89.31 (7)
Co1–C13	2.075 (2)	Co1–Co2–C3	49.59 (7)
Co1–C14	2.074 (2)	Co1–Co2–CP2[b]	136.2
Co1–C15	2.090 (2)	C2–Co2–C3	91.86 (11)
Co1–CP1[b]	1.721	C2–Co2–CP2	130.8
Co2–C21	2.113 (2)	C3–Co2–CP2	129.1
Co2–C22	2.119 (2)	Co1–C1–O1	175.88 (20)
Co2–C23	2.081 (2)	Co2–C2–O2	176.07 (20)
Co2–C24	2.079 (2)	Co1–C3–Co2	81.02 (9)
Co2–C25	2.092 (2)	Co1–C3–H3A	118.7 (12)
Co2–CP2[b]	1.724	Co1–C3–H3B	114.9 (15)
C1–O1	1.156 (3)	Co2–C3–H3A	113.1 (13)
C2–O2	1.148 (3)	Co2–C3–H3B	119.4 (16)
C3–H3A	1.03 (2)	H3A–C3–H3B	108.1 (19)
C3–H3B	0.86 (2)	C15–C11–C12	108.47 (21)
C11–C12	1.381 (3)	C11–C12–C13	108.34 (20)
C12–C13	1.400 (4)	C12–C13–C14	108.18 (21)
C13–C14	1.405 (3)	C13–C14–C15	107.93 (21)
C14–C15	1.405 (3)	C14–C15–C11	107.07 (20)
C15–C11	1.422 (3)	C11–C15–C16	125.36 (23)
C15–C16	1.496 (3)	C14–C15–C16	127.51 (23)
C21–C22	1.397 (3)	C25–C21–C22	108.62 (19)
C22–C23	1.416 (3)	C21–C22–C23	107.93 (20)
C23–C24	1.406 (3)	C22–C23–C24	107.96 (19)
C24–C25	1.412 (3)	C23–C24–C25	108.50 (19)
C25–C21	1.424 (3)	C24–C25–C21	106.98 (20)
C25–C26	1.491 (3)	C21–C25–C26	126.16 (21)
		C24–C25–C26	126.76 (21)
		C1–Co1–Co2–C2	−173.7
		CP1–Co1–Co2–CP2	139.9
		C1–Co1–Co2–CP2	−14.7
		Cp1–Co1–Co2–C2	−19.0
		C1–Co1–Co2–C3	93.3
		CP1–Co1–Co2–C3	−112.0
		C2–Co2–Co1–C3	93.0
		CP2–Co2–Co1–C3	−108.0
		C1–Co1–CP1–C15	−13.4
		C2–Co2–CP2–C25	−17.1
		C3–Co1–CP1–C15	130.8
		C3–Co2–CP2–C25	122.3

[a] In this and all subsequent tables the esd's of all parameters are given in parentheses, right justified to the least significant digit(s) given. The esd's are calculated including the correlation terms derived from the inverted least-squares matrix. Distances and angles are uncorrected for thermal motion. [b] CP1 and CP2 are the centroids of the two cyclopentadienide rings.

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(9) Takusagawa, F.; Fumagalli, A.; Koetzle, T. F.; Herrmann, W. A. *Inorg. Chem.* **1981**, *20*, 3060.

(10) Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 861.

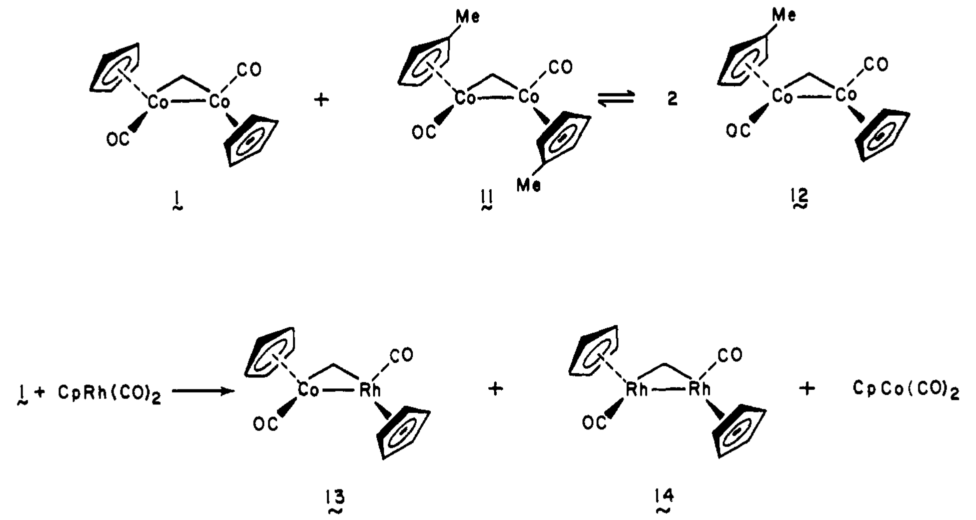
(11) Korswagen, R.; Alt, R.; Speth, D.; Ziegler, M. L. *Angew. Chem.* **1981**, *93*, 1073.

(12) Casey, C. P.; Fagan, P. J.; Miles, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 1134.

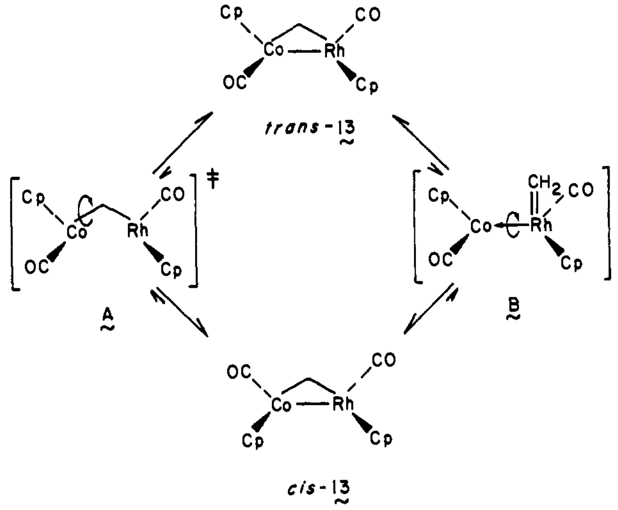
(13) A graphic method was used to derive these values: Shanan-Atidi, H.; Bar-Eli, K. H. *J. Phys. Chem.* **1970**, *74*, 961.

(14) Herrmann, W. A.; Krueger, C.; Goddard, R.; Bernal, I. *J. Organomet. Chem.* **1977**, *140*, 73.

Scheme II



Scheme III



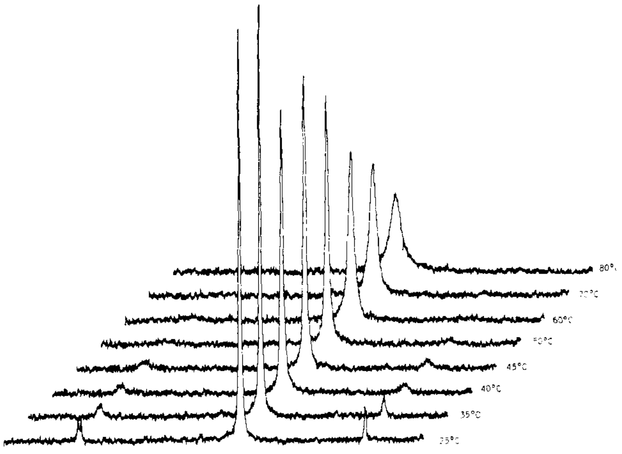


Figure 3. ^{1}H NMR spectra of **13** (μ-CH_2 region only) in the range from 25 to 80 °C showing cis–trans isomerization rapid on the NMR time scale.

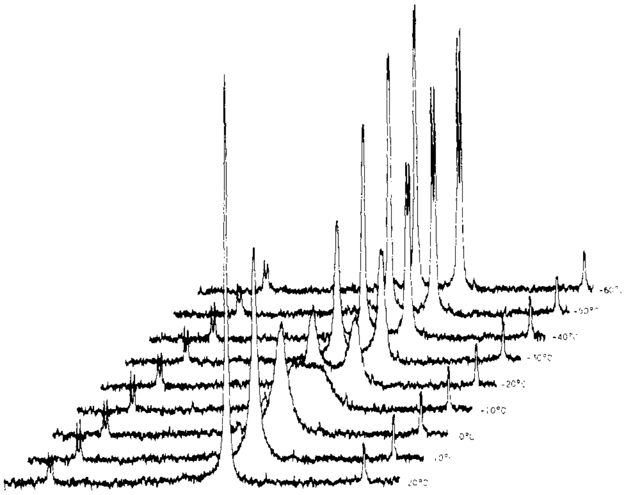


Figure 4. ^{1}H NMR spectra of **13** (μ-CH_2 region only) in the range from 20 to −60 °C showing the rapid equilibration of the two diastereotopic methylene hydrogens of *trans*-**13**.

tone-d_6 solution. While these results do not provide conclusive evidence that **1** is in equilibrium with a mononuclear carbene complex, they certainly make the consideration of such an intermediate in the reactions of **1** necessary.

The preparation of the heteronuclear Co/Rh complex **13** also allows a more detailed study of the previously described cis–trans isomerization. Scheme III shows two conceivable limiting structures for the transition state or intermediate in this reaction. Cleavage of the metal–metal bond of **13**, leading to A, and rotation around a metal–carbon bond followed by reformation of the metal–metal bond, accomplishes the isomerization. The metal–metal bond should be stronger in **13** than in the homonuclear cobalt dimer **10** due to the difference in electronegativity of the two metal centers and consistent with the notion that metal–metal bond strengths increase upon going down a column in the periodic table.

Alternatively a metal–carbon bond of **13** (presumably the weaker Co–C bond) can be broken, leading to B. Rotation around the metal–metal bond and subsequent reclosure again accomplishes the observed interconversion. The bond strengths of the Co–C bond in Co/Co complex **11** and Co/Rh complex **13** should be similar.

With this in mind we studied the cis–trans isomerization of heteronuclear complex **13** by variable-temperature NMR spectrometry. When a solution of **13** in acetone-d_6 was heated in the probe of a 180-MHz NMR spectrometer, broadening and finally coalescence of the resonances for the two isomers was observed (Figure 3). A simple calculation[13] yields the free energies of activation for the two related processes: $\Delta G_{\text{cis}\rightarrow\text{trans}}{}^{\ddagger} = 17.0$ kcal/mol, $\Delta G_{\text{trans}\rightarrow\text{cis}}{}^{\ddagger} = 18.2$ kcal/mol. Comparison with the corresponding values for homonuclear **11** shows these to be identical within the error limits of such an analysis.[15] In accord with Knox's postulate in the ruthenium system,[10] we therefore

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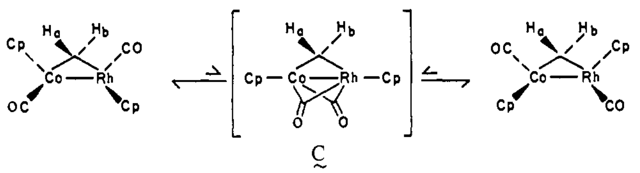
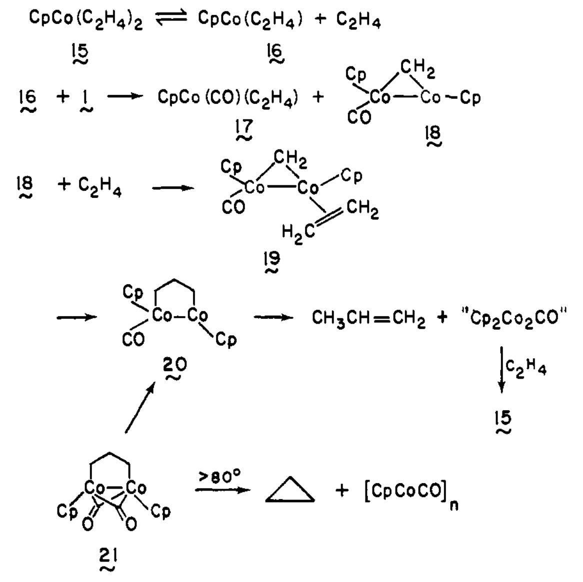
(15) Binsch, G.; Kessler, H. *Angew. Chem.* **1980**, *92*, 445.

Scheme IV



Scheme V



favor a structure resembling B as the transition state or intermediate for the cis–trans isomerizations of the μ-alkylidene dimers.

Cooling Co/Rh complex **13** below ambient temperature reveals another dynamic process. Figure 4 shows the μ-CH_2 region of the variable-temperature ^1H NMR spectra of **13** at low temperatures. The single resonance broadens and then resharpens to form two doublets (due to coupling to ^{103}Rh, $I = {}^1/_2$) of equal intensity. These are the resonances for the two protons of the μ-CH_2 group in the trans isomer, which are diastereotopic. The interconversion of the two enantiomers of *trans*-**13**, which equilibrates these protons, is apparently rapid on the NMR time scale at room temperature. The coalescence temperature of ca. 263 K was used to estimate a $\Delta G^{\ddagger} = 13.0$ kcal/mol for this process. Processes of this kind are well precedented[16] and thought to proceed via CO-bridging structures like the proposed intermediate C in Scheme IV.

Reaction of 1 with Ethylene. One of the most interesting reactions[17] of the parent μ-CH_2 complex **1** is its homologation with ethylene, leading to propene (eq 1).

$$1 + C_2H_4 \rightarrow CH_3{-}CH{=}CH_2 + CpCo(CO)(C_2H_4) \quad (1)$$

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 of methane (3%). The organometallic product of this reaction is a sensitive material which is stable in solution only under ethylene. On the basis of its IR and ^1H NMR spectra we assign to it the carbonyl/ethylene complex structure **17** (Scheme V); it is formed in 95% yield (NMR). Support for this assignment is provided by formation of the same material in the reaction between neutral dimer $[CpCo(CO)]_2$ and ethylene. This leads initially to the known compounds $CpCo(CO)_2$ and $CpCo(C_2H_4)_2$ (**15**), which then more slowly symproportionate to the thermodynamic product **17**.

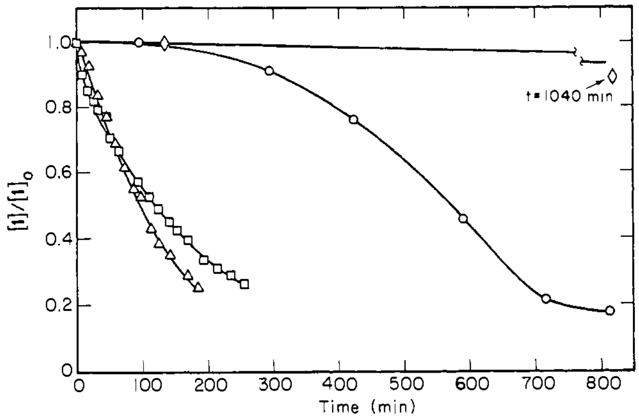


Figure 5. Concentration vs. time plots for reaction of **1** with 4.5 atm of C_2H_4 in C_6D_6 at 62 °C: (○) no other additives, (△) 0.11 M $CpCo(C_2H_4)_2$ added, (□) 0.66 M unsaturated dimer $[CpCo(CO)]_2$ added, and (◇) 4 atm of C_2F_4 added.

As reported for the corresponding reaction of μ-$CH_2Fe_2(CO)_8$ with ethylene,[18] 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 (Figure 5). Second, *the reaction is inhibited strongly by ligands other than CO* (see, for example, the effect of C_2F_4 shown in Figure 5), *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 $[CpCoCO]_2$. Monitoring by NMR showed the initial transformation of this unsaturated cobalt dimer to $CpCo(C_2H_4)_2$ (**15**), as described above, followed by rapid conversion of **1** to propylene. Addition of independently prepared **15** to the reaction produced a similarly dramatic acceleration in rate (Figure 5).

It seems clear from these experiments that the reaction of **1** with ethylene is autocatalytic, and the catalyst is coordinatively unsaturated $CpCo(C_2H_4)$ (**16**). This material is generated rapidly by ethylene loss from $CpCo(C_2H_4)_2$. We propose the pathway summarized in Scheme V as a likely mechanism for the autocatalytic reaction. The "activation" steps in this mechanism involve dissociation of ethylene from diethylene complex **15** to give coordinatively unsaturated **16**. This species is capable of abstracting CO, in a bimolecular step,[20] from μ-methylene complex **1**, allowing ethylene to enter the cobalt coordination sphere. The use of $[CpCo(C_2H_4)]_2$ to accelerate preparation of the unsaturated μ-alkylidene dimers **3**, **6**, and **8** provides support for this part of the reaction sequence. It is informative to note that the thermal decomposition of saturated dimer **5** is an autocatalytic reaction, too, whereas its unsaturated derivative **6** decomposes in a clean first-order process (see below).

Abstraction of CO from **1** leads to coordinatively unsaturated dinuclear complex **18** (Scheme V) which reacts with ethylene to give propylene. It seems likely that this occurs by π complexation followed by insertion to give **20**, a coordinatively unsaturated relative[4] of metallacyclopentane **21**, as suggested by Pettit and his co-workers for the related iron system.[18] The metal fragments

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[16] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; p 1226.

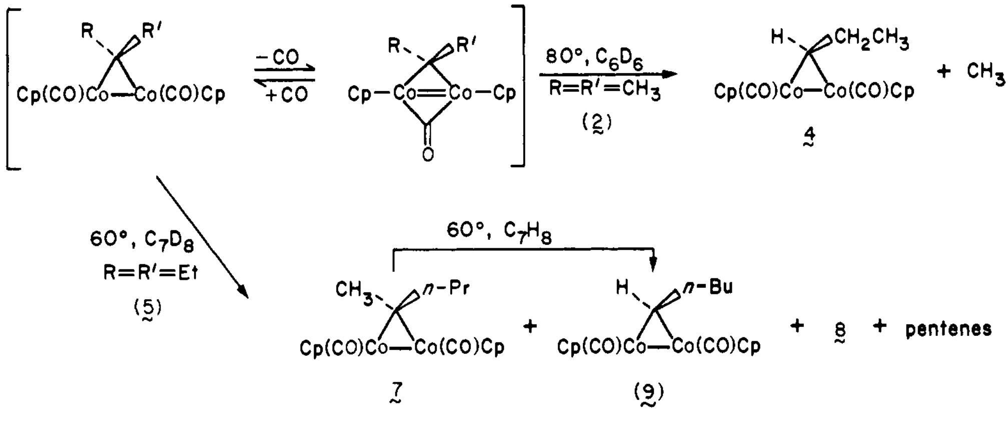
[17] **1** also reacts with H_2, alkynes, and strong protic acids (see ref 5a), but these reactions have not yet been studied in detail.

[18] Sumner, C. E., Jr.; Riley, P. E.; Davis, R. E.; Pettit, R. *J. Am. Chem. Soc.* **1980**, *102*, 1752.

[19] For a related example of such a process (apparently intramolecularly assisted by an appended amine ligand) reported very recently, see: Aumann, R.; Henkel, G.; Krebs, B. *Angew. Chem.* **1982**, *94*, 218.

[20] Similar metal-assisted CO dissociations have recently been reported: (a) Albers, M. O.; Coville, N. J.; Ashworth, T. V.; Singleton, E.; Swanepoel, H. E. *J. Chem. Soc., Chem. Commun.* **1980**, 489. (b) Casey, C. P.; Shusterman, A. J. *J. Mol. Catal.* **1980**, *8*, 1.

Scheme VI



are then scavenged by ethylene to regenerate diethylene complex **15** and a second molecule of carbonyl ethylene complex **17**. Supporting evidence for this hypothesis is provided by additional experiments involving dimetallacyclopentane **21**. As reported earlier,[4] thermolysis of **21** leads to propene and cyclopropane in about a 4:1 ratio. Thermolysis of **21** in the presence of $[CpCo(CO)]_2$ leads to a significant increase in this ratio (propene/cyclopropane = 9.0), presumably because the unsaturated dimer increases (as it does with **1**) the amount of reaction proceeding by initial CO removal to give **20** (Scheme V). Unfortunately, we have been unable to find conditions which might facilitate the trapping of **20** to give **21**; as with other ligands, added CO completely inhibits the reaction of **1** with ethylene, presumably by converting cobalt ethylene π complexes **15**, **16**, and **17** to $CpCo(CO)_2$, which is not capable of functioning as a catalyst for the reaction.

Thermolysis of Dinuclear Alkylidene Complexes. When a solution of saturated 2-propylidene complex **2** (cf. scheme VI) in benzene-d_6 was heated to 80 °C for 10 h, loss of one CO to give the corresponding doubly bonded complex **3** was observed quite soon; following that, decomposition began to occur and propene was produced in 79% yield. However, during NMR monitoring of this reaction we were also surprised to discover that a small amount (7%) of the *unbranched* 1-propylidene complex **4** appeared during the course of the reaction. Curious to know whether this apparent metal-migration reaction could occur over a longer carbon chain, we heated a solution of 3-pentylidene complex **5** under similar conditions. Once again, heating at 60 °C in toluene-d_8 for several hours led to the formation of pentenes and small amounts of the various *n*-pentylidene isomers **6–9**. Finally, heating 2-pentylidene complex **7** at 60 °C for 7 h gave ca. 3% of 1-pentylidene isomer **9**. No reverse isomerization was observed on heating **4** or **9**; only alkene and intractable organometallic products were formed. Examination of the time course of these reactions indicated that they are autocatalytic, similar to the reaction of parent μ-CH_2 complex **1** with ethylene. However, when the unsaturated 3-pentylidene complex **6** was used as starting material, the decomposition followed good first-order kinetics (Figure 6), but only unsaturated 2-pentylidene (**8**) and no 1-pentylidene complex (**9**) was formed. This is probably due to the decreased availability of CO in this system, which leads to decomposition of the unsaturated 1-pentylidene dimer rather than trapping with CO to form **9**. These observations suggest that these reactions, once initiated, proceed by product-assisted removal of a CO ligand from the starting material.

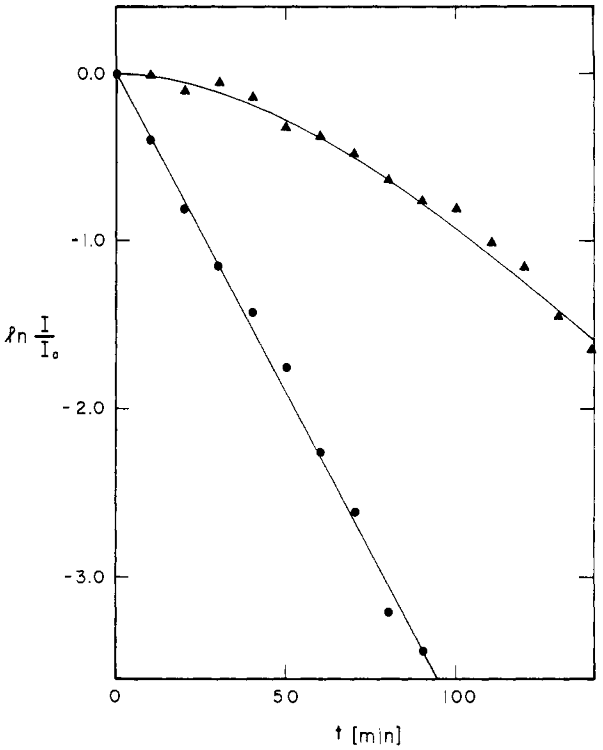
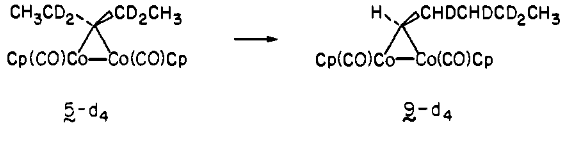


Figure 6. First-order kinetics plots for the thermal reactions of 3-pentylidene dimers in toluene-d_8 at 60 °C: (▲) **5**, (●) **6**.

Scheme VII

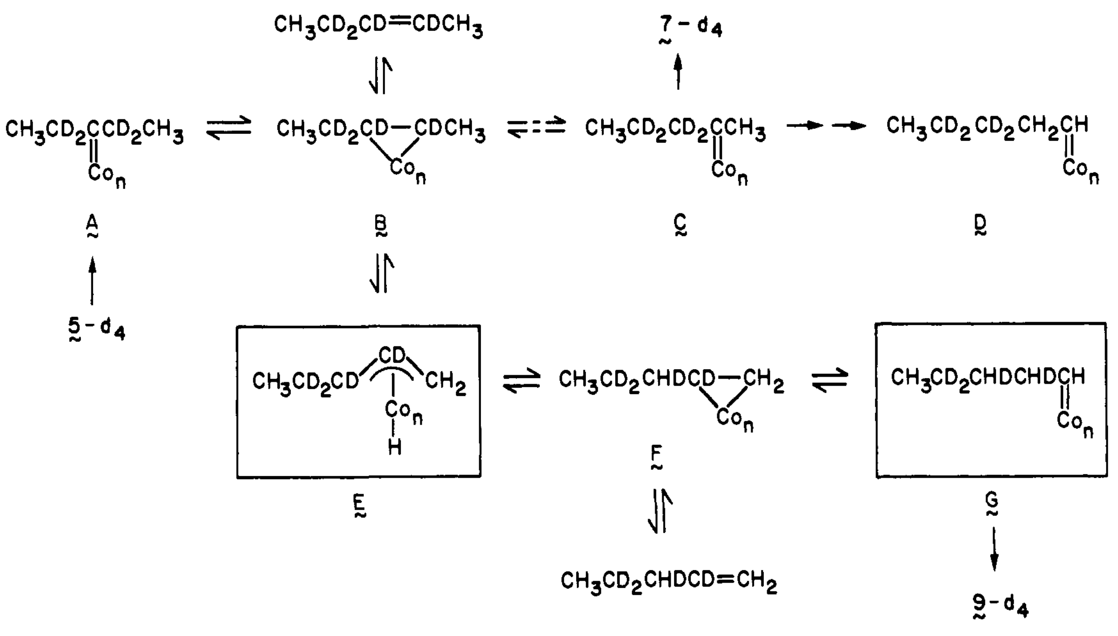


Because of this, further kinetic study appeared unprofitable, and we turned to isotope labeling experiments to probe the mechanism of the rearrangement. Labeled 3-pentylidene complex **5**-d_4 (≥99.5% deuterated at the α positions) was prepared by conversion of completely α-deuterated 3-pentanone to the corresponding diiodide followed by reaction with radical anion $Na[CpCo(CO)]_2$. A solution of this material was heated until NMR monitoring showed it had almost all reacted. The 1-pentylidene product **9** formed was then isolated by column chromatography and its ^1H NMR spectrum examined. This showed clean and specific conversion to the complex labeled as illustrated in Scheme VII.

In principle **9** could be formed by two successive one-carbon migrations of the metal fragment of the kind which must transform 2-propylidene **3** into 1-propylidene **4** (Scheme VI). However the labeling pattern of **9**-d_4 is not consistent with that sequence. Furthermore, the relative amounts of products formed and the approximate rates at which 3- and 2-pentylidene complexes **5** and **7** rearrange seem to discredit **7** as an important intermediate in the two-carbon migration from **5** to **9**.

In considering mechanisms which can be responsible for these migration reactions, a significant question is whether the dinuclear fragment remains intact during the rearrangement. The obvious crossover experiment is rendered useless, however, in light of the

Scheme VIII



earlier described exchange reactions (Scheme II) which occur at the same temperature and destroy the molecular integrity necessary for analysis of such experiments. The mechanism we propose (Scheme VIII) therefore accounts in general terms for the products and labeling results but does not specify whether these transformations occur in the coordination sphere of a mononuclear or dinuclear complex.

As shown in Scheme VIII, following loss of CO in **5**-d_4 to give intermediate A, we believe the next step involves migration of metal and a hydrogen atom in opposite directions (probably via a β-elimination/reductive elimination sequence), leading to π complex B. Given that one-carbon migration occurs in the closely related rearrangement of 2-propylidene complex **2**, it must be possible to do the same sort of process in reverse, leading to C. However, the labeling results rule out this direct 1,2 metal/H interchange as the *predominant* path in the formation of **9**, because that would lead to the (unobserved) labeling pattern shown in the scheme as D resulting directly from C. Instead, π complex B apparently more rapidly undergoes insertion into the methyl C–H bond, leading to π-allyl complex E. Reductive elimination leads to F, and then 1,2 metal/H interchange can occur, leading to G and the labeling pattern actually found in **9**.

The π complexes B and F are obvious precursors for the pentenes formed as major products in this reaction. However, given the often-demonstrated reversibility of π complex formation between low-valent metals and olefins, if this mechanism is correct it suggests that free olefin becomes reincorporated into the manifold of intermediates (i.e., there is a viable pathway for conversion of alkenes into dinuclear carbene complexes.[19] If the reentry rate is slow enough, it may be difficult to detect incorporation of olefin in the time required for complete rearrangement of a given internal alkylidene, but we decided to test this prediction. First, we carried out the thermolysis of deuterium-labeled 2-propylidene complex **2**-d_6 in the presence of unlabeled propene. Isolation of the 1-propylidene product **4** and mass spectral analysis showed that it did, in fact, contain a small but significant amount (ca. 6%) of alkylidene-h_6, without contamination by mixed H/D species which might have arisen by a hydrogen (rather than alkylidene ligand) exchange process. Second, we examined the rearrangement of unlabeled 3-pentylidene complex **5** in the presence of an excess of propene. In this experiment, small but detectable amounts (ca. 1%) of 1-propylidene complex **4** appeared in place of 1-pentylidene rearrangement product **9** formed in the absence of propene. This demonstrates, therefore, the possibility of alkene isomerization by a new pathway: formation of a π complex, hydrogen/metal rearrangement to give an alkylidene complex, hydrogen/metal rearrangement to a new π complex, and release of rearranged alkene from the metal. In our complexes, competing isomerization by the more conventional alkene-to-π-allyl complex mechanism is more rapid, but the alkylidene route may possibly be dominant in other systems.

Summary and Conclusions

A class of μ-alkylidene complexes of cobalt has been prepared and characterized. It appears that relatively subtle changes in substitution of the μ-CR_2 group have strong effects on the preferred structure of these compounds. The barriers associated with interconversions between different structures are low, resulting in high flexibility of the complex framework.

The thermal chemistry of these compounds is marked by autocatalytically initiated processes. Unimolecular loss of CO to open a coordination site is apparently less facile than removal of that ligand by unsaturated products of the reaction in a bimolecular step. This mode of activation has been observed in a few other cases[20] but is probably much more widespread in organometallic chemistry than presently recognized. These results emphasize 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.*

A ubiquitous question concerning the mechanism of these reactions is whether the reactive intermediates are really mononuclear species or whether the dimer framework is conserved during the conversion. This uncertainty is very much reminiscent of the earlier work on acyclic[21] and cyclic[4] cobalt dimers studied in our laboratory, and its clarification has to await further studies of reaction mechanisms of both mono- and dinuclear compounds in this series.

Finally, the "alkylidene walk" along a saturated hydrocarbon chain suggests an alternative mechanism for alkene isomerization as well as the demonstration that the conversion of alkenes into μ-alkylidene ligands is a viable process. This transformation may well be involved in olefin metathesis systems.

Experimental Section

General. ^1H NMR spectra were recorded on a Varian EM-390 spectrometer, or at 250, 200, or 180 MHz on spectrometers equipped with Cryomagnets Inc. magnets and Nicolet Model 1180 data collection systems. ^{13}C NMR spectra were recorded at 45 MHz on a spectrometer

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(21) (a) Schore, N. E.; llenda, C. S.; Bergman, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 7436; **1977**, *99*, 1781. (b) White, M. A.; Bergman, R. G. *J. Chem. Soc., Chem. Commun.* **1979**, *1056*; Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113.

equipped with a Bruker superconducting magnet and a Nicolet Corp. Fourier transform computer package. All high-field instruments were constructed by Rudi Nunlist in the UC Berkeley NMR laboratory. IR spectra were obtained on a Perkin-Elmer Model 283 infrared spectrophotometer. Analyses of the volatile products of decomposition reactions were performed on an analytical Perkin-Elmer 3920 gas chromatograph, connected to a Spectra Physics integrator, using a 20 ft × $^1/_8$ in. stainless steel column packed with 1% DBTCP on Chromosorb P. All manipulations involving organometallic compounds, including chromatographic separations, were carried out in a Vacuum Atmosphere inert atmosphere box under N_2, prescrubbed and continuously circulated through a purifier, unless indicated otherwise.

All solvents were purified by stirring over sodium benzophenone ketyl, followed by distillation under N_2. Hexane was purified by shaking with concentrated sulfuric acid containing 5% concentrated nitric acid, followed by washing with water, saturated sodium carbonate solution, and water again. After drying with $CaCl_2$, the hexane was dried with *n*-BuLi followed by distillation as mentioned above.

Elemental analyses were performed by the UC Berkeley College of Chemistry microanalytical laboratory. $CpCo(CO)_2$ was prepared according to published procedures[22] and reduced to the known Na[η^5CpCo(CO)]$_2$ with sodium amalgam.[6] $CpRh(CO)_2$ was prepared according to published procedures[23,24] from rhodium trichloride obtained on loan from Matthey Bishop, Inc. $CpCo(C_2H_4)_2$ was prepared by reaction of Cp_2Co with Li powder in the presence of ethylene.[7] Diiodomethane was obtained from Aldrich and thoroughly degassed before use. The higher *gem*-diiodoalkanes were prepared by the method of Pross and Sternhell,[25] i.e., treating the hydrazone of the corresponding ketone or aldehyde with iodine in the presence of base.[25] 1,1-Diiodopropane and 2,2-diiodopropane have been prepared by these authors and were identified by comparison of their ^{1}H NMR spectra with the reported values. The other diiodides exhibited the following ^{1}H NMR spectra in $CDCl_3$: 1,1-diiodopentane δ 5.13 (t, 1 H), 2.36 (m, 2 H), 1.40 (m, 4 H), 0.94 (m, 3 H); 2,2-diiodopentane 3.03 (s, 3 H), 2.15 (m, 2 H), 1.69 (m, 2 H), 1.06 (t, 3 H); 3,3-diiodopentane 2.28 (q, 4 H), 1.15 (t, 6 H); 1,1-diiodo-3,3-dimethylbutane 5.08 (t, 1 H), 3.85 (d, 2 H), 0.95 (s, 9 H). CD_2I_2 (99 atom % D) was obtained from Merck, Sharp & Dohme and degassed before use. C_2H_4 and C_3H_6 were obtained from Matheson. C_2F_4 was obtained from PCR Research Chemicals. Before use these gases were condensed in a trap and oxygen removed by evacuation.

(μ-Methylene)bis((η^5-cyclopentadienyl)carbonylcobalt) (1). In the drybox 0.17 mL of diiodomethane (0.515 g, 2.11 mmol) was added all at once to a stirred suspension of 1.0 g of crude Na[CpCo(CO)]$_2$ (2.14 mmol)[6b] in 20 mL of THF. The pale green suspension immediately turned blue green (the color[21a] of $Cp_2Co_2(CO)_2$), and then dark red. The IR spectrum at this time showed CO stretches at 2020 and 1960 cm^{-1} ($CpCo(CO)_2$ and a new material). Hexane (40 mL) was added to precipitate NaI and the mixture was filtered. After evaporation of the solvent the residue was chromatographed on neutral alumina II, eluting first with hexane and then with hexane/benzene. The second fraction (dark red) was collected and the solvent evaporated under reduced pressure. The solid residue was recrystallized once from pentane to yield 330 mg of analytically pure **1** (48% yield): mp 68 °C; IR (THF) 1966 (w), 1957 (br s), 1924 (w) cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.90 (s, 2 H), 4.64 (s, 10 H, trans), 7.80 (s, 1 H), 6.22 (s, 1 H), 4.52 (s, 10 H, cis); ^{13}C NMR (C_6D_6) δ 207.8, 104.4, 86.5 (trans), 85.2 (cis); MS, (15 ev), *m/e* 318 (M$^+$). Anal. Calcd for $C_{13}H_{12}Co_2O_2$: 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.

(μ-(2-Propylidene))bis((η^5-cyclopentadienyl)carbonylcobalt) (2) and (μ-(2-Propylidene))(μ-carbonyl)bis((η^5-cyclopentadienyl)cobalt) (3). 2,2-Diiodopropane (0.2 mL, 1.74 mmol) was added all at once to a suspension of 1.0 g of Na[CpCo(CO)]$_2$ (2.14 mmol) in 15 mL of THF. The solution immediately turned dark blue green, then purple and finally brown (after ca. 15 min). Hexane (30 mL) was added and the precipitated NaI filtered off. The solvent was evaporated and the solid residue chromatographed on neutral alumina II, eluting first with hexane to afford a first fraction of $CpCo(CO)_2$. Further elution with hexane/benzene (10:1) yielded a brown fraction, and finally elution with hexane/benzene (1:1) afforded a very translucent purple fraction. The solvent from the two latter fraction was evaporated under reduced pressure and both materials recrystallized once from hexane. The dark brown fraction yielded a total of 150 mg of analytically pure **2** (20% yield): mp 97–98 °C; IR (toluene) 1937 (s), 1853 (w), 1813 (s) cm^{-1}; IR (KBr) 1847 (s), 1796 (v s) cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.54 (s, 10 H), 2.18 (s, 6 H); MS, (20 eV) *m/e* 346 (M$^+$). Anal. Calcd for $C_{15}H_{16}Co_2O_2$: C, 52.05; H, 4.66; Co, 34.1. Found: C, 52.29; H, 4.62; Co, 33.8.

The purple fraction afforded 15 mg of dark red crystals of **3** (2% yield): mp 65 °C dec; IR (C_6D_6) 1797 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.11 (s, 10 H), 3.24 (s, 6 H); MS, (20 eV) *m/e* 318 (M$^+$). Anal. Calcd for $C_{14}H_{16}Co_2O$: C, 52.85; H, 5.07; Co, 37.1. Found: C, 52.93; H, 5.02; Co, 38.0.

(μ-(1-Propylidene))bis((η^5-cyclopentadienyl)carbonylcobalt) (4). 1,1-Diiodopropane (0.6 mL, 5.2 mmol) was added all at once to a stirred suspension of 1.08 g of Na[CpCoC(CO)]$_2$ in 20 mL of THF. The color of the solution changed immediately to blue green and then to dark red. Hexane (40 mL) was added and the precipitated NaI filtered off. The solvent was evaporated and the residue was chromatographed on neutral alumina II, eluting with hexane. The second fraction (dark red) was collected and the solvent evaporated under reduced pressure. The residue was crystallized from pentane to afford 390 mg of dark red crystals of **4** (49% yield): mp 50–51 °C; IR (C_6D_6) 1990 (wk), 1945 (s) cm^{-1}; ^{1}H NMR (C_6D_6) δ 8.03 (t, 1 H, *J* = 7.9 Hz), 4.64 (s, 10 H), 2.44 (m, 2 H), 1.23 (t, 3 H, *J* = 7.2 Hz) (trans, 95%), 9.17 (m), 4.48 (s) (cis, 5%); MS, (20 eV) *m/e* 346 (M$^+$). Anal. Calcd for $C_{15}H_{16}Co_2O_2$: C, 52.05; H, 4.66; Co, 34.1. Found: C, 52.26; H, 4.73; Co, 34.1.

(μ-(3-Pentylidene))bis((η^5-cyclopentadienyl)carbonylcobalt) (5). 3,3-Diiodopentane (0.4 mL, ca. 2.7 mmol) was added all at once to a stirred suspension of 1.1 g of Na[CpCo(CO)]$_2$ (2.35 mmol) in 20 mL of THF. After the solution had turned brown (approximately 15 min), 40 mL of hexane was added and the solution filtered to remove NaI. The solvent was evaporated and the solid residue chromatographed on neutral alumina II, eluting first with hexane and then with benzene. The second (brown) and third (purple) fraction were combined. This solution was then exposed to 1 atm of CO to convert all the **6** into **5**. The solvent was then removed under reduced pressure and the solid recrystallized from Et_2O to yield a first crop of 120 mg of pure **5**. The solvent was removed from the mother liquor and the residue recrystallized from hexamethyldisiloxane to yield a second crop of 40 mg of pure **5** (21% combined yield): mp 77.5–80.5 °C; IR (toluene) 1938 (s), 1856 (v wk), 1813 (wk) cm^{-1}; IR (KBr) 1926 (s), 1810 (v wk) cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.62 (s, 10 H), 2.37 (m, 4 H), 1.09 (t, 6 H, *J* = 7.3 Hz); MS, (20 eV) *m/e* 374 (M$^+$). Anal. Calcd for $C_{17}H_{20}Co_2O_2$: C, 54.56; H, 5.39; Co, 31.5. Found: C, 54.80; H, 5.39; Co, 31.3.

(μ-(3-Pentylidene))-(μ-carbonyl)bis((η^5-cyclopentadienyl)cobalt) (6). This preparation was identical with the one for **5** (see above) except that the third (purple) fraction was collected separately. Removal of solvent and one recrystallization from pentane afforded 13 mg of pure **6** (2% yield): mp 96 °C dec; IR (C_6D_6) 1795 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.12 (s, 10 H), 3.90 (m, 4 H), 0.07 (t, 6 H, *J* = 7.3 Hz); MS, (20 eV) *m/e* 346 (M$^+$). Anal. Calcd for $C_{16}H_{20}Co_2O$: C, 55.51; H, 5.82; Co, 34.0. Found: C, 55.70; H, 5.77; Co, 33.2.

(μ-(2-Pentylidene))bis((η^5-cyclopentadienyl)carbonylcobalt) (7). 2,2-Diiodopentane (1.0 g, ca. 3.1 mmol) was added all at once to a stirred suspension of 1.5 g of Na[CpCo(CO)]$_2$ (3.6 mmol) in 20 mL of THF. After the color had changed to brown, 50 mL of hexane was added and the precipitated NaI filtered off. The solvent was evaporated and the residue chromatographed on neutral alumina II, eluting first with hexane and then with benzene. The second (brown) and third (purple) fractions were combined and this solution exposed to 1 atm of CO. The solvent was then evaporated under reduced pressure and the residue recrystallized once from pentane to yield 170 mg of pure **7** (14% yield): mp 58–61 °C; IR (toluene) 1936 (s), 1856 (wk), 1811 (m) cm^{-1}; IR (KBr) 1938 (s), 1810 (v wk) cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.60 (s, 10 H), 2.43 (m, 2 H), 2.17 (s, 3 H), 1.54 (m, 2 H), 0.99 (t, 3 H, *J* = 7.3 Hz); MS, (20 eV) *m/e* 374 (M$^+$). Anal. Calcd for $C_{17}H_{20}Co_2O_2$: C, 54.56; H, 5.39; Co, 31.5. Found: C, 54.90; H, 5.37; Co, 31.3.

(μ-(2-Pentylidene))(μ-carbonyl)bis((η^5-cyclopentadienyl)cobalt) (8). A mixture of 38 mg of **7** (0.102 mmol) and 20 mg of $CpCo(C_2H_4)_2$[7] was dissolved in 6 mL of hexane and stirred at room temperature for 3 h; at this point the solution appeared purple. The solution was chromatographed on alumina II, eluting with benzene. The purple fraction was collected and the solvent evaporated. One recrystallization of the residue from hexane yielded 18 mg of pure **8** (51% yield): mp 70 °C dec; IR (toluene) 1796 cm^{-1}; ^{1}H NMR (toluene-d_8) δ 4.10 (s, 10 H) 3.81 (m, 2 H), 3.26 (s, 3 H), 0.91 (t, 3 H, *J* = 7.4 Hz), −0.16 (m, 2 H); MS, (20 eV) *m/e* 346 (M$^+$). Anal. Calcd for $C_{16}H_{20}Co_2O$: C, 55.51; H, 5.82; Co, 34.0. Found: C, 55.65; H, 5.88; Co, 34.2.

(μ-(1-Pentylidene))bis((η^5-cyclopentadienyl)carbonylcobalt) (9). 1,1-Diiodopentane (0.7 g, 2.16 mmol) was added all at once to a stirred suspension of 1.0 g of Na[CpCo(CO)]$_2$ (2.14 mmol) in 20 mL of THF. After the solution had turned red, 40 mL of hexane was added and the solution filtered. The solvent was evaporated and the residue chromatographed on neutral alumina II, eluting with hexane. The dark red

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

(23) Fischer, E. O.; Bittler, K. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1961**, *16B*, 225.

(24) McCleverty, J. A.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

(25) Pross, A.; Sternhell, S. *Aust. J. Chem.* **1970**, *23*, 988.

fraction was collected and the solvent removed under reduced pressure. One recrystallization of the residue from pentane afforded 295 mg of analytically pure **9** (38% yield): mp 59.5–61.5 °C; IR (toluene) 1992 (wk), 1948 (s) cm^{-1}; ^{1}H NMR (C_6D_6) δ 8.13 (t, 1 H, J = 7.9 Hz), 4.66 (s, 10 H), 2.51 (m, 2 H) 1.55 (m, 4 H), 1.04 (t, 3 H, J = 7.1 Hz) (trans, 96%), 9.28 (m), 4.50 (s) (cis, 4%); MS, (20 eV) m/e 374 (M$^+$). Anal. Calcd for $C_{17}H_{20}Co_2O_2$: C, 54.56; H, 5.39; Co, 31.5. Found: C, 54.75; H, 5.33; Co, 31.3.

(μ-(1-(3,3-Dimethyl)butylidene))bis((η^5-cyclopentadienyl)carbonylcobalt) (10). 1,1-Diiodo-3,3-dimethylbutane (0.7 g) (containing a small vinyl/iodide impurity, presumably 1-iodo-3,3-dimethylbutene^{25}) was added all at once to a stirred suspension of 1.0 g of Na[CpCo(CO)]$_2$ (2.14 mmol) in 20 mL of THF. The solution turned brown. Hexane (40 mL) was added and the precipitated NaI filtered off. Removal of solvent and chromatography on neutral alumina II afforded a dark brown material which was recrystallized once from pentane to yield 90 mg of pure **10** (11% yield): mp 83–85 °C; IR (toluene) 1991 (m), 1950 (s), 1912 (wk) cm^{-1}; IR (KBr) 1945 cm^{-1}; ^{1}H NMR (CD_3COCD_3) δ 8.28 (t, 1 H, J = 7.5 Hz), 4.95 (s, 10 H), 2.52 (d, 2 H), 1.00 (s) (trans, 80%), 9.75 (t, 1 H, J = 7.8 Hz), 5.06 (s, 10 H), 2.28 (d, 2 H); 1.00 (s) (cis, 20%). Anal. Calcd for $C_{18}H_{22}Co_2O_2$: C, 55.69; H, 5.71; Co, 30.4. Found: C, 55.86; H, 5.82; Co, 30.2.

2-d_6. 2,2-Diiodopropane-d_6 (0.6 g, 2.0 mmol) (prepared from acetone-d_6) was added all at once to a stirred suspension of 1.03 g of Na[CpCo(CO)]$_2$ (2.20 mmol) in 20 mL of THF. Hexane (40 mL) was added and the solution filtered. Removal of solvent and chromatography on alumina II afforded a brown and a purple fraction which were combined and exposed to 1 atm of CO. Evaporation of the solvent and recrystallization from pentane yielded 150 mg of pure **2**-d_6 (19% yield): ^{1}H NMR (C_6D_6) δ 4.54 (s, 10 H); MS, (20 eV) m/e 352 (M$^+$); d$_6$, 95.6%, d$_5$, 4.4%.

5-d_4. 2,2,4,4-Tetradeuterio-3,3-diiodopentane (0.8 g, 2.44 mmol) (prepared from 3-pentanone,^{25} after three cycles of base-catalyzed H/D exchange at the α positions;^{26} no α hydrogen detected in the ^{1}H NMR spectrum) was added to a suspension of 1.01 g of Na[CpCo(CO)]$_2$ (2.16 mmol) in 20 mL of THF. After 30 min, 40 mL of hexane was added and the precipitated NaI filtered off. The solvent was evaporated and the residue chromatographed on alumina II. The second (brown) and third (purple) fraction were combined and exposed to 1 atm of CO. Solvent removal and recrystallization from pentane yielded 141 mg of pure **5**-d_4 (18% yield): ^{1}H NMR (C_6D_6) δ 4.62 (s, 10 H), 1.07 (s, br, 6 H); MS, (20 eV) m/e 378 (M$^+$), 377 not detected.

1-d_2. CD_2I_2 (0.3 mL, 3.7 mmol) was added to a suspension of 1.0 g of Na[CpCo(CO)]$_2$ (2.14 mmol) in 20 mL of THF and this mixture was stirred for 30 min. The NaI formed was precipitated with 40 mL of hexane. The solvent was evaporated and the residue chromatographed on neutral alumina II, eluting first with hexane and then with benzene. The second (dark red) fraction was collected and the solvent removed under reduced pressure. One recrystallization from hexane at −60 °C yielded 348 mg of pure **1**-d_2 (51% yield): ^{1}H NMR (C_6D_6) δ 4.64 (s, 10 H); MS, (15 eV) m/e 320 (M$^+$); d$_2$; 98.7%, d$_1$, 1.3%.

(μ-Methylene)bis(η^5-(methylcyclopentadienyl)carbonylcobalt) (11). MeCpCo(CO)$_2$ (10 g, 51.5 mmol) was added to a mixture of 20 mL of THF and 44 mL of 0.75% sodium amalgam and stirred for 1 h. This mixture was extracted with 2 200-mL portions of THF, and the combined extracts were filtered and evaporated to dryness to leave 11.0 g of a green air-sensitive solid, presumably a mixture of NaCo(CO)$_4$ [IR (THF) 1890 (br, v s), 1860 (m)] and (Na[MeCpCo(CO)]$_2$ [1740 (m), 1690 (m), 1655 (s) cm^{-1}].

Diiodomethane (0.3 mL, 3.7 mmol) was added to a stirred suspension of 1.0 g of that material. After 30 min, 40 mL of hexane was added to precipitate the NaI. Filtration and removal of solvent yielded a solid residue which was chromatographed on neutral alumina II, using hexane as eluent. The second (dark red) fraction was collected and the hexane evaporated under reduced pressure. One recrystallization of this material from hexane afforded 250 mg of analytically pure **11** (0.72 mmol, 31% yield based on MeCpCo(CO)$_2$): mp 57.5–58.5 °C; IR (toluene) 1950 cm^{-1}; IR (KBr) 1978 (m), 1938 (s) cm^{-1}; ^{1}H NMR (C_6D_6) δ 6.80 (s, 2 H), 4.58–4.57 (m, 8 H), 1.75 (s, 6 H); MS, (20 eV) m/e 346 (M$^+$). Anal. Calcd for $C_{15}H_{16}Co_2O_2$: C, 52.05; H, 4.66; Co, 34.05. Found: C, 52.44; H, 4.81; Co, 33.2.

Reaction of 3 with CO. **3** (5 mg) was placed in a 50-mL flask and dissolved in 3 mL of hexane. The flask was fitted with a vacuum stopcock and evacuated after freezing this solution in liquid nitrogen. CO (at 570 torr) was admitted to the thawed solution under stirring. The solution turned brown immediately. The hexane was then removed under reduced pressure and the solid residue determined to be **2** by IR spectroscopy (solution in hexane: 1947 (s), 1850 (w), 1823 (s) cm^{-1}) and MS [(20 eV), m/e 346 (M$^+$)].

Variable-Temperature NMR Study of 10. An NMR tube was charged with ca. 3 mg of **10** and 0.5 mL of acetone-d_6, vacuum transferred by using a vacuum line. CO was then admitted to the tube (at ca. 500 torr, to inhibit the thermal decomposition of **10**) and the tube sealed off. The tube was then placed in the probe of a 180-MHz ^{1}H NMR spectrometer, and spectra were taken in the temperature range from 25 to 70 °C. The Cp resonances of the two isomers were used to determine the coalescence temperature of 55 °C. This was used to calculate the free energies of activation by a graphic method described by Shanan-Atidi and Bar-Eli.^{13}

Reaction of 1 with 11. An NMR tube was charged with ca. 3 mg of **1** (0.009 mmol) and ca. 5 mg of **11** (0.014 mmol), and 0.5 mL of benzene-d_6 was vacuum transferred in. The tube was sealed under vacuum and an initial spectrum taken which showed resonances consistent with a mixture of **1** and **11**. The tube was then immersed in an oil bath kept at 62 °C and the progress of the reaction monitored sporadically by ^{1}H NMR spectroscopy. Over the course of 2 days new resonances consistent with the mixed dimer **12** grew in and finally reached a nearly statistical ratio (1:2.3:1.55) [^{1}H NMR for **12**; δ 6.85 (s, 2 H) 4.66 (s, 5 H), 4.55 (m, 4 H), 1.73 (s, 3 H)]. Small amounts of CpCo(CO)$_2$ and MeCpCo(CO)$_2$ were also formed. The tube was then opened and the mixture of methylene dimers reisolated by column chromatography. The MS of this material showed parent ions for all three dimers (20 eV: m/e 346, 332, 318). The HRMS on the m/e 332 peak was consistent with structure **12** (calcd for $C_{14}H_{14}O_2Co_2$; 331.9658; found, 331.9659).

Reaction of 1 with CpRh(CO)$_2$. A glass vessel with vacuum stopcock was charged with 120 mg of CpRh(CO)$_2$ (0.54 mmol) and 85 mg of **1** (0.27 mmol). Benzene (3 mL) was added and this mixture heated to 63 °C for 2.5 days under stirring. The resulting mixture was poured on a column (2 × 75 cm, neutral alumina II) and eluted with hexane/benzene 3:1. The first fraction (yellow) was a mixture of CpCo(CO)$_2$ and CpRh(CO)$_2$ (identified by TLC). The second fraction (red) contained **1** (identified by IR). The third fraction was brown and left a dark solid upon removal of the solvent. One recrystallization of this material from hexane yielded 37 mg of pure **13** (38% yield based on **1**): mp 67.5 °C; IR (toluene) 1977 (vw), 1962 (br, s) cm^{-1}; ^{1}H NMR (acetone-d_6) δ 6.84 (s, 2 H) 5.37 (d, 5 H, J_{H-Rh} = 0.62 Hz), 5.07 (s, 5 H) (trans isomer, 88%), 7.70 (q, 1 H, J_{H-Rh} = 3.24 Hz, J_{H-H} = 0.34 Hz), 6.17 (q, 1 H, J_{H-Rh} = 1.13 Hz), 5.52 (d, 5 H, J_{H-Rh} = 0.52 Hz), 5.14 (s, 5 H) (cis isomer, 12%); MS, (15 eV) m/e 362 (M$^+$). Anal. Calcd for $C_{13}H_{12}O_2CoRh$: C, 43.12; H, 3.34; Co, 16.3; M_r 361.9215. Found: C, 42.79; H, 3.35; Co, 16.0; M_r 361.9227. Further elution yielded a fourth (orange) fraction. The solvent was evaporated and the residue recrystallized from hexane to yield 25 mg of pure **14** (23% yield based on **1**): ^{1}H NMR (acetone-d_6) δ 7.05 (q, 2 H, J_{H-Rh} = 0.54 Hz), 5.47 (t, 10 H, J_{H-Rh} = 0.29 Hz) (trans isomer, 87%), 7.73 (t, 1 H, J_{H-Rh} = 2.92 Hz), 6.53 (s, br, 1 H), 5.54 (t, 10 H, J_{H-Rh} = 0.34 Hz) (cis isomer, 13%) (lit.^{14} ^{1}H NMR 7.07 (q, 2 H, J_{H-Rh} = 0.55 Hz), 5.48 (t, 10 H, J_{H-Rh} = 0.31 Hz); MS, (20 eV) m/e 406 (M$^+$); HRMS calcd for $C_{13}H_{12}O_2Rh_2$, M_r 405.8928; found, M_r 405.8945.

Variable-Temperature NMR Study of 13. An NMR tube was charged with ca. 4 mg of **13**, and 0.5 mL of acetone-d_6 was vacuum transferred in. C_2F_4 (0.044 mmol) was then condensed into the tube with a glass bulb of known volume and a pressure gauge (the C_2F_4 was added to inhibit the thermal decomposition of **13** at higher temperatures; see Results and Discussion). Following that the tube was sealed under vacuum. The tube was placed in the probe of a ^{1}H NMR spectrometer (180 MHz for ^{1}H), and spectra were taken in the temperature range from −70 to +80 °C. For the cis–trans isomerization the Cp resonances of the Cp ligand on Co were used to determine the coalescence temperature of 50 °C and the free energy of activation was calculated by using a graphic method.^{13} For the low-temperature equilibration of the μ-CH$_2$ protons of *trans*-**13**, the free energy of activation was determined by using the exchange rate at the coalescence temperature (−10 °C) and the Eyring equation.

Reaction of 1 with C_2H_4. An NMR tube was charged with 15 mg of **1**, and 0.5 mL of benzene-d_6 was vacuum transferred in. C_2H_4 (0.384 mmol) was then condensed in and the tube sealed under vacuum (this corresponds to ca. 4.5 atm of C_2H_4 in the tube at room temperature). The tube was immersed in a $CHCl_3$ bath kept at gentle reflux (62 °C) and the progress of the reaction periodically monitored by ^{1}H NMR spectroscopy. After 15 h all the **1** had reacted and its resonances were replaced by those of propene and one major organometallic product formed in ca. 95% yield (NMR). On the basis of its ^{1}H NMR spectrum (δ 4.41 (s, 5 H), 2.4 (br, 4 H) at 90 MHz and 4.41 (s, 5 H), 2.55 (br, 2 H), 2.15 (br, 2 H) at 250 MHz) and comparison to independently synthesized material (see below), we assign to it the structure CpCo(CO)(C_2H_4). This material is stable in solution only under ethylene; attempts at isolation were unsuccessful. The yield of propene was determined in an independent experiment. A small glass vessel with a vacuum stopcock was charged with 15.5 mg of **1** and 1.0 mL of benzene.

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(26) Shiner, V. J., Jr.; Cross, S. *J. Am. Chem. Soc.* **1957**, *79*, 3599.

C_2H_4 (0.521 mmol) was condensed in and the vessel closed under vacuum. This solution was heated to 70 °C for 20 h. The volatile products were isolated with a Toepler pump and analyzed quantitatively by gas chromatography. The amount of C_2H_4 present was corrected for the fraction converted to propene and used as internal standard. Yields: propene, 65%; methane, 3%. No cyclopropane was detected.

(η^5-Cyclopentadienyl)(carbonyl)(ethylene)cobalt (17). An NMR tube was charged with 10 mg of $[CpCo(CO)]_2$, and 0.5 mL of benzene-d_6 was vacuum transferred in. C_2H_4 (0.288 mmol) was condensed in and the tube sealed under vacuum. The tube was placed in the probe of a 250-MHz NMR spectrometer kept at 30 °C and the progress of the reaction monitored by ^1H NMR spectroscopy. The resonance of the starting material at δ 4.39 was rapidly replaced by the resonances of $CpCo(CO)_2$ (4.40 ppm) and $CpCo(C_2H_4)_2$ (4.29 (s, 5 H), 2.55 (m, 4 H), 0.68 (m, 4 H) ppm) which in turn were slowly replaced by the resonances of **17**: δ 4.41 (s, 5 H) 2.55 (br, 2 H) 2.15 (br, 2 H). The tube was warmed to 45 °C for 20 h to drive the reaction to completion. After this **17** accounted for 80% of the Cp-containing products. The tube was then opened and an IR spectrum recorded as quickly as possible. This exhibited a strong CO stretching frequency at 1974 cm^{-1}. These spectral data are consistent with the structure $CpCo(CO)(C_2H_4)$.

Reaction of 1 with C_2H_4 in the Presence of C_2F_4. An NMR tube was charged with 18 mg of **1**, and 0.5 mL of benzene-d_6 was vacuum transferred in. Both C_2H_4 and C_2F_4 (0.332 mmol each) were then condensed in and the tube sealed under vacuum. The tube was then heated to 62 °C and the progress of the reaction monitored periodically by ^1H NMR spectroscopy. Even after 214 hours the reaction was only 60% complete (without C_2F_4 the reaction is complete after 15 h). The ^{19}F NMR spectrum showed no new resonance besides that of C_2F_4. Propene was the major organic product, and only $CpCo(CO)_2$ (no $CpCo(CO)(C_2H_4)$) was detected.

Reaction of 1 with C_2H_4 in the Presence of CO. An NMR tube was charged with 25 mg of **1**, and 0.5 mL of benzene-d_6 was vacuum transferred in. C_2H_4 (0.405 mmol) and CO (0.203 mmol) were then condensed in and the tube was sealed. The tube was heated to 62 °C and the progress of the reaction monitored by ^1H NMR spectroscopy. $CpCo(CO)_2$ was the only tractable product of this reaction; i.e., no propene or $CpCo(CO)(C_2H_4)$ were formed. The reaction is slower than the reaction of **1** with C_2H_4 (i.e., the half-life is ca. 20 h).

Reaction of 1 with C_2H_4 in the Presence of $[CpCo(CO)]_2$ or $CpCo(C_2H_4)_2$. Two NMR tubes were prepared containing (a) 10 mg of **1**, 10 mg of $[CpCo(CO)]_2$, 0.5 mL of benzene-d_6, and 0.384 mmol of C_2H_4, and (b) 10 mg of **1**, 10 mg of $CpCo(C_2H_4)_2$, 0.5 mL of benzene-d_6, and 0.384 mmol of C_2H_4. Each tube was placed in the probe of an NMR spectrometer kept at 62 °C and the progress of the reaction monitored by ^1H NMR spectroscopy (see Figure 5). These reactions exhibited no initiation period. Both were observed by NMR spectroscopy to produce propene and $CpCo(CO)(C_2H_4)$ as major products.

Rearrangement of 2. An NMR tube was charged with 10 mg of **2**, and 0.5 mL of benzene-d_6 was vacuum transferred in. The tube was sealed under vacuum and then heated to 80 °C. ^1H NMR spectra were taken periodically. After 10 h the resonances of **2** had decreased and the resonances of **3** and propene had grown in. There was also a new set of resonances which was assigned to **4** by comparison with the NMR spectrum of material made by independent synthesis from Na[CpCoCO] and 1,1-diiodopropane. The yield of this material was 7% (NMR) at its maximum. The absolute yield of propene was determined in an independent experiment. A small glass vessel with vacuum stopcock was charged with 22.6 mg of **2** (0.0653 mmol) and 4 mL of benzene. The solution was degassed and then heated to 80 °C for 16 h. The volatile products were isolated by using a Toepler pump and quantitated by gas chromatography by using a subsequentially added known amount of C_2H_4 as standard. Yield of propene, 79%.

Rearrangement of 5. An NMR tube was charged with 10 mg of **5**, 0.5 mL of benzene-d_6 was transferred in, and the tube was sealed under vacuum. The tube was then heated to 75 °C and the reaction monitored periodically by ^1H NMR spectroscopy. After 3 h all the **5** had reacted and the complex spectrum was consistent with the presence of small amounts of **6**, **8**, and **9** (comparisons made with independently prepared complexes). At earlier stages of the reaction traces of **7** were also observed. Also present were several isomeric pentenes, cobalt-containing clusters, and $CpCO(CO)_2$. The yields of these products at their respective maximum concentrations were as follows: **7**, 2%; **8**, 3%; **9**, 12% (NMR).

Rearrangement of 7. An NMR tube was charged with 10 mg of **7**, 0.4 mL of benzene-d_6 was vacuum transferred in, and the tube was sealed under vacuum. The tube was then heated to 62 °C and the reaction monitored periodically by ^1H NMR spectroscopy. The resonances of **7** were slowly replaced by the usual decomposition products (pentenes, $CpCo(CO)_2$, clusters) as well as **8** and **9**. The maximum concentration of **9** was reached after 6.5 h and corresponded to a yield of 3% (NMR). No trace of **5** or **6** was detected by NMR.

Table II. Crystal Data and Data Collection Details

mol formula	$C_{15}H_{16}Co_2O_2$
M_r	346.16
a, b, c, Å[a]	8.0529 (23), 9.5160 (28), 9.9330 (45)
α, β, γ, deg	69.678 (31), 74.769 (30), 83.704 (23)
V, Å^3	688.6 (5)
space group	$P1$
Z	2
d(calcd), g cm^{-3}	1.669
μ(calcd), cm^{-1}	23.99
size, mm	0.15 × 0.17 × 0.18
radiation	Mo Kα (λ = 0.71073 Å)
method	θ–2θ
scan speed, deg s^{-1} t	0.69–6.7
scan width	$\theta = 0.55 + 0.347 \tan \theta$
background	measured over an additional 0.25 (θ) added to each end of the scan
standard	3 reflctns measured every 2 h, no decay in intensity
2θ range, deg	3–45
no. of reflctns collected	1796
no. of unique reflctns	1796

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 24 reflections with 2θ near 28°.

Thermal Decomposition of 9. An NMR tube was charged with 10 mg of **9** and 0.5 mL of benzene-d_6 and the tube sealed. The tube was heated to 60 °C and the reaction monitored by NMR spectroscopy. After 1 h the reaction had progressed to ca. 30% completion. Only pentenes and organometallic decomposition products (i.e., $CpCO(CO)_2$, clusters) were found. No indication of any rearranged alkylidene dimers was detected. After 7 h the reaction was complete. Again there was no indication of any **5**, **6**, **7**, or **8**.

Kinetics of the Rearrangement of 5 and 6. Two NMR tubes were prepared with (a) 12 mg of **5**, 3 mg of Cp_2Fe (as internal standard), and 0.5 mL of toluene-d_8, and (b) 10 mg of **6**, 3 mg of Cp_2Fe, and 0.5 mL of toluene-d_8. These tubes were placed in the probe of a 200-MHz ^1H NMR spectrometer maintained at 60 °C. Spectra were taken at 10-min intervals and the resonances of **5** and **6** integrated against Cp_2Fe. The data plotted according to first-order kinetics are shown in Figure 6.

Rearrangement of 5-d_4. An NMR tube was charged with 12 mg of **5**-d_4, 0.4 mL of benzene-d_6 was vacuum transferred in, and the tube was sealed under vacuum. After 3 h at 75 °C and 1 h at 65 °C, the ^1H NMR spectrum indicated that almost all **5**-d_4 had reacted. The tube was then opened and the contents chromatographed to reisolate the fraction containing the saturated μ-alkylidene dimers. This fraction was redissolved in benzene-d_6 and an NMR spectrum recorded. The labeled **9** formed exhibited the following ^1H NMR spectrum (benzene-d_6): δ 8.13 (d, br, 1 H), 4.66 (s, 10 H), 2.49 (t, br, 1 H), 1.89 (s, br, 1 H), 1.05 (s, br, 3 H). The spectrum also indicated the presence of some unreacted **5**-d_4 (ca. 15% of the sample). No **7**-d_4 was detected.

Rearrangement of 2-d_6 in the Presence of Propene. An NMR tube was charged with a solution of 10 mg of **2**-d_6 in 0.4 mL of benzene-d_6. Propene (0.377 mmol) was condensed in and the tube sealed under vacuum. This tube was heated to 90 °C for 2.5 h. The NMR spectrum showed that all **2**-d_6 had reacted and there was no indication that any **4**-d_0 formed. The tube was opened and the contents chromatographed. The fraction containing the saturated μ-alkylidene dimers was isolated and submitted for MS (20 eV); m/e 352 (M^+, **4**-d_6, 94%), 346 (M^+, **4**-d_0, 6%). No ions with intermediate m/e values were detected.

Rearrangement of 5 in the Presence of Propene. A thick-walled NMR tube was charged with 15 mg of **5**, and 0.5 mL of benzene-d_6 was vacuum transferred in. Propene (0.681 mmol) was condensed in (corresponding to ca. 10 atm in the tube at room temperature) and the tube sealed. This tube was then heated to 65 °C and the reaction monitored by ^1H NMR spectroscopy. After ca. 2 h the ^1H NMR spectrum indicated the presence of **4** in ca. 1% yield (on the basis of chemical shift of the μ-alkylidene protons). No **9** was detected at any time during the reaction. Further heating led to decomposition of the **4** formed.

Crystal and Molecular Structure Determination of 11. Well-formed shiny black crystals of **11** were obtained by sublimation under high vacuum. Crystals were mounted in thin-wall glass capillaries in air and the capillaries were flame sealed. Preliminary precession photographs indicated triclinic ($P\bar{1}$) Laue symmetry and showed that many of the

Table III. Positional and Thermal Parameters and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Co1	0.29404 (4)	0.28470 (3)	−0.22804 (3)	0.01009 (5)	0.00930 (4)	0.00705 (3)	−0.00158 (7)	−0.00475 (6)	−0.00618 (5)
Co2	0.20504 (4)	0.26422 (3)	0.03852 (3)	0.00991 (5)	0.00822 (3)	0.00669 (3)	−0.00001 (7)	−0.00551 (6)	−0.00493 (5)
O1	0.6489 (2)	0.2876 (2)	−0.2279 (2)	0.0103 (3)	0.0267 (3)	0.0181 (2)	−0.0027 (5)	−0.0071 (4)	−0.0199 (4)
O2	−0.1474 (2)	0.2344 (2)	0.0444 (2)	0.0110 (3)	0.0226 (3)	0.0165 (2)	−0.0040 (5)	−0.0071 (4)	−0.0146 (4)
C1	0.5043 (3)	0.2840 (3)	−0.2225 (2)	0.0150 (4)	0.0130 (3)	0.0085 (2)	−0.0007 (6)	−0.0047 (5)	−0.0094 (4)
C2	−0.0045 (3)	0.2437 (3)	0.0386 (2)	0.0140 (4)	0.0117 (3)	0.0075 (2)	−0.0009 (6)	−0.0060 (5)	−0.0058 (4)
C3	0.2319 (3)	0.4376 (3)	−0.1368 (2)	0.0170 (4)	0.0089 (3)	0.0087 (2)	0.0007 (6)	−0.0085 (5)	−0.0061 (4)
C11	0.2627 (3)	0.1131 (3)	−0.3088 (2)	0.0186 (4)	0.0119 (3)	0.0109 (2)	−0.0019 (6)	−0.0093 (5)	−0.0134 (4)
C12	0.1028 (3)	0.1592 (3)	−0.2434 (2)	0.0147 (4)	0.0156 (3)	0.0113 (3)	−0.0115 (6)	−0.0047 (5)	−0.0137 (4)
C13	0.0815 (3)	0.3125 (3)	−0.3166 (2)	0.0118 (4)	0.0191 (4)	0.0141 (3)	0.0050 (6)	−0.0129 (5)	−0.0190 (5)
C14	0.2298 (3)	0.3615 (3)	−0.4308 (2)	0.0188 (4)	0.0127 (3)	0.0089 (2)	0.0012 (6)	−0.0148 (5)	−0.0059 (4)
C15	0.3446 (3)	0.2386 (3)	−0.4261 (2)	0.0136 (4)	0.0141 (3)	0.0079 (2)	−0.0005 (6)	−0.0064 (5)	−0.0108 (4)
C16	0.5174 (4)	0.2350 (3)	−0.5283 (3)	0.0176 (5)	0.0252 (5)	0.0109 (3)	−0.0007 (9)	−0.0033 (6)	−0.0167 (6)
C21	0.2519 (3)	0.0892 (3)	0.2262 (2)	0.0171 (4)	0.0094 (3)	0.0089 (2)	0.0003 (6)	−0.0121 (5)	−0.0020 (4)
C22	0.4090 (3)	0.1377 (3)	0.1260 (2)	0.0139 (4)	0.0135 (3)	0.0102 (3)	0.0075 (6)	−0.0127 (5)	−0.0085 (4)
C23	0.4224 (3)	0.2921 (3)	0.1020 (2)	0.0124 (4)	0.0135 (3)	0.0093 (2)	−0.0030 (6)	−0.0093 (5)	−0.0075 (4)
C24	0.2743 (3)	0.3369 (2)	0.1906 (2)	0.0148 (4)	0.0108 (3)	0.0086 (2)	−0.0009 (6)	−0.0094 (5)	−0.0080 (4)
C25	0.1658 (3)	0.2125 (3)	0.2670 (2)	0.0132 (4)	0.0117 (3)	0.0066 (2)	0.0002 (6)	−0.0077 (5)	−0.0047 (4)
C26	−0.0019 (4)	0.2079 (3)	0.3769 (3)	0.0183 (5)	0.0161 (4)	0.0089 (3)	−0.0029 (7)	−0.0038 (6)	−0.0059 (5)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
CP1	0.2043	0.2370	−0.3452		H3A	0.325 (3)	0.508 (2)	−0.146 (2)	4.5 (6)
CP2	0.3047	0.2197	0:1824		H3B	0.142 (3)	0.492 (2)	−0.157 (2)	4.0 (6)

[a] The form of the anisotropic thermal parameter is $\exp[-(B(1,1)*h^2 + B(2,2)*k^2 + B(3,3)*l^2 + B(1,2)*hk + B(1,3)*hl + B(2,3)*kl)]$.
[b] Estimated standared deviations in the least significant digits are shown in parentheses; CP1 and CP2 are the centroids of the five-atom planes C11–C15 and C21–C25, respectively.

crystals were intergrown doublets or multiplets. Finally, a small (0.15 × 0.17 × 0.18) single crystal was located, transferred to an Enraf-Nonius CAD4 automated diffractometer,[27] and centered in the beam. Automatic peak search and indexing methods yielded a triclinic reduced primitive cell. Inspection of the Niggli values[28] showed no indication of a conventional unit cell of higher symmetry. Final cell dimensions and details of the data collection procedures are given in Table II.

The 1796 unique raw intensity data were converted to values of the structure factor amplitude and their esd's by correction for scan speed, background, and Lorentz and polarization effects.[29–31] Inspection of the azimuthal scan data showed only a ±3% variation in intensity. No absorption correction was performed.

The structure was solved by analysis of the three-dimensional Patterson synthesis and refined by standard full-matrix least-squares procedures. Following refinement of all non-hydrogen atoms with anisotropic thermal parameters ($R^{32} = 3.87\%$,[32] $R_w = 6.25\%$), a difference Fourier synthesis clearly showed the positions of all hydrogen atoms. The hydrogen atoms of the bridging methylene group were allowed to refine and all other hydrogen atoms were included in structure factor calculations in their idealized positions but not refined. In the final cycles of least squares a secondary extinction parameter was also refined. The final residuals for 181 variables refined against the 1520 data for which $F^2 > 3\sigma(F^2)$ were $R = 1.85\%$, $R_w = 2.49\%$, and GOF = 1.439. The *R* value for all 1769 data was 2.82%.

The quantity minimized by the least-squares program was $\sum w(F_o - F_c)^2$, where *w* is the weight of a given observation. The *p* factor,[32] used to reduce the weight of intense reflections, was set to 0.025 throughout the refinement. The analytical forms for the scattering factor tables for the neutral atoms were used,[33] and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[34] Inspection of the residuals ordered in ranges of $(\sin\theta)/\lambda$, $|F_o|$, and parity and value of the individual indexes showed no unusual features or trends. The largest peak in the final difference Fourier map had an electron density of 0.26 e^2/A^3. All of the largest peaks were near the two Co atoms. The positional and thermal parameters of the refined atoms are given in Table III. The positions of the hydrogen atoms and a listing of the values of F_o and F_c are available as supplementary material.

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(27) Instrumentation at the University of California Chemistry Department X-ray Crystallographic Facility (CHEXRAY) consists of two Enraf-Nonius CAD-4 diffractometers, one controlled by a DEC PDP 8/a with an RK05 disk and the other by a DEC PDP 8/e with an RL01 disk. Both use Enraf-Nonius software as described in the *CAD-4 Operation Manual*, Enraf-Nonius, Delft, Nov 1977, updated Jan 1980.

(28) Roof, R. B., Jr., "A Theoretical Extension of the Reduced-Cell Concept in Crystallography", Publication LA-4038, Los Alamos Scientific Laboratory, Los Alamos, NM, 1969.

(29) All calculations were performed on a PDP 11/60 equipped with 128 kilowords of memory, twin RK07 28 MByte disk drives, Versatec printer/plotter and TU10 tape drive, using locally modified Nonius-SDP[3] software operating under RSX-11M.

(30) Structure Determination Package User's Guide, April, 1980, Molecular Structure Corp., College Station, TX 77840.

(31) The data reduction formulae are

$$F_o^2 = \frac{\omega}{Lp}(C - 2B) \qquad \sigma_o(F_o^2) = \frac{\omega}{Lp}(C + 4B)^{1/2}$$

$$F_o = F_o^2 \qquad \sigma_o(F) = \frac{\sigma_o(F_o^2)}{2F_o}$$

where *C* is the total count in the scan, *B* the sum of the two background counts, the scan speed used in deg/min, and

$$\frac{1}{Lp} = \frac{\sin 2\theta\,(1 + \cos^2 2\theta_m)}{1 + \cos^2 2\theta_m - \sin^2 2\theta}$$

is the correction for Lorentz and polarization effects for a reflection with scattering angle 2θ and radiation monochromatized with a 50% perfect single-crystal monochrometer with scattering angle $2\theta_m$.

(32) Note:

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$R_w = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w F_o^2}\right]^{1/2}$$

$$\mathrm{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{(n_o - n_v)}\right]^{1/2}$$

where n_o is the number of observations, n_v the number of variable parameters, and the weights *w* were given by

$$w = \frac{4F_o^2}{\sigma^2(F_o^2)} \qquad \sigma^2(F_o^2) = [\sigma_o^2(F_o^2) + (pF^2)^2]$$

where *p* is the factor used to lower the weight of intense reflections.

(33) Cromer, D. T.; Waber, J. T. In "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(34) Cromer, D. T., in ref 33; Table 2.3.1.

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26291) and to the Matthey-Bishop Corp. for a generous loan of rhodium trichloride. K. H. Theopold acknowledges an Ephraim Weiss Scholarship (1980–1981) and a D. O. Sumek and S. M. Tasheira Scholarship (1981–1982) from the University of California, Berkeley. The X-ray structure analysis was performed by Dr. F. J. Hollander of the U. C. Berkeley X-ray diffraction facility (CHEXRAY). Funds for the analysis were provided by the above NSF grant; partial funding for the equipment in the facility was provided by NSF Grant CHE 79-07027.

Registry No. 1, 77674-08-9; **1**-d_2, 84040-86-8; **2**, 84064-05-1; **2**-d_6, 84064-10-8; **3**, 84049-85-4; **4**, 84064-06-2; **4**-d_6, 84049-88-7; **5**, 84040-83-5; **5**-d_4, 84064-11-9; **6**, 79255-87-1; **7**, 84064-07-3; **8**, 84049-86-5; **9**, 84064-08-4; **9**-d_4, 84040-88-0; *cis*-**10**, 84040-84-6; *trans*-**10**, 84064-13-1; **11**, 84064-09-5; **12**, 84064-25-5; *trans*-**13**, 79390-72-0; *cis*-**13**, 77674-11-4; *trans*-**14**, 65138-22-9; *cis*-**14**, 84064-12-0; **15**, 69393-67-5; **16**, 77674-13-6; **18**, 84049-87-6; $Na[CpCo(CO)]_2$, 62602-00-0; CD_2I_2, 15729-58-5; $MeCpCo(CO)_2$, 12145-31-2; $NaCo(CO)_4$, 14878-28-5; $Na[MeCpCo(CO)]_2$, 84040-87-9; $CpRh(CO)_2$, 12192-97-1; $CpCo(CO)(C_2H_4)$, 77674-12-5; $[CpCo(CO)]_2$, 58496-39-2; diiodomethane, 75-11-6; 2,2-diiodopropane, 630-13-7; 1,1-diiodopropane, 10250-52-9; 3,3-diiodopropane, 66688-39-9; 2,2-diiodopentane, 66688-37-7; 1,1-diiodopentane, 66688-35-5; 1,1-diiodo-3,3-dimethylbutane, 84040-85-7; 2,2-diiodopropane-d_6, 79255-38-2; 2,2,4,4-tetradeuterio-3,3-diiodopentane, 79255-39-3.

Supplementary Material Available: A listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

Single Cubane-Type MFe_3S_4 Clusters (M = Mo, W): Synthesis and Properties of Oxidized and Reduced Forms and the Structure of $(Et_4N)_3[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_4(3,6\text{-}(C_3H_5)_2C_6H_2O_2)]$

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Abstract: Reaction of the solvated cubane-type clusters $[MFe_3S_4(SR)_3((C_3H_5)_2cat)(MeCN)]^{2-}$ (M = Mo, W; R = Et, p-C_6H_4Cl; $(C_3H_5)_2cat$ = 3,6-diallylcatecholate) with the ligands L = p-$ClC_6H_4S^-$, PhO^-, CN^- and PEt_3 affords the ligated clusters $[MFe_3S_4(SR)_3((C_3H_5)_2cat)L]^{2-,3-}$. Examples of each, except phosphine clusters, have been isolated as Et_4N^+ salts in 54–77% yields. $(Et_4N)_3[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_4((C_3H_5)_2cat)]$ crystallizes in monoclinic space group $C2/c$ with $a = 33.918$ (8) Å, $b = 16.674$ (4) Å, $c = 27.374$ (5) Å, $\beta = 95.98$ (2)°, and $Z = 8$. On the basis of 5511 unique data ($F_o^2 > 2.5\sigma(F_o)^2$) the structure was refined to $R = 6.6\%$. The structure provides the first definitive proof of a *single* MFe_3S_4 cubane-type cluster, which in this compound approaches C_s symmetry. Solvated clusters exhibit chemically reversible one-electron reduction reactions, and solutions of $[MFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_3((C_3H_5)cat)(MeCN)]^{3-}$ are readily prepared by reduction of solvated 2− clusters with sodium acenaphthylenide. The reduced clusters are paramagnetic (probable $S = 2$ ground state) and form 1:1 adducts with PEt_3 and CO. ^1H NMR spectra demonstrate that all oxidized and reduced ligated clusters have structures of effective C_s symmetry in solution. Other results relevant to the reactions of oxidized and reduced clusters and π donor properties of the latter are presented. The availability and spectroscopic characterization of reduced clusters, with substitutionally labile solvate molecules at the Mo atom site, provide an opportunity to examine reactions of nitrogenase substrates at that site.

Evolvement of the chemistry of MFe_3S_4 clusters (M = Mo, W) is detailed in recent reports from this laboratory,[1-6] in which we describe our interest in these species as the only examples of mixed-metal $M'_nM_{4-n}S_4$ cubane-type clusters and as preliminary models of the Mo atom coordination unit in nitrogenase. An important aspect of this research continues to be synthesis and physicochemical and reactivity characterization of *single* cubane species. These are not accessible from cluster assembly reactions which afford various types of bridged *double* cubanes[3,7-10] (e.g., $[M_2Fe_6S_8(\mu_3\text{-}SR)_3(SR)_6]^{3-}$) depending on conditions.

Our approach to the synthesis of single cubanes is outlined in Figure 1. Reaction 1, in which the Fe(III)-bridged double cubane $[M_2Fe_7S_8(SR)_{12}]^{3-}$ [8,9] (**1**-M) is treated with a 3,6-disubstituted catechol ($R_{3,6} = CH_2CH{=}CH_2$, n-Pr), results in bridge disruption and formation of the doubly bridged double cubane $[M_2Fe_6S_8(SR)_6(R_{3,6}\text{-cat})_2]^{4-}$ [1,5,11] (**2**-M). In coordinating solvents this species, in reaction 2, experiences bridge cleavage to form the solvated single cubane $[MFe_3S_4(SR)_3(R_{3,6}\text{-cat})(solv)]^{2-}$ [1,5] (**3**-M). This cluster undergoes the thiolate ligand substitution reaction 3,[5] and the solvent displacement reaction 4 with ligands $L^{0,1-}$ to afford single cubanes $[MFe_3S_4(SR)_3(R_{3,6}\text{-cat})L]^{2-,3-}$.[4,5] The structures of two key intermediate clusters **2**-Mo (R = Et, Ph) have been established by X-ray diffraction.[1,5,12]

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(1) Armstrong, W. H.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 6246.

(2) Palermo, R. E.; Power, P. P.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 173.

(3) Christou, G.; Mascharak, P. K.; Armstrong, W. H.; Papaefthymiou, G. C.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2820.

(4) Armstrong, W. H.; Mascharak, P. K.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 1699.

(5) Armstrong, W. H.; Mascharak, P. K.; Holm, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 4373.

(6) Holm, R. H. *Chem. Soc. Rev.* **1981**, *10*, 455.

(7) Wolff, T. E.; Berg, J. M.; Hodgson, K. O.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1979**, *101*, 4140.

(8) Wolff, T. E.; Berg, J. M.; Power, P. P.; Hodgson, K. O.; Holm, R. H. *Inorg. Chem.* **1980**, *19*, 430.

(9) Wolff, T. E.; Power, P. P.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1980**, 102, 4694.

(10) Christou, G.; Garner, C. D. *J. Chem. Soc., Dalton Trans.* **1980**, 2354.

(11) A different cluster product, $[MoFe_3S_4(SEt)_3Fe(cat)_3]^{3-}$, is obtained from the reaction of **1**-Mo (R = Et) with catechol itself: Wolff, T. E.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1981**, *20*, 174.

(12) Armstrong, W. H. Ph.D. Thesis, Stanford University, 1982.

0002-7863/83/1505-0475$01.50/0