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Carbon–Carbon Bond Formation in Dinuclear Dialkyl Complexes. Reactions of $[CpCo(CO)R]_2$ (R = CH_3, CH_2CH_3, CH_2CF_3) and $(C_{11}H_{10})Co_2(CO)_2(CH_3)_2$ with Carbon Monoxide and Triphenylphosphine

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Abstract: The full details of the synthesis, thermal decomposition, and carbonylation of dialkyldicobalt dimers $[CpCo(CO)R]_2$ are reported. The dinuclear dimethyl complex **2a** gives acetone and cobalt clusters on thermal decomposition; the very sensitive mononuclear complex $CpCo(CO)Me_2$ (**7a**) can be detected as an intermediate. The bis(trifluoroethyl) complex $[CpCo(CO)(CH_2CF_3)]_2$ (**2c**) rearranges to **7c** (R = CH_2CF_3), which does not go on to ketone and can be isolated. Carbonylation of the dinuclear dimethyl and diethyl complexes **2a** and **2b** proceeds even more cleanly to ketones, giving a quantitative yield of $CpCo(CO)_2$ as the final organometallic product. However, this reaction proceeds by a mechanism different from that of the thermal decomposition. In the carbonylation an initial very rapid reaction leads to the diacyl complex $[CpCo(CO)(COR)]_2$; this goes on to ketone at a rate faster than can be attributed to **7**. Crossover experiments provide strong evidence that complexes **2a**, **2b**, and **2c** are in rapid equilibrium with small amounts of the paramagnetic, 17-electron monomers CpCo(CO)R. The corresponding complex $(C_{11}H_{10})Co_2(CO)_2Me_2$ (**13a**), containing a bridging ligand in which two Cp rings are connected by a CH_2 group, has also been synthesized. This material is more stable than **2a**; it undergoes carbonylation to acetone only at temperatures near 70 °C. It reacts with PPh_3 at 25 °C but instead of leading to ketone gives the rearranged product $[C_{11}H_{10}][Co(CO)_2][Co(PPh_3)Me_2]$ (**14**). The PPh_3 + **13a** $\rightleftharpoons$ **14** reaction is reversible at room temperature, with an equilibrium constant of 33 M^{-1}. Kinetic studies on this system are consistent with a mechanism involving the reversible formation of a transient intermediate which can be trapped by PPh_3. Taken together, the results require that at least three chemical pathways are accessible to complexes of type **2**: reversible cleavage to paramagnetic monomers, alkyl transfer from one cobalt atom to another, and carbonylation to give dinuclear diacyl complexes, which can rapidly proceed on to form ketone.

Introduction

The identification of a small but significant number of potentially reversible "primary reaction steps" in organometallic chemistry—such as oxidative addition/reductive elimination, alkene insertion/β-elimination, and CO migratory insertion/deinsertion—provided an important stimulus to the development of mechanistic understanding in this field.[1] However, a significant characteristic of these primary steps is that they were all initially defined for reactions at a single metal center. In the mid-1970's interest began to focus on metal-mediated transformations that require more than one metal center.[2] Two important questions arose: (1) Do the primary steps in the mechanisms of these reactions actually involve direct participation of di- or polynuclear centers, or do they involve smaller amounts of (possibly mononuclear) fragments as the critical reactive species? (2) Is there a class of "primary reaction steps" for di- and/or polynuclear metal centers analogous to those identified for mononuclear systems?

Because these questions had not been answered in any direct way even for the smallest polynuclear complexes, we set out to address them in systems containing two metal centers. Our initial goal was the synthesis and study of a class of simple dinuclear complexes containing a metal–metal bond and one σ-bound organic ligand attached to each metal. We sought such a system that could be induced to decompose with the release of organic molecules containing both of the σ-bound fragments, so that the mechanisms of these transformations might be investigated.

We found such a system in the course of our studies on the chemical reduction and alkylation of cyclopentadienyl-substituted cobalt carbonyl complexes. Reduction of $CpCo(CO)_2$ leads to dinuclear radial anion **1** (Scheme I), whose $(Ph_3P)_2N^+$ salt we were able to characterize crystallographically.[3] This material can be oxidized to neutral cobalt dimer $[CpCoCO]_2$ (**3**) and also undergoes a quite general set of alkylation reactions. For example, treatment of **1** with primary alkyl halides and sulfonates leads to dinuclear dialkyl complexes **2** having one alkyl group attached to each metal center; organic dihalides lead to dinuclear metallacycles of varying ring size. On heating or treatment with phosphines nearly all these molecules release organic compounds containing new carbon–carbon bonds.[4-9]

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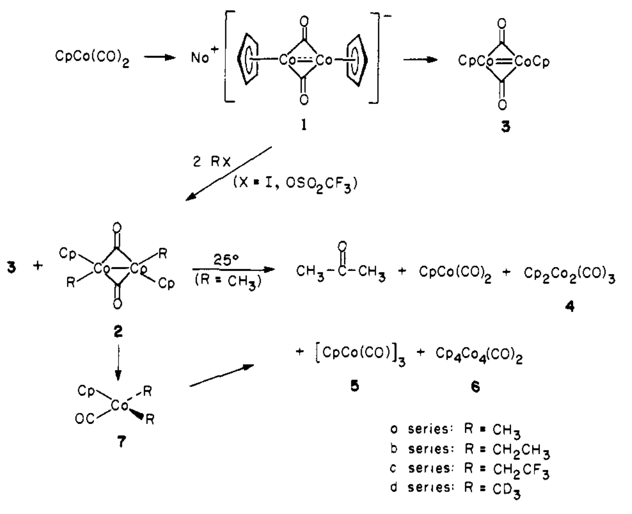
Scheme I



The dinuclear metallacycles and their reactions have been studied and described in detail.[4] We have also utilized the stereochemistry of the metallacycle-forming reaction to examine the mechanism of the reaction of the radical anion **1** with organic halides.[5] Reactions of the dinuclear dialkyl complexes, however, have been more difficult to understand. Some of our preliminary results have been reported in communication form, and the application of crossover experiments to the study of these reactions has been discussed in a review.[6-9] This paper reports the experimental details of the synthesis and carbonylation reactions of the dinuclear dialkyl complexes [CpCo(CO)(R)]$_2$ (**2a** and **2b**, R = CH$_3$ and CH$_2$CH$_3$). Included are studies of the corresponding trifluoroethyl complex **2c** (R = CH$_2$CF$_3$), whose chemistry differs from that of **2a** and **2b** in some interesting ways. We also report details of the chemistry of a related system in which the two Cp rings of the dinuclear complex are linked by a CH$_2$ group (**13**), along with some additional experiments on the mechanism of phosphine-induced decomposition of this material.

Synthesis and Chemistry of Dinuclear Complexes [CpCo(CO)R]$_2$

Preparation and Characterization of [CpCo(CO)CH$_3$]$_2$. Treatment of the sodium salt of **1** (Scheme I) with 2 equiv of methyl trifluoromethanesulfonate in THF produces a deep bluish green solution displaying an IR band at 1790 cm^{-1} due to[3] neutral dimer **3** and a band of roughly equal intensity at 1820 cm^{-1}. The same new band is exhibited by solutions formed by treatment of **1** with methyl iodide, but in this case no concomitant formation of **3** is observed. The material responsible for the new IR band is thermally very sensitive in solution; it decomposes with a half-life of a few hours at room temperature. However, it may be isolated and purified by column chromatography under an N$_2$ atmosphere provided that solutions of the material are kept cold and removal of solvent is carried out under high vacuum below room temperature. The compound thus obtained in 48% yield is a dark green solid, indefinitely stable at room temperature under nitrogen, displaying NMR absorptions at δ 5.09 and −0.72 in THF-d_8 (δ 4.63 and −0.35 in C$_6$D$_6$) in a 5:3 intensity ratio.

These data are consistent with complex **2a** illustrated in Scheme I, a doubly alkylated dinuclear neutral complex with bridging carbonyl groups. The IR band at 1820 cm^{-1} is always accompanied by a weaker absorption at 1854 cm^{-1}; the presence of cis and trans isomers is a possible explanation for this observation (no stereochemical implications are intended by the drawings in Scheme I and following). In toluene-d_8 at room temperature, both NMR absorptions are rather broad (width at half-height ca. 2.5 Hz), and they maintain their shape down to −55 °C, with only small changes in chemical shift. Preparation of **2d**, fully deuterated at the methyl groups, is easily achieved by treating **1** with methyl-d_3 iodide. Purified **2d**, obtained in 47% yield, possesses only a single NMR absorption at δ 4.62 in C$_6$D$_6$, also with a width of 2.5 Hz at half height, thus ruling out the possibility that long-range coupling between the CH$_3$ and C$_5$H$_5$ groups might be responsible for the broad NMR signals in **2a**.

The gross structure of **2a** is supported by elemental analysis and solution molecular weight measurement. Its thermal instability has prevented us from observing a molecular ion in several attempts at mass spectrometry and ion cyclotron resonance. The only fragments identified with m/e >200 are those derived from the various cobalt clusters arising from the decomposition of **2a** in the inlet of the mass spectrometer. However, a number of lower molecular weight peaks confirm the presence of the C$_5$H$_5$Co-CH$_3$CO fragment in purified **2a**.

Conversion of [CpCo(CO)(CH$_3$)]$_2$ to Acetone. Complex **2a** decomposes readily upon dissolution in cyclohexane, benzene, or THF. Although insoluble material appears in all three solvents, the decomposition is cleanest in THF. Complete disappearance of **2a** takes several days at room temperature and yields a brown solution with at least six new IR absorptions in the carbonyl region and five new peaks corresponding to cyclopentadienyl protons in the NMR. Vacuum transfer of all volatile material from this mixture affords a reddish orange solution that contains only (η^5-cyclopentadienyl)dicarbonylcobalt (IR 1955 and 2020 cm^{-1}; NMR δ 5.18) and acetone, the only organic product, identified by IR, NMR, GC, and reduction to 2-propanol.

The nonvolatile portion of the product mixture may be separated into fractions soluble and insoluble in cyclohexane. The soluble portion displays IR bands at 1800 and 1965 cm^{-1} and an NMR absorption at δ 4.83 characteristic[10] of bis(η^5-cyclopentadienyl)tricarbonyldicobalt (**4**; Scheme I). Also present in the solution and possessing a single NMR peak at δ 4.76 is tris(η^5-cyclopentadienyl)tricarbonyltricobalt (**5**). The latter material, purified by column chromatography, displays a characteristic pattern[11,12] of five IR bands when redissolved in THF.

The brown, cyclohexane-insoluble product displays NMR signals at δ 4.83 and 4.94 in toluene, identical with the spectrum reported[10,12] for tetrakis(η^5-cyclopentadienyl)dicarbonyltetracobalt (**6**). Only a broad IR adsorption below 1700 cm^{-1} is observed in a nujol mull of **6**; in THF two broad bands at 1685 and 1700 cm^{-1} are seen. This tetranuclear cluster is by far the major organometallic product of the decomposition of **2a** in THF, being formed in 54% yield (by integration of C$_5$H$_5$ resonances vs. residual solvent peaks in the ^{1}H NMR). Approximate NMR yields of the other complexes are 11% CpCo(CO)$_2$, 7% **4**, and 7% **5**. Remarkable, however, is the yield of acetone, estimated to be 85% by NMR.

The decomposition of **2a** can be monitored readily by ^{1}H NMR or IR spectrometry. These studies demonstrate that neither acetone nor the cobalt clusters **5** and **6** appear immediately upon dissolution of **2a** in a solvent. The first signals observed are those due to CpCo(CO)$_2$, together with new absorptions in the cyclopentadienyl and methyl regions of the NMR in a 5:6 intensity ratio. Simultaneously, an additional IR band in the terminal carbonyl region of the spectrum appears (2001 cm^{-1} in THF; 2012 cm^{-1} in cyclohexane). The material responsible for these absorptions builds up in solution, maximizing in concentration after about 90 min at 35 °C, and appears to be the immediate precursor to the acetone formed in this reaction. On the basis of these data and the chemical behavior of this material (vide infra) we assign to it structure **7a** (R = CH$_3$; Scheme I).

The decomposition of **2a** follows first-order kinetics in both benzene and THF. The process can be easily followed by IR or NMR, generating the rate data in Table I. Decomposition in cyclohexane is too fast to follow at room temperature. The conversion of intermediate **7** to acetone proceeds with a rate

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Table I. Kinetics of Decomposition of **2**

complex	solv	T, °C	rate const s^{-1} × 10^{-4}	method
2a	C_6D_6	35	2.4^a	NMR
2a	C_6D_6	35	1.6^a	NMR
2a	THF	10	0.084	IR
2a	THF	33	0.67	IR
2b	THF	23	0.82	IR
2c	THF-d_8	23	0.39^a	NMR
2c	THF-d_8	23	0.37^a	NMR

^{a}Correlation coefficients for these four runs were 0.97, 0.96, 0.999, and 0.997, respectively; the measured rate constants reflect the degree of reproducibility from run to run at identical starting concentrations of **2**.

constant of 4.5 × 10^{-6} s^{-1} in THF-d_8 at 35 °C.

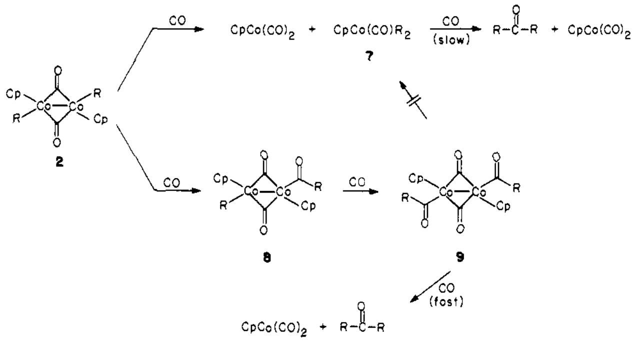
Synthesis and Thermal Decomposition of [CpCo(CO)CH$_2$CH$_3$]$_2$ (2b) and [CpCo(CO)CH$_2$CF$_3$]$_2$ (2c). The diethyl (**2b**) and bis(trifluoroethyl) (**2c**) analogues of **2a** were prepared by treatment of radical anion **1** with the appropriate alkyl iodides. Following air-free chromatography, **2b** was isolated in 33% yield as a dark-green solid; **2c** was obtained as a brown solid in 30% yield; both were obtained analytically pure.

The thermal decomposition of **2b** differed slightly from that of **2a**, mainly because of the presence of β-hydrogens on the alkyl groups. As with **2a**, the decomposition of **2b** was first-order in complex but the rate was faster than that of **2a** (Table I). The organic products of the decomposition were 3-pentanone (32%), ethane (54%), and ethylene (14%). The organometallic products were CpCo(CO)$_2$, [CpCo(CO)]$_2$, [CpCo(CO)]$_3$, and [Cp$_4$Co$_4$(CO)$_2$]. During the decomposition, the IR bands due to **2b** (ν_{CO} 1847, 1813 cm^{-1}) disappeared and a band at 2000 cm^{-1}, which may be due to CpCo(CO)(CH$_3$CH$_2$)$_2$ (**7b**), grew in. Bands attributable to the organometallic products listed above were also observed. Due to the complexity of the NMR spectrum of the decomposition solution, NMR signals that might be assigned to CpCo(CO)(CH$_3$CH$_2$)$_2$ could not be discerned (the methylene protons are expected to be diastereotopic).

Both the NMR spectrum and thermal decomposition of bis(trifluoroethyl) complex **2c** are quite informative. **2c** shows no detectable ^{1}H NMR signals at normal concentrations at room temperature. However, at −50 °C, the spectrum consists of a sharp cyclopentadienyl singlet and a methylene quartet. As the sample is warmed, the peaks broaden until they disappear at +10 °C. No new peaks appear up to +34 °C, where the complex begins to decompose. Cooling the sample back down to −50 °C causes the peaks to reappear, indicating a reversible process is occurring. We suggest that a paramagnetic monomer/diamagnetic dimer equilibrium is responsible for the broadening of the NMR spectrum. As the sample is warmed, the equilibrium shifts to generate a higher concentration of paramagnetic monomer, which has (presumably) strongly shifted and highly broadened resonances. The averaged spectrum due to this exchange process is thus very broad at room temperature. This process was invoked by Cotton and co-workers to explain the broadening and disappearance of the signals due to [CpCr(CO)$_3$]$_2$ in its temperature-dependent NMR spectrum.[13] This behavior was not observed in the NMR spectra of **2a** and **2b**, indicating that the equilibrium constant for dissociation of the dimer is smaller in these systems.

Decomposition of the bis(trifluoroethyl) complex **2c** also followed first-order kinetics. Like diethyl complex **2b**, its rate was somewhat more rapid than that of **2a** (Table I) but dramatically different in that the decomposition stopped with the production of the mononuclear dialkyl complex **7c**. Due presumably to the increased metal–carbon bond strengths in this product, no conversion of **7c** to ketone was observed, and isolation of this material was possible. Thus, when **2c** was dissolved in THF-d_8 and allowed to decompose, its NMR signals at δ 5.42 and 0.25 disappeared and signals due to CpCo(CO)$_2$ (δ 5.19) and CpCo(CO)(CF$_3$CH$_2$)$_2$ (**7c**) (δ 5.42 (s, 5 H)), 2.40 (8 lines, 2 H), 1.10 (8 lines, 2 H) appeared. Likewise IR analysis showed the ν_{CO} bands of **2c** (1875, 1845 cm^{-1}) decreasing in intensity and bands due to CpCo(CO)$_2$ (2020, 1955 cm^{-1}) and CpCo(CO)(CF$_3$CH$_2$)$_2$ (2040 cm^{-1}) growing in. Decomposition in benzene led to a black precipitate (presumably cluster complexes) and a solution of CpCo(CO)$_2$ and **7c**. Evaporation and sublimation gave analytically pure mononuclear bis(trifluoroethyl) complex, identified based on IR, NMR, mass spectral, and analytical data. The NMR spectrum of **7c** shows a 16-line signal for the methylene protons because they are diastereotopic.

Scheme II



Carbonylation Reactions. Complexes **2a**, **2b**, and **2c** react quickly with CO, the carbonylation reactions being complete within a few minutes at room temperature. The reactions of **2a** and **2b** follow a similar course but that of **2c** differs.

Dinuclear bis(trifluoroethyl) complex **2c** was allowed to react with CO in a sealed NMR tube, and the reaction was monitored by NMR spectroscopy. Absorptions due to **2c** disappeared and were replaced by those due to CpCo(CO)$_2$ and CpCo(CO)(CF$_3$CH$_2$)$_2$, which were formed in equal amounts. The yield was quantitative. No further reaction occurred, the carbonylation reaching completion within 15 min at room temperature.

The carbonylation of dinuclear dialkyl complexes **2a** and **2b** leads ultimately to CpCo(CO)$_2$ and acetone and 3-pentanone, respectively, in quantitative yield. However, although **7** is formed in this reaction, the ketone-forming process does *not* occur via the sole intermediacy of this complex, as was observed in the thermal decomposition. As described below, NMR, IR, and kinetic data show that **2a** and **2b** are converted to ketone in a rapid process involving dinuclear, acyl-containing intermediates, which circumvents the mononuclear intermediates CpCo(CO)R$_2$.

Upon treatment of a 0.1 M solution of **2a** in THF-d_8 with an excess of CO (1–10 atm, 4–40 equiv) the NMR signals of the dimethyl complex **2a** (δ 5.14, −0.71) disappeared within a few minutes at room temperature and were replaced by several new signals. These were due (vide infra; Scheme II) to the presence of (a)**7a** (δ 5.01, 0.45), (b) CpCo(CO)$_2$ (δ 5.19), (c) acetone (δ 2.09), and (d) *E,Z* isomers of the new complex **9a** (two sets of signals, each consisting of a cyclopentadienyl singlet and an acyl singlet (δ 5.11 (5 H), 2.32 (3 H), and 4.93 (5 H), 2.50 (3 H)). The first set of signals was three times as intense as the second.

During the course of the carbonylation, a new methyl signal at δ −0.97 grew in and then disappeared. The chemical shift of this signal was characteristic of a methyl bound to cobalt and was assigned to the dinuclear alkyl–acyl complex **8a** (Scheme II). The acyl methyl signal of **8a** appeared at δ 2.32, overlapping one of the acyl signals due to **9a**. In toluene-d_8, however, the acyl signals were separated by a few hertz and thus conversion of **8a** to **9a** could be observed.

When the carbonylation of **2a** was monitored by infrared spectroscopy, its CO stretching bands at 1854 and 1820 cm^{-1} decreased in intensity and were replaced by new bands at 1865, 1830, and 1675 cm^{-1} (assigned to **9a**). The shapes and intensities of the bridging CO bands at 1865 and 1830 cm^{-1} resembled those of the bands at 1854 and 1820 cm^{-1} due to **2a**. The 1675 cm^{-1} band was assigned as an acyl CO stretching absorption. Bands characteristic of **7a** (2001 cm^{-1}) and CpCo(CO)$_2$ (2020, 1955

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cm^{-1}) were also observed. **9a** was isolated as a brown solid (ca. 70% yield) from the carbonylation reaction mixture by low-temperature column chromatography under an inert atmosphere, although it could not be obtained absolutely pure due to its extreme thermal instability.

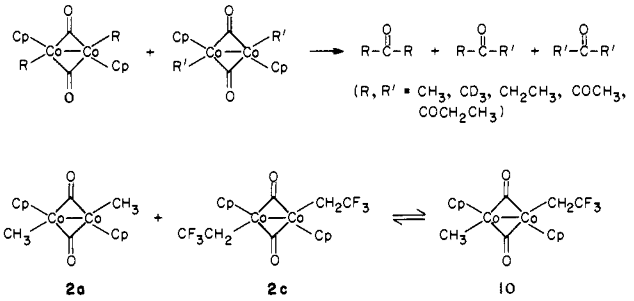
Similar results were obtained when $[CpCo(CO)(CH_2CH_3)]_2$ (**2b**) was treated with CO. When the carbonylation was carried out in THF-d_8, NMR signals due to **2b** (δ 5.12, 0.90 (CH_3), 0.22 (CH_2)) were replaced by signals assigned to the *E* and *Z* isomers of **9b** (δ 5.15 (5 H), 2.93 (2 H), 0.65 (3 H) and 4.94 (5 H), 3.09 (2 H), 0.81 (3 H)). Again, one isomer (having the set of signals listed first) was present in concentration about 3 times higher than the second. However, unlike the carbonylation of **2a**, neither a monoacyl intermediate nor $CpCo(CO)(CH_2CH_3)_2$ (**7b**) were observed in the product mixture. Infrared data collected during the carbonylation of **2b** were similar to those observed during the carbonylation of **2a**. During the carbonylation the bands due to **2b** at 1847 and 1813 cm^{-1} disappeared and were replaced by new bands at 1862, 1828, and 1666 cm^{-1} due to **9b**.

Studies of the rates and products of decomposition of diacyl complexes **9a** and **9b** provide information about the pathways leading to ketone in these systems. When either **9a** or **9b** was allowed to decompose in the presence of CO, quantitative formation of $CpCo(CO)_2$ and acetone or 3-pentanone, respectively, was observed. These reactions were surprisingly rapid, *proceeding at reasonable rates even at 0 °C in THF-d_8*. Decomposition in the absence of CO gave similar results, except that some cobalt clusters were observed as final organometallic products in addition to $CpCo(CO)_2$. Kinetic studies demonstrated the rate of carbonylation of **9a** is first order in complex; there is essentially no effect on the rate caused by the addition of excess CO (at 0.5 atm of CO, $k_{obsd} = 5.5 \times 10^{-5}$ s^{-1}; at 9.5 atm of CO, $k_{obsd} = 3.23 \times 10^{-5}$ s^{-1} (0 °C)). The most critical feature of these observations is that *none of the mononuclear dimethyl complex **7a** is formed during the decomposition of diacyl complex **9a**, and the rate of conversion of **9a** to acetone is much faster than the rate at which **7a** is converted to acetone.* This is most dramatically demonstrated by observation of mixtures of **7a** and **9a**, which show **9a** being converted rapidly to acetone while signals due to **7a** undergo no detectable change in intensity. These data require that conversion of dinuclear dimethyl complex **2a** to acetone and $CpCo(CO)_2$ can take place by two distinct routes, one (slower) process involving the intermediacy of the mononuclear complex **7a** and another, more rapid reaction that involves the dinuclear diacyl complexes (*E*)- and (*Z*)-**9a**.

Crossover Experiments on the Thermal Decomposition and Carbonylation Reactions of 2. To determine whether the two alkyl groups in each molecule of ketone product were associated with the same molecule of starting complex **2**—i.e., whether the ketone-forming reaction was inter- or intramolecular—several crossover experiments were performed. As will be demonstrated, the molecularity of the product-forming step is masked by rapid exchange of alkyl groups between different molecules of starting dinuclear complex **2**. We believe this alkyl exchange involves reversible metal–metal bond cleavage of the type suggested to explain the variable-temperature line broadening seen for complex **2c** discussed earlier in this paper.

The crossover experiments were carried out by both isotope labeling and "structure labeling" techniques. In one experiment, hexadeuterio complex **2d** (cf. Scheme I) was prepared by alkylation of radical anion **1** with CD_3I. A 50:50 mixture of solutions of dimethyl complex **2a** and its hexadeuterio analogue **2d** were then allowed to decompose to acetone. Because we were concerned about possible label scrambling by proton transfer in the weakly acidic ketone, the acetone product was reduced to isopropyl alcohol with $LiAlH_4$ before analysis by mass spectroscopy. This revealed that the product of the decomposition contained 27% acetone-d_0, 46% acetone-d_3, and 27% acetone d_6—i.e., an almost statistical (1:2:1) mixture (Scheme III). In a second experiment, separate samples of **2a** and **2d** were allowed to decompose in cyclohexane, where conversion to mononuclear dimethyl complex **7** occurs more rapidly than **7** goes on to ketone. The two samples containing mostly **7** were then mixed, allowed to proceed on to acetone, and then reduced and analyzed. A much smaller amount of crossover was observed in this experiment—47% acetone-d_0, 7% -d_3, and 45% -d_6. This demonstrates that the methyl scrambling process takes place before or during formation of the mononuclear complex **7**.

Scheme III



Additional experiments involved binary mixtures utilizing complexes **2a**, **2b**, and **2c**, as well as dinuclear acyl complexes **9a** and **9b**. When dinuclear dimethyl complex **2a** was mixed with diethyl complex **2b**, the overall rate of decomposition was similar to that observed for the two individual materials. A complicated mixture of products was formed, including ethane, ethylene, acetone, 2-butanone, and 3-pentanone. When the mixture was carbonylated, a complicated mixture of acyl complexes was formed, but as summarized in Scheme III, the final ketone product mixture contained a quantitative yield of acetone, 2-butanone, and 3-pentanone, formed in a 1:2:1 ratio. Finally, diacetyl complex **9a** was isolated and mixed with its homologue, dipropionyl complex **9b**. As indicated previously, each of these separate complexes undergoes rapid conversion to ketone even at 0 °C. Decomposition of the mixture of these materials produced clean, quantitative conversion to a 1:2:1 mixture of acetone, 2-butanone, and 3-pentanone, in both the presence and absence of carbon monoxide.

Experiments with the dimethyl and bis(trifluoroethyl) complexes **2a** and **2c** demonstrated that alkyl scrambling occurs even before any substantial conversion to mononuclear dialkyl complex **7** has taken place, because in this case the mixed complex **10** (Scheme III) can be observed spectroscopically. When **2a** and **2c** were mixed in THF and an IR spectrum recorded at room temperature, in addition to the bridging carbonyl bands for the starting isomers at 1820 and 1845 cm^{-1}, a new stronger band at 1833 cm^{-1}, consistent with the formation of mixed dialkyl dimer **10** (Scheme III), was immediately observed. NMR observation confirmed this assignment and demonstrated that the scrambling reaction occurs rapidly even at low temperature. In these experiments, **2a** and **2b** were mixed carefully at −40 °C in THF-d_8 and the solution then observed by NMR at −50 °C. New NMR resonances assignable to a statistical amount of the mixed dimer **10** were observed immediately. Similar observations were made in the presence of CO. Once again, observation by NMR (this time at −20 °C) showed complete scrambling of alkyl groups.

Decomposition of the mixed complex **10** occurs more rapidly than that of either the symmetrical dimers **2a** or **2c**. Although the products of this reaction were not examined thoroughly, NMR resonances of the reacting solutions indicated that the immediate product of the decomposition of **10** was the mixed mononuclear complex $CpCo(CO)(CH_3)(CH_2CF_3)$. Under CO, resonances assignable to the mixed dinuclear acyl complex $Cp_2Co_2(CO)_2(COCH_3)(CH_2CF_3)$ were observed. This was quickly converted to the corresponding mixed mononuclear acyl complex $CpCo(CO)(COCH_3)(CH_2CF_3)$, which led to methyl trifluoroethyl ketone and $CpCo(CO)_2$ (see Experimental Section).

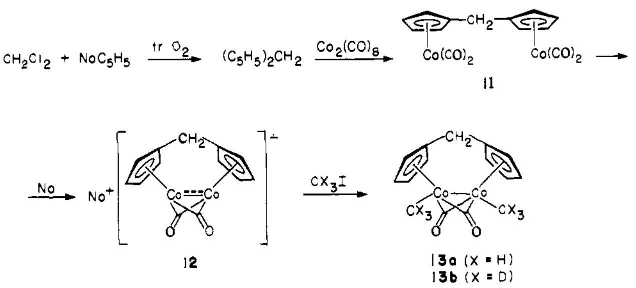
All these observations are consistent with the hypothesis that rapid and reversible cleavage of dimers **2** into paramagnetic, mononuclear CpCo(CO)R fragments is occurring rapidly and reversibly even at −50 °C, and this is responsible for the alkyl scrambling as well as for the NMR line broadening discussed in an earlier section of this paper.[14]

Table II. Analysis of Acetone Produced on Carbonylation of **13a** and **13b** in the Presence and Absence of PPh_3

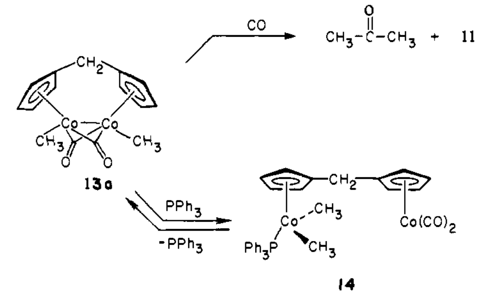
					acetone, %		
$[13]_0$, M	**13a**	**13b**	*T*, C	conditns	d_0	d_3	d_6
0.25	53	47	70	*a*	40	28	32
0.05	55	45	70	*a*	52	5	43
0.25	46	54	25	*b*	38	16	46
0.05	49	51	25	*c*	49	1	50
0.25	69	31	70	*d*	69	3	28

[a] Carbonylation carried out by using 3.3 atm of CO for 8 h in toluene solvent. Acetone vacuum transferred at completion of reaction and analyzed by GC/MS or purified by preparative GC and analyzed by MS. [b] Starting complexes treated with 2.5 M PPh_3 for 8 h in benzene solvent, then diluted to ca. 0.05 M, and carbonylated and the acetone analyzed as in *a*. [c] Starting complexes treated with 0.5 M PPh_3 for 8 h in benzene and then carbonylated as in *a*. [d] Starting complexes treated with 2.5 M PPh_3 for 8 h in benzene, then diluted to ca. 0.05 M, and carbonylated as in *a*.

Scheme IV



Scheme V



Phosphine- and CO-Induced Decomposition of a Dinuclear Dialkyl Complex Containing a Bridging Cp_2CH_2 Ligand

To restrict the ability of $[CpCo(CO)R]_2$ dimers to undergo the rapid metal–metal bond cleavage reaction discussed above, we decided to prepare the analogous complex in which the two cyclopentadienyl ligands were attached to one another by a CH_2 group. In such a complex the entropy gain on metal–metal bond cleavage would be substantially lowered because two independent fragments would not be produced, and we hoped this would shift the equilibrium toward the intact dimer. Our results indicate that this is indeed the case. However, modifications in the observed chemistry caused by the change in ligand, although interesting, raise some questions about the comparability of the two different types of systems.

The Cp_2CH_2 ligand was prepared by treating sodium cyclopentadienide with methylene chloride,[15] as shown in Scheme IV. One characteristic of this preparation, not evident from literature descriptions, is that yields are quite sensitive to oxygen. The reaction proceeds best when a trace of oxygen is allowed into the system, indicating that a free radical mechanism, rather than a conventional substitution, is involved. Formation of **11**, the dinuclear analogue of $CpCo(CO)_2$, is straightforward, as is reduction to the bridged radical anion **12**. Alkylation of the radical anion caused serious difficulties, however. We were able to obtain low yields of the dimethyl complex **13a**, but in contrast to our experience with the parent radical anion **1**, alkylation with other reagents was unsuccessful. We therefore were restricted to experiments on **13a** and its deuterated analogue **13b** in our chemical and mechanistic studies.

As expected, the bridged dimethyl compound is strikingly stable compared to its unbridged analogue **2a**, requiring temperatures near 70 °C to undergo decomposition. Unfortunately, this decomposition reaction is considerably less clean than that associated with **2a**, leading to some acetone but mostly dark, insoluble material which we have not been able to characterize. In contrast, reaction with carbon monoxide proceeds cleanly at 70 °C, leading to acetone and dinuclear tetracarbonyl complex **11** in quantitative yield (Scheme V).

Perhaps most surprising is the reaction of dimethyl complex **13a** with triphenylphosphine. During our study of the carbonylation of **2a**, discussed above, we briefly examined the reaction of **2a** with triphenylphosphine. A reaction was observed to take place at room temperature, but it was much more complicated than the carbonylation. Only about a 58% yield of acetone was obtained, along with a complex mixture of materials which included (as judged by observation of the IR and ^1H NMR spectra of the reaction mixture) $CpCo(CO)PPh_3$ (61%), $CpCo(PPh_3)_2$ (9%), and $CpCo(PPh_3)Me_2$ (<5%); in addition, $CpCo(CO)_2$ was present at early reaction times. We were initially surprised to see this dicarbonyl appear in spite of the insufficiency of CO in the system.

The reaction of PPh_3 with **13a** has illuminated this result to some extent. Treatment of **13a** with PPh_3 causes reaction to proceed at a reasonable rate even at room temperature. In the presence of excess triphenylphosphine, only one product is observed. The close similarity of both ^1H NMR and IR spectra of this material to both well-known compounds $CpCo(CO)_2$ and $CpCo(PPh_3)Me_2$ make it clear that the product is the unsymmetrical complex **14** shown in Scheme V. Although we have had difficulty obtaining **14** free of excess phosphine (see below), it was clear from monitoring the reaction by both ^1H NMR and IR spectrometry that excess PPh_3 converts **13a** to this species in essentially quantitative yield.

As outlined above, the most rapid pathway for reaction of the unbridged complexes **2** involves cleavage to species in which one alkyl and one carbonyl group remain attached to each cobalt. In light of this, it is striking that phosphine-induced decomposition leads to **14**, in which the two carbonyl groups and two methyl groups are each found attached to a single metal center. To better understand this process, kinetic and crossover labeling studies were carried out in the presence of excess phosphine. The reaction is first order in substrate, and the rate increases with increasing phosphine concentration, consistent with a preequilibrium step to form a coordinatively unsaturated intermediate, followed by attack of PPh_3 at one of the cobalt atoms of this species. As might be expected for a system in which the two cobalt atoms are held permanently in proximity by a bridge, crossover experiments (Table II) showed that a substantial fraction of the conversion of **13** to **14** was intramolecular. The intermolecular component can be increased by raising the starting concentration of **13**, thus increasing the probability of interaction between two dimeric molecules. A similar result was obtained from crossover experiments on the carbonylation reaction.

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(14) Several attempts were made to detect these species by ESR spectroscopy. Although ESR signals were observed in both solutions and frozen glasses, their appearance was not very reproducible, and in general the lines were broad, obscuring any hyperfine coupling which may have been present.

(15) Shaltegger, H.; Neuenschwander, M.; Meuche, D. *Helv. Chim. Acta* **1965**, *48*, 955.

Table III. Observed Rate Constants as a Function of Phosphine Concentration ([L]) for the Reaction of Dimethyl Dimer **13a** with Triphenylphosphine at 25.4 °C

$[A_0]$ (dimethyl dimer), M	[L], M	10^4k_{obsd}
0.076	0.93	3.06 ± 0.18[a]
0.076	0.59	3.19 ± 0.2[a]
0.01	0.091	2.80 ± 0.1
0.005	0.0443	2.28 ± 0.03
0.005	0.0443	2.19 ± 0.26
0.0025	0.0222	1.91 ± 0.18
0.0025	0.0222	1.59 ± 0.20

[a] Obtained from a correction of data from ref 7.

These data were published in preliminary form[7] in 1979. In the process of completing the study, we increased our efforts to obtain analytically pure samples of **14** and also worked on improving the fit of our kinetic data to the rate law derived from the preequilibrium mechanism we proposed[7] for the conversion of symmetrical dimethyl complex **13** to unsymmetrical rearranged product **14**. As it turned out, both of these problems were connected. When we began to do experiments on reactions of **13a** with lower concentrations of PPh_3, we noticed that it was difficult to carry the reactions to completion. Most strikingly, when one such "inhibited" sample, run in benzene-d_6, was diluted with additional solvent, the amount of observed starting complex **13a** increased at the expense of the product **14**. These experiments made it clear that the reaction was reversible—i.e., that back-exchange of methyl and CO, with dissociation of PPh_3, in **14** to give **13a** occurs at an accessible rate at room temperature. Attempts to remove PPh_3 from isolated **14** most likely resulted in additional dissociation of phosphine from the complex.

This equilibrium complicates the analysis of the mechanism using the steady-state assumption, because preequilibration with a transient intermediate now must be taken into account from both the starting material and product sides of the reaction. For simplicity, let us use A to represent the concentration of starting dimethyl complex **13a**, L to represent $[PPh_3]$, C to represent the concentration of product **14**, and B to represent the concentration of the hypothetical intermediate or set of intermediates to which the steady-state assumption is applied (see eq 5 below). The phenomenological system, which defines how concentration vs. time data (under pseudo-first-order conditions) must be plotted for the reversible interconversion of A and C (eq 1), is given by eq 2 (k_{obsd} = rate constant for approach to equilibrium; A_0 = concentration of A at time 0 and A_e = concentration of A at equilibrium). The reaction of **13** with PPh_3 was examined under

$$A + L \xrightleftharpoons[k_r]{k_f} C \tag{1}$$

$$\ln([A_0] - [A_e])/([A] - [A_e]) = k_{obsd}t \tag{2}$$

pseudo-first-order conditions for several half-lives to discover the dependence of the observed rate constant on the triphenylphosphine concentration. All plots exhibited a good fit to the above relationship and the results are summarized in Table III and Figure 1.

In the previous study,[7] the kinetic data were fit to a mechanism in which an intermediate B (assumed to form by cleavage of one cobalt–carbonyl bond and the metal–metal bond, leaving one metal center coordinatively unsaturated) was followed by a fast phosphine trapping step (eq 3). This led to an expression for the

$$A \xrightleftharpoons[k_{-1}]{k_1} B \xrightarrow{k_2[L]} C \tag{3}$$

overall rate k_{obsd} given by eq 4, assuming $d[L]/dt = 0$ and the

$$k_{obsd} = k_1k_2[L]/(k_{-1} + k_2[L]) \tag{4}$$

concentration of B is small. This scheme must now be amended by the inclusion of a back step with rate constant k_{-2} (eq 5).

$$A \xrightleftharpoons[k_{-1}]{k_1} B \xrightleftharpoons[k_{-2}]{k_2[L]} C \tag{5}$$

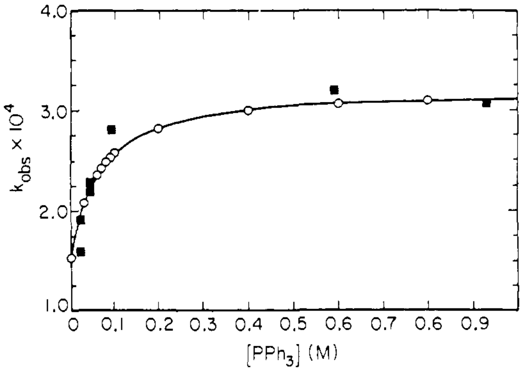


Figure 1. Plot of k_{obsd} vs. the concentration of PPh_3 for the conversion of **13** to the equilibrium mixture of **13** and **14**. Squares represent experimental data; circles and solid line represent the theoretical curve predicted from the best-fit microscopic rate constants.

Steady-state analysis of this situation assuming $(d[B]/dt) = 0$, after suitable algebraic manipulation leads to eq 6. Therefore,

$$\ln \frac{[A_e]k_1k_2[L]/k_{-1}k_{-2}}{[A] - [A_e]} = \ln \frac{[A_0] - [A_e]}{[A] - [A_e]} = \frac{k_1k_2[L] + k_{-1}k_{-2}}{k_{-1} + k_2[L]}t \tag{6}$$

the value of k_{obsd} in this system is given by eq 7. The microscopic

$$k_{obsd} = \frac{k_1k_2[L] + k_{-1}k_{-2}}{k_{-1} + k_2[L]} \tag{7}$$

rate constants can be obtained by substituting for k_1k_2 or $k_{-1}k_{-2}$ by using the equilibrium expression. This leads to eq 8 and 9.

$$K_{eq}[L] + 1/k_{obsd} = \frac{k_2}{k_{-1}k_{-2}}[L] + \frac{1}{k_{-2}} \tag{8}$$

$$\frac{[L] + 1/K_{eq}}{k_{obsd}} = \frac{1}{k_1}[L] + \frac{k_{-1}}{k_1k_2} \tag{9}$$

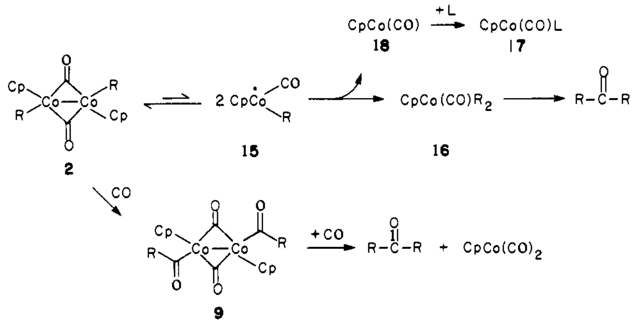
In both expressions 8 and 9, the quantity on the left side is experimentally known and can be plotted vs. [L]. Such plots gave good straight lines with slope = $k_2/k_{-1}k_{-2}$ and intercept = $(k_{-2})^{-1}$ for eq 8 and slope = $1/k_1$ and intercept = k_{-1}/k_1k_2 for eq 9. Analysis of the kinetic data in this way yields the following microscopic rate and equilibrium constants: $k_1 = (3.10 \pm 0.06) \times 10^{-4}$, $k_{-2} = (1.53 \pm 0.19) \times 10^{-4}$, $k_2/k_{-1} = 16.1 \pm 2.0$, and $K_{eq} = k_1k_2/k_{-1}k_{-2} = 33 \pm 2$ M^{-1}. These constants lead to the theoretical curve shown in Figure 1.

In light of the fact that the PPh_3 + **13a** $\rightleftharpoons$ **14** reaction proceeds in both directions at comparable overall rates, our guess as to the identity of B must be reevaluated, and this is done in the Discussion. In addition, the crossover experiments carried out on the reaction of **13** with PPh_3 (Table II) must be viewed in a somewhat different light than they were in the preliminary communication.[7] The analyses were carried out by treating **13** with PPh_3, diluting the solution, carbonylating the "product", and analyzing the resulting acetone by mass spectroscopy. It is now clear that these experiments constitute carbonylations of the PPh_3 + **13a** $\rightleftharpoons$ **14** mixture, with different concentrations of PPh_3 present in solution. The interpretation of these results is considered further in the following section.

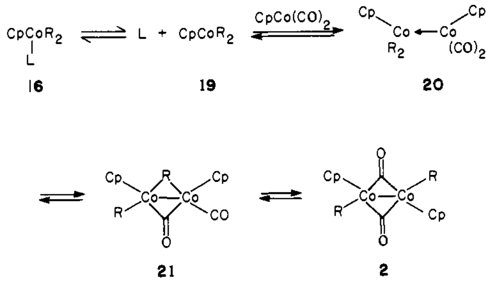
Discussion

We first discussed the mechanism of ketone-forming processes in these systems in a review article written several years ago.[9] At that point it was clear that two independent pathways leading from dinuclear dialkyl complex **2** to ketone were available; these are illustrated briefly in Scheme VI. One proceeded via initial carbonylation of dimer **2**, leading to diacyl complex **9**; this is discussed in more detail below. The second involved the formation of mononuclear dialkyl carbonyl complex **16** as an NMR detectable intermediate, which proceeded on to ketone by migratory insertion and reductive elimination.

Scheme VI



Scheme VII



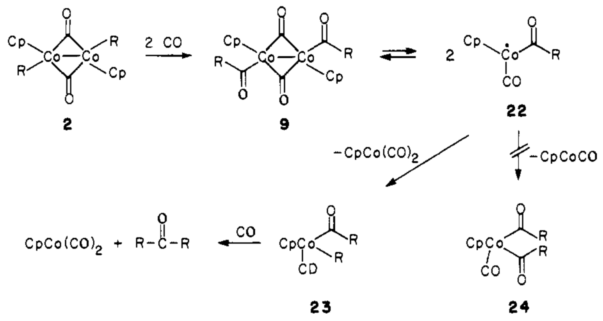
We believe the evidence is quite strong that paramagnetic CpCo(CO)R monomers **15** are rapidly and reversibly formed from the dialkyl dimer **2**. To account for the formation of mononuclear complex **16** in an economical way, we postulated[9] that transfer of an alkyl group could occur between two molecules of the paramagnetic intermediate, leading to **16** and CpCo(CO) (**18**), which can be trapped by a dative ligand L or aggregate to form cobalt clusters.

On the basis of these judgments we predicted that the closely analogous system **13a** (Scheme V), containing linked Cp rings, on treatment with a dative ligand L would initially form the intermediate $(CH_3)_2(CO)Co(C_5H_4\text{–}CH_2\text{–}C_5H_4)Co(CO)L$; like **16** this should then undergo insertion and reductive elimination to give acetone. We were quite surprised to find that **14** was formed instead.

To account for this result, we postulated the formation of a phosphine adduct that could have led to paramagnetic intermediates capable of transferring alkyl groups in the proper way to give the product **14**. However, the discovery that the **13a** $\rightleftharpoons$ **14** reaction is easily reversible has suggested a simpler and in many ways more satisfying mechanism. For the purpose of emphasis, we consider first (Scheme VII) the "reverse" interaction of a cobalt dialkyl (**16**) with $CpCo(CO)_2$ to give the dinuclear dialkyl complex **2**. The kinetic studies discussed in the section immediately preceding this one suggest that this requires dissociation of phosphine at some step during the reaction. It seems likely that PPh_3 is lost initially, leading to intermediate **19**. This coordinatively unsaturated intermediate might then react with $CpCo(CO)_2$, forming the datively metal–metal bonded complex **20**. Conversion to **2** then requires only exchange of R and CO groups between metal centers, either in one step or two as shown in the scheme. This seems a likely mechanism for the process observed in the **13a** $\rightleftharpoons$ **14** reaction. That it also occurs in the parent system, at least to some extent, is indicated by the brief observations we were able to make on the complicated reaction between **2** and PPh_3, discussed earlier. In addition, we have obtained preliminary NMR results that indicate that $CpCo(PPh_3)Me_2$ reacts with $CpCo(CO)_2$ to give dimer **2a** and its thermal decomposition products.

In view of the fact that the **13a** $\rightleftharpoons$ **14** reaction is reversible, how do we interpret the crossover experiments? The presence of the bridging ligand not only makes metal–metal bond cleavage slower but also ensures that bond cleavage/recombination will not result in the sort of scrambling reaction which takes place in the parent system **2**. Therefore, some other process must be responsible for the partial intermolecularity observed in the carbonylation of **13a** $\rightleftharpoons$ **14**. We suggest two possible explanations. The first is that at high concentrations of **13a** $\rightleftharpoons$ **14**, occasionally the set of interactions outlined in Scheme VII might occur between cobalt atoms on different molecules, rather than between cobalt atoms attached to the same bridging ligand, resulting in intermolecular interchange of alkyl groups. Alternatively, complex **14** might undergo methyl interchange between two $Co(PPh_3)Me_2$ moieties in different molecules, as has been established[16] for the parent compound $CpCo(PPh_3)Me_2$. Both of these processes should be dependent upon the concentration of dinuclear complex present in solution; information presently available does not allow us to distinguish between them.

Scheme VIII



Clearly something different happens in the CO-induced conversion of **2** to ketone, since this reaction avoids mononuclear dialkyl complexes **16** (L = CO; Scheme VI). Here we feel our earlier mechanism, involving paramagnetic intermediates, still provides a compelling way to account for the experimental observations. As shown in Scheme VIII, the first step is conversion of dialkyl complex **2** in a stepwise fashion to diacyl **9**. We do not yet know the mechanism of this interesting process; it may occur either by direct interaction of CO with the dimer or by CO-induced migratory insertion in dissociated CpCo(CO)R fragments, followed by recombination of the paramagnetic mononuclear acyl complexes so generated. In any case, once formed, acyl complexes **9** are undoubtedly in equilibrium with these mononuclear paramagnetic species (**22**). Interestingly, we see no evidence for the formation of mononuclear diacyl complex **24** nor for biacetyl, the potential reductive elimination product from this species. This suggests that acyl, and by inference perhaps alkyl, transfer between paramagnetic complexes such as **22** and **15** is not facile and thus provides additional support for the mechanism outlined in Scheme VI for the generation of **16** from **2**. A much larger driving force, however, exists for the transfer of an alkyl (rather than acyl) group between two molecules of **22**. The reason is that such a process generates two coordinatively saturated complexes: $CpCo(CO)_2$ and the alkyl/acyl complex **23**. Complex **23** is presumably identical with the intermediate generated in the reaction of **16** (L = CO) with CO to give acetone and therefore should be a very efficient source of ketone. Its direct formation from **22** accounts for the absence of **16** itself on the pathway from **9** to ketone.

In summary, several different types of chemistry are accessible to dinuclear dialkyl complexes of general structure **2**, although the final ketone-forming steps seem inevitably to involve mononuclear precursors in this system. Fragmentation of dimers to paramagnetic mononuclear species is a very efficient process, and we believe the two major pathways leading to acetone from dinuclear dimethyl complex **2a** involve alkyl transfer between such intermediates. The second important type of chemistry observed is alkyl transfer between adjacent even-electron cobalt centers. This can be clearly observed in the chemistry of bridged complex **13**, and reactions analogous to those which convert **13** into **14** (Scheme VII) may be occurring to some extent when unbridged complexes **2** react with phosphine or CO. Most intriguing is the discovery that this second alkyl-transfer process is reversible. If the thermodynamics can be controlled by properly varying the

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[16] Bryndza, H. E.; Evitt, E. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 4948.

metals or substituents attached to them, it may be possible to construct polynuclear systems of general structure $(MR)_n$ by treating complexes ML_x with mononuclear polyalkyl complexes MR_y. This is an exciting possibility that we hope to explore in the future.

Experimental Section

General Data. All manipulations of air- or water-sensitive materials were conducted under a prescrubbed recirculating atmosphere of N_2 in a Vacuum Atmospheres HE-553 Dri-Lab with attached MO-40-1 Dri-Train or using standard Schlenk or vacuum line techniques.

Infrared (IR) spectra were recorded on Perkin-Elmer 257 and 283 and Beckman IR 4210 grating spectrophotometers using NaCl solution cells (0.10-mm path length). Nuclear magnetic resonance (NMR) spectra were recorded on Varian T-60 and A60A (60-MHz) spectrometers, a Varian EM-390 90-MHz spectrometer, or high-field (180- and 200-MHz) spectrometers equipped with a Bruker magnet and Nicolet Model 1180 data collection system with electronics assembled by Mr. Rudi Nunlist (U.C. Berkeley).

Low-resolution mass spectra were recorded on an A.E.I. MS-12 spectrometer interfaced with a Finnegan 2300 data system. High-resolution mass spectra were recorded on a Du Pont CEC 21-110 system. Molecular weights were obtained from Dornis u. Kolbe Mikroanalytisches Laboratorium (Mülheim, West Germany).

Preparative column chromatography was performed on silica gel 60 (0.063–0.20-mm silica, E. Merck and Co.) dried and degassed for 30 min on a vacuum line. Columns were typically packed in the air and degassed before use by flushing the column with degassed solvent using Schlenk techniques. Gas chromatography was performed on Varian 90P, Perkin-Elmer 3920, and Varian 1400 gas chromatographs.

Reagent grade solvents were purified as follows: methylene chloride and hexanes (Baker "Analyzed Reagent" Grade) were distilled from CaH_2 and degassed by bubbling with N_2 for 5 min. Tetrahydrofuran (THF), diethyl ether, and benzene (all Baker "Analyzed Reagent" Grade) were vacuum transferred, under static conditions, from purple sodium benzophenone ketyl solutions. Triphenylphosphine (Alfa) was recrystallized from hexane and dried for 16 h at high vacuum (25 °C); carbon monoxide (Matheson) was used as supplied. Methyl iodide ($-d_0$ and $-d_3$) was vacuum transferred from CaH_2 onto a clean (concentrated HNO_3, distilled H_2O, and reagent grade acetone washed) copper wire and degassed before use with three freeze–pump–thaw cycles. Cyclopentadiene was cracked at atmospheric pressure from the commercial (Dow) dimer and stored at −78 °C until used. Dicobalt octacarbonyl (Alfa) was used as supplied. Sodium (Alfa) was taken from a mineral oil storage container, washed with pentane and ethanol (absolute), and used directly. Elemental analyses were performed by the California Institute of Technology and U.C. Berkeley microanalytical laboratories.

$Na[CpCoCO]_2$ was prepared as described earlier[3] and was normally used in crude form. For an estimation of the percent of radical anion salt in this material, a sample was prepared and the amount of NaCp and THF were estimated by NMR integration vs. a known amount of added internal standard. This gave a maximum value of 74% $Na[CpCoCO]_2$, which was used in calculating yields (which are thus minimum values) in each of the preparations described below.

$[CpCo(CO)(CH_3)]_2$. $Na[CpCo(CO)]_2$ (1.43 g, 3.24 mmol) was suspended in THF (10 mL) and CH_3I (0.60 mL, 9.6 mol) was added with stirring. The mixture was allowed to stir for 5 min at room temperature, and then petroleum ether (20 mL) was added. The mixture was filtered, and solvent was removed from the filtrate under vacuum to yield 0.74 g of dark green solid. This material was dissolved in benzene and applied to a 2.5 × 10 cm silica gel–benzene column. The first band eluted was orange and contained $CpCo(CO)_2$. The second band, dark green in color, contained $[CpCo(CO)(CH_3)]_2$, which was isolated as a dark green solid upon removal of solvent: yield 0.52 g (48%); NMR (THF-d_8) δ 5.14 (s, 5 H), −0.71 (s, 3 H); IR (THF) ν_{CO} 1854, 1820 cm^{-1}. Anal. Calcd for $C_{14}H_{16}Co_2O_2$: C, 50.32; H, 4.83; Co, 35.27; mol wt, 334. Found: C, 50.49; H, 4.87; Co, 35.09; mol wt (cryoscopic in benzene), 341, 343.

$[CpCo(CO)(CH_3CH_2)]_2$. $Na[CpCo(CO)]_2$ (0.35 g, 0.79 mmol) was suspended in THF (4 mL) in a 100-mL three-necked flask. A dropping funnel containing CH_3CH_2I (0.29 mL, 3.6 mmol) in THF (1 mL), a dropping funnel containing 10 mL of petroleum ether, and a filtration apparatus were attached to the three openings in the flask. The assembly was removed from the drybox, and the flask was cooled to −10 °C. The CH_3CH_2I solution was added dropwise, and the mixture was stirred at −10 °C for 5 h. Petroleum ether was added, and the mixture was filtered. Solvent was removed from the filtrate under vacuum yielding 0.16 g of a dark green solid. This material was chromatographed as described for $[CpCo(CO)(CH_3)]_2$ and $[CpCo(CO)(CH_3CH_2)]_2$ was isolated as a dark green solid: yield 0.070 g (25%); NMR (THF-d_8) δ 5.12 (s, 5 H), 0.90 (t, J = 7 Hz, 3 H), 0.22 (q, J = 7 Hz, 2 H); IR (THF) ν_{CO} 1847, 1813 cm^{-1}. Anal. Calcd for $C_{16}H_{20}Co_2O_2$: C, 53.06; H, 5.57; Co, 32.5. Found: C, 54.63; H, 5.83; Co, 32.7.

$[CpCo(CO)(CF_3CH_2)]_2$. $Na[CpCo(CO)]_2$ (0.38 g, 0.86 mmol) was suspended in THF (3 mL) and CF_3CH_2I (0.40 mL, 2.9 mmol) was added with stirring. The reaction solution was allowed to stir for a few minutes at room temperature, and then petroleum ether (6 mL) was added to the solution. The mixture was filtered and solvent was removed from the filtrate under vacuum yielding a black solid. The material was dissolved in benzene and chromatographed on silica gel by using a 10:1 benzene–petroleum ether mixture. The first band (orange-yellow) eluted from the column contained $CpCo(CO)_2$ and $CpCo(CO)(CF_3CH_2)_2$. The second band was brown in color and contained $[CpCo(CO)(CF_3CH_2)]_2$. The product was isolated as a dark brown solid upon removal of solvent under vacuum: yield 0.31 g (22%); NMR (THF-d_8) δ 5.42 (s, 5 H), 0.25 (q, J_{H-F} = 15 Hz, 2 H); IR (THF) ν_{CO} 1875, 1845 cm^{-1}. Anal. Calcd for $C_{16}H_{14}Co_2F_6O_2$: C, 40.87; H, 3.03; Co, 25.1. Found: C, 40.90; H, 3.38; Co, 25.5.

$CpCo(CO)(CF_3CH_2)_2$. $[CpCo(CO)(CF_3CH_2)]_2$ was dissolved in benzene and allowed to decompose at room temperature. IR analysis showed the major decomposition products were $CpCo(CO)_2$ and $CpCo(CO)(CF_3CH_2)_2$. An insoluble black precipitate was also formed during the decomposition. The solution was filtered, and solvent was removed from the filtrate under vacuum (most of the $CpCo(CO)_2$ codistilled with the solvent). The brown residue was chromatographed on silica gel using petroleum ether as the eluent. The first band eluted from the column contained $CpCo(CO)(CF_3CH_2)_2$ that was isolated as a yellow oil upon removal of solvent. The oil crystallized when it came into contact with a crystal of $CpCo(CO)(CF_3CH_2)_2$. NMR analysis showed this material contained petroleum ether of crystallization that could not be pumped away under vacuum. Analytically pure material was obtained by sublimation at room temperature and <0.001 mm: ^{1}H NMR (benzene-d_6) δ 4.29 (s, 5 H), 1.79 (8 lines, J_{A-B} = 12.4 Hz, J_{A-F} = 14.5 Hz, 2 H), 0.66 (8 lines, J_{A-B} = 12.4 Hz, J_{B-F} = 14.5 Hz, 2 H); ^{19}F NMR (benzene-d_6) δ 0.08 (t, J_{HF} = 14.5 Hz); IR (THF) ν_{CO} 2040 cm^{-1}; mass spectrum, parent peak at m/e 318. Anal. Calcd for $C_{10}H_9CoF_6O$: C, 37.75; H, 2.85; Co, 18.5. Found: C, 38.04; H, 2.96; Co, 18.7.

Thermal Decomposition of $[CpCo(CO)(CH_3)]_2$. A. $[CpCo(CO)(CH_3)]_2$ (0.009 g, 0.027 mmol) was dissolved in toluene-d_8 (0.27 mL), and the solution was filtered into an NMR tube. $[CpCo(CO)(CH_3)]_2$ was allowed to decompose at room temperature, and the reaction was monitored by ^{1}H NMR. Absorptions due to $[CpCo(CO)(CH_3)]_2$ (δ 4.52, −0.47) disappeared, and absorptions due to $CpCo(CO)(CH_3)_2$ (δ 4.37, 0.54) grew in. $CpCo(CO)(CH_3)_2$ began to decompose to produce acetone before the conversion of $[CpCo(CO)(CH_3)]_2$ to $CpCo(CO)(CH_3)_2$ was complete. The final products of the decomposition were acetone (85%), $CpCo(CO)_2$, $[CpCo(CO)]_3$, and $Cp_4Co_4(CO)_2$.

B. $[CpCo(CO)(CH_3)]_2$ (0.002 g, 0.006 mmol) was dissolved in THF (0.25 mL), and the solution was transferred to an IR solution cell. The decomposition of $[CpCo(CO)(CH_3)]_2$ was monitored by following the disappearance of the ν_{CO} band at 1820 cm^{-1}. A band at 2001 cm^{-1} was observed during the course of the decomposition that was assigned to $CpCo(CO)(CH_3)_2$. The product solution contained $CpCo(CO)_2$ (2020, 1955 cm^{-1}), $[CpCo(CO)]_3$ (1955, 1845, 1810, 1760, 1705 cm^{-1}), and $Cp_4Co_4(CO)_2$ (1705, 1685 cm^{-1}). TLC analysis of the product solution verified the presence of these complexes in the solution.

Thermal Decomposition of $[CpCo(CO)(CH_3CH_2)]_2$. A. In the drybox, $[CpCo(CO)(CH_3CH_2)]_2$ (0.020 g, 0.055 mmol) was placed in an NMR tube equipped with a ground glass joint. Toluene-d_8 (0.40 mL) and benzene (0.020 mL) were vacuum transferred onto the solid, and the tube was sealed. An NMR spectrum was recorded at −30 °C. The sample was then allowed to stand at room temperature, and the NMR spectrum was recorded periodically. At the end of the reaction there were a large number of Cp absorptions between δ 5.0 and 4.0. Integration revealed that the total area under these peaks comprised 72% of the area of the original Cp absorption of $[CpCo(CO)(CH_3CH_2)]_2$. Likewise, the area under the ethyl absorptions accounted for 74% of the area of the ethyl absorptions originally present in solution. Two of the organic products were ethane and ethylene, which would be present in the gas phase as well as in solution. This could account for the remainder of the organic product. The third organic product was 3-pentanone present in 32% yield. GC analysis (8 ft ≥ $^{1}/_{8}$ in. Poropak Q; 70 °C; flow, 83 mL/min) of the gases above the solution showed a 4:1 ratio of ethane to ethylene (the 4:1 ratio of ethane to ethylene was also observed in the NMR spectrum). IR, NMR and TLC analysis of the product mixture indicated $CpCo(CO)_2$, $[CpCo(CO)]_2$, $[CpCo(CO)]_3$, and $Cp_4Co_4(CO)_2$ were present in the solution. All products were identified by comparison with authentic samples.

B. $[CpCo(CO)(CH_3CH_2)]_2$ (0.0042 g, 0.012 mmol) was dissolved in THF (0.30 mL), and the solution was transferred to an IR solution cell. The decomposition was monitored by following the disappearance of the

ν_{CO} bands at 1847 and 1813 cm^{-1} over the course of 12.5 h. A band at 2000 cm^{-1} was observed during the course of the reaction that may be due to CpCo(CO)(CH$_3$CH$_2$)$_2$. The compounds observed in solution when the reaction was complete were CpCo(CO)$_2$, [CpCo(CO)]$_2$ (1790 cm^{-1}), [CpCo(CO)]$_3$, and Cp$_4$Co$_4$(CO)$_2$.

Reaction of [CpCo(CO)(CH$_3$)]$_2$ with [CpCo(CO)CF$_3$CH$_2$)]$_2$. A. [CpCo(CO)(CH$_3$)]$_2$ (0.015 g, 0.045 mmol) and [CpCo(CO)(CF$_3$CH$_2$)]$_2$ (0.020 g, 0.045 mmol) were each dissolved in THF-d_8, and an NMR spectrum of each solution was recorded. The NMR samples were taken into the drybox, cooled to −40 °C, and mixed. NMR spectra of the mixture were recorded at −50 °C. Absorptions due to [CpCo(CO)(CH$_3$)]$_2$ (δ 5.14, −0.71) and [CpCo(CO)(CF$_3$CH$_2$)]$_2$ (δ 5.42, 0.25) were observed in addition to several new absorptions that have been assigned to [Cp$_2$Co$_2$(CO)$_2$(CH$_3$)(CF$_3$CH$_2$)] (δ 5.32 (s, 5 H), 5.26 (s, 5 H), 0.18 (q, J_{HF} = 15 Hz, 2 H), −0.66 (s, 3 H)). [Cp$_2$Co$_2$(CO)$_2$(CH$_3$)(CF$_3$CH$_2$)] decomposed rapidly to yield a compound identified as CpCo(CO)(CF$_3$CH$_2$)(CH$_3$), based on its NMR spectrum (δ 5.15 (s, 5 H), 2.32 (8 lines, J_{AB} = 13 Hz, J_{HF} = 14.5 Hz, 1 H), 0.76 (8 lines, 1 H), 0.62 (s, 3 H)). CpCo(CO)$_2$ (δ 5.19) and [CpCo(CO)]$_2$ (δ 4.80) were also produced in the decomposition of [Cp$_2$Co$_2$(CO)$_2$(CF$_3$CH$_2$)(CH$_3$)].

B. [CpCo(CO)(CH$_3$)]$_2$ and [CpCo(CO)(CF$_3$CH$_2$)]$_2$ were each dissolved in THF, and IR spectra were recorded of each solution. The two solutions were mixed so that about equal amounts of each complex would be present in the reaction solution. The reaction was monitored by IR spectroscopy. [CpCo(CO)(CH$_3$)]$_2$ (ν_{CO} 1820 cm^{-1}) and [CpCo(CO)(CF$_3$CH$_2$)]$_2$ (ν_{CO} 1845 cm^{-1}) reacted very quickly (within a few minutes at room temperature) to yield [Cp$_2$Co$_2$(CO)$_2$(CH$_3$)(CF$_3$CH$_2$)] (ν_{CO} 1833 cm^{-1}). [Cp$_2$Co$_2$(CO)$_2$(CH$_3$)(CF$_3$CH$_2$)] then completely decomposed over the course of 40 min at room temperature to yield CpCo(CO)$_2$ (ν_{CO} 2020, 1955 cm^{-1}) [CpCo(CO)]$_2$ (ν_{CO} 1790 cm^{-1}) and presumably CpCo(CO)(CH$_3$)(CF$_3$CH$_2$), which probably has ν_{CO} at 2020 cm^{-1}, under the CpCo(CO)$_2$ band.

Reaction of [CpCo(CO)(CH$_3$)]$_2$ with [CpCo(CO)(CF$_3$CH$_2$)]$_2$ in the Presence of CO. An NMR sample containing [CpCo(CO)(CH$_3$)]$_2$ and [CpCo(CO)(CF$_3$CH$_2$)]$_2$ was prepared exactly as described above except that after the two solutions containing the complexes were mixed, the NMR tube was sealed under CO (0.30 mmol, 3 atm at 25 °C). The reaction was monitored by NMR spectroscopy at −20 °C and then at 34 °C. The initial products of the reaction were [Cp$_2$Co$_2$(CO)$_2$(CH$_3$)(CF$_3$CH$_2$)] and [Cp$_2$Co$_2$(CO)$_2$(COCH$_3$)(CF$_3$CH$_2$)] (δ 5.32 (s), 5.17 (s), 2.40 (s), −0.15 (q, J_{H-F} = 15 Hz)). These complexes decomposed quickly to yield CpCo(CO)(CH$_3$)(CF$_3$CH$_2$), which then reacted with CO to produce CpCo(CO)(COCH$_3$)(CF$_3$CH$_2$) (δ 5.22 (s, 5 H), 2.65 (s, 3 H), 2.53 (8 lines, J_{A-B} = 13 Hz, J_{H-F} = 14.5 Hz, 1 H), 1.24 (8 lines, 1 H). CpCo(CO)(COCH$_3$)(CF$_3$CH$_2$) then underwent reductive elimination to yield CF$_3$CH$_2$COCH$_3$ and CpCo(CO)$_2$.

Reaction of [CpCo(CO)(CH$_3$)]$_2$ with [CpCo(CO)(CH$_3$CH$_2$)]$_2$. A. [CpCo(CO)(CH$_3$)]$_2$ (0.010 g, 0.030 mmol) and [CpCo(CO)(CH$_3$CH$_2$)]$_2$ (0.011 g, 0.030 mmol) were each dissolved in a mixture of THF-d_8 (0.35 mL) and benzene (0.02 mL), and an NMR spectrum was recorded of each solution. The NMR samples were taken into the drybox, cooled to −40 °C, and mixed. A spectrum was recorded of the mixture at −50 °C. Only peaks due to [CpCo(CO)(CH$_3$)]$_2$ and [CpCo(CO)(CH$_3$CH$_2$)]$_2$ were observed. The mixture was allowed to decompose. Qualitatively, it decomposed at about the same rate as each complex would independently. The product mixture was complex. CpCo(CO)(CH$_3$)$_2$ (δ 5.05 (s, 5 H), 0.43 (s, 6 H)) and a complex that may have been CpCo(CO)(CH$_3$)(C$_2$H$_5$) (CH$_3$ singlet at δ 0.24) were present in about equal concentrations. The organic products observed were ethylene and ethane (in about equal amounts), acetone, 2-butanone, and 3-pentanone.

B. IR spectra were recorded of solutions of [CpCo(CO)(CH$_3$)]$_2$ (0.032 M in toluene) and [CpCo(CO)(C$_2$H$_5$)]$_2$ (0.032 M in toluene). Equal amounts of the two solutions were combined, and a spectrum of the mixture was recorded. The ν_{CO} bands of the complexes were not resolvable and only two bands, at 1850 and 1815 cm^{-1}, were observed. After 1 h at room temperature, some decomposition had occurred but the rate of decomposition was similar to that of each complex alone in solution.

Reaction of [CpCo(CO)(CH$_3$)]$_2$ with [CpCo(CO)(CH$_3$CH$_2$)]$_2$ in the Presence of CO. In the drybox, [CpCo(CO)(CH$_3$)]$_2$ (0.007 g, 0.021 mmol) and [CpCo(CO)(CH$_3$CH$_2$)]$_2$ (0.008 g, 0.021 mmol) were placed in an NMR tube equipped with a ground glass joint. On the vacuum line, THF-d_8 (0.38 mL) and benzene (0.02 mL) were distilled into the tube and the tube was sealed under CO (0.30 mmol, 3 atm at 25 °C). The tube was thawed at −78 °C, and NMR spectra were recorded at −50 °C. The NMR spectrum of the reaction mixture was complex. Peaks due to [Cp$_2$Co$_2$(CO)$_2$(COCH$_3$)(CH$_3$)], [CpCo(CO)(COCH$_3$)]$_2$ (*E* and *Z* isomers), [CpCo(CO)(COCH$_2$CH$_3$)]$_2$ (*E* and *Z* isomers), and CpCo(CO)(CH$_3$)$_2$ were observed. A peak having a chemical shift differing from the methyl singlet of [Cp$_2$Co$_2$(CO)$_2$(COCH$_3$)(CH$_3$)] by only 2 Hz was observed. This may be the methyl absorption of [Cp$_2$Co$_2$(CO)$_2$(COCH$_2$CH$_3$)(CH$_3$)]. The carbonylation reaction was allowed to go to completion, and the products of this reaction were CpCo(CO)$_2$ and acetone, 2-butanone, and 3-pentanone in a 1:2:1 molar ratio (as shown by NMR). The NMR solution was analyzed by GC (20 ft × $^1/_8$ in. 8% Carbowax 600 on Chrombsorb G, 70 °C) to verify the identity of the ketone products and their molar ratio. The yields of ketone and CpCo(CO)$_2$ were quantitative.

Reaction of [CpCo(CO)(CH$_3$)]$_2$ with CO. A. In the drybox, [CpCo(CO)(CH$_3$)]$_2$ (0.015 g, 0.045 mmol) was placed in an NMR tube. On the vacuum line, THF-d_8 (0.40 mL) and benzene (0.02 mL) were distilled onto the sample under vacuum. The tube was sealed under CO (0.30 mmol, 3 atm at 25 °C), and the sample was allowed to thaw at −78 °C. The reaction was monitored by NMR spectroscopy at −30 °C. The reaction was quite slow at −30 °C, so during the time a spectrum was recorded, little reaction took place. The reaction was allowed to proceed at room temperature by removing the tube from the cooled probe periodically and allowing it to stand at room temperature for a few minutes before the next spectrum was recorded. After all the [CpCo(CO)(CH$_3$)]$_2$ had reacted, the solution contained a mixture of CpCo(CO)(CH$_3$)$_2$, CpCo(CO)$_2$, acetone, [Cp$_2$Co$_2$(CO)$_2$(CH$_3$)(COCH$_3$)], and *E* and *Z* isomers of [CpCo(CO)(COCH$_3$)]$_2$. If the reaction was allowed to continue, [Cp$_2$Co$_2$(CO)$_2$(CH$_3$)(COCH$_3$)] reacted with CO to produce [CpCo(CO)(COCH$_3$)]$_2$. Then [CpCo(CO)(COCH$_3$)]$_2$ decomposed quickly to yield acetone and CpCo(CO)$_2$. CpCo(CO)(CH$_3$)$_2$ reacted with CO more slowly to produce the same two products. Acetone and CpCo(CO)$_2$ were obtained in quantitative yield.

B. [CpCo(CO)(CH$_3$)]$_2$ (0.010 g, 0.030 mmol) was dissolved in THF (1 mL) in a 25-mL three-necked flask equipped with a vacuum stopcock, a rubber septum, and a stopcock having a hose adaptor that was connected to a balloon. An aliquot of the solution was taken, and then the apparatus was removed from the drybox. The solution was degassed, and the flask was evacuated on the vacuum line. The solution was cooled to −23 °C, and an atmosphere of CO was established over the solution. The balloon was inflated with CO to act as a reservoir. The reaction was allowed to stir at −23 °C and was monitored by IR spectroscopy. Aliquots were taken by syringe and loaded into an argon flushed solution cell. After 1.5 h at −23 °C, most of the [CpCo(CO)(CH$_3$)]$_2$ had been converted to [CpCo(CO)(COCH$_3$)]$_2$. After 2.75 h, most of the [CpCo(CO)(COCH$_3$)]$_2$ had decomposed.

Isolation and Characterization of [CpCo(CO)(COCH$_3$)]$_2$. [CpCo(CO)(CH$_3$)]$_2$ (0.050 g, 0.15 mmol) was dissolved in THF (3 mL). The solution was treated with CO at −23 °C as described above for the reaction of [CpCo(CO)(CH$_3$)]$_2$ with CO. The reaction was monitored by IR spectroscopy, and when all the starting complex had reacted, solvent was removed from the solution under vacuum, yielding a dark-brown solid. This solid was taken into the drybox and purified by column chromatography. A small (0.7 × 7 cm) silica gel–toluene column was prepared, capped with a septum, and cooled in a −40 °C freezer. Flasks containing toluene and THF were also cooled. The residue was dissolved in cold toluene and applied to the cold chromatography column. A green band (probably containing unreacted [CpCo(CO)(CH$_3$)]$_2$ and possibly some [CpCo(CO)]$_2$) was eluted and discarded. Cold THF was applied to the column, and a brown band was collected. Solvent was removed from this fraction under vacuum, yielding a brown solid identified as [CpCo(CO)(COCH$_3$)]$_2$ on the basis of its IR and NMR spectra. The instability of the complex in solution precluded complete purification. (Some decomposition occurred after chromatography, while solvent was being removed from the solution containing [CpCo(CO)(COCH$_3$)]$_2$.) The NMR spectrum (THF-d_8) of the solid showed two Cp resonances and two acetyl resonances: δ 5.11 (s, 5 H), 2.32 (s, 3 H) and 4.93 (s, 5 H), 2.50 (s, 3 H). The first set of signals was 3 times as intense as the second set. The IR spectrum (THF) showed ν_{CO} bands at 1865, 1830, and 1675 cm^{-1}.

The Thermal Decomposition of [CpCo(CO)(COCH$_3$)]$_2$. [CpCo(CO)(COCH$_3$)]$_2$ (0.005 g, 0.013 mmol) was dissolved in THF-d_8 (0.4 mL), and the solution was transferred to an NMR tube. The tube was cooled to −78 °C, and then an NMR spectrum was recorded at −40 °C. The reaction was allowed to proceed at room temperature by removing the tube from the cooled probe periodically and allowing it to stand at room temperature for a few minutes before the next spectrum was recorded. The acetyl peaks due to [CpCo(CO)(COCH$_3$)]$_2$ disappeared and were replaced by the methyl resonance of acetone. The organometallic products consisted of CpCo(CO)$_2$ and cobalt clusters. The yield of acetone was quantitative.

The Effect of CO Pressure on the Rate of Decomposition of [CpCo(CO)(COCH$_3$)]$_2$. [CpCo(CO)(CH$_3$)]$_2$ (0.024 g, 0.072 mmol) was dissolved in a mixture of THF-d_8 (0.68 mL) and benzene (0.02 mL). This solution was divided into three NMR tubes, and each tube was sealed containing a different amount of CO (0.094, 0.47, 0.94 mmol; 1, 5, and

10 atm at 25 °C). The tubes were allowed to thaw at −78 °C and were stored at −78 °C when spectra were not being recorded. In each sample, $[CpCo(CO)(CH_3)]_2$ was allowed to react completely, forming mostly $[CpCo(CO)(COCH_3)]_2$. The disappearance of $[CpCo(CO)(COCH_3)]_2$ was then monitored at 0 °C by observing the decrease in intensity of the acetyl signals. The THF-d_7 peak at δ 3.63 served as the internal standard.

The Reaction of $CpCo(CO)(CH_3)_2$ with CO. $[CpCo(CO)(CH_3)]_2$ (0.009 g, 0.027 mmol) was dissolved in toluene-d_8 (0.27 mL), and the solution was filtered into an NMR tube. The decomposition of $[CpCo(CO)(CH_3)]_2$ was monitored by NMR. When all the $[CpCo(CO)(CH_3)]_2$ had decomposed, the molar ratio of $CpCo(CO)(CH_3)_2$ to acetone was 1.36:1. The NMR tube was taken into the drybox, and the solution was transferred to an NMR tube equipped with a ground glass joint. The solution was degassed, and the tube was sealed under CO (0.30 mmol, 3 atm at 25 °C). The reaction of $CpCo(CO)(CH_3)_2$ with CO was monitored by NMR spectroscopy at ambient temperature.

The Reaction of $[CpCo(CO)(CH_3CH_2)]_2$ with CO. The reaction of $[CpCo(CO)(CH_3CH_2)]_2$ with CO was carried out and monitored as described above for $[CpCo(CO)(CH_3)]_2$. The differences between the two reactions were as follows: (1) qualitatively, the carbonylation reaction proceeded more quickly when $[CpCo(CO)(CH_3CH_2)]_2$ was the substrate; (2) no $CpCo(CO)(CH_3CH_2)_2$ was observed in the carbonylation product mixture; (3) no $[Cp_2Co_2(CO)_2(CH_3CH_2)(COCH_2CH_3)]$ intermediate was observed. The initial products of the carbonylation were (*E*)- and (*Z*)-$[CpCo(CO)(COCH_2CH_3)]_2$, $CpCo(CO)_2$, and 3-pentanone. Allowing the reaction to continue produced $CpCo(CO)_2$ and 3-pentanone as the only products (quantitative yield).

Isolation and Characterization of $[CpCo(CO)(COCH_2CH_3)]_2$. The formation and isolation of $[CpCo(CO)(COCH_2CH_3)]_2$ was carried out exactly as described for $[CpCo(CO)(COCH_3)]_2$. $[CpCo(CO)(COCH_2CH_3)]_2$ seemed to be slightly more stable than is methyl analogue and so was isolated almost pure after column chromatography (as shown by NMR). The NMR spectrum (THF-d_8) consisted of two sets of signals: δ 5.15 (s, 5 H), 2.93 (q, 2 H), 0.65 (t, 3 H) and 4.94 (s, 5 H), 3.09 (q, 2 H), 0.81 (t, 3 H). The set of signals listed first was three times as intense as the second set. These signals have been assigned to *E* and *Z* isomers of $[CpCo(CO)(COCH_2CH_3)]_2$. The IR spectrum (THF) of the material showed ν_{CO} bands at 1862, 1828, and 1666 cm^{-1}.

The Thermal Decomposition of $[CpCo(CO)(COCH_2CH_3)]_2$ in the Presence and Absence of CO. $[CpCo(CO)(COCH_2CH_3)]_2$ (0.020 g, 0.048 mmol) was dissolved in THF-d_8 (0.60 mL), and benzene (0.04 mL) was added to the mixture. The solution was divided into two NMR tubes. One was sealed under CO (0.30 mmol, 3 atm at 25 °C), and the other was sealed under 1 atm of nitrogen. The tubes were thawed at −78 °C and were stored at −78 °C when spectra were not being recorded. The thermal decomposition and carbonylation of $[CpCo(CO)(COCH_2CH_3)]_2$ were followed at 27 °C by monitoring the disappearance of the methylene protons. The THF-d_7 peak at δ 3.63 served as the internal standard. In the absence of CO, 3-pentanone, $CpCo(CO)_2$, $[CpCo(CO)]_2$, and cobalt clusters were produced. Yields were quantitative. In the presence of CO, 3-pentanone and $CpCo(CO)_2$ were the only products. Again, the yields were quantitative.

Thermal Decomposition of a Mixture of $[CpCo(CO)(COCH_3)]_2$ and $[CpCo(CO)(COCH_2CH_3)]_2$. Two solutions containing approximately equal amounts of $[CpCo(CO)(COCH_3)]_2$ and $[CpCo(CO)(COCH_2CH_3)]_2$ in THF-d_8 were mixed in an NMR tube. The thermal decomposition of the mixture was monitored by NMR spectroscopy at −30 °C. The products of the decomposition were $CpCo(CO)_2$, cobalt clusters, acetone, 2-butanone, and 3-pentanone. The molar ratio of the three ketones appeared to be 1:2:1, respectively. The identity of the ketones was verified by GC analysis of the reaction solution (20 ft × $^1/_8$ in. 8% Carbowax 600 on Chromsorb G, 70 °C). The total yield of ketone was 93%.

The Reaction of $[CpCo(CO)(CF_3CH_2)]_2$ with CO. $[CpCo(CO)(CF_3CH_2)]_2$ (0.030 g, 0.064 mmol) was transferred into an NMR tube, and THF-d_8 (0.40 mL) and benzene (0.02 mL) were distilled into the tube under vacuum. The tube was sealed under CO (0.30 mmol, 3 atm at 25 °C) and allowed to thaw at −78 °C. An NMR spectrum of the solution was recorded at −50 °C. The tube was removed from the probe and allowed to warm to room temperature for a few minutes. Spectra were recorded periodically at −50 °C. The reaction was complete within 15 min at room temperature. The only two products observed were $CpCo(CO)_2$ and $CpCo(CO)(CF_3CH_2)_2$ that were present in equal amounts. The yield was quantitative.

Dicyclopentadienylmethane. The following procedure is a modification of the methods described by Schaltegger.[15] A 1-L round-bottomed flask, previously flushed with argon and equipped with a magnetic stirring bar, was charged with 300 mL of dry THF (degassed by bubbling dry nitrogen through the solution) and 15.1 g (0.66 mol) of sodium metal. The flask was equipped with a jacketed, constant-pressure addition funnel flushed with argon. The funnel was cooled to −78 °C using an acetone/dry ice bath and charged with 70 mL of cyclopentadiene, prepared from the dimer by atmospheric cracking under nitrogen. The cold cyclopentadiene was then added dropwise over a 1.5-h period to the stirred reaction mixture. Immediate evolution of hydrogen was observed and the flask was maintained at room temperature by external cooling with an ice bath. After 6 h all of the sodium had dissolved. The clear, slightly violet solution was stored under argon overnight.

The additional funnel was then filled with 21 mL of methylene chloride (dried over nonactivated, 4A molecular sieves), and the solution was added dropwise over a 15-min period. When the addition was complete, the reaction vessel was equipped with a reflux condenser, topped by a positive pressure of argon, and placed in a water bath at 40–50 °C. The reaction was maintained at this temperature for 2.9 h. The solution was then cooled to room temperature, and ~50 mL of ice water was added slowly over a 5-min period with stirring. The addition of water caused most of the salts formed during the course of the reaction to clump together at the bottom of the reaction vessel. Stirring was discontinued, and the solution was decanted. The solution was then washed with three 100-mL portions of water and two 100-mL portions of saturated sodium chloride solution and dried over magnesium sulfate for 15 min at 0 °C.

The dried solution was filtered and concentrated by the use of a rotary evaporator at room temperature to give 28.9 g (61%) of a clear, gold oil. Care must be taken not to heat the product after isolation since polymerization can be induced; attempted vacuum distillation at 60 °C (0.15 mm) resulted in the loss of 90% of the material to polymerization. The material was therefore not purified further. A ^{1}H NMR spectrum of the crude product showed that it contained dicyclopentadienylmethane as the major component as a mixture of three olefin isomers as well as a small amount (~5%) of dicyclopentadiene as a contaminant: ^{1}H NMR ($CDCl_3$) δ 2.9 (m), 3.6 (m), 6.3 (m). The product could be stored without difficulty under N_2 at −10 °C.

[μ-Bis(η^5-cyclopentadienyl)methane]bis(dicarbonylcobalt(I)) (11). In the drybox a 500-mL round-bottom flask equipped with a magnetic stir bar was charged with 24.6 g (71.9 mmol) of dicobalt octacarbonyl. A serum-capped condenser was placed on the flask, and the system was removed from the drybox. A solution of 9.09 g (63.1 mmol) of dicyclopentadienylmethane (added as a 44% solution, by weight, in CH_2Cl_2 containing some dicyclopentadiene) and 300 mL of dry, degassed CH_2Cl_2 was added, via cannula, to the cobalt carbonyl. The flask was then placed in a preequilibrated 50 °C oil bath and heated at reflux for 18 h, after which time IR analysis showed no $Co_2(CO)_8$ remained. The reaction mixture was cooled to room temperature and the solvent removed on a rotary evaporator without external heating. The product mixture was suspended in 250 mL of dry, degassed hexane and filtered through a medium grade sintered glass Schlenk filter into a 500-mL round-bottom flask. The resulting red solution was concentrated on a rotary evaporator and the residual oil placed on a 2.5 × 50 cm column of degassed silica gel, packed in degassed hexane, with a syringe.

The column was developed under air-free conditions as a fast moving yellow band (minor) and a slower moving black band eluted from the column. The remaining slow moving red band was washed from the column with diethyl ether and concentrated on a high vacuum manifold to yield 27.1 g (59.3 mmol, 94% yield) of **11** as a deep red oil: IR (THF) 2017, 1952 cm^{-1}; NMR (C_6D_6/C_6D_5H) δ 2.77 (s, 2 H), 4.54 (AA′BB′ m, 8 H). Anal. Calcd for $C_{15}H_{10}Co_2O_4$: C, 48.42; H, 2.71. Found: C, 48.53; H, 2.81.

[μ-Bis(η^5-cyclopentadienyl)methane]bis(carbonylmethylcobalt(II)) (13). In the drybox a 500-mL round-bottom flask equipped with a 4-mm Teflon needle valve sealed to the bottom was charged with 500 g (146 mmol) of 0.67% sodium amalgam. A magnetic stir bar was added as was 300 mL of dry, degassed THF followed by 12.5 g (33.6 mmol) of **11**. The solution was capped with a rubber septum, taken from the drybox, connected to a pressure relief bubbler, and stirred for 5 h, after which time the IR spectrum of the reaction solution showed no starting **11** remained. During this reaction the solution color changed from red to green. The amalgam was then released through the bottom of the vessel and the solution taken into the drybox where it was filtered through a medium grade sintered glass frit. The solvent was removed by vacuum, and the resulting brittle green foam, containing some THF, **12**, and $NaCo(CO)_4$, was used directly in the alkylation step described below. Because of its extreme air sensitivity this complex was not purified further. IR spectrum (THF): $NaCo(CO)_4$, 1889, 1855 cm^{-1}; **12**, 1643 cm^{-1}.

In the drybox 2.5 g (< 7.4 mmol) of crude **12** was dissolved in 20 mL of dry, degassed THF in a 100-mL round-bottom flask containing a magnetic stir bar. A total of 5.0 g (35 mmol) of CH_3I was added, via syringe, to the stirring solution. The solution was stirred for 2 min, diluted with 40 mL of hexane, quickly filtered through a medium grade scintered glass frit, and concentrated to dryness. The resulting green-brown solid was dissolved in 1.5 mL of benzene, taken from the drybox, and chromatographed, under air-free conditions, on 1.5 × 50 cm of silica gel packed with 60%/40% hexane/benzene preequilibrated at −10 °C. The column was developed with the same solvent mixture to elute minor orange and green fractions before collecting a brown band of **13**. Immediately following the brown fraction, a major red fraction containing mostly **11** was collected and concentrated for recovery.

Solvent was removed from crude **13** on a vacuum line and the resulting solid rechromatographed on silica gel (1 × 15 cm) in the drybox. Hexane was used to elute a small amount of **11** as a yellow band, and then diethyl ether was used to elute the otherwise stationary **13**. Removal of the solvent on a vacuum line left green-black air-sensitive needles of **13** (230 mg, 0.66 mmol): IR (THF) 1830 (s), 1863 (m) cm^{-1}; NMR (C_6D_6/C_6D_5H) δ 4.57 (t, 4 H), 4.82 (t, 4 H) [AA′BB′], 2.03 (s, 2 H), −0.35 (s, 6 H); mass spectrum, *m/e* 346, 316, 302, 288, 275, 274, 215, 201, 177, 111, 149, 148, 142, 141, 133, 67, 58, 44, 43. Anal. Calcd for $C_{15}H_{16}Co_2O_2$: C, 52.05; H, 4.66; M_r, 345.9817. Found: C, 52.18; H, 4.86; M_r, 345.9817.

By this same method **13-*d*$_6$** was prepared from **12** and CD_3I: IR (Et_2O) 1838 (s), 1869 (m) cm^{-1}; NMR (C_6D_6/C_6D_5H) δ 4.57 (t, 4 H), 4.82 (t, 4 H) [AA′BB′], 2.03 (s, 2 H); mass spectrum analysis showed >99% $C_{15}H_{10}D_6Co_2O_2$.

Reaction of 13 with CO. Solutions of **13**, while indefinitely stable under air free conditions in solutions at room temperature, decomposed under an atmosphere of CO in several hours to form acetone and **11** quantitatively, as analyzed by NMR. In the drybox a 5-mm NMR tube fused to a 14/20 ground glass joint was charged with 10 mg (0.029 mmol) of **13** and dissolved in ca. 500 μL of benzene-*d*$_6$. The solution was capped with a 4-mm Teflon needle valve and the assembly placed on the vacuum line below an 81.22-mL known volume bulb. The manifold was evacuated and the tube degassed with three freeze–pump–thaw cycles. The bulb was then filled with 458 torr of CO gas (by manometer), and the contents of the bulb were allowed to equilibrate with the NMR tube at liquid N_2 temperatures. The tube was then sealed containing 0.146 mmol of CO gas. The tube was thawed and placed in the heated (70 °C) probe of an NMR spectrometer. The products were analyzed by NMR chemical shift and spiking information as well as IR and mass spectral methods in the case of the acetone.

Crossover Experiments with 13a and 13b. Crossover experiments were conducted by combining **13a** and **13b** in a stock solution. This solution was measured into a 12-mL heavy walled Schlenk bomb with 4-mm Teflon stopcock, and more solvent was added as required by the experiment. In a typical experiment a total of 10.0 mg (0.0287 mmol, 121 μL) of the combined **13a** materials (from a solution containing 20.0 mg (0.0578 mmol) of **13a** and 21.2 mg (0.0602 mmol) of **13b** and 500 μL of solvent: the mixture thus was of a 49/51 **13a**/**13b** composition containing 0.0824 mg/mL of **13a**) was placed in the bomb. The bomb was stripped of the ether solvent, and the desired amount of benzene was added (350 μL for solution concentration of 0.25 M, 1.74 mL for 0.05 M) and the bomb charged with 75 mg (0.286 mmol) PPh_3 and allowed to stand in a 25 °C bath for 8 h. The resulting solution was diluted to 0.05 M in the drybox, degassed on a vacuum line, charged with 1.62 mmol (600 torr in 160 mL at 298 °C, 3.3 atm in bomb at 25 °C) of CO, and heated for 8 h at 70 °C. The solution was stripped of CO on a vacuum line, and the resulting volatiles were vacuum transferred off of the **11** and PPh_3 products. The acetone was collected by preparative VPC and analyzed by mass spec.

When the donor ligand was CO, the solution of **13a** + **13b** was degassed on a vacuum line (three freeze–pump–thaw cycles) and the ligand condensed into the vessel by using known volume bulbs to measure the desired amount of compound.

Reaction of Dimer 13a with Triphenylphosphine. 1. Sample Preparation. In the drybox a 5-mm Pyrex NMR tube fused to a 14/20 ground glass joint was charged with a known volume of a 0.0099 M benzene-*d*$_6$ solution of bridging dimethyl dimer (**13a**). The solution was transferred by using a volumetric pipette (0–1.0 mL), and the stock benzene-*d*$_6$ solution of the dimethyl compound (**13a**) was stored in a 2-mL volumetric test tube equipped with a ground glass joint. The test tube was sealed between uses with a ground glass stopper and parafilm, and the solution was frozen in the drybox freezer. The stock solution had been prepared by dissolving 6.9 ± 0.3 mg (20.0 μmol) of recrystallized dimethyl compound (**13a**) in benzene-*d*$_6$ and bringing the solution up to volume.

The solution in the NMR tube was then frozen by using a cold toluene solution (−30 to −40 °C) that had been stored in the freezer. A known volume of a 0.0886 M benzene-*d*$_6$ solution of triphenylphosphine was placed on top of the frozen solution again by using a volumetric pipette. The stock triphenylphosphine solution had been prepared by dissolving 116.2 ± 0.1 mg (0.443 mmol) of recrystallized triphenylphosphine with benzene-*d*$_6$ in a 5-mL volumetric flask sealed to a 4-mm Teflon stopcock. The purpose of the stopcock was to prevent concentration changes due to solvent evaporation during storage.

The total volume of each sample was 1.0 mL. In those cases where the desired concentration could not be achieved by mixing the stock solutions alone, the sample volume was brought to 1.0 mL using benzene-*d*$_6$.

With both solutions unmixed and frozen, the NMR tube was fitted with a 4-mm Teflon stopcock equipped with 14/20 ground glass joints. The assembly was quickly removed from the drybox, and the end of the NMR tube was placed in a liquid-nitrogen bath. The sample was placed on a vacuum line evacuated to $\leq 10^{-3}$ torr, and a calculated amount of tetramethylsilane (MeSi) ($^1/_3$ × mol of dimethyl compound in sample) was vacuum transferred onto the kinetic sample as an internal standard by using a known volume bulb and a differential pressure gauge. The tube was then hermetically sealed under vacuum. Since freeze–pump–thaw cycles would result in mixing of the solution, they were not carried out. The prepared sample was then stored in a freezer until needed.

2. Data Collection. Having prepared the sample, a typical kinetic run was carried out in the following manner. The tube was removed from a cold bath, quickly warmed to room temperature by vigorous shaking in a water bath, and then placed in the thermostated probe (T = 25.4 ± 0.1 °C) of a 200-MHz ^{1}H NMR spectrometer. The temperature of the probe was calibrated by using a standard methanol sample obtained from Varian Associates. The sample was then allowed to equilibrate in the probe for at least 5 min while the field was shimmed. Generally 25 to 30 spectra were collected at 9-min intervals for the first half of the run and 18-min intervals during the second half. The progress of the reaction was monitored by observing the decrease in the methyl resonance for **13a** (singlet at δ −0.3) and the increase in the intensity of the methyl absorption of the product **14** (doublet at δ 0.45 (J = 5.8 Hz)). Peak areas and positions were calculated relative to the added internal standard, TMS.

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Registry No. 1, 62602-00-0; **2a**, 61276-02-6; **2b**, 73411-69-5; **2c**, 92284-17-8; **2d**, 92284-18-9; **3**, 58496-39-2; **4**, 53450-14-9; **5**, 53450-15-0; **6**, 53450-16-1; **7a**, 61156-12-5; **7b**, 92284-19-0; **7c**, 92284-20-3; **8a**, 73411-72-0; (*E*)-**9a**, 73411-70-8; (*Z*)-**9a**, 73465-73-3; (*E*)-**9b**, 75023-46-0; (*Z*)-**9b**, 74098-47-8; **10**, 92284-21-4; **11**, 71674-53-8; **12**, 92284-22-5; **13a**, 71729-49-2; **13b**, 92284-23-6; **14**, 92284-24-7; $CpCo(CO)_2$, 12078-25-0; $CpCo(CO)(CF_3CH_2)(CH_3)$, 92284-25-8; $[Cp_2Co_2(CO)_2(COCH_3)(CF_3CH_2)]$, 92284-26-9; $CpCo(CO)(COCH_3)(CF_3CH_2)$, 92284-27-0; $CF_3CH_2COCH_3$, 2366-70-3; $CpCo(CO)(CH_3)(C_2H_5)$, 92284-28-1; $[Cp_2Co_2(CO)_2(COCH_2CH_3)(CH_3)]$, 92284-29-2; $Co_2(CO)_8$, 10210-68-1; acetone, 67-64-1; 2-butanone, 78-93-3; 3-pentanone, 96-22-0; dicyclopentadienylmethane, 79249-50-6; cyclopentadiene, 542-92-7; methylene chloride, 75-09-2.