positional and thermal parameters are given in Table III.[29]

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(29) See paragraph at the end of paper regarding supplementary material.

Synthesis, Crystal and Molecular Structure, and Chemistry of (μ-Trimethylene)bis(η-cyclopentadienyl)bis(μ-carbonyl)dicobalt, a Five-Membered Dicobaltacycle[†]

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Treatment of Na[CpCo(CO)]$_2$ with 1,n-dihaloalkanes leads in certain cases to double alkylation, giving dinuclear metallacycles containing two adjacent cobalt atoms. This paper reports the synthesis and study of several such systems and an in-depth investigation of the five-membered dimetallacycle 1 prepared from 1,3-diiodopropane. The molecular structure of 1 was determined by X-ray diffraction, using 1016 reflections (R = 2.47). The crystals were orthorhombic (space group $Fdd2$), with unit-cell parameters a = 16.7983 Å, b = 45.576 Å, c = 6.9565 Å. The complex has an "open envelope" ring structure, with a dihedral angle of 32.9°; the Co–Co bond distance is 2.413 Å. Thermolysis of 1 (80–100°) gives cyclopropane and propene. Reaction of 1 with CO or phosphines (L) occurs at lower temperature, leading to a product distribution which is dependent upon the concentration of L. At low [L], the reaction leads to cyclopropane mixed with a small amount of propene and CpCo(L)(CO). High [L] produces CpCo(L)(CO) and mononuclear metallacyclopentanones 6, 7, or 8 depending on the entering ligand. Thermolysis of the metallacyclopentanones leads again to cyclopropane and propene rather than to cyclobutanone. Kinetic and isotope labeling studies on the reaction of 1 with dative ligands suggest a mechanism involving initial formation of dicobaltacyclohexanones A and B. B then is postulated to rearrange to a mononuclear carbonylmetallacyclobutane complex (C) which can either eliminate C$_3$ hydrocarbons or undergo CO insertion, leading to metallacyclopentanone.

Introduction

Metallacycles—heterocycles containing a transition metal in the ring—have been a subject of intensive study by organometallic chemists. The longest known members of this class of complexes are the carbon-unsaturated "metalloles" formed during metal-induced oligomerization or cyclotrimerization of acetylenes.[1,2] More recently, carbon-saturated metallacycles have been implicated in important processes such as C–H activation,[3] olefin metathesis,[4] alkene dimerization,[5] and metal-catalyzed isomerization of organic small-ring compounds.[6] The synthesis of stable, isolable members of this class of complexes has helped in elucidating their properties and understanding the role they play in the processes mentioned above.

There is increasing evidence that many metal-mediated processes depend on catalysts or intermediates containing more than one metal.[7] Despite this, the majority of metallacycles studied so far contain only one metal in the ring. An interesting departure from this trend is the provocative series of carbon-unsaturated metallacycles formed by sequential insertion of alkynes into a dinuclear molybdenum system[8] and the class of dimetallacyclopropanes (μ-methylene complexes) which have been prepared and studied recently.[9]

(1) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; p 525 ff.

(2) See, for example, the following papers and the references cited therein: (a) Collman, J. P.; Kang, J. W.; Little, W. F.; Sullivan, M. F. *Inorg. Chem.* 1968, 7, 1298. (b) Maitlis, P. M. *Acc. Chem. Res.* 1976, 9, 93. (c) Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* 1979, 101, 1123. (d) Dickson, R. S.; Mok, C.; Connor, G. *Aust. J. Chem.* 1977, 30, 2143. (e) Vollhardt, K. P. C. *Acc. Chem. Res.* 1977, 10, 1. (f) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* 1977, 99, 1666.

(3) DiCosimo, R.; Moore, S. S.; Sowinski, A. F.; Whitesides, G. M. *J. Am. Chem. Soc.* 1982, 104, 124 and references cited there.

(4) Grubbs, R. H. In "Progress in Inorganic Chemistry"; Lippard, S. J., ed.; Wiley: New York, 1978; Vol. 24.

(5) McLain, S. J.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* 1980, 102, 5610.

(6) (a) Paquette, L. A. *Acc. Chem. Res.* 1971, 4, 280. (b) Bishop, K. C., III *Chem. Rev.* 1976, 76, 461. (c) Halpern, J. In "Organic Synthesis via Metal Carbonyls"; Wender, I.; Pino, P., Eds.; Wiley: New York, 1977; Vol. II, p 705.

(7) (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* 1975, 84, 959; 1976, 85, 451. (b) Sinfelt, J. H. *Acc. Chem. Res.* 1977, 10, 15. (c) Muetterties, E. L.; Stein, J. *J. Chem. Rev.* 1979, 79, 479. (d) Johnson, B. F. G.; Lewis, J. *Pure Appl. Chem.* 1975, 44, 43. (e) Ozin, G. A. *Catal. Rev.—Sci. Eng.* 1977, 16, 191.

(8) (a) Knox, S. A. R.; Stansfield, F. D.; Stone, F. G. A.; Winter, M. J.; Woodward, P. *J. Chem. Soc., Chem. Commun.* 1978, 221. (b) Green, M.; Norman, N. C.; Orpen, A. G. *J. Am. Chem. Soc.* 1981, 103, 1269.

[†] This paper is submitted in memory of Rowland Pettit, a brilliant chemist and good friend. We have chosen this manuscript because of the interest we shared in the chemistry of dinuclear metallacycles, but we hope it will serve as our tribute to Pettit's many important contributions to organotransition-metal chemistry from its early days to the most recent times.
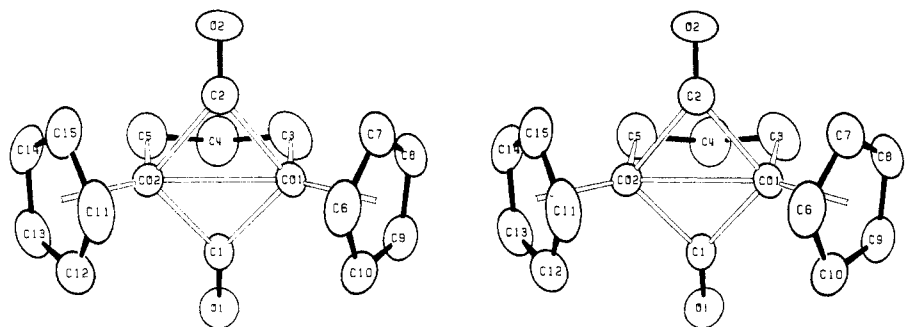
Figure 1. ORTEP stereopair drawing of one molecule of $Co_2(CO)_2(C_3H_6)(C_5H_5)_2$ (1), showing the atomic labeling scheme. View is approximately parellel to the molecular mirror plane. Thermal ellipsoids are scaled to represent the 50% probability surface.

The work reported in this paper was initiated in the belief that saturated dinuclear metallacycles would have a chemistry at least as rich and important as their mononuclear relatives. It was stimulated by our earlier development of a method for preparing dinuclear dialkylcobalt complexes.[10] We describe the full details of synthesis and chemistry of the first saturated five-membered dimetallacycle, including its crystal and molecular structure.

Results and Discussion

Preparation of Dicobaltacycles. As described earlier, the dinuclear radical anion $Na[Cp_2Co_2(CO)_2]$ can be doubly alkylated with a variety of alkyl monohalides and sulfonates.[10] We have now extended this reaction, using dihaloalkanes to prepare metallacycles containing the dicobalt moiety. For example, when 1,3-diiodopropane was added to a suspension of $Na[Cp_2Co_2(CO)_2]^{10a,11}$ in THF at room temperature, an immediate color change to an intense blue-green indicated reaction. 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 1955 cm^{-1} ($CpCo(CO)_2$), 1790 cm^{-1} ($Cp_2Co_2(CO)_2$), and 1815 cm^{-1}. The latter value is reminiscent of the IR carbonyl frequency of the earlier prepared dialkyl dimers.[10b] Column chromatography on alumina yielded a first fraction of yellow $CpCo(CO)_2$ and a second dark green fraction of a new material. Analytical data and spectroscopic characterization of this material are consistent with structure 1 (Scheme I), a cobalt dimer in which the two metal atoms are bridged by a trimethylene chain and two CO ligands. Complex 1 was isolated in 42% yield based on $Na[Cp_2Co_2(CO)_2]$. It forms air-stable black needles, and solutions of it can be exposed to air without any signs of decomposition.

Because the analogous acyclic dialkyl dimers decompose in solution at room temperature,[10b] we were surprised by the high thermal stability of 1. Solutions of 1 in benzene decompose at an appreciable rate only at 100 °C. To test the influence of ring size on this thermal stability, we attempted the preparation of analogous metallacycles with larger and/or smaller rings. Reaction of $Na[Cp_2Co_2(CO)_2]$
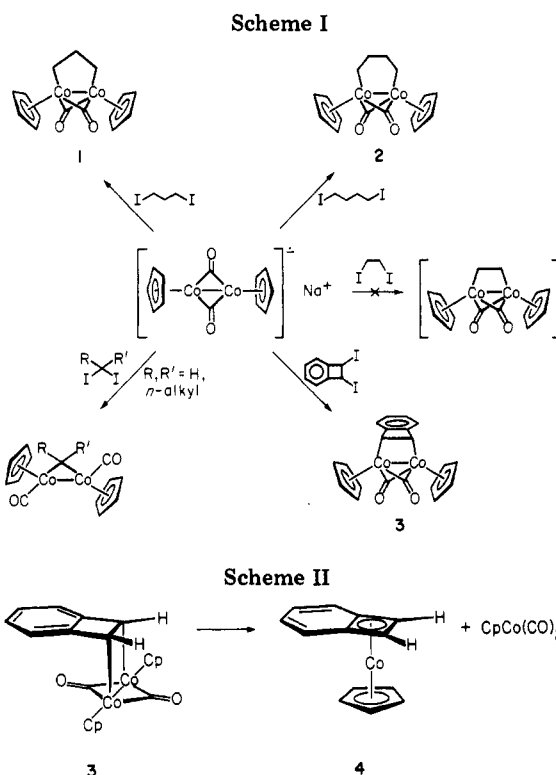
Scheme I

Scheme II

with 1,4-diiodobutane afforded a new material, to which we assign structure 2 (Scheme I) on the basis of analytical and spectroscopic data. This six-membered metallacycle proved to be much more sensitive thermally than 1. Solutions of 2 decompose rapidly at room temperature, and its preparation and chromatographic isolation in 18% yield had to be carried out at ca. -10 °C (see Experimental Section for details). Treatment of $Na[Cp_2Co_2(CO)_2]$ with 1,2-diiodoethane did not result in the formation of the expected four-membered metallacycle (Scheme I). If it is indeed formed, its decomposition, most likely to C_2H_4 and unsaturated cobalt fragments, must be very fast.

Such a decomposition pathway might be energetically less favorable for a strained olefin. We therefore attempted to generate a four-membered metallacycle by using the diiodide of benzocyclobutadiene (Scheme I). This reaction indeed afforded the expected metallacycle 3 in 16% yield after chromatography on alumina. However, this molecule is also relatively thermolabile and rearranges to the previously prepared[12] mononuclear η^4-benzocyclobutadiene complex 4 at ambient temperature (Scheme II). Finally, treatment of $Na[Cp_2Co_2(CO)_2]$ with gem-diiodides led to

(9) See, for example, the following papers and references cited therein: (a) Herrmann, W. A.; Plank, J.; Ziegler, M. L.; Balbach, B. *J. Am. Chem. Soc.* **1980**, *102*, 5906. (b) Theopold, K. H.; Bergman, R. G. *Ibid.* **1981**, *103*, 2489.

(10) (a) Schore, N. E.; Ilenda, C. S.; Bergman, R. G. *J. Am. Chem. Soc.* **1976**, *98*, 7436; **1977**, *99*, 1781. (b) White, M. A.; Bergman, R. G. *J. Chem. Soc., Chem. Commun.* **1979**, 1056. (c) Bergman, R. G. *Acc. Chem. Res.* **1980**, *13*, 113. Some of the results reported here were described earlier in preliminary form: (d) Theopold, K. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1980**, *102*, 5694.

(11) The material used throughout this study was the crude product of the reduction of $CpCo(CO)_2$ with Na amalgam. The actual concentration of $Na[Cp_2Co_2(CO)_2]$ in this material is ca. 70% by weight.

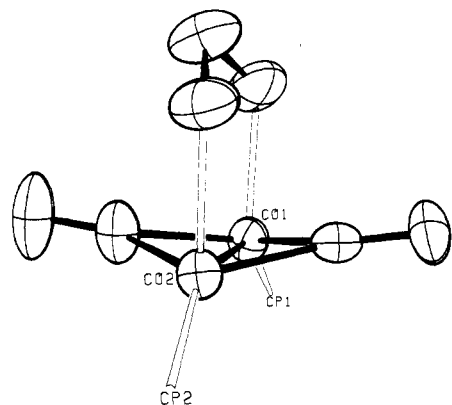(12) Duclos, R. T.; Vollhardt, K. P. C.; Yee, L. S. *J. Organomet. Chem.* **1979**, *174*, 109.

Figure 2. ORTEP drawing showing a view of 1 along the metal–metal bond axis. Cyclopentadienyl rings have been omitted for clarity.

dimetallacyclopropanes (Scheme I). These compounds are quite stable thermally; i.e. their solutions can be heated to 60–70 °C before decomposition begins. Preliminary results on the chemistry of these μ-alkylidene dimers has been described elsewhere.[9b,13]

To our knowledge, 1 and 2 are the first saturated dinuclear five- and six-membered metallacycles, and complete structural characterization seemed warranted. Due to its greater stability 1 was chosen for the structure determination. Suitable crystals were grown by diffusion of pentane into a solution of 1 in toluene at room temperature. A total of 1016 reflections were measured, and the structure was refined to an R value of 2.4%. (See Table II, Experimental Section, and supplementary information for details of the structure determination.) The crystal structure consists of well-separated molecules of 1. There are no unusually short intermolecular contacts. Figure 1 shows an ORTEP stereodrawing of the molecule with the atom numbering scheme. Figure 2 shows a view along the Co–Co bond (Cp rings omitted for clarity).

Selected distances and angles are compiled in Table I. The individual molecules possess approximate noncrystallographic mirror symmetry with the mirror plane normal to the Co–Co bond. Each cobalt is bound to one carbon of the C_3H_6 moiety, a η^5-cyclopentadienyl ligand, two bridging carbonyls, and the other cobalt. The Cp rings are "slipped" relative to the cobalt atoms so that Co1–C8 < Co1–C9 $\approx$ Co1–C7 < Co1–C6 $\approx$ Co1–C10; i.e. the cobalt is closer to the edge near the C_3H_6 ligand. This is presumably due to steric interaction between these two ligands. The carbonyl oxygens are coplanar with the Co_2–C planes to which they belong, and these planes are bent away from the Cp ligands. The geometry of the five-membered ring is that of an opened envelope with a dihedral angle (Co1–C3–C4–C5) of 32.9°. Since the ¹H NMR spectrum shows the four α protons and two β protons to be respectively equivalent in the temperature range from 25 to –80 °C, the ring flip that equilibrates these protons must be fast on the NMR time scale (in addition, the average cis and trans H_α/H_β coupling constants must be very similar). This is not surprising given the reported barrier to planarity in cyclopentane of 5.2 kcal/mol.[14]

Chemistry of Bimetallacycle 1. The thermal chemistry of 1 reflects its cyclic structure. When solutions of 1 in benzene were heated to 100 °C, the metallacycle slowly decomposed to yield propene (73%), cyclopropane (18%), and traces of propane (1%). The organometallic products

(13) Theopold, K. H.; Bergman, R. G. *Organometallics* **1982**, *1*, 219.
(14) Carreira, L. A.; Jiang, G. J.; Person, W. B.; Willis, J. N. *J. Chem. Phys.* **1972**, *56*, 1440.

Table I. Selected Distances (Å) and Angles (Deg)[a]

Bond Distances

Co1–Co2	2.413 (1)	C1–O1	1.154 (4)
Co1–C1	1.885 (3)	C2–O2	1.164 (4)
Co1–C2	1.872 (3)		
Co1–C3	2.044 (4)	C3–C4	1.528 (5)
Co1–C6	2.144 (4)	C4–C5	1.494 (5)
Co1–C7	2.107 (4)	C6–C7	1.400 (5)
Co1–C8	2.053 (3)	C7–C8	1.388 (6)
Co1–C9	2.090 (3)	C8–C9	1.419 (5)
Co1–C10	2.131 (3)	C9–C10	1.412 (5)
Co1–Cp1	1.732[b]	C10–C6	1.417 (6)
Co2–C1	1.875 (3)	C11–C12	1.395 (6)
Co2–C2	1.884 (3)	C12–C13	1.418 (5)
Co2–C5	2.038 (4)	C13–C14	1.437 (5)
Co2–C11	2.140 (4)	C14–C15	1.382 (6)
Co2–C12	2.141 (3)	C15–C11	1.414 (5)
Co2–C13	2.102 (3)		
Co2–C14	2.060 (3)		
Co2–C15	2.107 (4)		
Co2–Cp2	1.737[b]		

Bond Angles

C1–Co1–C2	98.19 (13)	Co2–Co1–C3	92.49 (10)
C1–Co1–C3	85.98 (17)	Co1–Co2–C5	92.55 (9)
C2–Co1–C3	82.40 (15)	Co1–C3–C4	133.9 (3)
Co1–Co2–Cp1	142.6[b]	Co2–C5–C4	114.8 (3)
C1–Co1–Cp1	126.6[b]	C3–C4–C5	118.1 (4)
C2–Co1–Cp1	125.5[b]		
C3–Co1–Cp1	124.8[b]	C10–C6–C7	107.7 (4)
		C6–C7–C8	108.2 (4)
C1–Co2–C2	98.12 (13)	C7–C8–C9	109.5 (3)
C1–Co2–C5	85.95 (17)	C8–C9–C10	106.1 (4)
C2–Co2–C5	82.54 (14)	C9–C10–C6	108.6 (3)
Co1–Co2–Cp2	143.1[b]		
C1–Co2–Cp2	127.7[b]	C15–C11–C12	108.5 (4)
C2–Co2–Cp2	124.9[b]	C11–C12–C13	108.9 (3)
C5–Co2–Cp2	124.2[b]	C12–C13–C14	105.5 (4)
		C13–C14–C15	109.6 (3)
Co1–C1–O1	139.62 (21)	C14–C15–C11	107.5 (4)
Co2–C1–O1	140.46 (21)		
Co1–C1–Co2	79.86 (14)		
Co1–C2–O2	140.71 (25)		
Co1–C2–Co2	79.96 (13)		

Torsional Angles

Cp1–Co1–Co2–Cp2	2.0	Co2–Co1–Cp1–C6	–23.4
C3–Co1–Co2–C5	0.0	Co1–Co2–Cp2–C11	6.8
C3–Co1–Co2–C1	82.6	Co1–Co2–C5–C4	16.0
C3–Co1–Co2–C2	–78.0	Co2–Co1–C3–C4	–15.6
C3–Co1–Co2–Cp2	–174.9	Co1–C3–C4–C5	31.9
C5–Co2–Co1–Cp1	177.0	Co2–C5–C4–C3	–32.1

[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.

of this reaction were $CpCo(CO)_2$ and cobalt-containing clusters (mainly $Cp_4Co_4(CO)_2$). This unusual resistance to decomposition by β-elimination resembles the behavior of other five-membered metallacycles.[15] Thermolysis of 1-d_2 (fully deuterated β-position) exhibited no scrambling of the label into the α-positions of recovered starting material, indicating that the trimethylene unit does not suffer skeletal rearrangement under these conditions. Likewise, the thermolysis of a 1:1 mixture of 1 and 1-d_4 (fully deuterated α-positions) gave cyclopropane having label distribution d_0, 45.7%, d_1, 4.1%, d_2, 2.1%, d_3, 9.0%, and d_4, 39.1%, and propene having label distribution d_0, 44%, d_1, 4.4%, d_2, 1.7%, d_3, 9.4%, and d_4, 40.1%. This

(15) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1973**, *95*, 4451.

Scheme III

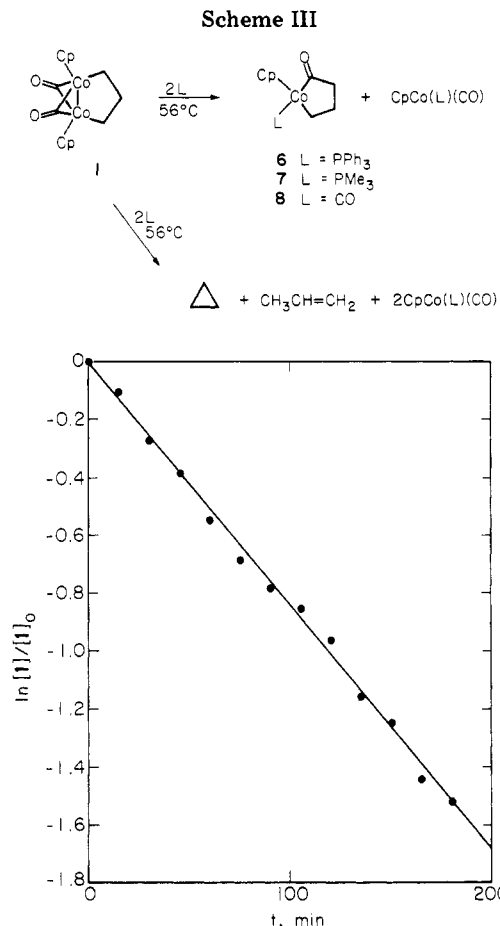**Figure 3.** First-order plot of the disappearance of **1** in the presence of excess triphenylphosphine ($[1]_0$ = 0.014 M, $[PPh_3]$ = 0.402 M; k_{obsd} = 14.1 × 10^{-5} s^{-1}).

demonstrates that the product hydrocarbons arise in predominantly intramolecular reactions.

The cleanest and in some ways most dramatic reaction of bimetallacycle **3** occurs upon treatment with CO and phosphines (Scheme III). Reaction with relatively high concentration of PPh_3, for example, occurs rapidly at 56 °C and leads to $CpCo(PPh_3)CO$ and the mononuclear metallacycle **6**. Similar treatment of **1** with PMe_3 leads to **7**, and carbonylation gives **8**. During carbonylation of $Cp_2Co_2(CO)_2Me_2$ it was possible to observe[10b] both binuclear diacyl complexes as well as the mononuclear dialkyl complex $CpCo(CO)Me_2$, but we have never been able to detect the alkyl/acyl complex $CpCo(COCH_3)(CH_3)CO$. Neither have we found $CpCo(COCH_3)(CH_3)(PR_3)$ in reactions of the dimethyl complex with phosphines; apparently these materials undergo too rapid reductive elimination to acetone. In sharp contrast, complex **6** is stable to 125 °C, and even at this temperature *cyclopropane and propylene*, rather than cyclobutanone, are the products of thermal decomposition. Trimethylphosphine complex **7** is even more stable, again leading to cyclopropane and propylene at temperatures near 175 °C.

Lowering the concentration of PPh_3 produces two effects. First, at sufficiently low $[PPh_3]$, substantial decreases in the reaction rate are observed. Second, significant amounts of cyclopropane (mixed with small amounts of propene) begin to be observed, the ratio of cyclopropane to **6** *increasing* as the phosphine concentration (and the reaction rate) drops. Control studies demonstrated that the C_3 products are not formed from unassisted thermal decomposition, which proceeds too slowly at 56 °C to produce detectable amounts of cyclopropane or propene;
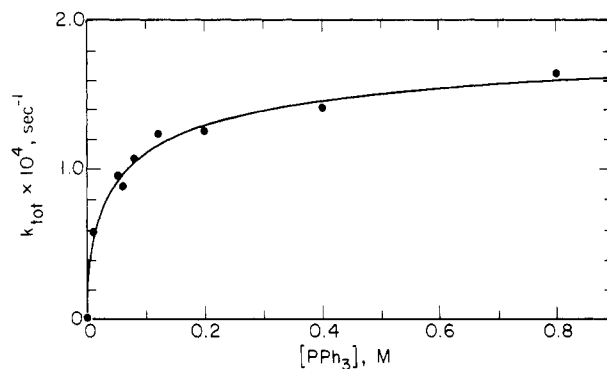

Figure 4. Dependence of the pseudo-first-order rate constant of the reaction of **1** with PPh_3 on the concentration of phosphine.
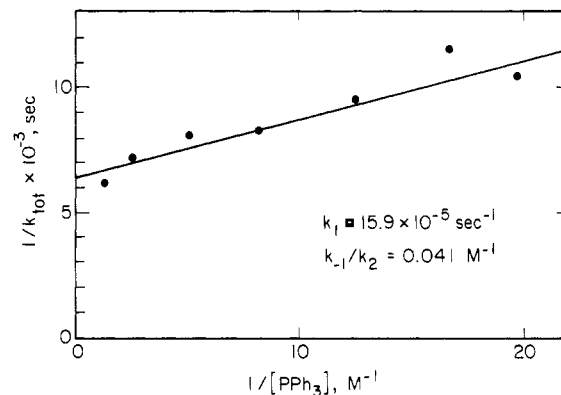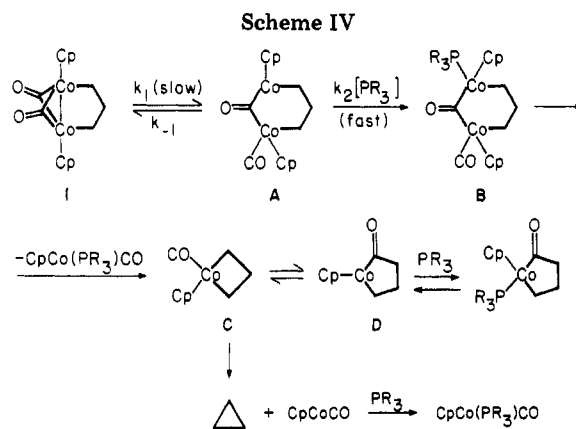

Figure 5. Plot of $1/k_{obsd}$ versus inverse phosphine concentration (according to eq 2).

Scheme IV

the formation of **6** and C_3 hydrocarbons are therefore *both* phosphine-induced reaction channels in this system.

Examination of the kinetics of the reaction between **1** and PPh_3 provides information about its mechanism. Operating at phosphine concentrations high enough that $[L] \simeq$ constant during each run, good pseudo-first-order decomposition of **1** is observed (see Figure 3). At high concentrations of PPh_3 the product is essentially exclusively **6**, and kinetic studies show a dependence of the reaction rate upon the concentration of PPh_3 (see Figure 4).

These observations are consistent with an initial reversible isomerization to an intermediate such as A in Scheme IV, followed by trapping of this intermediate by phosphine. Formulation of the appropriate rate law under the steady-state assumption for A leads to eq 1. Under

$$-\frac{d[1]}{dt} = \frac{k_1 k_2 [L]}{k_{-1} + k_2 [L]}[1] = k_{obsd}[1] \qquad (1)$$

Scheme V

Scheme VI
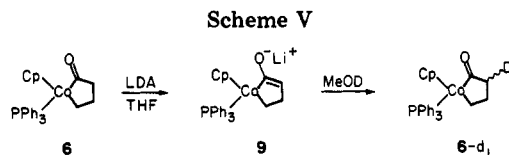
conditions where [L] = constant, the pseudo-first-order rate constant k_{obsd} depends on [L] according to eq 2. The

$$\frac{1}{k_{obsd}} = \frac{k_{-1}}{k_1 k_2} \frac{1}{[L]} + \frac{1}{k_1} \tag{2}$$

corresponding plot of $1/k_{obsd}$ vs. inverse phosphine concentration (Figure 5), does indeed yield a straight line. The intercept and slope of this line determine k_1 (15.9 × 10^{-5} s^{-1}) and the ratio k_{-1}/k_2 (0.041 M^{-1}).

If this mechanism is correct, the employment of a different trapping agent for A in this reaction should not affect the overall rate, provided its concentration is high enough to trap A every time it is formed (i.e., $k_{obsd} = k_1$). Accordingly the rate constant for the reaction of 1 with the much more nucleophilic PMe₂Ph (0.443 M) is 9.8 × 10^{-5} s^{-1}. This compares reasonably well with the k_1 derived from the PPh₃ reaction (when [PPh₃] = 0.402, k_{obsd} = 14.1 × 10^{-5} s^{-1}), considering the use of two different techniques in collecting the data (see Experimental Section).
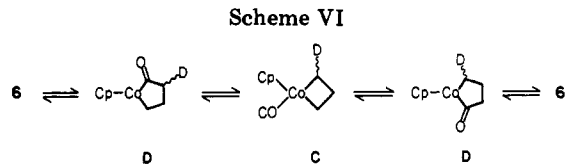
Evidence against certain other reversible processes in this system (e.g., a metal–metal bond cleavage/alkyl transfer preequilibrium (eq 3)) was provided by the
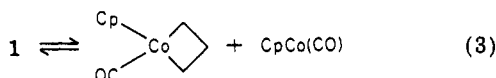
thermolysis of a mixture of 1 and its MeCp analogue 5. The reaction was carried to ca. 10% conversion; mass spectral analysis of recovered starting material showed only a very small amount (ca. 1%) of the mixed dimer, indicating that such a process is not significant under these circumstances.

In order to explain the phosphine-dependent product ratio, partitioning of intermediate B or C (Scheme IV) must also be dependent on the phosphine concentration. We cannot decide at this point whether B or C is the immediate precursor of cyclopropane, but there must be a PPh₃-independent route to cyclopropane, competitive with attack of phosphine on an intermediate to form cobaltacyclopentanone 6. Since thermolysis of 6 afforded mostly cyclopropane, presumably via species D and C, we currently favor C as the species that eliminates cyclopropane in the reaction of 1 with PPh₃.

In order to test this conclusion and to determine whether C and D equilibrate rapidly relative to the extrusion of cyclopropane, we prepared 6-d_1 with the deuterium label α to the carbonyl function. Cobaltacyclopentanone 6 was deprotonated with lithium diisopropylamide (LDA) to form the enolate 9. Addition of MeOD generated 6-d_1 (Scheme V). Entry from 6 into the D ⇌ C manifold provides a pathway for scrambling this label into the position adjacent to the metal center (Scheme VI). No scrambling was observed when a solution of 6-d_1 was heated to 100 °C until decomposition occurred. This would only be consistent with the mechanism outlined in Scheme IV, if at low phosphine concentrations the trapping of D with phosphine were too slow to compete with the formation of cyclopropane from C. To test this, we heated a solution of 6-d_1 at 110 °C in C₆D₆ in the presence of excess phosphine ([PPh₃] = 0.8 M). Under these con-

ditions monitoring by ¹H NMR indicated a slow equilibration of the deuterium label between the two positions α to the ketone and α to the metal, as predicted by the mechanism in Scheme IV.

Summary and Conclusions

Some similarities, but also significant differences, have been observed between the chemical behavior of the acyclic dinuclear dialkylcobalt complexes reported earlier,[10] and the related cyclic dimetallacycles discussed in this paper. Reactions of both types of complexes result ultimately in the formation of new carbon–carbon bonds. This does not occur via intact dinuclear intermediates but instead involves transient mononuclear intermediates which are formed by transfer of one of the alkyl groups from one metal center to the other. One of the most rapid processes in the acyclic system, reversible dissociation of the starting complex to two CpCo(CO)R fragments, is clearly less favorable in the cyclic system, because considerably less entropy is gained upon cleavage of the metal–metal bond (a "diradical", or dicobalt(II) intermediate, would be generated in the dimetallacycle case). This may be the reason for the greater thermal stability of the dimetallacyclopentane. We cannot say whether diradical-type species intervene in the conversion of 1 to C (Scheme IV), but our present results certainly do not require such an intermediate.

Important differences also exist in the behavior of the mononuclear species generated after metal-to-metal alkyl transfer. Perhaps most interesting is the contrast between the behavior of cobaltacyclopentanones D and the analogous acyclic intermediate CpCo(COR)R. The latter must undergo reductive elimination to ketone extremely rapidly even below room temperature; CpCo(L)(COR)R complexes are never detected in the carbonylation of CpCo(L)R₂ or [CpCo(CO)R]₂. Finally, metallacyclobutane complex C is a critical intermediate in the mechanism outlined in Scheme IV; circumstantial evidence for its involvement is very compelling. For that reason, it is frustrating that stable complexes of this type appear to be completely unknown in the cobalt triad. Synthesis of metallacyclobutanes, with M = Co, Rh, or Ir, therefore represents a challenge which, if successfully met, should provide important information about the conclusions reached in this study.

Experimental Section

General Techniques. ¹H NMR spectra were recorded on a Varian EM-390 spectrometer or at 250 MHz or 200 MHz on spectrometers equipped with Cryomagnets Inc. magnets and Nicolet Model 1180 data collection systems. ¹³C NMR spectra were recorded at 45 MHz on a spectrometer equipped with a Bruker superconducting magnet and a Nicolet Corp. Fourier Transform Computer package. All high-field instruments were constructed by Mr. Rudi Nunlist in the UC Berkeley NMR laboratory. IR spectra were obtained on a Perkin-Elmer Model 283 infrared spectrophotometer. Analysis of the volatile products of the decomposition reactions was 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 15% DBTCP on Chromosorb P. All manipulations

involving air-sensitive organometallic compounds, including chromatographic separations, were carried out in a Vacuum Atmospheres 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. Before transfer to the drybox, the solvents so obtained were frozen and the flasks evacuated. Hexane was purified by stirring with concentrated sulfuric acid two times for 12 h, followed by stirring with a saturated solution of $KMnO_4$ in 10% sulfuric acid and washing with water, saturated sodium carbonate solution, and water again. After the solution was dried with $CaCl_2$, the hexane was stirred over sodium benzophenone ketyl followed by distillation as mentioned above.

Elemental analysis were performed by the UC Berkeley College of Chemistry microanalytical laboratory. $CpCo(CO)_2$ was prepared according to published procedures[16] and reduced to the known $Na[\eta^5\text{-}CpCo(CO)]_2$ with Na amalgam.[10a,11]

(μ-Trimethylene)bis(η^5-cyclopentadienyl)bis(μ-carbonyl)dicobalt (1). In the dry box, 1.0 g of 1,3-diiodopropane (3.4 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. The pale green suspension immediately turned blue-green. The IR spectrum at this time showed CO stretches at 2020 and 1955 cm^{-1} ($CpCo(CO)_2$), 1815 cm^{-1} (1), and 1790 cm^{-1} ($Cp_2Co_2(CO)_2$), causing the intense blue-green color.[10a] After 30 min the solution appeared brown-green, and the IR spectrum showed that all $Cp_2Co_2(CO)_2$ had decomposed. A 40-mL sample of hexane was then added to precipitate NaI and the mixture 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 green) was collected and the solvent evaporated under reduced pressure. The solid residue was recrystallized from toluene/hexane to yield 314 mg of analytically pure 1 (42% yield): mp 170 °C dec; IR (THF) 1850 (wk), 1815 (s), 1785 (wk) cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.71 (s, 10 H), 1.66 (t, 4 H), 0.68 (q, 2 H, J_{HH} = 7.1 Hz); ^{13}C NMR (C_6D_6) δ 254.8, 91.75, 31.9, 20.5; MS (15 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, 52.33; H, 4.91; Co, 33.7.

(μ-Tetramethylene)bis(η^5-cyclopentadienyl)bis(μ-carbonyl)dicobalt (2). This reaction was carried out under inert gas by using Schlenk techniques to facilitate cooling. A solution of 1 g of 1,4-diiodobutane in 5 mL of THF was added to a suspension of 1 g of $Na[Cp_2Co_2(CO)_2]$ in 15 mL of THF which was cooled to 10 °C. After 20 min this solution was exposed to ca. 1 atm of CO to convert $Cp_2Co_2(CO)_2$ to $CpCo(CO)_2$. The solvent was then evaporated. The residue was taken up in cold toluene (0 °C) and the mixture transferred to a column (Alumina II, 2 × 30 cm, cooled to –10 °C) and eluted with pentane/Et_2O (10:1). The green fraction was collected and the solvent evaporated, while the solution was kept below –10 °C. The resulting green solid was recrystallized from toluene/pentane (1:2) to yield 140 mg of analytically pure 2 (18% yield): mp 100 °C dec; IR (THF) 1848 (wk), 1828 (s), 1783 (vwk) cm^{-1}; ^{1}H NMR (toluene-d_8, –20 °C) δ 4.43 (s, 10 H), 1.16 (m, 4 H), 0.91 (m, 4 H). Anal. Calcd for $C_{16}H_{18}Co_2O_2$: C, 53.36; H, 5.04; Co, 32.7. Found: C, 52.88; H, 5.00; Co, 32.4.

(μ-Benzocyclobutene)bis(η^5-cyclopentadienyl)bis(μ-carbonyl)dicobalt (3). A 930-mg (2.6-mmol) sample of 1,2-diiodo-3,4-benzocyclobutene was added to a stirred suspension of 0.86 g of $Na[Cp_2Co_2(CO)_2]$ (1.84 mmol) in 15 mL of THF. After the solution was stirred for 20 min, 30 mL of hexane was added and the green-brown solution filtered. The solvent was evaporated under vacuum and the residue chromatographed on SiO_2 (1 × 20 cm, eluent benzene/hexane (1:1)). The second, dark green, fraction was collected, the solvent evaporated, and the solid residue recrystallized from toluene/hexane to yield 120 mg of analytically pure 3 as black needles (yield 16%): mp 104 °C; IR (THF) 1853 (vwk), 1817 (s), 1786 (sh, vwk) cm^{-1}; ^{1}H NMR (THF-d_8) δ 6.85 (m, 4 H), 4.88 (s, 10 H), 3.25 (s, 2 H). Anal. Calcd for $C_{20}H_{16}Co_2O_2$: C, 59.14; H, 3.97; Co, 29.02. Found: C, 59.29; H, 4.13; Co, 29.1.

Formation of (η^4-Benzocyclobutadiene)(η^5-cyclopentadienyl)cobalt (4). An NMR tube was charged with ca 10 mg of 3 and 0.5 mL of THF-d_8 transferred on. The tube was then sealed. After 3 days at room temperature the resonances of the starting material were replaced by those of $CpCo(CO)_2$ and a set of resonances consistent with 4: δ 7.01 (m, 2 H), 6.63 (m, 2 H), 4.56 (s, 5 H), 2.92 (s, 2 H). The yield of 4 as determined by the integration of the ^{1}H NMR spectrum using the residual solvent peaks as internal standard was ca. 75%. The tube was then opened and the mixture filtered through Alumina II using hexane as eluent. The solvent was evaporated and the residue heated to ca. 50 °C under vacuum to remove the $CpCo(CO)_2$. The ^{1}H NMR spectrum in C_6D_6 and the mass spectrum of the so obtained material were identical with the reported values for 4.[12]

(η^5-Cyclopentadienyl(triphenylphosphine)cobaltacyclopentanone (6). To a solution of 360 mg of 1 (1.04 mmol) in 10 mL of THF was added 2.3 g of PPh_3 (8.77 mmol), and the solution was kept at 60 °C for 15 h. The solvent was evaporated and the residue chromatographed on silica gel. Elution with benzene yielded first a dark red fraction of $CpCo(PPh_3)CO$ (identified by its ^{1}H NMR and IR spectra). Further elution with THF yielded an orange fraction containing 6. Evaporation of solvent and recrystallization from toluene/pentane gave 455 mg of analytically pure 2 (1.0 mmol, 96% yield): mp 177.5–178.5 °C dec; IR (C_6H_6) 1645 cm^{-1}; ^{1}H NMR (C_6D_6) δ 7.76 (m, 6 H), 7.08 (m, 9 H), 4.63 (s, 5 H), 3.34 (m, 1 H), 2.61 (m, 1 H), 1.61 (m, 4 H); MS (20 eV), m/e 456 (M$^+$). Anal. Calcd for $C_{27}H_{26}CoOP$: C, 71.05; H, 5.74; Co, 12.9; P, 6.79. Found: C, 71.10; H, 5.88; Co, 12.6; P, 6.66.

(η^5-Cyclopentadienyl)(trimethylphosphine)cobaltacyclopentanone (7). A 100-mg (0.29-mmol) samples of 1 was dissolved in 3 mL of toluene. Into the degassed solution was vacuum transferred ca. 3.3 mmol of PMe_3, and this mixture was heated to 70 °C for 3 h. Excess PMe_3 and solvent were pumped off, and the residue was chromatographed on SiO_2. With benzene a first fraction of $CpCo(CO)PMe_3$ was eluted, and further elution with benzene/THF yielded a yellow fraction of 7. This material was recrystallized from pentane to yield 70 mg (0.26 mmol, 90%) of orange air-sensitive crystals: mp 124 °C; IR (C_6H_6) 1640 cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.57 (s, 5 H), 3.7–0.8 (m, 6 H), 0.9 (d, 9 H, J_{PH} = 10 Hz); MS (20 eV), m/e 270 (M$^+$). Anal. Calcd for $C_{12}H_{20}CoOP$: C, 53.34; H, 7.46; Co, 21.8; P, 11.46. Found: C, 53.23; H, 7.33; Co, 22.0; P, 11.19.

(η^5-Cyclopentadienyl)carbonylcobaltacyclopentanone (8). A solution of 37 mg of 1 in 1 mL of benzene in an open NMR tube was placed in a steel bomb, pressurized with CO (750 psi), and kept at ca. 70 °C for 3 days. The color of the solution changed to a reddish brown. Chromatography of the solution on SiO_2 yielded a first fraction of $CpCo(CO)_2$ with benzene and a second light yellow fraction of 8 upon elution with THF. This fraction was evaporated to dryness to yield pure 8 as volatile yellow oil: IR (THF) 2005 (s), 1700 (m) cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.53 (s, 5 H), 2.94 (m, 1 H), 2.35 (m, 3 H), 1.40 (m, 2 H); MS (20 eV), m/e 222 (M$^+$). High-resolution MS calcd for $C_{10}H_{11}CoO_2$: m/e 222.0091. Found: m/e 222.0093.

Thermolysis of 1. An NMR tube was charged with 10 mg of 1. Approximately 0.5 mL of C_6D_6 was vacuum transferred in and the tube sealed off. The tube was then heated to 100 °C and the progress of the reaction monitored periodically by ^{1}H NMR spectroscopy. After 20 h the resonances of 1 were replaced by those of $CpCo(CO)_2$, propene, and cyclopropane as major products. Because the NMR signals at this point were rather broad, the volatile materials were vacuum transferred into another NMR tube. The ^{1}H NMR spectrum again confirmed the presence of $CpCo(CO)_2$, propene, and cyclopropane. No cyclobutanone was detected. An IR spectrum of the solid residue showed CO stretches for $CpCo(CO)_2$, some unconverted 1, and $Cp_4Co_4(CO)_4$. The absolute yield of C_3 hydrocarbons was determined in an independent experiment. A 23.5-mg sample of 1 (0.0679 mmol) was dissolved in benzene and the solution degassed and then heated to 110 °C for 2 days to ensure complete reaction. The volatile products of this reaction were isolated by using a Toepler pump and quantitated by gas chromatography by using an added known amount of C_2H_4 as standard. The absolute yields were as follows: propene, 73%; cyclopropane, 18%; propane, 1%.

Thermolysis of 6. An NMR tube was charged with 15 mg of 6, 0.5 mL of C_6D_6 vacuum transferred in, and the tube sealed

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

under vacuum. The tube was then heated to 120 °C and the reaction monitored periodically by ^{1}H NMR spectroscopy. After 12 h the reaction was complete and the resonance of 6 had been replaced by those of CpCo(CO)PPh$_3$ (the only organometallic product), cyclopropane, and propene. An IR spectrum of this solution showed only one CO stretching vibration at 1920 cm^{-1} (consistent with CpCo(CO)PPh$_3$). The yield of C$_3$ hydrocarbons was determined in an independent experiment. A 23.5-mg sample of 2 (0.052 mmol) was dissolved in benzene and the solution degassed and then heated to 110 °C for 4 days. The volatile products of this reaction were isolated by using a Toepler pump and the absolute amounts of cyclopropane and propene determined by GC. A known amount of C$_2$H$_4$ was added to the gas mixture prior to GC analysis. The absolute yields were as follows: cyclopropane, 46.6%; propene, 34.4%.

Kinetics of the Reaction of 1 with PPh$_3$. Solutions of 1 and excess PPh$_3$ (i.e., [PPh$_3$]/[1] ≥ 5, to maintain pseudo-first-order conditions) in benzene were heated to 56.2 °C in an acetone bath maintained at a gentle reflux. The progress of the reaction was monitored by IR spectroscopy using the CO bands of 1 (1815 cm^{-1}) and 2 (1645 cm^{-1}). Spectra were taken in the absorbance mode to facilitate the use of peak heights as a measure of concentration, and four scans were averaged to determine each point. The reactions were monitored for 2 half-lives and yielded good first-order plots (see Figure 3 for a typical plot). In a typical experiment 10.0 mg of 1 (0.029 mmol) and 104.8 mg of PPh$_3$ (0.4 mmol) were dissolved in benzene to give a total volume of 2.00 mL. This solution was transferred to a glass tube fitted with a joint and equipped with a stirring bar. The tube was stoppered with a rubber septum and immersed in gently refluxing acetone. IR spectra were taken every 15 min by removing aliquots of the reaction mixture with a syringe and transferring them into an IR cell which had previously been flushed with argon.

Kinetics of the Reaction of 1 with PMe$_2$Ph. An NMR tube was charged with 8 mg of 1 (0.023 mmol) and a solution of 49 mg of PMe$_2$Ph (0.355 mmol) in C$_6$D$_6$ to give a total volume of 0.80 mL. Me$_4$Si was added as internal standard by using a glass bulb of known volume on a vacuum line. The tube was then sealed under vacuum. The tube was maintained at 56 °C in the probe of an NMR spectrometer (201 MHz for ^{1}H NMR), and spectra were taken every 7 min. A total of 30 points were taken over 2 half-lives monitoring the disappearance of the Cp resonance of 1. A first-order plot of these data yielded a straight line with K_{obsd} = 9.77 (±0.16) × 10^{-5} s^{-1}.

1,3-Diiodo-2,2-dideuteriopropane. A 10.02-g (0.1-mol) of malonic-d_4 acid (Aldrich, 99 atom % D) was dissolved in 150 mL of CHCl$_3$ (refluxed over P$_2$O$_5$ and distilled). A 14.2-mL sample of CH$_3$OD (Aldrich, 99.5 % D) and 1 mL of D$_2$SO$_4$ were added, and this mixture was refluxed for 10 h. The solution was washed with D$_2$O, the CHCl$_3$ evaporated, and the residue distilled to yield 11.02 g (83%) of the pure dimethyl ester (bp$_{19}$ = 75–78 °C). A solution of this ester in 40 mL of THF was added to a stirred suspension of 4 g of LiAlH$_4$ in ca. 300 mL of dry THF. The solution was heated to reflux for 30 min and after being cooled, 20 mL of saturated Na$_2$SO$_4$ solution was added. The solution was again heated to reflux and filtered hot. The solid residue was extracted twice with hot THF, and the combined filtrates were evaporated to leave behind a viscous oil. This was distilled under vacuum to yield 3.7 g (0.047 mol, 56%) of the desired diol (bp$_1$ 72 °C). The diol was added to a stirred solution of 7.72 g (0.0244 mmol) of P$_2$I$_4$[17] in 300 mL of CS$_2$ and cooled to 0 °C under argon. After the solution was stirred for 4 days, workup and distillation under vacuum yielded 3.85 g (0.013 mmol, 28%) of the desired diiodide (bp$_{2.5}$ 50–51 °C; ^{1}H NMR (CCl$_4$) δ 3.2 (s, br). [Lit.[18] (for the protio compound) bp$_{19}$ 110 °C; ^{1}H NMR (CCl$_4$) δ 3.2 (t, 4 H) 2.25 (m, 2 H).] No hydrogen could be detected in the β-position by ^{1}H NMR spectroscopy, i.e., D incorporation ≥95%.

Preparation and Thermolysis of (μ-2,2-Dideuteriotrimethylene)bis(η^5-cyclopentadienyl)bis(μ-carbonyl)dicobalt (1-d_2). A solution of ca. 30 μL of 1,3-diiodo-2,2-dideuteriopropane in 0.5 mL of THF was added to a stirred suspension of 80 mg of

Na[CpCo(CO)]$_2$ in 2 mL of THF. Workup as described previously yielded ca. 10 mg of 1-d_2: ^{1}H NMR (C$_6$D$_6$) δ 4.72 (s, 10 H), 1.67 (s, br, 4 H). A solution of 1-d_2 in C$_6$D$_6$ was heated to 80 °C in an NMR tube and the sample periodically checked by ^{1}H NMR spectroscopy. After 24 h the thermal decomposition to cyclopropane and propene had progressed to ca. 10%, and no scrambling of the label could be detected.

Thermolysis of a Mixture of 1 and 1-d_4. As described above dimethyl malonate was reduced with LiAlD$_4$ (99% D) to 1,1,3,3-tetradeuterio-1,3-propanediol, the diol was converted to the corresponding diiodide (1,1,3,3-tetradeuterio-1,3-diiodopropane) with P$_2$I$_4$[17] and this treated with Na[CpCo(CO)]$_2$ to yield 30 mg of 1-d_4: ^{1}H NMR (C$_6$D$_6$) δ 4.71 (s, 10 H), 0.65 (s, br, 2 H); MS (20 eV), m/e 350 (M$^+$); isotopic enrichment (by MS): 98% d_4, 2% d_3.

A solution of 11.5 mg of 1 (0.033 mmol) and 13.1 mg of 1-d_4 (0.037 mmol) in 2.5 mL of benzene was heated to 110 °C for 3 days. The volatile products of this reaction were isolated by using a Toepler pump and analyzed by GC–MS. The distribution for propenes was as follows: d_0, 44%; d_1, 4.4%; d_2, 1.7%; d_3, 9.9%; d_4, 40.1%. The distribution for the cyclopropanes was as follows: d_0, 45.7%; d_1, 4.1%; d_2, 2.1%; d_3, 9.0%; d_4, 39.1%. A GC–MS analysis of independently generated cyclopropane-d_4 and propene-d_4 (from thermolysis of pure 1-d_4) showed that contribution to the peaks at m/e 42–45 due to fragmentation of d_4 hydrocarbons was negligible.

(μ-Trimethylene)bis(η^5-methylcyclopentadienyl)bis(μ-carbonyl)dicobalt (5). A 10-g (51.5-mmol) sample MeCpCo(CO)$_2$ was added to a mixture of 20 mL of THF and 44 mL of 0.75% Na amalgam and stirred for 1 h. This mixture was extracted with two 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: IR (THF) 1890 (br, vs) and 1860 (m) (Na-Co(CO)$_4$) and 1740 (m), 1690 (m), and 1655 (s) cm^{-1} (Na-[MeCpCo(CO)]$_2$).

A 0.3-mL sample of 1,3-diiodopropane (2.6 mmol) was added to a stirred suspension of 1.12 g of this material in 20 mL of THF. After the solution was stirred for 1 h, hexane was added and the solution filtered to remove NaI. The solvent was evaporated and the residue chromatographed on neutral Alumina II (20 × 1 cm). Elution with hexane yielded first a fraction of MeCpCo(CO)$_2$ and further elution with hexane/benzene (1:1) afforded a dark green fraction of 5. The solvent was evaporated and the solid recrystallized from toluene/hexane (1:1) to yield 210 mg (0.56 mmol, yield 11% based on MeCpCo(CO)$_2$) of analytically pure 5: mp 102–103.5 °C; ^{1}H NMR (C$_6$D$_6$) δ 4.6–4.3 (m, 8 H), 1.80 (s, 6 H), 1.47 (t, 4 H, J_{HH} = 7.2 Hz), 0.67 (m, 2 H); IR (benzene) 1840 (wk), 1803 (s), 1775 (wk) cm^{-1}; MS (20 eV); m/e 374 (M$^+$). Anal. Calcd for C$_{17}$H$_{20}$O$_2$Co$_2$: C, 54.56; H, 5.39; Co, 31.15. Found: C, 54.84; H, 5.45; Co, 31.9.

Crossover between 1 and 5. An NMR tube was charged with 12 mg of 1 (0.035 mmol) and 13 mg of 5 (0.035 mmol). Approximately 0.6 mL of C$_6$D$_6$ was transferred in and the tube sealed under vacuum. This solution was then heated to 80 °C and monitored periodically by ^{1}H NMR spectroscopy. After 24 h the ^{1}H NMR spectrum showed some decomposition of the metallacycles but no new resonances which could be interpreted as those of a mixed (MeCp/Cp) dimer. The tube was then opened and the mixture of metallacycles reisolated by chromatography. A mass spectrum of this mixture showed a small peak (ca. 1%) at m/e 360 (the M$^+$ ion of a mixed dimer) in addition to the starting metallacycles. A high-resolution MS of the same mixture was consistent with the assignment of this peak to a mixed dimer. Calcd. for C$_{16}$H$_{18}$O$_2$Co$_2$: m/e 359.9971. Found: m/e 359.9972.

Preparation of 6-d_1. A solution of 50 mg of 6 in 5 mL of THF was slowly added to a solution to 35 mg of LDA (∼3 equiv) in 5 mL of THF kept at −78 °C in an acetone/dry ice bath. After being stirred for 1 h, the solution had turned red-brown. Three drops of CH$_3$OD (≥99.5% D) were added to the cold solution. The color of the solution immediately changed back to the light orange color characteristic of 6. The solvent was evaporated under vacuum and the solid residue chromatographed on a small SiO$_2$ column. The material so obtained was recrystallized from toluene/pentane to yield 35 mg of 6-d_1: ^{1}H NMR (C$_6$D$_6$) δ 7.76 (m, 6 H), 7.08 (m. 9 H), 4.63 (s, 5 H), 3.34 (m, 0.87 H), 2.61 (m, 0.08 H) 1.61 (m, 4 H); MS (20 eV) m/e 457 (M$^+$).

(17) Lauwers, M.; Regnier, B.; Van Eenoo, M.; Denis, J. N.; Krief, A. *Tetrahedron Lett.* 1979, 80, 1801.

(18) "Handbook of Chemistry and Physics", 55th ed.; CRC Press: Cleveland, OH, 1975; p C-442.

Table II. Crystal Data and Data Collection Details

mol formula	$C_{15}H_{16}Co_2O_2$
mol wt, amu	346.16
a, b, c,[a] Å	16.7983 (20), 45.576 (6), 6.9565 (16)
V, Å³	5326 (3)
space group, Z	Fdd2, 16
d(calcd), g cm⁻³	1.727
μ(calcd), cm⁻¹	25.8
size, mm	0.20 × 0.30 × 0.55
scan method; speed (θ)	θ, 2θ; 0.74-6.7 deg s⁻¹ (θ)
scan width	$\Delta\theta = 0.6 + 0.347 \tan\theta$
bkgd	measd over an additional 0.25 (Δθ) added to each end of the scan
stds	three reflctns measd every 2 h; no decay in intensity
2θ range, deg	3-45
no. of reflctns collected	1016
no. of unique reflctns	959

[a] Unit cell parameters and their esd's were derived by a least-squares fit to the setting angles of the unresolved Mo Kᾱ (λ = 0.710 73 Å) components of 24 reflections with 2 near 28°.

Thermolysis of 6-d_1. An NMR tube was charged with 5 mg of 6-d_1, and ca. 0.5 mL of C_6D_6 transferred in and the tubed sealed under vacuum. This tube was kept in an oil bath maintained at 100 °C and periodically monitored by ¹H NMR spectroscopy. After 20 h the formation of cyclopropane and CpCo(PPh₃)CO indicated decomposition. At this time the relative integrals of the alkyl resonances of 6-d_1 had not changed noticeably.

Thermolysis of 6-d_1 at High PPh₃ Concentration. An NMR tube was charged with 7.7 mg of 6-d_1 and 129.1 mg of PPh₃ (0.493 mmol). C_6D_6 was transferred on and the tube sealed under vacuum. The total volume of the sample was 0.70 mL corresponding to a phosphine concentration of [PPh₃] = 0.704 M. The tube was immersed in an oil bath heated first to 80 °C, then to 105 °C, and finally to 120 °C. The progress of the reaction was monitored by ¹H NMR spectroscopy. After 11 h at 120 °C 30% of the starting material had decomposed to CpCo(CO)PPh₃ and C_3 hydrocarbons. The remaining metallacycle was reisolated chromatographically and a ¹H NMR spectrum recorded and carefully integrated. The ratio of the two protons α to the carbonyl function had dropped from the initial 10.9 to 1.63, and the total integral of both α protons relative to the Cp had increased to 1.6 (compared to the initial 1.0).

Crystal Structure of 1. Dark, shiny air-stable crystals, primarily of a bladelike habit were obtained by slow diffusion of pentane into a solution of 1 in toluene at room temperature. The crystal used for data collection was a columnar fragment of approximate dimensions 0.20 × 0.30 × 0.55 mm cleaved from a thick blade. This was mounted on a glass fiber, in air by using cyanoacrylate cement. Preliminary precession photographs indicated orthorhombic Laue symmetry and an F-centered cell and yielded rough cell dimensions. The systematic absences suggested Fdd2 or Fddd as possible space groups.

The crystal was then transferred to an Enraf-Nonius CAD4 automated diffractometer[19] and centered in the beam. Our standard peak search and automatic indexing procedure yielded a primitive triclinic cell of one-fourth the volume of the preliminary cell. Inspection of the Niggli values[20] showed that the F-centered orthorhombic lattice was obtainable from the primitive cell and the transformation was made. The systematic absences (h0l, h + l = 4n, 0kl, k + l = 4n, hk0, h = 2n and k = 2n) were consistent only with the noncentric space group Fdd2. The final

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(19) 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 softward as described in the *CAD-4 Operation Manual*, Enraf-Nonius, Delft, Nov 1977, updated Jan. 1980.

(20) 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.

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	0.18382 (2)	0.06435 (1)	0.0000 (0)	0.00175 (1)	0.00033 (0)	0.0136 (1)	0.00024 (1)	0.0008 (1)	0.00061 (3)
Co2	0.32735 (2)	0.06229 (1)	0.0008 (1)	0.00175 (1)	0.00028 (0)	0.0134 (1)	-0.0007 (1)	-0.0007 (1)	0.00018 (3)
O1	0.2511 (1)	0.02143 (6)	0.2529 (6)	0.0033 (1)	0.00062 (2)	0.0386 (10)	-0.00003 (6)	-0.0004 (6)	0.0064 (2)
O2	0.2613 (1)	0.11535 (5)	-0.1531 (5)	0.0041 (1)	0.00026 (1)	0.0232 (7)	-0.00003 (5)	-0.0008 (5)	0.0015 (2)
C1	0.2535 (2)	0.04035 (9)	0.1428 (7)	0.0017 (1)	0.00040 (2)	0.0226 (11)	0.00004 (7)	0.0004 (7)	0.0020 (3)
C2	0.2582 (2)	0.09215 (8)	-0.0837 (6)	0.0026 (1)	0.00034 (2)	0.0115 (8)	0.00001 (7)	0.0007 (6)	-0.0009 (2)
C3	0.1811 (2)	0.09076 (9)	0.2374 (7)	0.0044 (2)	0.00073 (2)	0.0144 (9)	0.00124 (10)	0.0042 (8)	-0.0001 (3)
C4	0.2596 (2)	0.09169 (11)	0.3484 (8)	0.0043 (2)	0.00081 (3)	0.0150 (10)	0.00003 (11)	0.0014 (8)	-0.0013 (3)
C5	0.3353 (2)	0.08845 (8)	0.2377 (7)	0.0036 (1)	0.00061 (2)	0.0156 (9)	0.00007 (9)	-0.0020 (8)	-0.0016 (3)
C6	0.1402 (2)	0.04570 (8)	-0.2626 (7)	0.0023 (1)	0.00067 (2)	0.0205 (9)	-0.00027 (9)	-0.0020 (8)	-0.0016 (3)
C7	0.1075 (2)	0.07357 (7)	-0.2326 (8)	0.0024 (1)	0.00050 (2)	0.0265 (10)	0.00002 (9)	-0.0062 (9)	0.0014 (3)
C8	0.0665 (2)	0.07315 (7)	-0.0593 (7)	0.0020 (1)	0.00044 (2)	0.0341 (15)	0.00048 (9)	-0.0022 (8)	0.0002 (3)
C9	0.0718 (2)	0.04476 (8)	0.0233 (8)	0.0021 (1)	0.00057 (2)	0.0275 (11)	-0.00024 (8)	0.0027 (8)	0.0011 (3)
C10	0.1178 (2)	0.02779 (7)	-0.1051 (7)	0.0022 (1)	0.00043 (2)	0.0285 (11)	-0.00030 (8)	-0.0011 (8)	0.0005 (3)
C11	0.3680 (2)	0.04165 (8)	-0.2575 (7)	0.0022 (1)	0.00080 (2)	0.0224 (10)	0.00036 (9)	0.0005 (8)	-0.0033 (3)
C12	0.3900 (2)	0.02441 (7)	-0.1005 (8)	0.0026 (1)	0.00037 (2)	0.0355 (12)	0.00031 (8)	0.0019 (9)	-0.0011 (3)
C13	0.4385 (2)	0.04138 (8)	0.0241 (7)	0.0023 (1)	0.00058 (2)	0.0241 (11)	0.00067 (8)	-0.0014 (8)	0.0000 (3)
C14	0.4452 (2)	0.06965 (7)	-0.0659 (7)	0.0020 (1)	0.00050 (2)	0.0317 (13)	-0.00065 (9)	0.0031 (7)	-0.0025 (3)
C15	0.4027 (2)	0.06971 (7)	-0.2362 (8)	0.0022 (1)	0.00061 (2)	0.0239 (10)	0.00002 (9)	0.0052 (8)	-0.0001 (4)
Cp1[b]	0.1008 (0)	0.0530 (0)	-0.1272 (0)						
Cp2[b]	0.4089 (0)	0.0494 (8)	-0.1272 (0)						

[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] $B = 4.0000\ (0)$ Å².

cell parameters and the details of the data collection procedure are given in Table II.

The 1016 raw intensity data were reduced to structure factor amplitudes and their esd's by corrections for background, scan speed, and Lorentz and polarization factors.[21-23] Inspection of azimuthal scan data indicated the necessity of an absorption correction, and so the faces of the crystal were identified and measured. The actual correction was applied after solution of the structure and before the final refinement. The maximum and minimum transmission factors were 0.630 and 0.525, respectively.

The locations of the two cobalt atoms were determined by analysis of the three-dimensional Patterson synthesis. Standard Fourier and least-squares techniques slowly revealed the remainder of the non-hydrogen atoms in the structure. The difficulty in attaining convergence was due to the near perfect pseudomirror plane located approximately normal to a at $x = 0.25$ which related one half of the molecule to the other. After refinement of all atoms with anisotropic thermal parameters ($R^{24} = 3.54\%$, $R_w = 5.29\%$) a difference Fourier showed peaks where many of the hydrogens were expected. The hydrogen positions were calculated based on their idealized geometry and included in structure factor calculations but not refined. Inversion of the structure followed by refinement led to a much higher R value, indicating that our original choice of enantiomer in the space group was the correct one.

The final residuals for 171 variables refined against the 921 data for which $F^2 > 3\sigma(F^2)$ were $R = 2.30\%$, $R_w = 3.21\%$, and GOF = 1.853. The R value for all 959 data was 2.47%.

The quantity minimized by the least-squares program was $\sum w(|F_o| - |F_c|)$, where w is the weight of a given observation. The p factor,[24] used to reduce the weight of intense reflections, was

set to 0.03 throughout the refinement. The analytical forms for the scattering factor tables for the neutral atoms were used,[25] and all non-hydrogen scattering factors were corrected for both the real and imaginary components of anomalous dispersion.[26]

The largest peak in the final difference Fourier map had an electron density of 0.30 e/A³. There was no apparent correlation of peaks with the structure.

The positional and thermal parameters of the non-hydrogen 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.

Registry No. 1, 74656-84-1; 1-d_2, 82665-65-4; 1-d_4, 82665-66-5; 2, 82665-62-1; **3**, 82665-63-2; 4, 71513-79-6; 5, 82665-64-3; 6, 74656-85-2; 6-d_1, 82665-67-6; 7, 74656-86-3; 8, 74725-89-6; Na[C$_p$Co(CO)]$_2$, 62602-00-0; CpCo(CO)$_2$, 12078-25-0; CpCo(CO)PPh$_3$, 12203-85-9; MeCpCo(CO)$_2$, 75297-02-8; Na[MeCpCo(CO)]$_2$, 82797-08-8; 1,3-diiodopropane, 627-31-6; 1,4-diiodobutane, 628-21-7; 1,2-diiodo-3,4-benzocyclobutene, 82665-59-6; propene, 115-07-1; cyclopropane, 2781-85-3; 1,3-diiodo-2,2-dideuteriopropane, 82665-60-9; malonic-d_4 acid, 813-56-9; dimethyl malonate-d_2, 36647-07-1; 2,2-dideuterio-1,3-propanediol, 38645-14-6; dimethyl malonate, 108-59-8; 1,1,3,3-tetradeuterio-1,3-propanediol, 41866-21-1; 1,1,3,3-tetradeuterio-1,3-diiodopropane, 82665-61-0.

Supplementary Material Available: Positional and thermal parameters and their estimated deviations for the hydrogen atoms, listing of observed and calculated structure factors, and stereoview of the unit cell in the crystal of complex 1 (7 pages). Ordering information is given on any current masthead page.

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(21) 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[22] software operating under RSM-11M.

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

(23) The data reduction formulae are $F_o^2 = (\omega/Lp)(C - 2B)$, $\sigma_o(F_o^2) = (\omega/Lp)(C + 4B)^{1/2}$, $F_o = F_o^2$, and $\sigma_o(F) = \sigma_o(F_o^2)/2F_o$ where C is the total count in the scan, B the sum of the two background counts, ω the scan speed used in deg/min, and $1/Lp = \sin 2\theta(1 + \cos^2 2\theta_m)/(1 + \cos^2 2\theta_m - \sin^2 2\theta)$ 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 $2\theta_m$.

(24) $R = (\sum||F_o| - |F_c||)/\sum|F_o|$, $R_w = \{[\sum w(|F_o| - |F_c|)^2]/\sum wF_o^2\}^{1/2}$, and GOF = $\{[w(F_o - F_c)^2]/(n_o - n_v)\}^{1/2}$, where n_o is the number of observations, n_v is the number of variable parameters, and the weights w were given by $w = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [\sigma_o^2(F_o^2) + (pF^2)^2]$, where p is the factor used to lower the weight of intense reflections.

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

(26) Cromer, D. T. ref 25, Table 2.3.1.