

pathways for this process were also not detectable by changing the partial pressure of **1**.

The reactivity of tetralin contrasts with that of its olefinic analogue, cyclohexene,¹⁷ in a number of ways. The rate of the retro-[2 + 4] reaction is more nearly comparable to that of dehydrogenation in tetralin, resulting in competitive formation of **6** and **7** with **2** and **3**. If the retro-[2 + 4] reaction in tetralin is concerted, disruption of the aromatic nature of the ring system may give rise to a higher energy transition state for ethylene loss. If the concerted pathway is shunned due to this situation, a stepwise carbon-carbon bond cleavage with subsequent loss of ethylene may be occurring. In either case, one would expect a higher activation energy for the ethylene-loss channel, one more nearly comparable to that of dehydrogenation. The observation of *o*-allyltoluene, the disproportionation product from the intermediate in a stepwise process, indicates that the nonconcerted reaction is energetically feasible. The occurrence of 1,2- instead of 1,4-dehydrogenation is perhaps not surprising since again the aromatic nature of the ring system must be destroyed for a concerted 1,4-hydrogen elimination to occur. Questions as to the energetics of these processes and their mechanisms are under active investigation.

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Synthesis of Metallacyclopentanes Containing Two Metals in the Ring. Thermal Decomposition to Cyclopropane and Ligand-Induced Conversion to Stable Mononuclear Metallacyclopentanones

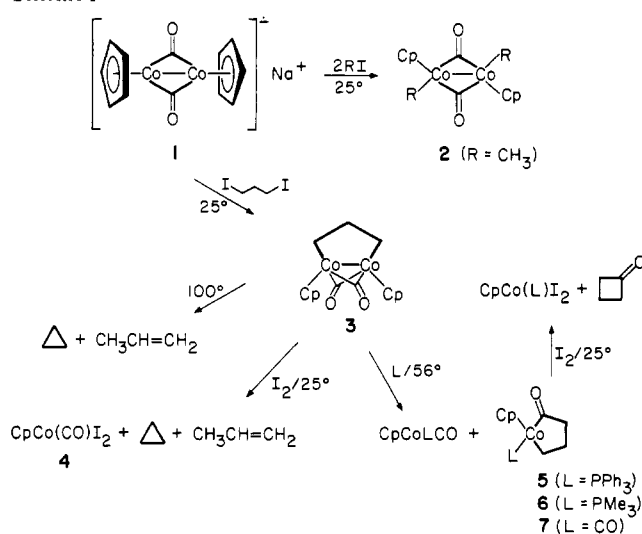
Sir:

During the past few years, much successful effort has been directed toward the synthesis of metallacycles and the study of their chemical reactions. This research has revealed similarities and differences between metallacycles and their noncyclic counterparts that has increased our understanding of the chemical behavior of both types of complexes; it has also allowed identification of metallacyclic intermediates in a number of important catalytic processes.¹

It is our view that metallacycles containing two, rather than just one, metal atoms will provide similar illumination of the chemistry of binuclear dialkyl complexes. We now report the successful synthesis of a five-membered ring metallacycle containing two cobalt atoms and a study of the reactions of this material.²

(1) See, for example: (a) Y. Wakatsuki, K. Aoki, and H. Yamazaki, *J. Am. Chem. Soc.*, **101**, 1123 (1979); (b) D. R. McAlister, J. E. Bercaw, and R. G. Bergman, *ibid.*, **99**, 1666 (1977); (c) M. Sohn, J. Blum, and J. Halpern, *ibid.*, **101**, 2694 (1979); (d) J. X. McDermott, J. F. White, and G. M. Whitesides, *ibid.*, **95**, 4451 (1973), and references cited therein; (e) R. H. Grubbs, A. Miyashita, M. Liu, and P. Burk, *ibid.*, **100**, 2418 (1978), and references cited therein; (f) S. J. McLain, C. D. Wood, and R. R. Schrock, *ibid.*, **101**, 4558 (1979); (g) R. J. Al-Essa, R. J. Puddephatt, M. A. Quysar, and C. F. H. Tipper, *ibid.*, **101**, 364 (1979), and references cited therein; (h) K. J. Ivin, J. J. Rooney, C. D. Stewart, M. L. H. Green, and R. Mahtab, *J. Chem. Soc., Chem. Commun.*, 604 (1978).

Scheme I



Our synthesis is based on an intramolecular version of the earlier-reported³ dialkylation of sodium di- μ -carbonyl-bis(η^5 -cyclopentadienyl)cobaltate (**1**) to give **2** and other alkyls (Scheme I). Addition of 1.5 equiv of 1,3-diiodopropane to a stirred suspension of green radical anion **1** in THF caused the color of the solution to change immediately, first to an intense blue-green and then to greenish brown. At the same time, the characteristic absorptions of **1** were replaced by a transient absorption at 1790 cm^{-1} [assigned⁴ to the neutral dimer $\text{Cp}_2\text{Co}_2(\text{CO})_2$] and a band at 1815 cm^{-1} . Column chromatography (aluminum oxide, air-free conditions) of the material so obtained afforded μ -trimethylenedi- μ -carbonyl-bis(η^5 -cyclopentadienyl)dibobalt (**3**) in 40% yield.^{5,6}

Our preliminary results on the chemistry of bimetallic cycle **3**, as well as on some of its reaction products, are summarized in Scheme I. Thermally, the material is surprisingly stable. Whereas the dimethyl derivative **2** undergoes solution thermal decomposition rapidly at temperatures near ambient, in benzene **3** decomposes only slowly at 100 °C (sealed tube). The product of this decomposition is primarily propene (73%), but substantial amounts of cyclopropane (17%), as well as traces of propane (1.4%), are produced (values given are absolute yields determined by gas chromatography, using an internal standard). Crossover experiments demonstrated the process is intramolecular: a 50:50 mixture of **3**-*d*₀ and **3**-*d*₄ (labeled in the α -CH₂ positions) gives only cyclopropane-*d*₀ and -*d*₄, uncontaminated with significant

(2) A few binuclear metallacycles are known or have been postulated as intermediates in certain organometallic transformations; see, for example: (a) S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc., Chem. Commun.*, 221 (1978); (b) D. J. S. Guthrie, I. U. Khand, G. R. Knox, J. Kollmeier, P. L. Pauson, and W. E. Watts, *J. Organomet. Chem.*, **90**, 93 (1975); (c) F. Garnier, P. Krausz, and J.-E. Dubois, *ibid.*, **170**, 195 (1979); (d) P. Pertici and G. Vitulli, *Tetrahedron Lett.*, 1897 (1979); (e) C. E. Sumner, Jr., P. E. Riley, R. E. Davis, and R. Pettit, *J. Am. Chem. Soc.*, **102**, 1752 (1980).

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

(4) (a) N. E. Schore, C. S. Ilenda, and R. G. Bergman, *J. Am. Chem. Soc.*, **99**, 1781 (1977); (b) W. I. Bailey, Jr., D. M. Collins, F. A. Cotton, J. C. Baldwin, and W. C. Kaska, *J. Organomet. Chem.*, **165**, 373 (1979).

(5) Data for **3**: mp 170 °C (dec); IR (THF) 1850 (w), 1815 (s), 1785 (w) cm^{-1} ; ¹H NMR (benzene-*d*₆) δ 4.71 (s, 10), 1.66 (t, 4), 0.68 (q, 2); ¹³C NMR (benzene-*d*₆) δ 254.8, 91.75, 31.9, 20.5; mass spectrum (MS) (15 eV), *m/e* 346 (*M*⁺). Anal. Calcd for C₁₅H₁₆Co₂O₂: C, 52.05; H, 4.66. Found: C, 52.33; H, 4.91.

(6) In preliminary results, we have also found that radical anion **1** reacts with methylene iodide to give the μ -methylene complex analogous to **3**. This material is isolated as dark red crystals in 48% yield: mp 68 °C; IR (THF) 1996, 1957, 1924 cm^{-1} ; MS (15 eV), *m/e* 318 (*M*⁺); high-resolution mass spectroscopy (HRMS) calcd for C₁₃H₁₂Co₂O₂, 317.9501; found, 317.9492. Substituted analogues of this complex have been prepared earlier; see, for example: (a) W. A. Herrmann, *Chem. Ber.*, **1**, 1077 (1978); (b) W. Herrmann and I. Schweizer, *Z. Naturforsch. B: Anorg. Chem., Org. Chem.*, **33B**, 911 (1978).

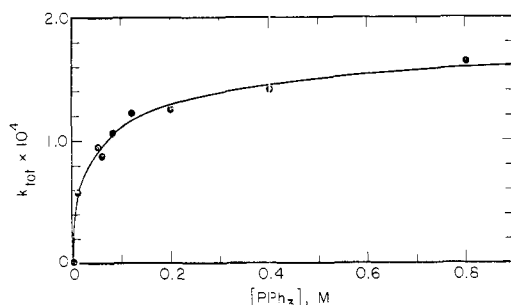
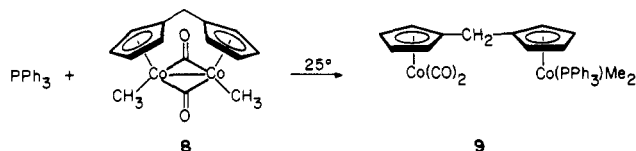


Figure 1. Dependence of the pseudo-first-order rate constant for disappearance of **3** upon the concentration of PPh_3 (benzene solution, 56°C).

Scheme II

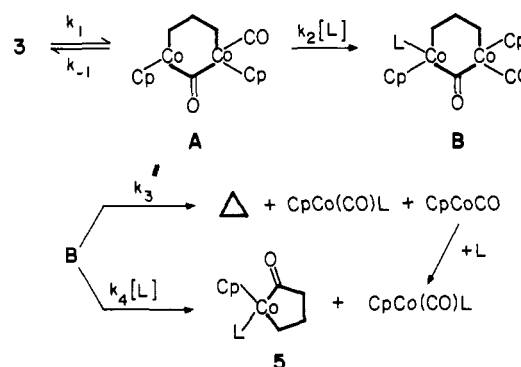


amounts of cyclopropane- d_2 . Treatment of **3** with I_2 leads to a 58% yield of three-carbon hydrocarbons containing a much higher proportion of cyclopropane (cyclopropane, 71%; propylene, 9%); the organometallic product of this reaction is the known⁷ diiodide **4** ($100 \pm 5\%$).

Reaction of bimetallic complex **3** takes place more rapidly upon treatment with CO and phosphines. Reaction with relatively high concentrations of PPh_3 , for example, occurs at 56°C , and leads to $\text{CpCo}(\text{PPh}_3)\text{CO}$ and the mononuclear metallacycle **5**. Similar treatment of **3** with PMe_3 leads to **6**, and carbonylation gives **7**.⁸ During carbonylation of **2**, it was possible to observe³ binuclear diacyl complexes as well as the mononuclear dialkyl complex $\text{CpCo}(\text{CO})\text{Me}_2$, but we have never been able to detect the alkyl/acyl complex $\text{CpCo}(\text{COCH}_3)(\text{CH}_3)\text{CO}$; apparently, this material undergoes reductive elimination to acetone too rapidly. In sharp contrast, complex **5** is stable to 125°C , and even at this temperature, cyclopropane and propylene, rather than cyclobutanone, are the products of thermal decomposition. Trimethylphosphine complex **6** is even more stable, again leading to cyclopropane and propylene at temperatures near 175°C . Oxidation of **5** with I_2 , however, occurs upon mixing at 25°C and leads to cyclobutanone in approximately 50% yield.⁹

Examination of the kinetics of the reaction between **3** and PPh_3 provides information about its mechanism. At high concentrations of PPh_3 , the product is essentially exclusively **5**, and kinetic studies show only a very weak dependence of the reaction rate upon the

Scheme III



concentration of PPh_3 (see Figure 1). Lowering the concentration of PPh_3 produces two effects. First, at sufficiently low $[\text{PPh}_3]$, 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 **5** increases as the phosphine concentration (and the reaction rate) decreases. At concentrations of PPh_3 below 0.01 M, the product is completely three-carbon hydrocarbons (94% cyclopropane, 6% propene), and no metallacycle is formed. Control studies demonstrated that the three-carbon products are not formed from unassisted thermal decomposition, which proceeds too slowly at 56°C to produce detectable amounts of cyclopropane or propene; the formations of both **5** and three-carbon hydrocarbons are therefore phosphine-induced reaction channels in this system.

As in our earlier investigation¹² of the phosphine-induced conversion of bridged dimethyl complex **8** to **9** (Scheme II), the kinetic observations made with **3** are consistent with initial reversible isomerization to an intermediate such as **A** in Scheme III, followed by reaction of this intermediate with phosphine (giving **B**). However, in order to explain the phosphine-dependent product ratio, partitioning of intermediate **B** must also be dependent on phosphine. Thus, we postulate a PPh_3 -independent route to cyclopropane (k_3 in Scheme III), competitive with attack of phosphine on **B** to give cobaltacyclopentanone **5**. This type of mechanism will explain the fact that both pathways are phosphine-induced, but the rate law for formation of **5** contains an additional term in $[\text{PPh}_3]$.

In summary, this study reveals some important parallels between the chemistry of mono- and binuclear metallacycles, e.g., the fact that migration of an alkyl group (or one end of the alkyl chain in the cyclic compound) from one metal to the other can be a significant process in both systems. However, there are also significant (and, at this point, not yet well understood) differences. Perhaps the most important of these is the formation of cyclopropane in the cyclic system; we have never before observed simple C-C bond formation in ligand-induced or thermal reactions of either mono- or binuclear cyclopentadienylcobalt complexes.³ Another difference is the dramatic effect of ligand on the products formed from **3**; no such effect was observed in either of the systems investigated previously.^{3,12} Studies aimed at understanding the nature of these differences are the subjects of a continuing investigation.

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(8) Spectral and analytical data for metallacyclopentanones. **5**: ^1H NMR δ 7.76 (m, 6), 7.08 (m, 9), 4.63 (s, 5), 3.34 (m, 1), 2.61 (m, 1), 1.64 (m, 4); IR (benzene- d_6) 1650 cm^{-1} ; HRMS calcd, 456.1053; found, 453.1067; mp $177.5\text{--}178.5^\circ\text{C}$. Anal. Calcd for $\text{C}_{27}\text{H}_{26}\text{CoOP}$: C, 71.05; H, 5.74. Found: C, 71.10; H, 5.88. **6**: ^1H NMR δ 4.57 (s, 5), 3.7–0.8 (m, 6), 0.9 (d, 9); IR (benzene) 1640 cm^{-1} ; MS (M^+), m/e 270; mp $108\text{--}110^\circ\text{C}$. Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{CoOP}$: C, 53.34; H, 7.46. Found: C, 53.81; H, 7.40. **7**: ^1H NMR δ 4.53 (s, 5), 2.94 (m, 1), 2.35 (m, 3), 1.40 (m, 2); IR (THF) 2005 (s) , $1700\text{ (m)}\text{ cm}^{-1}$; HRMS calcd for $\text{C}_{10}\text{H}_{11}\text{CoO}_2$, 222.0091; found, 222.0093.

(9) A referee has suggested that the reluctance of these (and other¹⁰) cyclic alkyl-acyl complexes to undergo rapid thermal reductive elimination, in contrast to the rapidity with which this apparently occurs in closely related acyclic systems, is due to "the difference in stability of cyclobutanone and acetone". This seems to us to be overly simplistic, in view of the fact that ethane is never observed to be formed from any of the dimethyl derivatives in this series (this includes binuclear, as well as mononuclear, carbonyl and phosphine derivatives^{3,11,12}), but the cyclic system finds it possible to produce the (more highly strained) product cyclopropane upon both thermal and oxidative decomposition. It seems to us inescapable that some factor in addition to the thermodynamic properties of the products strongly influences the effect of structure on the rates of these reactions.

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