(m, Ph), 4.72 (d, J_{PH} = 1.8 Hz, C_5H_5), 1.57 (d, J_{PH} = 8.5 Hz, PMe), 0.97 (d, J_{PH} = 8.5 Hz, PMe). Anal. Calcd for $C_{36}H_{31}MoO_2P$: C, 69.45; H, 5.02. Found: C, 69.39; H, 5.03.

(η-Cyclopentadienyl)(η^3-triphenyloxocyclobutenyl)carbonyl(triphenyl phosphite)molybdenum(II) (11b). (η-Cyclopentadienyl)(η^3-triphenylcyclopropenyl)dicarbonylmolybdenum (**6a**) (0.15 g, 0.31 mmol) was dissolved in benzene (30 mL). Triphenyl phosphite (100 μL, 0.38 mmol) was added, and the solution was heated to reflux overnight and then cooled to room temperature. Florisil (4 g) was added, and the solvent was removed in vacuo. The coated Florisil was added to the top of a Florisil column prepared in hexane. The product eluted with 50:50 methylene chloride/ether and was crystallized from CH_2Cl_2/hexane to give yellow crystals (0.11 g, 45%): mp 195–201 °C dec; IR (CH_2Cl_2 ν_{CO} 1933, $\nu_{C=O}$ 1663 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.9–6.5 (m, 30 H, Ph), 4.67 (d, J_{PH} = 1.1 Hz, C_5H_5). Anal. Calcd for $C_{46}H_{35}MoO_5P$: C, 69.52; H, 4.44. Found: C, 69.32; H, 4.77.

X-ray Diffraction Studies. Crystalline samples of **6a** and **6b** of a quality suitable for diffraction studies were obtained by recrystallization from CH_2Cl_2/hexane at −30 °C. Unit-cell parameters, as reported in Table I, were obtained from angular settings of 25 reflections (20° ≤ 2θ ≤ 30°) containing Friedel related reflections to judge optical alignment. Systematic absences uniquely defined the space groups of **6a** and **6b**. During data reduction corrections were made for decay and *Lp* effects, but none for absorption were required.

Standard heavy-atom methods were used to locate the Mo atom in both **6a** and **6b**, and the remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. In the final cycles of blocked-cascade refinement, all non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were placed in idealized, updated locations (d(C–H) = 0.96 Å, U = 1.2 × attached carbon U). Additionally, in **6a** the three phenyl rings were treated as rigid, planar rings (d(C–C) = 1.395 Å).

Atomic coordinates for **6a** and **6b** are provided in Tables II and III, respectively. Selected bond distances and angles are given in Table IV. Additional crystallographic data are available as supplementary material.[29]

Acknowledgment. R.P.H. is grateful to the National Science Foundation, to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Alfred P. Sloan Foundation, for generous support of this work. R.P.H. is also grateful for preprints from, and free and helpful discussions with Professor R. R. Schrock (MIT). Dartmouth's Varian XL-300 NMR spectrometer and the University of Delaware diffractometer were purchased with funds from the National Science Foundation.

Registry No. **6a**, 82661-45-8; **6b**, 97689-46-8; **6c**, 97689-44-6; **8**, 97689-41-3; **9a**, 82661-46-9; **9b**, 92144-96-2; **11a**, 82661-47-0; **11b**, 97689-45-7; $W(CO)_6$, 14040-11-0; $Mo(CO)_6$, 13939-06-5; cyclopentadienylthallium, 34822-90-7; triphenylcyclopropenyl hexafluorophosphate, 42134-08-7; triphenylcyclopropenyl chloride, 58090-78-1; ammonium hexafluorophosphate, 16941-11-0; *tert*-butyldiphenylcyclopropenyl hexafluorophosphate, 97689-43-5.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes, fractional coordinates and isotropic thermal parameters for the hydrogen atoms, anisotropic thermal parameters, and bond distances and angles for **6a** (Tables 1S–5S) and **6b** (Tables 6S–10S) (41 pages). Ordering information is given on any current masthead page.

Reactions of Cyclopropenyl Cations with Group 6 Metal Carbonyl Anions. Synthesis of η^3-Oxocyclobutenyl Complexes of Chromium, Molybdenum, and Tungsten[†]

Russell P. Hughes,*[1a,2] Wolfgang Kläui,*[1b] John W. Reisch,[1a] and Arnold Müller[1b]

Department of Chemistry, Dartmouth College, Hanover, New Hampshire 03755, and Institut für Anorganische Chemie der Technischen Hochschule Aachen, 5100 Aachen, Federal Replublic of Germany

Received January 9, 1985

Reactions of $Na[M(C_5H_5)(CO)_3]$ (M = Mo, W) with the triphenylcyclopropenyl cation lead to apparent redox chemistry, affording the dinuclear compounds $[M(C_5H_5)(CO)_3]_2$ as the only organometallic products. In contrast reactions of the pentamethylcyclopentadienyl analogues $Na[M(C_5Me_5)(CO)_3]$ (M = Cr, Mo, W) with symmetrically substituted cyclopropenyl cations lead to oxocyclobutenyl complexes **4**; unsymmetrically substituted cyclopropenyl cations give exclusively complexes **5**, containing unsymmetrically substituted oxocyclobutenyl ligands. Similarly the molybdenum anion $[MoL(CO)_3]^-$ (L = $[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$) reacts with the triphenylcyclopropenyl cation to give the oxocyclobutenyl complex **6**. Spectroscopic properties of the oxocyclobutenyl complexes and reaction mechanisms are discussed.

Introduction

The reactions of cyclopropenyl cations, or their equivalents, with transition-metal centers have been investigated for a number of years and have been shown to give rise to a variety of products. The three-membered ring may be maintained intact in the form of 3-η^1-,[3-6] η^2-[7-9] or η^3-cyclopropenyl ligands,[10-22] or ring cleavage may occur to

---

[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III→3 and 13.)

(1) (a) Dartmouth College. (b) Technische Hochschule Aachen.

(2) Alfred P. Sloan Research Fellow 1980–1984.

(3) Desimone, D. M.; Desrosiers, P. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 4842–4846.

(4) Desrosiers, P. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1981**, *103*, 5593–5594.

(5) Gompper, R.; Bartmann, E.; Nöth, H. *Chem. Ber.* **1979**, *112*, 218–233.

(6) Gompper, R.; Bartmann, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 456–457.

(7) Mealli, C.; Midollini, S.; Moretti, S.; Sacconi, L.; Silvestre, J.; Albright, T. A. *J. Am. Chem. Soc.* **1982**, *104*, 95–107.

afford metallacyclobutadiene,[23-27] oxocyclobutenyl,[10-13,16,22,28-32] and a number of other metallacyclic systems.[33-35] The metallacyclobutadiene/η^3-cyclopropenyl valence isomers have assumed recent significance in view of their probable role as intermediates in alkyne metathesis reactions.[36-43] A theoretical survey of many of the transition-metal-promoted reactions of cyclopropenyl cations has appeared.[44]

Previously we have described the oxidative addition reaction of cyclopropenyl cations to zerovalent molybdenum and tungsten centers to afford ultimately the η^3-cyclopropenyl complexes **1**.[10,22] In some cases ring expansion reactions to give the η^3-oxocyclobutenyl compounds **2** were also observed. Since the oxocyclobutenyl ligand has proven to be a useful precursor for a number of cyclobutadiene complexes,[45-48] and in view of the potential catalytic significance of η^3-cyclopropenyl compounds of the group 6 metals (vide supra), we sought to establish whether compounds of general structure **1** and **2** might be synthesized more readily by reactions of cyclopropenyl cations with the nucleophilic anions $[M(C_5R_5)(CO)_3]^-$ (R = H, Me; M = Cr, Mo, W), and related species. Unpublished observations, quoted in a review article,[32a] indicated that reaction between (unspecified) cyclopropenyl cations and $Na[Mo(C_5H_5)(CO)_3]$ did not yield metal carbonyl species incorporating the three-membered-ring system. A subsequent exception, involving the reaction of the extremely bulky cation $[C_3\text{-}t\text{-}Bu_3]^+$ with $[M(C_5H_5(CO)_3]^-$ (M = Mo, W), was shown to yield the unusual hydrido complexes **3**, which result from apparent exo attack at the C_5H_5 ligand, followed by oxidative addition of the resultant endo-CH bond to the metal.[32b]

Some of the results reported here were the subject of a preliminary communication.[10]

Results and Discussion

The reactions of THF solutions of the sodium salts of the metal carbonyl anions $[M(C_5H_5)(CO)_3]^-$ (M = Mo, W) with the triphenylcyclopropenyl cation under rigorously anaerobic conditions afforded the metal–metal bonded dimers $[M(C_5H_5)(CO)_3]_2$ as the only organometallic products. Carrying out these reactions at −78 °C or changing the counterion to bis(triphenylphosphine)nitrogen (PPN^+) in the case of the Mo derivative did not change the course of the reaction. Similar apparent redox reactions have been observed in other metal carbonyl anion reactions with cyclopropenyl cations, and in some cases the accompanying benzene derivative resulting from reduction of the cation has been isolated.[3,10] These results confirm those reported earlier by King.[32a]

In contrast, the analogous reactions of the sodium salts of the pentamethylcyclopentadienyl derivatives $[MCp^*(CO)_3]^-$ ($Cp^* = C_5Me_5$) with the triphenylcyclopropenyl cation resulted in formation of the η^3-oxocyclobutenyl complexes **4**. Yields were reproducibly excellent (80–95%) for the Mo complex **4b** and moderate (50–60%) for the chromium and tungsten analogues **4a** and **4c**, respectively. No infrared absorptions characteristic of the known η^3-cyclopropenyl complex **1a**[10,22] were observed in the spectrum of the crude reaction product **4b**. Compounds **4** were readily characterized spectroscopically. For example, the IR spectrum of **4b** exhibited two strong terminal metal carbonyl stretching bands (CH_2Cl_2 solution) at 1987 and 1928 cm^{-1} and a characteristic[13,22,28] oxocyclobutenyl ketone absorption at 1664 cm^{-1}; these values can be compared with those for the corresponding Cp analogue **2a**[10,22] of 2001, 1945, and 1677 cm^{-1}. Lowering of terminal CO stretching frequencies on substitution of Cp by Cp* is not surprising since Cp* is expected to be a better donor, and we have shown that substitution of one CO ligand in **2a** by a better donor tertiary phosphine or phosphite ligand lowers the oxocyclobutenyl ketone frequency (**2c**, 1651 cm^{-1}; **2d**, 1663 cm^{-1}).[22] Similar variations in the oxocyclobutenyl ketone frequency have been observed for phosphine- and phosphite-substituted oxocyclobutenyl complexes of cobalt[28] and iron.[11,16] The $^{13}C\{^1H\}$ NMR spectra of compounds **4** exhibited a single resonance for the two CO ligands, a

---

(8) Mealli, C.; Midollini, S.; Moretti, S.; Sacconi, L. *Angew. Chem., Int. Ed. Engl.* **1980**, *11*, 931.

(9) McClure, M.D.; Weaver, D.L. *J. Organomet. Chem.* **1973**, *54*, C59–C61.

(10) Hughes, R. P.; Lambert, J. M. J.; Reisch, J. W.; Smith, W. L. *Organometallics* **1982**, *1*, 1403–1405.

(11) Hughes, R. P.; Hubbard, J. L.; Lambert, J. M. J.; Whitman, D. W.; Rheingold, A. L., manuscript in preparation.

(12) Drew, M. G. B.; Brisdon, B. J.; Day, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1310–1316.

(13) Chiang, T.; Kerber, R. C.; Kimball, S. D.; Lauher, J. W. *Inorg. Chem.* **1979**, *18*, 1687–1691.

(14) Hayter, R. G. *J. Organomet. Chem.* **1968**, *13*, P1–P3.

(15) (a) Rausch, M. D.; Tuggle, R. M.; Weaver, D. L. *J. Am. Chem. Soc.* **1970**, *92*, 4981–4982. (b) Tuggle, R. M.; Weaver, D. L.; *Inorg. Chem.* **1971**, *10*, 1504–1510.

(16) Jens, K. J.; Valeri, T.; Weiss, E. *Chem. Ber.* **1983**, *116*, 2872–2880.

(17) Gowling, E. W.; Kettle, S. F. A. *Inorg. Chem.* **1964**, *3*, 604–605.

(18) Jolly, P. W.; Wilke, G. "The Organic Chemistry of Nickel"; Academic Press: New York, 1974; Vol. 1, p 373.

(19) Weaver, D. L.; Tuggle, R. M. *J. Am. Chem. Soc.* **1969**, *91*, 6506–6507.

(20) Olander, W. K.; Brown, T. L. *J. Am. Chem. Soc.* **1972**, *94*, 2139–2140.

(21) Schneider, M.; Weiss, E. *J. Organomet. Chem.* **1976**, *121*, 345–353.

(22) Hughes, R. P.; Reisch, J. W.; Rheingold, A. L. *Organometallics*, preceding paper in this issue.

(23) Frisch, P. D.; Khare, G. P. *Inorg. Chem.* **1979**, *18*, 781–786.

(24) Tuggle, R. M.; Weaver, D. L. *Inorg. Chem.* **1972**, *11*, 2273–2242.

(25) A number of polynuclear compounds containing $\mu\text{-}C_3R_3$ ligands has been prepared via cyclopropenyl cations.[26,27] These can also be regarded as metallacyclobutadiene derivatives.

(26) Bailey, P. M.; Keasey, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1825–1830.

(27) Frisch, P. D.; Posey, R. G.; Khare, G. P. *Inorg. Chem.* **1978**, *17*, 781–786.

(28) Donaldson, W. A.; Hughes, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 4846–4859.

(29) Coffey, C. E. *J. Am. Chem. Soc.* **1962**, *84*, 118.

(30) King, R. B.; Efraty, A. *J. Organomet. Chem.* **1970**, *24*, 241–245.

(31) Potenza, J.; Johnson, R.; Mastropaolo, D.; Efraty, A. *J. Organomet. Chem.* **1974**, *64*, C13–C15.

(32) (a) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417–427. (b) Green, M.; Hughes, R. P. *J. Chem. Soc., Chem. Commun.* **1975**, 862–863.

(33) Frisch, P. D.; Khare, G. P. *J. Am. Chem. Soc.* **1978**, *100*, 8267–8269.

(34) McClure, M. D. Ph.D. Dissertation, Carnegie-Mellon University, 1975.

(35) Macunias, G. M. Ph.D. Dissertation, Carnegie-Mellon University, 1975.

(36) Pederson, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808–6809.

(37) Churchill, M. R.; Wasserman, H. J. *J. Organomet. Chem.* **1984**, *270*, 201.

(38) Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pederson, S. F.; Schrock, R. R. *Organometallics* **1983**, *2*, 1046–1048.

(39) Churchill, M. R.; Ziller, J. W.; Pederson, S. F.; Schrock, R. R. *J. Chem. Soc., Chem. Commun.* **1984**, 485–486.

(40) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, 485–486.

(41) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563–1573.

(42) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574–1583.

(43) Strutz, H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1600–1601.

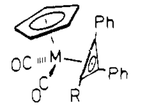
(44) Jemmis, E. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2570–2575.

(45) Donaldson, W. A.; Hughes, R. P.; Davis, R. E.; Gadol, S. M. *Organometallics* **1982**, *1*, 812–819.

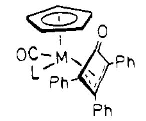
(46) Chidsey, C. E.; Donaldson, W. A.; Hughes, R. P. *J. Organomet. Chem.* **1979**, *169*, C12.

(47) Donaldson, W. A.; Hughes, R. P. *J. Magn. Reson.* **1981**, *43*, 170–172.

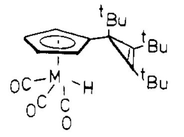
(48) Hughes, R. P.; Reisch, J. W.; Rheingold, A. L. *Organometallics* **1984**, *3*, 1761–1763.



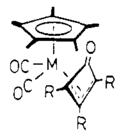
1 a. M=Mo; R=Ph
b. M=Mo; R=^{t}Bu
c. M=W; R=^{t}Bu



2 a. M=Mo; L=CO
b. M=W; L=CO
c. M=Mo; L=PMe$_2$Ph
d. M=Mo; L=P(OPh)$_3$



3 a. M=Mo
b. M=W



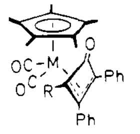
4 a. M=Cr; R=Ph
b. M=Mo; R=Ph
c. M=W; R=Ph
d. M=Mo R=Me

characteristic[28] ketone resonance, and two resonances for the remaining oxocyclobutenyl ring carbon atoms, consistent with the presence of a molecular symmetry plane and similar to the spectra of compounds **2a**,**b**[22] and oxocyclobutenyl complexes of other transition metals.[10-13,16,28] Their ^{1}H NMR spectra showed resonances for the Cp* and phenyl groups in the expected intensity ratio.

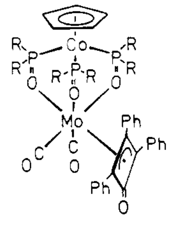
A similar reaction of the $[MoCp^*(CO)_3]^-$ anion with the trimethylcyclopropenyl cation afforded the analogous trimethyloxocyclobutenyl compound **4d**; low yields of a (trimethyloxocyclobutenyl)cobalt complex have been reported previously.[30]

Unsymmetrically substituted cyclopropenyl cations also reacted with $[MCp^*(CO)_3]^-$ (M = Cr, Mo, W) to yield oxocyclobutenyl complexes **5**. Notably, of the two substitution patterns possible for the oxocyclobutenyl rings of compounds **5**, only the unsymmetrically substituted isomer shown was observed. Monitoring of the ^{1}H NMR spectrum of the crude reaction product failed to identify any resonances which could be ascribed to the symmetrically substituted four-membered ring.[49] That the unique substituent in compounds **5** indeed occupies a site adjacent to the ketone group is clearly evident from the $^{13}C\{^1H\}$ NMR spectra, which show resonances for two distinct CO ligand environments together with four different resonances for the carbon atoms of the oxocyclobutenyl ring. Exclusive observation of this oxocyclobutenyl substituent pattern is also completely consistent with results obtained in reactions of unsymmetrically substituted cyclopropenyl cations with $[Co(CO)_4]^-$[28] and $[Fe(CO)_3(NO)]^-$.[11,49]

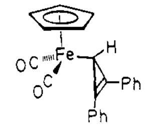
The oxygen tripod ligand $L^- = [(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-$, a monoanionic six-electron donor, is formally equivalent to a cyclopentadienyl ligand but should possess different electronic properties. It was of interest, therefore, to compare the reactivity of $[MoL(CO)_3]^-$[50] with that of its Cp and Cp* analogues toward the triphenylcyclopropenyl cation. The reaction proceeded readily to afford the oxocyclobutenyl complex **6** as a yellow air-stable crystalline material. This compound shows the expected IR bands for the oxygen tripod ligand$_{51}$ together with two bands for the cis-dicarbonyl unit at 1972 and 1895 cm^{-1} and a ketone stretch at 1688 cm^{-1}. The P=O stretching frequency occurs at 1115 cm^{-1} which is 55 cm^{-1} lower than that in Na(L), indicating considerable reduction of the P=O bond order upon coordination to Mo. The CO stretching frequencies in **6** are lower than those in the Cp and Cp* analogues **2a** and **4b**, respectively, demonstrating that L is indeed a good donor ligand. It is surprising, however, that the ketone stretching absorption in **6** is not shifted to a lower frequency than that observed for **2a**. Interestingly, the ^{1}H NMR spectrum of **6** shows that the equivalence of the six OC_2H_5 groups is lost upon formation of the oxocyclobutenyl complex. This clearly indicates that the oxygen tripod ligand L, unlike the freely rotating Cp and Cp* ligands, is rigidly bound to the molybdenum center.



5 a. M=Mo; R=H
b. M=Mo; R=^{t}Bu
c. M=Mo; R=Me
d. M=W; R=H
e. M=Cr; R=^{t}Bu



6. R=OEt



7

The reaction of the triphenylcyclopropenyl cation with $[MoL(CO)_3]^-$ is sensitive to the bulk of the oxygen tripod ligand. Changing the six OC_2H_5 groups in L^- to O-*i*-Pr groups yields a highly crowded ligand.[52] Using this ligand, formation of the corresponding oxocyclobutenyl complex is largely suppressed, and the main organometallic products observed instead are the dimer $[MoL[CO)_3]_2$ and other as yet unidentified $MoL(CO)_3$ species resulting from apparent redox reactions.

The mechanism of formation of these oxocyclobutenyl complexes deserves some brief comment. In a detailed study of the formation of oxocyclobutenyl complexes of cobalt, we have shown unambiguously that the immediate precursor to the oxocyclobutenyl ring is a (2-cyclopropene-1-carbonyl)cobalt intermediate.[28] It was also suggested that, in the reaction of $[Co(CO)_4]^-$ with cyclopropenyl cations, this intermediate was formed by direct electrophilic attack of the cyclopropenyl cation at a carbon monoxide ligand, rather than at the metal center;[28] this hypothesis was based on circumstantial evidence, however.

It is quite clear that the expected site of nucleophilic attack at an unsymmetrically substituted cyclopropenyl cation is at a non-phenylated position; in this unusual situation the phenyl group *destabilizes* the localization of positive charge on an adjacent carbon atom in the tran-

---

[49] Symmetrically substituted oxocyclobutenyl complexes of iron are formed by exogenous ligand-promoted ring expansion of the η^3-cyclopropenyl rings in $[Fe(\eta\text{-}C_3Ph_2R)(CO)_2(NO)]$ (R = H, Me). Hughes, R. P.; Lambert, J. M. J.; Hubbard, J. L., to be submitted for publication.

[50] Kläui, W.; Müller, A.; Scotti, M. *J. Organomet. Chem.* **1983**, *253*, 45.

[51] Kläui, W.; Dehnicke, K. *Chem. Ber.* **1978**, *111*, 451.

[52] Eberspach, W.; ElMurr, N.; Kläui, W. *Angew Chem., Int. Ed. Eng.* **1982**, *21*, 915.

[53] Cross, G. L.; Boll, W. A.; Heyn, H.; Dev, V. *J. Am. Chem. Soc.* **1968**, *90*, 173–178.

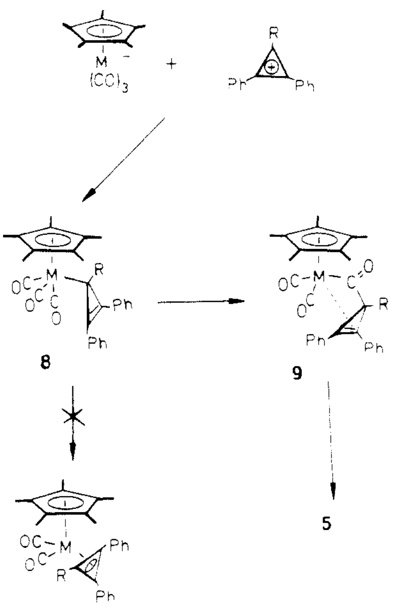
[54] Zimmerman, H. E.; Aasen, S. M. *J. Org. Chem.* **1978**, *43*, 1493–1506.

[55] Farnum, D.; Burr, M. *J. Am. Chem. Soc.* **1960**, *82*, 2651.

[56] Birdwhistell, R.; Hackett, P. Manning, A. R. *J. Organomet. Chem.* **1978**, *157*, 239–241.

[57] Kläui, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1403.

Scheme I



sition state for nucleophilic attack at the C_3 ring.[58] Examples of this site selectivity involving organic nucleophiles have been reported,[58-60] but only one organometallic system has been well characterized; the $[Fe(C_5H_5)(CO)_2]^-$ anion is reported to react selectively with the diphenylcyclopropenyl cation to yield 7[6].

On the basis of these precedents, the mechanism shown in Scheme I is proposed to account for the selective formation of isomers **5** from unsymmetrically substituted cyclopropenyl cations. Direct attack of the metal center at the C_3 ring should afford the 3-η^1-cyclopropenyl species **8**, which can then undergo a cyclopropenyl migration reaction to CO, yielding the 2-cyclopropene-1-carbonyl species **9**.[61] This contains the known[28] prerequisite ligand for subsequent ring expansion to give final product **5**. It should be emphasized that **9** must contain the unique substituent, R, directly adjacent to the ketone group in order for **9** to yield *only* the unsymmetrically substituted oxocyclobutenyl ring observed in **5**.[62] On the basis of these observations we cannot rule out the possibility that **9** is formed directly, without the intermediacy of **8**. However, if **8** is indeed an intermediate, cyclopropenyl migration to produce **9**, and then **5**, must occur to the complete exclusion of CO dissociation to afford η^3-cyclopropenyl complexes. The latter are not observed as reaction products, and we have demonstrated previously that η^3-triphenylcyclopropenyl analogues **1a** require much more forcing conditions in order to generate oxocyclobutenyl complexes **2**.[22] Indeed η^3-*tert*-butyldiphenylcyclopropenyl complexes **1a** and **1b** are inert toward ring expansion to the corresponding oxocyclobutenyl ligand.[22,63]

It is not clear why this reaction to give oxocyclobutenyl complexes works well for metal carbonyl anions bearing the pentamethylcyclopentadienyl ligand and the oxygen tripod ligand but fails utterly for the cyclopentadienyl analogues, yielding apparent redox products. One possibility is that the metal–carbon bond in the cyclopentadienyl analogue of **8** is sufficiently weak to undergo homolysis with the resultant exclusion of either cyclopropenyl migration or CO dissociation; the products (**2** or **1**) of either of these latter pathways are thermally stable.[22] If a redox SET reaction between anion and cation is responsible for radical formation, it is not clear why the Cp* analogues should not also be excellent reducing agents.

Experimental Section

General Procedures. Reactions were carried out in conventional oven dried Schlenk glassware under an atmosphere of dinitrogen which was deoxygenated over BASF catalyst and dried over P_4O_{10} or in a Vacuum Atmospheres glovebox equipped with a HE-493 gas purification system. Hydrocarbon and ethereal solvents were dried by distillation from sodium or potassium benzophenone ketyl. Methylene chloride was distilled from P_4O_{10}. All solvents were stored and transferred under purified dinitrogen.

The 300-MHz ^1H NMR spectra and 75-MHz $^{13}C\{^1H\}$ NMR spectra were obtained on a Varian XL-300 spectrometer, and some lower field ^1H and $^{13}C\{^1H\}$ spectra were measured on JEOL C 60 HL and Bruker WP 80 instruments, respectively. Chemical shifts are reported in parts per million downfield from internal tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 599 spectrometer and calibrated against the 1601 cm^{-1} peak of polystyrene. Electron-impact (70 eV) mass spectra were run on a Varian MAT CH5 spectrometer. Microanalyses were performed by Spang, Eagle Harbor, MI.

Triphenylcyclopropenyl hexafluorophosphate,[22] **trimethylcyclopropenyl tetrafluoroborate,**[53] **methyldiphenylcyclopropenyl tetrafluoroborate,**[54] ***tert*-butyldiphenylcyclopropenyl hexafluorophosphate,**[54] **and diphenylcyclopropenyl perchlorate**[55] were prepared by literature procedures. *Caution!* The latter perchlorate salt should be prepared on a small scale (<1 g) and should not be air-dried. We have experienced a small but severe explosion when a dry sample was probed with a nichrome spatula.

The dinuclear complexes $[M(C_5H_5)(CO)_3]_2$ (M = Mo, W) and $[M(C_5Me_5)(CO)_3]_2$ (M = Mo, W) were prepared by the literature method.[56] $Na[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]$ (≡ NaL) was prepared as described previously.[57]

Reaction of $[MoCp(CO)_3]^-Na^+$ with Triphenylcyclopropenyl Hexafluorophosphate. A sodium amalgam was prepared by using Na (0.15 g, 6.53 mmol) and mercury (20 mL). Dry THF (25 mL) and the $[MoCp(CO)_3]_2$ dimer (0.53 g, 1.2 mmol) were added. The mixture was stirred for 1 h, the mercury was drained off, and the solution was filtered through filter cel. The filter cel was washed with THF (2 × 7 mL), and the washings were added to the filtrate. The solution was cooled to −80 °C, and solid triphenylcyclopropenyl hexafluorophosphate (1.0 g, 2.4 mmol) was added. The mixture was stirred at −80 °C for 3 h and then allowed to warm to ambient temperature. Florisil (3 g) was added, and the solvent was removed in vacuo. The coated Florisil was added to the top of a Florisil column (30 g) prepared in hexane. A red band eluted with methylene chloride which was evaporated in vacuo to give the starting dimer (0.42 g, 80%): IR (CH_2Cl_2) ν_{CO} 1955, 1909 cm^{-1}.

Reaction of $[WCp(CO)_3]^-Na^+$ with Triphenylcyclopropenyl Hexafluorophosphate. A sodium amalgam was prepared by using Na (0.201 g, 8.74 mmol) and mercury (20 mL). Dry THF (20 mL) and the $[WCp(CO)_3]_2$ dimer (0.875 g, 1.31 mmol) were added. The mixture was stirred for 1 h, the mercury was drained off, and the solution was filtered through filter cel. The filter cel was washed with THF (2 × 7.5 mL), and the washings were added to the filtrate. The solution was cooled to −80 °C, and triphenylcyclopropenyl hexafluorophosphate (1.01 g, 2.44 mmol) was added. The mixture was stirred at −80 °C for 90 min, then allowed to warm to ambient temperature, and stirred overnight. Florisil (3 g) was added, and the solvent was removed.

---

(58) Johnson, R. W.; Widlanski, T.; Breslow, R. *Tetrahedron Lett.* **1976**, 4685–4686.

(59) Breslow, R.; Hover, H.; Chang, H. W. *J. Am. Chem. Soc.* **1962**, *84*, 3168–3174.

(60) Padwa, A.; Blacklock, T. J.; Cordova, D. M.; Loza, R. *J. Am. Chem. Soc.* **1980**, *102*, 5648–5656.

(61) It should be noted that this migration must occur by a 1,2-shift from M to CO and cannot occur with allylic rearrangement of the migrating group. Migration of cyclopropenyl groups from CO to Re has been observed to occur with allylic rearrangement.[3,4]

(62) A detailed study of the exogenous ligand-induced ring expansion reactions of $[Fe(\eta\text{-}C_3Ph_2R)(CO)_2(NO)]$ (R = H, Me) to give *both* symmetrically and unsymmetrically substituted oxocyclobutenyl rings is the subject of a forthcoming paper.[49]

(63) Similar inertness of mono- and tri-*tert*-butylcyclopropenyl ligands toward ring expansion has been observed for $[Fe(\eta\text{-}C_3R_2\text{-}t\text{-}Bu)(CO)_2(NO)]$ (R = Ph, *t*-Bu).[49]

The coated Florisil was added to the top of a Florisil column (30 g) prepared in hexane. An orange band eluted with methylene chloride, which was evaporated in vacuo to give the starting dimer (0.79 g, 90%): IR (CH_2Cl_2) ν_{CO} 1962, 1909 cm^{-1}.

(η-Pentamethylcyclopentadienyl)(η^3-triphenyloxocyclobutenyl)dicarbonylchromium(II) (4a). NaH (0.120 g, 50:50 oil, 2.6 mmol) was washed with hexane (3 × 5 mL) and vacuum dried. THF (10 mL) and pentamethylcyclopentadiene (0.40 mL, 2.4 mmol) were added. The mixture was heated to 60 °C overnight. The yellow solution was cooled to ambient temperature and transferred via filter cannula to a dry tared Schlenk flask. Hexacarbonylchromium (0.524 g, 2.38 mmol) was added, and the mixture was refluxed overnight. The solution was cooled to −80 °C, and solid triphenylcyclopropenyl hexafluorophosphate (0.98 g, 2.38 mmol) was added. The solution was stirred cold for 45 min, then allowed to warm to ambient temperature, and stirred for 3 h. Florisil (3 g) was added, and the solvent was removed. The coated Florisil was added to the top of a Florisil column (2.5 × 25 cm) prepared in hexane. Elution with methylene chloride/ether (80:20) afforded a yellow band, which was evaporated in vacuo. Crystallization of the residue from CH_2Cl_2/hexane afforded the product as yellow, air-stable crystals (0.52 g, 41%): mp 196 °C dec; IR (CH_2Cl_2) ν_{CO} 1975, 1920, $\nu_{C=O}$ 1675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 15 H, Ph), 1.67 (s, 15 H, C_5Me_5); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 241.9 (CrCO), 168.4 (C=O); 134.7 (Ph), 134.5 (Ph), 130.9 (Ph), 130.6 (Ph), 128.4 (Ph), 127.9 (Ph), 127.6 (Ph), 127.0 (Ph), 125.8 (Ph), 101.0 (C_5Me_5), 96.0 (CPh), 74.5 (CPh), 8.4 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{34}H_{30}CrO_3$: C, 75.82; H, 5.61. Found: C, 75.74; H, 5.90.

(η-Pentamethylcyclopentadienyl)(η^3-triphenyloxocyclobutenyl)dicarbonylmolybdenum(II) (4b). A sodium alamagam was prepared with mercury (20 mL) and sodium (0.10 g, 4.3 mmol). Dry THF (30 mL) and bis(η-pentamethylcyclopentadienyl)-hexacarbonyldimolybdenum (0.61 g, 0.968 mmol) were added. The mixture was stirred for 45 min and the color changed from bright orange to yellow. The mercury was drained off, and the solution was filtered through filter cel in a Schlenk filter. The filter cel was washed with THF (2 × 6 mL), and the washings were added to the filtrate. The solution was cooled to −80 °C, and solid triphenylcyclopropenyl hexafluorophosphate (0.76 g, 1.84 mmol) was added. The solution was stirred cold for 1 h, then allowed to warm to ambient temperature, and stirred overnight. Florisil (4 g) was added, and the solvent was removed in vacuo. The coated Florisil was added to the top of a Florisil column (2.5 × 25 cm) prepared in hexane. Elution with ether gave a yellow band which was evaporated. Crystallization of the residue from CH_2Cl_2/hexane gave the product as yellow crystals (0.92 g, 86%): mp 197–199 °C; IR (CH_2Cl_2) ν_{CO} 1987, 1928, νC=O 1664 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.4–7.0 (m, 15 H, Ph), 1.77 (s, 15 H, C_5Me_5); ^{13}C{^{1}H}) NMR ($CDCl_3$) δ 231.5 (MoCO), 167.9 (C=O), 135.1 (Ph), 134.0 (Ph), 131.2 (Ph), 127.5 (Ph), 126.3 (Ph), 125.2 (Ph), 103.2 (C_5Me_5), 88.3 (*C*Ph), 68.4 (*C*Ph), 8.7 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{34}H_{30}MoO_3$: C, 70.10; H, 5.19. Found: C, 69.98; H, 5.24.

(η-Pentamethylcyclopentadienyl)(η^3-triphenyloxocyclobutenyl)dicarbonyltungsten(II) (4c) was prepared similarly to **4b** but starting with the corresponding tungsten dimer, in 38% yield: mp 209–212 °C dec; IR (CH_2Cl_2) ν_{CO} 1993, 1930, $\nu_{C=O}$ 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.39 (m, 15 H, Ph), 2.00 (s, 15 H, $C_5\mathit{Me}_5$); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 219.5 (WCO), 171.0 (C=O), 135.7 (Ph), 127.5 (Ph), 133.9 (Ph), 132.1 (Ph), 129.6 (Ph), 128.6 (Ph), 127.5 (Ph), 126.2 (Ph), 124.9 (Ph), 101.0 (C_5Me_5), 80.8 (*C*Ph), 59.3 (*C*Ph), 8.6 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{34}H_{30}O_3W$: 60.91; H, 4.51. Found: C, 61.31; H, 4.69.

(η-Pentamethylcyclopentadienyl)(η^3-trimethyloxocyclobutenyl)dicarbonylmolybdenum(II) (4d) was prepared similarly to **4b** but using trimethylcyclopropenyl tetrafluoroborate, in 70% yield: mp 184–190 °C; IR (CH_2Cl_2) ν_{CO} 1971, 1907, $\nu_{C=O}$ 1654 cm^{-1}; ^{1}H NMR δ 2.02 (s, 3 H, Me), 1.90 (s, 15 H, C_5Me_5), 1.64 (s, 6 H, Me); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 233.1 (MoCO), 172.0 (C=O), 102.4 ($C_5\mathit{Me}_5$), 88.1 (*C*Me), 64.3 (*C*Me), 9.25 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{19}H_{24}MoO_3$: C, 57.58; H, 6.10. Found: C, 57.49; H, 6.13.

(η-Pentamethylcyclopentadienyl)(η^3-2,3-diphenyloxocyclobutenyl)dicarbonylmolybdenum(II) (5a) was prepared similarly to **4b** but using diphenylcyclopropenyl perchlorate, in 67% yield: mp 188–190 °C; IR (CH_2Cl_2) ν_{CO} 1987, 1924, $\nu_{C=O}$ 1663 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.19 (m, 10 H, Ph), 3.56 (s, 1 H), 1.85 (s, 15 H, C_5Me_5); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 232.3 (MoCO), 231.0 (MoCO), 170.0 (C=O), 135.2 (Ph), 134.3 (Ph), 129.5 (Ph), 127.9 (Ph), 126.4 (Ph), 103.4 (C_5Me_5), 85.7 (*C*Ph), 79.0 (*C*Ph), 47.6 (*C*H), 9.3 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{28}H_{26}MoO_3$: C, 66.40; H, 5.17. Found: C, 66.40; H, 5.18.

(η-Pentamethylcyclopentadienyl)(η^3-2-*tert*-butyl-3,4-diphenyloxocyclobutenyl)dicarbonylmolybdenum(II) (5b) was prepared similarly to **4b** but using *tert*-butyldiphenylcyclopropenyl hexafluorophosphate, in 71% yield: mp 198–201 °C dec; IR (CH_2Cl_2) ν_{CO} 1970, 1910, $\nu_{C=O}$ 1656 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 10 H, Ph), 1.84 (s, 15 H, $C_5\mathit{Me}_5$), 1.05 (s, 9 H, $C\mathit{Me}_3$). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 235.0 (MoCO), 232.0 (MoCO), 167.8 (C=O), 134.2 (Ph), 131.9 (Ph), 128.1 (Ph), 127.4 (Ph), 127.1 (Ph), 125.1 (Ph), 102.0 (C_5Me_5), 90.6 (*C*Ph), 83.5 (*C*Ph), 83.5 (*C*Ph), 68.7 ($\mathit{C}CMe_3$), 33.5 (CMe_3), 30.5 ($C\mathit{Me}_3$), 9.1 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{32}H_{34}MoO_3$: C, 68.32; H, 6.09. Found: C, 68.11; H, 6.44.

(η-Pentamethylcyclopentadienyl)(η^3-2-methyl-3,4-diphenyloxocyclobutenyl)dicarbonylmolybdenum(II) (II) (5c) was prepared similarly to **4b** but using methyldiphenylcyclopropenyl tetrafluoroborate, in 31% yield: mp 163–164 °C; IR (CH_2Cl_2) ν_{CO} 1982, 1920, $\nu_{C=O}$ 1972 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.7–7.0 (m, 10 H, Ph), 1.90 (s, 3 H, Me), 1.85 (s, 15 H, C_5Me_5); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 233.0 (MoCO), 232.1 (MoCO), 171.2 (C=O), 135.0 (Ph), 134.7 (Ph), 128.5 (Ph), 128.2 (Ph), 128.0 (Ph), 127.8 (Ph), 127.2 (Ph), 125.7 (Ph), 102.9 (C_5Me_5), 87.9 (*C*Ph), 68.9 (*C*Ph), 63.4 (*C*Me), 10.1 (Me), 9.1 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{29}H_{28}MoO_3$: C, 66.92; H, 5.42. Found: C, 66.77; H, 5.38.

(η-Pentamethylcyclopentadienyl)(η^3-2,3-diphenyloxocyclobutenyl)dicarbonyltungsten(II) (5d) was prepared in a similar manner to **4c** but using the diphenylcyclopropenyl perchlorate salt, in 12% yield: mp 187–190 °C; IR (CH_2Cl_2) ν_{CO} 1982, 1915, $\nu_{C=O}$ 1671 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.08 (m, 10 H, Ph), 3.40 (s, 1 H, CH), 2.01 (s, 15 H, C_5Me_5). Anal. Calcd for $C_{28}H_{26}O_3W$: C, 56.58; H, 4.41. Found: C, 56.48; H, 4.46.

(η-Pentamethylcyclopentadienyl)(η^3-2-*tert*-butyl-3,4-diphenyloxocyclobutenyl)dicarbonylchromium(II) (5e) was prepared in a similar manner to **4a** but using the *tert*-butyldiphenylcyclopropenyl hexafluorophosphate salt, in 30% yield: mp 188–189 °C; IR (CH_2Cl_2) ν_{CO} 1968, 1914, $\nu_{C=O}$ 1671 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 10 H, Ph), 1.68 (s, 15 H, C_5Me_5), 1.08 (s, 9 H, CMe_3). ^{13}C{^{1}H} NMR ($CDCl_3$) δ 245.2 (CrCO), 242.8 (CrCO), 167.8 (C=O), 135.2 (Ph), 134.1 (Ph), 131.8 (Ph), 128.4 (Ph), 127.8 (Ph), 126.2 (Ph), 101.3 (C_5Me_5), 98.3 (*C*Ph), 89.3 (*C*Ph), 34.5 ($\mathit{C}Me_3$), 31.0 ($C\mathit{Me}_3$), 9.2 ($C_5\mathit{Me}_5$). Anal. Calcd for $C_{32}H_{34}CrO_3$: C, 74.01; H, 6.61. Found: C, 73.63; H, 6.94.

Preparation of $[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]Mo[CO_2(\eta^3\text{-}C_3Ph_3CO)]$ (6). A mixture of $Mo(CO)_6$ (0.150 g, 0.56 mmol) and NaL (0.315 g, 0.56 mmol) in acetonitrile (10 mL) was heated to reflux for 3 h. The resultant dark red solution was cooled to room temperature, the solvent removed in vacuo, and the solid residue dissolved in 10 mL of hot methylene chloride (40 °C). After 30 min solid $[C_3Ph_3]BF_4$ (0.200 g, 0.56 mmol) was added and the reaction mixture was stirred for 30 min. Chromatography was conducted on alumina. Some side products were eluted first with CH_2Cl_2. With 1:1 tetrahydrofuran/diethylether as eluant a yellow band developed which was collected. Evaporation of the solvent and crystallization of the residue from hexane yielded **6** (0.204 g, 37%) as bright yellow, air-stable crystals: IR (KBr) ν_{CO} 1972, 1895, $\nu_{C=O}$ 1688, $\nu_{P=O}$ 1115 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.2 (m, CH_3, 18 H), 3.5–4.3 (m, br, OCH_2, 12 H), 4.9 (s, C_5H_5, 5 H), 7.0–7.9 (m, Ph, 15 H); ^{13}C{^{1}H} NMR (67.9 MHz, CD_3COCD_3) δ 16.6 (CH_3), 61.0–62.1 (m, OCH_2), 80.2 (CPh), 90.3 (C_5H_5), 126.9, 127.8, 129.8, 131.9, 136.0, 136.8 (Ph), 169.8 (C=O), 224.2 (C≡O); mass spectrum (electron impact, 70 eV, 200 °C), *m/e* (relative intensity) 984 (M^+ (^{98}Mo), 0.5), 928 ($M^+ - 2$ CO, 10), 900 ($M^+ -$ 3 CO, 30), 631 (LMo^+, 10), 450 ($M^+ - 3$ CO, 5), 449 (M^+ - L, 15), 267 ($C_3Ph_3^+$, 40), 178 ($C_2Ph_2^+$, 100). Anal. Calcd for $C_{41}H_{50}CoMoO_{12}P_3$; C, 50.12; H, 5.13. Found: C, 50.07; H, 5.18.

Acknowledgment. R.P.H. is grateful to the National Science Foundation, to the donors of the Petroleum research Fund, administered by the American Chemical Society, and to the Alfred P. Sloan Foundation, for generous support of this work. Dartmouth's Varian XL-300 NMR spectrometer was purchased with funds from the National Science Foundation.

Registry No. **4a**, 97689-54-8; **4b**, 82665-10-9; **4c**, 97689-55-9; **4d**, 92144-97-3; **5a**, 97689-56-0; **5b**, 97689-57-1; **5c**, 97689-58-2; **5d**, 97689-59-3; **5e**, 97689-60-6; **6**, 97689-61-7; $[MoCp(CO)_3]_2$, 12091-64-4; $[MoCp(CO)_3]^-Na^+$, 12107-35-6; $[WCp(CO)_3]^-Na^+$, 12107-36-7; $[WCp(CO)_3]_2$, 12091-65-5; $Cr(CO)_6$, 13007-92-6; $Mo(CO)_6$, 13939-06-5; $[(C_5H_5)Co\{P(O)(OC_2H_5)_2\}_3]^-Na^+$, 70850-86-1; $[Mo(C_5Me_5)(CO)_3]_2$, 56200-14-7; $[W(C_5Me_5)(CO)_3]_2$, 70605-19-5; $[C_3Ph_3]PF_6$, 42134-08-7; C_5Me_5H, 41539-64-4; $[C_3Me_3]BF_4$, 12306-61-5; $[C_3Ph_3]BF_4$, 741-16-2; diphenylcyclopropenyl perchlorate, 37647-36-2; *tert*-butyldiphenylcyclopropenyl hexafluorophosphate, 97674-31-2; methyldiphenylcyclopropenyl tetrafluoroborate, 65102-02-5.

Reaction of Bis(cyclopentadienyldicarbonylmolybdenum) with Carbon Monoxide. Evidence against Facile Ligand Dissociation from the Cyclopentadienyltricarbonylmolybdenum Radical

Nataliya N. Turaki and John M. Huggins*

Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208

Received January 14, 1985

The reactions of $(MeCp)_2Mo_2(CO)_4$ and $(Cp)_2Mo_2(CO)_4$ mixtures, as well as $MeCpMo(CO)_2{\equiv}Mo(CO)_2Cp$, with carbon monoxide were studied. The products were invariably the corresponding hexacarbonyl dimers $(RC_5H_4)_2Mo_2(CO)_6$ (R = H, CH_3) with no evidence for the respective crossover products. The absence of crossover was verified under a variety of conditions of solvent and temperature. These results are interpreted as excluding a mechanism involving metal–metal bond homolysis. Arguments are presented for direct CO dissociation in the formation of $Cp_2Mo_2(CO)_4$ from $Cp_2Mo_2(CO)_6$ for both the thermal and photochemical pathways.

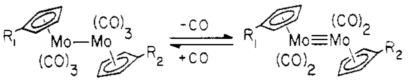
Introduction

The ligand substitution behavior of dinuclear metal carbonyl complexes with metal–metal single bonds has been a topic of considerable recent interest.[1] Attention has been drawn to these reactions by earlier studies[2] suggesting that the thermal and photochemical substitution reactions of the $M_2(CO)_{10}$ dimers (M = Mn, Re) occur by ligand substitution at the 17-electron intermediates formed by metal–metal bond homolysis. It is now clear from a series of elegant crossover experiments by Muetterties, Atwood and co-workers that the thermal substitution reactions of these dimers occur by a CO-dissociative mechanism that does not involve metal-metal bond cleavage.[3] Furthermore, a number of flash photolysis and low-temperature matrix photolysis experiments have established that CO dissociation and metal-metal bond homolysis are competitive primary photoprocesses and that both pathways can lead to substitution.[4] On the other hand, a number of other studies clearly indicate that 17-electron radicals, when formed, show exceptional ligand lability.[1,5–7] Indeed associative substitution has been demonstrated for the isolable complexes $V(CO)_6$ and $Mn(CO)_3(PBu_3)_2$ as well as some transient radicals.[5,6,7a,b] In this context the formation of $[CpMo(CO)_2]_2$ (**2**) from $[CpMo(CO)_3]_2$ (**1**), eq 1,[8,9] represents a unique example of

Table I. Dimer Ratios for the Decarbonylation of an Equimolar Mixture of 1a and 1c in Refluxing Toluene[a]

time, min	$[\mathbf{1b}]^2/[\mathbf{1a}][\mathbf{1c}]$	% **2a–c**
3	0.43	2.1
6	1.33	4.1
9	2.44	6.1
12	3.26	7.0
15	3.39	12.7
30	3.73	31.9

[a] The dimer ratios were calculated from the relative peak areas of the UV-detector (254 nm) output from the HPLC system correcting for differences in molar absorptivity.



(1)

1a, R_1 = H, R_2 = H
b, R_1 = H, R_2 = CH_3
c, R_1 = CH_3, R_2 = CH_3

2a, R_1 = H, R_2 = H
b, R_1 = H, R_2 = CH_3
c, R_1 = CH_3, R_2 = CH_3

---

(1) (a) Muetterties, E. L.; Burch, R. R.; Stolzenberg, A. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 89. (b) Brown, T. L. *Ann. N.Y. Acad. Sci.* **1980**, *333*, 80. (c) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press; New York, 1978; pp 184–193.

(2) (a) McCullen, S. B.; Brown, T. L. *Inorg. Chem.* **1981**, *20*, 3528. (b) Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095. (c) Byers, B. H.; Brown, T. L. *Ibid.* **1975**, *100*, 3260. (d) Fawcett, J. P.; Poë, A. *J. Chem. Soc., Dalton Trans.* **1976**, 2039. (e) Poë, A. *Inorg. Chem.* **1981**, *20*, 4029.

(3) (a) Stolzenberg, A. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1983**, *105*, 822. (b) Coville, N. J.; Stolzenberg, A. M.; Muetterties, E. L. *Ibid.* **1983**, *105*, 2499. (c) Sonnenberger, D.; Atwood, J. D. *Ibid.* **1980**, *102*, 3484. (d) Atwood, J. D. *Inorg. Chem.* **1981**, *20*, 4031.

(4) (a) Hepp, M. F.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 5934. (b) Dunkin, I. R.; Harter, P.; Shields, C. J. *Ibid.* **1984**, *106*, 7248. (c) Yesaka, H.; Kobayashi, T.; Yusufuku, K.; Nagakura, S. *Ibid.* **1983**, *105*, 6249. (d) Rothberg, L. J.; Cooper, N. J.; Peters, K. S.; Vaida, V. *Ibid.* **1982**, *104*, 3537. (e) Leopold, D. G.; Vaida, V. *Ibid.* **1984**, *106*, 3720. (f) Hughey, J. L.; Anderson, C. P.; Meyer, T. J. *J. Organomet. Chem.* **1977**, *125*, C49.

(5) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 4032.

(6) McCullen, S. B.; Walker, H. W.; Brown, T. L. *J. Am. Chem. Soc.* **1982**, *104*, 4007.

(7) (a) Zizelman, P. M.; Amatore, C.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3771. (b) Hershberger, J. W.; Amatore, C.; Kochi, J. K. *J. Organomet. Chem.* **1983**, *250*, 345. (c) Hershberger, J. W.; Klinger, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 3035. (d) Hoffman, N. W.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 613. (e) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 947.

0276-7333/85/2304-1766$01.50/0 © 1985 American Chemical Society