which contained actually, as shown by NMR[9], spectroscopy, both cis/trans isomers stable in neutral medium.

The addition of **2** to **8** in the presence of $HBF_4 \cdot Et_2O$ in CH_2Cl_2 led to the formation of **11** (61%; Scheme III). The ^1H NMR spectrum of **11** indicated[11] the selectivity of the addition to the intracyclic C=C bond and the presence of only one diastereoisomer.

The proposed relative configuration of **11** is based on the following rationale pertaining to the addition of a bulky nucleophile to forms I and II of the protonated *l*-carvone (Scheme IV): (i) forms I and II are expected to be in equilibrium at room temperature,[12] (ii) it has been established[7,13] for a six-membered ring that nucleophilic addition occurs antiparallel to the axial hydrogen atom H_a or H'_a at the adjacent carbon atom, and therefore nucleophilic addition to C-3 in forms I and II should occur as shown by A and B, respectively, in Scheme IV, (iii) the antiparallel addition of a bulky $Fe(\eta^2\text{-}CS_2)$ complex to form I is obviously disfavored with respect to the antiparallel addition to form II due to the axial position of the bulky 1-methylethenyl group in I. Therefore **11** should result from the addition to form II in the sense indicated by B.

The present study shows that the addition of a nucleophilic $Fe(\eta^2\text{-}CS_2)$ complex, in acidic medium, to α,β-unsaturated substrates is regiospecific and reaches a high stereoselectivity when the bulky nucleophile **2** is used. We are currently investigating ways to remove the metallic moiety from the sulfur-containing organic part of the cationic adducts.

Registry No. **1**, 64424-57-3; **2**, 64424-68-6; **3a**, 107-02-8; **3b**, 78-94-4; **3c**, 94-41-7; **3d**, 96-33-3; **4a**, 82665-43-8; **4b**, 82665-45-0; **4c**, 82665-47-2; **4d**, 82665-49-4; **5c**, 82665-51-8; **6c**, 82665-52-9; **7**, 591-11-7; **8**, 2244-16-8; *cis*-**9**, 82665-54-1; *trans*-**9**, 82729-18-8; *cis*-**10**, 82665-56-3; *trans*-**10**, 82729-20-2; **11**, 82665-58-5.

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[9] Data for complex **10**: mp 154–155 °C. Anal. Calcd: C, 58.80; H, 4.12; Fe, 6.24; P, 6.79. Found: C, 58.49; H, 4.19; Fe, 6.12; P, 6.66. IR (Nujol) 2042, 1985, 1790 cm^{-1}. NMR (δ, CD_2Cl_2): *cis*-**10**, ^1H (100 MHz) 1.38 (d, $CHCH_3$, $^3J_{HH}$ = 6.5 Hz), ^{13}C (20.115 MHz) 287.6 (t, CS_2), 172.7 (C=O), 79.6 ($CHCH_3$), 59.1 (CHS), 33.2 (CH_2), 20.6 (CH_3); *trans*-**10**, ^1H 1.22 (d, $CHCH_3$, $^3J_{HH}$ = 6 Hz), ^{13}C 288.3 (t, CS_2), 172.7 (C=O), 80.1 ($CHCH_3$), 59.1 (CHS), 33.2 (CH_2), 18.9 (CH_3). The *trans* configuration has been assigned to the major isomer in agreement with the nature of the major adduct[10] of thiols with **7**.

[10] Ducher, S.; Michet, A. *Bull. Soc. Chim. Fr.* **1973**, 1037.

[11] Data for complex **11**: mp 118–121 °C. IR (Nujol) 2038, 1970, 1715 cm^{-1}; ^1H NMR (CD_2Cl_2, 100 mHz) δ 4.58 ($C{=}CH_2$), 4.28 (SCH), 1.52 (s, $CH_3C{=}C$), 0.62 (d, CH_3CH, $^3J_{HH}$ = 5.8 Hz). Anal. Calcd: C, 61.89; H, 4.74; Fe, 5.89; P, 6.53. Found: C, 61.35; H, 4.73; Fe, 5.39; P, 6.03.

[12] Barieux, J. J.; Gore, J.; Richer, J. C. *Bull. Soc. Chim. Fr.* **1974**, 1020.

[13] (a) Chamberlain, P.; Whitman, G. H. *J. Chem. Soc., Perkin Trans. 2* **1972**, 130. (b) Allinger, N. L.; Riew, C. K. *Tetrahedron Lett.* **1966**, 1269.

Reinvestigations of Some Reactions of Metal Carbonyl Anions with Cyclopropenium Cations. Conversion of η^3-Cyclopropenyl to η^3-Oxocyclobutenyl Ligands

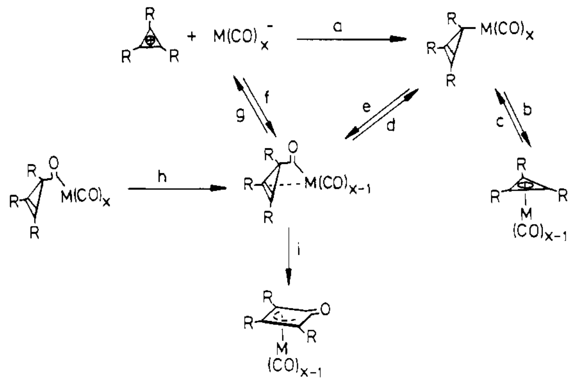
Russell P. Hughes,*[1a] James M. J. Lambert, John W. Reisch, and Wayne L. Smith[1b]

Department of Chemistry, Dartmouth College
Hanover, New Hampshire 03755

Received June 15, 1982

Summary: Contrary to some previous reports, cyclopropenium cations react with metal carbonyl anions to give both η^3-cyclopropenyl and η^3-oxocyclobutenyl complexes. External ligand induced conversions of η^3-cyclopropenyl to η^3-oxocyclobutenyl skeletons are also reported.

Scheme I



Curiously, there are no reported examples of the reaction of a cyclopropenium cation with a metal carbonyl *anion* to yield a (η^3-cyclopropenyl)metal compound, although a number of such compounds have been prepared by oxidative addition pathways involving *neutral* metal precursors.[2-8] As shown in Scheme I reactions of cyclopropenium cations with metal carbonyl anions can evolve along a variety of paths which we and others are attempting to define. Path a has been characterized for a single system; reaction of $[C_3Ph_3]^+$ with $[Fe(CO)_2(\eta\text{-}C_5H_5)]^-$ affords crystallographically characterized $[Fe(CO)_2(3\text{-}\eta^1\text{-}C_3Ph_3)(\eta\text{-}C_5H_5)]$, but this compound is resistant to decarbonylation (path b) to yield the corresponding η^3-cyclopropenyl compound or to thermal ring expansion (path e, i) to afford an oxocyclobutenyl ligand.[9,10] We have previously reported that substituted (3-η^1-cyclopropenyl)pentacarbonylrhenium compounds could be prepared by a synthetic sequence involving paths h and d and that path d proceeded with an unprecedented allylic rearrangement of the migrating cyclopropenyl group; no evidence for reverse cyclopropenyl migration (path e) or decarbonylation (path b) was observed in this system.[11,12] Finally an extensive study of the reactions of $[Co(CO)_4]^-$ with cyclopropenium cations has provided evidence for a surprising reaction pathway involving an apparent direct

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[1] (a) Alfred P. Sloan Research Fellow, 1980–1984. (b) On leave from Colby College, Waterville, ME 04901.

[2] Gowling, E. W.; Kettle, S. F. A. *Inorg. Chem.* **1964**, *3*, 604–605.

[3] Olander, W. K.; Brown, T. L. *J. Am. Chem. Soc.* **1972**, *94*, 2139–2140.

[4] Rausch, M. D.; Tuggle, R. M.; Weaver, D. L. *J. Am. Chem. Soc.* **1970**, *92*, 4981–4982.

[5] Chiang, T.; Kerber, R. C.; Kimball, S. D.; Lauher, J. W. *Inorg. Chem.* **1979**, *18*, 1687–1691.

[6] Hayter, R. G. *J. Organomet. Chem.* **1968**, *13*, P1–P3.

[7] Drew, M. G. B.; Brisdon, B. J.; Day, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1310–1316.

[8] Unsymmetrically η^2-bound cyclopropenyl ligands have also been reported. (a) McClure, M. D.; Weaver, D. L. *J. Organomet. Chem.* **1973**, *54*, C59–C61. (b) Mealli, C.; Midollini, S.; Moretti, S.; Sacconi, L. *Angew. Chem., Int. Ed. Engl.* **1980**, *11*, 931. (c) Mealli, C.; Midollini, S.; Moretti, S.; Sacconi, L.; Silvestre, J.; Albright, T. A. *J. Am. Chem. Soc.* **1982**, *104*, 95–107.

[9] Gompper, R.; Bartmann, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 456–457.

[10] Gompper, R.; Bartmann, E.; Noth, H. *Chem. Ber.* **1979**, *112*, 218–233.

[11] Desrosiers, P. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1981**, *103*, 5593–5594.

[12] DeSimone, D. M.; Desrosiers, P. J.; Hughes, R. P. *J. Am. Chem. Soc.* **1982**, *104*, 4842.

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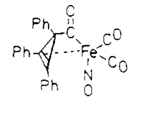
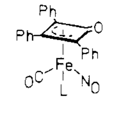
attack on coordinated CO (path f) followed by ring expansion to afford the η^3-oxocyclobutenyl ligand (path i); evidence for the dissociative path g was also defined in this system.[13] This communication reports reinvestigations of some previously reported reactions of metal carbonyl anions with cyclopropenium cations, together with some newly characterized systems; in a number of cases previous reports are shown to be incorrect or incomplete.

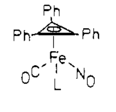
The reaction of Na[Fe(CO)$_3$NO] with [C$_3$Ph$_3$]Br in methanol was reported to afford low yields (14%) of a maroon complex for which structures **1** and **2a** were suggested; chemical oxidation of this compound to regenerate [C$_3$Ph$_3$]$^+$ was considered to indicate that the cyclopropenyl ring was still intact, thus favoring structure **1**.[14] In our hands, this same reaction (20 °C) afforded a 50% overall yield of a 1:1 mixture of orange **2a**[15] and maroon **3a**,[16] which could be separated by column chromatography. A much cleaner reaction, affording almost quantitative yields of a 1:4 ratio of **2a**/**3a**, was obtained by using PPN[Fe(CO)$_3$NO][17] and [C$_3$Ph$_3$]PF$_6$ in methanol. While **2a** and **3a** did not interconvert at 20 °C, the pure η^3-cyclopropenyl compound **3a** reacted with PPh$_3$ in refluxing benzene to yield a 1:1 mixture of **3b**,[16] the product of phosphine substitution, and the ring-expanded oxocyclobutenyl complex **2b**.[15] Similarly **3a** reacted with PMe$_2$Ph to yield a 1:1 mixture of **3c**[16] and **2c**.[15] In contrast the known cobalt complex [Co(CO)$_3$(η^3-C$_3$Ph$_3$)][5] cleanly afforded only [Co(CO)$_2$(PPh$_3$)(η^3-C$_3$Ph$_3$)][18] on thermal reaction with PPh$_3$; no ring expansion was observed.



1.

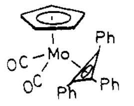


2a. L=CO
2b. L=PPh$_3$
2c. L=PMe$_2$Ph

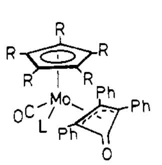


3a. L=CO
3b. L=PPh$_3$
3c. L=PMe$_2$Ph

The η^3-cyclopropenyl complex **4** was reported[6] to be formed in low overall yield (3%) from the reaction of [Mo(CO)$_3$(MeCN)$_3$] with [C$_3$Ph$_3$]Cl, followed by treatment of the known intermediate[6,7] [MoCl(CO)$_2$(MeCN)$_2$(η^3-C$_3$Ph$_3$)] with Li[C$_5$H$_5$]. We report that a one-pot reaction of [Mo(CO)$_3$(MeCN)$_3$] with [C$_3$Ph$_3$]Cl in MeCN (15 h, 70 °C), followed by replacement of the solvent by THF and treatment with Tl[C$_5$H$_5$] (20 °C), afforded **4**[19] (19%) together with the oxocyclobutenyl complex **5a**[20] (28%). A reaction sequence which maintained the first oxidative addition step at 20 °C (72 h) afforded only **4** (40%). Treatment of **4** with PMe$_2$Ph in refluxing benzene rapidly afforded only the ring-expanded product **5b**.[20] Neither **4** nor **5a** was formed in the reaction of [Mo(CO)$_3$(η-C$_5$H$_5$)]$^-$ (Na$^+$ or PPN$^+$ salt) with [C$_3$Ph$_3$]PF$_6$ (THF; −60 °C to 20 °C); only [Mo(CO)$_3$(η-C$_5$H$_5$)]$_2$ and [C$_3$Ph$_3$]$_2$ were obtained in an apparent redox reaction. Surprisingly, the reaction of Na[Mo(CO)$_3$(η-C$_5$Me$_5$)] with [C$_3$Ph$_3$]PF$_6$ under identical conditions cleanly produced **5c**[20] (86%).

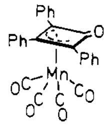


4.



5a. R=H; L=CO
5b. R=H; L=PMe$_2$Ph
5c. R=Me; L=CO

Apparently analogous redox chemistry, to give [Mn$_2$(CO)$_{10}$] and [C$_3$Ph$_3$]$_2$, has been reported in the reaction of Na[Mn(CO)$_5$] and [C$_3$Ph$_3$]BF$_4$.[3] In our hands these two products were indeed observed, but low yields (10%) of the oxocyclobutenyl complex **6**[21] could also be isolated by careful column chromatography. A somewhat higher yield route to **6** (20%) was afforded by the reaction of PPN[Mn(CO)$_5$] with [C$_3$Ph$_3$]PF$_6$ (CH$_2$Cl$_2$, CH$_3$CN, or THF; 20 °C).



6.

Formation of **3a** constitutes an example of direct formation of a η^3-cyclopropenyl complex from a metal carbonyl anion and a cyclopropenium cation. **3a** appears to possess the same physical properties as the compound originally proposed[14] to have structure **1** or **2a**. The presence of a freely rotating, intact cyclopropenyl ring is evidenced by a single ^{13}C NMR resonance for the three cyclopropenyl ring carbon atoms,[22] and it is not surprising, therefore, that oxidation of this compound affords free [C$_3$Ph$_3$]$^+$.[14] It is not clear whether **2a** and **3a** result from different initial sites of electrophilic attack on [Fe(CO)$_3$NO]$^-$ (**3a** by direct attack at the metal and **2a** by attack at CO, as observed for [Co(CO)$_4$]$^-$)[13] or whether they are formed by competitive pathways arising from a common intermediate. The effect of the cation (Na$^+$ or PPN$^+$) on

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

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

(15) **2a**: IR (hexane) ν_{CO} 2060 (sh), 2053, 2025 (sh), 2016, $\nu_{C=O}$ 1720, ν_{NO} 1798 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.5–8.3 (m, Ph); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 210.41 (CO), 164.68 (C=O), 132.31, 131.00, 128.64 (br, Ph), 100.44 (CPh), 94.84 (CPh). **2b**: IR (CH$_2$Cl$_2$) ν_{CO} 1990, $\nu_{C=O}$ 1677, ν_{NO} 1752 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.79–7.71 (m, Ph). **2c**: IR (hexane) ν_{CO} 1992, $\nu_{C=O}$ 1679, ν_{NO} 1754 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.3–8.2 (m, Ph), 1.24 (d, J_{PH} = 7.8 Hz, PMe), 1.15 (d, J_{PH} = 8.0 Hz, PMe).

(16) **3a**: IR (hexane) ν_{CO} 2033, 1992, ν_{NO} 1760 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 6.76–8.74 (m); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 213.09 (CO), 131.86, 129.21, 128.89, 128.32 (Ph), 54.95 (CPh). **3b**: IR (CH$_2$Cl$_2$) ν_{CO} 1953, ν_{NO} 1708 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.95–7.54 (m); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 221.10 (d, J_{P-C} = 2 Hz, CO), 135.34, 134.52, 133.67, 132.90, 129.41, 128.24, 127.59, 126.65 (Ph), 51.80 (d, J_{PC} = 2 Hz, CPh). **3c**: IR (hexane) ν_{CO} 1960, ν_{NO} 1719 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 6.8–7.5 (m, Ph), 1.42 (d, J_{PH} = 8.1 Hz, PMe), 1.39 (d, J_{PH} = 7.8 Hz, PMe).

(17) PPN$^+$ = bis(triphenylphosphin)iminium. A facile synthesis of PPN(Fe(CO)$_3$NO] is described by: Stevens, R. E.; Yanta, T. J.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 4981–4982.

(18) IR (hexane): ν_{CO} 2001, 1954 cm^{-1}.

(19) **4**: IR (CH$_2$Cl$_2$) ν_{CO} 1961, 1901 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.30 (m, Ph), 5.00 (s, C$_5$H$_5$); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 229.53 (CO), 135.38, 128.89, 128.29, 126.24 (Ph), 90.33 (C$_5$H$_5$), 34.01 (CPh).

(20) **5a**: IR (CH$_2$Cl$_2$) ν_{CO} 2001, 1945; $\nu_{C=O}$ 1677 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.36 (m, Ph), 5.20 (s, C$_5$H$_5$); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 227.78 (CO), 168.33 (C=O), 135.54, 132.53, 131.00, 128.52, 127.99, 125.84 (Ph), 95.20 (C$_5$H$_5$), 89.36 (CPh), 70.12 (CPh). **5b**: IR (CH$_2$Cl$_2$) ν_{CO} 1896, $\nu_{C=O}$ 1651 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.1–7.9 (m, Ph), 4.72 (d, J_{PH} = 1.8 Hz, C$_5$H$_5$), 1.57 (d, J_{PH} = 8.5 Hz, PMe), 0.97 (d, J_{PH} = 8.5 Hz, PMe). **5c**: IR (CHCl$_3$) ν_{CO} 1987, 1928, $\nu_{C=O}$ 1644 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.0–7.4 (m, Ph), 1.77 (s, C$_5$Me$_5$); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 231.5 (CO), 167.9 (C=O), 135.1, 134.0, 131.2, 127.5, 126.3, 125.2 (Ph), 103.2 (C_5Me$_5$), 88.3 (CPh), 68.4 (CPh), 8.7 (C$_5$$Me_5$).

(21) **6**: IR (hexane) ν_{CO} 2070, 2017, 1985, 1972 cm^{-1}; ^{1}H NMR (CDCl$_3$) 7.0–7.94 (m, Ph); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 216.87 (CO), 169.74 (C=O), 131.76, 130.14, 129.21, 128.52, 128.19, 127.95, 127.71, 127.50 (Ph), 124.78 (CPh), 116.39 (CPh).

(22) Also observed in **2b**,[16] **3c**,[16] and **4**.[19] Theoretical calculations put the barrier to rotation about the metal–ring axis in the isoelectronic [Fe(CO)$_3$(η-C$_3$H$_3$)]$^-$ at ca. 6–7 kcal·mol^{-1}.[23]

(23) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546–7557.

(24) A similar thermal conversion of a η^3-cyclopropenyl to η^3-oxocyclobutenyl ligand is implicit in the results reported in ref 7.

both yields and product ratios is interesting[25] and is under further investigation.

That a η^3-cyclopropenyl ligand can serve as a direct precursor to a η^3-oxocyclobutenyl ligand is evidenced by the phosphine-promoted conversion of **2a** to **2b** and **3b** (or **2c** and **3c**) and by transformation of **4** to **5b**. These reactions are presumably initiated by pathway c (Scheme I) followed by competition between path b or a sequence of paths e and i; in the case of the iron compounds, both pathways are competitive, for molybdenum the ring expansion route dominates, whereas for cobalt no ring expansion occurs. A similar thermal conversion of a η^3-cyclopropenyl to a η^3-oxocyclobutenyl ligand on molybdenum is evidenced by formation of only **4** under mild conditions, but a mixture of **4** and **5a** under more vigorous thermal conditions.[24] The reasons for the different reactivities of the anions $[Mo(CO)_3(\eta\text{-}C_5R_5)]^-$ (R = H, Me) toward $[C_3Ph_3]^+$ are unclear; notably $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$ has been shown previously to react with $[C_3\text{-}t\text{-}Bu_3]^+$ via attack at the cyclopentadienyl ring.[27]

Once again, it cannot be distinguished whether the manganese compound **6** arises via direct attack at Mn (path a, e, i) or by attack at CO (path f, i). Whichever path is followed, formation of **6** demonstrates a notable difference between Mn and Re chemistry; the (2-cyclopropene-1-carbonyl)rhenium system undergoes exclusive cyclopropenyl migration to Re (path d), with no observable ring expansion (path i), and (3-η^1-cyclopropenyl)rhenium complexes show no tendency to form oxocyclobutenyl compounds (path e, i).[11,12]

Reactions of metal carbonyl anions with cyclopropenium cations clearly proceed via an array of reaction pathways, but the underlying reasons for choice of reaction path are still obscure. Nevertheless, under suitable conditions these reactions can provide good synthetic routes to oxocyclobutenyl compounds, which are useful precursors to cationic cyclobutadiene compounds[28,29] and to new η^1- and η^3-cyclopropenyl compounds, whose chemistry is currently under continuing investigation.

Acknowledgment. We are grateful to the National Science Foundation (Grants CHE 7717877 and CHE 8022854) and the Alfred P. Sloan Foundation for support of this research. Helpful discussions with Dr. Neil G. Connelly (Bristol University) are also acknowledged with gratitude.

Registry No. 2a, 82661-39-0; **2b**, 82661-40-3; **2c**, 82661-41-4; **3a**, 82661-42-5; **3b**, 82661-43-6; **3c**, 82661-44-7; **4**, 82661-45-8; **5a**, 82661-46-9; **5b**, 82661-47-0; **5c**, 82665-10-9; **6**, 82661-48-1; $Na[Fe(CO)_3NO]$, 25875-18-7; $[C_3Ph_3]Br$, 4919-51-1; $Mo(CO)_3(MeCN)_3$, 15038-48-9; $[C_3Ph_3]Cl$, 82661-38-9; $[Mo(CO)_3(\eta\text{-}C_5H_5)]Na$, 12107-35-6; $[Mo(CO)_3(\eta\text{-}C_5H_5)]PPN$, 67486-18-4; $[C_3Ph_3]PF_6$, 82661-49-2; $[Mo(CO)_3(\eta\text{-}C_5H_5)]_2$, 12091-64-4; $[C_3Ph_3]_2$, 4997-62-0; $Na[Mo(CO)_3(\eta\text{-}C_5Me_5)]$, 82661-50-5; $Na[Mn(CO)_5]$, 13859-41-1; $[C_3Ph_3]BF_4$, 741-16-2; $PPN[Mn(CO)_5]$, 52542-59-3.

Supplementary Material Available: Table of microanalysis data for **2a–c**, **3a–c**, **5a–c**, and **6** (1 page). Ordering information is given on any current masthead page.

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[25] The nature of the cation is known to affect the IR spectroscopic properties of metal carbonyl anions and can also affect the rates of some of their reactions. The rate of the CO migratory insertion reaction can also be influenced by the nature of cations present in solution.[26]

[26] See: Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982,** *104,* 1521–1530 and references cited therein.

[27] Green, M.; Hughes, R. P. *J. Chem. Soc., Chem. Commun.* **1975,** 862–863.

[28] Donaldson, W. A.; Hughes, R. P.; Davis, R. E.; Gadol, S. M. *Organometallics* **1982,** *1,* 812–819.

[29] Hughes, R. P.; Reisch, J. W., manuscript in preparation.

New Syntheses of Mixed-Metal Clusters from $H_2Os_3(CO)_{10}$. Crystal and Molecular Structure of the Paramagnetic Cluster $H_3(\eta^5\text{-}C_5H_5)CoOs_3(CO)_9$ and Its Diamagnetic Structural Analogue $H_3(\eta^5\text{-}C_5H_5)NiOs_3(CO)_9$

Sheldon G. Shore,* Wen-Liang Hsu,
Clemens R. Weisenberger, and Maureen L. Caste

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Melvyn Rowen Churchill* and Clifford Bueno

Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214

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Summary: Reactions of $H_2Os_3(CO)_{10}$ with metal carbonyls in the presence of H_2 and also in the absence of H_2 provide convenient routes to a number of new mixed-metal clusters and improved yields of some previously reported clusters. The X-ray structure determination of the paramagnetic cluster $H_3(\eta^5\text{-}C_5H_5)CoOs_3(CO)_9$ and its diamagnetic structural analogue $H_3(\eta^5\text{-}C_5H_5)NiOs_3(CO)_9$ is reported.

An earlier report[1] from this laboratory suggested a relatively simple approach to the preparation of mixed-metal systems containing a triosmium unit and is based upon the use of the electronically unsaturated cluster $H_2Os_3(CO)_{10}$ as a starting material. A simple high-yield preparation of $H_2FeOs_3(CO)_{13}$ and a good yield preparation of $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$ were reported. More recently we have found that when the latter reaction is conducted in the presence of molecular hydrogen, the yield of $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$ is greatly diminished but two additional products are formed.

$$(\eta^5\text{-}C_5H_5)Co(CO)_2 + H_2Os_3(CO)_{10} + H_2 \xrightarrow[90°\text{ C, 53 h}]{\text{toluene}} \underset{4\%}{H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}} + \underset{33\%}{H_3(\eta^5\text{-}C_5H_5)CoOs_3(CO)_9} + \underset{32\%}{H_4(\eta^5\text{-}C_5H_5)CoOs_3(CO)_9} \tag{1}$$

The conditions chosen for reaction 1 permit formation of significant yields of $H_3(\eta^5\text{-}C_5H_5)CoOs_3(CO)_9$. However, this compound will react with H_2 to convert to $H_4(\eta^5\text{-}C_5H_5)CoOs_3(CO)_9$. Thus after a prolonged period of time the principal product from reaction 1 is $H_4(\eta^5\text{-}C_5H_5)CoOs_3(CO)_9$. On the other hand, the conversion of $H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}$ to the other clusters in the presence of H_2 at 1 atm is not favorable.[2]

$$\underset{30\%\text{ consumed}}{H_2(\eta^5\text{-}C_5H_5)CoOs_3(CO)_{10}} + H_2 \xrightarrow[90\text{ °C, 3 days}]{\text{toluene}} \underset{7\%}{H_3(\eta^5\text{-}C_5H_5)CoOs_3(CO)_9} + \underset{23\%}{H_4(\eta^5\text{-}C_5H_5)CoOs_3(CO)_9} \tag{2}$$

It is possible that in reaction 1 H_2 is assisting in CO displacement from the reactants and that the primary path of the reaction does not proceed through $H_2(\eta^5\text{-}C_5H_5)$-

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[1] Plotkin, J. S.; Alway, D. G.; Weisenberger, C. R.; Shore, S. G. *J. Am. Chem. Soc.* **1980,** *102,* 6157.

[2] This result contrasts with the earlier observation that most of $H_2FeRu_3(CO)_{13}$ (82%) is converted to $H_4FeRu_3(CO)_{12}$ in the presence of H_2. See: Koepke, J. W.; Johnson, J. R.; Knox, S. A. R.; Kaesz, H. D. *Ibid.* **1975,** *97,* 3947.

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