law expressed in eq 7. The k_1/k_{-1} ratios are equivalent to

$$-d[M_x(CO)_y]/dt = (k_1[OR^-] + k_{-1})[M_x(CO)_y] \quad (7)$$

the equilibrium constants for adduct formation determined from spectral changes as seen in Figure 1. The relevant rate data are summarized in Table I along with similar data obtained earlier[4] for $Fe(CO)_5$.

The three substrates $Ru_3(CO)_{12}$, $Fe_3(CO)_{12}$, and $Ru(CO)_5$ are all remarkably reactive toward each of the oxygen nucleophiles (OH^- being the more reactive) especially in comparison to $Fe(CO)_5$.[11] Given that adduct formation is faster for $Ru(CO)_5$ than for $Ru_3(CO)_{12}$, the cluster apparently provides no special advantage over the monomer in accomodating the developing negative charge in the reaction transition state. Preliminary kinetics studies in this laboratory on the reactions of osmium carbonyls with methoxide confirm this with $Os(CO)_5$ being considerably more reactive than $Os_3(CO)_{12}$. Furthermore under comparable conditions, the mononuclear complexes follow the order $Os(CO)_5 > Ru(CO)_5 \gg Fe(CO)_5$ while the trinuclear complexes follow the order $Fe_3(CO)_{12} > Ru_3(CO)_{12} > Os_3(CO)_{12}$. The failure of a cluster effect to be evidenced for the heavier metals accentuates the dramatic reversal of form for the iron carbonyls. One possible rationale for the surprising high reactivity of the triiron complex is that the presence of the bridging carbonyls (which are a structural feature of $Fe_3(CO)_{12}$[12] but not of $Ru_3(CO)_{12}$) raises the reactivity of this species from that of $Fe(CO)_5$ to give rates fortuitously comparable to the ruthenium species.

The observation that $Ru(CO)_5$ is orders of magnitude more reactive than $Fe(CO)_5$ toward the formation of hydroxycarbonyl adducts provides an important clue in explaining a startling observation regarding homogeneous catalysis of the water-gas shift reaction. Under high CO pressures (>25 atm) and at 125 °C, very low concentrations of ruthenium carbonyl ($<10^{-4}$ M) aqueous trimethylamine solutions are reported to display extraordinarily high catalytic activities for H_2 production via the WGSR.[13] Under these conditions the ruthenium species are proposed to be largely mononuclear. Under similar conditions, catalysts prepared from $Fe(CO)_5$ in aqueous trimethylamine solutions are nearly 4 orders of magnitude less active.[2d] Mechanistic studies of the WGSR catalysis by $Fe(CO)_5$ in alkaline alcohol solutions have identified the reaction of base with $Fe(CO)_5$ as the rate-limiting step of the catalysis cycle.[4,14] In the context of this mechanism, the much greater susceptibility of $Ru(CO)_5$ to hydroxide attack would explain the extraordinary activity of the mononuclear ruthenium catalyst.

In summary, these studies provide important insight in interpreting the roles of nucleophilic activation in the metal carbonyl catalysis of two different reactions[2,3d] involving carbon monoxide as a reductant. Continuing studies are directed toward further evaluation of the roles played by mononuclear and polynuclear metal centers in activating CO toward various nucleophiles and toward a more complete elucidation of the reaction mechanisms of these and subsequent reactions.

(11) The rates of $Fe(CO)_5$ plus CH_3O^- reactions have been qualitatively confirmed by independent studies in this laboratory. Notably all these systems including $Fe(CO)_5$ are many orders of magnitude more reactive with OH^- than is free CO, which reacts slowly with aqueous base at elevated temperatures (Iwata, M. *Chem. Abstr.* **1969**, *70*, 6989v).

(12) Dahl, L. F.; Blount, J. F. *Inorg. Chem.* **1965**, *4*, 1373–5.

(13) (a) Sleigar, W. A. R.; Sapienza, R. S.; Easterling, B. *ACS Symp. Ser.* **1981**, *No. 152*, 325–44. (b) Reported initially by R. Pettit, T. Cole, W. Slegier, K. Cann, and C. Summer at the Symposium on the Production and Conservation of Energy: Catalysis, 178th National Meeting of the American Chemical Society, Washington, DC, Sept 1979.

(14) King, A. D.; King, R. B.; Young, D. B. *J. Am. Chem. Soc.* **1980**, *102*, 1028–32.

Ruthenium used in these studies was provided on loan by Johnson-Matthey Inc. Dr. Haim Cohen, formerly of these laboratories, carried out preliminary rate measurements of the $Ru_3(CO)_{12}$ system.

Department of Chemistry   **David C. Gross**
University of California   **Peter C. Ford***
Santa Barbara, California 93106

Stepwise Formation of Triosmium Edge Double-Bridged μ-H,μ-O=C(Nu) Decacarbonyl Complexes, Nu = NRR', OR, or R. Reversal of Barrier Heights in the Fluxional Behavior of the Anions [Ru₃(μ-O=CNMe₂)(μ-CO)₃(CO)₇]⁻ and [Os₃(μ-O=CNMe₂)(CO)₁₀]⁻

Sir:

We wish to report studies on the reaction of nucleophiles with $Os_3(CO)_{12}$ (**1**)[1] and $Ru_3(CO)_{12}$[1a,2] at room temperature and below, which we believe play an important role in the transformations of carbon monoxide at these polynuclear metal centers.[3] The system studied initially is that using primary or secondary amines with **1**. Our observations and the experimental conditions employed are summarized in Scheme I. The ionic intermediates shown in this scheme were identified through spectroscopic studies described as follows.

When **1** is treated at 0 °C with $LiNMe_2$, it is initially converted to a salt of the anion [**2a**]⁻. When the solution warms to room temperature, carbon monoxide is evolved from [**2a**]⁻, forming [**3a**]⁻ quantitatively within about 1 h. Loss of the carbonyl group is accompanied by the transformation of the η^1-carboxamido ligand into the μ form.

Spectroscopic data in accord with these structural assignments were determined for the [PPN]⁺ salts[4] of [**2a**]⁻ and [**3a**]⁻. In [PPN][**2a**] a strong IR absorption is seen at 1549 cm⁻¹ (THF solution),[5] which may be attributed to the $\nu(C=O)$ absorption of the η^1-C(O)NMe₂ group. Coordination of the oxygen atom to the metal center causes this absorption to shift to 1503 cm⁻¹ in [PPN][**3a**] (CH_2Cl_2 solution).[6] The ^1H NMR spectrum of [PPN][**2a**] shows a singlet for the dimethylamino group that is temperature dependent (δ (THF-d_8) 3.36 at −40 °C and 2.62 at 35 °C). The spectrum of [PPN][**3a**] shows two separate singlets that are temperature independent (δ (THF-d_8) 3.08, 2.69). Coordination of the acyl oxygen and restricted rotation at the C–NMe₂ bond are re-

(1) (a) Kaesz, H. D.; Szostak, R.; Lin, Y. C.; van Buskirk, G.; Humphries, A. P. "Abstracts of Papers", American Chemical Society/Chemical Society of Japan Chemical Congress, Honolulu, HI, April 1979; American Chemical Society: Washington, D.C., 1979, INOR 174. (b) Lin, Y. C. Ph.D. Dissertation, University of California, Los Angeles, 1981. Kaesz, H. D.; Lin, Y. C., manuscripts in preparation.

(2) Szostak, R.; Strouse, C. E.; Kaesz, H. D. *J. Organomet. Chem.* **1980**, *191*, 243.

(3) (a) Keim, W.; Berger, M.; Schlupp, J. *J. Catal.* **1980**, *61*, 359. (b) Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959. (c) Dombek, B. D. *Ibid.* **1981**, *103*, 6508.

(4) (a) [PPN][Cl] = bis(triphenylphosphine)iminium chloride; Alfa Division, Ventron, Danvers, MA 01923. The Chemical Abstracts recommended name for [PPN]⁺ is bis(triphenylphosphoranediyl)nitrogen(1+). (b) A solution of the [PPN]⁺ salt is prepared by adding an equivalent amount of $NaOCH_3/HOCH_3$ at 0 °C to a solution of **1** in $HNMe_2$/THF (1:3) followed by adding a slight excess of [PPN][Cl]. The solvent is removed, the residue is redissolved at 0 °C in THF, and the resulting solution is filtered.

(5) Carbonyl absorptions for [PPN][**2a**] (cm⁻¹): 2087 w, 2026 s, 2008 m, 1993 vs, 1959 m.

(6) Carbonyl absorptions for [PPN][**3a**] (there is a systematic shift of the carbonyl absorptions to lower energy) (cm⁻¹): 2063 w, 2006 s, 1990 s, 1971, 1937 m, 1925 m.

Scheme I
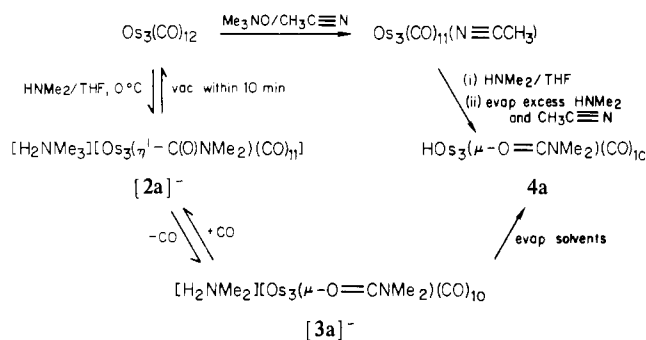
sponsible for the appearance of two separate signals for the dimethylamino group, as observed in the neutral product **4a**.[1] The neutral complex **4a** is obtained in high yield by protonation of [PPN][**3a**] with CF_3SO_3H/Et_2O; **4a** is also obtained in the reaction of $Os_3(CO)_{11}(N\equiv CCH_3)$ with Me_2NH as shown in Scheme I.[7]

In the reaction of **1** with $MeLi/Et_2O$ an analogous sequence of intermediate anions $[Os_3[\eta^1-C(O)Me](CO)_{11}]^-$ ([**2b**]$^-$) and $[Os_3[\mu-O\!=\!C(Me)](CO)_{10}]^-$ ([**3b**]$^-$) is obtained.[8] Acidification of the latter gives $HOs_3[\mu-O\!=\!C(Me)](CO)_{10}$ (**4b**) in 50% yield.[9] The lithium salt of [**2b**]$^-$ exists as a tight ion pair; its acyl IR absorption at 1546 cm^{-1} is seen to shift to 1609 cm^{-1} upon the addition of "Kryptofix-221".[10] The transformation of [Li][**2b**] to [Li][**3b**] requires 30 h, which is accelerated to 10 h upon the addition of the cryptate. Ion pairing in [Li][**2b**] thus retards loss of the carbonyl group.

In the reaction with alkoxides dissolved in their corresponding alcohol as solvent, **1** is instantaneously and completely converted to the anionic complex [**2c**]$^-$; this intermediate must be stabilized by addition of [PPN][Cl][4a] or "Kryptofix 221".[10,11a,b] The stabilized anion [**2c**]$^-$ is observed over a 3-h period to convert partially into the two new anions [**3**]$^-$ and [**5**]$^-$. The stoichiometry of these anions is established from that of the products obtained by neutralization. Protonation of the anion mixture with CF_3SO_3H in Et_2O gives the new complex $HOs_3[\mu-O\!=\!C(OR)](CO)_{10}$ (**4c**)[12] and the known

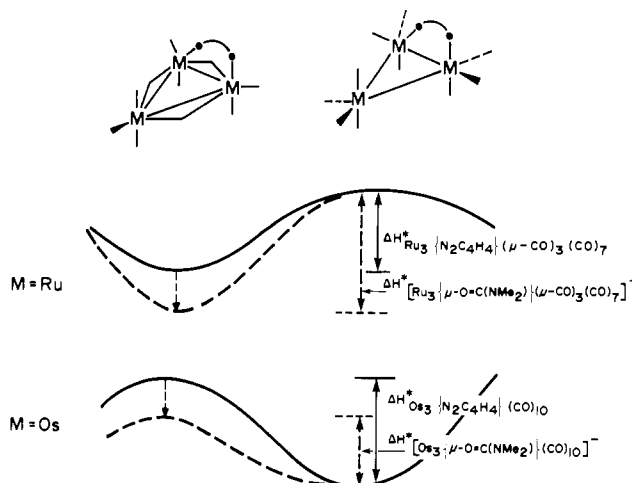**Figure 1.** Schematic representation of the enthalpies of activation for the neutral diazene complexes $Ru_3(N_2C_4H_4)(\mu\text{-}CO)_3(CO)_7$[21] and $Os_3(N_2C_4H_4)(CO)_{10}$[22] with those of the isoelectronic and isostructural anions $[Ru_3[\mu-O\!=\!C(NMe_2)](\mu\text{-}CO)_3(CO)_7]^-$ and $[Os_3[\mu-O\!=\!C-(NMe_2)](CO)_{10}]^-$ isolated in this work.

$HOs_3[\mu-(OR)](CO)_{10}$ (**5**)[13] each in about 10% yield; starting material is recovered in 80% yield.[12a] Complex **4c** is an isomer of $HOs_3(\mu-O_2CR)(CO)_{10}$ obtained in the reaction of **1** with acetic acid.[14]

The remarkably low temperatures at which a CO group is evolved from the η^1-C(O)Nu complexes, transforming these into the bridged μ-O$=$C(Nu) derivatives, indicate some labilization of either geminal or vicinal CO groups in the former (usually temperatures around 100 °C or more are required to obtain evolution of CO from trinuclear cluster complexes of osmium). The labilization is reminiscent of base catalysis in the substitution of mononuclear complexes observed earlier by Basolo and Morris.[15] If geminal, this would be analogous to the cis labilization observed in the substitution of acyl complexes by Brown and Bellus[16] and surely is also related to the labilization of CO groups in formate complexes.[17] Labilization of the type we have observed here must also be responsible for the decomposition of intermediate η^1-formyl derivatives observed in the low-temperature reaction of hydride with $Os_3(CO)_{12}$.[18]

Reaction of $Ru_3(CO)_{12}$ with $C(NMe_2)_4$[19] gives the [C-$(NMe_2)_3]^+$ salt of $[Ru_3[\mu-O\!=\!C(NMe_2)](CO)_{10}]^-$ ([**6**]$^-$) in high yield. In the carbonyl-stretching region of the infrared,[20]

(7) (a) Shapley, J. R.; Pearson, G. A.; Tachikawa, M.; Schmidt, G. E.; Churchill, M. R.; Hollander, F. J. *J. Am. Chem. Soc.* **1977**, *99*, 8064. (b) A high-yield synthesis of carboxamido complexes has recently been reported in the reaction of amides with $Os_3(CO)_{10}(N\equiv CCH_3)_2$ (refluxing nonane, 40 h): Johnson, B. F. G.; Lewis, J.; Odiaka, T. I.; Raithby, P. R. *J. Organomet. Chem.* **1981**, *216*, C56.

(8) The following IR absorptions in C_2Cl_4 (cm^{-1}) are observed. For [Li][**2b**]: ν(CO) 2094 w, 2034 s, 2017 m, 2001 vs, 1966 m; ν(C$=$O) 1564 w. For the [Li-cryptate]$^+$ salt: ν(CO) 2088 w, 2026 s, 2010 m, 1994 vs, 1960 m; ν(C$=$O) 1609 w. For [Li-cryptate][**3b**]: ν(CO) 2067 w, 2009 s, 1994 vs, 1978 m, 1934 m.

(9) (a) Acyl complexes of this type have been prepared in low yields by the oxidative addition at 130 °C of aldehydes to **1**, although this route does not work for acetaldehyde: Azam, K. A.; Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1981**, 91. (b) Acyl complexes are obtained in much better yields in the reaction of aldehydes with Os_3-$(CO)_{10}(N\equiv CCH_3)_2$ in refluxing cyclohexane.[7b]

(10) 4,7,13,16,21-Pentaoxa-1,10-diazabicyclo[8.8.5]tricosane, MCB Inc., Cincinnati, OH 45212.

(11) (a) In absence of the stabilizing agents, the intermediate anion [**2c**]$^-$ rapidly decomposes; we have not traced the organic products, but $Os_3(CO)_{12}$ is re-formed at close to its original concentration. (b) IR of [PPN][**2c**] (THF solution, cm^{-1}): ν(CO) 3094 vw, 2030 s, 2020 s, 1999 vs, 1963 m, 1950 w; ν(C$=$O) 1631 w. (c) Partitioning of the reaction into **4c** and **5** is dependent on the temperature at which intermediate anion [**2c**]$^-$ is formed. At 0 °C, treatment with nucleophile followed by acidification leads to a product mixture richer in **4c**, **4c:5** = 4:1. When this two-step sequence is carried out at 40 °C, the product isolated is exclusively **5**. The temperature affects principally the partitioning of the intermediate anion [**2c**]$^-$ into [**3c**]$^-$ and [$Os_3[\mu$-(OR)](CO)$_{10}]^-$ ([**5**]$^-$). Once formed, however, the anion [**3c**]$^-$ is stable in the absence of CO: if the mixture of the two anions [**3c**]$^-$ and [**5**]$^-$ formed at room temperature is warmed to 40 °C for 2 h and then returned to room temperature, the yield of **4c** upon acidification is unchanged from that obtained in the sequence carried out exclusively at room temperature.

(12) (a) These products are separated by chromatography on silica gel (Merck 600) with hexane as eluant. (a) The following spectroscopic data are observed for **4c**. IR (cm^{-1}): ν(CO) (hexane) 2111 w, 2073 vs, 2060 s, 2029 vs, 2013 s, 2006, 1988 w, 1985 w, 1985 m; ν(C$=$O) (C$_2$Cl$_4$) 1482; ν(C$-$O) (KBr) 1222, 1168. ^{1}H NMR (CDCl$_3$): δ 3.66 (CH$_3$), -14.05 (Os$-$H$-$Os). Mass spectrum: M$^+$, multiplet centered around m/e 911.

(13) Johnson, B. F. G.; Lewis, J.; Kilty, P. A. *J. Chem. Soc. A* **1968**, 2859.

(14) Crooks, G. R.; Johnson, B. F. G.; Lewis, J.; Williams, I. G.; Gamlen, G. *J. Chem. Soc. A* **1969**, 2761.

(15) Basolo, F.; Morris, D. E. *J. Am. Chem. Soc.* **1968**, *90*, 2536.

(16) Brown, T. L.; Bellus, P. A. *Inorg. Chem.* **1978**, *17*, 3726.

(17) Darensbourg, D. J.; Fischer, M. B.; Schmidt, R. E., Jr.; Baldwin, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 1297.

(18) (a) Pruett, R. L.; Schoening, R. C.; Vidal, J. L.; Fiato, R. A. *J. Organomet. Chem.* **1979**, *182*, C57. (b) Use of a different complex hydride for the initial nucleophilic attack followed by acidification leads to isolation of $Os_3[\mu$-CH$_2$,μ-(CO)](CO)$_{10}$; see: Steinmetz, G. R.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1981**, *103*, 1278.

(19) (a) Weingarten, H.; White, H. *J. Am. Chem. Soc.* **1966**, *88*, 2885. (b) The use of $C(NMe_2)_4$ for the formation of the η^1-carboxamido group has previously been reported for mononuclear complexes by: Petz, W. *J. Organomet. Chem.* **1975**, *90*, 223. Reactions leading to heterotrimetallic complexes have been reported by: Petz, W.; Kruger, C.; Goddard, R. *Chem. Ber.* **1979**, *112*, 3413.

(20) Absorptions for [C(NMe$_2$)$_3$][**6**] in the carbonyl stretching region (THF, cm^{-1}): ν(CO) 2060 w, 2008 s, 1986 s, 1974 s, 1946 sh, 1932 m; ν(C$-$O) 1813 sh, 1796 m; ν(C$=$N) in [C(NMe$_2$)$_3$]$^+$ 1601 m, 1577 w.

this salt exhibits a medium to strong band at 1796 cm^{-1} (with a shoulder at 1813 cm^{-1}). This indicates bridging carbonyl groups not observed in the salt of the osmium analogue [C-(NMe$_2$)$_3$][3a], whose carbonyl absorptions are essentially the same as those seen for the [PPN]$^+$ salt.[5b] A structural similarity is thus indicated with the 1,2-diazene complexes M$_3$-(C$_4$H$_4$N$_2$)(CO)$_{10}$, M = Ru[21] or Os[22] (see Figure 1), which are isoelectronic with the μ-O=C(NMe$_2$)-substituted anions; the structure of Ru$_3$(C$_4$H$_4$N$_2$)(CO)$_{10}$ has been determined by X-ray diffraction.[21] Fluxional behavior is observed for each of the anions as also noted for the 1,2-diazene complexes but with a significant difference as explained below. For [C-(NMe$_2$)$_3$][6] in THF a limiting spectrum is seen in the ^{13}C NMR[23a] at -95 °C with three peaks at 262.7, 257.6, and 246.1 ppm, confirming the presence of three carbonyl bridging groups.[23b] Coalescence of these resonances with those of the terminally bonded carbonyl groups occurs by various stages and is still not complete at +65 °C. By contrast, the osmium analogue [C(NMe$_2$)$_3$][3a] does not yield a limiting spectrum at -95 °C and shows averaging among all ten carbonyl groups at +26 °C.

The barrier for averaging of the carbonyl groups in the triosmium complex is thus *lower* than it is in the homologous triruthenium anion, a *reversal* in the relative barrier heights usually observed between cluster complexes of these two metals.[24] This is illustrated schematically in Figure 1. For the triruthenium anion, the ground state is known to be the bridged form, while for the triosmium anion the ground state is the all-terminal structure. The fluxional processes in these species are of course more complicated than can be represented by a single energy profile. We have simplified the diagram to make a point.

For neutral derivatives such as the 1,2-diazene complexes, the barrier height for tautomerism is higher in the triosmium cluster than in the triruthenium analogue. This is represented by the labeled vertical solid arrows in Figure 1. In the anions, the greater charge-carrying ability of the bridging carbonyls causes a stabilization of the bridged structure, represented by the dotted reaction coordinates falling at lower energy for the two bridged forms. The barrier toward the overall fluxional process is *increased* in the triruthenium anion but *decreased* in the triosmium anion relative to those in the corresponding neutral diazene complexes. This results in a *reversal* of the usual relationships between barriers to exchange in the complexes of these two metals, as represented by the vertical dashed double-arrows in Figure 1.

(21) Cotton, F. A.; Hanson, B. E.; Jamerson, J. D. *J. Am. Chem. Soc.* **1977,** *99,* 6588.
(22) Cotton, F. A.; Hanson, B. E. *Inorg. Chem.* **1977,** *16,* 2820.
(23) (a) JEOL FX90Q F-T NMR spectrometer, ^{13}C with Cr(acac)$_3$ added as a paramagnetic relaxation agent, at 22.50 MHz relative to Me$_4$Si. (b) ^{13}C NMR for [C(NMe$_2$)$_3$][6]: at -95 °C, 262.7 (1 CO), 257.6 (1 CO), 246.1 (1 CO), 211.4 (1 CO), 210.6 [O=CN(CH$_3$)$_2$], 209.1 (1 CO), 206.0 (1 + 1 CO), 204.3 (1 + 1 CO), 202.7 (1 CO) ppm; at +65 °C, 220.7 (9 CO), 212.7 [O=CN(CH$_3$)$_2$], 211.2 (1 CO) ppm; for spectra at both temperatures 164.4 [C(NMe$_2$)$_3$], 41.0 (CH$_3$), 40.4 [C(NMe_2)$_3$], 33.6 (CH$_3$). (c) ^{13}C NMR for [C(NMe$_2$)$_3$][3a]: at -95 °C, 192.7 (1 CO), 190.5 (1 CO), 189.8 (1 CO), 189.0 [O=CN(CH$_3$)$_2$], 188.0 and 185.0 (both broad, 7 CO) ppm; at +26 °C, 190.6 [O=CN-(CH$_3$)$_2$], 187.2 (10 CO); for spectra at both temperatures 164.2 [C-(NMe$_2$)$_3$], 41.3 (CH$_3$), 40.2 [C(NMe_2)$_3$], 33.9 (CH$_3$).
(24) A similar situation exists for the anions [M$_3$(μ-H,μ-CO)(CO)$_{10}$]$^-$, where the range from a single resonance to a limiting spectrum is -50 to -105 °C for M = Os, but $+32$ to -115 °C for M = Ru. Cf. respectively: Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C. *J. Chem. Soc., Dalton Trans.* **1978,** 1358. Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Süss, G. *Ibid.* **1979,** 1356.

from the UCLA Academic Computing Center.

Department of Chemistry   **A. Mayr**
University of California   **Y. C. Lin**
Los Angeles, California 90024   **N. M. Boag**
                                               H. D. Kaesz*

Synthesis of Edge Double-Bridged Ru$_3$(μ-H,μ-X)(CO)$_{10}$, X = O=C(Me), Cl, Br, I, and of Ru$_3$(μ-H,μ_3-I)(CO)$_9$: A New Series of Reactive Complexes for Triruthenium Cluster Chemistry. Crystal and Molecular Structure of Ru$_3$(μ-H,μ-Br)(CO)$_{10}$

Sir:

Recent studies of the stepwise formation of edge double-bridged trinuclear cluster complexes[1] led us to the synthesis of the new acyl derivative Ru$_3$[μ-H,μ-O=C(Me)](CO)$_{10}$ (1).[2,3] In this work we consistently observed a minor product that eluted, together with unreacted Ru$_3$(CO)$_{12}$, ahead of the main product. Trial and error led us to a procedure in which the yield of the minor product was optimized to 30%,[4,5] sufficient

(1) Mayr, A.; Lin, Y. C.; Boag, N. M.; Kaesz, H. D. *Inorg. Chem.*, companion paper in this issue.
(2) (a) Ru$_3$(CO)$_{12}$ in THF at -30 °C is treated with MeLi stabilized with ca. 22.5% LiBr (1.5 M in diethyl ether, Alfa Products, Thiokol/Ventron Division). IR spectra in a cell precooled to -50 °C under a dry-dinitrogen atmosphere indicate an anionic η^1-C(O)Me complex, identified by the characteristic carbonyl stretch at 1575 cm^{-1}; the other bands in the carbonyl stretching region are at 2080 w, 2061 w, 2012 vs, 1990 vs, and 1962 br, sh cm^{-1}. The mixture is permitted to warm to 0 °C over a 15-min period and stirred for an additional 1 h. The reaction is acidified with CF$_3$SO$_3$H (dropwise) and the solvent removed under oil pump vacuum. Extraction of the residue was performed in hexane and elution through a silica gel column (Merck 60). (b) IR and ^{1}H NMR for 1 are given in Table I. ^{13}C NMR (relative to internal Me$_4$Si, in C$_6$D$_6$/Cr(acac)$_3$): O=CMe 285.1; CO groups 206.1 (1), 205.9 (1), 200.5 (1), 200.2 (1), 195.1 (1), 194.0 (1), 190.7 (1 + 1), 188.4 (1), 183.9 (1); Me 46.8.
(3) The reaction of phenyllithium with Ru$_3$(CO)$_{12}$ has been previously reported to give the unusual orthometalated carbene complex HRu$_3$-[C$_6$H$_4$-*o*-C(Ph)](CO)$_{10}$ in low yield: Parkins, A. W.; Fischer, E. O.; Huttner, G.; Regler, D. *Angew. Chem., Int. Ed. Engl.* **1970,** *9,* 633. Also mentioned was an orange oil. In repeating this work, we confirm this observation; through preliminary spectroscopic studies we believe this material to be the acyl derivative HRu$_3$[μ-O=C(Ph)](CO)$_{10}$.
(4) (a) Treatment of THF solutions of Ru$_3$(CO)$_{12}$ with MeLi/LiBr[2a] at -30 °C followed within 5 min by acidification with excess CF$_3$SO$_3$H results in a mixture that upon workup gives 1 in 20% yield and 2a in 30% yield. Spectroscopic data are presented in Table I. Less than 5% of the starting material is recovered; the balance represents various polynuclear species among which we could identify [HRu$_6$(CO)$_{18}$]$^-$.[4b] (b) Eady, C. R.; Jackson, P. F.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; McPartlin, M.; Nelson, W. J. H. *J. Chem. Soc., Dalton Trans.* **1980,** 383.
(5) (a) Nucleophilic attack of coordinated carbonyl groups by MeLi followed by protonation has been shown to generate carbyne, vinylidine, and hydroxycarbene complexes, as shown in ref 5b, 5c, and 5d, respectively. In the synthesis of 2a one such type of complex may well be an intermediate susceptible to substitution by bromide ion in the presence of excess acid. (b) Nitay, M.; Priester, W.; Rosenblum, M. *J. Am. Chem. Soc.* **1978,** *100,* 3620. (c) Dawkins, G. M.; Green, M.; Jeffery, J. C.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1980,** 1120. (d) Fisher, E. O.; Riedel, A. *Chem. Ber.* **1968,** *101,* 156. Darst, K. P.; Lukehart, C. M. *J. Organomet. Chem.* **1979,** *171,* 65. Chatt, J.; Leigh, G. J.; Pickett, C. J.; Stanley, D. R. *Ibid.* **1980,** *184,* C64.