Inorg. Chem. **1996,** *35,* 923−928 **923**

Synthesis, Characterization, and Comparative Properties of $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ and $[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$

Gishun Hsu, Scott R. Wilson, and John R. Shapley*

School of Chemical Sciences and Materials Research Laboratory, University of Illinois,
Urbana, Illinois 61801

Received July 13, 1995⊗

The reaction of $[PPN]_2[Re_6C(CO)_{19}]$ with $Mo(CO)_6$ and $Ru_3(CO)_{12}$ under sunlamp irradiation provided the new mixed-metal clusters $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ and $[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$, which were isolated in yields of 85% and 61%, respectively. The compound $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 20.190$ (7) Å, $b = 16.489$ (7) Å, $c = 27.778$ (7) Å, $\beta = 101.48$ (2)°, and $Z = 4$ (at $T = -75$ °C). The cluster anion is composed of a Re_6C octahedral core with a face capped by a $Mo(CO)_4$ fragment. There are three terminal carbonyl ligands coordinated to each rhenium atom. The four carbonyl ligands on the molybdenum center are essentially terminal, with one pair of carbonyl ligands (C72−O72 and C74−O74) subtending a relatively large angle at molybdenum (C72−Mo−C74 = 147.2(9)°), whereas the remaining pair of carbonyl ligands (C71−O71 and C73−O73) subtend a much smaller angle (C71−Mo−C73 = 100.5(9)°). The ^{13}C NMR spectrum of ^{13}CO-enriched $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ shows signals for four sets of carbonyl ligands at −40 °C, consistent with the solid state structure, but the carbonyl ligands undergo complete scrambling at ambient temperature. The ^{13}C NMR spectrum of ^{13}CO-enriched $[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$ at 20 °C is consistent with the expected structure of an octahedral $Re_6C(CO)_{18}$ core capped by a $Ru(CO)_3$ fragment. The visible spectrum of $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ shows a broad, strong band at 670 nm ($\epsilon = 8100$), whereas all of the absorptions of $[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$ are at higher energy. An irreversible oxidation wave with E_p at 0.34 V is observed for $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$, whereas two quasi-reversible oxidation waves with $E_{1/2}$ values of 0.21 and 0.61 V (*vs* Ag/AgCl) are observed for $[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$. The molybdenum cap in $[Re_6C(CO)_{18}Mo(CO_4)]^{2-}$ is cleaved by heating in donor solvents, and by treatment with H_2, to give largely $[H_2Re_6C(CO)_{18}]^{2-}$. In contrast, $[Re_6C(CO)_{18}Ru(CO)_3]^{2-}$ shows no tendency to react under similar conditions.

Introduction

The synthesis of a number of mixed-metal clusters involving rhenium has been effected by utilizing the cluster $[Re_7C(CO)_{21}]^{3-}$ [1,2] as a pseudo-Cp ligand to react with metal complex electrophiles.[3] A variety of stable heterometallic derivatives $[Re_7C(CO)_{21}ML_n]^{2-}$, where M = Cu,[4] Ag,[4] Au[4,5] Pd,[3,6] Pt,[3] Hg,[7] Rh,[3,8] and Ir,[3,9] have been reported. In contrast, the related octahedral cluster compound $[Re_6C(CO)_{19}]^{2-}$ [10,11] apparently forms only weak complexes with copper triad electrophiles.[11] Our previous observation of the facile conversion of $[Re_6C(CO)_{19}]^{2-}$ to $[H_2Re_6C(CO)_{18}]^{2-}$ under sunlamp irradiation in the presence of hydrogen (eq 1),[10] has prompted

$$[Re_6C(CO)_{19}]^{2-} + H_2 \xrightarrow[CH_2Cl_2]{h\nu} [H_2Re_6C(CO)_{18}]^{2-} + CO \quad (1)$$

us to utilize this unique photoreactivity for synthetic purposes. We report in this paper the reactions of $[Re_6C(CO)_{19}]^{2-}$ with $Mo(CO)_6$ and $Ru_3(CO)_{12}$ under irradiation to provide the new mixed-metal clusters $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ and $[Re_6C(CO)_{18}Ru(CO)_3]^{2-}$ (eqs 2, 3) These are the first large rhenium carbonyl

$$[Re_6C(CO)_{19}]^{2-} + Mo(CO)_6 \xrightarrow[CH_2Cl_2]{h\nu} [Re_6C(CO)_{18}Mo(CO)_4]^{2-} + 3CO \quad (2)$$

$$[Re_6C(CO)_{19}]^{2-} + {}^{1}/_{3}Ru_3(CO)_{12} \xrightarrow[THF]{h\nu} [Re_6C(CO)_{18}Ru(CO)_3]^{2-} + 2CO \quad (3)$$

cluster derivatives to contain either a group 6 or a group 8 transition metal cap. The structure of $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ has been fully characterized by a low-temperature single-crystal X-ray crystallographic study, and both compounds have been examined by solution ^{13}C NMR spectroscopy. Furthermore, we compare the relative reactivity and some physical properties of the two cluster compounds.

Experimental Section

General Procedures. All operations were conducted by using standard Schlenk techniques under a nitrogen atmosphere unless otherwise noted. The $[(Ph_3P)_2N]^+$ (PPN^+) salt of $[Re_6C(CO)_{19}]^{2-}$ was prepared as described previously.[10] $Mo(CO)_6$ was obtained from Strem

---

⊗ Abstract published in *Advance ACS Abstracts,* January 15, 1996.

(1) Ciani, G.; D'Alfonso, G.; Freni, M.; Romiti, P.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1982**, 339.
(2) Hayward, C.-M. T.; Shapley, J. R. *Organometallics* **1988**, *7*, 448.
(3) Henly, T. J.; Shapley, J. R.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1988**, *7*, 441.
(4) Beringhelli, T.; D'Alfonso, G.; Freni, M.; Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1985**, *295*, C7.
(5) Henly, T. J.; Shapley, J. R.; Rheingold, A. L. *J. Organomet. Chem.* **1986**, *310*, 55.
(6) Henly, T. J.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1988**, *27*, 2551.
(7) Henly, T. J.; Shapley, J. R. *Organometallics* **1989**, *8*, 2729.
(8) Simerly, S. W.; Shapley, J. R. *Inorg. Chem.* **1990**, *29*, 3634.
(9) (a) Ma, L.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1990**, *29*, 5133. (b) Ma, L.; Szajek, L. P.; Shapley, J. R. *Organometallics* **1991**, *10*, 1662. (c) Ma, L.; Shapley, J. R. *Inorg. Chim. Acta* **1993**, *212*, 303. (d) Ma, L.; Wilson, S. R.; Shapley, J. R. *J. Am. Chem. Soc.* **1994**, *116*, 787.
(10) Hsu, G.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1991**, *30*, 3881.
(11) Beringhelli, T.; D'Alfonso, G.; Molinari, H.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1992**, 689.

0020-1669/96/1335-0923$12.00/0

Chemicals and used without further purification. $Ru_3(CO)_{12}$ was prepared by a previously reported procedure.[12] A GE 275 W sunlamp was the light source used for photolysis; it was placed ca. 10 cm from the flask. Dichloromethane, THF, and triglyme were distilled from calcium hydride, sodium/benzophenone, and sodium, respectively.

Physical Measurements. Elemental analyses were performed by the Microanalytical Laboratory of the School of Chemical Sciences. Fast atom bombardment (FAB) mass spectra were obtained in the School Mass Spectrometry Laboratory; the matrix used was Magic Bullet (dithioerythritol−dithiothreitol). Infrared (IR) spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrometer. UV−vis spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. ^{13}C NMR spectra were obtained on a General Electric QE-300 spectrometer at 75 MHZ and were referenced to the carbonyl resonance at δ 206.0 in acetone-d_6 and to the central methylene peak at δ 53.8 in dichloromethane-d_2. Cyclic voltammetric experiments were conducted using a BAS 100A electrochemical analyzer with a cell incorporating a platinum disk as the working electrode, Ag/AgCl as the reference electrode, a platinum counter electrode, and $[Bu_4N][PF_6]$ as the supporting electrolyte. The dichloromethane solutions were ~1 mM in complex and 0.1 M in supporting electrolyte. All measurements were conducted with a scan rate of 100 mV s^{-1}. Under our experimental conditions, the Fc^+/Fc couple was measured at $E_{1/2} = 0.24$ V ($\Delta E_p = 77$ mV).

Synthesis of $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$. $[PPN]_2[Re_6C(CO)_{19}]$ (35 mg, 0.013 mmol) and $Mo(CO)_6$ (38 mg, 0.14 mmol) were placed in a 250 mL Pyrex Schlenk tube and dissolved in dichloromethane (75 mL). The flask was irradiated under an argon atmosphere. The heat generated by the sunlamp was sufficient to maintain the solvent at reflux. The reaction was monitored by IR for the appearance of the characteristic band of $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ at 2002 cm^{-1} and the disappearance of the characteristic band of $[Re_6C(CO)_{19}]^{2-}$ at 1978 cm^{-1}. After 8 h of irradiation, the solvent was removed under vacuum. Unreacted $Mo(CO)_6$ was removed by sublimation at ambient temperature. The residue was extracted with dichloromethane (2 × 50 mL) to give a green solution. The solution was concentrated to ca. 3 mL, and a layer of ether was allowed to diffuse slowly into the dichloromethane solution. Black crystals of $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ (32 mg, 0.011 mmol, 85%) were obtained after washing with ether and drying in vacuo. Anal. Calcd for $C_{95}H_{60}N_2O_{22}P_4Re_6Mo$: C, 39.10; H, 2.07; N, 0.96. Found: C, 38.77; H, 2.09; N, 1.01. IR (dichloromethane): ν_{CO} 2056 (vw), 2002 (s), 1991 (vs), 1970 (w, sh), 1946 (vw, sh), 1915 (w) cm^{-1}. Negative ion FAB mass spectrum (^{187}Re, ^{98}Mo): *m/z* 2386 ($[PPN][Re_6C(CO)_{18}Mo(CO)_4]$), 2358 ($[PPN][Re_6C(CO)_{18}Mo(CO)_4] - CO$), 2176 ($[PPN][Re_6C(CO)_{18}]$), 1848 − xCO, $x = 0-5$ ($Re_6C(CO)_{18}Mo(CO)_4 - x$CO), 1638 ($Re_6C(CO)_{18}$). UV−vis (THF): λ_{max} (ϵ) 380 (23 100), 450 (14 000), 670 (8100) nm.

$[PPN]_2[Re_6{}^*C(CO)_{18}Mo(CO)_4]$ resulted when $[PPN]_2[Re_6{}^*C({}^*CO)_{19}]$ ($^*C$ ~ 50% ^{13}C) was reacted with unenriched $Mo(CO)_6$. ^{13}C NMR (75 MHz, acetone-d_6, 20 °C): δ 418.6 (s, 1 C, μ_6-C). $[PPN]_2[Re_6{}^*C({}^*CO)_{18}Mo({}^*CO)_4]$ was obtained by reacting $[PPN]_2[Re_6{}^*C({}^*CO)_{19}]$ with $Mo({}^*CO)_6$ (ca. 50% ^{13}C). $Mo({}^*CO)_6$ was prepared by reacting $Mo(CO)_3(NCCH_2CH_3)_3$[13] with ^{13}CO. ^{13}C NMR (75 MHz, CD_2Cl_2, −40 °C): δ 212.7 (s, 4C, $Mo(CO)_4$), 198.8 (s, 9C), 194.9 (s, 6C), 191.0 (s, 3C).

Synthesis of $[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$. $PPN_2[Re_6C(CO)_{19}]$ (52 mg, 0.019 mmol) and $Ru_3(CO)_{12}$ (36 mg, 0.057 mmol) were placed in a Pyrex flask. THF (20 mL) was added, and the flask was irradiated under an argon atmosphere. The heat generated by the sunlamp was sufficient to maintain the solvent at reflux. The IR bands characteristic of $[Re_6C(CO)_{19}]^{2-}$ were slowly replaced by the those of $[Re_6C(CO)_{18}Ru(CO)_3]^{2-}$. The reaction was terminated after 22 h of irradiation. The solvent was removed, and the solid residue was washed with ether and dried in vacuo. Crystallization of the residue by solvent diffusion from dichloromethane/ether gave black crystals of $[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$ (33 mg, 0.011 mmol, 61%), which were washed with ether and dried. Anal. Calcd for $C_{94}H_{60}N_2O_{21}P_4Re_6Ru$: C, 38.99; H, 2.09; N, 0.97. Found: C, 38.91; H, 2.10; N, 0.96. IR (acetone): ν_{CO} 2062 (w), 2017 (m), 1995 (vs), 1975 (w), 1969 (w), 1953 (vw, sh), 1936 (vw, sh), 1916 (w), 1885 (vw) cm^{-1}. Negative ion FAB mass spectrum (^{187}Re, ^{102}Ru): *m/z* 2362 ($[PPN][Re_6C(CO)_{18}Ru(CO)_3]$), 2334 ($[PPN][Re_6C(CO)_{18}Ru(CO)_3] - CO$), 1824 ($[Re_6C(CO)_{18}Ru(CO)_3]$), 1796 ($[Re_6C(CO)_{18}Ru(CO)_3] - CO$). UV−vis (THF): λ_{max} (ϵ) 322 (20 700), 390 (9700), 516 (5300) nm.

$[PPN]_2[Re_6{}^*C({}^*CO)_{18}Ru({}^*CO)_3]$ was prepared from $[PPN]_2[Re_6{}^*C({}^*CO)_{19}]$ and $Ru_3({}^*CO)_12$ ($^*C$ ~ 50% ^{13}C). ^{13}C NMR (75 MHZ, acetone-d_6, 20 °C): δ 419.2 (s, 1 C, μ_6-C), 200.2 (s, 9 C), 193.4 (s, 9 C), 188.0 (s, 3 C, $Ru(CO)_3$).

Photochemical Stability of $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ and $[Re_6C(CO)_{18}Ru(CO)_3]^{2-}$. Typically, 10−15 mg samples of $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ and $[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$ were dissolved in THF (40 mL) in a Pyrex flask. The flasks were irradiated for up to 1 h with no reversion to $[Re_6C(CO)_{19}]^{2-}$. Prolonged irradiation (2−3 h) resulted in small amounts of decomposition products (by IR), which were not identified.

Thermal Stability. $[PPN_]2[Re_6C(CO)_{18}Mo(CO)_4]$ (17 mg, 0.0058 mmol) was dissolved in triglyme (25 mL). The green solution was heated with an oil bath at 60 °C for 1 h. The IR bands of $[Re_6C(CO)_{19}]^{2-}$ at 1990 (vs) and 1975 (s) cm^{-1} began to appear. Heating was continued at 100 °C for an additional 2 h. $[PPN]_2[Re_6C(CO)_{19}]$ was precipitated by adding 2-propanol. Recrystallization from dichloromethane/2-propanol produced $[PPN]_2[Re_6C(CO)_{19}]$ (12 mg, 0.0044 mmol, 77%), which was identified by spectroscopic data previously described.[10]

$[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$ (15 mg, 0.0053 mmol) was dissolved in triglyme (20 mL), and the solution was heated with an oil bath at 75 °C for 2 h. Unassignable IR bands appeared. Additional heating at 100 °C for 3 h resulted in complete decomposition as observed by IR and by the change from a lavender to a colorless solution.

Reaction with CO. A 10−15 mg sample of $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ or $[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$ was dissolved in THF (40 mL). $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ did not react with CO (1 atm) at room temperature or under irradiation for 1 h. Prolonged irradiation resulted in some decomposition. $[Re_6C(CO)_{18}Ru(CO)_3]^{2-}$ did not react with CO (60 psig) at room temperature over 7 days. Irradiation of $[Re_6C(CO)_{18}Ru(CO)_3]^{2-}$ under CO (1 atm) for 1 h also did not produce any reaction.

Reaction with Acetonitrile. $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ (15 mg, 0.0053 mmol) was dissolved in acetonitrile (25 mL). The reaction mixture was stirred at room temperature for 4 days. The characteristic IR bands for $[Re_6C(CO)_{19}]^{2-}$ were observed. The solvent was removed, and crystallization of the residue from dichloromethane/2-propanol gave $[PPN]_2[Re_6C(CO)_{19}]$ (12 mg, 0.044 mmol, 84%).

$[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$ (10 mg, 0.0036 mmol) was dissolved in acetonitrile (30 mL). The solution was stirred at room temperature for 8 days. The only IR bands observed were those of $[Re_6C(CO)_{18}Ru(CO)_3]^{2-}$.

Reaction with H_2 under Irradiation. $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ (16 mg, 0.0055 mmol) was dissolved in THF (40 mL). H_2(g) was bubbled through the solution, and the reaction mixture was irradiated for 1 h. Conversion to $[H_2Re_6C(CO)_{18}]^{2-}$ was complete. The solution was concentrated, and a layer of 2-propanol was added. Slow diffusion resulted in red crystals of $[PPN]_2[H_2Re_6C(CO)_{18}]$ (12 mg, 0.0045 mmol, 82%), identified by spectroscopic data consistent with those previously described.[2,10,14]

$[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$ (10 mg, 0.0036 mmol) was dissolved in THF (50 mL), and H_2(g) was bubbled through the solution. The mixture was irradiated for 3 h with no reaction as monitored by IR. After 5 h, some decomposition of the starting material in the form of a precipitate appeared, but there was no formation of $[H_2Re_6C(CO)_{18}]^{2-}$ observed by IR.

Reaction with H_2 by Heating. $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ (16 mg, 0.0055 mmol) was placed in a pressure bottle with THF (60 mL). H_2 (40 psig) was introduced, and the reaction mixture was heated at 50 °C for 4 days. The distinct IR bands for $[H_2Re_6C(CO)_{18}]^{2-}$ were the only bands observed. Concentration of the solution to ca. 4 mL followed by introduction of 2-propanol as diffusing solvent gave $[PPN]_2[H_2Re_6C(CO)_{18}]$ (13 mg, 0.0047 mmol, 86%).

Reaction of $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ with H_2 bubbling through a THF solution at reflux or through a triglyme solution at 75 °C resulted

---

[12] Bruce, M. I.; Jensen, C. M.; Jones, N. L. *Inorg. Synth.* **1990**, *28*, 216.

[13] Kubas, G. J.; Van Der Sluys, L. S. *Inorg. Synth.* **1990**, *28*, 29.

[14] Ciani, G.; D'Alfonso, G.; Romiti, P.; Sironi, A.; Freni, M. *J. Organomet. Chem.* **1983**, *244*, C27.

Table 1. Crystallographic Data for $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$

formula	$C_{95}H_{60}N_2O_{22}P_4MoRe_6$	fw	2918.56
space group	$P2_1/c$	temp, °C	−75
a, Å	20.191(7)	λ, Å	0.710 73 (Mo Kα)
b, Å	16.489(7)	ρ_{calcd}, g cm^{-3}	2.139
c, Å	27.778(7)	μ, cm^{-1}	83.63
β, deg	101.48(2)	transm coeff	0.223−0.105
V, Å^3	9063(10)	R^a	0.051
Z	4	$R_w{}^b$	0.058

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$, where $w = k/([\sigma(F_o)]^2 + [pF_o]^2)$ and $k = 1.55$, $p = 0.02$.

in the formation of a mixture of $[H_2Re_6C(CO)_{18}]^{2-}$ and $[Re_6C(CO)_{19}]^{2-}$ as observed by IR.

$[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$ (15 mg, 0.0052 mmol) was dissolved in triglyme (15 mL). H_2(g) was bubbled through the solution, and the solution was heated successively at 75 °C for 3 h and at 100 °C for 2 h. There was no reaction as observed by IR.

X-ray Crystallographic Study of $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$. Crystals of $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ suitable for diffraction studies were grown by solvent diffusion of 2-propanol into a dichloromethane solution. A dark, opaque, prismatic crystal (dimensions 0.2 × 0.3 × 0.4 mm) with well-developed faces (face ($\bar{1}00$) was slightly damaged) was mounted with oil (Paratone-N, Exxon) to a thin glass fiber. Data collection was carried out at −75 °C on an Enraf-Nonius CAD4 automated κ-axis diffractometer. Pertinent crystallographic data are summarized in Table 1. Unit cell parameters were obtained by a least-squares fit of 25 machine-centered reflections ($21° < 2\theta < 24°$). A total of 11 089 independent reflections, 6901 observed with $I > 2.58\sigma(I)$, in the range $2° < 2\theta < 44°$ were measured at variable rates over a period of 99 h with no change in the appearance of the sample. Data were corrected numerically for absorption and for anomalous dispersion, Lorentz, and polarization effects.

The structure was solved by direct methods (SHELXS-86); correct positions for the metal atoms were deduced from an E map. Subsequent least-squares difference Fourier calculations (SHELX-76) revealed positions for the remaining non-hydrogen atoms. Hydrogen atoms were included as fixed contributors in idealized positions. In the final cycle of least squares, anisotropic thermal coefficients were refined for all metal and phosphorus atoms, and a common isotropic thermal parameter was varied for the hydrogen atoms. Successful convergence was indicated by the maximum shift/error for the final cycle. The highest peaks in the final difference Fourier map were in the vicinity of the metal atoms, +3.34 e/Å^3. Final agreement factors were $R = 0.051$ and $R_w = 0.058$. Positional parameters for the cluster anion are listed in Table 2, and selected bond distances and angles are listed in Table 3. Complete lists of atom coordinates and thermal coefficients are provided as Supporting Information.

Results and Discussion

Synthesis and Characterization. The photoinduced reaction of $[PPN]_2[Re_6C(CO)_{19}]$ with $Mo(CO)_6$ in dichloromethane resulted in the formation of $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$, which was subsequently isolated in 85% yield. The choice of a noncoordinating solvent was essential for the productive formation of $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$. The analogous reaction of $[PPN]_2[Re_6C(CO)_{19}]$ and $Ru_3(CO)_{12}$ in THF gave $[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$, which was isolated in 61% yield. An attempted thermal reaction of $[Re_6C(CO)_{19}]^{2-}$ and $Ru_3(CO)_{12}$ was not successful up the decomposition point of $[Re_6C(CO)_{19}]^{2-}$ (150 °C). The new clusters were readily formulated on the basis of FAB negative ion mass spectra. In each case, the highest mass ions observed were $[M - PPN]^-$ and $[M - PPN - CO]^-$; additional ions related to the cluster core were seen at lower mass numbers.

Under conditions similar to those for the reaction with $Mo(CO)_6$, the reactions of $[Re_6C(CO)_{19}]^{2-}$ with $Cr(CO)_6$ and $W(CO)_6$ did not yield the analogous $[Re_6C(CO)_{18}M(CO)_4]^{2-}$ products. Two factors appear relevant to the formation of a stable $[Re_6C(CO)_{18}M(CO)_4]^{2-}$ complex. First, it is necessary for $M(CO)_6$ to extrude two carbonyl ligands overall to give a $M(CO)_4$ cap. The loss of carbonyl ligands by $M(CO)_6$ in a poor donor solvent is likely to be assisted by the unsaturated species $[Re_6C(CO)_{18}]^{2-}$, which can capture a carbonyl ligand to regenerate $[Re_6C(CO)_{19}]^{2-}$. In the case of $W(CO)_6$, the relatively strong W−CO bonds should hinder the carbonyl loss. Second, the heterometal cap must not undergo cleavage once formed. In the case of a $Cr(CO)_4$ derivative, the rhenium−chromium bond strength may not be sufficient to provide a stable compound under the reaction conditions.

Table 2. Selected Positional Parameters for $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$

	x/a	y/b	z/c
Re1	0.73586(3)	0.09605(5)	0.94043(4)
Re2	0.72209(3)	−0.08040(5)	0.95934(5)
Re3	0.71368(3)	0.03181(5)	1.06908(4)
Re4	0.79810(3)	−0.08035(5)	1.08450(5)
Re5	0.18435(3)	0.09814(5)	1.06917(5)
Re6	0.82238(3)	−0.01162(5)	0.95373(5)
Mo	0.63556(6)	0.0315(1)	0.9456(1)
C	0.7703(6)	0.011(1)	1.0123(9)
C11	0.7020(7)	0.194(1)	0.954(1)
O11	0.6834(5)	0.2533(9)	0.9662(8)
C12	0.7798(7)	0.158(1)	0.901(1)
O12	0.8047(5)	0.1965(9)	0.8714(8)
C13	0.7027(8)	0.082(1)	0.849(1)
O13	0.6847(6)	0.0772(10)	0.7923(9)
C21	0.7123(9)	−0.104(2)	0.864(1)
O21	0.7117(6)	−0.119(1)	0.8087(9)
C22	0.6684(8)	−0.148(1)	0.979(1)
O22	0.6402(5)	−0.1925(9)	0.9906(8)
C23	0.7566(9)	−0.179(2)	0.973(1)
O23	0.7724(7)	−0.247(1)	0.9715(10)
C31	0.7367(7)	0.011(1)	1.165(1)
O31	0.7441(5)	−0.0022(9)	1.2211(8)
C32	0.6974(7)	0.136(1)	1.100(1)
O32	0.6885(5)	0.1990(9)	1.1182(8)
C33	0.6580(8)	−0.028(1)	1.085(1)
O33	0.6298(5)	−0.0693(9)	1.1049(7)
C41	0.8388(8)	−0.046(1)	1.169(1)
O41	0.8614(5)	−0.0291(89)	1.2198(8)
C42	0.8478(8)	−0.161(1)	1.082(1)
O42	0.8768(6)	−0.209(1)	1.0798(9)
C43	0.7622(8)	−0.158(1)	1.126(1)
O43	0.7371(6)	−0.1991(9)	1.1504(8)
C51	0.8093(8)	0.141(1)	1.154(1)
O51	0.8073(5)	0.1621(9)	1.2091(8)
C52	0.8841(7)	0.093(1)	1.098(1)
O52	0.9257(6)	0.0905(10)	1.1174(8)
C53	0.8233(8)	0.203(1)	1.039(1)
O53	0.8309(6)	0.267(1)	1.0150(8)
C61	0.8104(8)	−0.012(1)	0.861(1)
O61	0.8011(6)	−0.009(1)	0.8011(9)
C62	0.864(1)	−0.098(2)	0.953(2)
O62	0.8905(8)	−0.153(1)	0.948(1)
C63	0.8746(9)	0.065(2)	0.954(1)
O63	0.9060(6)	0.113(1)	0.9555(9)
C71	0.5807(8)	−0.027(1)	0.966(1)
O71	0.5478(6)	−0.059(1)	0.9840(9)
C72	0.6120(8)	0.116(1)	1.001(1)
O72	0.5915(6)	0.1648(10)	1.0293(8)
C73	0.6025(8)	0.105(1)	0.879(1)
O73	0.5821(6)	0.156(1)	0.8395(9)
C74	0.6205(9)	−0.039(2)	0.862(1)
O74	0.6053(6)	−0.0726(9)	0.8120(8)

The reaction of $[Re_6C(CO)_{19}]^{2-}$ and $Fe_3(CO)_{12}$ in THF under photolytic conditions provided some conversion to $[Re_6C(CO)_{18}Fe(CO)_3]^{2-}$, as identified by mass spectrometry. However, prolonged irradiation resulted in more insoluble decomposition products, and it was not possible to isolate the compound in pure form. The analogous reaction of $[Re_6C(CO)_{19}]^{2-}$ and $Os_3(CO)_{12}$ did not yield an osmium-capped cluster. Again, the success of the reaction is apparently related on the one hand to the ability to generate an appropriate capping reagent, in this case to the propensity for $M_3(CO)_{12}$ to undergo

Table 3. Selected Bond Distances (Å) and Angles (deg) for the Cluster Anion in $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$

Distances			
Re1−Re2	2.969(1)	Re4−Re5	3.003(1)
Re1−Re3	2.981(1)	Re4−Re6	3.069(1)
Re1−Re5	3.042(1)	Re5−Re6	2.994(1)
Re1−Re6	2.957(1)	Re1−Mo	3.004(2)
Re2−Re3	2.931(1)	Re2−Mo	2.999(2)
Re2−Re4	2.953(1)	Re3−Mo	2.962(2)
Re2−Re6	3.031(1)	Mo−C71	1.92(2)
Re3−Re4	2.954(1)	Mo−C72	1.99(2)
Re3−Re5	3.002(1)	Mo−C73	1.91(2)
Re−$C_{carbide}$	2.12(2) (av)	Mo−C74	2.02(3)
Re−CO	1.90(3) (av)		

Angles			
Mo−C71−O71	174(2)	C71−Mo−C72	82.5(9)
Mo−C72−O72	171(2)	C71−Mo−C73	100.5(9)
Mo−C73−O73	176(2)	C71−Mo−C74	81.2(9)
Mo−C74−O74	169(2)	C72−Mo−C73	77.6(10)
Re2−C23−O23	168(2)	C72−Mo−C74	147.2(9)
Re3−C33−O33	168(2)	C73−Mo−C74	77.6(10)
Re1−Mo−C71	165.6(7)	Re1−Re2−Mo	60.43(4)
Re1−Mo−C72	100.5(6)	Re1−Re3−Mo	60.72(4)
Re1−Mo−C73	93.9(7)	Re2−Re1−Mo	60.27(4)
Re1−Mo−C74	102.3(7)	Re2−Re3−Mo	61.18(4)
Re2−Mo−C71	109.0(7)	Re3−Re1−Mo	59.32(4)
Re2−Mo−C72	136.9(7)	Re3−Re2−Mo	59.90(4)
Re2−Mo−C73	136.1(7)	Re4−Re2−Mo	120.15(5)
Re2−Mo−C74	75.6(7)	Re6−Re2−Mo	119.48(5)
Re3−Mo−C71	107.6(7)	Re6−Re1−Mo	121.79(5)
Re3−Mo−C72	77.9(7)	Re1−Re2−Re3	60.68(3)
Re3−Mo−C73	139.7(7)	Re1−Re3−Re2	60.28(3)
Re3−Mo−C74	134.3(7)	Re2−Re1−Re3	59.03(3)
Re1−Mo−Re2	59.29(4)	Re4−Re5−Re6	61.56(3)
Re1−Mo−Re3	59.96(4)	Re4−Re6−Re5	59.36(3)
Re2−Mo−Re3	58.92(4)	Re5−Re4−Re6	59.08(3)

photochemical fragmentation, and on the other hand to the stability of the capped product under the reaction conditions. The thermal redox condensation reaction of $[Ru_6C(CO)_{16}]^{2-}$ with excess $Ru_3(CO)_{12}$ at 162 °C gives $[Ru_{10}C(CO)_{24}]^{2-}$.[15] However, it appears that the thermal reaction is not a viable route to $[Re_6C(CO)_{18}Ru(CO)_3]^{2-}$, in part because it is stable only to ca. 100 °C.

Structural Features of $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$. From X-ray data obtained at −75 °C, the crystal structure of $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ was determined; details are given in Table 1. An ORTEP diagram of the cluster anion $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ is shown in Figure 1. The ion is composed of an octahedral $Re_6C(CO)_{18}$ core (with three terminal carbonyl ligands per rhenium atom and an interstitial carbide ligand) capped by a $Mo(CO)_4$ moiety. Selected bond distances and angles for the cluster anion are given in Table 3. The rhenium−rhenium and the rhenium−carbide distances are in accord with those of other heterometal-capped rhenium clusters, such as $[Re_7C(CO)_{21}Ag]^{2-}$ in $[\{Re_7C(CO)_{21}Ag\}_2(\mu\text{-Br})]^{5-}$,[4] $[Re_7C(CO)_{21}Au(PPh_3)]^{2-}$,[5] $[Re_7C(CO)_{21}Pt(C_4H_7)]^{2-}$,[3] $[Re_7C(CO)_{21}Pd(C_9H_9)]^{2-}$,[6] and $[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]^{2-}$.[9a] The molybdenum capping moiety is bonded to a triangular rhenium face in a rather symmetrical fashion with rhenium−molybdenum bond distances of 3.004(2), 2.999(2), and 2.962(2) Å. These are similar to those of $[Re_7C(CO)_{21}Ir(C_2H_4)(CO)]^{2-}$, which shows rhenium−iridium distances ranging from 2.904(8) to 3.032(9) Å,[9a] and to the rhenium (core)−rhenium (cap) distances in $[Re_6C(CO)_{18}Re(CO)_3P(OPh)_3]^{2-}$.[16] The rhenium−metal distances associated with capping moieties that do not bear carbonyl ligands are shorter, as in the cases of $[Re_7C(CO)_{21}Ag]^{2-}$ (2.832−2.927 Å),[4] $[Re_7C(CO)_{21}Au(PPh_3)]^{2-}$ (2.856(1)−2.893(1) Å),[5] and $[Re_7C(CO)_{21}Pd(C_9H_9)]^{2-}$ (2.786(3)−2.952(3) Å).[6] Each of the rhenium atoms forming the face capped by $Mo(CO)_4$ has two terminal carbonyl ligands pointing toward and one carbonyl ligand pointing away from the cap, a common feature for compounds with a capped $Re_6C(CO)_{18}$ core.

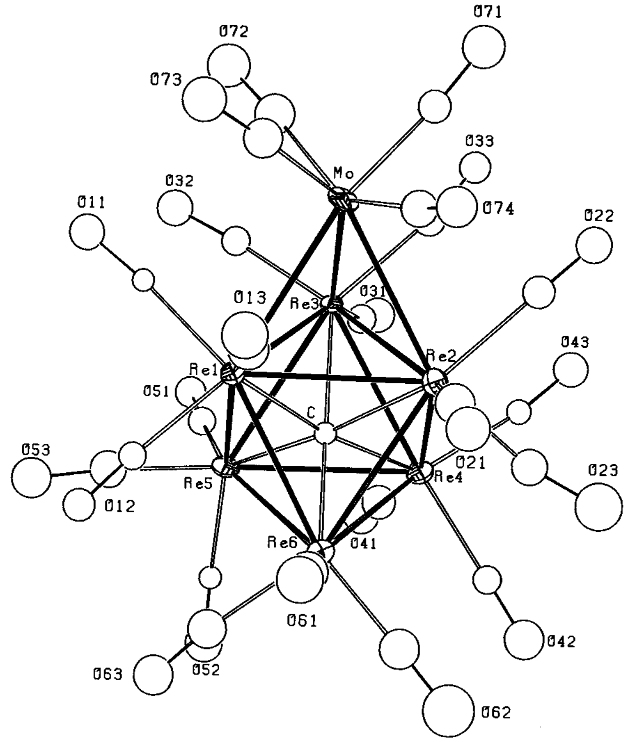

Figure 1. ORTEP diagram of the anion in $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ showing 35% probability ellipsoids.

The complex $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ represents the third known cluster with seven metal atoms and twenty-two ligands, the previous two being the homometallic carbido rhenium clusters $[Re_7C(CO)_{21}P(OPh)_3]^{16}$ and $[Re_7C(CO)_{22}]^{-}$.[17] In all of these cases, the structure of the metal framework is the same, namely, an octahedral Re_6C core with one capping metal fragment, but the ligand distribution differs. In the case of $[Re_7C(CO)_{22}]^{-}$, each of the seven rhenium centers has three terminal carbonyls, and the "extra" carbonyl is found in a position bridging an edge of the triangular face opposite the capped face of the octahedral core.[17] However, for $[Re_7C(CO)_{21}P(OPh)_3]^{-}$, each of the six core rhenium centers bears only the set of three terminal carbonyls, and the extra ligand is placed on the capping $Re(CO)_3P(OPh)_3$ moiety.[16] The structure of $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ is closely related to that of $[Re_7C(CO)_{21}P(OPh)_3]^{-}$, not only in the placement of four ligands on the capping metal center but also in its detailed geometry. In each case, the capping ML_4 unit has local C_{2v} symmetry, with one coplanar pair of ligands (pseudo-trans) subtending a relatively large angle at M and the other coplanar (pseudo-cis) pair forming a relatively small angle. The values are 147.2(9)° [C72−Mo−C74] and 100.5(9)° [C71−Mo−C73] for $Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ compared with 160.7(7)° and 95.6(6)° for $[Re_7C(CO)_{21}P(OPh)_3]^{-}$. The molybdenum−carbon distances for the pseudo-trans carbonyl ligands (Mo−C72 = 1.99(2) Å and Mo−C74 = 2.02(3) Å) are longer than those for the pseudo-cis carbonyl ligands (Mo−C71 = 1.92(2) Å and Mo−C73 = 1.91(2) Å). The trans carbonyl ligands (C72−O72 and C74−O74) are bent by ca. 10° and lean toward Re3

---

(15) Chihara, T.; Komoto, R.; Kobayashi, K.; Yamazaki, H.; Matsuura, Y. *Inorg. Chem.* **1989**, *28*, 964.

(16) Simerly, S. W.; Wilson, S. R.; Shapley, J. R. *Inorg. Chem.* **1992**, *31*, 5146.

(17) Beringhelli, T.; D'Alfonso, G.; De Angelis, M.; Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1987**, *322*, C21.

and Re2, respectively, with C74···Re2 = 3.17 Å and C72···Re3 = 3.20 Å.

The bonding interactions of a ML_4 fragment capping a cluster triangular face have been discussed.[18] A C_{2v} geometry appears to be favored for the ML_4 fragment, with a slight preference for the conformation that orients the plane containing the pseudo-trans ligands to bisect an edge of the triangle. This is the conformation adopted by $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ and $[Re_7C(CO)_{21}P(OPh)_3]^-$ as well as by several other examples of ML_4 caps.[18,19] In $[Re_7C(CO)_{21}P(OPh)_3]^-$ this configuration clearly allows for significant semibridging interactions involving the pseudo-trans carbonyls and the adjacent rhenium centers (average Re−C−O = 165(2)° and average Re···C = 3.0(1) Å). In the case of $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$, the structural manifestation of such secondary bonding is not so obvious, since the pseudo-trans carbonyls are only slightly bent and the Re···C distances are quite long. Nevertheless, it has been emphasized that such secondary interactions strongly stabilize the C_{2v} geometry for a $M(CO)_4$ unit capping a cluster triangular face.[18] Although analogous bonding symmetries are involved in coordinating a metal fragment to a triangle of metal atoms as to a planar carbocycle, such as $C_5H_5^-$ or C_6H_6, recent analyses of $(C_nR_n)M(CO)_4$ piano-stool structures show only small deviations from local C_{4v} symmetry are expected or observed.[20,21]

Both $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ and $[Re_6C(CO)_{18}Ru(CO)_3]^{2-}$ are 98-electron compounds, and both adopt the capped-octahedral geometry that is commonly observed for heptanuclear clusters.[22,23] This electron count and geometry are readily rationalized by Mingos' polyhedral skeletal electron pair theory augmented by the capping principle.[24,25] Given their mode at formation as well as some of their properties, these compounds are probably best viewed as complexes of the 84-electron octahedral core $[Re_6C(CO)_{18}]^{2-}$ with the neutral 14-electron $Mo(CO)_4$ or $Ru(CO)_3$ cap. Of course, the formal distribution of electrons as $[Re_6(CO)_{18}]^{4-}$ and $[M(CO)_n]^{2+}$ gives the same overall result. In either case the frontier orbitals for the conical fragment $Ru(CO)_3$ (a_1 + e) are expected to provide a good match for the three orbitals (also a_1 + e) projecting from the cluster face, leading to three strong bonding interactions. However, the three frontier orbitals for the C_{2v}-$Mo(CO)_4$ fragment (b_1, b_2, a_1) are more widely distributed in energy[18] and likely make a poorer match for the orbitals of the supporting Re_3 triangle. One could then view the bonding from the Re_6C core to the Mo cap as more "diene-like" ($[Re_6C(CO)_{18}]^{2-}$ donates 4 e to $Mo(CO)_4$) than "dienide-like" ($[Re_6C(CO)_{18}]^{4-}$ donates 6 e to $[Mo(CO)_4]^{2+}$). In fact, the C_{2v} distortion seen for $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ approaches that observed for $[Mo(CO)_4(\eta^4\text{-diene})]$ complexes,[26,27] as shown in Figure 2.

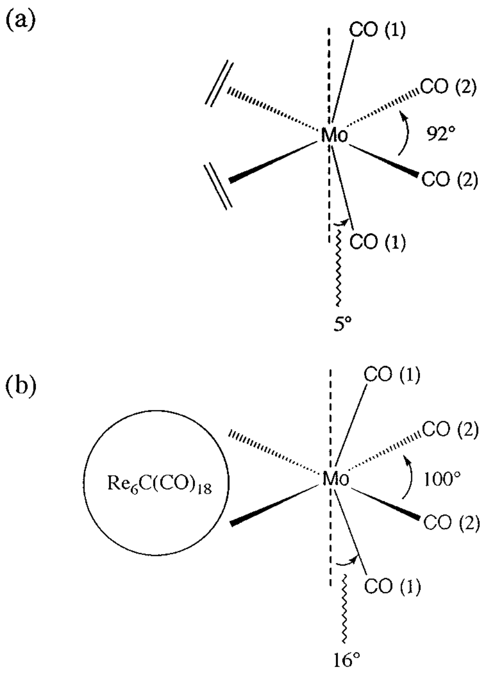

Figure 2. (a) Diagram of $Mo(CO)_4(\eta^4\text{-}C_{16}H_{16})$[26] showing the coordination shell of the metal: Mo−CO (1) = 2.046(3) Å (av) and Mo−CO (2) = 1.974(3) Å (av). (b) Diagram of $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ shown with emphasis on the coordination around the molybdenum center: Mo−CO (1) = 2.00(3) Å (av) and Mo−CO (2) = 1.92(2) Å (av).

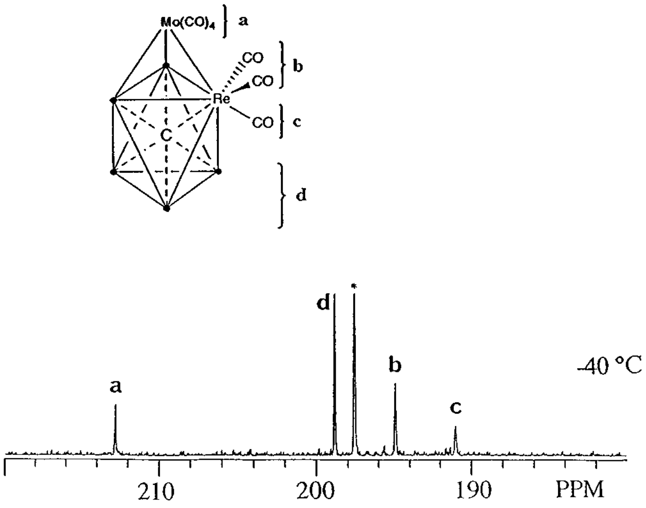

Figure 3. ^{13}C NMR spectrum (carbonyl region) of $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ in CD_2Cl_2 at −40 °C, with suggested assignments. The asterisk denotes unreacted $[PPN]_2[Re_6C(CO)_{19}]$.

Solution Structures and Stereodynamics. The ^{13}C NMR spectrum of $[PPN]_2[Re_6{}^*C({}^*CO)_{18}Ru({}^*CO)_3]$ at 20 °C exhibits a pattern that corresponds to the expected monocapped octahedral structure, with allowance for rapid localized exchange at each $Re(CO)_3$ center. The resonances for the carbonyl ligands bonded to the ruthenium atom occu at δ 188.0 (3C), those for the two tiers of carbonyl ligands associated with the rhenium atoms of the capped and uncapped triangular faces occur at δ 193.4 (9C) and δ 200.2 (9C), respectively, and that for the carbide ligand occurs at δ 419.2 (1C). The temperature dependence of the spectrum was not examined. The specific assignments are done by comparison with those made for $[Re_7C(CO)_{20}(NO)]^{2-}$, which also shows no evidence at room temperature for metal-to-metal carbonyl ligand migration.[28]

The ^{13}C NMR spectrum (carbonyl region) of $[PPN]_2[Re_6{}^*C({}^*CO)_{18}Mo({}^*CO)_4]$ at −40 °C is shown in Figure 3. The resonance for the carbide ligand is found at δ 418.6. The

---

(18) Evans, D. G.; Mingos, D. M. P. *Organometallics* **1983**, *2*, 435.
(19) Johnston, V. J.; Einstein, F. W. B.; Pomeroy, R. K. *Organometallics* **1988**, *7*, 1867.
(20) Poli, R. *Organometallics* **1990**, *9*, 1892.
(21) Lin, Z.; Hall, M. B. *Organometallics* **1993**, *12*, 19.
(22) Mingos, D. M. P.; May, A. S. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990; Chapter 2.
(23) Mingos, D. M. P.; Wales, D. J. *Introduction to Cluster Chemistry*; Grimes, R. N., Ed.; Prentice Hall: Englewood Cliffs, NJ, 1990.
(24) Mingos, D. M. P. *Acc. Chem. Res.* **1984**, *17*, 311.
(25) Mingos, D. M. P.; Forsyth, M. I. *J. Chem. Soc., Dalton Trans.* **1977**, 610.
(26) (a) Connop, A. H.; Kennedy, F. G.; Knox, S. A. R.; Mills, R. M.; Riding, G. H.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1980**, 518. (b) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2331.
(27) Blau, R. J.; Siriwardane, U. *Organometallics* **1991**, *10*, 1627.
(28) Hayward, C.-M. T.; Folkers, J. P.; Shapley, J. R. *Inorg. Chem.* **1988**, *27*, 3685.

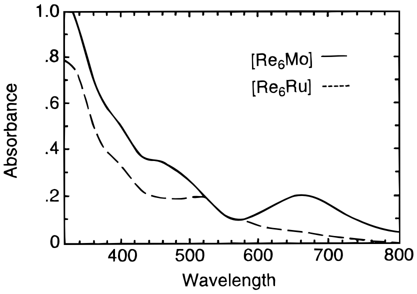

Figure 4. Electronic absorption spectra in THF for (a) $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ (2.5×10^{-5} M)[—] and (b) $[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$ (3.7×10^{-5} M) [- - -].

carbonyl spectrum is readily assigned with respect to the solid state structure. The signal at δ 212.7 (4C) is due to the carbonyl ligands (a) bonded to the molybdenum atom, which are undergoing localized exchange at this temperature. The resonance at δ 198.8 (9C) is assigned to the tier of carbonyl ligands (d) bonded to the basal plane of rhenium atoms. The resonances at δ 194.9 and 191.0 are attributed to carbonyl ligands on the rhenium atoms supporting the Mo cap, which are pointing toward (b) and away (c) from it, respectively. As the temperature is raised, all of the signals broaden, and at 20 °C, a single broad signal at δ 199 is observed for the exchange-averaged carbonyl ligands.

The fluxional behavior of $[Re_6C(CO)_{18}Re(CO)_3P(OPh)_3]^-$,[16] which also has four ligands on the capping metal, is very similar to that of $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$. In each case, three sets of limiting signals are exhibited: (i) carbonyls on the cap, (ii) carbonyls on the three rhenium atoms bonded to the capping atom, and (iii) carbonyls on the remaining basal triangle of rhenium atoms. The fluxional process is more facile for $[Re_6C(CO)_{18}Re(CO)_3P(OPh)_3]^-$, which may be attributable to the more distinct semibridging interactions of the capping center with the rhenium atoms of the $Re_6C(CO)_{18}$ core. In studies with $Cr(CO)_4(\eta^4\text{-diene})$ compounds,[29] it was found that a rotation of the diene ligands around the axis through the chromium and the center of gravity of the four carbonyl ligands reasonably explained the carbonyl scrambling. Occurrence of a similar process with the $Mo(CO)_4$ cap would provide for site exchange of the carbonyl ligands on molybdenum, leading ultimately to complete exchange of carbonyl ligands between the molybdenum cap and the $Re_6C(CO)_{18}$ core.

Electronic Absorption Spectra. The strongly different colors of the two title compounds prompted a comparison of their visible absorption spectra. The spectra recorded for solutions in THF of green $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ and lavender $[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$ are displayed in Figure 4. The distinctive feature for the molybdenum compound is the broad, strong, low-energy absorption centered at 670 nm (ϵ = 8,100). Heterometallic dinuclear compounds typically display two characteristic absorptions, an intense $\sigma \rightarrow \sigma^*$ band in the near-ultraviolet and a much weaker $d\pi \rightarrow \sigma^*$ band in the visible.[30] For example, these occur for $(\eta^5\text{-}C_5H_5)Mo(CO)_3Re(CO)_5$ at 365 nm ($\epsilon = 6500$) and 454 nm ($\epsilon = 640$).[31] Although the low-energy band observed for $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ is several times more intense than typical $d\pi \rightarrow \sigma^*$ bands, it likely has an origin similar to that of a Re-to-Mo charge-transfer transition.

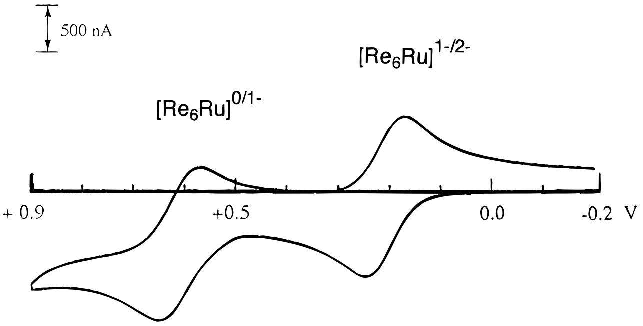

Figure 5. Positive-scan cyclic voltammogram of $[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$ in CH_2Cl_2 with 0.1 M $[Bu_4N][PF_6]$ (scan rate 100 mV s^{-1}; Ag/AgCl reference).

Cyclic Voltammetry. The positive scan cyclic voltammogram of $[PPN]_2[Re_6C(CO)_{18}Ru(CO)_3]$ (Figure 5) shows two quasi-reversible oxidation waves with $E_{1/2}$ values of 0.21 V (ΔE_p = 77 mV) and 0.61 V (ΔE_p = 81 mV) vs Ag/AgCl. The redox characteristics are very similar to those of the isostructural and isoelectronic $[Re_7C(CO)_{21}]^{3-}$, which also has two quasi-reversible oxidation waves with $E_{1/2}$ = 0.08 and 0.42 V,[3] and comparable to those of $[Re_7C(CO)_{20}NO]^{2-}$, 0.62 and 0.96 V, which has the same overall charge.[28] The cyclic voltammetric trace of $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ exhibits an irreversible oxidation wave with E_p at 0.34 V. The additional carbonyl ligand shifts the oxidation potential higher by ca. 130 mV. The ability of an extra carbonyl to remove electron density can be seen, for instance, with $[Re_7C(CO)_{21}Re(CO)_3]^{2-}$, which has a oxidation potential that is 220 mV higher than that of $[Re_7C(CO)_{21}Rh(CO)_2]^{2-}$.[3]

Comparative Reactivity. The molybdenum cap in $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ underwent cleavage upon heating in triglyme at 60 °C or upon treatment with acetonitrile at room temperature. The core cluster $[Re_6C(CO)_{19}]^{2-}$ was isolated in 77% and 84% yields, respectively, but the fate of the residual $Mo(CO)_3$ fragment could not be determined. $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ reacted with H_2 (1 atm) under photolytic conditions to give $[H_2Re_6C(CO)_{18}]^{2-}$ in 82% yield, but the thermal reactions with H_2 (1 atm) provided a mixture of $[H_2Re_6C(CO)_{18}]^{2-}$ and $[Re_6C(CO)_{19}]^{2-}$. The complex $[Re_6C(CO)_{18}Ru(CO)_3]^{2-}$ is relatively robust and did not undergo a discernible decapping reaction with CO, H_2, or CH_3CN under similar conditions.

The thermal reaction of $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ with H_2 is particularly interesting because the outcome is dependent on the H_2 pressure. At 1 atm of H_2, a mixture of $[Re_6C(CO)_{19}]^{2-}$ and $[H_2Re_6C(CO)_{18}]^{2-}$ was formed, but at 3.7 atm of H_2, only $[H_2Re_6C(CO)_{18}]^{2-}$ was observed. Since $[Re_6C(CO)_{19}]^{2-}$ does not react with H_2 under thermal activation,[10] this result suggests that cleavage of $[Re_6C(CO)_{18}Mo(CO)_4]^{2-}$ occurs to give the unsaturated intermediate $[Re_6C(CO)_{18}]^{2-}$, which then reacts with H_2 or competes for CO from the former $Mo(CO)_4$ cap.

Acknowledgment. This research was supported by National Science Foundation Grant DMR 89-20538 to the Materials Research Laboratory at the University of Illinois.

Supporting Information Available: Complete tables of positional parameters and thermal parameters for the crystallographic study of $[PPN]_2[Re_6C(CO)_{18}Mo(CO)_4]$ (13 pages). Ordering information is given on any current masthead page.

IC950887D

---

(29) Kreiter, C. G.; Kotzian, M.; Schubert, U.; Bau, R.; Bruck, M. A. *Z. Naturforsch.* **1984**, *39B*, 1553.

(30) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979; pp 59−65.

(31) Ginley, D. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1975**, *97*, 4908.