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Systematic and Efficient Syntheses of $Ru_6(CO)_{18}^{2-}$, $Ru_6C(CO)_{16}^{2-}$, $Os_6(CO)_{18}^{2-}$, and $Os_{10}C(CO)_{24}^{2-}$. Isolation and Characterization of $Os_6C(CO)_{17}$

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Treatment of $Ru_3(CO)_{12}$ or $Os_3(CO)_{12}$ with sodium in ether solvents at various reaction temperatures provides efficient preparations of several large anionic carbonyl clusters of ruthenium and osmium. The combination of $Ru_3(CO)_{12}$ and 1 equiv of sodium (Ru_3:Na = 1:1) affords $Ru_6(CO)_{18}^{2-}$ in refluxing tetrahydrofuran (66 °C) but $Ru_6C(CO)_{16}^{2-}$ in refluxing diglyme (162 °C). Under the latter conditions $Ru_6(CO)_{18}^{2-}$ is converted quantitatively to $Ru_6C(CO)_{16}^{2-}$. Treatment of $Os_3(CO)_{12}$ with sodium (Os_3:Na = 1:1) in diglyme at 162 °C yields $Os_6(CO)_{18}^{2-}$. Pyrolysis of $Os_6(CO)_{18}^{2-}$ in triglyme (216 °C) gives $Os_{10}C(CO)_{24}^{2-}$ as the major product. The decanuclear compound also is formed from the direct reaction of $Os_3(CO)_{12}$ with sodium (Os_3:Na = 1.66:1 or 1:1) in tetraglyme at 230–260 °C. Oxidation of $Ru_6C(CO)_{16}^{2-}$ and $Os_6(CO)_{18}^{2-}$ with aqueous ferric chloride in a carbon monoxide atmosphere produces $Ru_6C(CO)_{17}$ and $Os_6(CO)_{18}$ in good yields. A compound formulated as $Os_6C(CO)_{17}$ is isolated in low yield from the similar oxidation of reaction mixtures produced upon pyrolysis of $Os_6(CO)_{18}^{2-}$. This is suggested as evidence for the formation of $Os_6C(CO)_{16}^{2-}$ under the conditions for conversion of $Os_6(CO)_{18}^{2-}$ to $Os_{10}C(CO)_{24}^{2-}$.

Introduction

Most of the known large carbonyl clusters of ruthenium and osmium have been prepared via the pyrolysis of $M_3(CO)_{12}$ (M = Ru, Os) or its derivatives (e.g.,[1] eq 1).[1-5] This method

$$Os_3(CO)_{12} \xrightarrow[\text{sealed tube}]{210\ °C} Os_5(CO)_{16} + Os_6(CO)_{18} + Os_7(CO)_{21} + Os_8(CO)_{23} \qquad (1)$$

usually affords a mixture of products, frequently of similar solubility properties, so that quantitative separation of various species is tedious. The difficulty in obtaining pure compounds in sufficient quantities tends to limit the possibilities for further examination of their reactivity.

Chini and co-workers have shown how "redox condensation" reactions (e.g., eq 2) may allow the systematic construction

$$Rh_6(CO)_{15}^{2-} + Rh(CO)_4^{-} \rightarrow Rh_7(CO)_{16}^{3-} + 3CO \qquad (2)$$

of large anionic clusters of metals in the cobalt and nickel triads.[6,7] Some recent reports suggest that the direct formation of anionic clusters may be relatively selective for the iron subgroup metals also. Thus, treatment of $Ru_3(CO)_{12}$ in tetrahydrofuran with aqueous potassium hydroxide leads to $Ru_6(CO)_{18}^{2-}$ in 80% yield,[8] and reducing $Ru_3(CO)_{12}$ with $Mn(CO)_5^-$ in refluxing diglyme gives $Ru_6C(CO)_{16}^{2-}$ in 60% yield.[9] The latter synthesis is closely related to that reported for $Fe_6C(CO)_{16}^{2-}$, which involves the reduction of $Fe(CO)_5$ with $Mn(CO)_5^-$ or $V(CO)_6^-$.[10] It was recently shown, however, that $Fe_6C(CO)_{16}^{2-}$ is generated cleanly by the condensation of $Fe(CO)_5$ with a stoichiometric amount of $Fe(CO)_4^{2-}$ (eq 3),[11] thereby avoiding the use of a different metal. Fur-

$$5Fe(CO)_5 + Fe(CO)_4^{2-} \xrightarrow[150\text{–}160\ °C]{\text{diglyme}} Fe_6C(CO)_{16}^{2-} \xrightarrow{Fe^{3+}} \underset{60\%}{Fe_5C(CO)_{15}} \qquad (3)$$

thermore, since $Fe(CO)_4^{2-}$ also is formed from $Fe(CO)_5$ by treatment with sodium,[12] this result suggests the use of sodium alone as the reducing agent. We have applied this idea to the preparation of large anionic clusters from $M_3(CO)_{12}$ (M = Ru, Os) and have developed systematic, efficient syntheses of $Ru_6(CO)_{18}^{2-}$, $Ru_6C(CO)_{16}^{2-}$, $Os_6(CO)_{18}^{2-}$, and $Os_{10}C(CO)_{24}^{2-}$. Oxidation of the anions $Ru_6C(CO)_{16}^{2-}$ and $Os_6(CO)_{18}^{2-}$ with ferric chloride provides the corresponding neutral compounds $Ru_6C(CO)_{17}$ and $Os_6(CO)_{18}$ in good yields. Proceeding similarly, we have isolated and characterized the new compound $Os_6C(CO)_{17}$ in order to provide evidence for the formation of $Os_6C(CO)_{16}^{2-}$ under the conditions that cause the conversion of $Os_6(CO)_{18}^{2-}$ to $Os_{10}C(CO)_{24}^{2-}$. The solid-state geometries established for the previously known compounds are shown in Figure 1.

Experimental Section

General Procedures. $Ru_3(CO)_{12}$[17] and $Os_3(CO)_{12}$[18] were prepared by using literature procedures. Sodium was used as a 40% dispersion in mineral oil (Alfa). Diethyl ether, diglyme, triglyme, tetraglyme, and tetrahydrofuran (THF) were freshly distilled from sodium/benzophenone ketyl before use. Diglyme and tetraglyme generally were dried a second time over active sodium/benzophenone and filtered directly into the reaction flask. Dichloromethane was dried by heating to reflux over phosphorus pentoxide and then distilled. Unless otherwise specified, all operations were carried out under a nitrogen atmosphere with the use of standard techniques.

Reactions were monitored by observing the infrared spectra of reaction mixtures in the 2200–1600-cm^{-1} region. Infrared spectra were recorded on a Perkin-Elmer Model 281B spectrophotometer and calibrated with cyclohexane (2138.5 cm^{-1}) and polystyrene. Mass

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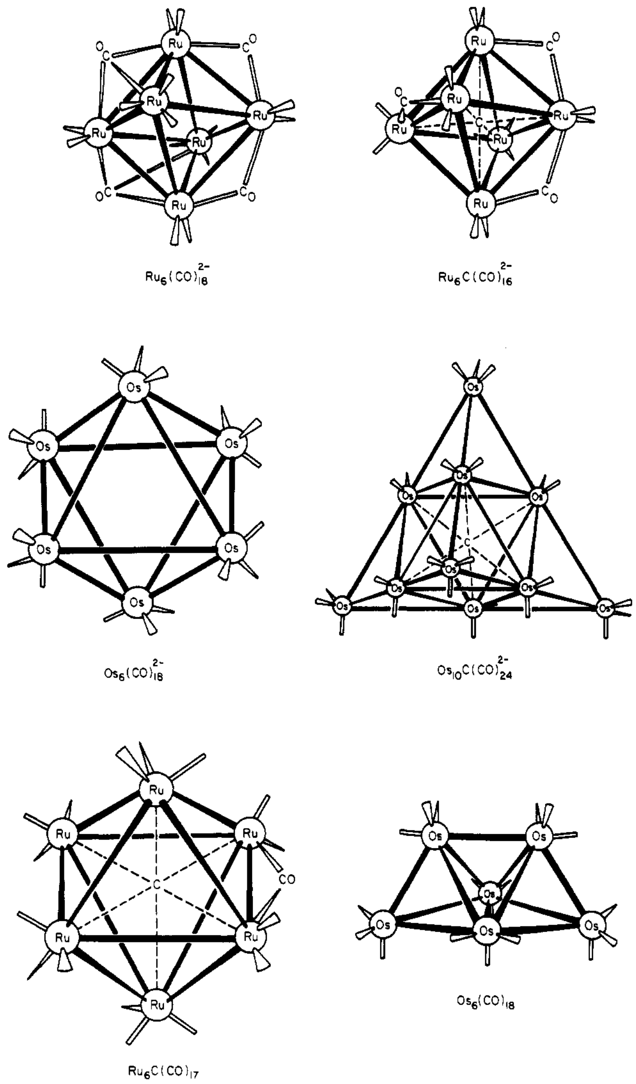

Figure 1. Geometries of six large ruthenium and osmium clusters as established by X-ray diffraction studies: $Ru_6(CO)_{18}^{2-}$,[13] $Ru_6C(CO)_{16}^{2-}$,[9] $Os_6(CO)_{18}^{2-}$,[14] $Os_{10}C(CO)_{24}^{2-}$,[3] $Ru_6C(CO)_{17}$,[15] and $Os_6(CO)_{18}$.[16]

spectra were obtained with electron-impact ionization (70 eV) on a Varian MAT CH-5 mass spectrometer by Dr. Richard Milberg. Simulated isotopic multiplets were calculated with the aid of the computer program MASPAN, written by Dr. M. A. Andrews in association with Professor H. D. Kaesz.[19] Elemental analyses were performed by the microanalysis laboratory of the School of Chemical Sciences.

Preparation of $[(Ph_3P)_2N]_2[Ru_6(CO)_{18}]$. To an oven-dried 50-mL three-necked flask were added sodium dispersion (38 mg, 0.66 mmol of Na) and a magnetic stir bar. This flask was then equipped with a serum rubber stopper, a reflux condenser, and a nitrogen inlet. Freshly distilled THF (25 mL) was introduced by means of a cannula through the serum stopper. The stopper was briefly removed, and $Ru_3(CO)_{12}$ (406 mg, 0.64 mmol) was added against a nitrogen flow. This mixture was refluxed for 5 h, yielding a dark brown solution. The cooled solution was added to 20 mL of aqueous $(Ph_3P)_2NCl$ (400 mg, 0.70 mmol). Upon partial evaporation of the solvent, a dark brown precipitate formed, which was collected and washed first with warm water (50 mL) and then with 2-propanol (20 mL) in order to remove excess $(Ph_3P)_2NCl$. Crystallization of the residue from dichloromethane/methanol by solvent diffusion at room temperature produced dark brown crystals of $[(Ph_3P)_2N]_2[Ru_6(CO)_{18}]$ (533 mg, 0.25 mmol, 78%). Anal. Calcd for $C_{90}H_{60}N_2O_{18}P_4Ru_6$: C, 49.41; H, 2.76; N, 1.28; P, 5.66. Found: C, 49.74; H, 2.74; N, 1.34; P, 5.71. IR (CH_2Cl_2): ν_{CO} 2001 (s), 1986 (s, br), 1933 (m), 1758 (w, br) cm^{-1}; lit.[8] ν_{CO} 2001 (s), 1981 (s), 1924 (w), 1749 (w, br) cm^{-1}. $Ru_6(CO)_{18}^{2-}$ was also isolated as the Et_4N^+ salt by following an analogous procedure.

Preparation of $[Et_4N]_2[Ru_6C(CO)_{16}]$. To an oven-dried 50-mL three-necked flask containing sodium dispersion (47 mg, 0.82 mmol of Na) were added dry diglyme (20 mL) and $Ru_3(CO)_{12}$ (508 mg, 0.79 mmol). The brown-red mixture was refluxed for 12 h and then was cooled and added to 80 mL of aqueous Et_4NCl (2.0 g, 12.0 mmol). A red precipitate formed after holding the mixture in an ice–water bath for several hours. This precipitate was filtered, washed with water (100 mL), and then dried in vacuo (yield: 472 mg, 0.36 mmol, 90%). The IR spectrum of this solid indicated it to be pure $[Et_4N]_2[Ru_6C(CO)_{16}]$. Red crystals were obtained from dichloromethane at −78 °C (93% recovery). Anal. Calcd for $C_{33}H_{40}N_2O_{16}Ru_6$: C, 29.86; H, 3.04; N, 2.11. Found: C, 29.73; H, 3.06; N, 1.97. IR (CH_2Cl_2): ν_{CO} 2030 (w), 1978 (s), 1952 (sh, m), 1918 (m), 1820 (sh, m), 1780 (m) cm^{-1}; lit.[9] ν_{CO} 2048 (w), 2032 (w), 1977 (s), 1952 (sh, m), 1918 (m), 1820 (sh, m), 1780 (m) cm^{-1}.

Pyrolysis of $[(Ph_3P)_2N]_2[Ru_6(CO)_{18}]$. $[(Ph_3P)_2N]_2[Ru_6(CO)_{18}]$ (90 mg, 0.041 mmol) was dissolved in diglyme (30 mL) and heated under reflux. The initially dark brown solution turned bright red after 1 h at 162 °C, indicating formation of $Ru_6C(CO)_{16}^{2-}$. Heating was stopped, and the solvent was removed under reduced pressure. The dry residue was characterized as pure $[(Ph_3P)_2N]_2[Ru_6C(CO)_{16}]$ (84 mg, 0.039 mmol, 96%) by its IR spectrum. Crystals of the $(Ph_3P)_2N^+$ salt were obtained from dichloromethane/diethyl ether by solvent diffusion at −20 °C. Anal. Calcd for $C_{89}H_{60}N_2O_{16}P_4Ru_6$: C, 49.86; H, 2.82; N, 1.31; P, 5.78. Found: C, 49.63; H, 2.83; N, 1.40; P, 5.94. $[Et_4N]_2[Ru_6(CO)_{18}]$ was converted quantitatively to $[Et_4N]_2[Ru_6C(CO)_{16}]$ by an analogous procedure.

Preparation of $Ru_6C(CO)_{17}$. To a 250-mL three-necked flask equipped with a dropping funnel, reflux condenser, and carbon monoxide inlet tube were added dichloromethane (200 mL) and $[Et_4N]_2[Ru_6C(CO)_{16}]$ (100 mg, 0.075 mmol). This mixture was stirred rapidly at 0 °C under carbon monoxide flush for 20 min. The dropping funnel was charged with a 10% aqueous solution (10 mL) of ferric chloride, which was added dropwise to the flask over a 10-min period. After vigorous stirring for 15 min, carbon monoxide bubbling was stopped and the mixture was allowed to warm to room temperature in air. The red dichloromethane layer was separated from the aqueous layer, dried over anhydrous magnesium sulfate, and rotary evaporated to yield a red solid. Crystallization of this residue from dichloromethane at −20 °C produced red crystals of $Ru_6C(CO)_{17}$ (56 mg, 0.051 mmol, 68%). Mass spectrum (^{102}Ru): m/z 1160 (M$^+$) as well as $1160 - 28x$, $x = 1$–17 (M$^+ - x$CO). Anal. Calcd for $C_{18}O_{17}Ru_6$: C, 19.75; Ru, 55.40. Found: C, 19.78; Ru, 55.61. IR (cyclohexane): ν_{CO} 2065 (s), 2046 (s), 2005 (w), 1995 (w), 1952 (w, br), 1851 (w) cm^{-1}; lit.[20] ν_{CO} 2064 (s), 2049 (s), 2007 (w), 1993 (w), 1958 (w), 1854 (w, br) cm^{-1}.

Preparation of $[Et_4N]_2[Os_6(CO)_{18}]$. A mixture of $Os_3(CO)_{12}$ (200 mg, 0.22 mmol) and sodium dispersion (15 mg, 0.26 mmol of Na) in diglyme (30 mL) was heated under reflux for 12 h, yielding an orange-brown solution. The solution was cooled and then added to 60 mL of aqueous Et_4NCl (600 mg, 3.6 mmol). The resulting mixture was held at 0 °C overnight in order to complete precipitation. The orange-brown solid was collected by filtration, washed with water (100 mL), and dried in vacuo. Deep orange crystals of $[Et_4N]_2[Os_6(CO)_{18}]$ were obtained from THF/diethyl ether by solvent diffusion at −20 °C (137 mg, 0.072 mmol, 65%). Anal. Calcd for $C_{34}H_{40}N_2O_{18}Os_6$: C, 21.43; H, 2.12; N, 1.47. Found: C, 21.56; H, 2.05; N, 1.63. IR (acetone): ν_{CO} 1997 (vs), 1915 (w) cm^{-1}; lit.[21] ν_{CO} 1992 (vs), 1915 (w) cm^{-1}. $Os_6(CO)_{18}^{2-}$ was also isolated as the $[(Ph_3P)_2N]^+$ salt by an analogous procedure.

Preparation of $Os_6(CO)_{18}$. To a 100-mL three-necked flask equipped with a dropping funnel, reflux condenser, and nitrogen inlet were added dichloromethane (70 mL) and $[Et_4N]_2[Os_6(CO)_{18}]$ (30 mg, 0.016 mmol). The dropping funnel was charged with a 10% aqueous solution (5 mL) of ferric chloride, which was added dropwise to the slurry over a 5-min period. After the mixture was stirred vigorously for 10 min, the brown dichloromethane layer was separated from the aqueous layer in air, dried over anhydrous magnesium sulfate, and concentrated to a small volume (<1 mL). Preparative-scale TLC

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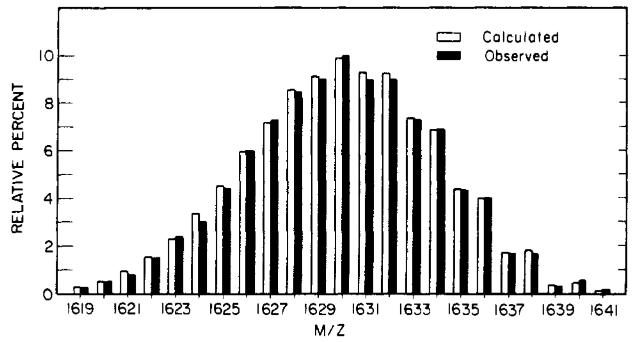

Figure 2. Comparison of observed and calculated isotope patterns for the molecular ion of $Os_6C(CO)_{17}$. The ion $^{192}Os_6{}^{12}C(^{12}C^{16}O)_{17}{}^+$ has *m/z* 1640.

(silica gel/hexanes) afforded only one significant product, a brown band identified as $Os_6(CO)_{18}$ (23 mg, 0.014 mmol, 88%). Mass spectrum (^{192}Os): *m/z* 1656 (M^+) as well as $1656 - 28x$, $x = 1$–18 ($M^+ - x$CO). IR (cyclohexane): ν_{CO} 2075 (s), 2063 (s), 2038 (s), 2031 (m, sh), 2001 (w), 1960 (w) cm^{-1}; lit.[21] ν_{CO} 2075 (vs), 2061 (vs), 2037 (s), 2029 (ms, sh), 1999 (w), 1958 (w) cm^{-1}. When this reaction was carried out under a carbon monoxide atmosphere, $Os_6(CO)_{18}$ was obtained in similar yield.

Isolation of $Os_6C(CO)_{17}$. A mixture of $Os_3(CO)_{12}$ (195 mg, 0.22 mmol) and sodium dispersion (14.2 mg, 0.24 mmol of Na) in diglyme (30 mL) was heated under reflux for 140 h, affording a dark brown solution. The solution was cooled to room temperature and added to 80 mL of aqueous Et_4NCl (1.0 g, 6.0 mmol). The resulting mixture was held at 0 °C overnight to complete precipitation. The brown precipitate was isolated by filtration, washed with water, and dried. The dry solid was placed in a 250-mL three-necked flask equipped with a dropping funnel, reflux condenser, and carbon monoxide inlet tube. Dichloromethane (200 mL) was introduced into the flask, and the resulting slurry was stirred vigorously under carbon monoxide flush. The dropping funnel was charged with a 10% aqueous solution (20 mL) of ferric chloride, which was then added dropwise to the flask. The mixture was stirred for 2 h; then the brown dichloromethane layer was separated from the aqueous layer. The dichloromethane solution was concentrated to a small volume (<1 mL), and its components were separated by preparative-scale TLC (silica gel/hexanes). Among other unidentified products[22] were found brown $Os_6(CO)_{18}$ (35 mg, 0.021 mmol, 20%) and purple $Os_6C(CO)_{17}$ (3 mg, 0.002 mmol, 2%). **$Os_6C(CO)_{17}$:** Mass spectrum (^{192}Os): *m/z* 1640 (M^+) as well as $1640 - 28x$, $x = 1$–17 ($M^+ - x$CO). The isotopic pattern for the molecular ion is shown in Figure 2. IR (cyclohexane): ν_{CO} 2070 (s), 2052 (s), 2030 (w), 2016 (w), 2004 (w), 2000 (w), 1993 (w) cm^{-1}.

Preparation of $[Et_4N]_2[Os_{10}C(CO)_{24}]$. A solution of $Os_3(CO)_{12}$ (190 mg, 0.21 mmol) and sodium dispersion (14.6 mg, 0.25 mmol of Na) in tetraglyme (25 mL) was heated at 230 °C for 70 h. The reaction mixture changed in color sequentially from orange to light red to dark red-brown. The characteristic strong infrared band of $Os_6(CO)_{18}{}^{2-}$ at 1997 cm^{-1} was observed after 2 h; this was slowly replaced by bands at 2033 and 1992 cm^{-1} due to $Os_{10}C(CO)_{24}{}^{2-}$. The cooled reaction mixture was added to 70 mL of aqueous Et_4NCl (800 mg, 4.8 mmol). This mixture was held at 0 °C for 5 h; then the dark red-brown precipitate was collected, washed with water, and dried in vacuo. Air-stable crystals of $[Et_4N]_2[Os_{10}C(CO)_{24}]$ (115 mg, 0.04 mmol, 63%) were obtained from dichloromethane/methanol by solvent diffusion at -20 °C. Anal. Calcd for $C_{41}H_{40}N_2O_{24}Os_{10}$: C, 17.30; H, 1.42; N, 0.98. Found: C, 17.36; H, 1.45; N, 1.22. IR (acetone): ν_{CO} 2034 (s), 1992 (s) cm^{-1}; lit.[3] ν_{CO} 2033 (s), 1986 (s) cm^{-1}.

When a stoichiometric ratio of $Os_3(CO)_{12}$:sodium (3.3:2) was used in this synthesis, the major product obtained was again the decaosmium carbide cluster, but in comparable yield (68%). Infrared spectra of the reaction mixture indicated the intermediate formation of $Os_6(CO)_{18}{}^{2-}$, as in the reaction described above. $Os_{10}C(CO)_{24}{}^{2-}$ was isolated also as the Ph_4As^+ and $(Ph_3P)_2N^+$ salts by analogous procedures.

Pyrolysis of $[Et_4N]_2[Os_6(CO)_{18}]$. $[Et_4N]_2[Os_6(CO)_{18}]$ (38 mg, 0.02 mmol) was dissolved in triglyme (20 mL) and heated under reflux for 24 h.[23] The resulting mixture was cooled, and a small amount of black intractable powder was filtered from the red-brown solution. Water (80 mL) was added, and the mixture was allowed to stand at 0 °C overnight. Crystallization of the isolated precipitate afforded pure $[Et_4N]_2[Os_{10}C(CO)_{24}]$ (12 mg, 0.0042 mmol, 35%). This filtrate was evaporated to dryness. Oxidation of the residue with a 10% aqueous solution of ferric chloride in a carbon monoxide atmosphere followed by TLC afforded a distribution of products similar to those observed during the isolation of $Os_6C(CO)_{17}$.

Results and Discussion

The reaction of $Ru_3(CO)_{12}$ with $Mn(CO)_5{}^-$ in refluxing tetrahydrofuran affords a complex mixture from which $Ru_6(CO)_{18}{}^{2-}$ was isolated in only 11% yield.[24] We have found that replacing the manganese complex by dispersed sodium under the same conditions leads to a relatively clean reaction and that pure salts of the dianion are obtained in about 80% yield (eq 4). This procedure provides an alternative to that

$$2Ru_3(CO)_{12} + 2Na \xrightarrow[65\ °C]{THF} Ru_6(CO)_{18}{}^{2-} \qquad (4)$$

employing aqueous potassium hydroxide as the reducing agent, for which an 80% yield also was reported.[8] The selective formation of a Ru_6 compound from Ru_3 precursor raises interesting mechanistic questions, but rather little information is yet available to provide answers. In view of the strongly basic conditions involved in both syntheses and the demonstration that $HRu_6(CO)_{18}{}^-$ does not readily deprotonate,[8] it seems unlikely that $HRu_3(CO)_{11}{}^-$ is an important intermediate. On the other hand, the recently reported[25] species $Ru_3(CO)_{11}{}^{2-}$ seems probable. The interaction of $Ru_3(CO)_{11}{}^{2-}$ and $Ru_3(CO)_{12}$ to form $Ru_6(CO)_{18}{}^{2-}$ would be an example of a "redox condensation" reaction as defined by Chini.[6,7]

Treatment of $Ru_3(CO)_{12}$ with sodium but raising the reaction temperature to 162 °C (refluxing diglyme) provides a direct route to the carbide cluster $Ru_6C(CO)_{16}{}^{2-}$ in better yield (80–90%) than that obtained by using $Mn(CO)_5{}^-$ as reductant.[9] Bradley and co-workers[9] proposed that $Ru_6(CO)_{18}{}^{2-}$ was an intermediate in the formation of $Ru_6C(CO)_{16}{}^{2-}$, and we have found that pyrolysis of the former in refluxing diglyme converts it quantitatively to the latter (eq 5).[26] Presumably

$$Ru_6(CO)_{18}{}^{2-} \xrightarrow[162\ °C]{diglyme} Ru_6C(CO)_{16}{}^{2-} + CO_2(?) \qquad (5)$$

the oxygen atom is removed as carbon dioxide. Since this reaction is exceptionally clean and involves the formation of an encapsulated carbide cluster from a noncarbide precursor of the same nuclearity, possible mechanistic pathways are being probed in ongoing work (vide infra).

Higher temperatures are required for the formation of large osmium clusters, but the interaction of $Os_3(CO)_{12}$ with sodium in refluxing diglyme provides an efficient preparation of $Os_6(CO)_{18}{}^{2-}$, crystalline salts of which were isolated in 65% yield. This complex was prepared previously by the reduction of $Os_6(CO)_{18}$,[27] which is the major product in the pyrolysis of $Os_3(CO)_{12}$.[1] It was reported that $Os_6(CO)_{18}{}^{2-}$ is oxidized by iodine to $Os_6(CO)_{18}$,[27] and we have found that aqueous

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[22] Thin-layer chromatographic methods have not proved adequate to separate these compounds for infrared or mass spectroscopic analyses.

[23] The reaction was terminated at this time to avoid product decomposition as evidenced by osmium mirror deposition on the reaction flask.

[24] Eady, C. R.; Johnson, B. F. G.; Lewis, J.; Malatesta, M. C.; Machin, P.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1976**, 945.

[25] Nagel, C. C.; Bricker, J. C.; Alway, D. G.; Shore, S. G. *J. Organomet. Chem.* **1981**, *219*, C9. The combination of $Ru_3(CO)_{12}$ and potassium in a 1:1 ratio provides $Ru_6(CO)_{18}{}^{2-}$ in ca. 80% yield: Shore, S. G., personal communication.

[26] This transformation has been observed also at Union Carbide: Dombek, B. D., personal communication.

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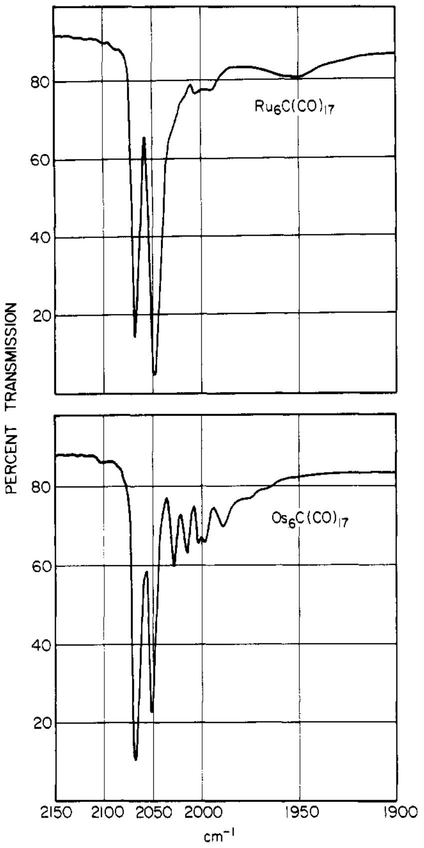


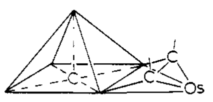
Figure 3. Infrared spectra of $Ru_6C(CO)_{17}$ and $Os_6C(CO)_{17}$ (cyclohexane solutions).

ferric chloride likewise affords the neutral compound in high yield (eq 6). Pyrolysis of $Os_6(CO)_{18}^{2-}$ in refluxing triglyme (216 °C) did not produce the anticipated hexanuclear carbide cluster $Os_6C(CO)_{16}^{2-}$ but instead gave $Os_{10}C(CO)_{24}^{2-}$ as the major product. The decanuclear carbide cluster also is formed from the direct combination of $Os_3(CO)_{12}$ and sodium in tetraglyme (230–260 °C). Comparable yields (60–70%) of isolated materials were obtained whether the Os_3:Na ratio was stoichiometric (1.67:1) or the same as in the synthesis of $Os_6(CO)_{18}^{2-}$ (1:1). However, in either case infrared spectra of the reaction mixtures indicate initial formation of $Os_6(CO)_{18}^{2-}$, which is then transformed into $Os_{10}C(CO)_{24}^{2-}$ after prolonged heating. The previous preparation of $Os_{10}C(CO)_{24}^{2-}$ was by the pyrolysis of solid $Os_3(CO)_{11}(NC_5H_5)$ with a reported yield of 80%.[3] Since the pyridine derivative is prepared in two steps from $Os_3(CO)_{12}$,[28] overall yields of the decanuclear cluster are likely to be comparable for the two alternative procedures.

$$2Os_3(CO)_{12} + 2Na \xrightarrow[162\ °C]{diglyme} Os_6(CO)_{18}^{2-} \xrightarrow{Fe^{3+}} Os_6(CO)_{18} \qquad (6)$$

The formation of $Os_{10}C(CO)_{24}^{2-}$ instead of $Os_6C(CO)_{16}^{2-}$ from the pyrolysis of $Os_6(CO)_{18}^{2-}$ at 216 °C suggested that, if $Os_6C(CO)_{16}^{2-}$ is generated as an intermediate, under the reaction conditions it is easily converted to the thermodynamically more stable $Os_{10}C(CO)_{24}^{2-}$. Ferric chloride oxidation (under CO) of a reaction mixture resulting from the prolonged interaction of $Os_3(CO)_{12}$ and sodium in refluxing diglyme (162 °C) gives a complex mixture of apparently neutral osmium clusters, as indicated by multiple TLC bands. However, a bright purple band could be separated and was isolated as a purple solid in ca. 2% yield. This compound is formulated as $Os_6C(CO)_{17}$ on the basis of its mass spectrum, which shows the appropriate isotope multiplet for the molecular ion (M^+; see Figure 2) as well as multiplets for the ions $[M - xCO]^+$, $x = 1$–17. Since $Ru_6C(CO)_{17}$ is generated in good yield by analogous oxidation of $Ru_6C(CO)_{16}^{2-}$, the isolation of $Os_6C(CO)_{17}$ provides evidence for the formation of $Os_6C(CO)_{16}^{2-}$ under the conditions appropriate for the conversion of $Os_6(CO)_{18}^{2-}$ to $Os_{10}C(CO)_{24}^{2-}$. At this time the very small amounts of $Os_6C(CO)_{17}$ available preclude an attempt to reduce it to $Os_6C(CO)_{16}^{2-}$ (cf. ref 29, $Ru_6C(CO)_{17}$ to $Ru_6C(CO)_{16}^{2-}$) in order to determine directly the stability of the latter.

The structure of $Os_6C(CO)_{17}$ is likely to be closely related to that of $Os_6C(CO)_{16}^{2-}$, since all of the known isoelectronic cluster pairs $M_n(CO)_x/M_n(CO)_{x-1}^{2-}$ display the same geometry for the metal framework, e.g., octahedral $Ru_6C(CO)_{17}/Ru_6C(CO)_{16}^{2-}$ (Figure 1). The IR (ν_{CO}) spectrum of $Os_6C(CO)_{17}$ is compared with that of $Ru_6C(CO)_{17}$ in Figure 3. No evidence for a bridging carbonyl is seen in the spectrum of the osmium cluster, but otherwise few structural deductions can be drawn. Lewis and co-workers[14] have pointed out that a capped-square-pyramidal geometry and an octahedral geometry have the same number of framework bonding electrons (Wade-Mingos theory). $H_2Os_6(CO)_{18}$[14] adopts the former structure, whereas $H_2Ru_6(CO)_{18}$[30] displays the latter. Also relevant is the structure of $Os_6C(CO)_{16}(C_2Me_2)$,[31] which shows a square-pyramidal Os_5C core (see **1**). These examples suggest that $Os_6C(CO)_{17}/Os_6C(CO)_{16}^{2-}$ may prefer a similar capped structure (see **2**) rather than the isoelectronic octahedral structure (**3**). This possibility is attractive in the sense that **2**, with an "exposed" carbon atom, seems likely to be closer to the intermediates actually involved in the process of splitting a carbonyl C–O bond. Furthermore, such a structure may be relatively susceptible to capping reactions, culminating in the fully capped and very stable $Os_{10}C(CO)_{24}^{2-}$. Structural and mechanistic studies are in progress in order to provide tests for these speculations.



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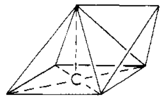

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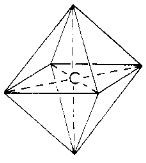

3

Conclusions

The preparations of $Ru_6(CO)_{18}^{2-}$ and $Os_6(CO)_{18}^{2-}$ reported here appear to be directly analogous to Chini's redox condensation procedures.[6,7] Pyrolysis of these anionic clusters generates anionic carbide clusters in reactions that are generally more selective than pyrolysis of neutral carbonyl clusters. Analogous to this latter step is the recent preparation of $Co_{11}C_2(CO)_{22}^{3-}$ and $Co_{13}C_2(CO)_{24}^{4-}$ from heating $Co_6C(CO)_{15}^{2-}$ in diglyme.[32] We are currently exploring the use of these relatively straightforward procedures for the preparation of large anionic carbonyl clusters with other transition metals.[33]

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Note Added in Proof. The evolution of carbon dioxide in the transformation of $Ru_6(CO)_{18}^{2-}$ to $Ru_6C(CO)_{16}^{2-}$ (eq 5) has been confirmed by trapping as barium carbonate (82% yield).

Registry No. $[(Ph_3P)_2N]_2[Ru_6(CO)_{18}]$, 62501-17-1; $[Et_4N]_2[Ru_6C(CO)_{16}]$, 73413-28-2; $[(Ph_3P)_2N]_2[Ru_6C(CO)_{16}]$, 73413-27-1; $[Et_4N]_2[Ru_6(CO)_{18}]$, 82639-14-3; $Ru_6C(CO)_{17}$, 27475-39-4; $[Et_4N]_2[Os_6(CO)_{18}]$, 82639-15-4; $Os_6(CO)_{18}$, 59069-01-1; $Os_6C(CO)_{17}$, 82706-16-9; $[Et_4N]_2[Os_{10}C(CO)_{24}]$, 82639-16-5; Na, 7440-23-5; $Ru_3(CO)_{12}$, 15243-33-1; $FeCl_3$, 7705-08-0; $Os_3(CO)_{12}$, 15696-40-9.

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Coordination Intercalation Reactions of the Layered Compounds $VOPO_4$ and $VOAsO_4$ with Pyridine

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Coordination intercalation compounds of the layered mixed oxides $VOPO_4$ and $VOAsO_4$ with pyridine and 4-substituted pyridines have been obtained. With pyridine, the tetragonal phases $VOPO_4(py)$ (a = 6.207 (1), c = 9.589 (2) Å) and $VOAsO_4(py)$ (a = 6.403 (1), c = 9.661 (1) Å) are formed. The lattice constants and infrared spectra show that pyridine is coordinated to vanadium and is perpendicular to the oxide layers. Little or no reduction of V^{5+} occurs, and the host layers are preserved on reaction. $VOPO_4$ also reacts with 4-phenylpyridine and 4,4′-bipyridine, although the reactions are slower and the products less crystalline than in the pyridine case.

Introduction

Intercalation reactions of neutral host lattices usually occur via electron transfer between the guest species and the host lattice. The reaction mechanism is well established for the intercalation chemistry of the transition-metal dichalcogenides with alkali metals[1] and organometallic compounds.[2] Formation of the "neutral" organic intercalation compounds such as $TaS_2(py)_{1/2}$ has also been shown to involve reduction of the host lattice and cointercalation of both neutral and protonated pyridine.[3] In contrast, we have shown recently[4] that molybdenum trioxide reacts with pyridine and 4,4′-bipyridine under anhydrous conditions to form layered compounds without reduction of Mo(VI). In these compounds the pyridine molecules are coordinated directly to molybdenum atoms, and the structure is built of layers of composition $MoO_3(py)$ or $MoO_3(4,4'\text{-bpy})_{1/2}$. These new compounds can be envisioned as resulting from intercalation of the layered hydrate $MoO_3{\cdot}H_2O$, which has a similar structure.[5] The coordinated water molecule in $MoO_3{\cdot}H_2O$ is replaced by the stronger donor ligand pyridine without major disruption of the host structure. In fact, $WO_3(py)$ was prepared by reaction of $WO_3{\cdot}H_2O$ with pyridine. These results for MoO_3 and WO_3 suggest the possibility of a broader class of coordination intercalation reactions for layered compounds that contain metal centers either with vacant coordination sites or with easily replaceable ligands. The layered compounds vanadyl phosphate and vanadyl arsenate satisfy these criteria and form coordination intercalation compounds. In this paper, we report the reactions of these host lattices with pyridine.

Table I. Lattice Constants of Tetragonal $MOXO_4$ Compounds

compd	a, Å	c, Å	ref
$VOPO_4$	6.014 (7)	4.434 (2)[a]	6
$VOAsO_4$	6.33	4.18	12
$NbOPO_4$	6.387 (1)	4.104 (1)	7
$NbOAsO_4$	6.57	4.08	13
$TaOPO_4$	6.425 (3)	4.001 (3)	8
$VOSO_4$	6.261 (3)	4.101 (3)	11
$VOMoO_4$	6.6078 (2)	4.264 (3)	9
$MoOPO_4$	6.1768 (3)	4.2932 (3)	10

[a] Samples of $VOPO_4$ prepared by other workers using slightly different methods were reported to have lattice parameters a = 6.20 and c = 4.11 Å.[14] Our values agree with the latter.

Vanadyl phosphate, $VOPO_4$, has two well-characterized polymorphs,[6] one of which (α-$VOPO_4$) is layered and is isostructural with a number of other compounds including $NbOPO_4$,[7] $TaOPO_4$,[8] $VOMoO_4$,[9] $MoOPO_4$,[10] and α-$VOSO_4$.[11] X-ray powder diffraction data and chemical behavior suggest that $VOAsO_4$[12] and $NbOAsO_4$[13] also have similar structures. The structure of α-$VOPO_4$ is tetragonal with space group *P4/n*. The *ab* plane is made up of octahedra and tetrahedra that are linked through corner sharing, as shown in Figure 1. Each octahedron is joined to four different tetrahedra. The tetragonal layers are joined along the *c* axis by corner sharing of the remaining two trans vertices of the octahedron, as shown in Figure 2. The six oxygen atoms around the vanadium form

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