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Multiply Bonded Octahalodiosmate(III) Anions. 5.[1] Cleavage of the Electron-Rich $\text{Os}\equiv\text{Os}$ Bond by Carbon Monoxide and Isocyanide Ligands

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The triply bonded diosmium(III) complexes $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{X}_8$ (X = Cl, Br) react with isocyanide ligands RNC (R = CHMe_2, CMe_3, xylyl, mesityl) in ethanol at room temperature to afford the 17-electron, paramagnetic, mononuclear osmium(III) species $(n\text{-Bu}_4\text{N})[\text{OsX}_4(\text{CNR})_2]$ in very high yield. A similar reaction with carbon monoxide in hot ethanol gives $(n\text{-Bu}_4\text{N})[\text{OsX}_4(\text{CO})(\text{EtOH})]$, which upon reaction with other monodentate donors loses ethanol and forms $(n\text{-Bu}_4\text{N})[\text{OsX}_4(\text{CO})\text{L}]$, where L = DMSO, THF, CH_3CN, py, PPh_3, PEt_3, or xylNC. The spectroscopic and electrochemical properties of these complexes, as well as single-crystal X-ray structural studies on $(n\text{-Bu}_4\text{N})[\text{OsCl}_4(\text{CNxyl})_2]$ and a crystal of composition $(n\text{-Bu}_4\text{N})[\text{OsCl}_{4-x}\text{Br}_x(\text{CO})(\text{DMSO})]$ ($x \simeq 1.32$) have shown that the anions possess *trans*-$[\text{OsX}_4(\text{CNR})_2]^-$ and *trans*-$[\text{OsX}_4(\text{CO})\text{L}]^-$ geometries. Crystal data for $(n\text{-Bu}_4\text{N})[\text{OsCl}_4(\text{CNxyl})_2]$ at 20 °C are as follows: monoclinic space group $P2_1/n$, $a = 11.6698$ (7) Å, $b = 31.786$ (3) Å, $c = 21.484$ (2) Å, $\beta = 102.111$ (5)°, $V = 7791$ (2) Å^3, and $Z = 2$. The structure was refined to $R = 0.047$ ($R_w = 0.056$) for 4658 data with $I > 3.0\sigma(I)$. Crystal data for $(n\text{-Bu}_4\text{N})[\text{OsCl}_{2.68}\text{Br}_{1.32}(\text{CO})(\text{DMSO})]$ at 20 °C: triclinic space group $P\bar{1}$, $a = 9.026$ (2) Å, $b = 10.479$ (1) Å, $c = 16.328$ (2) Å, $\alpha = 95.35$ (1)°, $\beta = 94.68$ (2)°, $\gamma = 110.63$ (1)°, $V = 1428.2$ (8) Å^3, and $Z = 2$. The structure was refined to $R = 0.041$ ($R_w = 0.062$) for 3188 data with $I > 3.0\sigma(I)$.

Introduction

The cleavage of quadruply bonded dimolybdenum(II) and dirhenium(III) complexes, as well as certain triply bonded dirhenium(II) species, by the π-acceptor CO, NO, and isocyanide ligands provides an excellent synthetic route to many mononuclear complexes.[2-4] In extending this synthetic strategy to diruthenium and diosmium compounds, we found[5] that the diruthenium(II,III) and diosmium(III) acetates $\text{Ru}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}$ and $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ react with alkyl isocyanides RNC (R = CHMe_2, CMe_3, C_6H_{11}) to give the homoleptic metal(II) complexes $[\text{M}(\text{CNR})_6](\text{PF}_6)_2$. In the case of the diamagnetic $[\text{Os}_2\text{X}_8]^{2-}$ anions (X = Cl, Br),[6-9] which like dirhenium(II) complexes contain an electron-rich triple bond, we have previously shown that the $\text{Os}\equiv\text{Os}$ bond readily undergoes fission in the presence of phosphine and heterocyclic tertiary amine ligands.[1] We now describe the reactions of the salts $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{X}_8$ (X = Cl, Br) with carbon monoxide and alkyl and aryl isocyanides to afford compounds of the types $(n\text{-Bu}_4\text{N})[\text{OsX}_4(\text{CO})\text{L}]$, where L represents a monodentate donor, and $(n\text{-Bu}_4\text{N})[\text{OsX}_4(\text{CNR})_2]$. These reactions proceed in high yield and provide the most convenient and general route to this class of paramagnetic 17-electron osmium(III) compounds.

Experimental Section

Starting Materials and Procedures. The complexes $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Br}_8$ and $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ were prepared by using procedures described previously.[7,8,10] The complex $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Cl}_8$ was prepared by a modification of the existing procedure.[7,8] A sample of $\text{Os}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ (0.100 g, 0.14 mmol) was suspended in ethanol, which had been chilled in an ice bath and saturated with gaseous HCl. The mixture was refluxed for 1.5 h, and the green solution that resulted was treated with an ethanol solution that contained an excess of $n\text{-Bu}_4\text{NPF}_6$ (0.200 g, 0.410 mmol). The solvent was then removed on a rotary evaporator, and the resulting green oil was dissolved in 20 mL of dichloromethane. An equal volume of ethanol was added, and then 60 mL of diethyl ether was carefully layered over the solution. A green microcrystalline product separated as the layers slowly diffused. This was filtered off, and the product was then washed with ethanol and diethyl ether and dried under vacuum; yield 0.165 g (96%). Its spectroscopic and electrochemical properties were identical with those reported previously.[7,8] Note that the use of $n\text{-Bu}_4\text{NPF}_6$ as the cation source in place of $n\text{-Bu}_4\text{NBr}$[7,8] prevents the possible partial substitution of bromide for chloride in the $[\text{Os}_2\text{Cl}_8]^{2-}$ anion. The absence of the PF_6^- anion in the product was confirmed by the absence of a ν(P-F) band at 840 cm^{-1}.

Xylyl isocyanide (2,6-dimethylphenyl isocyanide from Fluka AG) was used as a 1.0 M solution in toluene as was mesityl isocyanide (2,4,6-trimethylphenyl isocyanide). The latter isocyanide as well as isopropyl and *tert*-butyl isocyanide were prepared by the method of Weber et al.[11] All other reagents were obtained from various commercial sources and were used as received. Solvents were thoroughly purged with nitrogen gas prior to use. All syntheses were carried out under an atmosphere of nitrogen.

A. Synthesis of Complexes of the Type $(n\text{-Bu}_4\text{N})[\text{OsX}_4(\text{CNR})_2]$. (i) $(n\text{-Bu}_4\text{N})[\text{OsCl}_4(\text{CNCMe}_3)_2]$. A sample of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Cl}_8$ (0.200 g, 0.174 mmol) was suspended in 10 mL of ethanol and the mixture stirred for 5 min. To this slurry was added an excess of *tert*-butyl isocyanide (0.37 mL, 3.48 mmol), and stirring was continued at room temperature for an additional 1 h. The yellow solution that resulted was evaporated to dryness on a rotary evaporator. The residue was dissolved in a minimal amount of dichloromethane ($\simeq$5 mL) and filtered. Diethyl ether (20 mL) was added to the filtrate, and the layers were allowed to diffuse together slowly overnight. During this period the complex precipitated as a mustard yellow powder and was recovered by filtration, washed with toluene and diethyl ether, and dried under vacuum; yield 0.211 g (83%). Anal. Calcd for $\text{C}_{26}\text{H}_{54}\text{Cl}_4\text{N}_3\text{Os}$: C, 42.16; H, 7.41. Found: C, 41.72; H, 7.61.

A procedure similar to A(i) was used to prepare other chloro complexes of this type. The quantities of the $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Cl}_8$ and RNC reagents that were used and the product yields are given in order.

(ii) $(n\text{-Bu}_4\text{N})[\text{OsCl}_4(\text{CNCHMe}_2)_2]$: 0.100 g (0.087 mmol); 0.16 mL (1.7 mmol); yield 0.093 g (77%). Anal. Calcd for $\text{C}_{24}\text{H}_{50}\text{Cl}_4\text{N}_3\text{Os}$: C, 40.40; H, 7.08. Found: C, 37.36; H, 6.90.

(iii) $(n\text{-Bu}_4\text{N})[\text{OsCl}_4(\text{CNxyl})_2]$: 0.100 g (0.087 mmol); 1.8 mL of a 1.0 M solution in toluene (1.8 mmol); yield 0.117 g (82%). Anal. Calcd for $\text{C}_{34}\text{H}_{54}\text{Cl}_4\text{N}_3\text{Os}$: C, 48.80; H, 6.50. Found: C, 48.22; H, 6.53.

(iv) $(n\text{-Bu}_4\text{N})[\text{OsCl}_4(\text{CNmes})_2]$: 0.100 g (0.087 mmol); 1.8 mL of a 1.0 M solution in toluene (1.8 mmol); yield 0.150 g (99%). Anal. Calcd for $\text{C}_{36}\text{H}_{58}\text{Cl}_4\text{N}_3\text{Os}$: C, 49.99; H, 6.76. Found: C, 50.05; H, 6.76.

(v) $(n\text{-Bu}_4\text{N})[\text{OsBr}_4(\text{CNCMe}_3)_2]$. A sample of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Br}_8$ (0.200 g, 0.133 mmol) was suspended in 10 mL of ethanol and the slurry stirred for 5 min. A large excess of *tert*-butyl isocyanide (0.50 mL, 4.72 mmol) was added and the mixture stirred at room temperature for 1 h. After about 10 min, a red solution had formed and an orange solid began to precipitate. The orange powder was filtered off, washed with toluene,

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ethanol, and diethyl ether, and dried under vacuum; yield 0.171 g (66%). Anal. Calcd for $\mathrm{C_{26}H_{54}Br_4N_3Os}$: C, 34.00; H, 5.93. Found: C, 35.00; H, 6.38.

A procedure similar to A(v) was used to prepare other red bromo complexes of this type. The quantities of the $(n\text{-}\mathrm{Bu_4N})_2\mathrm{Os_2Br_8}$ and RNC reagents that were used and the product yields obtained are given in order.

(vi) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsBr_4(CNCHMe_2)_2}]$: 0.200 g (0.133 mmol); 0.24 mL (2.64 mmol); yield 0.231 g (99%). Anal. Calcd for $\mathrm{C_{24}H_{50}Br_4N_3Os}$: C, 32.37; H, 5.66. Found: C, 32.17; H, 5.98.

(vii) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsBr_4(CNxyl)_2}]$: 0.200 g (0.133 mmol); 2.8 mL of a 1.0 M solution in toluene (2.8 mmol); yield 0.258 g (96%). Anal. Calcd for $\mathrm{C_{34}H_{54}Br_4N_3Os}$: C, 40.24; H, 5.36. Found: C, 40.67; H, 5.50.

(viii) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_4(CNmes)_2}]$: 0.200 g (0.133 mmol); 3.6 mL of a 1.0 M solution in toluene (3.6 mmol); yield 0.262 g (96%). Anal. Calcd for $\mathrm{C_{36}H_{58}Br_4N_3Os}$: C, 41.47; H, 5.61. Found: C, 41.26; H, 5.91.

B. Synthesis of Complexes of the Type $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsX_4(CO)L}]$. (i) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_4(CO)(EtOH)}]$. Carbon monoxide gas was bubbled through a suspension of $(n\text{-}\mathrm{Bu_4N})_2\mathrm{Os_2Cl_8}$ (0.100 g, 0.087 mmol) in ethanol (10 mL) and the mixture refluxed for 3 h. The orange solution that resulted was cooled to room temperature and filtered to remove trace amounts of insoluble material. The solvent was evaporated to dryness under vacuum, and the resulting red solid was redissolved in 10 mL of dichloromethane. This extract was then carefully layered with diethyl ether (25 mL) and set aside overnight in a freezer (≃0 °C). The red microcrystalline product that resulted was filtered off, washed twice with diethyl ether, and dried under vacuum; yield 0.105 g (96%). Anal. Calcd for $\mathrm{C_{19}H_{42}Cl_4N_3O_2Os}$: C, 33.73; H, 6.26. Found: C, 34.46; H, 7.00.

(ii) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_4(CO)(CNxyl)}]$. A sample of $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_4(CO)(EtOH)}]$ (0.100 g, 0.158 mmol) was treated with 10 mL of dichloromethane, the mixture stirred for 5 min, and 0.2 mL of a 1.0 M solution of 2,6-xylyl isocyanide in toluene (0.2 mmol) added. The solution was then stirred for 30 min at room temperature. At the end of this time, 20 mL of diethyl ether was added with stirring. The red powder was filtered off, washed with toluene and diethyl ether, and then dried under vacuum; yield 0.080 g (69%). The identity of this product was based upon its spectroscopic and electrochemical properties.

If the reaction solution was allowed to stand overnight prior to the precipitation of the product with diethyl ether, then some of the bis(xylyl isocyanide) complex (see A(iii)) was also formed.

A procedure similar to B(ii) was used to prepare other chloro complexes of this type. In all cases these reactions involved the use of 0.100 g of $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_4(CO)(EtOH)}]$. The quantities of ligand that were used and the product yields obtained are given in order.

(iii) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_4(CO)(PPh_3)}]\cdot 0.5\mathrm{CH_2Cl_2}$: 0.15 g (0.57 mmol) of $\mathrm{PPh_3}$; yield 0.116 g (85%). Anal. Calcd for $\mathrm{C_{35.5}H_{53}Cl_5NOOsP}$: C, 47.00; H, 5.78. Found: C, 46.47; H, 6.12. The presence of the $\mathrm{CH_2Cl_2}$ was confirmed by ^{1}H NMR spectroscopy.

(iv) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_4(CO)(PEt_3)}]$: 0.10 mL (1.0 mmol) of $\mathrm{PEt_3}$; yield 0.076 g (67%).

(v) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_4(CO)(NCCH_3)}]$: 0.10 mL (2.43 mmol) of $\mathrm{CH_3CN}$; yield 0.062 g (61%).

(vi) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_4(CO)(py)}]$: 0.10 mL (1.24 mmol) of pyridine; yield 0.075 g (69%).

(vii) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_4(CO)(DMSO)}]$: 0.10 mL (1.40 mmol) of DMSO; yield 0.067 g (63%). Anal. Calcd for $\mathrm{C_{19}H_{42}NO_2OsS}$: C, 33.53; H, 6.22. Found: C, 32.60; H, 4.27.

(viii) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_4(CO)(THF)}]$: 0.10 mL (1.24 mmol) of THF; yield 0.090 g (85%).

(ix) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsBr_4(CO)(EtOH)}]$. This complex was prepared from $(n\text{-}\mathrm{Bu_4N})_2\mathrm{Os_2Br_8}$ (0.100 g, 0.066 mmol) in a manner similar to that described for its chloro analogue (see B(i)). The crude product was recrystallized from dichloromethane/diethyl ether (1:3 by volume) to give dark red crystals of the complex; yield 0.101 g (94%). Anal. Calcd for $\mathrm{C_{19}H_{42}Br_4NO_2Os}$: C, 28.16; H, 5.22; Br, 39.44. Found: C, 28.42; H, 5.33; Br, 39.93.

(x) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsBr_4(CO)(DMSO)}]$. A sample of $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsBr_4(CO)EtOH}]$ (0.100 g, 0.123 mmol) and 5 mL of dichloromethane was stirred for 5 min. To this solution was added 0.1 mL of dimethyl sulfoxide (0.110 g, 1.40 mmol) and the mixture stirred for 30 min at room temperature. At the end of this period the stirring was stopped, and 25 mL of diethyl ether was added. The red powder that precipitated was filtered off, washed twice with 20 mL portions of diethyl ether, and dried under vacuum; yield 0.104 g (98%).

The following bromo complexes were prepared by the use of a procedure similar to that of B(x). Product yields and microanalyses (when obtained) are given.

(xi) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsBr_4(CO)(CNxyl)}]$: yield 0.103 g (92%). As in the case of the chloride analogue, extended reaction times or reflux conditions gave rise to a small amount of the bis(isocyanide) complex.

Table I. Crystallographic Data for $(n\text{-}\mathrm{Bu_4N})_2[\mathrm{OsCl_4(CNxyl)_2}]$ (**1**) and $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_{2.68}Br_{1.32}(CO)(DMSO)}]$ (**2**)

	1	**2**
chem formula	$\mathrm{OsCl_4N_3C_{34}H_{42}}$	$\mathrm{OsBr_{1.32}Cl_{2.68}SO_2NC_{19}H_{42}}$
fw	824.75	739.21
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	11.6698 (7)	9.026 (2)
b, Å	31.786 (3)	10.479 (1)
c, Å	21.484 (2)	16.328 (2)
α, deg	90	95.35 (1)
β, deg	102.111 (5)	94.68 (2)
γ, deg	90	110.63 (1)
V, Å^3	7791 (2)	1428.2 (8)
Z	8	2
T, °C	20	20
λ, Å	Mo Kα (0.71073)	Mo Kα (0.71073)
ρ_{calcd}, g cm^{-3}	1.406	1.719
μ(Mo Kα), cm^{-1}	35.78	63.46
transm coeff	1.00–0.78	1.00–0.37
R^a	0.047	0.041
$R_w{}^b$	0.056	0.062

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, $w = 1/\sigma^2(|F_o|)$.

(xii) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsBr_4(CO)(PPh_3)}]$: yield 0.119 g (92%).

(xiii) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsBr_4(CO)(PEt_3)}]$: yield 0.105 g (95%).

(xiv) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsBr_4(CO)(py)}]$: 0.095 g (90%). Anal. Calcd for $\mathrm{C_{22}H_{41}Br_4N_2OOs}$: C, 30.75; H, 4.81. Found: C, 30.59; H, 5.19.

(xv) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsBr_4(CO)(NCCH_3)}]\cdot\mathrm{CH_2Cl_2}$: yield 0.068 g (61%). Anal. Calcd for $\mathrm{C_{20}H_{41}Br_4Cl_2N_2OOs}$: C, 26.50; H, 4.56. Found: C, 26.28; H, 5.37. The presence of $\mathrm{CH_2Cl_2}$ was confirmed by ^{1}H NMR spectroscopy.

(xvi) $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsBr_4(CO)(THF)}]$: yield 0.083 g (80%).

Preparation of Single Crystals of $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_4(CNxyl)_2}]$ (1) and $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_4(CO)(DMSO)}]$ (2). Crystals of **1** were obtained by the diffusion of THF vapor into a dilute dichloromethane solution of the complex, while those of **2** were grown by the slow evaporation of a dichloromethane/toluene solution (1:1 by volume) in air over a period of at least 1 week.

X-ray Crystal Structure Determinations. The structures of **1** and **2** were determined by the application of standard procedures. The basic crystallographic parameters for these complexes are listed in Table I. The cell constants were determined by means of least squares analyses on 25 reflections with $15 < \theta < 19°$ for **1** and $20 < \theta < 23°$ for **2**. For each structure determination, three standard reflections were measured every 5000 s of beam exposure during data collection; there were no systematic variations in the intensities. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package.

For both complexes, the data were collected at +20 °C. The crystals of **1** and **2** were found to belong to the monoclinic space group $P2_1/n$ (No. 14) and the triclinic space group $P\bar{1}$ (No. 2), respectively. Lorentz and polarization corrections were applied to both sets of data. The structures were solved by the use of the Patterson heavy-atom method, which revealed the positions of the Os atoms. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses.

There are three crystallographically independent osmium-containing anions in the structure of **1**. One osmium atom, Os(1), resides on a general position with a multiplicity of 4, while the other two, Os(2) and Os(3), each of multiplicity 2, reside about special positions (1, 0, 1 and $^1/_2$, 0, $^1/_2$) and have $\bar{1}$ symmetry. Two crystallographically independent $[(\mathrm{C_4H_9})_4\mathrm{N}]^+$ cations are at general positions (each of multiplicity 4).

In the structure of **2** there is no crystallographically imposed symmetry. The only complication encountered in the structure solution was the recognition that the crystals contained significant amounts of bromide distributed randomly over the four chloride ligand sites; i.e., the true composition of the crystal was $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_{4-x}Br_x(CO)(DMSO)}]$. This conclusion was based upon (1) the anomalously small thermal parameters associated with the chloride ligands and the failure of the structure to refine satisfactorily ($R \simeq 0.10$) on the assumption that the composition was $(n\text{-}\mathrm{Bu_4N})[\mathrm{OsCl_4(CO)(DMSO)}]$ and (2) the subsequent spectroscopic characterization of this batch of crystals (see Discussion). With the recognition of the mixed halide composition and the assumption that the positions of the Cl and Br atoms were coincident, the multiplicities of the four bromines were allowed to vary and the individual chlorine multiplicities were constrained to one minus the associated bromine multiplicities. The bromine multiplicities Br(1), Br(2), Br(3), and Br(4) converged to 0.381, 0.146, 0.486 and 0.305, respectively, in

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters for the Atoms of the $[OsCl_4(CNxyl)_2]^-$ Anion of **1** and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*,[a] Å^2
Os(1)	0.00301 (5)	0.25413 (2)	0.21058 (3)	4.40 (1)
Cl(11)	−0.1564 (3)	0.2362 (1)	0.1225 (2)	3.90 (9)
Cl(12)	−0.0159 (4)	0.1870 (1)	0.2564 (2)	5.4 (1)
Cl(13)	0.1647 (4)	0.2702 (1)	0.2958 (2)	5.2 (1)
Cl(14)	0.0195 (4)	0.3215 (1)	0.1652 (2)	5.2 (1)
N(110)	−0.191 (1)	0.2880 (5)	0.2790 (6)	6.3 (4)
N(120)	0.181 (1)	0.2145 (4)	0.1373 (6)	5.6 (4)
C(110)	−0.118 (1)	0.2769 (5)	0.2554 (7)	4.6 (4)
C(111)	−0.296 (1)	0.2972 (6)	0.2994 (8)	6.7 (5)
C(112)	−0.384 (2)	0.2631 (7)	0.2816 (9)	9.2 (6)
C(113)	−0.495 (2)	0.2764 (9)	0.302 (1)	12.6 (9)
C(114)	−0.479 (2)	0.3154 (8)	0.335 (1)	16.4 (8)
C(115)	−0.414 (3)	0.3461 (7)	0.349 (1)	17 (1)
C(116)	−0.297 (2)	0.3355 (7)	0.3321 (9)	10.6 (6)
C(120)	0.118 (1)	0.2302 (5)	0.1647 (7)	4.8 (4)
C(121)	0.252 (1)	0.1914 (5)	0.1047 (1)	5.2 (4)
C(122)	0.363 (2)	0.2073 (6)	0.0987 (8)	6.8 (5)
C(123)	0.426 (2)	0.1814 (7)	0.0653 (9)	8.5 (6)
C(124)	0.383 (2)	0.1432 (7)	0.040 (1)	9.2 (7)
C(125)	0.273 (2)	0.1285 (7)	0.048 (1)	8.8 (7)
C(126)	0.201 (2)	0.1521 (6)	0.0801 (8)	7.2 (6)
C(1121)	−0.359 (2)	0.2239 (8)	0.249 (1)	11.8 (9)
C(1161)	−0.194 (3)	0.3644 (8)	0.346 (1)	14 (1)
C(1221)	0.394 (2)	0.2506 (7)	0.124 (1)	9.4 (6)
C(1261)	0.082 (2)	0.1378 (7)	0.088 (1)	10.0 (7)
Os(2)	1	0	1	4.62 (2)
Cl(21)	1.1651 (4)	0.0189 (1)	1.0831 (2)	4.9 (1)
Cl(22)	1.0194 (4)	0.0642 (1)	0.9467 (2)	5.6 (1)
N(210)	0.814 (1)	0.0379 (4)	1.0696 (6)	5.6 (4)
C(210)	0.886 (2)	0.0247 (5)	1.0457 (7)	5.2 (5)
C(211)	0.715 (2)	0.0462 (6)	1.0959 (8)	6.3 (5)
C(212)	0.625 (2)	0.0145 (8)	1.085 (1)	8.8 (7)
C(213)	0.525 (2)	0.0259 (9)	1.109 (1)	12.1 (8)
C(214)	0.518 (2)	0.0634 (9)	1.141 (1)	11.9 (8)
C(215)	0.606 (2)	0.0942 (7)	1.151 (1)	10.5 (7)
C(216)	0.711 (2)	0.0843 (6)	1.127 (1)	8.9 (7)
C(2121)	0.646 (2)	−0.0262 (7)	1.052 (1)	10.1 (8)
C(2162)	0.814 (2)	0.1151 (7)	1.140 (1)	10.6 (7)
Os(3)	$^1/_2$	0	$^1/_2$	4.69 (2)
Cl(31)	0.3344 (4)	0.0133 (1)	0.4150 (2)	5.4 (1)
Cl(32)	0.4667 (4)	0.0659 (1)	0.5472 (2)	5.2 (1)
N(310)	0.673 (1)	0.0445 (5)	0.4289 (7)	7.5 (4)
C(310)	0.608 (1)	0.0282 (5)	0.4548 (8)	5.6 (5)
C(311)	0.767 (2)	0.0593 (6)	0 4024 (8)	7.0 (5)
C(312)	0.864 (2)	0.0346 (7)	0.412 (1)	8.8 (6)
C(313)	0.962 (2)	0.0523 (8)	0.386 (1)	9.8 (7)
C(314)	0.946 (2)	0.0882 (7)	0.352 (1)	9.3 (6)
C(315)	0.843 (2)	0.1124 (8)	0.344 (1)	10.4 (8)
C(316)	0.747 (2)	0.0971 (7)	0.369 (1)	9.0 (6)
C(3121)	0.867 (2)	−0.0095 (7)	0.444 (1)	11.2 (9)
C(3161)	0.627 (2)	0.1228 (8)	0.358 (1)	12.9 (8)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$.

Table III. Positional Parameters and Equivalent Isotropic Displacement Parameters for the Atoms of the $[OsCl_{2.68}Br_{1.32}(CO)(DMSO)]^-$ Anion of **2** and Their Estimated Standard Deviations

atom	*x*	*y*	*z*	*B*,[a] Å^2
Os	0.24961 (5)	0.08831 (4)	0.22297 (3)	3.624 (90
Cl(1)[b]	0.4985 (2)	0.0852 (2)	0.1804 (1)	5.61 (5)
Cl (2)[b]	0.2871 (3)	0.2920 (2)	0.1622 (2)	5.01 (6)
Cl(3)[b]	−0.0099 (2)	0.0862 (2)	0.2553 (1)	6.78 (5)
Cl(4)[b]	0.1967 (3)	−0.1300 (2)	0.2726 (2)	7.20 (6)
S(20)	0.1593 (3)	−0.1333 (3)	0.0587 (2)	4.66 (7)
O(10)	0.405 (1)	0.240 (1)	0.3852 (6)	8.9 (3)
O(20)	0.1306 (9)	−0.0125 (8)	0.1037 (5)	6.6 (2)
C(10)	0.341 (1)	0.178 (1)	0.3238 (6)	5.1 (3)
C(21)	0.203 (2)	−0.083 (1)	−0.0414 (9)	8.0 (4)
C(22)	−0.038 (2)	−0.256 (1)	0.0278 (9)	6.4 (4)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. [b] Atoms labeled as Cl represent mixed chloride/bromide sites such that the Cl + Br multiplicities equal 1.00. For further details see the Experimental Section.

Table IV. Important Bond Distances (Å) and Bond Angles (deg) for One of the Three Crystallographically Independent $[OsCl_4(CNxyl)_2]^-$ Anions in the Structure of **1**[a]

	Distances		
Os(1)–Cl(11)	2.427 (3)	Os(1)–C(120)	1.97 (2)
Os(1)–Cl(12)	2.380 (4)	N(110)–C(110)	1.14 (2)
Os(1)–Cl(13)	2.392 (4)	N(110)–C(111)	1.41 (2)
Os(1)–Cl(14)	2.376 (4)	N(120)–C(120)	1.15 (2)
Os(1)–C(110)	2.00 (2)	N(120)–C(121)	1.40 (2)
	Angles		
Cl(11)–Os(1)–Cl(12)	89.4 (1)	Cl(13)–Os(1)–C(110)	94.4 (5)
Cl(11)–Os(1)–Cl(13)	178.0 (1)	Cl(13)–Os(1)–C(120)	87.5 (5)
Cl(11)–Os(1)–Cl(14)	90.4 (1)	Cl(14)–Os(1)–C(110)	89.9 (5)
Cl(11)–Os(1)–C(110)	87.6 (5)	Cl(14)–Os(1)–C(120)	91.2 (5)
Cl(11)–Os(1)–C(120)	90.5 (5)	C(110)–Os(1)–C(120)	177.9 (6)
Cl(12)–Os(1)–Cl(13)	90.1 (1)	Os(1)–C(110)–N(110)	176 (2)
Cl(12)–Os(1)–Cl(14)	179.3 (1)	Os(1)–C(120)–N(120)	177 (2)
Cl(12)–Os(1)–C(110)	89.4 (5)	C(110)–N(110)–C(111)	169 (2)
Cl(12)–Os(1)–C(120)	89.5 (5)	C(120)–N(120)–C(121)	174 (2)
Cl(13)–Os(1)–Cl(14)	90.1 (1)		

[a] Structural parameters are for the anion that resides on a general position. Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Important Bond Distances (Å) and Bond Angles (deg) for the $[OsCl_{2.68}Br_{1.32}(CO)(DMSO)]^-$ Anion in the Structure of **2**[a]

	Distances[b]		
Os–Cl(1)	2.415 (2)	Os–C(10)	1.795 (9)
Os–Cl(2)	2.366 (3)	S(20)–O(20)	1.517 (6)
Os–Cl(3)	2.436 (2)	S(20)–C(21)	1.80 (1)
Os–Cl(4)	2.399 (2)	S(20)–C(22)	1.79 (1)
Os–O(20)	2.130 (8)	O(10)–C(10)	1.13 (1)
	Angles[b]		
Cl(1)–Os–Cl(2)	89.69 (8)	Cl(3)–Os–O(20)	86.1 (3)
Cl(1)–Os–Cl(3)	175.78 (7)	Cl(3)–Os–C(10)	90.8 (4)
Cl(1)–Os–Cl(4)	90.78 (8)	Cl(4)–Os–O(20)	90.4 (2)
Cl(1)–Os–O(20)	89.8 (3)	Cl(4)–Os–C(10)	91.4 (4)
Cl(1)–Os–C(10)	93.3 (4)	O(20)–Os–C(10)	176.5 (5)
Cl(2)–Os–Cl(3)	89.09 (9)	O(20)–S(20)–C(21)	104.0 (5)
Cl(2)–Os–Cl(4)	174.59 (8)	O(20)–S(20)–C(22)	103.0 (5)
Cl(2)–Os–O(20)	84.2 (2)	C(21)–S(20)–C(22)	97.9 (6)
Cl(2)–Os–C(10)	94.0 (4)	Os–O(20)–S(20)	123.5 (3)
Cl(3)–Os–Cl(4)	90.06 (9)	Os–C(10)–O(10)	176.3 (9)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Atoms labeled as Cl represent mixed chloride/bromide sites such that the Cl + Br multiplicities equal 1.00. For further details see the Experimental Section.

accord with the stoichiometry $(n\text{-}Bu_4N)[OsCl_{2.68}Br_{1.32}(CO)(DMSO)]$. Convergence led to very satisfactory thermal parameters for the halides. In the subsequent discussion of this structure, these halide sites are, for convenience, labeled Cl(1), Cl(2), Cl(3), and Cl(4).

In both structure solutions, an empirical absorption correction was applied,[12] the linear absorption coefficient being 35.78 cm^{-1} for **1** and 63.46 cm^{-1} for **2**. No corrections were made for extinction. The structures were refined by full-matrix least-squares techniques where the function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. All non-hydrogen atoms were refined anisotropically and corrections for anomalous scattering were applied.[13] Hydrogen atoms were not included.

Positional parameters and their errors for the atoms of the osmium-containing monoanions of **1** and **2** are listed in Tables II and III. Some important intramolecular bond distances and angles for these two structures are given in Tables IV and V. Tables giving full details of

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(12) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158.

(13) (a) Cromer, D. T. *International Tables for X-ray Crystallogrphy*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution, see: Cromer, D. T.; Waber, J. T. Ibid. Table 2.2B.

Table VI. Spectral and Magnetic Properties for Osmium(III) Complexes of the Types (n-Bu_4N)[$OsX_4(CNR)_2$] and (n-Bu_4N)[$OsX_4(CO)L$]

	IR data,[a] cm^{-1}				ESR data[c]	
complex anion	ν(C≡N)	ν(C≡O)	ν(Os—X)	μ_{eff},[b] μ_B	$g_\parallel$	$g_\perp$
$[OsCl_4(CNCHMe_2)_2]^-$	2155		301	1.75	1.18	2.49
$[OsCl_4(CNCMe_3)_2]^-$	2136		298	1.67	1.20	2.57
$[OsCl_4(CNxyl)_2]^-$	2116		296	1.70	1.30	2.49
$[OsCl_4(CNmes)_2]^-$	2119		302	1.60	1.30	2.47
$[OsBr_4(CNCHMe_2)_2]^-$	2146		216	1.83	1.17	2.51
$[OsBr_4(CNCMe_3)_2]^-$	2141		216	1.85	1.18	2.53
$[OsBr_4(CNxyl)_2]^-$	2120		214	1.59	1.30	2.48
$[OsBr_4(CNmes)_2]^-$	2120		216	1.75	1.31	2.49
$[OsCl_4(CO)(EtOH)]^-$		1987[d]	313	1.72	1.56	2.33
$[OsCl_4(CO)(DMSO)]^-$		1965	314		1.59	2.40
$[OsCl_4(CO)(THF)]^-$		1989[d]	310		1.62	2.39
$[OsCl_4(CO)(NCCH_3)]^-$		1998[d]	314		1.57	2.43
$[OsCl_4(CO)(py)]^-$		1983[e]	313		1.60	2.47
$[OsCl_4(CO)(PPh_3)]^-$		2001[f]	309		1.56	2.42
$[OsCl_4(CO)(PEt_3)]^-$		2008	305		1.57	2.43
$[OsCl_4(CO)(CNxyl)]^-$	2197	2015	304		1.63	2.41
$[OsBr_4(CO)(EtOH)]^-$		1990	225	1.91	1.64	2.43
$[OsBr_4(CO)(DMSO)]^-$		1981	225		1.61	2.47
$[OsBr_4(CO)(THF)]^-$		1988	225		1.66	2.49
$[OsBr_4(CO)(NCCH_3)]^-$		2004	229		1.66	2.48
$[OsBr_4(CO)(py)]^-$		1998[e]	225		1.59	2.50
$[OsBr_4(CO)(PPh_3)]^-$		2001	217		1.59	2.50
$[OsBr_4(CO)(PEt_3)]^-$		2008	217		1.66	2.58
$[OsBr_4(CO)(CNxyl)]^-$	2193	2017	220		1.61	2.47

[a] Spectra were recorded as Nujol mulls. All peaks were of high intensity. [b] Magnetic moments (±0.1 μ_B) determined at ambient temperature on dichloromethane solutions by the Evans method (see ref 14). [c] X-Band ESR spectra recorded at −160 °C in toluene/dichloromethane glasses. [d] A single band at this same frequency also observed in a dichloromethane solution of the complex. [e] A value of 1984 cm^{-1} for ν(CO) has been reported previously for the Et_4N^+ salt.[20] [f] A value of 1995 cm^{-1} has been reported previously.[29]

the crystal data and data collection parameters (Tables S1 and S2), the positional parameters for all atoms (Tables S3 and S4), the thermal parameters (Tables S5 and S6), and complete listings of bond distances (Tables S7 and S8) and bond angles (Tables S9 and S10) are available as supplementary material.

Physical Measurements. Infrared spectra (4000–200 cm^{-1}) were recorded as Nujol mulls supported on KBr or polyethylene plates with a Perkin-Elmer 1800 FTIR spectrometer. Electronic absorption spectra (800–200 nm) were measured on dichloromethane solutions with the use of an IBM 9420 UV/vis spectrophotometer. Electrochemical experiments were carried out by using a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane or dichloromethane/acetone (10:1 by volume) solutions that contained 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the Ag/AgCl electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions, $E_{1/2} = +0.47$ V for the ferrocenium/ferrocene couple, which was used as an internal standard. Conductivities were measured with the use of an Industrial Instruments Inc. Model RC 16B2 conductivity bridge. X-Band ESR spectra of toluene/dichloromethane glasses (1:1 by volume) were recorded at −160 °C with the use of a Varian E-109 spectrometer. Magnetic moments were determined on dichloromethane solutions of the complexes at room temperature by the Evans method.[14] Negative ion FAB mass spectra were recorded in glycerol or 3-nitrobenzyl alcohol matrices on a Kratos MS-50 spectrometer.

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results

The reactions between the triply bonded diosmium(III) compounds (n-$Bu_4N)_2Os_2X_8$ (X = Cl, Br) and alkyl and aryl isocyanide ligands in ethanol occur quite rapidly at room temperature with resulting cleavage of the Os≡Os bond and the formation of the mononuclear, paramagnetic, 17-electron complexes (n-Bu_4N)[$OsX_4(CNR)_2$] (eq 1).

$$(n\text{-}Bu_4N)_2Os_2X_8 + 4RNC \xrightarrow{EtOH} 2(n\text{-}Bu_4N)[OsX_4(CNR)_2] \qquad (1)$$

$$R = CHMe_2,\ CMe_3,\ xyl,\ mes$$

The reactions proceed in very high yield, in some cases essentially quantitatively, and appear to be complete within 15 min, although a reaction time of an hour was used to ensure complete reaction in all cases. The use of a noncoordinating solvent such as dichloromethane gives these same products, with no appreciable decrease in the yield. A very large excess of the isocyanide ligand (up to a 50-fold excess) does not appear to give a more highly substituted product such as $OsX_3(CNR)_3$ or $[OsX_2(CNR)_4]^+$, although such species have been prepared by other procedures.[4,15]

The analogous reactions of carbon monoxide with suspensions of (n-$Bu_4N)_2Os_2X_8$ in ethanol proceed very slowly at room temperature, but under reflux conditions they afford (n-Bu_4N)[$OsX_4(CO)(EtOH)$] in quantitative yield (eq 2). The ethanol

$$(n\text{-}Bu_4N)_2Os_2X_8 + 2CO \xrightarrow{EtOH} 2(n\text{-}Bu_4N)[OsX_4(CO)(EtOH)] \qquad (2)$$

ligand is quite labile in these complexes and is readily displaced by ligands such as CH_3CN, py, THF, DMSO, PEt_3, PPh_3, and xylNC as shown in eq 3. In the reactions between (n-$Bu_4N)_2Os_2X_8$ and CO, we found no evidence for the formation

$$(n\text{-}Bu_4N)[OsX_4(CO)(EtOH)] + L \xrightarrow{CH_2Cl_2} (n\text{-}Bu_4N)[OsX_4(CO)L] + EtOH \qquad (3)$$

of the bis(carbonyl) complexes (n-Bu_4N)[$OsX_4(CO)_2$]. Attempts to incorporate a second carbonyl group included an increase in the reaction time, an increase in the carbon monoxide pressure in the reaction vessel, use of noncoordinating reaction solvents, and reaction of the isolated ethanol-containing adduct with carbon monoxide. In the reactions of (n-Bu_4N)[$OsX_4(CO)(EtOH)$] with xylNC to produce (n-Bu_4N)[$OsX_4(CO)(CNxyl)$], the use of an extended reaction time (several hours) or reflux conditions led to the formation of some (n-Bu_4N)[$OsX_4(CNxyl)_2$].

Some of the key spectroscopic, magnetic and electrochemical data for the complexes described in this report are summarized in Tables VI and VII. Solutions of the (n-Bu_4N)[$OsX_4(CNR)_2$] complexes in acetonitrile and (n-Bu_4N)[$OsX_4(CO)L$] in acetone (ca. 1×10^{-3} M) possess conductivities typical of 1:1 electrolytes; for example, $\Lambda_m = 116\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$ for (n-Bu_4N)[$OsBr_4(CNCHMe_2)_2$] and $\Lambda_m = 125\ \Omega^{-1}\ \mathrm{cm}^2\ \mathrm{mol}^{-1}$ for (n-Bu_4N)-

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Table VII. Cyclic Voltammetric Data for Osmium(III) Complexes of the Types (n-Bu$_4$N)[OsX$_4$(CNR)$_2$] and (n-Bu$_4$N)[OsX$_4$(CO)L]

	voltammetric half-wave potentials,[a] V			voltammetric half-wave potentials,[a] V	
complex anion	$E_{1/2}$(ox)	$E_{1/2}$(red)	complex anion	$E_{1/2}$(ox)	$E_{1/2}$(red)
[OsCl$_4$(CNCHMe$_2$)$_2$]$^-$	+0.81 (120)	−0.88 (130)	[OsBr$_4$(CNCHMe$_2$)$_2$]$^-$	+0.80 (110)	−0.77 (120)
[OsCl$_4$(CNCMe$_3$)$_2$]$^-$	+0.75 (110)	−0.92 (110)	[OsBr$_4$(CNCMe$_3$)$_2$]$^-$	+0.81 (110)	−0.76 (120)
[OsCl$_4$(CNxyl)$_2$]$^-$	+0.91 (100)	−0.73 (120)	[OsBr$_4$(CNxyl)$_2$]$^-$	+0.89 (100)	−0.60 (100)
[OsCl$_4$(CNmes)$_2$]$^-$	+0.86 (100)	−0.74 (130)	[OsBr$_4$(CNmes)$_2$]$^-$	+0.87 (110)	−0.63 (110)
[OsCl$_4$(CO)(EtOH)]$^-$	+1.49[b,c]	−0.18 (110)	[OsBr$_4$(CO)(EtOH)]$^-$	+1.45[b,c]	−0.12 (110)
[OsCl$_4$(CO)(DMSO)]$^-$	+1.29 (100)	−0.31 (160)	[OsBr$_4$(CO)(DMSO)]$^-$	+1.19 (120)	−0.21 (200)
[OsCl$_4$(CO)(THF)]$^-$	+1.41[b,c]	−1.14 (100)	[OsBr$_4$(CO)(THF)]$^-$	+1.43[b,c]	−1.14 (100)
[OsCl$_4$(CO)(NCCH$_3$)]$^-$	+1.46[b]	−0.23 (120)	[OsBr$_4$(CO)(NCCH$_3$)]$^-$	+1.40[b,c]	−1.16 (100)
[OsCl$_4$(CO)(py)]$^-$	+1.34 (80)	−0.31 (100)	[OsBr$_4$(CO)(py)]$^-$	+1.27 (90)	−0.26 (80)
[OsCl$_4$(CO)(PPh$_3$)]$^-$	+1.22[b,e]	−0.48[d,f]	[OsBr$_4$(CO)(PPh$_3$)]$^-$	+1.10 (80)	−0.41[d,g]
[OsCl$_4$(CO)(PEt$_3$)]$^-$	+1.04[b]	−0.54 (100)	[OsBr$_4$(CO)(PEt$_3$)]$^-$	+1.07[b]	−0.42 (70)
[OsCl$_4$(CO)(CNxyl)]$^-$	+1.36 (120)	−0.33 (130)	[OsBr$_4$(CO)(CNxyl)]$^-$	+1.33[b,h]	−0.27 (80)

[a] Versus Ag/AgCl. Recorded on solutions in 0.1 M TBAH–CH$_2$Cl$_2$ by the use of a Pt-bead electrode. Data obtained at v = 200 mV s^{-1}. Under our experimental conditions $E_{1/2}$ for the ferrocenium/ferrocene couple is +0.47 V vs Ag/AgCl. Numbers in parentheses are ΔE_p values (i.e., $E_{p,a} - E_{p,c}$). [b] $E_{p,a}$ value. [c] Coupled product wave at $E_{p,c} \simeq +1.1$ V. [d] $E_{p,c}$ value. [e] Coupled reduction at $E_{p,c} = +0.17$ V with $i_{p,c} < i_{p,a}$. [f] Coupled product wave at $E_{p,a} = -0.17$ V. [g] Coupled product wave at $E_{p,a} = -0.10$ V. [h] The wave due to the coupled reduction is overlayed by another process at $E_{p,c} \simeq +1.14$ V that probably arises from a chemical product which is produced following the one-electron oxidation.

[OsCl$_4$(CO)(DMSO)]. The IR spectra (2200–1900 cm^{-1}) of the bis(isocyanide) complexes (Table VI) show a single intense vibration due to ν(CN) of the coordinated π-acceptor ligands in accord with a centrosymmetric trans octahedral geometry. A single band is observed both for Nujol mulls as well as solutions of these complexes in dichloromethane. The trans configuration of these species is also confirmed by the presence of a single, fairly intense peak at ca. 300 cm^{-1} (X = Cl) or 215 cm^{-1} (X = Br) corresponding to the one IR-active ν(OsX) mode.[17] The carbonyl complexes (n-Bu$_4$N)[OsX$_4$(CO)L] likewise show one ν(CO) band (Table VI), which is located in the frequency range 2017–1965 cm^{-1}. The xylyl isocyanide complexes (n-Bu$_4$N)[OsX$_4$(CO)(CNxyl)] have the highest C≡O stretching frequencies of this series, a result that accords with the xylNC ligand being the best π-acceptor of the ligands (L) that were used.

The electronic absorption spectra of the isocyanide and carbonyl complexes (recorded on CH$_2$Cl$_2$ solutions) are very similar within each set of complexes but are very dependent upon the nature of the halogen. Thus, (n-Bu$_4$N)[OsCl$_4$(CNR)$_2$] shows an intense band at ca. 350 nm with several weaker features to lower energies, while for the related bromide complexes there are a pair of intense absorptions at ca. 470 and 440 nm, with a much weaker feature at ca. 540 nm.[18] These spectral shifts most likely correlate with the transitions being primarily X(π) → Os in character.[15,19] The same general features and spectral shifts are seen in the electronic absorption spectra of the carbonyl-containing species.[18] In the case of the pyridine complex (n-Bu$_4$N)[OsCl$_4$(CO)(py)], its solutions in CH$_2$Cl$_2$ show an intense absorption at 378 nm, with prominent shoulders at 400, 435, and 470 nm; these are probably the counterparts of the bands seen at 381 and 432 nm in the spectrum of (Et$_4$N)[OsCl$_4$(CO)(py)] (recorded as a KBr disk).[20] Magnetic moment measurements as well as X-band ESR spectral studies (Table VI) confirm the complexes to be low-spin d^5 Os(III) species and, therefore, formally 17-electron compounds. The ESR spectra resemble those reported previously for (n-Bu$_4$N)[OsX$_4$(PEt$_3$)$_2$] in which the anion has a trans octahedral geometry,[1,19] as well as for the mixed carbonyl–pyridine complexes Cs[OsCl$_4$(CO)(py)], (Et$_4$N)[OsCl$_4$(CO)(py)], and (Et$_4$N)[OsBr$_4$(CO)(py)],[21] although the $g_\parallel$ value of 1.80 reported for (Et$_4$N)[OsBr$_4$(CO)(py)] does not agree very well with the value of 1.59 that we found for the n-Bu$_4$N$^+$ salt (Table VI).

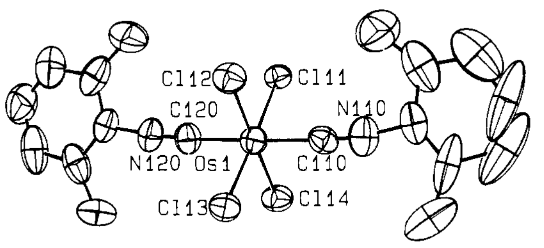

Figure 1. ORTEP representation of the structure of the *trans*-[OsCl$_4$(CNxyl)$_2$]$^-$ anion. The thermal ellipsoids are drawn at the 50% probability level. The anion featured is that which resides on a general position; two other crystallographically independent anions are on special positions ($\bar{1}$ symmetry).

The cyclic voltammetric properties of the isocyanide and carbonyl complexes are characteristic of octahedral Os(III) species.[1,15,19] Solutions of the complexes in 0.1 M TBAH–CH$_2$Cl$_2$ show two processes that are associated with the Os(IV)/Os(III) and Os(III)/Os(II) couples (Table VII), although for most of the monocarbonyl complexes the Os(III) → Os(IV) oxidation is irreversible. The $E_{1/2}$(ox) and $E_{1/2}$(red) values for (n-Bu$_4$N)[OsX$_4$(CNR)$_2$] follow the order xylNC ≃ mesNC > Me$_2$CHNC ≃ Me$_3$CNC. This trend is in accord with the greater π-accepting ability of the aryl isocyanide ligands, which renders the metal center more positively charged, thereby making the oxidation (to Os(IV)) more difficult; this is paralleled by an increasing accessibility of the reduction to Os(II) as the LUMO drops in energy. While there is little dependence of $E_{1/2}$(ox) upon the nature of X, the values of $E_{1/2}$(red) are uniformly at least 0.1 V more positive in the case of X = Br. In general, the carbonyl complexes display much less reversible electrochemical behavior than their bis(isocyanide) analogues. In all instances, both redox processes are shifted to considerably more positive potentials in accord with a fairly significant electron-withdrawing effect of the carbonyl ligand. This leads to a much greater stabilization of the 18-electron dianionic form, a trend that is particularly apparent with the EtOH, THF, and CH$_3$CN adducts. With the more basic PEt$_3$ ligand the $E_{p,a}$ and $E_{1/2}$(red) values are the most negative of those for any of the series of carbonyl complexes. In most cases, the value of $E_{1/2}$(red) is at least 50 mV more positive for the bromide derivative of each pair of (n-Bu$_4$N)[OsX$_4$(CO)L] (X = Cl or Br) complexes.

The structural identity of the sets of bis(isocyanide) and mono(carbonyl) complexes was confirmed by X-ray crystal

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(17) When the isopropyl isocyanide and xylyl isocyanide complexes were heated in ethanol and toluene for periods of up to 48 h, we found no evidence for isomerization to the cis isomers.

(18) Within the spectral region 650–300 nm, representative spectra are as follows (λ_{max} values are in nm with ϵ_{max} values in parentheses): (n-Bu$_4$N)[OsCl$_4$(CNCHMe$_2$)$_2$], 351 (4500), 370 (3700), 400 (sh), 428 (sh), 460 (sh); (n-Bu$_4$N)[OsBr$_4$(CNCHMe$_2$)$_2$], 380 (2900), 405 (3600), 436 (7900), 461 (10400), 525 (1950); (n-Bu$_4$N)[OsCl$_4$(CO)(EtOH)], 350 (sh), 380 (3700), 408 (3300), 438 (sh), 478 (sh); (n-Bu$_4$N)[OsBr$_4$(CO)(EtOH)], 316 (1400), 332 (1660), 462 (5700), 516 (7000), 650 (490).

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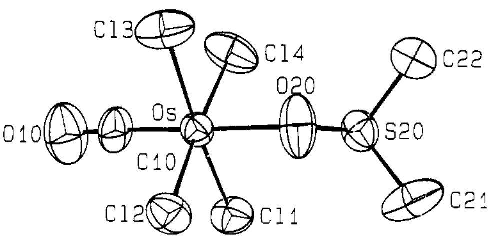

Figure 2. ORTEP representation of the structure of the *trans*-$[OsCl_{4-x}Br_x(CO)(DMSO)]^-$ anion. The thermal ellipsoids are drawn at the 50% probability level. The chlorine atoms Cl(1)–Cl(4) actually represent mixed chloride/bromide sites (for further details see Experimental Section).

structure determinations of two representative structures, viz., $(n\text{-}Bu_4N)[OsCl_4(CNxyl)_2]$ and $(n\text{-}Bu_4N)[OsCl_4(CO)(DMSO)]$. During the course of the structure refinement of the carbonyl complex, it became apparent that the crystal was that of a mixed chloride–bromide salt, a result which necessitated a modification in the synthetic procedure we used to prepare $(n\text{-}Bu_4N)_2Os_2Cl_8$ (see Experimental Section and Discussion). The ORTEP representations of the structures of the anions in the aforementioned salts are shown in Figures 1 and 2. Crystallographic details and the important structural parameters are given in Tables I–V.

Discussion

The cleavage of the Os≡Os bond in $(n\text{-}Bu_4N)_2Os_2X_8$ (X = Cl, Br) by isocyanide ligands RNC (R = $CHMe_2$, CMe_3, xylyl, mesityl) and by CO in ethanol to give $(n\text{-}Bu_4N)[OsX_4(CNR)_2]$ and $(n\text{-}Bu_4N)[OsX_4(CO)(EtOH)]$ provides a high yield and general synthetic route to these new mononuclear, paramagnetic Os(III) complexes. The course of the reactions with the isocyanide ligands resembles[22] the photochemical cleavage of the quadruple bond of $[Re_2Cl_8]^{2-}$ in acetonitrile to produce $[ReCl_4(NCCH_3)_2]^-$. In the case of the products from the carbonylation reactions, we had anticipated that the dicarbonyl complexes $(n\text{-}Bu_4N)[OsX_4(CO)_2]$ would be the major products. This was based upon an analogy with the isocyanide systems and a previous report[23] that salts of the *trans*-$[OsX_4(CO)_2]^-$ anions (X = Br, I) can be prepared. However, the reaction conditions we used, which involved refluxing ethanol to enhance the solubility of $(n\text{-}Bu_4N)_2Os_2X_8$ in the reaction mixture,[24] are likely to favor the loss of one of the carbonyl ligands in these relatively labile 17-electron species and its substitution by some other nucleophile such as ethanol. This labilization has been demonstrated previously[20] in the case of $(n\text{-}Bu_4N)[OsBr_4(CO)_2]$ by its conversion to $(n\text{-}Bu_4N)[OsBr_4(CO)(py)]$ upon reaction with pyridine. Even when we carried out the reaction at room temperature and monitored its course by IR spectroscopy, we found no spectroscopic evidence[23] for the formation of $[OsX_4(CO)_2]^-$, although the percent conversion under these conditions is very low. Accordingly, it might well be that the dissociation of the Os≡Os bond is solvent (ethanol) assisted, and that the reactions with RNC ligands and with CO give the same type of product, viz., $(n\text{-}Bu_4N)[OsX_4(CNR)(EtOH)]$ and $(n\text{-}Bu_4N)[OsX_4(CO)(EtOH)]$, respectively. While the former complex could react with an additional equivalent of isocyanide to form the bis(isocyanide) complex with loss of ethanol, the $[OsX_4(CO)(EtOH)]^-$ anions are presumably unreactive toward further CO.

In the early stages of our work we attempted to structurally characterize by X-ray crystallography what we now know to be $(n\text{-}Bu_4N)[OsCl_4(CO)(EtOH)]$.[25] However, while refinement revealed clearly the square-pyramidal $[OsCl_4(CO)]$ unit, we were unable to identify the ligand in the sixth position and so terminated the structure determination. Subsequently, through the use of negative ion FABMS we were able to confirm the composition of the anion in $(n\text{-}Bu_4N)[OsCl_4(CO)(EtOH)]$ through the observation of the parent ion at m/z = 406 and the $[OsCl_4(CO)]^-$ fragment ion at m/z = 360. Furthermore, the lability of the ethanol ligand was demonstrated through the reactions of $(n\text{-}Bu_4N)[OsX_4(CO)(EtOH)]$ with various monodentate donors. Indeed, the use of $(n\text{-}Bu_4N)[OsX_4(CO)(EtOH)]$ as a precursor to other complexes of the type $(n\text{-}Bu_4N)[OsX_4(CO)L]$, where L = DMSO, THF, CH_3CN, py, PPh_3, PEt_3, or xylNC, demonstrates this to be an excellent procedure for preparing this general class of complexes. A few complexes of this type have been prepared previously by procedures that involve the carbonylation of salts of the $[OsX_6]^{2-}$ ions. In addition to the previously mentioned dicarbonyls $(n\text{-}Bu_4N)[OsX_4(CO)_2]$ (X = Br, I),[23] examples include salts of the $[OsX_5(CO)]^{2-}$ anions (X = Cl, Br, I),[26–28] the pyridine complexes $(Et_4N)[OsCl_4(CO)(py)]$ and $(n\text{-}Bu_4N)[OsX_4(CO)(py)]$ (X = Br, I),[20] and the compounds $(n\text{-}Bu_4N)[OsX_4(CO)(H_2O)]$ (X = Cl, Br),[29] $(n\text{-}Bu_4N)[OsCl_4(CO)(PPh_3)]$,[29] and $(n\text{-}Bu_4N)[OsX_4(CO)(pdma)]$ (X = Cl, Br, I; pdma represents the *monodentate* *o*-phenylenebis(dimethylarsine) ligand).[29]

Although salts of the 17- and 18-electron mixed halide–carbonyl anions of the types *trans*-$[OsX_4(CO)_2]^-$ and *cis*-$[OsX_4(CO)_2]^{2-}$ have been isolated,[23,26] our attempts to reduce the complex anions $[OsX_4(CO)L]^-$ to $[OsX_4(CO)L]^{2-}$ were not successful. We encountered a similar lack of success in stabilizing the $[OsX_4(CNR)_2]^{2-}$ anions, even though the electrochemical properties of the monoanions indicate that the Os(III)/Os(II) couple is quite reversible. The problem here may be associated with our failure to find a suitable stabilizing cation.

The single-crystal X-ray structure of the xylyl isocyanide complex $(n\text{-}Bu_4N)[OsCl_4(CNxyl)_2]$ confirmed that the anion possesses a trans octahedral geometry (Figure 1) and therefore resembles closely the structure of $(Ph_4P)[OsCl_4(PEt_3)_2]$.[19] The crystal structure of $(n\text{-}Bu_4N)[OsCl_4(CNxyl)_2]$ revealed the presence of three crystallographically independent osmium anions, two of which possess $\bar{1}$ symmetry, while the third has no crystallographically imposed symmetry. The structural parameters for the latter anion, which are given in Table IV, are essentially the same as for those with the crystallographically imposed inversion centers (see Table S7). The angles that define the octahedral $OsCl_4C_2$ geometry are within 4.5° of 90°, while the angles that characterize the Os–C–N–C units show a close approach to linearity; the maximum deviation from 180° is for the angle C(210)–N(210)–C(211), which is 168 (2)°. The Os–Cl bond lengths span the range 2.374 (4)–2.427 (3) Å and can be compared with Os–Cl distances of from 2.375 (3) to 2.386 (2) Å in $[OsCl_4(PEt_3)_2]^-$.[19] The Os–C bond lengths of 1.97 (2)–2.00 (2) Å are similar to that of 2.00 (3) Å which has been reported[30] for the osmium(II) complex *trans*-$OsBr_2(CNCMe_3)_4$.

A structure determination on a crystal grown from a solution of $(n\text{-}Bu_4N)[OsCl_4(CO)(DMSO)]$ in dichloromethane/toluene showed the structure of this complex to be similar to that of the aforementioned xylyl isocyanide derivative, but with a trans set of CO and O-bound DMSO ligands in place of the two xylNC ligands (Figure 2). There is nothing unusual about the parameters associated with these two ligands, and therefore, the structural details of this complex (Table V) generally merit little further discussion. However, one point that needs to be mentioned concerns our finding that the true composition of the crystal is in reality $(n\text{-}Bu_4N)[OsCl_{2.68}Br_{1.32}(CO)(DMSO)]$. As discussed in the Experimental Section, during the course of the structure refinement it became apparent that our assumption that the halide sites were exclusively chloride led to unsatisfactory thermal pa-

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rameters. For satisfactory convergence, we found it was necessary to model the halide sites such that the individual Cl multiplicities were constrained to be one minus the associated Br multiplicities. This assumption was supported by the spectroscopic properties of this batch of crystals, which provided convincing evidence for serious contamination by bromide. Specifically, the negative ion FABMS of the sample of (n-Bu_4N)[$OsCl_4(CO)(EtOH)$] showed clusters of peaks at $m/z = 450$ and $m/z = 494$ that are due to $[OsCl_3Br(CO)(EtOH)]^-$ and $[OsCl_2Br_2(CO)(EtOH)]^-$; these had intensities of 58% and 16%, respectively, relative to the parent peak for $[OsCl_4(CO)(EtOH)]^-$ ($m/z = 406$, RI = 100%). In accord with these findings, we determined that some preparative batches of (n-$Bu_4N)_2Os_2Cl_8$ exhibited a weak band at 250 cm^{-1} in their low-frequency IR spectra that could be assigned[7] to the ν(Os–Br) mode of the bromide contaminant; the much more intense ν(Os–Cl) mode was located at 346 cm^{-1}. The source of the bromide is obviously the n-Bu_4NBr that is added during the synthesis of (n-$Bu_4N)_2Os_2Cl_8$ from the reaction of $Os_2(O_2CCH_3)_4Cl_2$ with ethanol/HCl(g) mixtures.[7,31] To avoid this occasional problem, n-Bu_4NPF_6 can be used in place of n-Bu_4NBr, as described in the modified procedure that is provided in the Experimental Section. This step gives a product that is free of a band at ca. 250 cm^{-1} in its IR spectrum.

Conclusions. As with the cleavage of the Os≡Os bond of (n-$Bu_4N)_2Os_2X_8$ (X = Cl, Br) by phosphine ligands,[1] we find that a similar reaction course ensures with isocyanide ligands and with carbon monoxide in ethanol. The mononuclear, paramagnetic, 17-electron osmium(III) complexes of the types (n-Bu_4N)[$OsX_4(CNR)_2$] and (n-Bu_4N)[$OsX_4(CO)(EtOH)$] are the major products and are obtained in very high yield. The ethanol ligand in the carbonyl complexes is readily displaced by other monodentate ligands, thereby providing an excellent general synthetic route to salts of the type (n-Bu_4N)[$OsX_4(CO)L$]. Crystal structure determinations on (n-Bu_4N)[$OsCl_4(CNxyl)_2$] and (n-Bu_4N)[$OsCl_{4-x}Br_x(CO)(DMSO)$] have shown the presence of trans octahedral geometries for the anions.

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Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters (Tables S1 and S2), the positional parameters for all atoms (Tables S3 and S4), the thermal parameters (Tables S5 and S6), and complete bond distances (Tables S7 and S8) and bond angles (Tables S9 and S10) for (n-Bu_4N)[$OsCl_4(CNxyl)_2$] and (n-Bu_4N)[$OsCl_{2.68}Br_{1.32}(CO)(DMSO)$] (24 pages); tables of observed and calculated structure factors (56 pages). Ordering information is given on any current masthead page.

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[31] Note that we found no evidence for bromide contamination in the crystal of (n-Bu_4N)[$OsCl_4(CNxyl)_2$] that was also subjected to an X-ray structure determination. Also, the spectroscopic properties of the other isocyanide and carbonyl complexes gave only occasional evidence for minor contamination by bromide.

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Synthesis, Separation, and Structural Characterization (X-ray) of the Two Diastereomers of $Ru_3(CO)_6[CH_3C{=}C(H)C(H){=}N\text{-}i\text{-}Pr]_2$, an Acyclic Trinuclear Complex That Is Isolobally Related to Cp_2Ru[1]

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Thermal reactions of $Ru_3(CO)_{12}$ (1 mmol) with the monoazadienes $R^1C(H){=}C(H)C(H){=}N$-i-Pr (6 mmol; $R^1 = CH_3$ (**a**), C_6H_5 (**b**)) in refluxing heptane yield the trinuclear 50e complexes $Ru_3(CO)_6[R^1C{=}C(H)C(H){=}N$-$i$-$Pr]_2$ (**5a,b**), containing two β-metalated monoazadien-4-yl ligands in a yield of 30% (**5a**) or 60% (**5b**). Compound **5** is formed via the intermediacy of the dinuclear complexes $Ru_2(CO)_6[R^1C{=}C(H)CH_2N$-$i$-Pr] (**1**) and ($\mu$-H)$Ru_2(CO)_5[R^1C{=}C(H)C(H){=}N$-$i$-Pr] (**2**). Alternatively, compound **5a** has been obtained in low yield by pyrolysis of $Ru_4(CO)_{10}[CH_3C{=}C(H)C(H){=}N$-$i$-$Pr]_2$ (**3a**). Compounds **5a,b** are both formed as a mixture of two diastereomers (*CC*/*AA*)- and (*CA*/*AC*)-**5a** have been separated by preparative HPLC on a reversed-phase column. Both diastereomers of **5a** have been characterized by X-ray crystal structures. Crystals of (*CA*/*AC*)-**5a** are monoclinic, space group $P2_1/n$, with $a = 8.684$ (1) Å, $b = 16.743$ (2) Å, $c = 16.852$ (2) Å, $\beta = 91.66$ (1)°, $Z = 4$, and $R = 0.025$. Crystals of (*CC*/*AA*)-**5a** are monoclinic, space group $P2/a$, with $a = 17.716$ (8) Å, $b = 8.581$ (3) Å, $c = 18.189$ (5) Å, $\beta = 118.56$ (3)°, $Z = 4$, and $R = 0.026$. Both diastereomers of **5a** consist of two azaruthenacyclopentadienyl fragments (which are isolobal to Cp) η^5-coordinated to a central ruthenium atom. The dimetallametallocenes **5a,b** are isolobally related to ruthenocene. Compounds **5a,b** are the first 50e trinuclear complexes of the iron triad which contain an open-chain, bent metal framework that is not stabilized by one or more ligands bridging the outer two metal centers. NOESY spectra showed that the bent geometry of both diastereomers of **5a** is retained in solution.

Introduction

The isolobal principle as formulated by Hoffmann[2] suggests that electronically and structurally related species may result from the formal interchange of a metal fragment for an isolobal carbon counterpart (and vice versa) by virtue of similarities in symmetry, shape, occupancy, and energy of their frontier orbitals. $Ru(CO)_3$ and CH^+ are isolobal and their formal interchange in the linear tetranuclear cluster $Ru_4(CO)_{10}[R^1C{=}C(H)C(H){=}NR^2]_2$ (**3**), with concomitant substitution of the NR by isoelectronic CH^- fragments, leads to the isolobal relation of **3** with $Ru_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ (Figure 1).[3]

It has been shown that the similarities between **3** and $Ru_2(CO)_4(\eta^5\text{-}C_5H_5)_2$ are not restricted to their structure. The formation path of **3**,[4] its dynamic behavior in solution,[5] and inter-

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