

Multiply Bonded Octahalodiosmate(III) Anions. 4.¹ Reactions with Nitrogen and Phosphorus Donor Ligands That Lead to Cleavage of the Os≡Os Bond

Phillip E. Fanwick, Iain F. Fraser, Stephen M. Tetrick, and Richard A. Walton*

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Salts of the octahalodiosmate(III) anions $[\text{Os}_2\text{X}_8]^{2-}$ ($\text{X} = \text{Cl}$ or Br) react with monodentate phosphines (PR_3) in alcohol solvents to give various mononuclear osmium(III) and osmium(II) species, viz. *trans*- $[\text{OsX}_4(\text{PR}_3)_2]^-$, *mer*- $\text{OsX}_3(\text{PR}_3)_3$, *trans*- $[\text{OsX}_2(\text{PR}_3)_4]^+$, *trans*- $\text{OsX}_2(\text{PR}_3)_4$, and $[\text{Os}_2(\mu\text{-X})_3(\text{PR}_3)_6]^+$. The actual complex that is isolated depends upon the reaction conditions and the phosphine used. Cleavage of the $\text{Os}\equiv\text{Os}$ bond of $[\text{Os}_2\text{Cl}_8]^{2-}$ also occurs upon reaction with $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$, $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, and $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ in ethanol to give *trans*- $\text{OsCl}_2(\text{L-L})_2$ complexes. Neat pyridine and 4-methylpyridine react to give *fac*- OsCl_3L_3 , whereas *trans*- $[\text{OsCl}_4\text{L}_2]^-$ is formed when DMF is used as the reaction solvent. The structure of the diosmium(II) complex $[\text{Os}_2(\mu\text{-Cl})_3(\text{PEt}_3)_6]\text{PF}_6$ has been determined by a single-crystal X-ray structure analysis on a crystal grown from THF-*n*-pentane. The complex crystallizes in the triclinic space group $P\bar{1}$ with the following unit cell parameters: $a = 13.856(2) \text{ \AA}$, $b = 18.551(3) \text{ \AA}$, $c = 11.174(2) \text{ \AA}$, $\alpha = 97.67(1)^\circ$, $\beta = 112.75(1)^\circ$, $\gamma = 84.52(1)^\circ$, $V = 2622(1) \text{ \AA}^3$, and $Z = 2$. The structure was refined to $R = 0.030$ ($R_w = 0.050$) for 6000 data with $F^2 > 3.0\sigma(F^2)$. The very long (nonbonded) $\text{Os}\cdots\text{Os}$ distance in this complex (3.47 \AA) contrasts with the dramatically shorter bond (2.56 \AA) in the tris(μ -hydrido) species $[\text{Os}_2(\mu\text{-H})_3(\text{PMe}_2\text{Ph})_6]^+$. This confacial bioctahedral structure is the first to be determined for a tris(μ -halo)-bridged diosmium(II) species.

Introduction

Reactions of the metal-metal quadruply bonded $[\text{Mo}_2\text{Cl}_8]^{4-}$ and $[\text{Re}_2\text{X}_8]^{2-}$ ($\text{X} = \text{Cl}$ or Br) anions with nitrogen and phosphorus donor ligands have been studied extensively² and generally proceed via substitution of halide by ligand to yield neutral complexes that contain a metal-metal quadruple bond. Recently, we described the synthetic, spectroscopic, and structural properties of the octahalodiosmate(III) anions $[\text{Os}_2\text{X}_8]^{2-}$ ($\text{X} = \text{Cl}$ or Br).^{1,3,4} It has yet to be established whether these complexes, which contain osmium-osmium triple bonds ($\sigma^2\pi^4\delta^2\delta^*2$ configuration), react with nitrogen and phosphorus donors to yield complexes in which a multiple bond is retained. Such studies have now been carried out and show that in all instances the $\text{Os}\equiv\text{Os}$ bond is cleaved. We describe herein the results of these investigations along with the spectroscopic and electrochemical properties of the resulting complexes.

Experimental Section

The octahalodiosmate(III) complexes $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{X}_8$ ($\text{X} = \text{Cl}$ or Br) and $(\text{PPN})_2\text{Os}_2\text{Cl}_8$ ($\text{PPN} = \text{bis}(\text{triphenylphosphine})\text{nitrogen}(1+)$) were prepared as described previously.¹ Potassium hexafluorophosphate was recrystallized from water prior to use. All other ligands and reagents were purchased from commercial sources and were used without subsequent purifications. Solvents were reagent grade and were deoxygenated prior to use. Reactions were carried out under an atmosphere of nitrogen unless otherwise noted.

A. Reactions of $(\text{PPN})_2\text{Os}_2\text{Cl}_8$. (i) $(\text{PPN})[\text{OsCl}_4(\text{py})_2]$ ($\text{py} = \text{Pyridine}$). $(\text{PPN})_2[\text{Os}_2\text{Cl}_8]$ (0.20 g, 0.12 mmol) and pyridine (0.05 mL, 0.62 mmol) were added to 10 mL of deoxygenated DMF and the reactants heated for 90 min under nitrogen. The solution was cooled, and the resulting red crystals were filtered off, washed with water, ethanol, and diethyl ether and dried under vacuum; yield 0.17 g (69%). This product did not give a satisfactory carbon microanalysis ($\sim 4\%$ low). Electronic absorption spectrum (CH_2Cl_2 ; λ_{max} , nm): 372 ($\epsilon = 7600$); 320 ($\epsilon = 8200$). IR spectrum (Nujol; cm^{-1}): 1115 (s) ($\nu(\text{P-N})$); 314 (m), 293 (s) ($\nu(\text{Os-Cl})$); 258 (m) ($\nu(\text{Os-N})$). Conductivity: $\Delta_m = 77 \text{ \Omega}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($7.2 \times 10^{-4} \text{ M}$ solution in CH_3NO_2). Magnetic moment: $\mu_{\text{eff}} = 1.8 \mu_B$ (in CH_2Cl_2). ESR spectrum (CH_2Cl_2 , -160°C): g values of ca. 2.5 and 2.29.

(ii) *fac*- $\text{OsCl}_3(\text{py})_3$. $(\text{PPN})_2[\text{Os}_2\text{Cl}_8]$ (0.10 g, 0.057 mmol) was refluxed in 10 mL of freshly distilled neat pyridine for 90 min. The excess pyridine was removed under vacuum at 60°C to leave a red-brown solid, which was dissolved in CH_2Cl_2 and filtered. A red-brown precipitate

formed upon addition of pentane to this filtrate. This was filtered off, washed with pentane and diethyl ether, and dried under vacuum; yield 0.05 g (80%). The spectral properties of this product are the same as those reported for $\text{OsCl}_3(\text{py})_3$ by Lewis et al.⁵

(iii) $(\text{PPN})[\text{OsCl}_4(\gamma\text{-pic})_2]$ ($\gamma\text{-pic} = \gamma\text{-Picoline}$). This brown-yellow crystalline compound was prepared as described above (paragraph A(i)) for the pyridine analogue; yield 59%. Electronic absorption spectrum (CH_2Cl_2 ; λ_{max} , nm): 360 ($\epsilon = 7500$); 318 ($\epsilon = 8300$). IR spectrum (Nujol; cm^{-1}): 1115 (s) ($\nu(\text{P-N})$); 300 (m), 289 (s) ($\nu(\text{Os-Cl})$); 233 (w) ($\nu(\text{Os-N})$). Conductivity: $\Delta_m = 92 \text{ \Omega}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ($6.8 \times 10^{-4} \text{ M}$ solution in CH_3NO_2). Magnetic moment: $\mu_{\text{eff}} = 1.9 \mu_B$ (in CH_2Cl_2). ESR spectrum (CH_2Cl_2 , -160°C): g values of 2.47 and 2.32.

(iv) *fac*- $\text{OsCl}_3(\gamma\text{-pic})_3$. This brown complex was prepared by a method similar to that used for the preparation of the pyridine derivative (paragraph A(ii)); yield 72%. The spectral properties of this product are the same as those reported previously for a sample of this complex prepared by a different procedure.⁵

(v) $[\text{Os}(\text{bpy})_3](\text{BPh}_4)_2$ ($\text{bpy} = 2,2'\text{-Bipyridine}$). $(\text{PPN})_2[\text{Os}_2\text{Cl}_8]$ (0.10 g, 0.057 mmol) was stirred at room temperature with an excess of 2,2'-bipyridine (0.10 g, 0.64 mmol) in 20 mL of deoxygenated methanol for 3 days. The resulting green solution was filtered and the filtrate treated with NaBPh_4 (0.08 g, 0.25 mmol) to form a dark green solid, which was washed several times with methanol and diethyl ether and then dried under vacuum. The product was recrystallized from CH_2Cl_2 ; yield 0.11 g (74%). The electronic absorption spectrum and the cyclic voltammogram of this complex in CH_2Cl_2 are identical with those reported previously.^{6,7}

(vi) *trans*- $\text{OsCl}_2(\text{dmpe})_2$ ($\text{dmpe} = 1,2\text{-Bis}(\text{dimethylphosphino})\text{ethane}$). A suspension of $(\text{PPN})_2\text{Os}_2\text{Cl}_8$ (0.10 g, 0.057 mmol) in ethanol (20 mL) was treated with a slight excess of dmpe (0.040 mL, 0.24 mmol) and refluxed for 2 h. The yellow solid that formed upon cooling the reaction mixture was filtered off, washed with ethanol and diethyl ether, and dried under vacuum. Recrystallization from CH_2Cl_2 afforded crystalline *trans*- $\text{OsCl}_2(\text{dmpe})_2$; yield 0.050 g (78%). Anal. Calcd for $\text{C}_{12}\text{H}_{32}\text{Cl}_2\text{OsP}_4$: C, 25.67; H, 5.75. Found: C, 25.20; H, 6.70.

(vii) *trans*- $\text{OsCl}_2(\text{dppm})_2$ ($\text{dppm} = \text{Bis}(\text{diphenylphosphino})\text{methane}$). A procedure very similar to that in paragraph A(vi) was used. The product was recrystallized from CH_2Cl_2 ; yield 34%. This complex has been prepared previously by Chatt and Hayter.⁸ The electrochemical properties for our sample are the same as those reported by Sullivan and Meyer⁹ for this complex.

(viii) *trans*- $\text{OsCl}_2(\text{dppe})_2$ ($\text{dppe} = 1,2\text{-Bis}(\text{diphenylphosphino})\text{ethane}$). A procedure very similar to that described in paragraph A(vi) afforded yellow *trans*- $\text{OsCl}_2(\text{dppe})_2$. The crude product was recrystallized from CH_2Cl_2 ; yield 33%. Anal. Calcd for $\text{C}_{33}\text{H}_{50}\text{Cl}_2\text{OsP}_4$: C, 55.70; H, 4.41. Found: C, 54.90; H, 4.56. The presence of lattice dichloromethane was

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confirmed by ^1H NMR spectroscopy in CDCl_3 ($\delta +5.30$).

B. Reactions of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Cl}_8$. (i) $(n\text{-Bu}_4\text{N})[\text{OsCl}_4(\text{py})_2]$. $(n\text{-Bu}_4\text{N})_2[\text{Os}_2\text{Cl}_8]$ (0.10 g, 0.06 mmol) and pyridine (0.02 mL, 0.25 mmol) were added to 10 mL of deoxygenated DMF and the reactants refluxed for 90 min under nitrogen. An excess of diethyl ether was added to the cooled solution to precipitate a yellow-brown solid. This was washed with diethyl ether and dried under vacuum; yield 0.09 g. The identity of this complex was confirmed by a single-crystal X-ray structure analysis. Electronic absorption spectrum (CH_2Cl_2 ; λ_{max} , nm): 372 ($\epsilon = 7100$); 320 ($\epsilon = 7700$). Conductivity: $\Lambda_M = 93 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ (5.4×10^{-4} M solution in acetone). The X-band ESR spectrum of this complex (CH_2Cl_2 , -160°C) was identical with that of the related PPN^+ salt (paragraph A(i)).

(ii) $(n\text{-Bu}_4\text{N})[\text{OsCl}_4(\text{PMe}_3)_2] \cdot 0.75\text{CH}_2\text{Cl}_2$. A sample of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Cl}_8$ (0.190 g, 0.165 mmol) was suspended in cold (0°C) *n*-propanol (5 mL). To this was added PMe_3 (0.080 mL, 0.79 mmol) via a syringe, and the resulting green suspension was stirred. After 10 min, the yellow suspension was allowed to warm to room temperature. *n*-Propanol (10 mL) was added to dissolve the yellow solid and the solution then filtered under nitrogen and recooled to 0°C . Pentane (50 mL) was slowly added with stirring via a syringe; this precipitated the product $(n\text{-Bu}_4\text{N})[\text{OsCl}_4(\text{PMe}_3)_2]$ as a bright yellow powder. After 15 min, the solid was removed by filtration, washed with diethyl ether, and vacuum-dried; yield 0.159 g (66%). Elemental microanalysis revealed that dichloromethane of crystallization was present. Anal. Calcd for $\text{C}_{22.75}\text{H}_{55.5}\text{Cl}_4.75\text{NOsP}_2$: C, 34.58; H, 7.08; Cl, 24.67. Found: C, 34.58; H, 7.44; Cl, 24.17. This complex is somewhat air-sensitive in the solid state, and dichloromethane solutions of this complex slowly decompose.

(iii) $\text{mer-OsCl}_3(\text{PMe}_3)_3$. Concentrated HCl (1 mL) was added to a suspension of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Cl}_8$ (0.127 g, 0.111 mmol) in methanol (10 mL). Trimethylphosphine (0.12 mL, 1.2 mmol) was added, and this mixture was refluxed for 1.5 h. The solution was evaporated to dryness, and the residue was dissolved in acetone and chromatographed on silica gel. Elution with acetone produces an orange solution that was evaporated to dryness. This was redissolved in dichloromethane followed by the addition of anhydrous sodium carbonate (1 g) to remove any water present. The mixture was filtered, the volume of the filtrate was reduced to about 5 mL, and pentane was added until the solution became cloudy. Refrigeration of this solution overnight yields dark orange crystals of $\text{mer-OsCl}_3(\text{PMe}_3)_3$; yield 0.080 g (69%). Anal. Calcd for $\text{C}_9\text{H}_{21}\text{Cl}_3\text{OsP}_3$: C, 20.60; H, 5.19. Found: C, 20.51; H, 5.34. A chlorine microanalysis (found: Cl, 21.91) was consistent with the presence of a trace of lattice CH_2Cl_2 (calcd for $\text{OsCl}_3(\text{PMe}_3)_3 \cdot \frac{1}{6}\text{CH}_2\text{Cl}_2$: C, 20.43; H, 5.12; Cl, 21.93). Electronic absorption spectrum (CH_2Cl_2 ; λ_{max} , nm): 494 ($\epsilon = 730$); 404 ($\epsilon = 1880$); 380 (sh); 334 ($\epsilon = 850$); 302 ($\epsilon = 1870$). Magnetic moment: $\mu_{\text{eff}} = 2.1 \mu_B$ (in CH_2Cl_2).

(iv) $\text{trans-OsCl}_2(\text{PMe}_3)_4\text{PF}_6$. Trimethylphosphine (0.10 mL, 0.98 mmol) was added to a suspension of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Cl}_8$ (0.178 g, 0.155 mmol) in methanol (10 mL). This mixture was stirred at room temperature for 20 h, the solvent was evaporated, and the dark residue was redissolved in acetone. This solution was treated with a solution of KPF_6 (0.5 g) in acetone (5 mL). After 30 min the solvent was evaporated and the residue was extracted with CH_2Cl_2 and the extract filtered to produce an intense pink filtrate. The solution volume was reduced to ca. 5 mL, and diethyl ether was added with stirring to precipitate $\text{trans-OsCl}_2(\text{PMe}_3)_4\text{PF}_6$ as a pink solid. This was removed by filtration and washed with diethyl ether. Purification was achieved by redissolving the product in methanol (10 mL) and then adding an equal volume of diethyl ether (10 mL). Refrigeration overnight yielded pink crystals of the product that were removed by filtration, washed with diethyl ether, and vacuum-dried; yield 0.117 g (53%). This complex was identified as $\text{trans-OsCl}_2(\text{PMe}_3)_4\text{PF}_6$ through a comparison of its spectral and magnetic properties with those reported for this complex by Werner and Gotzlig.¹⁰ Magnetic moment: $\mu_{\text{eff}} = 2.2 \mu_B$ (in CH_2Cl_2).

(v) $\text{trans-OsCl}_2(\text{PMe}_3)_4$. A sample of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Cl}_8$ (0.201 g, 0.175 mmol) was suspended in ethanol (10 mL). Trimethylphosphine (0.32 mL, 3.1 mmol) was added, the solution was refluxed for 4 h and then cooled to room temperature, and the ethanol was removed in vacuo to leave a yellow residue. This was extracted with hot toluene and filtered and the filtrate reduced to a volume of 5 mL. An equal amount of *n*-pentane was added, and this solution was refrigerated overnight. The orange crystals of $\text{trans-OsCl}_2(\text{PMe}_3)_4$ that formed were removed by filtration, washed with *n*-pentane and diethyl ether, and then vacuum-dried; yield 0.120 g (61%). The complex was identified as $\text{trans-OsCl}_2(\text{PMe}_3)_4$ through a comparison of its NMR (^1H and $^{31}\text{P}\{^1\text{H}\}$) spectral properties with those reported in the literature for this complex.¹⁰

(vi) $(n\text{-Bu}_4\text{N})[\text{OsCl}_4(\text{PET}_3)_2] \cdot 0.5\text{CH}_2\text{Cl}_2$. $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Cl}_8$ (0.124 g, 0.153 mmol) was suspended in ethanol (10 mL). To this was added PET_3

(0.10 mL, 0.68 mmol) with stirring. *n*-Pentane (20 mL) was added after 5 min with stirring to precipitate the product as a yellow powder. This solid was filtered off and was recrystallized from dichloromethane/diethyl ether; yield 0.142 g (81%). Anal. Calcd for $\text{C}_{28.5}\text{H}_{67}\text{Cl}_5\text{NOsP}_2$: C, 40.12; H, 7.92. Found: C, 39.99; H, 8.42.

(vii) $[\text{Os}_2\text{Cl}_3(\text{PET}_3)_6]\text{PF}_6$. A quantity of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Cl}_8$ (0.102 g, 0.089 mmol) was suspended in ethanol (10 mL). Triethylphosphine (0.21 mL, 1.35 mmol) was added, and this mixture was refluxed for 6 h. The resulting solution was evaporated to dryness, and the yellow residue was dissolved in acetone and filtered. An excess of KPF_6 (0.5 g) dissolved in acetone (5 mL) was added to the yellow filtrate. This mixture was stirred for 30 min and then evaporated to dryness. Extraction of the yellow residue with *tert*-butyl chloride, followed by filtration, yielded a yellow filtrate, which was evaporated to dryness. The residue was redissolved in dichloromethane (3 mL), 2-propanol (15 mL) was added, and the solution was refrigerated. Pale yellow needles of $[\text{Os}_2\text{Cl}_3(\text{PET}_3)_6]\text{PF}_6$ were filtered off, washed with diethyl ether, and vacuum-dried; yield 0.104 g (87%). Anal. Calcd for $\text{C}_{36}\text{H}_{90}\text{Cl}_3\text{F}_6\text{Os}_2\text{P}_7$: C, 32.25; H, 6.77. Found: C, 32.24; H, 7.27.

(viii) $\text{trans-OsCl}_2(\text{PMe}_2\text{Ph})_4$. A sample of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Cl}_8$ (0.205 g, 0.178 mmol) was suspended in ethanol (10 mL). A large excess of PMe_2Ph (0.50 mL, 3.50 mmol) was added, and the solution was refluxed for 1.5 h, whereupon a yellow solution resulted. This was evaporated to dryness and the residue stirred as a suspension in 2-propanol. Filtration yielded $\text{trans-OsCl}_2(\text{PMe}_2\text{Ph})_4$ as a pale yellow powder. This was washed with 2-propanol and *n*-pentane and then vacuum-dried; yield 0.173 g (60%). The spectroscopic and electrochemical properties were identical with those reported previously for this complex.¹¹

(ix) $[\text{Os}_2\text{Cl}_3(\text{PMePh}_2)_6]\text{PF}_6 \cdot 0.33\text{CH}_2\text{Cl}_2$. A quantity of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Cl}_8$ (0.106 g, 0.0923 mmol) was suspended in ethanol (10 mL) and treated with PMePh_2 (0.35 mL, 1.89 mmol). The mixture was refluxed for 20 h and then evaporated to dryness, and the dark brown residue was extracted into hot acetone. Filtration yielded a yellow solution, to which KPF_6 (0.5 g) was added with stirring. The resulting solution was then evaporated to dryness after 30 min and the residue extracted with chlorobenzene. This yielded a yellow filtrate, which was again evaporated to dryness, and the residue was dissolved in dichloromethane (5 mL). 2-Propanol (25 mL) was added, and this solution was then refrigerated. Yellow crystals of $[\text{Os}_2\text{Cl}_3(\text{PMePh}_2)_6]\text{PF}_6$ were removed by filtration, washed with diethyl ether, and vacuum-dried; yield 0.100 g (59%). Anal. Calcd for $\text{C}_{78.33}\text{H}_{78.66}\text{Cl}_{3.66}\text{F}_6\text{Os}_2\text{P}_7$: C, 50.54; H, 4.23; Cl, 6.98. Found: C, 50.55; H, 4.55; Cl, 7.25.

C. Reactions of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Br}_8$. (i) $(n\text{-Bu}_4\text{N})[\text{OsBr}_4(\text{PMe}_3)_2]$. A sample of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Br}_8$ (0.201 g, 0.134 mmol) was dissolved in acetone (10 mL), trimethylphosphine (0.13 mL, 1.28 mmol) was added via a syringe, and the solution was refluxed for 30 min. This affords a yellow solution, which was cooled to room temperature and filtered, and *n*-pentane was added to the filtrate with stirring to precipitate a bright yellow solid that was removed by filtration. The crude $(n\text{-Bu}_4\text{N})[\text{OsBr}_4(\text{PMe}_3)_2]$ was dissolved in dichloromethane (5 mL) and filtered. Diethyl ether (25 mL) was added to the yellow filtrate, and this solution was refrigerated. The yellow microcrystalline product that results was removed by filtration and washed several times with diethyl ether followed by drying under vacuum; yield 0.130 g (54%). Anal. Calcd for $\text{C}_{22}\text{H}_{54}\text{Br}_4\text{NOsP}_2$: C, 29.21; H, 6.02. Found: C, 28.89; H, 6.33. As with the chloro analogue, this complex is slightly air-sensitive in the solid state and in solution.

(ii) $\text{mer-OsBr}_3(\text{PMe}_3)_3$. Concentrated aqueous HBr (3 mL) was added to a suspension of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Br}_8$ (0.203 g, 0.135 mmol) in ethanol (15 mL) followed by the addition of trimethylphosphine (0.16 mL, 1.57 mmol). The dark red-purple solution that formed within 15 min was then cooled to room temperature. Removal of the solvent in vacuo yielded a red oil, which was dissolved in ethanol and filtered. The red-purple filtrate was reduced in volume to ca. 10 mL, water (15 mL) was added, and the solution cooled to 0°C . The brick red solid that precipitated was removed by filtration, washed with water and *n*-pentane, and vacuum-dried; yield 0.070 g (39%). Anal. Calcd for $\text{C}_9\text{H}_{21}\text{Br}_3\text{OsP}_3$: C, 16.42; H, 4.14. Found: C, 15.97; H, 4.31. Electronic absorption spectrum (CH_2Cl_2 ; λ_{max} , nm): 544 ($\epsilon = 2840$); 448 ($\epsilon = 1780$); 401 ($\epsilon = 1550$); 342 ($\epsilon = 1670$); 291 ($\epsilon = 1330$). Magnetic moment: $\mu_{\text{eff}} = 2.1 \mu_B$ (in CH_2Cl_2).

(iii) $\text{trans-OsBr}_2(\text{PMe}_3)_4$. A suspension of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Br}_8$ (0.210 g, 0.104 mmol) in ethanol (10 mL) was treated with trimethylphosphine (0.17 mL, 1.69 mmol). The reaction mixture was refluxed for 2 h, the solution that resulted was cooled to room temperature, and the solvent was evaporated. The yellow residue was washed with acetone, and the pale yellow solid was dissolved in dichloromethane (3 mL) and filtered.

(11) Coombe, V. T.; Heath, G. A.; Stephenson, T. A.; Whitelock, J. D.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* 1985, 947.

Acetone (15 mL) was added to the yellow filtrate, and this was refrigerated. Orange crystals of *trans*-OsBr₂(PMe₃)₄ were removed by filtration, and then washed with acetone and vacuum-dried; yield 0.082 g (45%). Anal. Calcd for C₁₂H₃₆Br₂OsP₄: C, 22.03; H, 5.55. Found: C, 22.41; H, 5.84.

(iv) *(n-Bu₄N)[OsBr₄(PEt₃)₂]*. A sample of *(n-Bu₄N)₂Os₂Br₈* (0.207 g, 0.138 mmol) was dissolved in dichloromethane (5 mL). Triethylphosphine (0.12 mL, 0.813 mmol) was added via a syringe. After 5 min, the orange-brown solution was filtered under nitrogen and then evaporated to dryness. The residue was dissolved in dichloromethane (5 mL) followed by the addition of 2-propanol (20 mL). Refrigeration overnight yielded orange crystals of *trans*-*(n-Bu₄N)[OsBr₄(PEt₃)₂]*, which were removed by filtration, washed with 2-propanol and diethyl ether, and vacuum-dried; yield 0.104 g (36%). Anal. Calcd for C₂₈H₆₆Br₄NOsP₂: C, 34.02; H, 6.73. Found: C, 33.50; H, 7.16.

(v) [Os₂Br₃(PEt₃)₆]PF₆. Yellow crystals of [Os₂Br₃(PEt₃)₆]PF₆ were prepared by a procedure very similar to that described for its chloride analogue (paragraph B(vii)); yield 91%. Anal. Calcd for C₃₆H₉₀Br₃F₆Os₂P₇: C, 29.34; H, 6.16. Found: C, 29.41; H, 6.40.

(vi) *trans*-OsBr₂(PMe₂Ph)₄. A mixture of *(n-Bu₄N)₂Os₂Br₈* (0.204 g, 0.136 mmol) and dimethylphenylphosphine (0.30 mL, 2.10 mmol) was refluxed in ethanol (15 mL) for 1 h, during which time a pale yellow solid precipitated. This was removed by filtration, washed several times with ethanol and diethyl ether, and then dried for a short time under vacuum; yield 0.169 g (ca. ~69%). The identity of this complex as *trans*-OsBr₂(PMe₂Ph)₄ was based upon its electrochemical and NMR spectral properties, which were similar to those displayed by the chloro analogue.

(vii) [Os₂Br₃(PMePh₂)₆]PF₆. Ethanol (15 mL) was added to a mixture of *(n-Bu₄N)₂Os₂Br₈* (0.201 g, 0.134 mmol), KPF₆ (0.1 g), and PMePh₂ (0.40 mL, 2.15 mmol). This was refluxed for 12 h and then cooled to room temperature, and the yellow solid was removed by filtration and washed several times with ethanol. Extraction of the solid into dichloromethane produced a yellow solution that was then evaporated to low volume (ca. 3 mL). Tetrahydrofuran (15 mL) was added, and this solution was refrigerated overnight. Yellow crystals of [Os₂Br₃(PMePh₂)₆]PF₆ that deposited were removed by filtration, washed with tetrahydrofuran and diethyl ether, and vacuum-dried; yield 0.170 g (65%). Anal. Calcd for C₇₈H₇₈Br₃F₆Os₂P₇: C, 47.64; H, 4.00. Found: C, 45.45; H, 4.16.

D. Preparation of *trans*-[OsBr₂(PR₃)₄]PF₆ Complexes. (i) *trans*-[OsBr₂(PMe₃)₄]PF₆. A sample of *trans*-OsBr₂(PMe₃)₄ (0.062 g, 0.0948 mmol) was dissolved in dichloromethane (5 mL). Solid NOPF₆ (0.034 g, 0.194 mmol) was added, which caused the solution to immediately change color from yellow to purple. After 5 min, the solution was filtered and diethyl ether was added to the stirred filtrate to induce precipitation of *trans*-[OsBr₂(PMe₃)₄]PF₆ as a purple solid. This product was removed by filtration and washed with diethyl ether. The crude material was dissolved in dichloromethane (10 mL) followed by the addition of diethyl ether (5 mL). Refrigeration overnight produced purple crystals of *trans*-[OsBr₂(PMe₃)₄]PF₆, which were filtered off, washed with diethyl ether, and vacuum-dried; yield 0.058 g (77%). Anal. Calcd for C₁₂H₃₆Br₂F₆OsP₅: C, 18.03; H, 4.54. Found: C, 18.32; H, 4.72. Magnetic moment: $\mu_{\text{eff}} = 2.2 \mu_{\text{B}}$ (in CH₂Cl₂).

(ii) *trans*-[OsBr₂(PMe₂Ph)₄]PF₆·Me₂CHOH. The complex *trans*-OsBr₂(PMe₂Ph)₄ (0.130 g, 0.144 mmol) was dissolved in dichloromethane (5 mL) and the resulting yellow solution treated with [(η^5 -C₅H₅)₂Fe]PF₆ (0.064 g, 0.193 mmol). The dark green solution was filtered, the filtrate was evaporated to low volume (ca. 3 mL), 2-propanol (15 mL) was added, and this solution was refrigerated. Dark green crystals of *trans*-[OsBr₂(PMe₂Ph)₄]PF₆·Me₂CHOH were harvested, washed with diethyl ether, and vacuum-dried; yield 0.125 g (78%). Anal. Calcd for C₃₃H₅₂Br₂F₆OOSp₅: C, 37.95; H, 4.73. Found: C, 37.74; H, 4.98. The presence of 2-propanol was inferred from the presence of a $\nu(\text{O-H})$ vibration at 3355 cm⁻¹ in the Nujol mull IR spectrum of this complex.

E. Preparation of Single Crystals of [Os₂(μ -Cl)₃(PEt₃)₆]PF₆. A batch of this complex was prepared as described in paragraph B(vii). Yellow crystals were obtained by dissolving a sample in tetrahydrofuran and layering *n*-pentane over this solution.

F. X-ray Structure Determination. Experimental details relating to this structure determination are available as supplementary material. Crystal data and information concerning the data collection and structure refinement are listed in Table I.

Further details concerning the data set, the structure solution, and the structure refinement may be obtained from Dr. P. E. Fanwick. Table II lists the positional parameters and their errors for non-ethyl-group atoms, while Table III lists important intramolecular bond distances and angles. Tables listing positional parameters and their errors for the ethyl carbon atoms (Table S1), positional parameters for the hydrogen atoms (Table S2), and thermal parameters (Table S3) and complete listings of

Table I. Crystallographic Data and Data Collection Parameters for [Os₂(μ -Cl)₃(PEt₃)₆]PF₆^a

| | |
|--|---|
| formula | Os ₂ Cl ₃ P ₇ F ₆ C ₃₆ H ₉₀ |
| fw | 1340.69 |
| space group | P $\bar{1}$ |
| <i>a</i> , Å | 13.856 (2) |
| <i>b</i> , Å | 18.551 (3) |
| <i>c</i> , Å | 11.174 (2) |
| α , deg | 97.67 (1) |
| β , deg | 112.75 (1) |
| γ , deg | 84.52 (1) |
| <i>V</i> , Å ³ | 2622 (1) |
| <i>Z</i> | 2 |
| <i>d</i> _{calcd} , g cm ⁻³ | 1.698 |
| cryst dimens, mm | 0.66 × 0.51 × 0.45 |
| temp, °C | 22.0 |
| radiation (wavelength, Å) | Mo K α (0.71073 Å) |
| monochromator | graphite |
| linear abs coeff, cm ⁻¹ | 52.59 |
| abs cor applied | empirical ^b |
| cryst radius, cm | 0.053 |
| diffractometer | Enraf-Nonius CAD4 |
| scan method | θ - 2θ |
| <i>h, k, l</i> limits | -14 to +14, 0 to +19, -12 to +11 |
| 2θ range, deg | 4.00-45.00 |
| scan width, deg | 0.75 + 0.35 tan θ |
| takeoff angle, deg | 1.90 |
| programs used | Enraf-Nonius SDP |
| <i>F</i> ₀₀₀ | 1336.0 |
| <i>p</i> factor used in weighting | 0.070 |
| no. of data colld | 6814 |
| data with <i>I</i> > 3.0 σ (<i>I</i>) | 6000 |
| no. of variables | 490 |
| largest shift/esd in final cycle | 0.67 |
| <i>R</i> ^c | 0.030 |
| <i>R</i> _w ^d | 0.050 |
| goodness of fit ^e | 1.335 |

^a Numbers in parentheses following certain data are estimated standard deviations occurring in the least significant digit. ^b Flack, H. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **1977**, *A33*, 890. ^c $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^d $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$. ^e Goodness of fit = $[\sum w(|F_o| - |F_c|)^2 / (N_{\text{observ}} - N_{\text{params}})]^{1/2}$.

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å²) for Non-Ethyl-Group Atoms and Their Estimated Standard Deviations^a

| atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> , Å ² |
|-------|-------------|-------------|-------------|---------------------------|
| Os(1) | 0.55555 (2) | 0.26153 (1) | 0.27988 (2) | 2.836 (5) |
| Os(2) | 0.29464 (2) | 0.24163 (1) | 0.22493 (2) | 2.819 (5) |
| Cl(1) | 0.4590 (1) | 0.16357 (8) | 0.3111 (1) | 3.52 (3) |
| Cl(2) | 0.3897 (1) | 0.25809 (8) | 0.0828 (1) | 3.18 (3) |
| Cl(3) | 0.4276 (1) | 0.33140 (8) | 0.3643 (1) | 3.41 (3) |
| P(1) | 0.6393 (1) | 0.18505 (9) | 0.1678 (1) | 3.44 (4) |
| P(2) | 0.6006 (1) | 0.37019 (9) | 0.2418 (1) | 3.42 (3) |
| P(3) | 0.6863 (1) | 0.2566 (1) | 0.4843 (1) | 4.02 (4) |
| P(4) | 0.1673 (1) | 0.33085 (9) | 0.1423 (1) | 3.63 (4) |
| P(5) | 0.2491 (1) | 0.23113 (9) | 0.3999 (1) | 3.64 (4) |
| P(6) | 0.2043 (1) | 0.14621 (9) | 0.0886 (1) | 3.77 (4) |
| P(7) | 0 | 1/2 | 1/2 | 5.63 (7) |
| P(8) | 0 | 0 | 1/2 | 6.11 (8) |
| F(71) | 0.1138 (3) | 0.4957 (4) | 0.5011 (6) | 9.8 (2) |
| F(72) | -0.0238 (5) | 0.4238 (3) | 0.4192 (7) | 11.1 (2) |
| F(73) | -0.0436 (5) | 0.5351 (4) | 0.3708 (5) | 11.5 (2) |
| F(81) | -0.0469 (5) | 0.0763 (3) | 0.5136 (9) | 15.5 (3) |
| F(82) | 0.0551 (7) | 0.0234 (4) | 0.4189 (8) | 18.2 (3) |
| F(83) | -0.0923 (7) | -0.0209 (6) | 0.387 (1) | 20.7 (4) |

^a Anisotropically refined atoms are given in the form of isotropic equivalent thermal parameters defined as $1/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos \gamma)B_{12} + ac(\cos \beta)B_{13} + bc(\cos \alpha)B_{23}]$. Data for ethyl-group atoms are available as supplementary material.

bond distances and bond angles (Tables S4 and S5, respectively) are available as supplementary material, as well as a figure (Figure S1) that shows the full atomic numbering scheme.

G. Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates with an IBM Instruments IR/32 Fourier

Table III. Important Bond Distances (Å) and Bond Angles (deg) for $[\text{Os}_2(\mu\text{-Cl})_3(\text{PEt}_3)_6]\text{PF}_6^a$

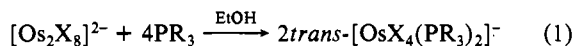
| (a) Distances | | | |
|-------------------|------------|-------------------|------------|
| Os(1)–Cl(1) | 2.492 (1) | Os(2)–Cl(1) | 2.502 (1) |
| Os(1)–Cl(2) | 2.492 (1) | Os(2)–Cl(2) | 2.485 (1) |
| Os(1)–Cl(3) | 2.498 (1) | Os(2)–Cl(3) | 2.504 (1) |
| Os(1)–P(1) | 2.294 (1) | Os(2)–P(4) | 2.301 (2) |
| Os(1)–P(2) | 2.304 (1) | Os(2)–P(5) | 2.311 (1) |
| Os(1)–P(3) | 2.309 (1) | Os(2)–P(6) | 2.291 (1) |
| (b) Angles | | | |
| Cl(1)–Os(1)–Cl(2) | 76.32 (4) | Cl(1)–Os(2)–P(4) | 167.55 (5) |
| Cl(1)–Os(1)–Cl(3) | 77.17 (4) | Cl(1)–Os(2)–P(5) | 93.11 (5) |
| Cl(1)–Os(1)–P(1) | 94.73 (5) | Cl(1)–Os(2)–P(6) | 92.25 (5) |
| Cl(1)–Os(1)–P(2) | 163.83 (5) | Cl(2)–Os(2)–Cl(3) | 77.43 (4) |
| Cl(1)–Os(1)–P(3) | 92.67 (5) | Cl(2)–Os(2)–P(4) | 94.20 (5) |
| Cl(2)–Os(1)–Cl(3) | 77.41 (4) | Cl(2)–Os(2)–P(5) | 164.92 (5) |
| Cl(2)–Os(1)–P(1) | 90.66 (5) | Cl(2)–Os(2)–P(6) | 93.37 (5) |
| Cl(2)–Os(1)–P(2) | 93.28 (5) | Cl(3)–Os(2)–P(4) | 93.39 (5) |
| Cl(2)–Os(1)–P(3) | 167.28 (5) | Cl(3)–Os(2)–P(5) | 89.86 (5) |
| Cl(3)–Os(1)–P(1) | 166.83 (5) | Cl(3)–Os(2)–P(6) | 167.09 (5) |
| Cl(3)–Os(1)–P(2) | 88.60 (5) | P(4)–Os(2)–P(5) | 94.63 (5) |
| Cl(3)–Os(1)–P(3) | 94.10 (5) | P(4)–Os(2)–P(6) | 96.35 (6) |
| P(1)–Os(1)–P(2) | 97.77 (5) | P(5)–Os(2)–P(6) | 97.77 (5) |
| P(1)–Os(1)–P(3) | 96.67 (5) | Os(1)–Cl(1)–Os(2) | 88.14 (4) |
| P(2)–Os(1)–P(3) | 96.00 (5) | Os(1)–Cl(2)–Os(2) | 88.49 (4) |
| Cl(1)–Os(2)–Cl(2) | 76.26 (4) | Os(1)–Cl(3)–Os(2) | 87.95 (4) |
| Cl(1)–Os(2)–Cl(3) | 76.88 (4) | | |

^a Numbers in parentheses are estimated standard deviations in the least significant digits.

transform spectrometer. Far-infrared spectra were measured as Nujol mulls on polyethylene plates with the use of an IBM Instruments IR/98 spectrometer. Cyclic voltammetry results were obtained as previously described¹² for dichloromethane solutions containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. Potentials were referenced to the silver/silver chloride electrode at room temperature. Conductivities were measured with the use of an Industrial Instruments Inc. Model RC 16B2 conductivity bridge. ¹H NMR spectra were recorded at 90 MHz with a Perkin-Elmer R32 spectrometer or at 200 MHz with a Varian XL-200 spectrometer. ³¹P{¹H} NMR spectra were recorded at 80.98 MHz with the same XL-200 spectrometer. Magnetic moments were recorded on CH₂Cl₂ solutions of the complexes at room temperature (~25 °C) by using the Evans method.¹³ X-Band ESR spectra were obtained on toluene-dichloromethane glasses (5/2, v/v) at -160 °C with a Varian E-109 spectrometer. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

Results and Discussion

(a) Reactions with Monodentate Phosphines. Monodentate phosphines react very rapidly at room temperature with ethanol suspensions of (*n*-Bu₄N)₂Os₂X₈ (X = Cl, Br) to yield solutions that contain the *trans*-[OsX₄(PR₃)₂]⁻ anions (PR₃ = PMe₃, PEt₃, PMe₂Ph, or PMePh₂) (eq 1). Cleavage of the Os≡Os bond in



[Os₂X₈]²⁻ by monodentate phosphines to give *trans*-[OsX₄(PR₃)₂]⁻ also occurs with diethyl ether, tetrahydrofuran (-78 °C), dichloromethane, and acetone as solvents. The effect of a different cation on the reaction pathway was also studied through the use of (PPN)₂Os₂Cl₈ (PPN = bis(triphenylphosphine)nitrogen(1+)) as a starting material; however, no difference in the reactivity of the (PPN)⁺ salt relative to that for the (*n*-Bu₄N)⁺ salt was observed. The use of less than a stoichiometric quantity of phosphine (<4 equiv) in dichloromethane solution results in a mixture of unreacted [Os₂X₈]²⁻ and *trans*-[OsX₄(PR₃)₂]⁻ as monitored by cyclic voltammetry and electronic absorption spectroscopy. Crystalline samples of salts of the *trans*-[OsX₄(PR₃)₂]⁻ anions were isolated from these solutions in the case of X = Cl or Br and PR₃ = PMe₃ or PEt₃. The isolation of other *trans*-[OsX₄(PR₃)₂]⁻ anions, where PR₃ = PMe₂Ph or PMePh₂, was not at-

Table IV. Cyclic Voltammetric Data for CH₂Cl₂ Solutions of Phosphine and Heterocyclic Amine Complexes of Osmium(III) and Osmium(II)

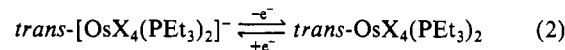
| complex | $E_{1/2}[\text{Os(IV)}/\text{Os(III)}]^a$ | $E_{1/2}[\text{Os(III)}/\text{Os(II)}]^a$ |
|--|---|---|
| (<i>n</i> -Bu ₄ N)[<i>trans</i> -OsCl ₄ (PEt ₃) ₂] | +0.16 (100) | |
| (<i>n</i> -Bu ₄ N)[<i>trans</i> -OsBr ₄ (PEt ₃) ₂] | +0.18 (110) | |
| <i>mer</i> -OsCl ₃ (PMe ₃) ₃ | +0.93 (115) | -0.52 ^b |
| <i>mer</i> -OsBr ₃ (PMe ₃) ₃ | +0.92 (110) | -0.37 ^b |
| <i>trans</i> -[OsCl ₂ (PMe ₃) ₄]PF ₆ | +1.46 (110) | +0.10 (110) |
| <i>trans</i> -[OsBr ₂ (PMe ₃) ₄]PF ₆ | +1.41 (120) | +0.14 (110) |
| <i>trans</i> -[OsBr ₂ (PMe ₂ Ph) ₄]PF ₆ | +1.46 (120) | +0.19 (100) |
| <i>trans</i> -OsCl ₂ (PMe ₃) ₄ | +1.46 (120) | +0.10 (115) |
| <i>trans</i> -OsBr ₂ (PMe ₃) ₄ | +1.42 (120) | +0.14 (120) |
| <i>trans</i> -OsCl ₂ (PMe ₂ Ph) ₄ | +1.41 (120) | +0.20 (110) |
| <i>trans</i> -OsBr ₂ (PMe ₂ Ph) ₄ | +1.38 (120) | +0.16 (105) |
| <i>trans</i> -OsCl ₂ (dmpe) ₂ | +1.45 (110) | +0.11 (120) |
| <i>trans</i> -OsCl ₂ (dppm) ₂ ^c | +1.65 ^d | +0.19 (125) |
| <i>trans</i> -OsCl ₂ (dppe) ₂ | +1.49 (120) | +0.22 (110) |
| (PPN)[<i>trans</i> -OsCl ₄ (py) ₂] | +0.29 (115) | -1.33 (110) |
| (PPN)[<i>trans</i> -OsCl ₄ (γ-pic) ₂] | +0.24 (120) | -1.42 (120) |
| <i>fac</i> -OsCl ₃ (py) ₃ | +0.88 (120) | -0.71 (110) |
| <i>fac</i> -OsCl ₃ (γ-pic) ₃ | +0.85 (120) | -0.80 (115) |
| complex | $E_{1/2}[\text{Os(III)Os(III)}/\text{Os(III)Os(II)}]^a$ | $E_{1/2}[\text{Os(III)Os(II)}/\text{Os(II)Os(II)}]^a$ |
| [Os ₂ Cl ₃ (PEt ₃) ₆]PF ₆ | +1.43 (115) | +0.83 (100) |
| [Os ₂ Br ₃ (PEt ₃) ₆]PF ₆ | +1.28 (100) | +0.75 (85) |
| [Os ₂ Cl ₃ (PMePh ₂) ₆]PF ₆ | +1.61 (120) | +1.06 (120) |
| [Os ₂ Br ₃ (PMePh ₂) ₆]PF ₆ | +1.57 (120) | +1.03 (120) |

^a Measured in 0.1 M TBAH-CH₂Cl₂ at a Pt-bead working electrode with $v = 200 \text{ mV s}^{-1}$, in V vs Ag/AgCl. Values of $E_{p,a} - E_{p,c}$ (in mV) at a sweep rate of 200 mV/s are given in parentheses. Under our experimental conditions $E_{1/2} = +0.47 \text{ V}$ for the ferrocenium/ferrocene couple. ^b $E_{p,c}$ value. ^c Data for this complex are in excellent agreement with that reported in ref 9. ^d $E_{p,a}$ value.

tempted although solid complexes of these anions can undoubtedly be obtained, if desired, in a manner similar to that described in the Experimental Section for the PEt₃ derivatives.

While mixed halide-phosphine anions of the *trans*-[MX₄(PR₃)₂]⁻ types are rather well-known for M = Ru,¹⁴ few previous examples have been reported for M = Os.^{15,16} The method we have developed that utilizes (*n*-Bu₄N)₂Os₂X₈ proceeds rapidly in quite high yield.

Cyclic voltammetry (CV) of the (*n*-Bu₄N)[OsX₄(PEt₃)₂] complexes in 0.1 M TBAH-CH₂Cl₂ reveals that both complexes have a reversible one-electron process corresponding to an oxidation at +0.18 V vs Ag/AgCl (Table IV). This represents the oxidation of these Os(III) anions to the neutral Os(IV) species *trans*-OsX₄(PEt₃)₂ (eq 2). Reduction of the previously reported



trans-OsCl₄(PEt₃)₂ occurs at a potential¹⁷ essentially identical with that reported here for the oxidation of *trans*-[OsCl₄(PEt₃)₂]⁻. These low-spin d⁵ Os(III) complexes give sharp ESR spectra at -160 °C in a 5/2 toluene-dichloromethane glass with $g_{\perp} = 2.55$ (X = Cl) and 2.44 (X = Br). Due to instrumental limitations, g_{\parallel} (<0.9) was not observed.

CV measurements on the trimethylphosphine derivatives (*n*-Bu₄N)[OsX₄(PMe₃)₂] indicate these complexes slowly decompose in solution even under nitrogen or argon. In the case of X = Cl, the complex has a process at $E_{1/2} = +0.29 \text{ V}$ that corresponds to a one-electron oxidation ($\Delta E_p = 120 \text{ mV}$). When this solution is allowed to stand, this couple is replaced by one at $E_{1/2} \approx +0.45 \text{ V}$, which may be due to the cis isomer of [OsCl₄(PMe₃)₂]⁻, together with additional processes, including ones at $E_{1/2} = +0.93 \text{ V}$ and $E_{p,c} = -0.53 \text{ V}$, which are probably due to the slow formation of some *mer*-OsCl₃(PMe₃)₃ (Table IV). For (*n*-

(12) Zietlow, T. C.; Klendworth, D. D.; Nimry, T.; Salmon, D. J.; Walton, R. A. *Inorg. Chem.* **1981**, *20*, 947.

(13) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(14) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, 1984; p 294.

(15) Douglas, P. G.; Shaw, B. L. *J. Chem. Soc. A* **1970**, 334.

(16) Pawson, D.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1975**, 417.

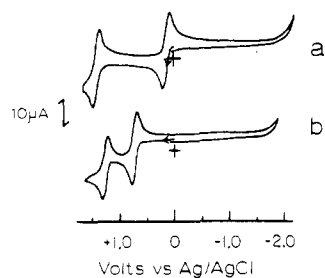
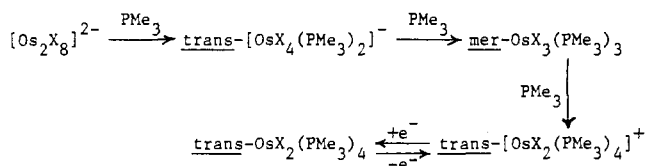


Figure 1. Cyclic voltammograms of (a) *trans*-OsBr₂(PMe₃)₄ and (b) [Os₂(μ-Br)₃(PEt₃)₆]PF₆ recorded in 0.1 M TBAH-CH₂Cl₂ at *v* = 200 mV s⁻¹ and 22 °C vs Ag/AgCl.

Scheme I



Bu₄N[OsBr₄(PMe₃)₂], the *E*_{1/2} value for the Os(IV)/Os(III) couple is +0.28 V, although like its chloro analogue this solution decomposed upon standing.

The reactions of the [Os₂X₈]²⁻ anions with a large excess of various monodentate phosphine were also studied and found to yield a variety of products depending upon reaction conditions and size of the phosphine. The initial products of osmium-osmium bond cleavage, viz. *trans*-[OsX₄(PR₃)₂]⁻, undergo further substitution of halide by phosphine (1 equiv) to generate dark orange (X = Cl) or reddish purple (X = Br) solutions of the neutral Os(III) complexes *mer*-OsX₃(PR₃)₃. Solids were isolated only in the case of the trimethylphosphine derivatives, which are reported here for the first time. The spectral, magnetic, and electrochemical properties for *mer*-OsX₃(PMe₃)₃ are similar to those reported for other phosphine derivatives of this type.¹⁷⁻¹⁹

Further reaction of *mer*-OsX₃(PR₃)₃ with PR₃ is dependent upon the phosphine used. The reactions at room temperature of trimethylphosphine with methanol (or ethanol) solutions of *mer*-OsX₃(PMe₃)₃ (generated in situ from (*n*-Bu₄N)₂Os₂X₈) yield pink (X = Cl) or purple (X = Br) solutions of the *trans*-[OsX₂(PMe₃)₄]⁺ cations. Reduction to *trans*-OsX₂(PMe₃)₄ occurs upon reacting (*n*-Bu₄N)₂Os₂X₈ with PMe₃ in refluxing ethanol. Previously, *trans*-OsCl₂(PMe₃)₄ had been prepared by reaction of OsCl₂(PPh₃)₃ with PMe₃ in hexane^{10,20} and oxidation to the *trans*-[OsCl₂(PMe₃)₄]⁺ cation was accomplished by using AgPF₆ as oxidant.¹⁰ The NMR spectral properties of the previously unreported *trans*-OsBr₂(PMe₃)₄ are consistent with this geometry, since only one resonance appears in the ³¹P{¹H} NMR spectrum (δ -55.2 in C₆D₆) and a broad singlet is present for the methyl protons in the ¹H NMR spectrum (at δ +1.62).

CV's of the *trans*-OsX₂(PMe₃)₄ complexes in 0.1 M TBAH-CH₂Cl₂ show the presence of two reversible one-electron couples corresponding to oxidations (Table IV and Figure 1).

The reaction chemistry of trimethylphosphine with [Os₂X₈]²⁻ can be summarized in Scheme I.

The reactions of (*n*-Bu₄N)₂Os₂X₈ with an excess of PMe₂Ph in refluxing ethanol proceed in a fashion similar to that found in the case of PMe₃ (vide supra) to afford yellow *trans*-OsX₂(PMe₂Ph)₄ in good yield. The chloro complex has been prepared previously by using other methods.^{11,21,22}

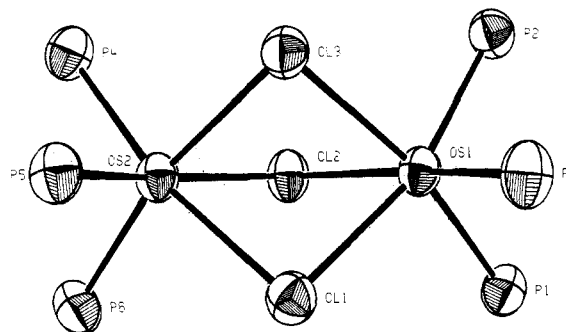


Figure 2. ORTEP view of the structure of the [Os₂(μ-Cl)₃(PEt₃)₆]⁺ cation showing the [Os₂Cl₃P₆] core. The thermal ellipsoids are drawn at the 50% probability level.

In contrast to the preceding results for the reactions between (*n*-Bu₄N)₂Os₂X₈ and PMe₃ or PMe₂Ph in refluxing ethanol, the corresponding reactions with PEt₃ and PMePh₂ terminate at the stage [Os₂X₃(PR₃)₆]⁺. These diosmium(II) cations can be isolated as their PF₆⁻ salts by metathesis. Chloride salts of such monocations (PR₃ = PMe₂Ph, PEt₂Ph, PMePh₂, and PEtPh₂) were first prepared by Chatt and Hayter⁸ through the reactions of (N-H₄)₂OsCl₆ with an excess of phosphine in water-ethanol mixtures and later (for PR₃ = PEt₃, PMe₂Ph, and PEtPh₂) by other methods.^{11,22} Our procedure offers the advantage of being easily adaptable to the bromo analogues.

The [Os₂X₃(PR₃)₆]⁺ cation can be anticipated to have a confacial bioctahedral structure with the three halide ligands bridging the two osmium centers. Consistent with this proposal is the observation of only one resonance in the ³¹P{¹H} NMR spectra (Table S6). This conclusion has now been confirmed through an X-ray crystal structure analysis of [Os₂Cl₃(PEt₃)₆]PF₆ (vide infra). An interesting feature of the chemistry of these complexes is seen in their electrochemical properties (Table IV and Figure 1). They display two reversible one-electron processes in their CV's, both of which correspond to oxidations. The first process is associated with the Os(II)Os(III)/Os(II)Os(II) couple, while the second process is due to the Os(III)Os(III)/Os(II)Os(III) couple. Such characteristics have recently been reported¹¹ for the PMe₂Ph derivative [Os₂Cl₃(PMe₂Ph)₆]⁺. We can confirm the generality of these redox characteristics for this class of diosmium cations.

(b) Crystal Structure of [Os₂(μ-Cl)₃(PEt₃)₆]PF₆. A single-crystal X-ray structure analysis on a crystal of the title complex grown from THF-*n*-pentane has confirmed that the cation possesses a confacial bioctahedral geometry. Important bond lengths and angles for the cation are listed in Table III, and an ORTEP representation of the [Os₂(μ-Cl)₃P₆]⁺ skeleton is shown in Figure 2. The basic structure resembles that seen previously in several diruthenium complexes that possess the [Ru₂(μ-Cl)₃]⁺ and [Ru₂(μ-Cl)₃]²⁺ cores and phosphine ligands, including those of the type [Ru₂(μ-Cl)₃(PR₃)₆]⁺ (PR₃ = PMe₃, PMe₂Ph, or PEt₂Ph).²³⁻²⁵ In these last three diruthenium cations, the Ru...Ru separation is, as expected, a little shorter (3.27-3.44 Å) than the corresponding nonbonding Os...Os distance (3.47 Å) in [Os₂(μ-Cl)₃(PEt₃)₆]PF₆. This is further reflected by changes in the angles at the bridging chloride ligands, which, like the M...M separations, increase in the order [Ru₂(μ-Cl)₃(PMe₃)₆]⁺ < [Ru₂(μ-Cl)₃(PMe₂Ph)₆]⁺ < [Ru₂(μ-Cl)₃(PEt₂Ph)₆]⁺, although the range of M-Cl-M angles is quite small (ca. 83-89°). Overall there is a striking similarity in the structural parameters for these compounds.

Of special note is the structural relationship between [Os₂(μ-Cl)₃(PEt₃)₆]⁺ and the tris(μ-hydrido) species [Os₂(μ-H)₃(PMe₂Ph)₆]⁺.²⁶ While both species possess similar structures,

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the latter contains a very short Os–Os distance (2.56 Å) that is compatible with the presence of a formal Os–Os triple bond.²⁶ This would follow from the adherence of this cation to a 36-electron valence count. The Os–P distances and P–Os–P angles in these two cations are very similar; data for $[\text{Os}_2(\mu\text{-Cl})_3(\text{PET}_3)_6]^+$ are given in Table III, while the average Os–P distances and P–Os–P angles for $[\text{Os}_2(\mu\text{-H})_3(\text{PMe}_2\text{Ph})_6]^+$ are 2.291 (4) Å and 93.4 (1)°, respectively.²⁶ Especially interesting is the fact that the replacement of a $\mu\text{-Cl}$ unit by $\mu\text{-H}$ leads to the shortening of the Os–Os distance by an average of ca. 0.30 Å. This is similar to the shortening of the Mo–Mo distance in the confacial bioctahedral anion $[\text{Mo}_2(\mu\text{-Cl})_3\text{Cl}_6]^{3-}$ upon its conversion to $[\text{Mo}_2(\mu\text{-H})(\mu\text{-Cl})_2\text{Cl}_6]^{3-}$.²

(c) Reactions with Bidentate Phosphines and Heterocyclic Amine Ligands. In an effort to synthesize complexes in which an osmium–osmium multiple bond is retained, several bidentate phosphine ligands were employed. Phosphines of the type $\text{R}_2\text{P}(\text{CH}_2)_n\text{PR}_2$ have been used to prepare a wide range of complexes that contain two metal atoms held in close proximity to one another.^{2,27} However, the $[\text{Os}_2\text{Cl}_8]^{2-}$ anion, as its PPN^+ salt, reacts with the phosphine ligands dppe, dpmm, and dmpe to form the mononuclear *trans*- $\text{OsCl}_2(\text{L-L})_2$ complexes. Electrochemical studies on these compounds in 0.1 M TBAH– CH_2Cl_2 reveal two oxidation processes (Table IV) with $E_{1/2}$ values of +0.1 to +0.2 V vs Ag/AgCl and $E_{1/2} = +1.45$ to +1.55 V vs Ag/AgCl (for the dpmm derivative this second oxidation is irreversible).

The salt $(\text{PPN})_2\text{Os}_2\text{Cl}_8$ reacts with neat pyridine and γ -picoline at room temperature to form, in high yield, red-brown *fac*- $\text{OsCl}_3(\text{py})_3$ and brown *fac*- $\text{OsCl}_3(\gamma\text{-pic})_3$, respectively.²⁸ These compounds have been prepared previously by heating $(\text{NH}_4)_2\text{Os}_2\text{Cl}_6$ with the amine in dimethylformamide.⁵ Their electrochemical properties (Table IV) are very similar to those reported previously for $\text{OsCl}_3(\text{py})_2(\text{PPh}_3)$ ($E_{1/2} = +0.96$ V and $E_{1/2} = -0.64$ V vs SCE).²⁹

When $(\text{PPN})_2\text{Os}_2\text{Cl}_8$ is heated with 6 equiv of pyridine or γ -picoline in dimethylformamide, the paramagnetic salts $(\text{PPN})[\text{OsCl}_4(\text{py})_2]$ and $(\text{PPN})[\text{OsCl}_4(\gamma\text{-pic})_2]$ are formed in good yield. The related reaction of $(n\text{-Bu}_4\text{N})_2\text{Os}_2\text{Cl}_8$ with pyridine affords $(n\text{-Bu}_4\text{N})[\text{OsCl}_4(\text{py})_2]$, whose properties are identical with those of the PPN^+ salt of this anion. While none of these complexes gave very satisfactory carbon microanalyses, the identity of $(n\text{-Bu}_4\text{N})[\text{OsCl}_4(\text{py})_2]$ has been confirmed by an X-ray structure analysis and the anion shown to contain a *trans* geom-

etry.³⁰ The redox behavior of these salts (Table IV) resembles that observed for *fac*- $\text{OsCl}_3(\text{py})_3$ and *fac*- $\text{OsCl}_3(\gamma\text{-pic})_3$ but with the potentials shifted by 0.6 V to more negative values relative to those of the last two complexes. This is similar to the shift in $E_{1/2}$ values between the Os(IV)/Os(III) couples of $(n\text{-Bu}_4\text{N})$ - $[\text{trans-OsX}_4(\text{PET}_3)_2]$ and *mer*- $\text{OsX}_3(\text{PMe}_3)_3$ (Table IV).

The reactions of $(\text{PPN})_2\text{Os}_2\text{Cl}_8$ with an excess of bpy in methanol at room temperature proceeds slowly to form a green solution, which, when treated with NaBPh_4 , affords the much studied and well-characterized $[\text{Os}(\text{bpy})_3](\text{BPh}_4)_2$.

(d) Concluding Remarks. The cleavage of the $\text{Os}\equiv\text{Os}$ bonds of the $[\text{Os}_2\text{X}_8]^{2-}$ anions (X = Cl or Br) by monodentate and bidentate phosphine and heterocyclic tertiary amine ligands serves as a convenient synthetic route to several groups of mononuclear complexes that contain these ligands, e.g. $[\text{OsX}_4\text{L}_2]^-$, OsX_3L_3 (L = py, γ -pic, or PR_3), and $\text{OsX}_2(\text{PR}_3)_4$, as well as some diosmium(II) complex cations of the type $[\text{Os}_2(\mu\text{-X})(\text{PR}_3)_6]^+$. In the case of the monodentate phosphines, these reactions proceed with rapid metal–metal bond cleavage to produce the fragments *trans*- $[\text{OsX}_4(\text{PR}_3)_2]^-$. Accordingly, these reactions contrast with those between the quadruply bonded $[\text{Re}_2\text{X}_8]^{2-}$ and the same phosphines since in these instances the retention of a metal–metal multiple bond is the rule.² The cleavage of the $\text{Os}\equiv\text{Os}$ bonds by neutral donor amine and phosphine ligands reflects their kinetic lability toward good σ -donors. Also, the formation of four new Os–L bonds is favored thermodynamically over the retention of the $\text{Os}\equiv\text{Os}$ bond. While several of the mononuclear chloro complexes can be prepared by other methods, the bromo complexes have all been prepared here for the first time and their ease of preparation from $[\text{Os}_2\text{Br}_8]^{2-}$ now makes these species accessible for further chemical reactivity studies.

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Supplementary Material Available: Experimental details relating to the crystal structure determination, listing of atomic positional parameters and their errors for the ethyl carbon atoms (Table S1), positional parameters for the hydrogen atoms (Table S2), anisotropic thermal parameters (Table S3), complete bond distances (Table S4) and bond angles (Table S5), NMR spectral data for the diosmium(II) phosphine complexes (Table S6), and a figure showing the full atomic numbering scheme (Figure S1) (17 pages); a table of observed and calculated structure factors (25 pages). Ordering information is given on any current masthead page.

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