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Synthesis, Crystal Structures, and Reactivity of Osmium(II) and -(IV) Complexes Containing a Dithioimidodiphosphinate Ligand

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Reduction of *trans*-$[OsL_2(O)_2]$ (**1**) ($L^- = [N(i\text{-}Pr_2PS)_2]^-$) with hydrazine hydrate afforded a dinitrogen complex **2**, possibly "$[OsL_2(N_2)(solv)]$" (solv = H_2O or THF), which reacted with RCN, R′NC, and SO_2 to give *trans*-$[OsL_2(RCN)_2]$ (R = Ph (**3**), 4-tolyl (**4**), 4-*t*-BuC_6H_4 (**5**)), *trans*-$[OsL_2(R'NC)_2]$ (R′ = 2,6-$Me_2C_6H_3$ (xyl) (**6**), *t*-Bu (**7**)), and $[Os(L)_2(SO_2)(H_2O)]$ (**8**) complexes, respectively. Protonation of compounds **2**, **3**, and **6** with HBF_4 led to formation of dicationic *trans*-$[Os(LH)_2(N_2)(H_2O)][BF_4]_2$ (**9**), *trans*-$[Os(LH)_2(PhCN)_2][BF_4]_2$ (**10**), and *trans*-$[Os(LH)_2(xylNC)_2][BF_4]_2$ (**11**), respectively. Treatment of **1** with phenylhydrazine and $SnCl_2$ afforded *trans*-$[OsL_2(N_2Ph)_2]$ (**12**) and *trans*-$[OsL_2Cl_2]$ (**13**), respectively. Air oxidation of compound **2** in hexane/MeOH gave the dimethoxy complex *trans*-$[OsL_2(OMe)_2]$ (**14**), which in CH_2Cl_2 solution was readily air oxidized to **1**. Compound **1** is capable of catalyzing aerobic oxidation of PPh_3, possibly via an Os(IV) intermediate. The formal potentials for the Os–L complexes have been determined by cyclic voltammetry. The solid-state structures of compounds **4**, **6**, *cis*-**8**, **13**, and **14** have been established by X-ray crystallography.

Introduction

Transition metal sulfur systems have attracted much attention due to their significance in catalysis, materials science, and biology.[1,2] To gain insight into the mechanisms of sulfur-containing catalysts, much effort has been devoted to develop molecular models based on metal thiolate and sulfido complexes.[3−5] Of special interest are group 8 thiolato compounds due in part to the finding that binary noble metal sulfides, notably RuS_2, are highly active in hydrodesulfurization processes.[6] Although sulfur-rich Os complexes containing thiophenolato,[7−9] dithiocarbamato,[10,11] and dithiolato[12,13] ligands are well-known, the catalytic activity of the OsS_4 core has not been well explored. This is in contrast with Os compounds with polydentate nitrogen ligands, e.g., porphyrins, tris(pyrazolyl)borate, tetraza macrocycles, and polypyridyl, which display rich redox and catalytic chemistry.[14]

Dichalcogenoimidodiphosphinates $[N(R_2PQ)_2]^-$ (R = alkyl or aryl; Q = O, S, or Se) (Chart 1), which are considered as

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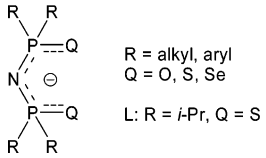
Chart 1



chalcogen analogues of acetylacetonates, can bind to metal ions with a high degree of electronic and geometric flexibilities.[15]

Although $[N(R_2PQ_2)_2]^-$ is known to form stable complexes with a range of main group and transition metals, the coordination chemistry of $Os-N(R_2PQ_2)_2$ is not well developed.[16,17] We are particularly interested in the isopropyl-substituted ligand $[N(i\text{-}Pr_2PS)_2]^-$ (denoted as L^-)[18] due to its high basicity and good solubility in organic solvents. Metal complexes with L^- are known to exhibit interesting structural chemistry and reactivity.[18,19] Previously, we reported that reduction of *trans*-$[OsL_2(O)_2]$ (**1**) with hydrazine gave a dinitrogen species, possibly "$[OsL_2(N_2)(solv)]$" (solv = THF or water) (**2**),[17] which may serve as a useful starting material for Os−L compounds. Herein, we describe the substitution reactions and air oxidation of compound **2** and the reduction of compound **1** with phenyl hydrazine, $SnCl_2$, and phosphines. The crystal structures and formal potentials of Os(II) and -(IV) complexes with L^- have been determined.

Experimental Section

General Considerations. Solvents were purified by standard procedures and distilled prior to use. All manipulations were carried out under nitrogen by standard Schlenk techniques. NMR spectra were recorded on a Bruker ALX 300 spectrometer operating at 300, 121.5, and 282.5 MHz for ^1H, ^{31}P, and ^{19}F, respectively. Chemical shifts (δ, ppm) were reported with reference to $SiMe_4$ (^1H), H_3PO_4 (^{31}P), and $CF_3C_6H_5$ (^{19}F). Infrared spectra (KBr) were recorded on a Perkin-Elmer 16 PC FT-IR spectrophotometer. Magnetic moments of paramagnetic compounds were determined by Evans method[20] at room temperature. Cyclic voltammetry was performed with a Princeton Applied Research (PAR) model 273A potentiostat. The working and reference electrodes were glassy carbon and Ag/$AgNO_3$ (0.1 M in acetonitrile), respectively, and the scan rate was 100 mV s^{-1}. Formal potentials ($E_{1/2}$) were measured in CH_2Cl_2 solutions with 0.1 M $[n\text{-}Bu_4N][PF_6]$ as supporting electrolyte and reported with reference to the ferrocenium−ferrocene couple ($Cp_2Fe^{+/0}$). Elemental analyses were preformed by Medac Ltd., Surrey, U.K. The dioxo compound *trans*-$[OsL_2(O)_2]$ (**1**) was prepared as described elsewhere.[17]

Preparation of *trans*-[Os(L)$_2$(RCN)$_2$] (R = Ph (3), Tolyl (4), 4-*t*-BuC$_6$H$_4$ (5)). The dinitrogen complex **2** was prepared as described previously.[17] To compound **1** (60 mg, 0.071 mmol) in THF (10 mL) was added hydrazine hydrate (0.1 mL), and the mixture was stirred for 2 h. The solvent was pumped off, and the residue was extracted into hexane (5 mL). To this hexane solution of compound **2** was added RCN (0.21 mmol), and the reaction mixture was stirred at room temperature for 30 h. The solvent was removed, and the residue was washed with cold hexane (−78 °C) and extracted with Et_2O (for compound **3**), hexane/Et_2O (1:1 v/v) (for compound **4**), or hexane/CH_2Cl_2 (1:1 v/v) (for compound **5**). Concentration and cooling at −10 °C afforded brown crystals.

3: 15 mg, 21% (based on compound **1** used). ^1H NMR (C_6D_6): δ 1.48 (m, 48H, $(CH_3)_2CH$), 2.49 (m, 8H, $(CH_3)_2CH$), 7.08−7.14 (m, 6H, H_o and H_p), 7.66−7.71 (m, 4H, H_m). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 58.73 (s). IR (KBr, cm^{-1}): 2175 (ν_{CN}). Anal. Calcd for $C_{40}H_{70}N_4OsP_4S_4$: C, 44.7; H, 6.5; N, 5.5. Found: C, 44.5; H, 6.5; N, 5.4.

4: 16 mg, 22% (based on compound **1** used). ^1H NMR (C_6D_6): δ 1.57 (m, 48H, $(CH_3)_2CH$), 2.10 (s, 6H, CH_3), 2.51 (m, 8H, $(CH_3)_2CH$), 6.93 (d, J = 8.2 Hz, 4H, H_o), 7.64 (d, J = 8.2 Hz, 4H, H_m). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 58.72 (s). IR (KBr, cm^{-1}): 2177 (ν_{CN}). Anal. Calcd for $C_{40}H_{70}N_4OsP_4S_4$: C, 45.8; H, 6.7; N, 5.3. Found: C, 45.3; H, 6.8; N, 5.3.

5: 22 mg, 28% (based on compound **1** used). ^1H NMR (C_6D_6): δ 1.27 (s, 18H, *t*-Bu), 1.56 (m, 48H, $(CH_3)_2CH$), 2.50 (m, 8H, $(CH_3)_2CH$), 7.29 (d, J = 8.4 Hz, 4H, H_o), 7.76 (d, J = 8.4 Hz, 4H, H_m). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 58.67 (s). IR (KBr, cm^{-1}): 2175 (ν_{CN}). Anal. Calcd for $C_{46}H_{82}N_4OsP_4S_4$: C, 48.7; H, 7.3; N, 4.9. Found: C, 48.4; H, 7.5; N, 4.8.

Preparation of *trans*-[OsL$_2$(R′NC)$_2$] (R′ = 2,6-Me$_2$C$_6$H$_3$ or Xyl (6), *t*-Bu (7)). To the above-described hexane solution of **2** was added 2 equiv of R′NC, and the reaction mixture was stirred at room temperature for 30 h. The solvent was removed in vacuo, and the residue was extracted with hexane (R = xyl) or CH_2Cl_2/hexane (R = *t*-Bu). Concentration and cooling at −10 °C afforded yellow crystals.

6: 21 mg, 28% (based on **1** used). ^1H NMR (C_6D_6): δ 1.34 (m, 48H, $(CH_3)_2CH$), 2.59 (m, 8H, $(CH_3)_2CH$), 2.99 (s, 12H, CH_3), 7.00−7.12 (m, 6H, phenyl protons). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 59.04 (s). IR (KBr, cm^{-1}): 2007, 2038 (ν_{CN}). Anal. Calcd for $C_{42}H_{74}N_4OsP_4S_4$: C, 46.8; H, 6.9; N, 5.2. Found: C, 46.8; H, 6.9; N, 4.9.

7: 12 mg, 17% (based on **1** used). ^1H NMR (C_6D_6): δ 1.54 (m, 48H, $(CH_3)_2CH$), 1.66 (s, 18H, *t*-Bu), 2.52 (m, 8H, $(CH_3)_2CH$). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 58.28 (s). IR (KBr, cm^{-1}): 2033 (ν_{CN}). Anal. Calcd for $C_{34}H_{74}N_4OsP_4S_4$: C, 41.6; H, 7.6; N, 5.7. Found: C, 41.6; H, 7.7; N, 5.5.

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Preparation of $[OsL_2(SO_2)(H_2O)]$ (8). Sulfur dioxide was bubbled into the above-described hexane solution of **2** for 3 min, during which the color changed from purple to reddish brown. The reaction mixture was stirred at room temperature for 30 min and evaporated to dryness. Recrystallization from CH_2Cl_2/hexane (1:2, v/v) at −10 °C afforded dark brown crystals. Yield: 19 mg, 30% (based on compound **1** used). ^{1}H NMR (C_6D_6): δ 1.25−1.68 (m, 48H, (C*H*$_3$)$_2$CH), 2.02 (m, 4H, (CH$_3$)$_2$C*H*), 2.54 (m, 4H, (CH$_3$)$_2$C*H*). ^{31}P{^{1}H} NMR (C_6D_6): δ 61.30 (d, J = 24 Hz, cis isomer), 59.37 (br s, cis isomer), 59.16 (br s, cis isomer), 58.49 (s, trans isomer), 56.40 (d, J = 24 Hz, cis isomer). In addition, a weak signal at δ 58.77 (s), possibly due to a *trans*-Os(L)$_2$ species, was observed in the ^{31}P{^{1}H} NMR spectrum. IR (cm^{-1}, KBr): 1266 (ν_{SO}). Anal. Calcd for $C_{24}H_{58}N_2O_3OsP_4S_5\cdot 1/2CH_2Cl_2\cdot H_2O$: C, 30.7; H, 6.4; N, 2.9. Found: C, 30.6; H, 6.6; N, 3.3. We were not able to obtain satisfactory nitrogen analysis of the compound.

Preparation of $[Os(HL)_2(N_2)(H_2O)](BF_4)_2$ (9). The above-described hexane solution of compound **2** was evaporated to dryness, and the residue was redissolved in 10 mL of Et_2O. To the solution was added 2 equiv of HBF_4 (20 μL of a 54% in Et_2O, 0.14 mmol) at 0 °C, at which the mixture was stirred for 30 min. The red precipitate was collected, washed with Et_2O, and dried in vacuo. Yield: 35 mg (80% based on **2**). The compound was found to be very air sensitive in solution. IR (KBr, cm^{-1}): 2044 (ν_{NN}). Anal. Calcd for $C_{24}H_{60}B_2F_8N_4OOsP_4S_4\cdot H_2O$: C, 27.3; H, 5.9; N, 5.3. Found: 27.1; H, 6.0; N, 5.0.

Preparation of *trans*-$[Os(HL)_2(PhCN)_2](BF_4)_2$ (10). To a solution of compound **3** (30 mg, 0.029 mmol) in Et_2O (15 mL) was added HBF_4 (9 μL of a 54% solution in Et_2O, 0.065 mmol) at −78 °C, and the mixture was stirred at room temperature for 15 min. The orange precipitate was collected, washed with Et_2O, and recrystallized from CH_2Cl_2/Et_2O to afford a yellowish orange microcrystalline solid. Yield: 19 mg, 54%. ^{1}H NMR ($CDCl_3$): δ 1.31 (m, 48H, (C*H*$_3$)$_2$CH), 2.87 (m, 8H, (CH$_3$)$_2$C*H*), 6.30 (br s, 2H, N*H*), 7.61−7.64 (m, 10H, phenyl protons). ^{31}P{^{1}H} NMR: 89.38 (s). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −149.79 (s). IR (KBr, cm^{-1}): 2194 (ν_{CN}), 3152 (ν_{NH}). Anal. Calcd for $C_{38}H_{68}B_2F_8N_4OsP_4S_4$: C, 38.1; H, 5.7; N, 4.7. Found: C, 38.2; H, 5.8; N, 4.5.

Preparation of *trans*-$[Os(HL)_2(xylNC)_2](BF_4)_2$ (11). This compound was prepared similarly as for compound **11** by protonation of compound **6** (30 mg, 0.028 mmol) in Et_2O (15 mL) with HBF_4 (8 μL of a 54% solution in Et_2O, 0.061 mmol). Recrystallization from CH_2Cl_2/Et_2O afforded pale orange crystals. Yield: 21 mg, 60%. ^{1}H NMR ($CDCl_3$): δ 1.17 (m, 48H, (C*H*$_3$)$_2$CH), 2.59 (s, 12H, CH$_3$), 2.75 (m, 8H, (CH$_3$)$_2$C*H*), 6.36 (br. s, 2H, NH), 7.22 (m, 6H, phenyl protons). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 89.80 (s). ^{19}F{^{1}H} NMR ($CDCl_3$): δ −149.62. IR (KBr, cm^{-1}): 2080 (ν_{CN}), 3098 (ν_{NH}). Anal. Calcd for $C_{42}H_{76}B_2F_8N_4OsP_4S_4$: C, 40.3; H, 6.1; N, 4.5. Found: C, 40.2; H, 6.2; N, 4.4.

Preparation of *trans*-$[OsL_2(N_2Ph)_2]$ (12). To a solution of **1** (60 mg, 0.071 mmol) in THF (8 mL) was added 4 equiv of phenylhydrazine hydrochloride (37 mg, 0.28 mmol) and 4 equiv of Et_3N (40 μL, 0.28 mmol). The reaction mixture was stirred at room temperature overnight, during which the color of solution turned from orange to brown. The solvent was removed, and the brown oily solid was washed with hexane and extracted into CH_2Cl_2/Et_2O (1:1, v/v). To the filtrate was added hexane, and the volume was reduced to ca. 5 mL. Cooling at −10 °C afforded yellowish brown crystals. Yield: 13 mg, 18%. ^{1}H NMR ($CDCl_3$): δ 1.01 (m, 48H, (C*H*$_3$)$_2$CH), 1.88 (m, 8H, (CH$_3$)$_2$C*H*), 7.01−7.45 (m, 10 H, phenyl protons). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 57.81 (s). IR (KBr, cm^{-1}): 1530 (s) (ν_{NN}). Anal. Calcd for $C_{36}H_{66}N_6OsP_4S_4\cdot CH_2Cl_2$: C, 41.1; H, 6.3; N, 7.9. Found: C, 41.0; H, 6.7; N, 7.9.

Preparation of *trans*-$[OsL_2Cl_2]$ (13). To a solution of compound **1** (60 mg, 0.071 mmol) in THF (10 mL) was added 2.5 equiv of $SnCl_2$ (34 mg, 0.18 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 20 min, during which the color of solution changed from red to green and finally purple. The solvent was removed, and the residue was extracted into toluene. Evaporation of the solvent afforded a dark solid, which was recrystallized from CH_2Cl_2/hexane to give dark purple crystals. Yield: 26 mg, 42%. ^{1}H NMR ($CDCl_3$): δ 1.23 (m, 2H, (CH$_3$)$_2$C*H*), 3.40 (m, 24H, (C*H*$_3$)$_2$CH), 3.64 (m, 6H, (CH$_3$)$_2$C*H*), 4.69 (m, 24H, (C*H*$_3$)$_2$CH). μ_{eff} ($CDCl_3$) = 1.8 μ_B. Anal. Calcd for $C_{24}H_{56}Cl_2N_2OsP_4S_4$: C, 32.5; H, 6.4; N, 3.2. Found: C, 32.3; H, 6.4; N, 3.0.

Preparation of *trans*-$[OsL_2(OMe)_2]$ (14). To the above-described hexane solution of compound **2** was added 5 mL of methanol, and the mixture was stirred vigorously under nitrogen until a homogeneous mixture was resulted. Upon exposure to air, an orange solution was formed. Slow evaporation at room temperature overnight afforded orange crystals, which were collected and washed with hexane. Yield: 25 mg, 40% (based on compound **1** used). ^{1}H NMR (C_6D_6): δ 2.44 (m, 24H, (C*H*$_3$)$_2$CH), 2.74 (m, 24H, (C*H*$_3$)$_2$CH), 3.84 (m, 8H, (CH$_3$)$_2$C*H*), 42.90 (s, 6H, OC*H*$_3$). ^{31}P-{^{1}H} NMR (C_6D_6): δ 34.65 (s). μ_{eff} ($CDCl_3/CD_3OD$, 1:1, v/v) = 1.6 μ_B. Anal. Calcd for $C_{26}H_{62}N_2O_2OsP_4S_4$: C, 35.6; H, 7.1; N, 3.2. Found: C, 35.6; H, 7.2; N, 3.2.

Preparation of *cis*-$[OsL_2(PMePh_2)_2]$ (15). To a solution of compound **1** (60 mg, 0.071 mmol) in THF (15 mL) was added 4 equiv of $PMePh_2$, and the mixture was stirred at room temperature for 30 h. The solvent was removed, and the orange solid was extracted with Et_2O/hexane (1:1, v/v). Concentration and cooling at −10 °C afforded orange crystals along with a white solid identified as $OPMePh_2$, which was removed by cold acetone. Yield: 21 mg, 24%. ^{1}H NMR (C_6D_6): δ 1.34−1.70 (m, 48H, (C*H*$_3$)$_2$CH), 2.15 (m, 4H, (CH$_3$)$_2$C*H*), 2.66 (d, $^2J_{PH}$ = 8.0 Hz, 6H, Me), 2.71 (m, 2H, (CH$_3$)$_2$C*H*), 3.61 (m, 2H, (CH$_3$)$_2$C*H*), 7.26 (m, 12H, phenyl protons), 7.99 (m, 8H, phenyl protons). ^{31}P{^{1}H} NMR (C_6D_6): δ −42.61 (m, $PMePh_2$), 49.16 (m, L), 50.10 (m, L). Anal. Calcd for $C_{50}H_{82}N_2OsP_6S_4\cdot 1/2Et_2O$: C, 49.9; H, 7.0; N, 2.2; Found: C, 49.9; H, 6.9; N, 2.1.

Os-Catalyzed Aerobic Oxidation of PPh_3. A mixture of PPh_3 (15 mg, 0.059 mmol) and compound **1** (5 mg, 0.0059 mmol) in $CHCl_3$ (5 mL) was stirred under 1 atm pressure of oxygen at room temperature for 2 d. The yield of triphenylphosphine oxide was determined to be 92% by ^{31}P NMR spectroscopy using PPh_4Cl as internal standard.

X-ray Crystallographic Analysis. Crystallographic data and experimental details for compounds **4**, **6**, *cis*-**8**, **13**, and **14** are summarized in Table 1. Intensity data were collected on a Bruker SMART APEX 1000 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The collected frames were processed with the software SAINT.[21] Structures were solved by the direct methods and refined by full-matrix least-squares on F^2 using SHELXL[22] software package. In **6**, the carbon atoms C(37)−C(42) and C(27) in the isopropyl groups were found to be disordered and were split into two positions with occupancies of 0.5 each. Selected bond lengths and angles for compounds **4**, **6**, **13**, and **14** are listed in Table 2, and those for *cis*-**8**, in Table 3.

(21) *Bruker SMART and SAINT+*, version 6.02a; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1998.
(22) Sheldrick, G. M. *SHELXTL-PLUS v.5.1 Software Reference Manual*; Bruker AXS Inc.: Madison, WI, 1997.

Table 1. Crystal Data and Structure Refinement Details for *trans*-[OsL_2(4-tolCN)$_2$] (**4**), *trans*-[OsL_2(xylNC)$_2$] (**6**), *cis*-[Os(L)$_2$(SO_2)(H_2O)] (*cis*-**8**), *trans*-[OsL_2Cl_2] (**13**), and *trans*-[OsL_2($OMe)_2$] (**14**)

param	**4**	**6**	*cis*-**8**	**13**	**14**
empirical formula	$C_{40}H_{70}N_4OsP_4S_4$	$C_{42}H_{74}N_4OsP_4S_4$	$C_{24}H_{58}N_2O_3OsP_4S_5$	$C_{24}H_{56}Cl_2N_2OsP_4S_4$	$C_{26}H_{62}N_2O_2OsP_4S_4$
fw	1049.32	1077.37	897.10	885.93	877.10
cryst system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	9.6387(6)	12.5973(12)	9.922(6)	9.6186(8)	9.4626(15)
b, Å	23.5292(14)	12.7653(12)	14.963(9)	15.4228(13)	10.1442(16)
c, Å	21.6939(13)	17.1029(17)	26.216(15)	12.8644(11)	19.756(3)
α, deg		102.619(2)			
β, deg	95.5140(10)	98.489(2)	94.050(14)	107.589(2)	90.433(3)
γ, deg		100.346(2)			
V, Å^3	4897.2(5)	2589.7(4)	3883(4)	1819.2(3)	1896.3(5)
Z	4	2	4	2	2
ρ_{calcd}, g cm^{-1}	1.423	1.382	1.535	1.617	1.536
temp, K	173(2)	250(2)	298(2)	100(2)	100(2)
F(000)	2152	1108	1824	896	896
μ(Mo Kα), cm^{-1}	2.936	2.778	3.745	4.076	3.777
no. of data/restraints/params	8742/0/478	8955/0/489	6533/0/352	4316/0/169	3690/0/178
goodness-of-fit on F^2	1.003	0.994	0.983	1.033	1.026
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0597, 0.0881	0.0338, 0.0814	0.0532, 0.0906	0.0355, 0.0652	0.0338, 0.0756
R_1, wR_2 (all data)	0.0947, 0.0952	0.0433, 0.0852	0.1124, 0.1037	0.0485, 0.0691	0.0406, 0.0786

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *trans*-[OsL_2X_2] Compounds

	X				
param	O (**1**)[17]	4-tolCN (**4**)	xylNC (**6**)	Cl (**13**)	OMe (**14**)
Os(1)−S(1)	2.463(1)	2.4137(19)	2.4461(11)	2.3970(10)	2.4153(11)
Os(1)−S(2)	2.457(1)	2.424(2)	2.4274(13)	2.3820(10)	2.4101(12)
Os(1)−S(3)		2.4181(19)	2.4383(11)		
Os(1)−S(4)		2.431(2)	2.4153(13)		
Os(1)−X	1.748(3)	1.967(6)	1.955(4)	2.3423(9)	1.934(3)
Os(1)−X		1.995(6)	1.971(4)		
P(1)−S(1)	2.046(1)	2.026(3)	2.0210(16)	2.0511(14)	2.0429(15)
P(2)−S(2)	2.043(1)	2.015(3)	2.0234(19)	2.0511(14)	2.0403(14)
P(3)−S(3)		2.027(3)	2.0257(18)		
P(4)−S(4)		2.007(3)	2.0296(18)		
N(1)/(3)−P(1)	1.593(3)	1.599(7)	1.582(4)	1.585(3)	1.598(4)
N(1)/(3)−P(2)	1.591(5)	1.589(6)	1.588(4)	1.595(3)	1.595(4)
N(2)/(4)−P(3)		1.597(7)	1.586(4)		
N(2)/(4)−P(4)		1.581(6)	1.591(4)		
S(1)−Os(1)−S(2)	99.8(1)	100.54(7)	100.17(4)	100.18(3)	99.83(4)
S(2)−Os(1)−S(3)/(1A)	80.2(1)	81.42(7)	80.98(4)	79.82(3)	80.17(4)
S(3)−Os(1)−S(4)		98.38(7)	99.31(4)		
S(4)−Os(1)−S(1)		79.70(7)	80.96(4)		
S(1)−Os(1)−S(3)/(1A)		177.71(7)	170.54(4)		
S(2)−Os(1)−S(4)		178.08(6)	171.49(5)		
P(1)−N(1)/(3)−P(2)	127.6(3)	134.3(4)	132.0(3)	130.5(2)	126.9(2)
P(3)−N(2)/(4)−P(4)		135.8(4)	128.9(3)		
Os(1)−S(1)−P(1)		116.75(11)	109.38(5)	112.14(5)	109.17(5)
Os(1)−S(2)−P(2)		110.40(10)	112.29(6)	110.77(5)	109.82(5)
Os(1)−S(3)−P(3)		115.17(11)	110.63(5)		
Os(1)−S(4)−P(4)		109.66(10)	111.46(6)		

Results and Discussion

Syntheses. (A) Os(II) Compounds. The syntheses of Os−L compounds are summarized in Scheme 1. As reported previously, treatment of *trans*-[$OsL_2(O)_2$] (**1**) with hydrazine hydrate afforded an oily solid **2** that exhibits an ν_{NN} peak at 2040 cm^{-1} in the IR spectrum.[17] It may be noted that reduction of *trans*-[Os(TPP)($O)_2$] (TPP = tetraphenylporphyrin dianion) and *trans*-[Os(salen)($O)_2$] (salen = *N*,*N*′-ethylenebis(salicylideneaminate)) afforded [Os(TPP)(N_2)(THF)][23] and [Os(salen)(N_2)(H_2O)],[24] the ν_{NN} of which were determined to be 2063 and 2030 cm^{-1}, respectively. Therefore, compound **2** was tentatively formulated as an Os(II) dinitrogen compound, possibly "[Os(L)$_2$(N_2)(solv)]" (solv = THF or H_2O). We have not been able to obtain a crystalline, analytically pure sample of compound **2** due to its lipophilic nature. The $^{31}P\{^1H\}$ NMR spectrum of a crude sample of compound **2** in benzene-d_6 displays two singlets at δ 58.14 and 58.49 ppm in a ca. 1:1 ratio. It is not clear whether the sample contained a single Os species with two types of magnetically inequivalent ^{31}P nuclei or a mixture of two Os species. Protonation of compound **2** afforded analytically pure *trans*-[Os($LH)_2$(N_2)(H_2O)][BF_4]$_2$ (**9**) in 80% yield (vide infra), indicating that compound **2** was predominantly

(23) (a) Che, C.-M.; Huang, J.-S.; Li, Z.-Y.; Poon, C.-K.; Tong, W.-F.; Lai, T.-F.; Cheng, C.-M.; Wang, C.-C.; Wang, Y. *Inorg. Chem.* **1992**, *31*, 5220. (b) Li, Z.-Y.; Huang, J.-S.; Chan, M. C.-W.; Cheung, K.-K.; Che, C.-M. *Inorg. Chem.* **1997**, *36*, 3064.

(24) Che, C.-M.; Cheng, W.-K.; Mak, T. C. W. *Inorg. Chem.* **1986**, *25*, 703.

Scheme 1

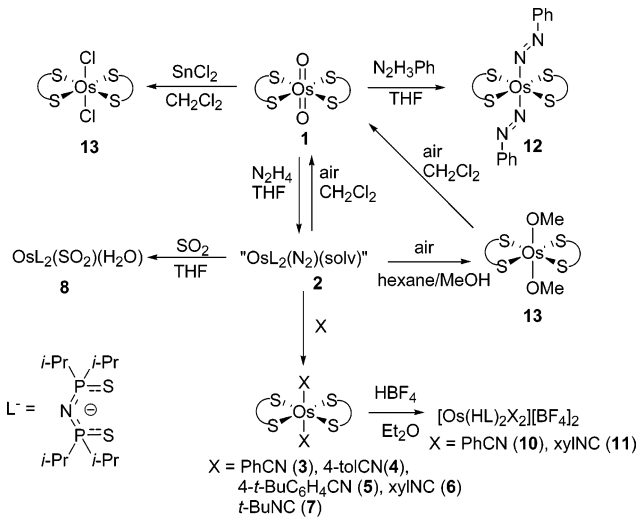


Table 3. Selected Bond Lengths (Å) and Angles (deg) for *cis*-[$OsL_2(SO_2)(H_2O)$] (*cis*-**8**)

Os(1)−S(1)	2.446(3)	Os(1)−S(2)	2.424(3)
Os(1)−S(3)	2.426(3)	Os(1)−S(4)	2.399(3)
Os(1)−S(5)	2.118(3)	Os(1)−O(1)	2.150(7)
O(2)−S(5)	1.443(7)	O(3)−S(5)	1.456(6)
P(1)−S(1)	2.033(4)	P(2)−S(2)	2.017(4)
P(3)−S(3)	2.028(4)	P(4)−S(4)	2.024(4)
S(1)−Os(1)−S(2)	93.48(9)	S(3)−Os(1)−S(4)	100.41(9)
S(1)−Os(1)−S(3)	82.23(9)	S(2)−Os(1)−S(4)	92.96(9)
S(1)−Os(1)−S(4)	90.32(9)	S(2)−Os(1)−S(3)	165.95(8)
O(1)−Os(1)−S(1)	82.3(2)	O(1)−Os(1)−S(2)	83.0(2)
O(1)−Os(1)−S(3)	83.2(2)	O(1)−Os(1)−S(4)	171.3(2)
S(5)−Os(1)−S(1)	172.75(9)	S(5)−Os(1)−S(2)	87.91(9)
S(5)−Os(1)−S(3)	94.75(10)	S(5)−Os(1)−S(4)	96.72(9)
O(1)−Os(1)−S(5)	90.8(2)	Os(1)−S(1)−P(1)	115.90(13)
Os(1)−S(2)−P(2)	114.37(13)	Os(1)−S(3)−P(3)	116.43(13)
Os(1)−S(4)−P(4)	111.79(13)	P(1)−N1−P(2)	136.0(5)
P(3)−N(2)−P(4)	139.0(6)		

composed of Os(II) dinitrogen complex(es). Despite its unknown composition, as-prepared **2** proved to be a useful starting material for Os−L compounds.

The dinitrogen ligand in compound **2** is labile and can be readily replaced by σ-donor/π-acid ligands such as nitriles and isocyanides. Thus, treatment of compound **2** with nitriles RCN and isonitriles R′NC afforded *trans*-[$OsL_2(RCN)_2$] (R = Ph (**3**), 4-tolyl (**4**), 4-*t*-BuC_6H_4 (**5**)) and *trans*-[$OsL_2(CNR')_2$] (R = 2,6-dimethylphenyl or xyl (**6**), *t*-Bu (**7**)), respectively. Compounds **6** and **7** are stable in both the solid state and in solutions whereas **3**−**5** are air sensitive in solutions. Treatment of **2** with SO_2(g) afforded [$Os(L)_2(SO_2)(H_2O)$] (**8**), isolated as an air-sensitive dark brown solid. The IR spectrum of compound **8** shows the S═O stretch at 1266 cm^{-1}, which is typical for *S*-bound SO_2 ligand. By comparison, the ν_{SO} for *cis*-[Ru{$N(PPh_2S)_2$}$_2$(PPh_3)(SO_2)] was observed at 1286 cm^{-1}.[25]

Attempts to activate the dinitrogen ligand in compound **2** by treatment with electrophiles such as trifluoroacetic anhydride were unsuccessful. Treatment of compound **2** with HBF_4 in Et_2O resulted in protonation of the L^- ligands and the formation of highly air-sensitive dicationic *trans*-[$Os(HL)_2(N_2)(H_2O)$][BF_4]$_2$ (**9**). Despite its 2+ overall charge, the ν_{NN} for dicationic compound **9** (2044 cm^{-1}) is virtually identical with that in neutral **2**. Similarly, protonation of compounds **3** and **6** with 2 equiv of HBF_4 in Et_2O gave cationic *trans*-[$Os(LH)_2(PhCN)_2$][BF_4]$_2$ (**10**) and *trans*-[$Os(LH)_2(xylNC)_2$][BF_4]$_2$ (**11**), respectively.

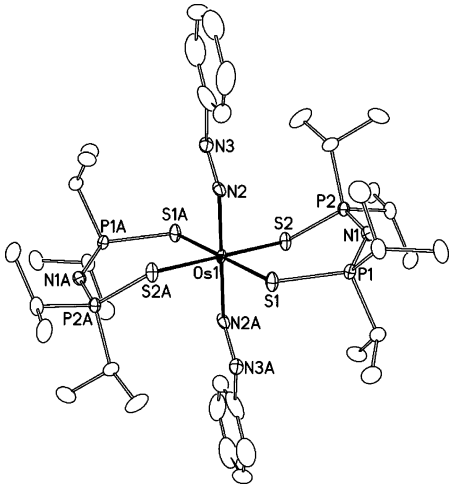


Figure 1. Molecular structure of *trans*-[$OsL_2(N_2Ph)_2$] (**12**). The ellipsoids are drawn at the 30% probability level.

(B) Os(IV) Compounds. Reduction of compound **1** with organohydrazines such as *tert*-butylhydrazine and 1,1-diphenylhydrazine resulted in intractable brown materials that did not crystallize. However, compound **1** reacted with phenylhydrazine and gave a dark yellow crystalline compound characterized as *trans*-[$OsL_2(N_2Ph)_2$] (**12**). A preliminary X-ray diffraction study showed that **12** contains two mutually *trans* N_2Ph^- ligands (Figure 1).[26] Unfortunately, it is not possible to analyze the N−N bond distance due to the disorder found in the N(3) atom in the axial N_2Ph^- group. The formulation of **3** as an Os(IV) bis(diazenido) compound is supported by the observation of an N═N band at 1530 cm^{-1} in the IR spectrum, which is typical for the diazenido compounds.[27] By comparison, the ν_{NN} for *trans*-[Mo(TPP)-$(N_2Ph)_2$] was observed at 1595 cm^{-1}.[28] In addition, no N−H signal was found in both the ^{1}H NMR and IR spectra. It may be noted that *cis*-[$Mo(N_2Ph)_2(S_2CNR_2)_2$] has been prepared from *cis*-[$Mo(O)_2(S_2CNR_2)_2$] and phenylhydrazine[29] whereas Os mono(diazenido) compounds were generally synthesized by either reaction of Os carbonyl compounds with R_2N^+ or reaction of Os hydride compounds with R_2N^+ followed by deprotonation with bases such as NaOH.[30]

(25) Leung, W.-H.; Zheng, H.; Chim, J. L. C.; Chan, J.; Wong, W.-T.; Williams, I. D. *J. Chem. Soc., Dalton Trans.* **2000**, 423.

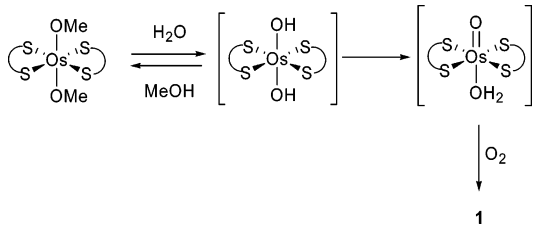
(26) Crystal data for compound **12**: $C_{66}H_{59}N_4P_5S_4Ru$; a = 9.8742(7), b = 10.6299(8), c = 12.0582(9) Å; α = 75.7600(10), β = 70.0860(10), γ = 79.9050(10)°; V = 1147.58(15) Å^3; triclinic, $P\bar{1}$ space group, Z = 1; ρ_{calcd} = 1.484 g cm^{-3}; T = 100(2) K; μ = 3.132 mm^{-1}; no. of data = 3937; R1 ($I > 2\sigma(I)$) = 0.0346, wR2 ($I > 2\sigma(I)$) = 0.0732, R1 (all data) = 0.0362, wR2 (all data) = 0.0739. N(3) in the N_2Ph ligands was found to be disordered, and the two sites were refined with occupancies 0.50 and 0.50.

(27) Johnson, B. F. G.; Haymore, B. L.; Dilworth, J. R. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, U.K., 1989; Chapter 13.3, p 99.

(28) Colin, J.; Bulter, G.; Weiss, R. *Inorg. Chem.* **1980**, *19*, 3828.

(29) Bishop, M. W.; Bulter, G.; Chatt, J.; Dilworth, J. R.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1979**, 1843.

Scheme 2



Reduction of **1** with $SnCl_2$ in THF gave the dichloride compound *trans*-[$Os(L)_2Cl_2$] (**13**). It may be noted that *trans*-[Os(TPP)Cl_2] has been prepared by reduction of *trans*-[Os(TPP)$(O)_2$] with $SnCl_2$.[31] Compound **13** is remarkably substitutionally inert. No substitution was found when **13** was reacted with nucleophiles such as azide, alkoxides, amides, and cyanide. An attempt to abstract the chlorides in **13** by treatment with silver triflate failed.

The Os(IV) bis(diazenido) compound **12** is diamagnetic whereas the dichloride compound **13** is paramagnetic with measured μ_{eff} of 1.8 μ_B which is similar to that for *trans*-[Os(TPP)Cl_2] (1.63 μ_B).[31] The diamagnetic behavior of compound **12** is consistent with the $(d_{xy})^2(d_{xz})^2$ or $(d_{xy})^2(d_{yz})^2$ ground electron configuration that has been found for bis(amido)osmium(IV) porphyrins, e.g., *trans*-[Os(TPP)$(NHPh)_2$].[23b] The splitting of the (d_{yz}, d_{zx}) set for *trans*-[M(TPP)$(NPh_2)_2$] (M = Ru, Os) has been explained in terms to the π interaction between the p_π orbital of the coplanar amido ligands and one of the metal d_π orbitals.[32] By contrast, the dialkoxyosmium(IV) porphyrins *trans*-[Os(TPP)$(OR)_2$], in which the alkoxy ligands act as pseudo double-faced π donors, are paramagnetic with the triplet $(d_{xy})^2(d_{yz})^1(d_{zx})^1$ ground state.[23a]

Air Oxidation of Compound 2. Previously, we reported that oxidation of compound **2** in Et_2O in air gave the dioxoosmium(VI) compound **1**.[17] However, when the oxidation of compound **2** was carried out in MeOH/hexane, orange crystals characterized as the Os(IV) dimethoxy compound *trans*-[$OsL_2(OMe)_2$] (**14**) were isolated. The measured μ_{eff} of 1.6 μ_B for compound **14** is similar to that of *trans*-[Os(salen)$(OMe)_2$] (1.33 μ_B)[24] but smaller than that of *trans*-[Os(TPP)$(OMe)_2$] (2.27 μ_B).[23a] Oxidation of compound **2** in ROH/hexane (R = Et, *i*-Pr) also gave red solutions, indicative of formation of the Os(IV) alkoxy species. Unfortunately, we were not able to crystallize these dialkoxy compounds due to their high solubility in organic solvents. It may be noted that *trans*-[Os(TPP)$(OR)_2$] (R = Me, Et, $PhCH_2$) have been synthesized from oxidation of [Os(TPP)(N_2)(THF)] in ROH/CH_2Cl_2 in air.[23a] Although compound **14** is stable in CH_2Cl_2/MeOH solution, it is readily oxidized in air to the dioxo compound **1** in CH_2Cl_2 solution. This is in contrast with *trans*-[Os(TPP)$(OMe)_2$][23a] and *trans*-[Os(salen)$(OMe)_2$][24]

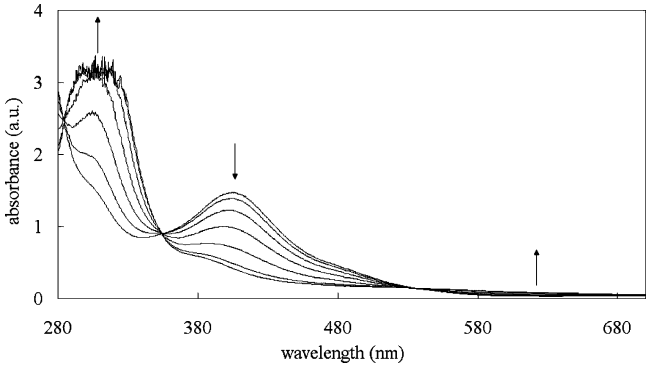


Figure 2. Optical spectral change for the air oxidation of *trans*-[$OsL_2(OMe)_2$] in CH_2Cl_2 solution (time interval = 2 min).

that are air stable in CH_2Cl_2 solutions. It seems likely that, in CH_2Cl_2 solution and in the absence of MeOH, compound **14** is in equilibrium with an Os(IV) dihydroxy or monooxo aquo species that can be readily air oxidized to compound **1**, possibly via an Os peroxo species. MeOH probably suppresses the exchange of the methoxy ligands in compound **14** with OH^-/H_2O, thus inhibiting its air oxidation (Scheme 2). Figure 2 shows the optical spectral trace for the oxidation of compound **14** in CH_2Cl_2 in air. The observation of isosbestic points at 285, 355, and 508 nm indicates that the air oxidation of compound **14** is a clean process and no intermediate(s) had accumulated during the oxidation.

NMR Spectroscopy. Compounds **3**−**7** exhibit a single ^{31}P resonance at ca. δ 58 ppm, which is very close to that of compound **1** (δ 60.7 ppm), indicative of the trans geometry of these Os(II) compounds. The $^{31}P\{^1H\}$ NMR spectrum of a recrystallized sample of compound **8**, which has been identified as *cis*-[$OsL_2(SO_2)(H_2O)$] by an X-ray diffraction study (vide infra), in C_6D_6 shows an intense singlet at δ 59.49 ppm characteristic of *trans*-Os$(L)_2$-type compounds along with four resonances at δ 61.30 (d), 59.37 (br s), 59.16 (br s), and 56.40 (d) ppm attributable to *cis*-**8**. This result suggests that while compound **8** prefers to crystallize in the trans form in the solid state, *cis*-**8** readily isomerizes to the trans isomer in C_6D_6. Similar cis−trans isomerization has been observed for [$RuL_2(PPh_3)X$]-type compounds previously. For example, [Ru{$N(Ph_2PS)_2$}$_2(PPh_3)$(py)] (py = pyridine) in $CDCl_3$ was found to contain a ca. 3:2 mixture of the cis and trans forms.[25] For compounds **10** and **11**, the ^{31}P resonances occur at more upfield positions (δ 89.38 and 89.90 ppm) than those of Os(II)−L compounds but are similar to that for free HL (δ 91.2 ppm). In addition, broad singlets assignable to the N*H* protons at δ 6.30 and 6.36 ppm, respectively, were observed in their ^1H NMR spectra. The NMR data confirmed that the nitrogen atom in L^- was protonated upon treatment of compounds **10** and **11** with HBF_4.

For the bis(phenyldiazenido) compound **12**, the resonances for the isopropyl protons occur at the normal diamagnetic region (δ 1.01 and 1.88 ppm). The $^{31}P\{^1H\}$ NMR spectrum displays a singlet at δ 57.81 ppm, consistent with its solid-state structure. Although compounds **13** and **14** are paramagnetic, they exhibit well-resolved ^1H NMR signals that are downfield shifted compared with diamagnetic Os−L compounds (e.g., the resonances for the Me_2CH protons

(30) (a) Haymore, B. L.; Ibers, J. A. *Inorg. Chem.* **1975**, *14*, 2784. (b) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Chem. Soc., Dalton Trans.* **1989**, 2353.
(31) Smieja, J. A.; Omberg, K. M.; Busuego, L. N.; Breneman, G. L. *Polyhedron* **1994**, *13*, 339.
(32) (a) Huang, J.-S.; Che, C.-M.; Li, Z.-Y.; Poon, C.-K. *Inorg. Chem.* **1992**, *31*, 1313. (b) Yang, S.-Y.; Leung, W.-H.; Lin, Z. *Organometallics* **2001**, *20*, 3198.

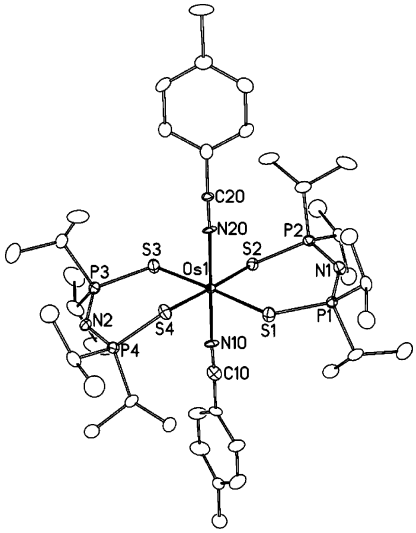


Figure 3. Molecular structure of *trans*-[OsL_2(4-tolCN)$_2$] (**4**). The ellipsoids are drawn at the 30% probability level.

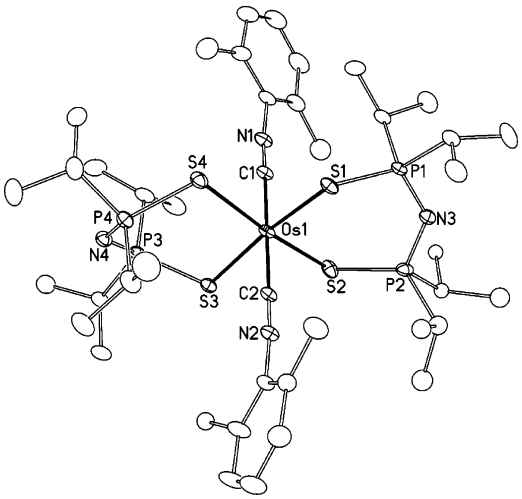


Figure 4. Molecular structure of *trans*-[OsL_2(xylNC)$_2$] (**6**). The ellipsoids are drawn at the 30% probability level.

occur at δ 3.84 and 3.40 and 3.64 ppm, respectively; cf. δ 2.51 ppm for compound **1**). The axial methoxy protons in compound **14** appears as a singlet at δ 42.90 ppm (cf. δ 34.23 for *trans*-[Os(TPP)(OMe)$_2$][23a]). The $^{31}P\{^1H\}$ NMR spectrum of **14** shows a singlet at δ 34.65 ppm whereas no ^{31}P resonant signals were observed for **13**.

Crystal Structures. The molecular structures of compounds **4**, **6**, *cis*-**8**, **13**, and **14** are shown in Figures 3−7, respectively. Selected bond lengths and angle for compounds **4**, **6**, **13**, and **14** are compiled in Table 2, and those of *cis*-**8**, in Table 3. The geometry around Os in compounds **4**, **6**, **13**, and **14** is pseudooctahedral with the two L^- ligands on the equatorial planes. The Os−SPNP′S′ rings in these complexes are nonplanar with boatlike confirmation. The P−S distances (2.026(2)−2.049(2) Å) are longer than those in the free ligand HL (1.941(1) and 1.949(1) Å)[18] whereas the P−N distances (1.586(5)−1.594(4) Å) are shorter than those in the latter (1.682(3) and 1.684(2) Å).[18] The Os−S distances for the Os(IV) compounds are similar to those of the Os(II) compounds. It is worth noting that the Os−S distances in the Os(II) compound **4** (2.414(2)−2.431(2) Å) are slightly

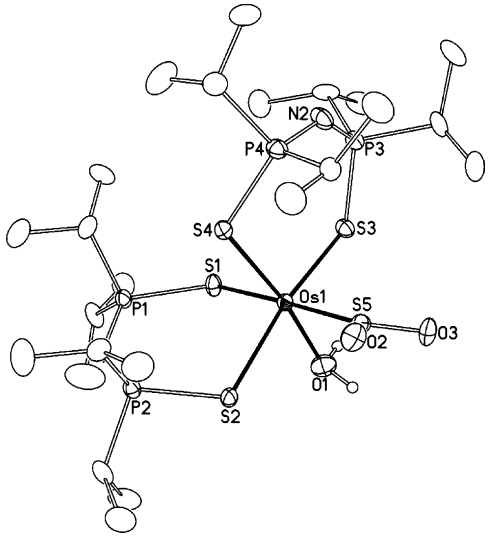


Figure 5. Molecular structure of *cis*-[$OsL_2(SO_2)(H_2O)$] (*cis*-**8**). The ellipsoids are drawn at the 30% probability level.

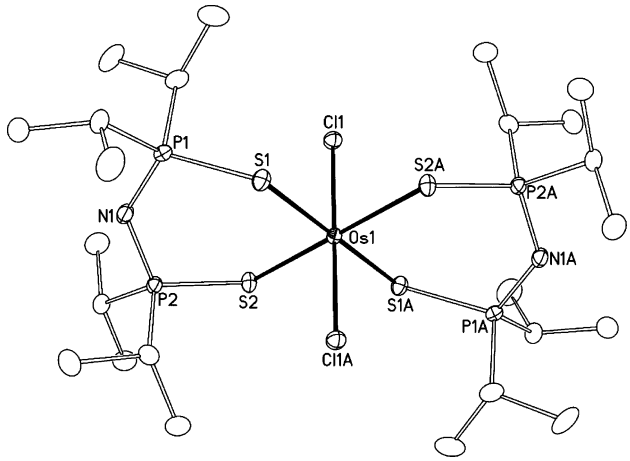


Figure 6. Molecular structure of *trans*-[OsL_2Cl_2] (**13**). The ellipsoids are drawn at the 30% probability level.

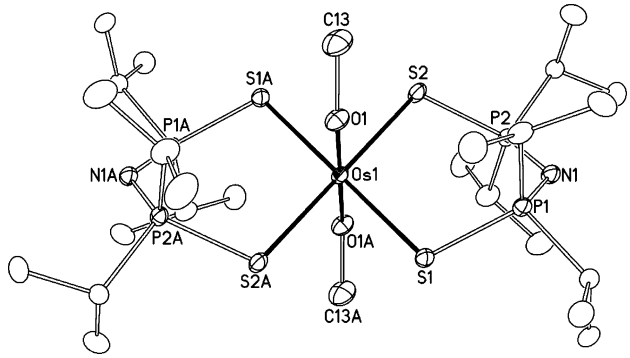


Figure 7. Molecular structure of *trans*-[$OsL_2(OMe)_2$] (**14**). The ellipsoids are drawn at the 30% probability level.

shorter than those in the dioxoosmium(VI) compound **1** (average 2.460 Å).[17] This result probably reflects strong Os−S interactions in the Os(II)−L compound. The Os−N distances in compound **4** (1.967(6) and 1.995(6) Å) and the Os−C distances in compound **6** [1.955(4) and 1.971(4) Å] are similar to those of related compounds, e.g., 2.081(8)−2.097(8) Å for *fac*-[$Os(PMe_2Ph)_3(MeCN)_3$]$^{2+}$ [33] and 2.00(3) Å for *trans*-[$OsBr_2(CN\text{-}t\text{-}Bu)_4$].[34] The Os−Cl distance in

Table 4. Formal Potentials ($E_{1/2}$)[a] for Os−L Complexes

complex	$E_{1/2}$/V vs $Cp_2Fe^{+/0}$		
	Os(V/IV)	Os(IV/III)	Os(III/II)
trans-[$OsL_2(PhCN)_2$] (**4**)		0.64	−0.63
trans-[$OsL_2(4\text{-tolCN})_2$] (**5**)		0.62	−0.67
trans-[$OsL_2(4\text{-}t\text{-}BuC_6H_4CN)_2$] (**6**)		0.64	−0.68
trans-[$OsL_2(xylNC)_2$] (**7**)		0.12[b]	
trans-[$Os(HL)_2(PhCN)_2][BF_4]_2$ (**11**)		0.93	0.33
trans-[OsL_2Cl_2] (**13**)		−0.62	
trans-[$OsL_2(OMe)_2$] (**14**)	0.31[b]		

[a] Potentials measured at a glassy carbon electrode in CH_2Cl_2 solutions with 0.1 M [n-Bu_4N][PF_6] as supporting electrolyte; scan rate = 100 mV s^{-1}. [b] Irreversible, E_{pa} value.

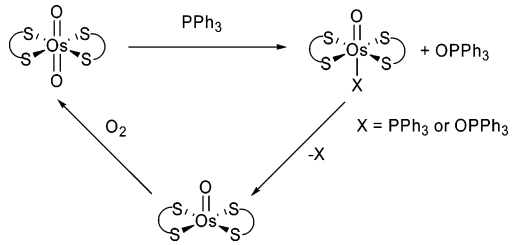
compound **13** (2.3423(9) Å) and the Os−O distance in compound **14** (1.934(3) Å) compare well with those of the porphyrin compounds *trans*-[Os(TPP)(OEt)$_2$] (1.915(4) Å)[23a] and *trans*-[Os(TPP)Cl_2] (2.294(2) Å).[31] The relatively short Os−O distance (cf. ca. 2.1 Å for normal Os−O single bonds) and large Os−O−C angle (127.9(3)°) in **14** are indicative of d_π(Os)−p_π(O) interaction.

The geometry about Os in *cis*-**8** is pseudooctahedral with the SO_2 and H_2O ligands cis to each other. The Os−S(*trans* to SO_2) distance (2.446(3) Å) is longer than the other Os−S distances (2.399(3)−2.426(3) Å) due to the trans influence of the SO_2 ligand. The Os−SO_2 distance of 2.118(3) Å is shorter than that in [Os(H)(SO_2)Cl(CO){$P(C_6H_{11})_3$}$_2$] (2.239(3) Å)[35] that has a trans-directing hydride ligand opposite to the SO_2 ligand. The Os−OH_2 distance of 2.150(7) Å is normal.

Electrochemistry. Formal potentials of Os−L complexes have been determined by cyclic voltammetry, and the results are summarized in Table 4. The cyclic voltammogram (CV) for compound **3** in CH_2Cl_2 shows two reversible couples at −0.63 and 0.64 V vs $Cp_2Fe^{+/0}$, which are assigned as the metal-centered Os(III/II) and Os(IV/III) couples, respectively. Similar Os(III/II) (−0.67 and −0.68 V, respectively) and Os(IV/III) (0.62 and 0.64 V, respectively) potentials were found for the bis(nitrile) compounds **4** and **5**. Unlike compounds **3**−**5**, the oxidation of the bis(isonitrile) complex **6** is irreversible (E_{pa} = 0.12 V). As one might expect, upon protonation the Os(III/II) and Os(IV/III) potentials for compound **3** were shifted to more anodic positions (0.33 and 0.93 V, respectively, for compound **10**). However, the anodic shift in the Os(III/II) potential ($\Delta E_{1/2}$ = 0.9 V) is more significant than that for the Os(IV/III) potential ($\Delta E_{1/2}$ = 0.31 V). This is probably due to the fact that the stability of the Os(II) state is more affected by the cationic charge (through weakening of Os-to-nitrile back-bonding) compared with that for the Os(III) and Os(IV) states.

The CV of the dichloride compound **13** exhibits a reversible couple at −0.62 V that is assigned as the Os(IV/III) couple. The Os(IV/III) potential for compound **13** is more negative than that of *trans*-[Os(TTP)Cl_2] (TTP = tetrakis(*p*-tolyl)porphyrin dianion) (−0.33 V)[36] but less positive than that of *trans*-[Os(Busalch)Cl_2] (Busalch = bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine) (−0.77 V).[37] The CV of the dimethoxy compound **14** displays an irreversible oxidation wave with E_{pa} = 0.12 V, which is tentatively assigned to the Os(IV/V) oxidation. By contrast, the Os(V/IV) couples for *trans*-[Os(TPP)$(OMe)_2$][38] and *trans*-[Os(salen)$(OMe)_2$][39] observed at 0.37 and 0.50 V, respectively, are reversible.

Scheme 3



1-Catalyzed Aerobic Oxidation of PPh_3. Treatment of compound **1** with excess PPh_3 (ca. 4 equiv) led to formation of an intractable paramagnetic material that did not crystallize. ^{31}P NMR spectroscopy indicated that ca. 1 equiv of Ph_3PO was produced, suggesting that the paramagnetic species is an Os(IV) compound. On the other hand, reaction of compound **1** with more basic phosphines led to formation of diamagnetic Os(II) phosphine compounds. For example, treatment of **1** with 4 equiv of $PMePh_2$ afforded air-sensitive *cis*-[$OsL_2(PMePh_2)_2$] (**15**). The $^{31}P\{^1H\}$ NMR spectrum of **15** displays three multiplets at δ −42.61, 49.16, and 50.10 ppm, consistent with the cis geometry of the compound. The facts that compound **1** can be reduced to an Os(IV) species by PPh_3 and that the Os(IV) compound **14** is readily air oxidized to give compound **1** suggest that catalytic oxidation of PPh_3 with compound **1** using oxygen as terminal oxidant is feasible. Indeed, stirring a solution of PPh_3 in chloroform at room temperature under 1 atm pressure of oxygen in the presence of 10 mol % of compound **1** gave Ph_3PO in 92% yield in 2 d. The dimethoxy compound **14** can also catalyze aerobic oxidation of PPh_3 with a similar efficiency (96%, 42 h). It seems likely that the catalytic cycle for the aerobic oxidation of PPh_3 involves the interconversion between compound **1** and an Os(IV) intermediate (Scheme 3). The catalytic activity of compound **1** is rather low compared with other metal−oxo catalysts, e.g., *cis*-[$Mo(O)_2(S_2CNEt_2)_2$][40] and [Ir(mes)$_3$(O)], where mes = 2,4,6-trimethylphenyl,[41] presumably due to the strong binding of PPh_3 or $OPPh_3$ to the Os center that inhibits the air oxidation of Os(IV) to Os(VI). Additional experimental work is needed to elucidate the mechanism of the Os-catalyzed aerobic oxidation of PPh_3.

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Concluding Remarks

We found that the dinitrogen compound **2** prepared by reduction of *trans*-$[OsL_2(O)_2]$ (**1**) with hydrazine hydrate is a useful starting material for Os−L compounds. Substitution of **2** with Lewis bases L′ such as nitriles and isonitriles afforded *trans*-$[OsL_2L'_2]$ whereas air oxidation of compound **2** in MeOH/hexane gave *trans*-$[OsL_2(OMe)_2]$. Reduction of **1** with phenylhydrazine and $SnCl_2$ afforded *trans*-$[OsL_2(N_2Ph)_2]$ and *trans*-$[OsL_2Cl_2]$, respectively. It appears that there is a close resemblance in chemistry between the OsS_4 core in the Os−L compounds and the OsN_4 and OsN_2O_2 cores in related porphyrin and Schiff base compounds, e.g., the $Os^{VI}(O)_2 \leftrightarrow Os^{IV}X_2 \leftrightarrow Os^{II}L_2$ interconversion. On the basis of the Os(IV/III) formal potential of $[Os^{IV}(chelate)Cl_2]$, the donor strength of chelate is ranked in the order $salen^{2-} > (L^-)_2 > TPP^{2-}$. A similar trend was obtained considering the IR N−N stretching frequencies for $[Os(chelate)(N_2)(solv)]$. Given the reported catalytic activity of Os salen[37] and porphyrin[42] compounds in organic transformations, one may anticipate that OsL_2 compounds may find applications in atom/group transfer reactions. Unlike the porphyrin and salen analogues, *trans*-$[OsL_2(OMe)_2]$ is air sensitive in CH_2Cl_2 solution and easily oxidized in air to dioxoosmium(VI) species. **1** can catalyze aerobic oxidation of PPh_3, and the catalytic cycle is believed to involve an interconversion between **1** and an Os(IV) intermediate.

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Supporting Information Available: Tables of crystal data, final atomic coordinates, anisotropic thermal parameters, and complete bond lengths and angles for compounds **4**, **6**, *cis*-**8**, **13**, and **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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