Protonation Reactions of *trans*-M(H)(SPh)(dppe)$_2$ (M = Ru, Os) To Give Thiol and Dihydrogen Complexes. X-ray Crystal Structure Determination of *trans*-Ru(H)(SPh)(dppe)$_2$ and *trans*-[Os(H)(O$_2$)(dppe)$_2$](O$_3$SCF$_3$)

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Received August 19, 1997

The compounds *trans*-M(H)(SPh)(dppe)$_2$ (M = Ru (**1Ru**), Os (**1Os**); dppe = 1,2-bis(diphenylphosphino)ethane) are synthesized by reaction of NaSPh with *trans*-[Ru(H$_2$)(H)(dppe)$_2$]BPh$_4$ or with *trans*-Os(H)(Br)(dppe)$_2$ in THF under Ar. They are characterized by ^{1}H and ^{31}P NMR, IR, FAB mass spectroscopy, elemental analyses, and cyclic voltammetry. The crystal structure determination of **1Ru** verifies the trans, octahedral geometry, which is distorted by ring−ring interactions. The thiophenoxide ligand is coordinated to the metal in a bent configuration, with the phenyl ring sandwiched between two phenyl rings of one of the dppe ligands. The reaction of complexes **1** with 1 equiv of HBF$_4$·Et$_2$O leads to the formation of the very reactive hydride thiol complexes *trans*-[M(H)(HSPh)(dppe)$_2$]BF$_4$ (M = Ru (**2Ru**), Os (**2Os**)). Analogous complexes to **1Os** and **2Os** with SC$_6$H$_4$-4-F instead of SPh are also described. In all cases there is no evidence for the existence of the tautomeric dihydrogen complex *trans*-[M(H$_2$)(SAr)(dppe)$_2$]$^+$. In the presence of excess acid the diprotonated complex *trans*-[Os(H$_2$)(HSPh)(dppe)$_2$](BF$_4$)$_2$ (**3Os**) is formed at 233 K where the T_1(min) of the H$_2$ ligand at 400 MHz is ∼34 ms so that 0.98 ≤ d_{HH} ≤ 1.24 Å. Under certain conditions the labile PhSH ligand of **3Os** is substituted by water to give *trans*-[Os(H$_2$)(OH$_2$)(dppe)$_2$](BF$_4$)$_2$ (**4Os**). The thiol complexes **2** react rapidly with H$_2$(g) to give the complexes *trans*-[M(H$_2$)H(dppe)$_2$]BF$_4$ (**5Ru, 5Os**). Complexes **3Os** and **4Os** also react with H$_2$ to give **5Os**. N$_2$ and O$_2$ (1 atm) displace the thiol in **2Os** in CH$_2$Cl$_2$ to produce *trans*-[Os(H)(L)(dppe)$_2$]$^+$ (L = η^1-N$_2$ (**6Os**), η^2-O$_2$ (**7Os**)). *trans*-[Os(H)(O$_2$)(dppe)$_2$]OTf·3C$_6$H$_6$ is characterized by X-ray diffraction.

Introduction

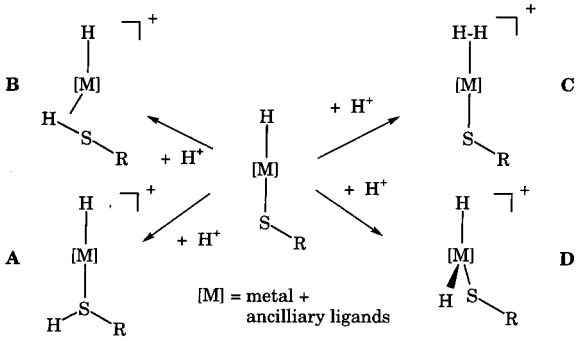
A question of fundamental importance is as follows: "Where does the proton go when a Brönsted acid is added to a complex containing both a thiolate and hydride ligand?" Four possible answers are represented by the structures of the products in Scheme 1 and are listed here with literature precedents: (**A**) on the sulfur to give a thiol complex;[1−3] (**B**) on the sulfur−metal bond to give an η^2-thiol ligand;[4] (**C**) on the metal−hydride bond to give an η^2-dihydrogen ligand;[2,5,6] (**D**) on the metal to give a dihydride.

In one series of complexes [M(H$_2$)(CO)(L)(PPh$_3$)$_2$]$^+$ and [M(H)(CO)(LH)(PPh$_3$)$_2$]$^+$ (M = Ru, Os; L = pyridine-2-thiolate, quinoline-8-thiolate), some of us were able to observe an equilibrium between dihydrogen thiolate (**C**) and hydride thiol (**A**) tautomeric forms (eq 1).[2]

$$\underset{\mathbf{C}}{[M](H_2)(SR)} \rightleftarrows \underset{\mathbf{A}}{[M](H)(HSR)} \qquad (1)$$

For one to observe such an equilibrium, the dihydrogen complex **C** must be very acidic because coordinated thiol ligands

Scheme 1



are very acidic. For example the quinoline-8-thiol ligand in the series just mentioned has a pK_a on the aqueous scale of about −1.[2] The benzenethiol ligand in the complex [Fe(C$_5$H$_5$)(CO)$_2$(SHPh)]$^+$ also has a pK_a value of less than zero,[7] whereas free PhSH has an aqueous pK_a value of 6.4.[8] We expected that the complexes *trans*-M(H)(SPh)(dppe)$_2$ (M = Ru (**1Ru**), Os (**1Os**)) would protonate at the M−H bond to produce dihydrogen complexes *trans*-[M(H$_2$)(SPh)(dppe)$_2$]$^+$ by analogy to the complexes *trans*-M(H)(Cl)(dppe)$_2$ which do give dihydrogen complexes *trans*-[M(H$_2$)(Cl)(dppe)$_2$]$^+$ (**8Ru, 8Os)** with pK_a

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S0020-1669(97)01050-1 CCC: $15.00
Published on Web 03/13/1998

values of 6.0 and 7.4, for M = Ru and Os, respectively.[9,10] However we report here that the expected dihydrogen complexes are not observed because the thiol hydride isomers *trans*-$[M(H)(HSPh)(dppe)_2]BF_4$ (M = Ru (**2Ru**), Os (**2Os**)) are more stable. In related work Wander et al. have reported that the anion $[Fe(SPh)(CO)_2(P(OPh)_3)_2]^-$ protonates at the metal to give $Fe(H)(SPh)(CO)_2(P(OPh)_3)_2$, which in turn protonates at the sulfur to give the very acidic complex $[Fe(H)(HSPh)(CO)_2(P(OPh)_3)_2]^+$.[1]

In keeping with the principle that dicationic dihydrogen complexes are unusually stable,[11,12] we also report the observation of the very acidic, dicationic dihydrogen thiol complex *trans*-$[Os(H_2)(HSPh)(dppe)_2](BF_4)_2$ (**3Os**). The related complex *trans*-$[Os(H_2)(SMe_2)(NH_2CH_2CH_2NH_2)_2](BF_4)_2$ has previously been characterized by ^{1}H NMR spectroscopy.[13]

Experimental Section

General Methods. Unless otherwise noted, air was excluded from the reactions by use of Schlenk techniques or Vacuum Atmospheres gloveboxes. In general, reactions were performed under argon, as was the purification of most of the charged complexes. The neutral complexes and $[Os(H)(N_2)(dppe)_2]^+$ were worked up under N_2. Solid $[Os(H)(O_2)(dppe)_2]^+$ (**7Os**) was generally handled in air.

Solvents were dried over the following reagents and distilled under dinitrogen: $CaSO_4$ for acetone, calcium hydride for dichloromethane, Linde type 4 Å molecular sieves for CD_2Cl_2, sodium for toluene, sodium/benzophenone ketyl for Et_2O, THF, benzene, and hexanes, and $Mg(OH)_x(OR)_{2-x}$ for alcohols. Except where noted, deuterated solvents were used as received from Cambridge Isotopes Laboratories. Prepurified gases were used as purchased from BOC. Phosphine ligands were used as purchased from Strem Chemicals or donated from Digital Specialty Co. Deuterations were performed with DOTf generated by reacting triflic anhydride with D_2O. *trans*-$OsH(Br)(dppe)_2$,[10] $RuCl_2(DMSO)_4$,[14] and *cis*-$RuCl_2(dppe)_2$[15] were prepared according to literature methods. Other reagents were obtained commercially and used as received.

Fast atom bombardment mass spectrometry (FAB MS) was carried out with a VG 70-250S mass spectrometer using a 3-nitrobenzyl alcohol (NBA) or magic bullet matrix with the sample dissolved in acetone. NMR was performed on a Varian Unity-400 operating at 400 MHz for ^{1}H, 61.47 MHz for ^{2}D, 161.90 MHz for ^{31}P, and 376.29 MHz for ^{19}F, a Varian Gemini 300 operating at 300 MHz for ^{1}H, 75.462 MHz for ^{13}C, 121.47 MHz for ^{31}P, and 282.33 MHz for ^{19}F, or a Varian Gemini 200 operating at 200 MHz for ^{1}H. Variable-temperature T_1 measurements were made at 300 or 400 MHz using the inversion recovery method with calibration of the 90°/180° pulse at each temperature. The temperature of the probes was calibrated with the temperature dependence of the chemical shifts of MeOH.[16] Reported chemical shifts refer to room-temperature conditions (19 °C) unless otherwise stated. All ^{31}P NMR spectra were proton decoupled unless specified otherwise. ^{31}P NMR chemical shifts were referenced to external 85% H_3PO_4. ^{1}H NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. ^{13}C spectra are ^{1}H-decoupled, and their chemical shifts are referenced relative to solvent peaks and reported relative to TMS. ^{19}F chemical shifts are referenced externally but reported relative to $CFCl_3$. Elemental analyses were performed by Guelph Chemical Laboratories Ltd.

A PAR model 273 potentiostat was used for cyclic voltammetry studies. The electrochemical cell contained a platinum working electrode, a tungsten secondary electrode, and a silver wire reference electrode in a Luggin capillary. The cyclic voltammograms were collected in dichloromethane containing 0.2 M *n*-Bu_4NPF_6 as the supporting electrolyte. Reported potentials are referenced to ferrocene, which was added to these solutions.

Preparation of *trans*-Ru(H)(SPh)(dppe)$_2$ (1Ru). $RuCl_2(dppe)_2$ (0.650 g, 0.671 mmol) and $NaBPh_4$ (1.020 g, 4.4 equiv) were stirred together in 10 mL of THF under an atmosphere of H_2 open to a mercury bubbler for 3 h. The initially deep red solution gradually lightened to become a pale yellow solution after 20 min. In a separate flask, $(PhS)_2$ (0.112 g, 0.513 mmol) and $NaBH_4$ (0.042 g, 2.2 equiv) were stirred together in 5 mL of THF and 5 mL of EtOH under an Ar atmosphere. Upon initial addition of the $NaBH_4$ to the solution, bubbles of H_2 were observed to rise from the solution. This solution was stirred for 5 days. The ruthenium-containing solution was filtered through Celite directly into the thiolate-containing solution, to give a deep yellow solution. The solvent was evaporated and the resulting yellow solids washed three times with MeOH, giving a bright yellow solid. Slow diffusion of ethanol into a saturated benzene solution of the complex produced analytically pure yellow crystals, suitable for X-ray crystallography (0.45 g, 80% yield). IR: 1918 cm^{-1} (m, ν_{RuH}). ^{1}H NMR (C_6D_6, 200 MHz): 7.5−6.3 (m br, 45H, Ph), 2.6 (m, 4H, CH_2), 1.8 (m, 4H, CH_2), −15.3 ppm (quint, 1H, $^2J_{HP}$ = 19.1 Hz, RuH). ^{31}P NMR (C_6D_6): 62.3 ppm (s). Anal. Calcd for $C_{58}H_{54}P_4RuS$: C, 69.11; H, 5.40. Found: C, 69.40; H, 5.41.

Preparation of *trans*-Os(H)(SPh)(dppe)$_2$ (1Os). Method 1. A slurry of NaSPh in THF (10 mL) was prepared by reacting NaO^{t}Bu (38 mg, 0.40 mmol) with PhSH (44 mg, 0.40 mmol). The complex *trans*-$Os(H)Br(dppe)_2$ (0.218 g, 0.204 mmol) was added, and the reaction mixture was refluxed for 3 h and then stirred for 50 h. The ^{31}P NMR spectrum showed that the reaction was complete. The suspension was chilled and filtered through THF-saturated Celite, and the solvent was removed from the yellow filtrate under reduced pressure. The resulting bright yellow powder was precipitated from THF (3 mL) by addition of cold Et_2O (10 mL) to give 0.28 g of crude product. This was dissolved in benzene (20 mL), and the salts were removed by filtering through benzene-saturated Celite. The volume of the filtrate was reduced under vacuum to 2 mL, Et_2O (4 mL) was added, and the mixture was briefly cooled. The bright yellow solid (0.18 g, 80% yield) was filtered out, washed with Et_2O (5 mL), and dried under vacuum.

Method 2. A white suspension of LiSPh was prepared by reacting HSPh (0.5 mL) in ether (10 mL) at 0 °C with ^{n}BuLi/hexanes (2.5 mL of 1.6 M). The ether was evaporated, THF was added, followed by $Os(H)Br(dppe)_2$ (0.49 g, 0.45 mmol) as above, and the mixture was refluxed for 48 h. IR: 2020 (m, ν_{OsH}). ^{1}H NMR (C_6D_6): 7.5−6.75 (m, 40H, PC_6H_5), 6.63 (m, 2H, SC_6H_5), 6.26 (m, 3H, SC_6H_5), 2.80 (m, 4H CH_2), 2.08 (m, 4H, CH_2), −16.6 (quint, 1H, $^2J_{HP}$ = 16.6 Hz, OsH). ^{31}P NMR (C_6D_6): 28.0 ppm (s). FAB MS: calcd for $C_{58}H_{54}{}^{32}SP_4{}^{192}Os$, *m*/*e* 1098; obsd, 1098 (M^+), 989 (M^+ − SPh). Anal. Calcd for $C_{58}H_{54}OsP_4S$: C, 63.49; H, 4.96. Found: C, 63.1; H, 4.9.

Preparation of *trans*-Os(H)(*p*-SC$_6$H$_4$F)(dppe)$_2$ (1Os-F). The preparation of this complex is analogous to the preparation of **1Os**. *p*-$LiSC_6H_4F$ was prepared by addition of ^{n}BuLi (8.5 mL of 1.5 M solution in hexanes, 13 mmol) to a solution of *p*-HSC_6H_4F (1.4 mL, 13 mmol) in 10 mL of Et_2O. The resulting white powder was collected by filtration, washed with Et_2O, and dried under vacuum.

To $Os(H)(Br)(dppe)_2$ (643 mg, 0.60 mmol) and *p*-$LiSC_6H_4F$ (166 mg, 1.24 mmol) under Ar was added about 50 mL of THF. The solution was refluxed for 17.5 h and then cooled, and the volume was reduced to 15−20 mL. ^{31}P NMR of the reaction mixture showed a single peak. Addition of Et_2O caused a bright yellow solid to precipitate out of solution. The remaining green-yellow liquid was removed by syringe, and the solid was dried under vacuum. It was then stirred overnight in toluene and filtered through toluene-saturated Celite. The volume of the solution was reduced, Et_2O was added, and the mixture was cooled; the Os(H)(*p*-SC_6H_4F)$(dppe)_2$ was collected by filtration and washed twice with Et_2O. The yield was increased by reducing

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the volume of the mother liquor, adding more Et_2O, cooling, and filtering again. Yield: 310 mg (0.28 mmol, 46%). ^{1}H NMR (CD_2Cl_2): 7.3 (d, $^2J_{HH}$ = 7 Hz, 8 H, *ortho* PPh), 7.0−7.1 (m, 24 H, *ortho* and *meta* PPh), 6.9 (t, $^2J_{HH}$ = 8, 8 H, *para* PPh), 6.1 (br, 2 H, *ortho* or *meta* SC_6H_4F), 5.7 (br, 2 H, *ortho* or *meta* SC_6H_4F), 2.8 (br, 4 H, PCH_2), 2.2 (br, 4 H, PCH_2), −17.0 ppm (quint, $^2J_{HP}$ = 16 Hz, 1 H, OsH). ^{31}P NMR (CD_2Cl_2): 30.4 ppm (s). ^{19}F NMR (CD_2Cl_2): −127.0 ppm (Ar F). Anal. Calcd for $C_{58}H_{53}FOsP_4S$: C, 62.41; H, 4.88. Found: C, 62.0; H, 4.9.

Preparation of *trans*-[Os(H)(HSPh)(dppe)$_2$]BF$_4$ (2Os). Excess HBF_4·Et_2O (25 μL, 0.14 mmol) was added with stirring to **1Os** (98 mg, 0.089 mmol) suspended in 15 mL of Et_2O. After 10 min, the deep yellow suspension had turned white. The white solid was collected by filtration and dried under vacuum. Yield: 60% to quantitative. ^{1}H NMR (CD_2Cl_2): 7.1−7.4 (m, 36H, PPh), 7.0 (t, $^2J_{HH}$ = 8, 1 H, *para* SPh), 6.7 (t, $^2J_{HH}$ = 8, overlaps peak at 6.6, 2 H, *meta* SPh), 6.6 (br, 4 H, *ortho* PPh), 5.8 (d, $^3J_{HH}$ = 8, 2H, *ortho* SPh), 4.4 (br quint, $^3J_{HP}$ = 4, 1 H, SH), 2.6 (br m, 4 H, PCH_2), 2.1 (br m, 4 H, PCH_2), −15.8 ppm (quint, $^2J_{HP}$ = 18 Hz, 1 H, OsH). ^{31}P NMR (CD_2Cl_2): 29.8 ppm (s).

The protonation can also be performed with HOTf instead of HBF_4·Et_2O. We were unsuccessful in obtaining acceptable elemental analysis on these very reactive thiol complexes.

Preparation of *trans*-[Os(H)(*p*-HSC$_6$H$_4$F)(dppe)$_2$]OTf (2Os-F). To a suspension of Os(H)(*p*-SC_6H_4F)(dppe)$_2$ (80 mg, 0.072 mmol) in about 20 mL of Et_2O was added HOTf (8 μL, 0.09 mmol). After 15 min of stirring, no color change was observed and so more HOTf (8 μL, 0.09 mmol) was added. Within 5 min, the color had changed from deep yellow to lavender. The solid was allowed to settle, and the solution was removed by syringe. The powder was washed once with Et_2O and then dried under vacuum. Yield: 36 mg (0.028 mmol, 40%). ^{1}H NMR (CD_2Cl_2): 7.4−6.9 (m; 32 H, PPh), 6.6 (br, 8 H, *ortho* PPh), 6.3 (t, J = 8, 2 H, *meta* SC_6H_4F), 5.9 (br m, 2 H, *ortho* SC_6H_4F), 4.5 (br m, 1 H, SH), 3.6 (s, 1 H, free *H*SC_6H_4F), 2.7 (br m, 4 H, PCH_2), 2.2 (br m, 4 H, PCH_2), −15.7 ppm (quint, $^2J_{HP}$ = 17 Hz, 1 H, OsH). ^{31}P NMR (CD_2Cl_2): 29.8 ppm (s). ^{19}F NMR (CD_2Cl_2): −77.3 (s, $SO_3CF_3^-$), −111.4 ppm (s, Ar F).

Identification of *trans*-[Os(H$_2$)(HSPh)(dppe)$_2$](BF$_4$)$_2$ (3Os). A CD_2Cl_2 solution of **1Os** (10−50 mg, 0.009−0.046 mmol) in an NMR tube was cooled to −78 °C. HBF_4·Et_2O (25 μL, 0.14 mmol) was added by syringe, and the sample was sealed and shaken briefly, until the yellow solution had turned colorless. The tube was then transferred to the NMR probe, which had been precooled to −30 °C. ^{1}H NMR (CD_2Cl_2): 11.6 (br, 35 H, H^+/H_2O), 7.4−7.1 (m, 37 H, PPh as well as SPh), 6.6 (br, 10 H, *ortho* PPh and possibly *meta* SPh), 5.9 (d, $^3J_{HH}$ = 7 Hz, 2 H, *ortho* SPh), 5.4 (quint br, 1 H, SH), 3.0 (br m, 4 H, PCH_2), 2.4 (br m, 4 H, PCH_2), −9.7 ppm (br, 2 H, Os(η^2-H_2)). VT T_1 of η^2-H_2 (ms)/temp (K): 55/193, 36/233, 34/253, 34/273, 34/283, 33/293, 30/298. ^{31}P NMR (CD_2Cl_2): 20.8 ppm (s).

After the sample had been kept at −78 °C for several hours, another ^{1}H NMR spectrum was taken at room temperature. ^{1}H NMR (hydride region): −9.7 (br, 1.6 H, **3Os**) −11.5 (m, 1 H, [Os(*H*$_2$)(Cl)(dppe)$_2$]$^+$),[10] −13.2 (br, 10 H, **4Os**), −15.7 (quint, $^2J_{HP}$ = 18 Hz, 4.5 H, **2Os**). In our solutions, **3Os** has never been the major species present at room temperature.

Identification of *trans*-[Os(H$_2$)(H$_2$O)(dppe)$_2$](OTf)$_2$ (4Os). To **1Os** (47 mg, 0.043 mmol) suspended in 10 mL of benzene was added CH_3OTf (7 μL, 0.062 mmol), with stirring. After 5 min the reaction mixture was clear. After a total of 20 min, it had become cloudy and slightly orange. HOTf (6 μL, 0.068 mmol) was added, and a precipitate formed. The volume of the solution was reduced, and the pale pink solid was collected by filtration and washed with Et_2O. On other occasions, the solution was removed by syringe rather than filtered. Yield: 58% to quantitative. ^{1}H NMR (CD_2Cl_2): 11.1 (br, H^+/H_2O), 7.5−7.6 (br, 8 H, *ortho* PPh), 7.4−7.1 (m, PPh and free HS*Ph*), 6.5 (br, 8 H, *ortho* PPh), 3.6 (s, 1 H, free *H*SPh), 3.2 (s, 2 H, Os(H_2O)), 2.9 (m, 4 H, PCH_2), 2.4 (m, 4 H, PCH_2), −13.3 ppm (br quint, $^2J_{HP}$ = 10 Hz, 2 H, Os(η^2-H_2)). T_1 of η^2-H_2 (ms)/temp (K): 47/294, 41/277, 38/252, 40/238, 50/221. ^{31}P NMR (CD_2Cl_2): 34.9 ppm (s). ^{19}F NMR (CD_2Cl_2): 277.1 (very small), −77.2 ppm (s, $SO_3CF_3^-$). FAB-MS: obsd, *m*/*e* 1170, 1097, 1021, 1003, 987 (largest peak); calcd, *m*/*e* 1097.30 [^{190}Os(H)(HSC$_6$H$_5$)(C$_{52}$H$_{48}$P$_4$)]$^+$, 1019.27 [^{190}Os(H)(O$_2$)(C$_{52}$H$_{48}$P$_4$)]$^+$, 1003.27 [^{190}Os(H)(O)(C$_{52}$H$_{48}$P$_4$)]$^+$, 987.28 [^{190}Os(H)(C$_{52}$H$_{48}$P$_4$)]$^+$.

HBF_4·Et_2O, instead of HOTf, can be used for the protonation; the complex can also be made directly by reaction of **1Os** with excess acid in dichloromethane or from **2Os**. The trace of water needed for the reaction may come from the slightly impure acid or from elsewhere.

Treatment of **1Os** with a 1:1 mixture of HOTf/DOTf in CD_2Cl_2 under Ar produces deuterated isotopomers of **4Os**. ^{1}H NMR (CD_2Cl_2): −13.3 (1:1:1 t, J_{HD} = 14 ± 1 Hz).

Identification of *trans*-[Os(H)(N$_2$)(dppe)$_2$]BF$_4$ (6Os). 2Os (120 mg, 0.101 mmol) was dissolved in 15−20 mL of CH_2Cl_2, and the solution was stirred for 30 min under N_2. Et_2O was then added to precipitate out a pale lavender powder, which was shown by ^{1}H NMR to contain both [Os(H)(N_2)(dppe)$_2$]$^+$ and **2Os** in the ratio 4:1. The remaining solid (85 mg) was redissolved in CH_2Cl_2 and stirred under N_2 for an additional 3.5 h. The volume of the solution was then reduced and Et_2O again added to precipitate out a pale lavender powder, which was washed twice with Et_2O. ^{1}H NMR showed this powder to consist of 7:3 [Os(H)(N_2)(dppe)$_2$]$^+$/**2Os**, as well as [Os(H)(H_2)(dppe)$_2$]$^+$ and Os(H)(Cl)(dppe)$_2$. Attempted recrystallization from CH_2Cl_2/ Et_2O under N_2 produced a mixture of hydrides. ^{1}H NMR (CD_2Cl_2, hydride region): −14.2 ppm ($^2J_{HP}$ = 17 Hz, Os*H*). ^{31}P NMR (CD_2Cl_2): 30.8 ppm (s). IR (Nujol mull): 2170 cm^{-1} (ν_{NN}).

Preparation of *trans*-[Os(H)(O$_2$)(dppe)$_2$]X (X = PF$_6$ or OTf) (7Os). Method 1 (PF$_6$ Salt). Os(H)Br(dppe)$_2$ (65 mg, 0.061 mmol) was suspended in ethanol under Ar. $NaPF_6$ (excess) was added and the reaction mixture was briefly opened to air. The pale yellow suspension was then sealed and stirred for 5 days, over which time its color changed to pale pink-brown. ^{31}P and ^{1}H NMR spectra of the reaction mixture confirmed that conversion to **7Os** was complete. The suspension was filtered in air and the filtrate washed with methanol to give a pale brown solid, which was air-dried overnight in a desiccator. The complex was also observed as the decomposition product of various reactions. The solid is air-stable for days. Yield: 62.4 mg (0.053 mmol, 87%); identification by NMR (see below).

Method 2 (OTf Salt). This reaction was conducted under Ar with traces of oxygen present. To **1Os** (35 mg, 0.023 mmol) suspended in 5 mL of benzene was added THF (0.8 mL) and then CH_3OTf (5 μL, 0.04 mmol). After 2 h of stirring, more CH_3OTf (2 μL, 0.02 mmol) was added and the mixture was again stirred for 2 h. The resulting peach solution was evaporated to dryness. The residue was dissolved in THF, and brown-red crystals were obtained by slow diffusion of benzene. The structure determined by single-crystal X-ray diffraction was confirmed by ^{1}H and ^{31}P NMR spectra of the remaining product. ^{1}H NMR (CD_2Cl_2): 7.4 (m, Ph), 7.3 (m, Ph), 7.2 (m, Ph; all overlapping, 32 H), 6.9 (br, 8 H, *ortho* Ph), 2.8 (m, 4 H, PCH_2), 2.1 (m, 4 H, PCH_2), −4.6 ppm (quint, $^2J_{HP}$ = 21 Hz, 1 H, Os*H*). ^{31}P NMR (CD_2Cl_2): 25.6 ppm (s).

X-ray Structure Determination of *trans*-Ru(H)(SPh)(dppe)$_2$. Crystals of *trans*-Ru(H)(SPh)(dppe)$_2$ were prepared by the slow diffusion of ethanol into a saturated solution of the complex in benzene in a purified N_2 atmosphere. A yellow crystal of dimensions 0.10 × 0.125 × 0.32 mm was mounted on a glass fiber and coated with epoxy to prevent exposure to the air. The mounted crystal was placed on an Enraf-Nonius CAD-4 diffractometer at 298 K. Unit cell parameters were determined by least-squares refinement of 15 reflections with 21.2 < 2θ < 22.5°. The unique space group $P2_1/n$ was determined. The data were corrected for Lorentz and polarization effects, and an absorption correction was applied using ψ-scan data. Minimum and maximum transmission coefficients were 0.4689 and 0.4893.

The structure was solved and refined using the SHELXTL/PC[17] package. Refinement was by full-matrix least-squares method on F^2 using all data (negative intensities included). The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0439P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were included in calculated positions and treated as riding atoms. The position of the hydride atom was refined with an isotropic thermal parameter.

(17) Sheldrick, G. M. *SHELXTL/PC V5.0*; Siemens Analytical X-ray Instruments Inc.: Madison, WI.

Table 1. Summary of Crystal Data, Details of Intensity Collection, and Least-Squares Refinement Parameters

	1Ru	**7Os**·3C_6H_6
empirical formula	$C_{58}H_{54}P_4RuS$	$C_{71}H_{67}F_3O_5OsP_4S$
a, Å	11.226(2)	13.259(2)
b, Å	33.260(7)	13.269(2)
c, Å	13.586(3)	18.201(3)
α, deg	90	86.13(1)
β, deg	104.01(3)	84.06(1)
γ, deg	90	85.48(1)
V, Å^3	4922(2)	3169.5(9)
Z	4	2
fw	1008.02	1403.39
cryst system	monoclinic	triclinic
space group	$P2_1/n$	$P\bar{1}$
T, K	293(2)	173(2)
λ, Å	0.710 73	0.710 73
ρ_{calc}, g cm^{-3}	1.360	1.471
μ, mm^{-1}	0.529	2.205
transm coeff	0.4689−0.4839	
$R(F_o)$ ($I > 2\sigma(I)$)[a]	0.0463	0.0490
$R_{2w}(F_o)$ (all data)[b]	0.1291	0.1039

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

Table 2. Selected Bond Lengths (Å) for **1Ru**

Ru(1)−S(1)	2.526(1)	Ru(1)−P(1)	2.332(1)
Ru(1)−P(2)	2.325(1)	Ru(1)−P(3)	2.340(1)
Ru(1)−P(4)	2.351(1)	Ru(1)−H(1Ru)	1.52(4)
S(1)−C(5)	1.754(5)	P(1)−C(1)	1.866(4)
P(1)−C(11)	1.846(5)	P(1)−C(21)	1.834(5)
P(2)−C(2)	1.852(5)	P(2)−C(31)	1.844(5)
P(2)−C(41)	1.833(5)	P(3)−C(3)	1.848(4)
P(3)−C(51)	1.829(5)	P(3)−C(61)	1.839(5)
P(4)−C(4)	1.857(4)	P(4)−C(71)	1.844(5)
P(4)−C(81)	1.829(4)	C(1)−C(2)	1.472(6)
C(3)−C(4)	1.516(6)		

Table 3. Selected Bond Angles (deg) for **1Ru**

P(1)−Ru(1)−S(1)	100.11(4)	P(2)−Ru(1)−S(1)	103.44(5)
P(4)−Ru(1)−S(1)	87.95(5)	P(3)−Ru(1)−S(1)	83.24(4)
P(1)−Ru(1)−P(3)	176.31(5)	P(2)−Ru(1)−P(3)	95.60(4)
P(2)−Ru(1)−P(1)	85.18(4)	P(1)−Ru(1)−P(4)	95.81(4)
P(2)−Ru(1)−P(4)	168.25(5)	P(3)−Ru(1)−P(4)	82.70(4)
H(1Ru)−Ru(1)−S(1)	173.7(14)	H(1Ru)−Ru(1)−P(1)	85.8(14)
H(1Ru)−Ru(1)−P(2)	78.9(14)	H(1Ru)−Ru(1)−P(3)	90.8(14)
H(1Ru)−Ru(1)−P(4)	89.5(14)	C(5)−S(1)−Ru(1)	117.8(2)
C(21)−P(1)−C(11)	99.7(2)	C(21)−P(1)−Ru(1)	125.4(2)
C(21)−P(1)−C(1)	99.7(2)	C(11)−P(1)−Ru(1)	118.4(2)
C(11)−P(1)−C(1)	101.7(2)	C(1)−P(1)−Ru(1)	108.1(2)
C(41)−P(2)−C(31)	100.3(2)	C(41)−P(2)−Ru(1)	122.9(2)
C(41)−P(2)−C(2)	104.8(2)	C(31)−P(2)−Ru(1)	121.4(2)
C(31)−P(2)−C(2)	97.2(2)	C(2)−P(2)−Ru(1)	106.5(2)
C(51)−P(3)−C(61)	100.2(2)	C(51)−P(3)−Ru(1)	120.9(2)
C(51)−P(3)−C(3)	101.2(2)	C(61)−P(3)−Ru(1)	123.6(2)
C(61)−P(3)−C(3)	101.9(2)	C(3)−P(3)−Ru(1)	105.6(2)
C(81)−P(4)−C(71)	100.8(2)	C(81)−P(4)−Ru(1)	119.5(2)
C(81)−P(4)−C(4)	103.3(2)	C(71)−P(4)−Ru(1)	122.8(2)
C(71)−P(4)−C(4)	98.1(2)	C(4)−P(4)−Ru(1)	108.81(14)
C(2)−C(1)−P(1)	113.1(3)	C(4)−C(3)−P(3)	107.7(3)
C(1)−C(2)−P(2)	112.3(3)	C(3)−C(4)−P(4)	111.3(3)

Crystal data are provided in Table 1, and selected bond lengths and angles are given in Tables 2 and 3.

X-ray Structure Determination of *trans*-[Os(H)(O$_2$)(dppe)$_2$]-OTf·3C$_6$H$_6$. Data were collected on a Siemens P4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The intensities of three standard reflections measured every 97 reflections showed less than 4% variation. The data were corrected for Lorentz and polarization and absorption effects.[18]

Table 4. Selected Bond Lengths (Å) for **7Os**

Os(1)−P(4)	2.351(2)	Os(1)−H(1Os)	1.29(4)
Os(1)−P(1)	2.360(2)	Os(1)−O(1)	2.061(4)
Os(1)−P(2)	2.368(1)	Os(1)−O(2)	2.064(3)
Os(1)−P(3)	2.380(1)	O(1)−O(2)	1.430(5)
P(1)−C(21)	1.818(6)	P(2)−C(31)	1.812(6)
P(1)−C(11)	1.822(5)	P(2)−C(41)	1.813(6)
P(1)−C(1)	1.858(5)	P(2)−C(2)	1.828(6)
P(3)−C(61)	1.821(6)	P(4)−C(71)	1.789(6)
P(3)−C(51)	1.834(5)	P(4)−C(81)	1.826(6)
P(3)−C(3)	1.837(6)	P(4)−C(4)	1.839(5)
C(1)−C(2)	1.528(7)	C(3)−C(4)	1.523(8)

Table 5. Selected Bond Angles (deg) for **7Os**

H(1Os)−Os(1)−O(1)	156(2)	H(1Os)−Os(1)−O(2)	164(2)
H(1Os)−Os(1)−P(4)	62(2)	H(1Os)−Os(1)−P(1)	78(2)
O(1)−Os(1)−P(4)	94.4(1)	O(1)−Os(1)−P(1)	125.9(1)
O(2)−Os(1)−P(4)	135.0(1)	O(2)−Os(1)−P(1)	85.4(1)
H(1Os)−Os(1)−P(2)	95(2)	H(1Os)−Os(1)−P(3)	94(2)
O(1)−Os(1)−P(2)	88.7(1)	O(1)−Os(1)−P(3)	83.2(1)
O(2)−Os(1)−P(2)	82.7(1)	O(2)−Os(1)−P(3)	88.6(1)
P(4)−Os(1)−P(1)	139.65(5)	P(4)−Os(1)−P(3)	84.02(5)
P(4)−Os(1)−P(2)	100.41(5)	P(1)−Os(1)−P(3)	99.77(5)
P(1)−Os(1)−P(2)	81.95(5)	P(2)−Os(1)−P(3)	171.05(5)
O(2)−O(1)−Os(1)	69.8(2)	O(1)−O(2)−Os(1)	69.6(2)
O(1)−Os(1)−O(2)	40.6(2)		
C(21)−P(1)−C(11)	104.0(3)	C(31)−P(2)−C(41)	104.4(3)
C(21)−P(1)−C(1)	101.6(3)	C(31)−P(2)−C(2)	105.1(3)
C(11)−P(1)−C(1)	104.9(3)	C(41)−P(2)−C(2)	101.6(3)
C(21)−P(1)−Os(1)	122.3(2)	C(31)−P(2)−Os(1)	115.4(2)
C(11)−P(1)−Os(1)	113.9(2)	C(41)−P(2)−Os(1)	124.1(2)
C(1)−P(1)−Os(1)	108.3(2)	C(2)−P(2)−Os(1)	103.8(2)
C(61)−P(3)−C(51)	104.2(3)	C(71)−P(4)−C(81)	102.5(3)
C(61)−P(3)−C(3)	103.9(3)	C(71)−P(4)−C(4)	102.3(3)
C(51)−P(3)−C(3)	102.6(3)	C(81)−P(4)−C(4)	103.3(3)
C(61)−P(3)−Os(1)	118.9(2)	C(71)−P(4)−Os(1)	119.2(2)
C(51)−P(3)−Os(1)	119.1(2)	C(81)−P(4)−Os(1)	119.6(2)
C(3)−P(3)−Os(1)	106.0(2)	C(4)−P(4)−Os(1)	107.6(2)

The structure was solved as above. The weighting scheme was $w = 1/[\sigma^2(F_o^2) + (0.0424P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were included in calculated positions and treated as riding atoms. The position of the hydride atom was refined with an isotropic thermal parameter. One of the C_6H_6 molecules is disordered over two sites with site occupancies 0.5:0.5, and the $CF_3SO_3^-$ anion is disordered over two sites with occupation parameters 0.62:0.38.

Crystal data are provided in Table 1, and selected bond lengths and angles are given in Tables 4 and 5.

Results and Discussion

Preparation of the Complexes *trans*-M(H)(SR)(dppe)$_2$. The new, deep yellow hydride complex *trans*-Ru(H)(SPh)(dppe)$_2$ (**1Ru**) is synthesized in four high-yield steps: (1) from $RuCl_3 \cdot 3H_2O$ to *cis*-$RuCl_2(DMSO)_4$; (2) to *cis*- and *trans*-$RuCl_2$(dppe)$_2$; (3) to *trans*-[Ru(H$_2$)(H)(dppe)$_2$]BPh$_4$ (**5Ru**);[15] (4) to complex **1Ru**. The dihydrogen ligand of **5Ru** is very labile and is easily displaced by the thiophenolate anion (eq 2), which

$$\textit{trans}\text{-}[Ru(H_2)(H)(dppe)_2]BPh_4 + NaSPh \rightarrow \textit{trans}\text{-}Ru(H)(SPh)(dppe)_2 + H_2 + NaBPh_4 \quad (2)$$

is conveniently generated by the reduction of PhSSPh with $NaBH_4$ in EtOH. A related complex, *trans*-Ru(H)(SPh)(dmpe)$_2$, is detected in solution by ^{1}H NMR when *cis*-Ru(H)$_2$(dmpe)$_2$ is reacted with PhSH.[19] This reaction is also thought to proceed via a dihydrogen complex, in this case *trans*-[Ru(H$_2$)(H)(dmpe)$_2$]-SPh. However this reaction proceeds further to produce *cis*- and *trans*-Ru(SPh)$_2$(dmpe)$_2$.

(18) Sheldrick, G. M. *SHELXA-90, Program for Absorption Correction*; University of Göttingen: Göttingen, Germany,

(19) Field, L. D.; Hambley, T. W.; Yau, B. C. K. *Inorg. Chem.* **1994**, *33*, 2009−17.

The new, yellow complex *trans*-Os(H)(SPh)(dppe)$_2$ (**1Os**) is synthesized in three high-yield steps: (1) from OsO_4 to $(NH_4)_2[OsBr_6]$; (2) to *trans*-Os(H)(Br)(dppe)$_2$;[10] (3) to complex **1Os**. The last step involves the displacement of bromide by thiophenolate in THF at reflux (eq 3). The synthesis of *trans*-Os(H)(*p*-SC_6H_4F)(dppe)$_2$ (**1Os-F**) is directly analogous to that of **1Os**.

$$\textit{trans}\text{-Os(H)(Br)(dppe)}_2 + \text{NaSPh} \rightarrow \textit{trans}\text{-Os(H)(SPh)(dppe)}_2 + \text{NaBr} \quad (3)$$

An alternative synthetic route similar to that of eq 2 failed to yield pure **1Os**. Reaction of $[Os(H_2)H(dppe)_2]BF_4$ **(5Os)** with LiSPh in THF leads primarily (90%) to deprotonation and formation of the dihydride complex $Os(H)_2(dppe)_2$[20] with only 10% formation of **1Os**. This result is somewhat unexpected, since PhS^- should not be a strong enough base to deprotonate **5Os**. The pK_a values of the PhSH and the dihydrogen complex are pK_a = 6.4 (measured on the aqueous scale)[8] and 13.6 (measured in THF and extrapolated to the aqueous scale),[21] respectively. This could be a thermodynamic effect where the basicity of the thiophenolate is enhanced in the THF solvent. It could also be a kinetic effect since it is known that deprotonation of **5Os** by a strong base is much faster ($t_{1/2} \ll 1$ min) than loss of H_2 ($t_{1/2} \gg 1$ h) at 20 °C.[21]

Properties of the Complexes *trans*-M(H)(SR)(dppe)$_2$. A C_6D_6 solution of each of the complexes causes a singlet to appear in the $^{31}P\{^1H\}$ spectra as expected for the trans stereochemistry. Accordingly, the ^1H spectra have quintets in the high-field region again indicating that the hydride couples to four equivalent phosphorus nuclei. The ^1H resonances of the thiolate ligands are found in the region between 6.3 and 7.0 ppm, somewhat upfield of the dppe ring protons. The presence of two different axial groups (hydride and thiolate) causes the methylene protons of the dppe to resonate in two distinct regions near 3 and 2 ppm.

The hydride stretch of **1Os** in Nujol at 2020 cm^{-1} is higher than that of **1Ru** at 1918 cm^{-1}. This indicates that the Os−H bond is stronger than the Ru−H bond. The FAB-MS of **1Os** reveals a parent ion and a fragment caused by loss of SPh^-.

The cyclic voltammograms of **1Ru** in CH_2Cl_2/*n*-Bu_4NPF_6 and **1Os** in THF/*n*-Bu_4NPF_6 show a reversible wave with a M(III)/M(II) reduction potential versus $FeCp_2^+/FeCp_2$ of 0.07 and −0.65 V, respectively. These translate into approximately 0.7 and 0.0 V vs NHE. The values are predicted to be 0.5 and 0.2 V, respectively, on the basis of Lever's empirical method which involves adding ligand parameters E_L.[22] Of the ligands X that we have examined in the series *trans*-M(H)(X)(dppe)$_2$ (X = H, Cl, SPh; M = Fe, Ru, Os), the SPh ligand has the most negative E_L value (−0.53 V vs −0.4 V for hydride[23] and −0.24 V for chloride) and therefore makes the metal in the complex the most reducing and potentially the most basic with respect to protonation (see below). A second reversible Os(IV)/Os(III) wave is observed for **1Os** at 0.25 V.

Complex **1Os** slowly reacts with CH_2Cl_2 or CD_2Cl_2 solvent to give *trans*-Os(H)(Cl)(dppe)$_2$ and $PhSCH_2SPh$. The latter product was identified by the CH_2 ^1H NMR resonance at 4.3 ppm. Usually chlorinated solvents react to replace the hydride ligand with a chloride ligand,[24] but in the case of **1Os,** the nucleophilicity of the thiolate ligand and steric hindrance to reaction at the hydride seem to determine the reaction outcome.

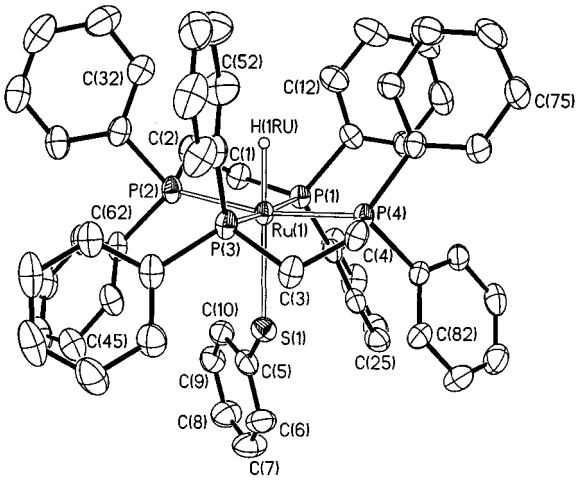

Figure 1. Crystallographic labeling scheme for **1Ru**. Thermal displacement parameters are at the 30% probability level.

X-ray Crystal Structure Determination of Ru(H)(SPh)(dppe)$_2$. The crystal structure determination of **1Ru** verifies the trans, octahedral geometry (Figure 1). The geometry is distorted by steric interactions as described below. The hydride position refined to a reasonable Ru−H distance of 1.52(4) Å.

The SPh ligand is coordinated to the metal in a bent configuration with a Ru−S−C(5) angle of 117.8(2)°. The phenyl ring is sandwiched between two phenyl rings of one of the dppe ligands. The Ru−S bond length of 2.526(1) Å is considerably longer than the average value of 2.238 Å observed for six ruthenium arenethiolates[24] and the 2.472(1) Å distance in the closely related complex *trans*-Ru(SPh)$_2$(dmpe)$_2$.[19] This is caused by a combination of two effects: the strong trans influence of the hydride ligand[25] and the steric crowding caused by the dppe ligands. The sulfur is pushed by interactions with the rings on P(1) and P(2) toward P(3) and P(4) so that the S−Ru−P angles are 100.11(4) and 103.44(5)° for the first two phosphorus atoms and 83.24(4) and 87.95(5)° for the last two. A similar distortion of octahedral geometry was reported for the complexes **8Ru**[9] and **8Os**[10] where the M−Cl bond tilts toward one dppe ligand because of Cl−ring interactions.

The ruthenium−phosphorus bonds are slightly longer to the dppe ligand toward which the M−S bond is tilted (Ru−P(3) = 2.340(1), Ru−P(4) = 2.351(1) Å) than to the other dppe ligand (Ru−P(1) = 2.332(1), Ru−P(2) = 2.325(1) Å). These Ru−P distances are very close to the ones observed in *trans*-Ru(SPh)$_2$(dmpe)$_2$[19] and *trans*-$[Ru(H_2)H(dppe)_2]BPh_4$[26] and shorter than those in *trans*-$[Ru(H_2)Cl(dppe)_2]PF_6$ (2.385(5) Å on average).[9]

Observation of the Complexes *trans*-[M(H)(SHPh)(dppe)$_2$]$^+$ (2Ru, 2Os). When a suspension of the complexes **1Ru** or **1Os** in Et_2O is treated with $HBF_4 \cdot Et_2O$ under Ar, then an unstable precipitate forms which is red (**2Ru**) or white (**2Os**), respectively.

$$\underset{\textbf{1Ru, 1Os}}{\textit{trans}\text{-M(H)(SPh)(dppe)}_2} + HBF_4 \cdot Et_2O \rightarrow \underset{\textbf{2Ru, 2Os}}{\textit{trans}\text{-[M(H)(SHPh)(dppe)}_2]BF_4} + Et_2O \quad (4)$$

The osmium complex is the more stable and has been character-

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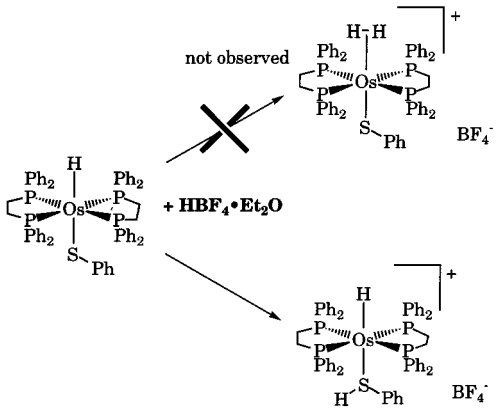
Scheme 2



ized in solution by ^{1}H and ^{31}P NMR. Prepared in this way, **2Os** reacts with both dichloromethane and THF, the two solvents in which it dissolves. When it is dissolved in CD_2Cl_2 under Ar, NMR spectra of the solution show that **2Os** predominates while $[Os(H_2)(Cl)(dppe)_2]^+$ (**8Os**)[10] is present in small and variable amounts.

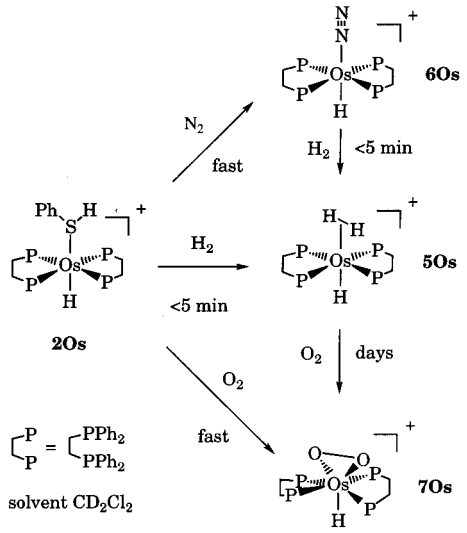
The trans stereochemistry of **2Os** is indicated by three spectral features. First, the complex has one singlet resonance in the $^{31}P\{^1H\}$ NMR spectrum at 29.8 ppm. Second, it has a binomial quintet at −15.8 ppm in the ^{1}H NMR spectrum for the hydride resonance. And third, it has a broad thiol resonance at 4.4 ppm which is also a binomial quintet with $^3J_{PH} = 4$ Hz. The T_1 of the hydride resonance is 420 ± 25 ms at 298 K, which rules out the possibility that **2Os** is a dihydrogen complex. The hydride peak integrates as expected in a 1:1 ratio to the broad quintet of the SH at 4.4 ppm.

The thiol ligand in this complex is very labile, and its exchange with free HSPh can be observed in a ^{1}H NMR spin saturation transfer experiment. Irradiation of the SH proton at 4.4 ppm causes an inversion of a singlet resonance at 3.4 ppm, which is due to the SH proton in free thiophenol.

When the protonation of **1Os** in CD_2Cl_2 is carried out at 193 K, complex **2Os** is the exclusive product (27.9 ppm in the ^{31}P NMR spectrum) apart from a small amount of $[Os(H_2)(Cl)(dppe)_2]^+$ (20.7 ppm). The latter is probably produced by reaction of **1Os** with CD_2Cl_2. Therefore it appears that protonation at sulfur is both kinetically and thermodynamically preferred over protonation at the Os−H bond (Scheme 2).

We anticipated that replacing the phenyl substituent of the thiolate with an electron-withdrawing *p*-fluorophenyl group might disfavor protonation at sulfur and favor protonation at the Os−H to produce the tautomeric *trans*-$[Os(H_2)(SAr)(dppe)_2]^+$ complex. However, like **1Os**, *trans*-Os(H)(*p*-SC_6H_4F)$(dppe)_2$ is singly protonated by HOTf in Et_2O to form the hydride thiol tautomer. *trans*-$[Os(H)(SC_6H_4\text{-}4\text{-}F)(dppe)_2]OTf$ (**2Os-F**) was identified by the similarity of its NMR spectra to those of **2Os**. For **2Os-F**, the ^{31}P NMR spectrum has a singlet at 29.8 ppm, while the ^{1}H NMR spectrum has a well-resolved quintet at −15.7 ppm for the hydride and broad quintet at 4.5 ppm for the thiol SH. All the ^{1}H chemical shifts are within 0.1 ppm of those for **2Os**. Apparently adding a *para* fluorine to the thiolate ring does not substantially reduce the basicity of the sulfur relative to that of the hydride.

Scheme 3



Red **2Ru** produces a yellow solution when dissolved in acetone-d_6 under Ar. The ^{1}H and ^{31}P NMR spectra both indicate the presence of a mixture of products. The major species, *trans*-$[Ru(H)(SHPh)(dppe)_2]^+$, shows in the $^{31}P\{^1H\}$ NMR spectrum a singlet at 64.1 ppm and in the ^{1}H NMR spectrum a quintet at −22.5 ppm ($^2J_{PH} = 19.3$ Hz) due to the hydride and a broad singlet at 3.8 ppm assigned to the SH resonance.

Reactions of Complexes 2 with Small Gas Molecules. Complexes **2** react rapidly with 1 atm of dihydrogen to give the dihydrogen complexes *trans*-$[M(H_2)H(dppe)_2]^+$ (**5Ru**, **5Os**) and free thiol (eq 5).

$$\textit{trans}\text{-}[M(H)(SHPh)(dppe)_2]^+ + H_2 \rightarrow \textit{trans}\text{-}[M(H)(H_2)(dppe)_2]^+ + HSPh \quad (5)$$

Complex **2Os** in CD_2Cl_2 reacts within seconds with H_2 to give the dihydrogen complex **5Os** (Scheme 3). Complex **2Ru** as a suspension in diethyl ether reacts to give **5Ru** as the major product. These are the first reports of a reaction where dihydrogen displaces a thiol ligand to produce a dihydrogen complex.[27]

Even dinitrogen displaces the thiol ligand of **2Os** in CD_2Cl_2 (Scheme 3). When **2Os** is dissolved in dichloromethane under an N_2 atmosphere, the major species observed by ^{1}H and ^{31}P NMR is *trans*-$[Os(H)(N_2)(dppe)_2]^+$ (**6Os**). Unfortunately, attempted crystallization only resulted in a pale lavender mixture of complexes. The dinitrogen stretching frequency is 2170 cm^{-1}, an unusually high frequency for a complex with a stable dihydrogen analogue. Most stable dihydrogen complexes of a d^6 metal ion have corresponding dinitrogen complexes with ν_{NN} in the range 2060−2150 cm^{-1}.[23] The dinitrogen complex was also observed in a reaction of **1Os** in CD_2Cl_2 under Ar with N_2-saturated CH_3OTf where, presumably, CH_3SPh is also produced.

The dinitrogen ligand in **6Os** is extremely labile and is replaced by dihydrogen after only a few seconds of bubbling H_2 through the solution. In contrast, N_2 does not displace H_2 from the complex when a solution of $[Os(H)(H_2)(dppe)_2]^+$ is shaken in a N_2-filled NMR tube.

O_2 reacts with **2Os**, **5Os**, or **6Os** to give the red-brown η^2-dioxygen complex *trans*-$[Os(H)(O_2)(dppe)_2]^+$ (**7Os**) (Scheme 3). This complex was also prepared by the reaction of *trans*-

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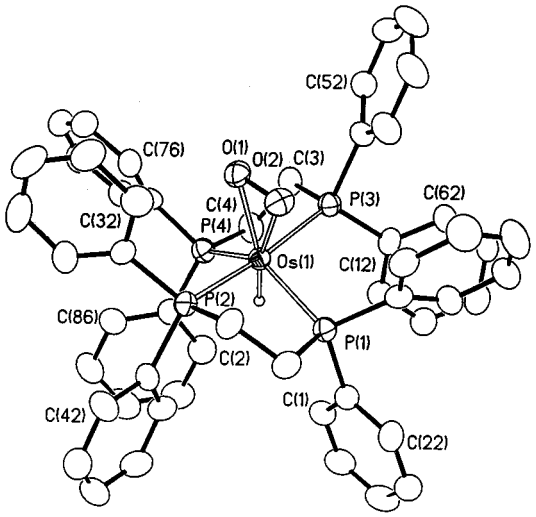

Figure 2. Crystallographic labeling scheme for the cation of **7Os**. Thermal displacement parameters are at the 50% probability level.

Os(H)(Br)(dppe)$_2$ with $NaPF_6$ in EtOH under a mixture of argon and air. The $[Os(H)(dppe)_2]^+$ binding site has a high affinity for dioxygen. This binding site also has a high affinity for CH_3CN,[28] but a 4.5-fold excess of CH_3CN does not displace O_2 from this complex in CD_2Cl_2 after 2 days at 20 °C.

Figure 2 shows the structure of the cation of **7Os**, and Tables 4 and 5 list selected bond lengths and angles. The Os−H(1Os) distance is artificially short at 1.29(4) Å. The O−O distance is 1.430(5) Å. The η^2-O_2 ligand is oriented along the P(1)−Os−P(4) axis, and the Os−P(1) and Os−P(4) bonds are bent away from the O−O bond, with a P(1)−Os−P(4) angle of 139.65(5)°. The P(2)−Os−P(3) angle is 171.05(5)°, oriented toward the η^2-dioxygen ligand. The structure of **5Os** is very similar to that of $[Os(H)(O_2)(dcpe)_2]^+$, which has an O−O bond distance of 1.45(1) Å along the P(2)−Os−P(4) axis, a P(2)−Os−P(4) angle of 136.3(1)° away from the O_2, and a P(1)−Os−P(3) angle of 169.2(1)° toward the O_2.[29]

The dihydrogen ligand of **5Os** has been located crystallographically in an orientation similar to that of this O_2 ligand, parallel to a P−Os−P axis.[30] However, the P−Os−P angle along this axis is 176.3° and so it does not bend as sharply away from the Os−(H−H) bonds as from the Os−(O−O) bonds. In these complexes, both electronic and steric forces contribute to the bending of one P−Os−P angle away from the π-bonding ligand. Electronically, the partial oxidative addition of the ligand imposes a distortion toward a 7-coordinate structure. Sterically, the alignment of the π-bonding ligand along the P−Os−P axis creates crowding that can only be relieved by a smaller P−Os−P angle or by longer metal−ligand distances. The P−Os−P angle is larger in $[Os(H)(H_2)(dppe)]^+$, consistent with the presence of a very small π-bonding ligand which has not been significantly reduced.

Observation of Dicationic Dihydrogen Complexes. When a large excess of HBF_4·Et_2O is added to **1Os** in CD_2Cl_2 at 193 K under Ar, two major peaks are observed in the high-field region of the ^{1}H NMR spectrum along with a small amount of the chloride complex **8Os** (Figure 3). Even under strongly acidic conditions the mixture consists of 70% **2Os,** as represented by the quintet at −15.7 ppm, and 30% *trans*-$[Os(H_2)(SHPh)(dppe)_2]^{2+}$ (**3Os**), the broad singlet at −9.5 ppm. ^{31}P NMR peaks at 27.9 and 18.8 ppm, respectively, correspond to these two resonances.

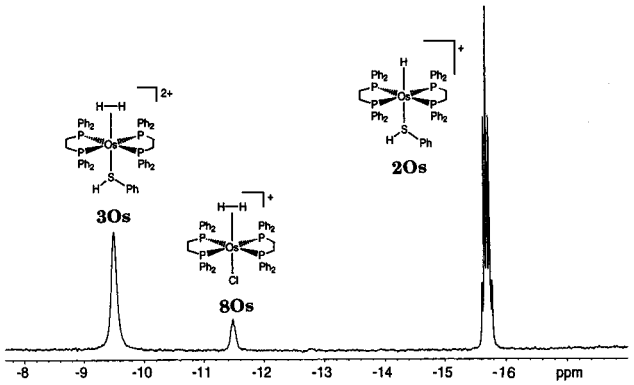

Figure 3. ^{1}H NMR spectrum in the high-field region at 253 K of **1Os** after reaction in CD_2Cl_2 at 193 K with a large excess of HBF_4·Et_2O.

$$\mathbf{1Os} + \text{excess } HBF_4\cdot Et_2O \xrightarrow{CD_2Cl_2,\ 193\ K} \mathbf{2Os} + \underset{\mathbf{3Os}}{\textit{trans}\text{-}[Os(H_2)(SHPh)(dppe)_2]^{2+}} + \mathbf{8Os} \quad (6)$$

The ^{1}H NMR signal at −9.5 is assigned to a coordinated dihydrogen because of its short minimum T_1 time of 34 ms at 272 K and 400 MHz. As the temperature is raised from 193 to 280 K, the T_1 of the dihydrogen resonance at −9.5 ppm goes to a minimum value of 34 ms (see Experimental Section) but then abruptly appears to get shorter as it starts to react to form another complex **4Os** (see below) above 280 K. An H−H distance of between 0.98 and 1.24 Å can be calculated from this T_1 value after correcting for other sources of dipolar relaxation and assuming fast or slow motion of the HH ligand, respectively.[20] Several attempts to measure the H,D coupling in this complex failed.

It is only possible to resolve the thiol proton resonance of **3Os** at low temperature (253 K); at other temperatures, it overlaps with other peaks. The assignment of the peaks due to **3Os** was confirmed by a heteronuclear ^{1}H{^{31}P} NMR experiment at 250 K in which the ^{31}P peak at 20.8 ppm (arising from **3Os**) was decoupled from the protons as a ^{1}H NMR spectrum was collected. This produced a ^{1}H NMR spectrum that showed sharpening of the peaks at 2.4 (CH_2), 3.0 (CH_2), 5.4 (SH), 5.9 (ortho SPh), and 6.6 ppm (ortho PPh). The ratios of the integrals of the peaks at 5.4 and 5.9 ppm relative to the integral of the hydride peak are 1:1 and 2:1, as expected.

In VT experiments starting at low temperature, a dihydrogen resonance at −13.2 ppm attributed to *trans*-$[Os(H_2)(OH_2)(dppe)_2]^{2+}$ **(4Os)** starts to appear at temperatures above 273 K and grows in intensity with increasing temperature, while the intensity of the resonance at −9.5 ppm decreases at the same time. The appearance of the peak at −13.2 ppm is accompanied by a set of new resonances for the ethylene backbone of **4Os** at 2.42 and 2.90 and of resonances at ∼3.6 ppm and ∼3.2 ppm (shifts are temperature-dependent by ±0.1 ppm) assigned to free PhSH and coordinated H_2O, respectively. The 3.2 ppm peak disappears 30 min after D_2O is added to the solution. In the ^{31}P NMR spectrum a new singlet at 33.1 ppm for **4Os** is observed. Complex **4Os** was prepared independently and the dihydrogen (or HD) ligand was characterized by a minimum ^{1}H T_1 value of 38 ms at 250 K and 300 MHz and an H−D coupling constant of 14 ± 1 (see Experimental Section). Therefore the thiol ligand in **3Os** is displaced by water,

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originating probably from the acid (eq 7). A similar reaction

$$\underset{\textbf{3Os}}{\textit{trans}\text{-}[Os(H_2)(SHPh)(dppe)_2]^{2+}} + H_3O^+ \rightleftarrows \underset{\textbf{4Os}}{\textit{trans}\text{-}[Os(H_2)(OH_2)(dppe)_2]^{2+}} + HSPh + H^+ \quad (7)$$

was described by Halcrow, Chaudret, and Trofimenko, who found that reaction of Ru(tris(pyrazol-1-yl)borate)(PCy_3)(H_2)(H) with $HBF_4 \cdot Et_2O$ or with HOTf gives [Ru(tris(pyrazol-1-yl)borate)(PCy_3)(H_2O)(H_2)]$^+$.[31] We have evidence that eq 7 can be partially reversed by cooling the sample below 273 K.[32]

Addition of HOTf or HBF_4 to **1Os** or **2Os** at 293 K produces a mixture of **2Os**, **3Os**, **4Os**, and free HSPh. Addition of excess PPh_3 (as a base) to this sample causes the conversion first of the **3Os** into **2Os** and then, when more PPh_3 is added, of the **4Os** into **2Os**. Since both **3Os** and **4Os** are deprotonated by PPh_3 but **3Os** is deprotonated first, its pK_a is probably well under 2.7, the pK_a of $HPPh_3^+$.

Reaction of the Dicationic Complexes with Dihydrogen. A remarkable feature of the complexes **2Os**, **3Os**, and **4Os** is their reactivity with H_2(g) (eq 8). Introduction of H_2(g) into

$$\textbf{2Os} + \textbf{3Os} + \textbf{4Os} + H^+ + \text{excess } H_2 \rightarrow \textbf{5Os} + HSPh + \textbf{4Os} + H^+ + \text{excess } H_2 \rightarrow \textbf{5Os} + HSPh + H_3O^+ \quad (8)$$

reaction mixtures containing the three complexes and acid in CD_2Cl_2 or CH_2Cl_2 solution leads to the rapid and quantitative formation of the complex $[Os(H_2)H(dppe)_2]^+$ **(5Os)** as the only product (aside from a little **8Os** formed in the side reaction of **2Os** with the solvent as discussed above). Of the three complexes **2Os**, **3Os**, and **4Os**, only **4Os** remains detectable in the spectrum after the introduction of H_2(g) into the mixture for less than 30 min. The labile thiol complexes **2Os** and **3Os** react quickly, and **4Os** reacts more slowly. Presumably the ultimate conversion of **4Os** to **5Os** involves the loss of the less labile aqua ligand and is therefore somewhat slower than the direct reaction of **2Os** or **3Os** with H_2(g). In all cases free PhSH was identified in the ^{1}H NMR spectrum as a reaction product by the appearance of a broad thiol proton resonance at ~3.6 ppm (s), while the water released probably contributes to the acid peak, observed at 13 ppm.

Conclusions

Although the thiolate ligand is strongly electron-donating to the metal, as indicated by the electrochemical results, protonation does not take place at the metal or metal−hydride of the new complexes *trans*-M(H)(SPh)(dppe)$_2$ (M = Ru, Os). Instead protonation at the sulfur is kinetically and thermodynamically preferred to give the very reactive complexes *trans*-[M(H)(SHPh)(dppe)$_2$]$^+$. The thiol ligand is very labile and can be displaced by H_2 to give the dihydrogen complexes *trans*-[M(H)(H_2)(dppe)$_2$]$^+$. Dioxygen and dinitrogen also displace the thiol in the osmium complex, thus producing a unique series of complexes containing molecular H_2, N_2 and O_2. Double protonation of **1Os** produces the first dihydrogen complex to contain a coordinated thiol, *trans*-[Os(H_2)(SHPh)(dppe)$_2$]$^{2+}$. The fact that a thiolate ligand can be displaced from a platinum-group metal by protonation and then reaction with dihydrogen suggests that the reactivation of "sulfur-poisoned" catalysts might be possible by such a reaction pathway.

Acknowledgment. We thank the NSERC Canada for an operating grant, Johnson-Matthey for a loan of ruthenium and osmium salts, and Digital Chemical Co. for a gift of dppe.

Supporting Information Available: Tables of crystal and structure refinement data, atomic coordinates, thermal parameters, and bond distances and angles for **1Ru** (9 pages). An X-ray crystallographic file, in CIF format, for the structure determination of **7Os** is available on the Internet only. Ordering and access information is given on any current masthead page.

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