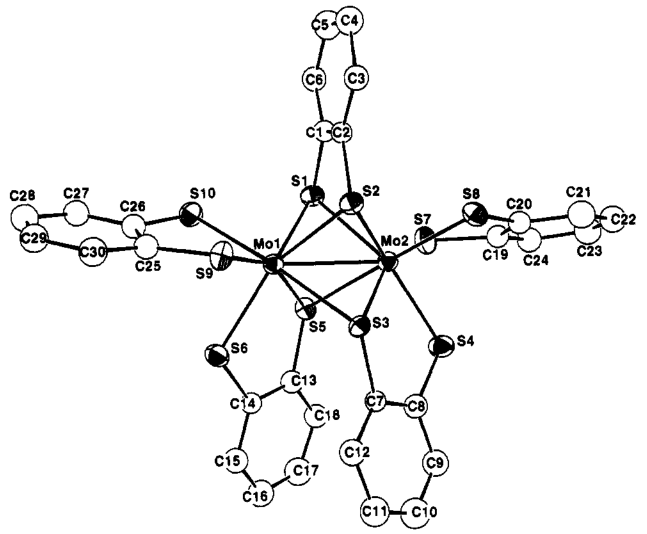

Figure 1. ORTEP drawing of the structure of the $Mo_2(bdt)_5$ molecule, showing the atom-labeling scheme.

structure is closely related to the structure[15] of $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4$, the primary difference being replacement of the symmetrically bridging S_2 ligand in the earlier structure by the bridging dithiolene containing S1 and S2 in the present structure. The two simple bidentate bdt ligands have mean Mo–S bond lengths of 2.38 Å. This compares closely to the mean Mo–S length of 2.37 Å observed[16] for $Mo(bdt)_3$ and for the corresponding terminal dithiolene ligands in $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4$. The ligand planes are also tipped from their respective Mo–S–S planes by 29.4 and 21.5°, much like the corresponding bdt ligands in $Mo(bdt)_3$, which are tipped between 13 and 30°. The two "half-bridging" bdt ligands act as simple chelating ligands to one Mo, with slightly elongated Mo–S bonds (mean 2.429 Å) and with the addition of a longer bridging bond (mean 2.579 Å) crossing over to the other Mo atom. The ligand planes of these bdt's are also tipped with respect to the Mo–S–S planes of the Mo atoms to which they chelate, by 14.8 and 18.5°. The fifth bdt ligand has both sulfur atoms (S1 and S2) located in symmetrical bridging positions, with the mean of the four Mo–S distances being 2.506 Å. The ligand plane of this bdt ligand is inclined a slight 2.6° from the vector connecting the two Mo atoms. Rather short S–S distances are observed between S1 and S5 (2.73 Å) and between S2 and S3 (2.71 Å). These distances are significantly longer than an S–S single bond (~2.05 Å) but much shorter than the sum of the van der Waals radii for nonbonded sulfurs (3.7 Å). A similar short S–S interaction (2.74 Å) was observed between the bridging sulfurs from the dithiolenes in $Mo_2(S_2)[S_2C_2(C_6H_5)_2]_4$ and between thiolate sulfur donor atoms bound to a single Mo center.[17,18]

The coordination geometry of the seven sulfur atoms bonded to each Mo has been compared to typical 7-coordination polyhedra (capped octahedron, CO; capped trigonal prism, CTP; pentagonal bipyramid, PB) by the method of Dollase[19] as implemented in a computer program written by Drew.[20] This program calculates the root-mean-square deviation of the observed coordinates from the ideal coordination polyhedra. For Mo1 the root-mean-square deviations from CTP, CO, and PB are 0.126, 0.132, and 0.239 Å, respectively. Thus, the geometry about Mo1 can be described equally well as a slightly distorted CTP, with S6 capping a rectangular face, or as a slightly distorted CO, with S1 capping a triangular face. An even more useful description of the geometry is the 3:4:3 arrangement of four donor atoms (S1, S2, S3, S5) parallel to a plane of three donor atoms (S6, S9, S10). As shown by Drew,[21] this geometry typically gives root-mean-square fits to CTP and CO similar to those observed in this case. If the geometry about Mo2 is combined with that about Mo1, it seems that the best overall description of the structure is a 3:4:3 double-decker sandwich. This structure is interestingly related to a number of $(CpMo)_2$"S_4" structures discussed by Rakowski DuBois and co-workers,[22] wherein the outer sets of three donors in the 3:4:3 arrangement are provided by the Cp ligands and the inner four sulfurs are provided by any of several combinations of sulfido, 1,1-alkanedithiolato, and 1,2-alkene- or 1,2-alkanedithiolato ligands.

The present structure reveals the versatility of "dithiolene" type ligands, confirms the proclivity of Mo(V) complexes to be dinuclear, and establishes unequivocally the stoichiometric and structural nature of the additional product of reactions which form tris(dithiolene)molybdenum complexes.

Supplementary Material Available: Tables SI–SV, listing bond distances, bond angles, and anisotropic thermal parameters for $Mo_2(bdt)_5$ and bond distances and angles for the THF solvate (8 pages); a table of observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
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Isolation and Characterization of the Redox Pair $[Re_2H_5(PMe_3)_6](PF_6)_n$ (n = 1 or 2)

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The dirhenium octahydride complexes of general stoichiometry $Re_2H_8(PR_3)_4$[1,2] are the most hydrogen rich of the known neutral dirhenium polyhydrides.[3] For two of these derivatives (PR_3 = PPh_3 and PMe_2Ph), studies of their chemistry have included various aspects of their redox[4] and protonation[5] behavior, as well as their reactions with certain nucleophiles (nitrile and isocyanide ligands)[4,6] and with copper(I),[7] gold(I),[8] and tin(II)[9] reagents; the latter lead to mixed Cu–Re, Au–Re, and Sn–Re clusters. With our development of a convenient synthetic route to a much wider range of complexes of the type $Re_2H_8(PR_3)_4$ (PR_3 represents a

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monodentate phosphine or half of a bidentate phosphine),[10] we are now in a position to examine how the chemistry of these complexes is dependent upon the phosphine ligand itself. In this report we describe certain aspects of the chemistry of the trimethylphosphine derivative $Re_2H_8(PMe_3)_4$ (**1**), specifically its protonation behavior and its reactions with trimethylphosphine.

Experimental Section

Starting Materials. The dirhenium octahydride complex $Re_2H_8(PMe_3)_4$ was prepared from $Re_2Cl_4(PMe_3)_4$ by a literature method.[10] Trimethylphosphine was obtained from Strem Chemicals. All other reagents and solvents were obtained from commercial sources and used without further purification. Solvents were dried by using standard techniques and thoroughly deoxygenated prior to use by a nitrogen purge.

Reaction Procedures. All reactions were performed under a dry nitrogen atmosphere with the use of standard vacuum-line techniques.

A. Protonation of $Re_2H_8(PMe_3)_4$ To Form $[Re_2H_9(PMe_3)_4]BF_4$. A quantity of $Re_2H_8(PMe_3)_4$ (0.048 g, 0.070 mmol) was dissolved in CH_2Cl_2 (2 mL) at 0 °C, and this solution was then treated with a small volume (0.020 mL) of an 85% solution of HBF_4 in diethyl ether. The resulting mixture was stirred briefly, whereupon an immediate darkening of the solution was observed. Upon the addition of an excess of deoxygenated diethyl ether (25 mL), a rust orange solid was obtained. This was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.040 g (74%). Anal. Calcd for $C_{12}H_{45}BF_4P_4Re_2$: C, 18.65; H, 5.88. Found: C, 18.53; H, 5.88.

B. Reaction of $Re_2H_8(PMe_3)_4$ with PMe_3. (i) $[Re_2H_5(PMe_3)_6]PF_6$. A mixture of $Re_2H_8(PMe_3)_4$ (0.103 g, 0.150 mmol) and KPF_6 (0.035 g, 0.190 mmol) was dissolved in methanol (10 mL), and a small quantity of PMe_3 (0.06 mL) was added. The solution was stirred at room temperature for 7.5 h before 30 mL of deoxygenated H_2O was added. The resulting rusty orange precipitate was filtered off, washed with deoxygenated H_2O and diethyl ether, and dried under vacuum; yield 0.118 g (80%). Anal. Calcd for $C_{18}H_{59}F_6P_7Re_2$: C, 22.08; H, 6.09. Found: C, 22.27; H, 6.58.

(ii) $[Re_2H_5(PMe_3)_6](PF_6)_2$. A quantity of $Re_2H_8(PMe_3)_4$ (0.053 g, 0.077 mmol) was dissolved in 10 mL of methanol, and 0.035 mL of PMe_3 was added. The mixture was stirred at room temperature for 5.5 h and then exposed to the air. Upon the addition of 40 mL of H_2O, the solution turned bright purple and a small amount of an orange solid formed. This solid was filtered off, and KPF_6 (0.050 g) was added to the purple filtrate. The purple precipitate that formed was filtered off, washed with H_2O and diethyl ether, and dried under vacuum; yield 0.054 g (62%). Anal. Calcd for $C_{18}H_{59}F_{12}P_8Re_2$: C, 19.23; H, 5.30. Found: C, 19.65; H, 5.92. All attempts to obtain a different salt of this purple complex were unsuccessful. The following counterions were tried: $[BPh_4]^-$, $[Re_2Cl_8]^{2-}$, $[PtCl_4]^{2-}$, $[ReO_4]^-$, triflate, and $[WO_4]^{2-}$.

C. Redox Reaction of $[Re_2H_5(PMe_3)_6](PF_6)_n$ (n = 1 or 2). (i) Reaction of $[Re_2H_5(PMe_3)_6]PF_6$ with $NOPF_6$. A mixture of $[Re_2H_5(PMe_3)_6]PF_6$ (0.049 g, 0.050 mmol) and $NOPF_6$ (0.013 g, 0.074 mmol) was stirred in 10 mL of CH_2Cl_2 for 5 min. The resulting purple solution was filtered into an excess of diethyl ether. The purple precipitate that formed was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.019 g (34%). The solid was shown to be $[Re_2H_5(PMe_3)_6](PF_6)_2$ on the basis of its spectroscopic and electrochemical properties.

(ii) Reaction of $[Re_2H_5(PMe_3)_6](PF_6)_2$ with Cobaltocene. A solution of cobaltocene (0.011 g, 0.058 mmol) in acetone (5 mL) was added to a solution of $[Re_2H_5(PMe_3)_6](PF_6)_2$ (0.013 g, 0.012 mmol) in 5 mL of acetone. The solution color changed from purple to orange almost immediately. This mixture was stirred for 5–10 min and then filtered into an excess of diethyl ether. The resulting orange precipitate was filtered off, washed with diethyl ether, and vacuum-dried; yield 0.006 g (55%). The orange solid was shown to be $[Re_2H_5(PMe_3)_6]PF_6$ based upon its spectroscopic and electrochemical properties.

D. Deprotonation Reactions. (i) $[Re_2H_9(PMe_3)_4]BF_4$. A solution of $[Re_2H_9(PMe_3)_4]BF_4$ (0.024 g, 0.031 mmol) in 2 mL of acetone was treated with 0.025 mL of NEt_3, and the mixture was stirred for ca. 5 min. Upon the addition of 15 mL of deoxygenated H_2O, an orange precipitate formed. The precipitate was filtered off, washed with H_2O, and dried under vacuum; yield 0.010 g (48%). This product was identified as $Re_2H_8(PMe_3)_4$ on the basis of its spectroscopic and electrochemical properties.[10]

(ii) $[Re_2H_5(PMe_3)_6]PF_6$. Reactions of $[Re_2H_5(PMe_3)_6]PF_6$ with stoichiometry amounts of NEt_3 (in CH_2Cl_2 or acetone) or with KO-*t*-Bu (in THF) led to recovery of the starting complex $[Re_2H_5(PMe_3)_6]PF_6$. There was no evidence for the formation of $Re_2H_4(PMe_3)_6$.

(iii) $[Re_2H_5(PMe_3)_6](PF_6)_2$. The reactions of $[Re_2H_5(PMe_3)_6](PF_6)_2$ with KO-*t*-Bu in CH_2Cl_2 yielded unreacted starting material and/or the reduction product $[Re_2H_5(PMe_3)_6]PF_6$. As in the case of section D(ii), we found no evidence for the formation of the tetrahydrido complex $Re_2H_4(PMe_3)_6$.

Physical Measurements. IBM Instruments IR/32 and Perkin-Elmer 1800 FTIR spectrometers were used to record infrared spectra of compounds as Nujol mulls supported on KBr plates in the region 4800–400 cm^{-1}. Electronic absorption spectra were recorded on IBM Instruments 9420 UV-visible and Hewlett-Packard HP 8451 A spectrophotometers. Electrochemical measurements were carried out by the use of a Bioanalytical Systems Inc. Model CV-1A instrument on dichloromethane solutions that contained 0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBAH) as the supporting electrolyte. A Pt-bead working electrode and a Pt-wire auxiliary electrode were utilized. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$ were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions the ferrocenium/ferrocene couple is at $E_{1/2} = +0.47$ V vs Ag/AgCl. Conductivity measurements were performed on solutions of the samples at a concentration of ca. 1.0×10^{-3} M. Measurements were made with an Industrial Instruments Inc. Model RC-16B2 conductivity bridge. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-200 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent (δ +5.35 in CD_2Cl_2, δ +3.35 (CH_3) and δ +4.75 (OH) in CD_3OD). Phosphorus resonances were referenced externally to 85% H_3PO_4. X-Band ESR spectra of dichloromethane solutions were recorded at ca. −160 °C with the use of a Varian E-109 spectrometer.

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

Results and Discussion

(a) Protonation of $Re_2H_8(PMe_3)_4$ (1). The treatment of **1** with $HBF_4\cdot Et_2O$ in CH_2Cl_2 gives the monoprotonation product $[Re_2H_9(PMe_3)_4]BF_4$ (**2**) in reasonably high yield ($\simeq$75%). This reaction is reversed upon the treatment of **2** with triethylamine in acetone. The conversion of **1** to **2** is analogous to the protonation of $Re_2H_8(PPh_3)_4$ under similar conditions to afford $[Re_2H_9(PPh_3)_4]BF_4$.[5] The ^1H NMR spectrum of **2** (recorded in CD_2Cl_2) consists of a doublet at δ +1.81 ($^2J_{PH}$ = 10.0 Hz) due to the methyl protons of the PMe_3 and a pentet at δ −5.43 ($^2J_{PH}$ = 10.0 Hz) arising from the hydride ligands. While the $^{31}P\{^1H\}$ NMR spectrum (recorded in CD_2Cl_2) consists of a singlet at δ −20.42, selective decoupling of the methyl protons in the ^{31}P NMR spectrum gives a 10-line pattern ($^2J_{PH}$ = 8.6 Hz) in which the intensity ratio is very similar to the theoretical ratio for the coupling of the phosphorus nuclei to *nine* equivalent hydride ligands.[11]

The conductivity of a solution of the complex in acetone (ca. 1×10^{-3} M) corresponds to that of a 1:1 electrolyte ($\Lambda_m = 140$ Ω^{-1} cm^2 mol^{-1}). The IR spectrum (Nujol mull) supports the formulation of the complex because of a strong band at 1058 cm^{-1} due to the $[BF_4]^-$ anion. The IR spectrum also displays a broad feature of medium intensity at 1968 cm^{-1} assigned to a ν(Re–H) mode and a strong band at 960 cm^{-1} due to the PMe_3 ligands. The cyclic voltammogram (CV) of $[Re_2H_9(PMe_3)_4]BF_4$ in 0.1 M TBAH–CH_2Cl_2 shows well-defined irreversible redox processes at $E_{p,a}$ = +0.71 V and $E_{p,c}$ = −1.61 V vs Ag/AgCl. There are additional irreversible processes at $E_{p,a}$ = +0.88 + 1.18 and +1.30 V which are probably attributable to chemical products that result from the irreversible oxidation at +0.71 V. While this CV is similar to that of $[Re_2H_9(PPh_3)_4]BF_4$,[5] it is quite different from the related behavior of the parent complex,[10] thereby implying that a significant structural difference exists between these two complexes. Nonetheless, the close relationship between the two complexes is demonstrated by the ease of the interconversion between **1** and **2**.

(b) Reaction of $Re_2H_8(PMe_3)_4$ with Trimethylphosphine. While the conversion of **1** to its monoprotonated derivative resembles closely the conversion of the triphenylphosphine complex $Re_2H_8(PPh_3)_4$ to $[Re_2H_9(PPh_3)_4]BF_4$, these two octahydrides differ in their behavior toward an excess of the corresponding

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[10] Fanwick, P. E.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 395.

[11] The observed ratio of 1:12:39:85:126:126:85:39:13:1 compares closely with the theoretical ratio of 1:9:36:84:126:126:84:36:9:1.

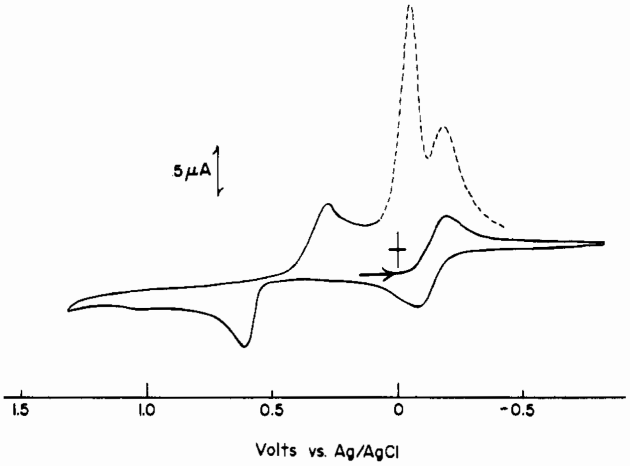


Figure 1. Single-scan cyclic voltammogram (scan rate 200 mV s^{-1}) of $[Re_2H_5(PMe_3)_6]PF_6$ (**3**) in 0.1 M TBAH–CH_2Cl_2. The oxidation at $E_{p,a}$ = +0.68 V vs Ag/AgCl has a coupled product wave at $E_{p,c}$ = +0.28 V. The second scan reveals an intense sharp wave at $E_{p,c}$ = –0.05 V which is presumably associated with the adsorption of a chemical product on the Pt electrode surface.

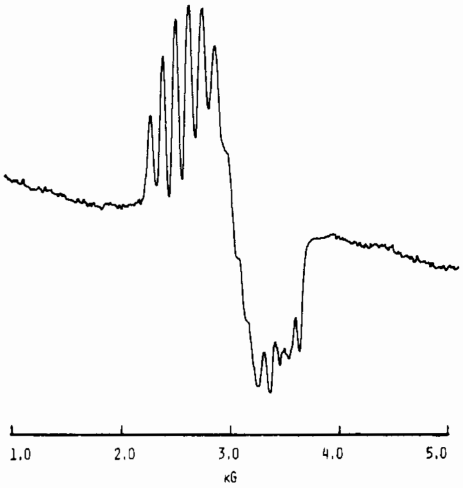


Figure 2. X-Band ESR spectrum of a solution of $[Re_2H_5(PMe_3)_6](PF_6)_2$ in dichloromethane at –160 °C.

parent phosphine. Whereas $Re_2H_8(PPh_3)_4$ does not appear to react further when stirred with a mixture of KPF_6 and excess PPh_3 in methanol, the reaction of **1** with PMe_3 affords two different products depending upon the reaction conditions used. In either case, the reagents are stirred in methanol at room temperature for 5–8 h. If KPF_6 is added at the beginning of the reaction, and the reagents are reacted under a nitrogen atmosphere, the addition of H_2O results in the precipitation of the orange salt $[Re_2H_5(PMe_3)_6]PF_6$ (**3**). If, however, the addition of the KPF_6 is delayed, and oxygen and H_2O are introduced into the system before the KPF_6 is added, the purple dicationic complex $[Re_2H_5(PMe_3)_6](PF_6)_2$ (**4**) is isolated.

Solutions of both complexes in 0.1 M TBAH–CH_2Cl_2 exhibit a reversible process at $E_{1/2}$ = –0.11 V and an irreversible oxidation at $E_{p,a}$ = +0.68 V vs Ag/AgCl in their CV's (Figure 1). As might be expected, the reversible process corresponds to an oxidation for **3** and a reduction for **4**. In view of the accessibility of the couple at $E_{1/2}$ = –0.11 V, it was anticipated that **3** and **4** could be interconverted quite easily with the appropriate choice of redox reagents. This was found to be the case. The orange complex $[Re_2H_5(PMe_3)_6]PF_6$ is readily oxidized to the purple complex $[Re_2H_5(PMe_3)_6](PF_6)_2$ by $NOPF_6$ in CH_2Cl_2, while the reduction of **4** with cobaltocene in acetone proceeds readily to yield **3**. The course of these reaction can be monitored quite conveniently by CV and ESR spectroscopy (vide infra).

The IR spectra (Nujol mull) of both **3** and **4** contain bands at ≃945 cm^{-1} for PMe_3 and at ≃845 cm^{-1} for $[PF_6]^-$. These spectra also display a band attributable to ν(Re–H) at 2006 (w) cm^{-1} and at 2015 (vw) cm^{-1} for **3** and **4**, respectively. Electronic absorption spectra were measured for these complexes on CH_2Cl_2 solutions. The orange complex **3** exhibits a band at λ_{max} = 450 nm (ϵ = 1200 M^{-1} cm^{-1}) with a shoulder at 550 nm. The purple complex **4**, on the other hand, shows bands at λ_{max} = 580 nm (ϵ = 5300 M^{-1} cm^{-1}) and 340 nm (ϵ = 1900 M^{-1} cm^{-1}). Conductivity measurements on 1 × 10^{-3} M solutions of the complexes in acetone confirm their mono- and dicationic nature. Complex **3** has Λ_m = 107 Ω^{-1} cm^2 mol^{-1}, while Λ_m = 200 Ω^{-1} cm^2 mol^{-1} for **4**. These values agree with their being 1:1 and 2:1 electrolytes, respectively.[12]

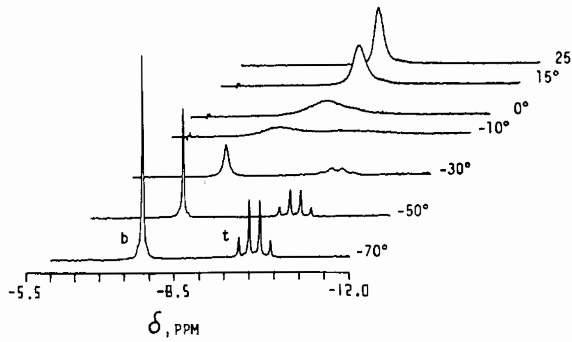
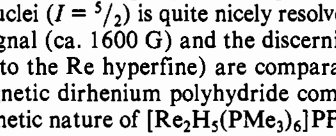


Figure 3. Variable-temperature ^1H NMR spectra of a solution of $[Re_2H_5(PMe_3)_6]PF_6$ in CD_3OD recorded in the hydride region.

Since **3** and **4** constitute a redox pair related by a one-electron transfer, complex **4** should be paramagnetic and contain one unpaired electron. The dicationic complex $[Re_2H_5(PMe_3)_6](PF_6)_2$ would then have a formal bond order of 2.5 if it is assumed that **3** adheres to the 18-electron rule and therefore has a Re–Re bond order of 3.0. The paramagnetic nature of **4** is reflected by its X-band ESR spectrum (measured in CH_2Cl_2 at –160 °C), which reveals a broad signal centered at 3040 G with g_{av} = 2.13 (Figure 2). The signal is fairly symmetrical, and the expected 11-line hyperfine pattern due to coupling of the unpaired electron to the two rhenium nuclei ($I = {}^5/_2$) is quite nicely resolved. The overall width of the signal (ca. 1600 G) and the discernible spacings of ≃120 G (due to the Re hyperfine) are comparable to those of other paramagnetic dirhenium polyhydride complexes.[4]

The diamagnetic nature of $[Re_2H_5(PMe_3)_6]PF_6$ is reflected in the extensive NMR spectral information it provided. The room-temperature ^1H NMR spectrum displays an apparent triplet[13] due to the methyl protons of the PMe_3 ligands at δ +1.71 in CD_2Cl_2 and at δ +1.77 in CD_3OD. The spectra also contain a broad singlet for the hydride ligands at δ –8.83 in CD_2Cl_2 and at δ –8.80 in CD_3OD. However, in both solvents the overall integration of the hydride region, relative to the methyl region, was lower than expected for the proposed stoichiometry. Therefore, further studies were necessary in order to determine the exact number of hydride ligands present.

Variable-temperature ^1H NMR spectroscopy (in CD_3OD) proved to be very informative. As the temperature is lowered (see Figure 3), the hydride resonance first broadens prior to coalescence near 5 °C, and then upon further cooling to –70 °C resolves into a singlet at δ –7.86 and a quartet at δ –10.10 ($^2J_{PH}$ = 42.0 Hz). Since only two resonances grow in, this complex can be assigned the symmetric structure I, in which there are three bridging hydrides and one terminal hydride located on each rhenium atom. This agrees well with the 3:2 relative intensity observed for these



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[12] Geary, W. J. *Coord. Chem. Ref.* **1971**, *7*, 81.

[13] Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley, New York, 1988; p 215.

two resonances. The singlet is assigned to the bridging hydrides, while the quartet arises from the terminal hydride ligands, each of which is split by the three phosphorus nuclei on the corresponding rhenium atom. This assignment is supported by comparison with the spectrum of the structurally characterized complex $[Re_2(\mu\text{-}H)_3H_2(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$,[6] which is very similar to that of **3** except that the terminal hydride resonance is seen as a triplet since, in this case, there are only two phosphine ligands bound to each rhenium center. A close resemblance is also seen with the ^1H NMR spectrum of $[Re_2(\mu\text{-}H)_3H_2(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]BF_4$,[14] although the latter complex shows two resonances for the bridging hydride ligands in its low temperature limit (−60 °C) in accord with the presence of inequivalent bridging Re–H bonds. Although these results support structure I, they do not of course unequivocally establish the actual number of hydride ligands present.

At room temperature, the $^{31}P\{^1H\}$ NMR spectrum displays a broad singlet at δ −31.3 in CD_2Cl_2 (δ −30.8 in CD_3OD) for the phosphorus atoms of the PMe_3 ligands and the expected septet near δ −143 for the $[PF_6]^-$ anion. Selective decoupling of the methyl protons of the PMe_3 ligands in the ^{31}P NMR spectrum gives a binomial sextet ($^2J_{PH}$ = 9.0 Hz), thereby confirming the presence of five hydride ligands. When a solution of **3** in CD_3OD is cooled to −40 °C the ^{31}P NMR spectrum splits into a doublet at δ −28.8 ($^2J_{PH}$ = 43.0 Hz). The splitting is comparable to that observed in the ^1H NMR spectrum for the terminal hydride resonance (vide supra). This doublet suggests that the phosphorus signal is split through coupling to only one adjacent hydride ligand. Therefore, I is further supported as being the correct structural formulation for this complex.

The reaction of **1** with PMe_3 that leads to the formation of $[Re_2H_5(PMe_3)_6]^+$ was also monitored by ^1H NMR spectroscopy. A sample of **1** was dissolved in CD_3OD, and an initial spectrum was recorded [δ −7.49 (pentet, Re–*H*), δ +1.66 (doublet, C*H*$_3$ of PMe_3)]. Four equivalents of PMe_3 was then injected into the NMR solution, and the progress of the reaction was monitored over time. Within 5 min the formation of the $[Re_2H_5(PMe_3)_6]^+$ cation had already begun, and within 4 h no octahydride remained; approximately 2 equiv of PMe_3 remained when the reaction was complete. An orange solid was isolated from the NMR solution following the addition of KPF_6 and H_2O, and the identity of this product as $[Re_2H_5(PMe_3)_6]PF_6$ (**3**) was confirmed by CV.

(c) Concluding Remarks. The reactions of the dirhenium octahydrides $Re_2H_8(PR_3)_4$ with additional phosphine can be anticipated to proceed as shown in eq 1. The first step has been

$$Re_2H_8(PR_3)_4 \xrightarrow[-H_2]{+PR_3} Re_2H_6(PR_3)_5 \xrightarrow[-H_2]{+PR_3} Re_2H_4(PR_3)_6 \qquad (1)$$

shown to occur in the case of $PR_3 = PMe_2Ph$,[15,16] and the resulting complex has been structurally characterized.[15] The second step has only been reported in the case of $Re_2H_8(PMe_2Ph)_4$ reacting with the phosphite ligand $P(OCH_2)_3CEt$, a reaction that affords $Re_2H_4(PMe_2Ph)_4[P(OCH_2)_3CEt]_2$.[14] This complex is readily converted into its conjugate acid $[Re_2H_5(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]^+$ upon treatment with $HBF_4{\cdot}Et_2O$.[14] One possibility is that in the reaction of $Re_2H_8(PMe_3)_4$ with PMe_3, the dirhenium tetrahydride $Re_2H_4(PMe_3)_6$ is formed but it is such a potent base (more so even than Caulton's complex)[14] that it is very rapidly protonated by the methanol solvent to form the weak acid $[Re_2H_5(PMe_3)_6]^+$, isolable as its $[PF_6]^-$ salt **3**. In the NMR experiment described in section b, we found no spectroscopic evidence for the presence of significant amounts of $Re_2H_4(PMe_3)_6$.[17] All attempts to deprotonate **3** and its one-electron-oxidized congener **4** failed (see Experimental Section). The dirhenium pentahydride complexes **3** and **4** constitute rare example of this class of complex; the complexes $[Re_2H_5(PMe_2Ph)_4[P(OCH_2)_3CEt]_2]BF_4$[14] and $[Re_2H_5(PPh_3)_4(CN\text{-}t\text{-}Bu)_2]PF_6$[4,6] are the only examples to have been reported previously.

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(17) Note added in proof. We have now succeeded in isolating $Re_2H_6(PMe_3)_5$ from the reaction of $Re_2H_8(PMe_3)_4$ with an excess of PMe_3 in benzene; H_2 is the byproduct of this reaction. When $Re_2H_6(PMe_3)_5$ is reacted with PMe_3 in CH_3OH, then $[Re_2H_5(PMe_3)_6]^+$ is the final product (by ^1H NMR spectroscopy). This reaction proceeds through an intermediate [δ −6.47 (sextet, Re–*H*, $J_{PH} \simeq 7.6$ Hz)], which could be the cation $[Re_2H_5(PMe_3)_5]^+$. This intermediate is captured by the excess PMe_3 present and converted into $[Re_2H_5(PMe_3)_6]^+$. Further mechanistic studies are under way.

Additions and Corrections

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Hyunkyu Kang, Shuncheng Liu, Shahid N. Shaikh, Terrence Nicholson, and Jon Zubieta*: Synthesis and Structural Investigation of Polyoxomolybdate Coordination Compounds Displaying a Tetranuclear Core. Crystal and Molecular Structures of $[n\text{-}Bu_4N]_2[Mo_4O_{10}(OMe)_4X_2]$ (X = –OMe, –Cl) and Their Relationship to the Catecholate Derivative $[n\text{-}Bu_4N]_2[Mo_4O_{10}(OMe)_2(OC_6H_4O)_2]$ and to the Diazenido Complexes of the *o*-Aminophenolate and the Naphthalene-2,3-diolate Derivatives $[n\text{-}Bu_4N]_2[Mo_4O_6(OMe)_2(HNC_6H_4O)_2(NNC_6H_5)_4]$ and $[n\text{-}Bu_4N]_2[Mo_4O_6(OMe)_2(C_{10}H_6O_2)_2(NNC_6H_5)_4]$. Comparison to the Structure of a Binuclear Complex with the $[Mo_2(OMe)_2(NNC_6H_5)_4]^{2+}$ Core, $[Mo_2(OMe)_2(H_2NC_6H_4O)_2(NNC_6H_5)_4]$.

Pages 920–933. The compound $[n\text{-}Bu_4N]_2$[III] and the previously reported compound $[n\text{-}Bu_4N]_2[Mo_4O_8(OEt)_4Cl_4]$ are incorrectly formulated as mixed-valence Mo(V)/Mo(VI) species. As previously indicated by Lincoln and Koch,[1] the latter complex is in fact the Mo(V) species $[n\text{-}Bu_4N]_2[Mo_4O_8(OEt)_2(HOEt)_2Cl_4]$, with coordinated alcohol, as well as alkoxy groups. Comparison of the Mo2–O6 distance for *III* to the corresponding Mo1–O3 distance for I (2.232 (5) Å vs 1.915 (2) Å) clearly establishes the former as an alcohol oxygen donor, rather than an alkoxy donor as previously suggested by us. The complexes of the type $[R_4N]_2[Mo_4O_8(OR)_2(HOR)_2Cl_4]$ exhibit the $[Mo_4O_8(OR)_2]^{2+}$ core with peripherally coordinated Cl^- and HOR ligands, not the $[Mo_4O_8(OR)_2]^{4+}$ core with Cl^- and OR^- ligands as originally formulated.

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—Jon Zubieta