Dirhenium Polyhydrides Containing Bridging 2-Mercaptoquinoline Ligands

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The dirhenium polyhydride complex $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4](BF_4)_2$ (**1**), where mq represents the 2-mercaptoquinoline ligand, can be deprotonated in two steps to afford the diamagnetic complexes $[Re_2H_5(\mu\text{-mq})_2(PPh_3)_4]BF_4$ (**2**) and $Re_2H_4(\mu\text{-mq})_2(PPh_3)_4$ (**3**) through the use of the bases PMe_3 and DBU, respectively. The treatment of **2** and **3** with $HBF_4 \cdot Et_2O$ regenerates **1**. The basic structure of the $[Re_2(\mu\text{-mq})_2(PPh_3)_4]$ unit is retained throughout these deprotonations/protonations as demonstrated by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. The neutral tetrahydrido complex **3** undergoes a two-electron oxidation when treated with the oxidants $[(\eta^5\text{-}C_5H_5)_2Fe]BF_4$ and $[(\eta^5\text{-}C_5H_5)_2\text{-}Fe]PF_6$ to afford the salts $[Re_2H_4(\mu\text{-mq})_2(PPh_3)_4](BF_4)_2$ (**4a**) and $[Re_2H_4(\mu\text{-mq})_2(PPh_3)_4](PF_6)_2$ (**4b**), respectively. The $[Re_2H_4(\mu\text{-mq})_2(PPh_3)_4]^{2+}/Re_2H_4(\mu\text{-mq})_2(PPh_3)_4$ couple has an $E_{1/2}$ value of -0.47 V vs Ag/AgCl as measured by the cyclic voltammetric technique on solutions of **3** and **4** in 0.1 M Bu_4NPF_6/CH_2Cl_2. The chemical reversibility of this process has been confirmed by the use of $(\eta^5\text{-}C_5H_5)_2Co$ to reduce **4a** back to **3**. An X-ray crystal structure on a salt of the $[Re_2H_4(\mu\text{-mq})_2(PPh_3)_4]^{2+}$ cation, established that this complex is very similar structurally to **1** (see *J. Am. Chem. Soc.*, **1995**, *117*, 9715). The most important structural differences are (1) the different numbers of hydrido ligands present and (2) the presence of a Re−Re single bond in **4a** (the Re−Re distance is 3.000(1) Å compared to 3.9034(8) Å in $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4]^{2+}$). Crystal data for $[Re_2H_4(\mu\text{-mq})_2(PPh_3)_4]\text{-}(ReO_4)_{1.18}(BF_4)_{0.82}\cdot3CH_2Cl_2$ at 203 K: monoclinic space group $P2_1/n$ (No. 14) with $a = 14.716(4)$ Å, $b = 43.908(13)$ Å, $c = 14.860(3)$ Å, $\beta = 110.164(19)°$, $V = 9013(4)$ Å^3, $Z = 4$. The structure was refined to $R = 0.071$ ($R_w = 0.159$) for 14128 data ($F_o^2 > 2\sigma(F_o^2)$).

Introduction

A large body of data now exists on dirhenium *polyhydride* complexes, a class of compounds which display a fascinating array of structures and reactivities.[1−25] In these systems, the bonding in the dinuclear units involves at least one Re−H−Re bridging unit. A common reaction pathway which accesses many of these dinuclear species involves the thermal or photochemical loss of H_2 from a mononuclear rhenium polyhydride complex to afford an electronic and coordinatively unsaturated species which subsequently dimerizes. A recent example is the facile thermal loss of H_2 from $ReH_5(triphos)$ to produce the dinuclear complex $Re_2(\mu\text{-H})_3H(triphos)_2$, where triphos $= CH_3C(CH_2PPh_2)_3$.[25] A new entry into dirhenium polyhydride chemistry has been provided by our finding[26] that when the mononuclear Re(V) polyhydride $ReH_4(mq)(PPh_3)_2$ (mq is the monoanion of 2-mercaptoquinoline) is treated with the electrophiles H^+ and Ph_3C^+, abstraction of H^- to afford the 16-electron $[ReH_3(mq)(PPh_3)_2]^+$ cation is followed by its dimerization to produce $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4]^{2+}$. This reaction course ensues in the absence of a complexing reagent, such as an alkyne, which can stabilize the mononuclear cation.[26] We have now examined the acid/base chemistry of $[Re_2H_6(\mu\text{-mq})_2\text{-}(PPh_3)_4]^{2+}$, a study which has provided access to other polyhydride species that contain the $\{Re_2(\mu\text{-mq})_2\}$ unit. These compounds differ from other dirhenium polyhydrides[1−25] in that they possess no Re−H−Re bridging bonds. A report on this chemistry and the structure of one of these new compounds is provided herein.

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Experimental Section

Starting Materials and Reaction Procedures. The compound $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4](BF_4)_2$ (**1**) was prepared as described in the literature except that $HBF_4 \cdot Et_2O$ was used in place of $HPF_6(aq)$.[26] The compounds $[(\eta^5\text{-}C_5H_5)_2Fe]BF_4$ and $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ were prepared by the literature method.[27] The following compounds were obtained from Aldrich Chemical Co.: 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU); $HBF_4 \cdot Et_2O$; $(\eta^5\text{-}C_5H_5)_2Co$. Trimethylphosphine was purchased from Strem Chemicals Inc. All liquid reagents and solvents were deoxygenated by purging with dinitrogen prior to use, and all reactions, unless otherwise noted, were performed under an atmosphere of dry dinitrogen.

Synthesis of $[Re_2H_5(\mu\text{-mq})_2(PPh_3)_4]BF_4$ (2). A mixture of trimethylphosphine (0.027 mL, 0.310 mmol), $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4](BF_4)_2$ (0.150 g, 0.078 mmol), and THF (10 mL) was stirred for 24 h. During this time, a red-brown solution formed and a similarly colored solid precipitated from the solution. The precipitate was collected via filtration, washed with diethyl ether, and dried under vacuum; yield 0.118 g (82%). Anal. Calcd for $C_{90}H_{85}BF_4N_2O_4P_4Re_2S_2$: C, 56.72; H, 4.49 (i.e. $[Re_2H_5(\mu\text{-mq})_2(PPh_3)_4]BF_4 \cdot 4H_2O$). Found: C, 55.88; H, 4.41. This complex displayed a broad, fairly intense $\nu(O-H)$ band at 3425 cm^{-1} in its IR spectrum (KBr pellet).

Synthesis of $Re_2H_4(\mu\text{-mq})_2(PPh_3)_4$ (3). A mixture of $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4](BF_4)_2$ (0.107 g, 0.056 mmol) and THF (7 mL) was treated with DBU (0.033 mL, 0.221 mmol) and allowed to stir for 3 h, whereupon a purple solution formed. The contents of the reaction vessel were filtered, and the resulting filtrate was layered with diethyl ether, which led to the slow formation of a purple crystalline solid. The solid was collected by filtration, washed with diethyl ether, and dried under vacuum; yield 0.089 g (91%). Anal. Calcd for $C_{90}H_{76}N_2P_4Re_2S_2$: C, 61.91; H, 4.39. Found: C, 61.03; H, 4.82.

An alternative route to $Re_2H_4(\mu\text{-mq})_2(PPh_3)_4$ involves the use of $[Re_2H_5(\mu\text{-mq})_2(PPh_3)_4]BF_4$ in place of $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4](BF_4)_2$. The reaction conditions and procedure were otherwise very similar; yield 85%.

Synthesis of $[Re_2H_4(\mu\text{-mq})_2(PPh_3)_4](BF_4)_2$ (4a). A mixture of $Re_2H_4(\mu\text{-mq})_2(PPh_3)_4$ (0.075 g, 0.043 mmol), $[(\eta^5\text{-}C_5H_5)_2Fe]BF_4$ (0.024 g, 0.088 mmol), and THF (10 mL) was stirred for 45 min, during which a yellow solid precipitated. A quantity of diethyl ether (15 mL) was added to the reaction mixture, which was stirred for a further 5 min. The yellow-green solid was collected by filtration, washed with diethyl ether, and dried under vacuum; yield 0.073 g (88%). Anal. Calcd for $C_{90}H_{82}B_2F_8N_2O_3P_4Re_2S_2$ (i.e. $[Re_2H_4(\mu\text{-mq})_2(PPh_3)_4](BF_4)_2 \cdot 3H_2O$): C, 54.77; H, 4.19. Found: C, 54.67; H, 4.14. This complex displayed a broad, fairly intense $\nu(O-H)$ band at 3420 cm^{-1} in its IR spectrum (KBr pellet).

When a quantity of complex **4a** (0.094 g, 0.049 mmol) was treated with cobaltocene (0.019 g, 0.100 mmol) in 5 mL of THF and the mixture stirred, conversion to the neutral purple complex **3** occurred; yield 0.067 g (78%).

Synthesis of $[Re_2H_4(\mu\text{-mq})_2(PPh_3)_4](PF_6)_2$ (4b). A procedure similar to that reported for **4a**, but with the use of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in place of $[(\eta^5\text{-}C_5H_5)_2Fe]BF_4$, afforded the yellow-green title complex **4b**; yield 96%. Anal. Calcd for $C_{90}H_{76}F_{12}N_2P_6Re_2S_2$: C, 53.09; H, 3.76. Found: C, 52.74; H, 3.99.

Protonation Reactions of 2 and 3. Both complexes were reconverted to $[Re_2H_6(\mu\text{-mq})_2(PPh_3)_4](BF_4)_2$ when treated with $HBF_4 \cdot Et_2O$.

(a) An excess of $HBF_4 \cdot Et_2O$ (0.15 mL) was added to a solution of **2** (0.055 g, 0.030 mmol) in dichloromethane (5 mL). The mixture was stirred for 10 min and then treated with an excess of diethyl ether (30 mL). A yellow precipitate of **1** formed and was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.042 g (73%).

(b) A procedure similar to (a) was used to convert **3** to **1**, but ^{31}P-$\{^1H\}$ NMR spectroscopy showed the product to be contaminated with appreciable amounts of **4a** (i.e. $[Re_2H_4(\mu\text{-mq})_2(PPh_3)_4](BF_4)_2$); total yield (**1** + **4a**) 65%.

X-ray Crystallography. Single crystals of composition $[Re_2H_4(\mu\text{-mq})_2(PPh_3)_4](ReO_4)_{1.18}(BF_4)_{0.82} \cdot 3CH_2Cl_2$ suitable for X-ray diffraction analysis were grown from a solution of complex **4a** in a CH_2Cl_2/C_2H_5-

$OC(O)CH_3$ (2/1) solvent mixture by the slow evaporation of the solvents at 25 °C under a nitrogen atmosphere. An orange platelike crystal having approximate dimensions $0.35 \times 0.23 \times 0.13$ mm was mounted on a glass fiber in a random orientation. The data collection was performed on an Enraf-Nonius CAD4 computer-controlled diffractometer with graphite-monochromatized Mo Kα radiation at 203 ± 1 K. The cell contents were based on 25 reflections obtained in the range $17° < \theta < 21°$ measured by the computer-controlled diagonal-slit method of centering. Three standard reflections were measured after every 5000 s of beam time during data collection to monitor the crystal stability. Calculations were performed on VAX computers. The structure was solved by using the Enraf-Nonius structure determination package (MolEN) and was refined using the SHELXL-93 program.[28] Lorentz and polarization corrections were applied to the data set. An empirical absorption correction was also applied,[29] but no correction for extinction was made.

The compound crystallized in the monoclinic crystal system. The space group of $P2_1/n$ was determined on the basis of systematic absences observed on the data set. The structure was solved by the use of the Patterson heavy-atom method to reveal the positions of the Re atoms. The remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. During the course of the structural analysis, the two $[BF_4]^-$ anions were found to be disordered with two $[ReO_4]^-$ anions which had formed during the slow crystal-growing procedure. This disordered model was included in the analysis, and the two anionic sites were finally refined to occupancies of 0.404-(5) and 0.596(5) for $[B(3)F_4]^-$ and $[Re(3)O_4]^-$ and of 0.413(6) and 0.587(6) for $[B(4)F_4]^-$ and $[Re(4)O_4]^-$, respectively. Three molecules of CH_2Cl_2 from the crystallization solvents were found to be present in the asymmetric unit. They were also included in the analysis and refined satisfactorily. All non-hydrogen atoms in this structure were refined with anisotropic thermal parameters, and corrections for anomalous scattering were applied to these atoms.[30] The positions of the hydride ligands were calculated by using the energy-minimizing program HYDEX,[31] and the positions of the hydrogen atoms on all organic groups were calculated by the use of the idealized geometries with C–H = 0.95 Å and $U = 1.3U_{eq}(C)$. They were added to the structure factor calculations, but their positions were not refined. The structure was refined by full-matrix least-squares calculations where the function minimized was $\sum w(F_o^2 - F_c^2)^2$ and the weighting factor w is defined as $w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 718.55P]$, where $P = (F_o^2 + 2F_c^2)/3$. The final residuals for the structure determination were $R = 0.071$ and R_w $(=[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}) = 0.159$ with GOF $= 1.19$. The largest remaining peak in the final difference Fourier map was 3.67 e/Å^3, the magnitude of which probably reflects the relatively poor quality of the crystal. The minimum negative peak was at -2.71 e/Å^3.

Physical Measurements. A Perkin-Elmer 1800 FTIR spectrometer was used to record the IR spectra of the compounds as mineral oil (Nujol) mulls or KBr pellets. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions, $E_{1/2} = +0.47$ vs Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were performed with a BAS Inc. Model CV-27 instrument in conjunction with a BAS Model RXY recorder. ^1H, $^{31}P\{^1H\}$, and ^{31}P NMR spectra were obtained with a Varian Gemini XL-200A spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuterated solvent, while phosphorus resonances were referenced externally to a sample of 85% H_3PO_4. Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

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Scheme 1. Reaction Chemistry of
[Re$_2$H$_6$(μ-mq)$_2$(PPh$_3$)$_4$](BF$_4$)$_2$ (**1**)
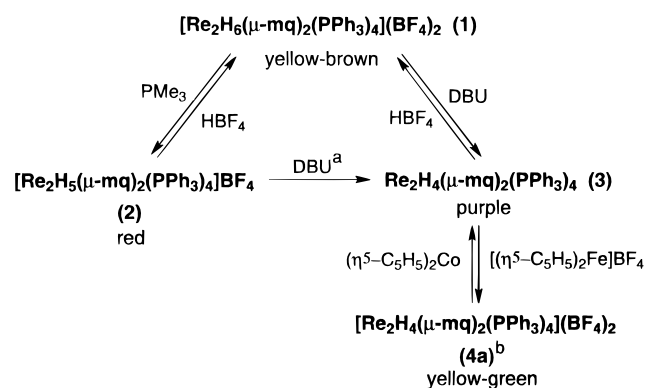
^{a} DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene. ^{b} The analogous [PF$_6$]$^-$ salt (**4b**) is formed when **3** is reacted with [(η^5-C$_5$H$_5$)$_2$Fe]PF$_6$.

Results and Discussion
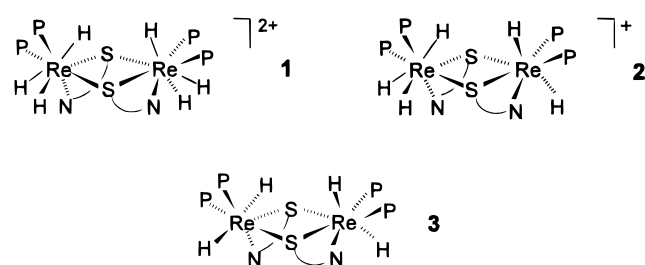
The reactions of the eight-coordinate rhenium(V) polyhydride complex ReH$_4$(mq)(PPh$_3$)$_2$[32] with the electrophiles H$^+$ and Ph$_3$C$^+$ result in the loss of H$^-$ and the dimerization of the 16-electron fragment [ReH$_3$(mq)(PPh$_3$)$_2$]$^+$ to produce stable salts of the [Re$_2$H$_6$(μ-mq)$_2$(PPh$_3$)$_4$]$^{2+}$ cation.[26] The complex [Re$_2$H$_6$-(μ-mq)$_2$(PPh$_3$)$_4$](BF$_4$)$_2$ (**1**) does not react with alkynes; this demonstrates the stability of the Re$_2$(μ-mq)$_2$ unit toward cleavage and the formation of the same alkylidyne complexes which are generated when the putative species {[ReH$_3$(mq)-(PPh$_3$)$_2$]$^+$} is produced *in the presence of alkynes*. Likewise, we find that the reactions of **1** with the bases PMe$_3$ and DBU do not give mononuclear [ReH$_3$(mq)(L)(PPh$_3$)$_2$]BF$_4$ (L = PMe$_3$, DBU). Instead, we observe a combination of deprotonation and redox reactions as shown in Scheme 1.

Our initial attempts to cleave **1** into mononuclear species were carried out in the presence of PMe$_3$. Under these conditions, the red-brown, singly deprotonated product [Re$_2$H$_5$(μ-mq)$_2$-(PPh$_3$)$_4$]BF$_4$ (**2**) was obtained in high yield. This complex, which behaves as a 1:1 electrolyte in acetonitrile (Λ_m = 171 Ω^{-1} cm^2 mol^{-1} for c_m = 1.0 × 10^{-3} M), can be deprotonated further by DBU to produce the neutral tetrahydrido complex Re$_2$H$_4$(μ-mq)$_2$(PPh$_3$)$_4$ (**3**) in essentially quantitative yield. Complex **3** can also be accessed by treating **1** with DBU.

Complex **3** is readily oxidized to the stable dicationic species [Re$_2$H$_4$(μ-mq)$_2$(PPh$_3$)$_4$]$^{2+}$, isolable as both its [BF$_4$]$^-$ salt **4a** and [PF$_6$]$^-$ salt **4b**, in the presence of [(η^5-C$_5$H$_5$)$_2$Fe]BF$_4$ and [(η^5-C$_5$H$_5$)$_2$Fe]PF$_6$, respectively. Solutions of these complexes in acetonitrile (c_m = 1.0 × 10^{-3} M) had conductivities in accord with 1:2 electrolyte behavior (Λ_m = 240 and 262 Ω^{-1} cm^2 mol^{-1} for **4a** and **4b**, respectively). The reversibility of the reaction **3** $\rightleftarrows$ **4** was demonstrated by the reduction of **4a** to **3** in the presence of 2 equiv of cobaltocene.

The protonation of **2** and **3** occurs upon their treatment with HBF$_4$·Et$_2$O to regenerate **1** (Scheme 1). This reaction proceeds cleanly in the case of **2**, but the conversion of **3** to **1** is complicated by the competing oxidation of **3** to **4a** due to the presence of small amounts of oxidants in the reaction medium. The oxidant appears to be adventitious O$_2$ and not H$^+$, since the yield of **1** increases relative to that of **4a** as the reaction mixture becomes more thoroughly deoxygenated. Under our reaction conditions, the lowest yield of **4a** was obtained in the case of a **1**:**4a** product ratio of 5:1, but we were unable to obtain **1** free from contamination by **4a** when using this protonation reaction.

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Chart 1. Representation of the Structural Relationships among **1**–**3**

The pentahydridodirhenium complex **2** displays an IR spectrum with an intense and characteristic ν(B–F) mode for the [BF$_4$]$^-$ anions at 1058 cm^{-1} and weak bands at 1966 and 1944 cm^{-1}, which are assigned to ν(Re–H). A cyclic voltammogram of a solution of **2** in 0.1 M TBAH–CH$_2$Cl$_2$ shows an irreversible oxidation at $E_{p,a} \approx$ +1.20 V, a couple at $E_{1/2}$ = +0.15 V, which corresponds to an oxidation of the bulk complex (ΔE_p (=$E_{p,a} - E_{p,c}$) = 100 mV), and a further coupled process which is characterized by $E_{p,c}$ = −0.55 V and $E_{p,a} \approx$ −0.40 V ($i_{p,c} > i_{p,a}$) vs Ag/AgCl.

The NMR spectral properties of **2** (recorded in CDCl$_3$) are quite complicated. The relatively low symmetry of this complex is reflected by the ^{31}P{^{1}H} NMR spectrum, which displays four distinct resonances of approximately equal intensity, two as broad singlets at δ +51.3 and +30.4 and two as doublets at δ +36.0 and +29.5 ($J_{P-P'}$ = 11.0 Hz). The ^{1}H NMR spectrum consists of three distinct Re–H resonances. There are doublets of doublets at δ −6.35 (J_{P-H} = 64 Hz, $J_{P'-H}$ = 21 Hz) and δ −1.93 (J_{P-H} = 60 Hz, $J_{P'-H}$ = 15 Hz), which are assigned to the two magnetically inequivalent hydrido ligands at the rhenium center that has been deprotonated, and a broad triplet (relative intensity 3) centered at δ −0.67, which is associated with the three hydrido ligands that are bound to the other rhenium atom. The magnetic equivalence of these three hydrides in the NMR spectrum implies the occurrence of a fluxional process. This was confirmed by recording the ^{1}H NMR spectrum of **2** in CD$_2$-Cl$_2$ over the temperature range +20 to −80 °C. Under these conditions, the two doublets of doublets remained unchanged but the triplet at δ −0.67 broadened, then collapsed as the temperature was lowered (coalescence temperature ca. −30 °C), and by the low temperature limit of −80 °C had been replaced by a very broad doublet at δ ca. −4.0 and another broad resonance at δ ca. +2.7 possessing relative intensities of ca. 1:2. Over this same temperature range, the ^{31}P{^{1}H} NMR spectrum (in CD$_2$Cl$_2$) changed very little except for a small downfield shift of the resonances at δ +51.3 and +36.0, so the fluxional process must involve only motion of the three hydrido ligands at the saturated rhenium center. The low-temperature ^{1}H NMR spectrum associated with the rhenium center that contains these three hydrido ligands resembles that reported previously[26] for the fluxional species [Re$_2$H$_6$(μ-mq)$_2$(PPh$_3$)$_4$]$^{2+}$ (**1**), *in which the halves of the dication are equivalent*. The ^{31}P{^{1}H} spectrum of **1** shows two separate resonances (doublets), while the ^{1}H NMR spectrum at room temperature has a broad feature at δ ca. +0.9 for the six hydrido ligands, which collapses when the temperature is lowered and splits out into two broad multiplets at δ ca. −2.35 and ca. +2.1 (intensity ratio 1:2) by −80 °C. Accordingly, we can confidently conclude that **2** is similar structurally to **1** but with a 3:2 distribution of terminal hydrido ligands (rather than 3:3 in the case of **1**). This structure change is represented in Chart 1.

As was mentioned previously, the purple neutral tetrahydrido complex **3**, which is the product of the double deprotonation of **1**, is readily oxidized to the yellow dicationic species **4**, which
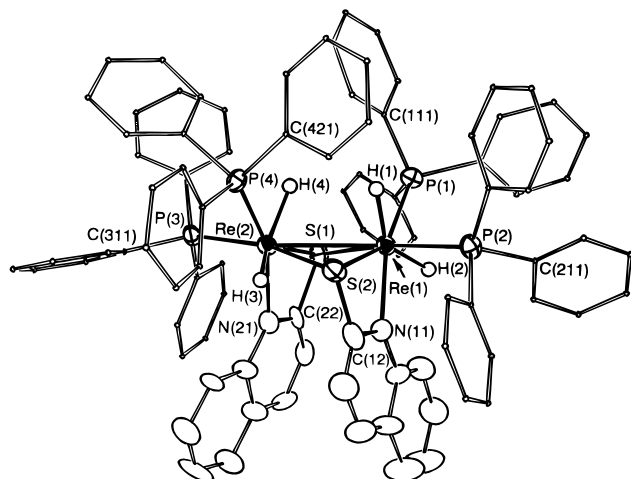
Figure 1. ORTEP[33] representation of the structure of the dirhenium cation [Re₂H₄(μ-mq)₂(PPh₃)₄]²⁺ present in complex **4a**. The thermal ellipsoids are drawn at the 50% probability level except for those of the hydrido ligands and the phenyl group atoms of the PPh₃ ligands, which are circles of arbitrary radius.

is isolable as its [BF₄]⁻ and [PF₆]⁻ salts **4a** and **4b**. Since the properties of **4a** and **4b** are essentially identical, except for the spectral changes associated with the different anions, only the properties of **4a** will be discussed. Both **3** and **4a** are diamagnetic and show identical cyclic voltammograms. Solutions of **3** and **4a** in 0.1 M TBAH−CH₂Cl₂ show a reversible one-electron oxidation at $E_{1/2}(ox) = +1.27$ V vs Ag/AgCl, with $\Delta E_p = 90$ mV, and a reversible two-electron process at $E_{1/2} = -0.47$ V vs Ag/AgCl, with $\Delta E_p = 120$ mV. The ease of oxidizing **3** to **4a** is reflected by the very low value for $E_{p,a} = -0.41$ V.

The IR spectrum of **3** shows the absence of [BF₄]⁻ and reveals a weak, broad ν(Re−H) mode at ca. 1960 cm⁻¹. In the case of **4a**, the ν(B−F) mode of [BF₄]⁻ appears at 1060 cm⁻¹ while a weak ν(Re−H) mode is located at 2012 cm⁻¹. The ¹H NMR spectra of **3** (recorded in CDCl₃) shows broad Re−*H* resonances at δ −6.25 and −2.88 which have the appearance of broad doublets (J_{P-H} ca. 63 Hz), although in reality they are probably unresolved doublets of doublets. The ³¹P{¹H} NMR spectrum of **3** (recorded in CDCl₃) consists of broad singlets at δ +52.3 and +30.3. These spectral features are in accord with the structure for **3** as shown in Chart 1, in which there is a symmetrical 2:2 distribution of terminal hydrido ligands. This is further supported by the ¹H and ³¹P{¹H} NMR spectra of **4a** (recorded in CDCl₃), which show doublets of doublets for the Re−*H* resonances at δ −5.39 ($J_{P-H} = 55$ Hz, $J_{P'-H} = 23$ Hz) and δ +2.26 ($J_{P-H} = 54$ Hz, $J_{P'-H} = 25$ Hz) and doublets in the ³¹P{¹H} NMR spectrum at δ +21.9 and +15.7 ($J_{P-P'} = 10.5$ Hz). The similarities between the NMR spectra and cyclic voltammograms of **3** and **4a** (and **4b**) imply a very close structural relationship; consequently, the two-electron redox process does not involve a major structural rearrangement. The structure for **4a**, and by implication that of **3**, has been confirmed by a single-crystal X-ray structure determination on a crystal of composition [Re₂H₄(μ-mq)₂(PPh₃)₄](ReO₄)₁.₁₈(BF₄)₀.₈₂·3CH₂-Cl₂, which was obtained from a solution of **4a** in a CH₂Cl₂/ethyl acetate (2/1) solvent mixture.

The nature of the anions in the crystal of **4a** was confirmed by the IR spectrum of the batch of crystals from which the single crystal was selected; bands at 1054 (s) and 906 (m-s) cm⁻¹ are assigned to the ν(B−F) and ν(Re−O) modes of the [BF₄]⁻ and [ReO₄]⁻ anions, respectively. The proportion of [BF₄]⁻ to [ReO₄]⁻ (0.82:1.18) was established by the successful refinement of the structure, with the constraint that the anion

Table 1. Crystallographic Data for [Re₂H₄(μ-mq)₂(PPh₃)₄](ReO₄)₁.₁₈(BF₄)₀.₈₂·3CH₂Cl₂ (**4a**)

empirical formula	Re₃.₁₈Cl₆S₂P₄F₃.₂₈O₄.₇₂N₂C₉₃B₀.₈₂H₈₂
fw	2367.24
space group	$P2_1/n$ (No. 14)
a, Å	14.716(4)
b, Å	43.908(13)
c, Å	14.860(3)
β, deg	110.164(19)
V, Å³	9013(4)
Z	4
T, K	203
λ(Mo Kα), Å	0.710 73
ρ_{calc}, g cm⁻³	1.745
μ(Mo Kα), cm⁻¹	57.12
transm coeff: max, min	0.46, 0.31
R^a	0.071
$R_w{}^b$	0.159
GOF	1.194

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$; $w = 1/[\sigma^2(F_o{}^2) + (0.0001P)^2 + 718.55P]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$.

Table 2. Selected Intramolecular Bond Distances (Å) and Angles (deg) for the Dirhenium Cation of [Re₂H₄(mq)₂(PPh₃)₄](ReO₄)₁.₁₈(BF₄)₀.₈₂·3CH₂Cl₂ (**4a**)^a

Distances			
Re(1)−S(1)	2.394(5)	Re(2)−S(2)	2.374(6)
Re(1)−S(2)	2.454(6)	Re(2)−S(1)	2.449(6)
Re(1)−P(1)	2.422(6)	Re(2)−P(3)	2.471(6)
Re(1)−P(2)	2.475(6)	Re(2)−P(4)	2.410(6)
Re(1)−N(11)	2.19(2)	Re(2)−N(21)	2.14(2)
Re(1)−H(1)	1.68(2)	Re(2)−H(3)	1.63(2)
Re(1)−H(2)	1.68(2)	Re(2)−H(4)	1.69(2)
S(2)−C(12)	1.76(3)	S(1)−C(22)	1.79(2)
N(11)−C(12)	1.39(3)	N(21)−C(22)	1.30(3)
N(11)−C(110)	1.38(3)	N(21)−C(210)	1.38(3)
Re(1)−Re(2)	3.000(1)		

Angles			
S(1)−Re(1)−S(2)	99.2(2)	S(2)−Re(2)−S(1)	99.9(2)
S(1)−Re(1)−P(1)	82.2(2)	S(2)−Re(2)−P(3)	168.3(2)
S(1)−Re(1)−P(2)	169.1(2)	S(2)−Re(2)−P(4)	84.1(2)
S(1)−Re(1)−N(11)	87.8(5)	S(2)−Re(2)−N(21)	89.9(5)
S(2)−Re(1)−P(1)	146.3(2)	S(1)−Re(2)−P(3)	86.2(2)
S(2)−Re(1)−P(2)	87.3(2)	S(1)−Re(2)−P(4)	143.6(2)
S(2)−Re(1)−N(11)	66.5(5)	S(1)−Re(2)−N(21)	65.7(5)
P(1)−Re(1)−P(2)	97.4(2)	P(3)−Re(2)−P(4)	97.0(2)
P(1)−Re(1)−N(11)	146.8(5)	P(3)−Re(2)−N(21)	83.5(5)
P(2)−Re(1)−N(11)	86.8(5)	P(4)−Re(2)−N(21)	150.6(5)
H(1)−Re(1)−H(2)	139(2)	H(3)−Re(2)−H(4)	137(2)
Re(2)−S(1)−Re(1)	76.5(2)	Re(2)−S(2)−Re(1)	76.8(2)

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

multiplicities for the formula unit totaled 2.0. An ORTEP[33] representation of the structurally significant tetrahydridodirhenium cation is shown in Figure 1, while key crystallographic data and important structural parameters are given in Tables 1 and 2.

The basic structure of the [Re₂H₄(μ-mq)₂(PPh₃)₄]²⁺ cation resembles closely the previously determined structure of the [Re₂H₆(μ-mq)₂(PPh₃)₄]²⁺ cation (**1**), as present in its [H₂PO₄]⁻ salt,[26] with the difference that there are two less terminal Re−H bonds present in the former species. The Re−P distances in **4a** are a little longer on average than they are in the structure of the [Re₂H₆(μ-mq)₂(PPh₃)₄]²⁺ cation; the range is 2.410(6)−2.475(6) Å for **4a** (Table 2) compared to 2.400(2)−2.419(2) Å for **1**.[26] Also, the disparity between the Re−P distances of the two PPh₃ ligands that are bound to each Re center in the structures of **4a** and **1** is greatest in **4a** (ca. 0.06 Å versus 0.02

(33) Johnson, C. K. ORTEP II. Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

Å). These structural features are in accord with the ^{1}H and ^{31}P{^{1}H} NMR spectral properties of **4a**, as discussed previously. While the Re−N distances in the structure of **4a** (2.19(2) and 2.14(2) Å) are not significantly different from the Re−N distance in the asymmetric unit of the analogous [Re$_2$H$_6$(μ-mq)$_2$-(PPh$_3$)$_4$]$^{2+}$ cation (2.191(6) Å),[26] the Re−S distances are much shorter in **4a**; the range is 2.374(6)−2.454(6) Å for **4a** (Table 2) compared to distances of 2.490(2) and 2.505(2) Å in the structure of [Re$_2$H$_6$(μ-mq)$_2$(PPh$_3$)$_4$](H$_2$PO$_4$)$_2$.[26] This result is probably a consequence of a stronger Re(μ-S)$_2$Re bridging unit because of the presence of a Re−Re single bond in **4a**. The Re−Re distance of 3.000(1) Å in the structure of **4a** can be contrasted with a nonbonding distance of 3.9034(8) Å in the structure of the hexahydridodirhenium cation.[26] The formation of a Re−Re bond in **4a**, which accords with the observed diamagnetism of the [Re$_2$H$_4$(μ-mq)$_2$(PPh$_3$)$_4$]$^{2+}$ species, results

in an opening of the S−Re−S bond angles; these angles are 99.2(2) and 99.9(2)° in the case of **4a** (Table 2) and 76.56(7)° in the structure of [Re$_2$H$_6$(μ-mq)$_2$(PPh$_3$)$_4$](H$_2$PO$_4$)$_2$.[26] This is also mirrored in the changes in the Re−S−Re angles which are much smaller in **4a** (76.5(2) and 76.8(2)°) than in **1** (102.8(1)°).