Reactions of the Polyhydride Complex $ReH_7(PPh_3)_2$ with Quinoline, 2-Hydroxyquinoline, and 2-Mercaptoquinoline. Preparation and Characterization of Hydrido Complexes of Rhenium(V) and Chloro Complexes of Rhenium(III)

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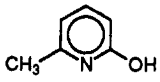
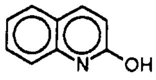
The thermal reactions of the heptahydride complex $ReH_7(PPh_3)_2$ with quinoline (qn), 2-hydroxyquinoline (Hhq), and 2-mercaptoquinoline (Hmq) afford the hydridorhenium(V) complexes $ReH_5(PPh_3)_2(qn)$, $ReH_4(hq)(PPh_3)_2$, and $ReH_4(mq)(PPh_3)_2$, respectively, when refluxing tetrahydrofuran or ethanol is used as the reaction solvent, whereas the paramagnetic chlororhenium(III) species $ReCl_3(qn)_2(PPh_3)$, $ReCl_2(hq)(PPh_3)_2$, and $ReCl_2(mq)(PPh_3)_2$ are formed in refluxing 1,2-dichloroethane solutions. The diamagnetic polyhydride complexes are fluxional at room temperature (by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy) and show cyclic voltammetric properties that are similar to those of other hydridorhenium(V) species. The structure of $ReH_4(hq)(PPh_3)_2$ (**1**) has been determined by X-ray crystallography and shown to be that of a distorted dodecahedron. The chlororhenium(III) species display very characteristic, well-defined, Knight-shifted ^1H NMR spectra. The crystal structure determination of $ReCl_2(mq)(PPh_3)_2$ (**2**) shows that the PPh_3 ligands are in a trans disposition relative to one another and confirms the presence of a chelating mq ligand. Crystal data for **1** (+20 °C): monoclinic space group $P2_1/c$ (No. 14), $a = 9.6655(8)$ Å, $b = 16.095(1)$ Å, $c = 24.562(2)$ Å, $\beta = 100.279(6)°$, $V = 3759.7(9)$ Å^3, $Z = 4$. The structure was refined to $R = 0.024$ ($R_w = 0.029$) for 3646 data with $I > 3.0\sigma(I)$. Crystal data for **2** (+20 °C): monoclinic space group $P2_1$ (No. 4), $a = 11.908(3)$ Å, $b = 16.779(8)$ Å, $c = 12.061(3)$ Å, $\beta = 99.73(2)°$, $V = 2374(2)$ Å^3, $Z = 2$. The structure was refined to $R = 0.054$ ($R_w = 0.070$) for 2774 data with $I > 3.0\sigma(I)$.

Introduction

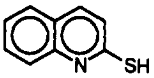
In several earlier studies[1–3] we investigated the reactions of the polyhydride complex $ReH_7(PPh_3)_2$ with several organic "acids", including pyridinecarboxylic acids, acetylacetone, 2-hydroxypyridines, and 2-mercaptopyridine, with the objective of generating reactive, coordinatively unsaturated, rhenium species following protonation of the starting material and the release of H_2. During the course of this work, we isolated and structurally characterized the first and, as far as we are aware, only example of eight-coordinate geometric isomers that retain their structural identity both in the solid state and in solution.[2,3] These novel isomeric forms were encountered in the case of the dihydrido complex $[ReH_2(mhp)_2(PPh_3)_2]PF_6$, where mhp is the monoanion of 2-hydroxy-6-methylpyridine (Hmhp, **I**).[2,3] We attributed the remarkable stability of these isomers to the presence of the methyl substituent in the 6-position of the pyridine ring of the mhp ligands, and we proposed[3] that it is the disposition of these two methyl groups relative to one another that provides a barrier to the "rotation" of the ReH_2 unit that is necessary to convert the least thermodynamically stable isomer to the most stable form.



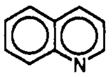
Hmhp (**I**)



Hhq (**II**)



Hmq (**III**)



qn (**IV**)

In order to better understand and more fully investigate the structural implications of varying the substituents on the pyridine ring of the 2-hydroxypyridine and 2-mercaptopyridine ligands in these types of protonation reactions, we have expanded this study to include the reactions of $ReH_7(PPh_3)_2$ with 2-hydroxyquinoline (Hhq, **II**) and 2-mercaptoquinoline (Hmq, **III**). We anticipated that the steric effects might be comparable to those found with Hmhp and, therefore, might provide a route to the eight-coordinate species $[ReH_2(hq)_2(PPh_3)_2]^+$ and $[ReH_2(mq)_2(PPh_3)_2]^+$. However, this proved not to be the case since only one hq and one mq ligand becomes incorporated into the coordination sphere. The details of this chemistry are now reported along with a comparison of the results obtained when the neutral quinoline (qn) ligand **IV** is used.

Experimental Section

Starting Materials. The starting materials $ReH_7(PPh_3)_2$ and $ReCl_3(PPh_3)_2(NCCH_3)$ were prepared as described in the literature.[4,5] Hexafluorophosphoric acid (60% by weight in water) and $HBF_4{\cdot}Et_2O$ were obtained from the Aldrich Chemical Co. The other reagents and solvents were also purchased from commercial sources. The solvents were thoroughly deoxygenated prior to use.

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

A. Reactions of $ReH_7(PPh_3)_2$ with Quinoline. (i) $ReH_5(PPh_3)_2(qn)$. A mixture of $ReH_7(PPh_3)_2$ (0.100 g, 0.14 mmol) and quinoline (0.05 mL, 0.40 mmol) in 5 mL of tetrahydrofuran was refluxed for 20 min. Diethyl ether (30 mL) was added to the cooled reaction mixture to precipitate a bright orange solid. The orange product was recrystallized from dichloromethane/methanol, washed with diethyl ether, and dried in vacuo; yield 0.075 g (64%). Anal. Calcd for $C_{45}H_{42}NP_2Re$: C, 63.96; H, 5.01. Found: C, 64.09; H, 4.76.

(ii) $ReCl_3(qn)_2(PPh_3)$. A solution of $ReH_7(PPh_3)_2$ (0.100 g, 0.14 mmol) and quinoline (0.05 mL, 0.40 mmol) in 5 mL of 1,2-dichloroethane was refluxed for 20 min. The solution was cooled, and an orange-red solid precipitated upon the addition of 50 mL of diethyl ether. The product

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was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.040 g (30%). Anal. Calcd for $C_{36}H_{29}Cl_3N_2PRe$: C, 53.17; H, 3.59; N, 3.44. Found: C, 52.29; H, 3.50; N, 3.32.

An alternative procedure for preparing this compound involves heating a solution of $ReH_5(PPh_3)_2(qn)$ (0.050 g, 0.058 mmol) in 5 mL of 1,2-dichloroethane at reflux for 5 min. The product was precipitated from a cooled solution by the addition of an excess of diethyl ether; yield 0.020 g. An improved yield of this product was obtained when this same reaction was carried out in the presence of an excess of added quinoline. A mixture of $ReH_5(PPh_3)_2(qn)$ (0.132 g, 0.156 mmol) and quinoline (0.100 mL, 0.848 mmol) was refluxed in 5 mL of 1,2-dichloroethane for 15 min. After the reaction mixture was allowed to cool to room temperature, the solvent was evaporated to leave an oil. A small quantity (ca. 1 mL) of dichloromethane was added to ensure that all the solid had dissolved before the addition of 40 mL of *n*-pentane. A red solid precipitated from the mixture. It was stirred for 20 min, and the product was filtered off, washed with 2 × 10 mL of *n*-pentane, and dried under a vacuum; yield 0.070 g (55%).

B. Reactions of $ReH_7(PPh_3)_2$ with 2-Hydroxyquinoline. (i) $ReH_4(hq)(PPh_3)_2$. A mixture of $ReH_7(PPh_3)_2$ (0.300 g, 0.42 mmol) and 2-hydroxyquinoline (0.150 g, 1.03 mmol) was refluxed in 15 mL of ethanol for 20 min. The reaction mixture was cooled to room temperature, and the insoluble bright yellow solid was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.230 g (64%). Anal. Calcd for $C_{45}H_{40}NOP_2Re$: C, 62.92; H, 4.69. Found: C, 62.03; H, 4.68.

(ii) $ReCl_2(hq)(PPh_3)_2$. A mixture of $ReH_7(PPh_3)_2$ (0.100 g, 0.14 mmol) and 2-hydroxyquinoline (0.04 g, 0.28 mmol) was refluxed in 5 mL of 1,2-dichloroethane for 20 min. The reaction mixture was allowed to cool to room temperature, and an excess of diethyl ether (30 mL) was added to precipitate a yellow solid. The product was filtered off, washed with a further quantity of diethyl ether, and dried under vacuum; yield 0.080 g (62%). Anal. Calcd for $C_{45.5}H_{37}Cl_3NOP_2Re$ (i.e. $ReCl_2(hq)(PPh_3)_2{\cdot}0.5CH_2Cl_2$): C, 56.44; H, 3.85; Cl, 10.98. Found: C, 55.51; H, 3.89; Cl, 10.93. The presence of dichloromethane of crystallization was confirmed by ^1H NMR spectroscopy (δ +5.29 in $CDCl_3$).

This same complex was formed when a solution of $ReH_4(hq)(PPh_3)_2$ (0.04 g, 0.05 mmol) in 5 mL of 1,2-dichloroethane was refluxed for 5 min. The solution was allowed to cool to room temperature, and the product precipitated upon the addition of ca. 30 mL of diethyl ether. It was purified by column chromatography (60–200 mesh silica, CH_2Cl_2 as eluant); yield 0.045 g (82%).

C. Reactions of $ReH_7(PPh_3)_2$ with 2-Mercaptoquinoline. (i) $ReH_4(mq)(PPh_3)_2$. A mixture of $ReH_7(PPh_3)_2$ (0.05 g, 0.07 mmol) and 2-mercaptoquinoline (0.025 g, 0.16 mmol) in 5 mL of tetrahydrofuran was refluxed for 20 min. The reaction mixture was cooled to room temperature, and a mustard-colored product precipitated upon the addition of an excess of diethyl ether (30 mL). The crude product was recrystallized from dichloromethane/methanol to afford bright yellow microcrystals; yield 0.04 g (66%). Anal. Calcd for $C_{45}H_{40}NP_2ReS$: C, 61.77; H, 4.61. Found: C, 61.97; H, 4.86.

(ii) $ReCl_2(mq)(PPh_3)_2$. A mixture of $ReH_7(PPh_3)_2$ (0.100 g, 0.140 mmol) and 2-mercaptoquinoline (0.04 g, 0.28 mmol) in 5 mL of 1,2-dichloroethane was refluxed for 20 min. The reaction mixture was cooled to room temperature, and an excess of diethyl ether was added to precipitate a brown solid. The solid was filtered off, washed with diethyl ether, and dried in vacuo; yield 0.025 g (19%).

An alternative route to this complex involved the reflux of a solution of $ReH_4(mq)(PPh_3)_2$ (0.050 g, 0.057 mmol) in 5 mL of 1,2-dichloroethane for 15 min, followed by the addition of 20 mL of diethyl ether and 20 mL of pentane to the cooled reaction mixture. A brown solid was filtered off, washed with diethyl ether, and dried under vacuum. Purification of the compound was accomplished through the use of column chromatography (60–200 mesh silica, CH_2Cl_2 as eluant) to produce red-orange microcrystals; yield 0.020 g (37%). Anal. Calcd for $C_{45.5}H_{37}Cl_3NP_2ReS$ (i.e. $ReCl_2(mq)(PPh_3)_2{\cdot}0.5CH_2Cl_2$): C, 55.52; H, 3.79. Found: C, 54.77; H, 3.62. The presence of dichloromethane of crystallization was confirmed by ^1H NMR spectroscopy (δ +5.29 in $CDCl_3$).

D. Reaction of $ReCl_3(PPh_3)_2(NCCH_3)$ with Quinoline. A mixture of $ReCl_3(PPh_3)_2(NCCH_3)$ (0.100 g, 0.12 mmol) and quinoline (0.5 mL, 4.2 mmol) in 5 mL of 1,2-dichloroethane was refluxed for 20 min until the solution turned deep red. A brown solid was precipitated from the reaction solution upon the addition of 30 mL of diethyl ether. The crude solid was purified by column chromatography (60–200 mesh silica, CH_2Cl_2 as eluant). The orange fraction was concentrated to ca. 2 mL and treated with 100 mL of *n*-pentane or *n*-heptane. The orange red product $ReCl_3(qn)_2(PPh_3)$ precipitated slowly when this mixture was kept at 0 °C for 24 h. The product was filtered off, washed with diethyl ether, and dried in vacuo; yield 0.50 g (45%). Its identity was established by a comparison of its spectroscopic and electrochemical properties with those exhibited by samples prepared by procedure A(ii).

E. Protonation of $ReH_5(PPh_3)_2(qn)$ and $ReH_4(hq)(PPh_3)_2$. (i) $[ReH(NCCH_3)_3(PPh_3)_2(qn)](BF_4)_2$. A mixture of $ReH_5(PPh_3)_2(qn)$ (0.050 g, 0.059 mmol) and 5 mL of acetonitrile treated with $HBF_4{\cdot}Et_2O$ (0.1 mL) was stirred at room temperature for 1 h. The solvent was evaporated under a vacuum to leave a dark oil. The addition of 10 mL of diethyl ether to the oil afforded a bright yellow solid. The yellow solid was filtered off, washed with diethyl ether, and dried in vacuo; yield 0.030 g (67%). Carbon microanalytical data for this product were reproducibly low; we attribute this to the incomplete combustion of the samples. Since the spectroscopic, electrochemical, and conductance properties of this product are in accord with this formulation, we conclude that it is relatively pure.

An analogous reaction with the use of HPF_6(aq) in place of $HBF_4{\cdot}Et_2O$ gave a similar result. The product (presumably $[ReH(NCCH_3)_3(PPh_3)_2(qn)](PF_6)_2$) again did not give a satisfactory carbon microanalysis.

(ii) $[ReH(NCCH_3)_4(PPh_3)_2](PF_6)_2$. A small quantity of HPF_6(aq) (0.1 mL) was added to a mixture of $ReH_4(hq)(PPh_3)_2$ (0.050 g, 0.058 mmol) and 5 mL of acetonitrile. After the reaction mixture had been stirred for ca. 1 h, the solvent was removed by evaporation under a vacuum. The oily residue that remained was treated with diethyl ether (10 mL) to produce a bright yellow solid. The product was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.045 g (66%). Anal. Calcd for $C_{44}H_{43}F_{12}N_4P_4Re$: C, 45.33; H, 3.72. Found: C, 44.60; H, 3.61. This product was further identified through a comparison of its spectroscopic and electrochemical properties with those of the previously reported[6] salt $[ReH(NCCH_3)_4(PPh_3)_2](BF_4)_2$.

F. Oxidation of $ReCl_3(qn)_2(PPh_3)$ and $ReCl_2(hq)(PPh_3)_2$ with $NOPF_6$. (i) $[ReCl_3(qn)_2(PPh_3)]PF_6$. A mixture of $ReCl_3(qn)_2(PPh_3)$ (0.050 g, 0.062 mmol) and $NOPF_6$ (0.010 g, 0.060 mmol) was stirred in 3 mL of dichloromethane for 10 min. The product was precipitated upon the addition of 20 mL of diethyl ether. The red solid was filtered off, washed with diethyl ether, and dried in vacuo; yield 0.035 g (59%).

(ii) $[ReCl_2(hq)(PPh_3)_2]PF_6$. A small quantity of dichloromethane (3 mL) was added to a mixture of $ReCl_2(hq)(PPh_3)_2$ (0.030 g, 0.032 mmol) and $NOPF_6$ (0.010 g, 0.060 mmol). The reaction mixture was stirred for 10 min, and an excess of diethyl ether (ca. 20 mL) was added to precipitate a purple solid. The solid was filtered off, washed with diethyl ether, and dried under vacuum; yield 0.025 g (71%). Anal. Calcd for $C_{45}H_{36}Cl_2F_6NOP_3Re$: C, 50.48; H, 3.39. Found: C, 49.90; H, 3.37.

Preparation of Single Crystals for X-ray Structure Determinations. Crystals of $ReH_4(hq)(PPh_3)_2$ (**1**) were grown at room temperature by carefully layering deoxygenated *n*-pentane over a dilute solution of the complex in benzene. Suitable yellow single crystals were isolated from this mixture after a period of ca. 5 weeks. Crystals of $ReCl_2(mq)(PPh_3)_2$ (**2**) were grown from 1,2-dichloroethane/*n*-pentane by a similar technique. These crystals were isolated after the mixture had been kept for ca. 4 weeks at 0 °C.

X-ray Crystallography. The structures of **1** and **2** were determined by the application of standard procedures. The basic crystallographic parameters for these complexes are listed in Table I. The cell constants are based on 25 reflections with $16 < \theta < 19°$ for **1** and $15 < \theta < 18°$ for **2**. Three standard reflections were measured after every 5000 s of beam exposure during data collection. While we observed no systematic variations in decay of these standards for **1**, there was a loss in intensity of 17.4% for **2**. A linear decay correction was applied. Lorentz and polarization corrections were applied to the data sets. An empirical absorption correction was applied,[7] the linear absorption coefficients being 33.93 cm^{-1} for **1** and 28.50 cm^{-1} for **2**. No corrections were made for extinction. Calculations were performed on a microVAX II computer using the Enraf-Nonius structure determination package. The structures of **1** and **2** were solved by the use of the Enraf-Nonius structure solution procedure MolEN.

All non-hydrogen atoms of **1** were refined with anisotropic thermal parameters. Corrections for anomalous scattering were applied to these

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Table I. Crystallographic Data for $ReH_4(hq)(PPh_3)_2$ (**1**) and $ReCl_2(mq)(PPh_3)_2 \cdot 3H_2O$ (**2**)

	1	**2**
chem formula	$ReP_2ONC_{45}H_{40}$	$ReCl_2SP_2O_3NC_{45}H_{42}$
fw	858.97	995.96
space group	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)
a, Å	9.6655(8)	11.908(3)
b, Å	16.095(1)	16.779(8)
c, Å	24.562(2)	12.061(3)
β, deg	100.279(6)	99.73(2)
V, Å^3	3759.7(9)	2374(2)
Z	4	2
T, °C	20	20
λ(Mo Kα), Å	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	1.517	1.393
μ(Mo Kα), cm^{-1}	33.93	28.50
transm coeff	1.00–0.86	1.00–0.40
R^a	0.024	0.054
$R_w{}^b$	0.029	0.070

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Table II. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for the Non-Phenyl Atoms of **1** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*
Re	0.14129(2)	0.01539(1)	0.25141(1)	2.668(4)
P(1)	0.1469(1)	0.00986(9)	0.34914(6)	2.91(3)
P(2)	0.0688(1)	0.0224(1)	0.15335(6)	2.98(3)
O(2)	−0.0008(4)	−0.0908(2)	0.2476(2)	3.60(9)
N(1)	0.2220(5)	−0.1089(3)	0.2460(2)	3.2(1)
C(2)	0.0990(6)	−0.1448(4)	0.2454(2)	3.7(1)
C(3)	0.0808(8)	−0.2325(4)	0.2427(3)	5.2(2)
C(4)	0.1949(9)	−0.2782(4)	0.2389(3)	6.0(2)
C(5)	0.4508(9)	−0.2865(5)	0.2357(3)	7.0(2)
C(6)	0.5741(9)	−0.2486(5)	0.2361(4)	7.5(2)
C(7)	0.5852(8)	−0.1618(5)	0.2391(3)	6.0(2)
C(8)	0.4660(6)	−0.1155(4)	0.2427(3)	4.3(2)
C(4a)	0.3279(8)	−0.2419(4)	0.2390(3)	5.1(2)
C(8a)	0.3381(6)	−0.1539(4)	0.2425(2)	3.7(1)
H(1)	0.275(6)	0.051(4)	0.221(2)	5(1)*
H(2)	0.305(6)	0.043(4)	0.284(2)	6(1)*
H(3)	0.001(6)	0.076(4)	0.254(3)	6(2)*
H(4)	0.162(7)	0.117(4)	0.262(3)	8(2)*

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Data for the phenyl atoms of the PPh_3 ligands are available as supplementary material. An asterisk denotes a value for an isotropically refined atom.

Table III. Positional Parameters and Equivalent Isotropic Displacement Parameters (Å^2) for the Non-Phenyl Atoms of **2** and Their Estimated Standard Deviations[a]

atom	*x*	*y*	*z*	*B*
Re(1)	0.21772(6)	0.09992	0.27532(6)	3.78(1)
Cl(1)	0.3840(4)	0.1704(3)	0.3644(5)	5.7(1)
Cl(2)	0.2267(5)	−0.0032(3)	0.4129(5)	5.7(1)
S	0.1660(5)	0.1884(4)	0.1181(5)	5.5(1)
P(1)	0.0974(4)	0.1774(3)	0.3843(4)	3.9(1)
P(2)	0.3385(5)	0.0209(4)	0.1690(5)	4.3(1)
N(1)	0.065(2)	0.049(1)	0.178(2)	7.9(6)*
C(2)	0.056(2)	0.111(2)	0.096(2)	8.2(6)*
C(3)	−0.041(2)	0.090(2)	0.003(2)	9.2(8)*
C(4)	−0.124(3)	0.049(2)	−0.022(3)	9.2(9)*
C(5)	−0.183(3)	−0.067(2)	0.046(3)	9.4(9)*
C(6)	−0.150(7)	−0.116(6)	0.121(7)	28(4)*
C(7)	−0.069(3)	−0.125(2)	0.229(3)	9.1(8)*
C(8)	0.026(4)	−0.070(3)	0.255(4)	13(1)*
C(4a)	−0.098(3)	−0.014(3)	0.069(3)	11(1)*
C(8a)	−0.010(2)	−0.005(1)	0.150(2)	5.9(5)*

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Data for the phenyl atoms of the PPh_3 ligands and the oxygen atoms of the water molecules of crystallization are available as supplementary material. An asterisk denotes a value for an isotropically refined atom.

atoms.[8] Hydrogen atoms of the PPh_3 and hq ligands were introduced at calculated positions (C–H = 0.95 Å, $B = 1.3\,B_C$), not refined but constrained to ride on their C atoms. The four hydrido ligands were located in the structure of **1** following anisotropic refinement of all non-hydrogen atoms. Their refinement gave reasonable Re–H bond distances. The highest peak in the final difference Fourier map had a height of 0.34 e/Å^3. The final residuals for **1** were $R = 0.024$ ($R_w = 0.029$) and GOF = 0.712.

While the structure solution and refinement of **2** were generally satisfactory and established the details of the geometry of the complex, problems arose in the refinement of the mq ligand from an apparent pseudo 2-fold rotation axis about N(1)–Re(1)–Cl(1).[9] As a consequence, the C and N atoms of the mq did not refine satisfactorily with the use of anisotropic thermal parameters. Furthermore, this problem was manifested in anomalously large thermal parameters for several of the carbon atoms, especially C(6), C(8), and C(4a) of the mq ligand and those of two of the phenyl rings associated with one of the PPh_3 ligands. However, since our primary interest lay in the determination of the gross structural features of **2** and the attendant Re–ligand parameters, this was not considered to be a major problem. Following location of all non-hydrogen atoms of the rhenium complex, three regions of electron density (each ~8e) remained that were located about general positions. These were modeled as oxygen atoms of lattice water molecules that were not at bonding distances to any of the atoms of the $ReCl_2(mq)(PPh_3)_2$ molecule.[10] The alternative possibility that at least some of this electron density might be due to chloride ions at half-occupancy was discounted since this complex is a nonelectrolyte (on the basis of conductivity measurements on acetonitrile solutions of **2**). With the exception of the C and N atoms of the 2-mercaptoquinoline ligand, all non-hydrogen atoms of **2** were refined with anisotropic thermal parameters. Corrections for anomalous scattering were applied to these atoms.[8] Hydrogen atoms of the PPh_3 and mq ligands were not included. The highest peak in the final difference Fourier map had a height of 1.26 e/Å^3. The final residuals for **2** were $R = 0.054$ ($R_w = 0.070$) and GOF = 2.010; for the other enantiomorph $R = 0.063$ ($R_w = 0.081$) and GOF = 2.232.

Positional parameters and their errors for the important non-hydrogen atoms of compounds **1** and **2** are listed in Tables II and III. Important intramolecular bond distances and angles are given in Tables IV and V. Full details of the crystal data, data collection parameters, and all structural parameters are available as supplementary material (Tables S1–S11).

Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates on a Perkin-Elmer Model 1800 Fourier transform (4000–450 cm^{-1}) spectrometer. Electrochemical measurements were carried out by the use of a Bioanalytical Systems Inc. Model CV-27 instrument in conjunction with a Bioanalytical Systems Inc. X-Y recorder. Voltammetric 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 a silver/silver chloride (Ag/AgCl) electrode and are uncorrected for junction potentials. Under our experimental conditions, $E_{1/2} = +0.47$ V vs Ag/AgCl for the ferrocenium/ferrocene couple. ^1H NMR spectra were recorded on a Varian XL-200 or Gemini-200 spectrometer and were referenced to the residual protons in the incompletely deuteriated solvents. $^{31}P\{^1H\}$ NMR spectra were also obtained on a Varian XL-200 spectrometer. Resonances were referenced externally to a sample of 85% H_3PO_4. An internal lock was used. Conductivity measurements were performed on either acetone or acetonitrile solutions of the complexes (1×10^{-3} M) by the use of an Industrial Instruments Inc. Model RC-16B2 conductivity bridge.

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

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(8) (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution see: Cromer, D. T.; Waber, J. T. *Ibid.*, Table 2.2B.

(9) We thank Dr. Larry R. Falvello for his advice in helping us overcome this crystallographic problem.

(10) We found no convincing evidence from IR spectroscopy and microanalytic data for the presence of significant amounts of H_2O of crystallization in the bulk samples. Consequently, these H_2O molecules are apparently a property of the crystal that was chosen for the structure analysis; a broad ν(O–H) band at ca. 3350 cm^{-1} was observed in the IR spectrum of the crystals.

Table IV. Important Bond Distances (Å) and Bond Angles (deg) for **1**[a]

	Distances		
Re–P(1)	2.393(1)	Re–H(1)	1.71(6)
Re–P(2)	2.388(1)	Re–H(2)	1.70(6)
Re–O(2)	2.184(4)	Re–H(3)	1.68(6)
Re–N(1)	2.160(5)	Re–H(4)	1.66(7)
	Angles		
P(1)–Re–P(2)	164.47(5)	O(2)–Re–H(3)	87(2)
P(1)–Re–O(2)	85.2(1)	O(2)–Re–H(4)	147(3)
P(1)–Re–N(1)	94.8(1)	N(1)–Re–H(1)	89(2)
P(1)–Re–H(1)	125(2)	N(1)–Re–H(2)	87(2)
P(1)–Re–H(2)	72(2)	N(1)–Re–H(3)	147(2)
P(1)–Re–H(3)	82(2)	N(1)–Re–H(4)	152(3)
P(1)–Re–H(4)	84(2)	H(1)–Re–H(2)	53(3)
P(2)–Re–O(2)	85.7(1)	H(1)–Re–H(3)	120(3)
P(2)–Re–N(1)	91.5(1)	H(1)–Re–H(4)	70(3)
P(2)–Re–H(1)	69(2)	H(2)–Re–H(3)	122(3)
P(2)–Re–H(2)	123(2)	H(2)–Re–H(4)	66(3)
P(2)–Re–H(3)	85(2)	H(3)–Re–H(4)	60(3)
P(2)–Re–H(4)	97(2)	Re–O(2)–C(2)	93.4(4)
O(2)–Re–N(1)	60.3(2)	Re–N(1)–C(2)	94.1(4)
O(2)–Re–H(1)	140(2)	O(2)–C(2)–N(1)	112.2(5)
O(2)–Re–H(2)	139(2)		

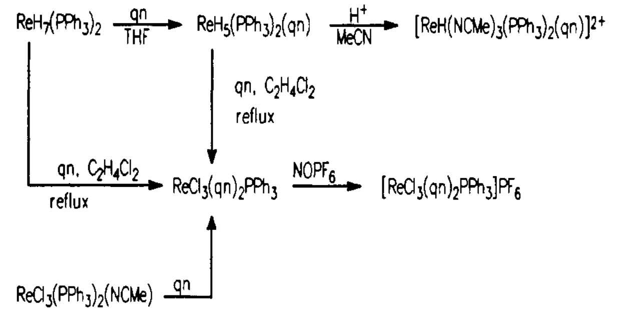
[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table V. Important Bond Distances (Å) and Bond Angles (deg) for **2**[a]

	Distances		
Re(1)–Cl(1)	2.399(5)	Re(1)–P(2)	2.469(6)
Re(1)–Cl(2)	2.387(6)	Re(1)–N(1)	2.16(3)
Re(1)–S	2.405(6)	S–C(2)	1.83(4)
Re(1)–P(1)	2.471(6)		
	Angles		
Cl(1)–Re(1)–Cl(2)	96.3(2)	Cl(2)–Re(1)–N(1)	91.6(8)
Cl(1)–Re(1)–S	97.5(2)	S–Re(1)–P(1)	90.0(2)
Cl(1)–Re(1)–P(1)	90.7(2)	S–Re(1)–P(2)	90.9(2)
Cl(1)–Re(1)–P(2)	89.3(2)	S–Re(1)–N(1)	74.6(8)
Cl(1)–Re(1)–N(1)	172.1(8)	P(1)–Re(1)–P(2)	179.1(2)
Cl(2)–Re(1)–S	166.1(2)	P(1)–Re(1)–N(1)	89.3(8)
Cl(2)–Re(1)–P(1)	88.5(2)	P(2)–Re(1)–N(1)	90.9(8)
Cl(2)–Re(1)–P(2)	90.6(2)		

[a] Numbers in parentheses are estimated standard derivatives in the least significant digits.

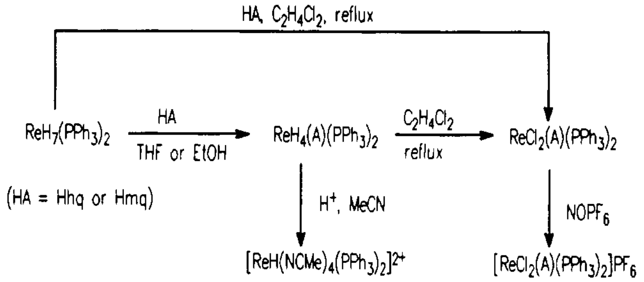
Scheme I. Reactions of $ReH_7(PPh_3)_2$ with Quinoline (qn)



Results

The reactions of $ReH_7(PPh_3)_2$ with quinoline (qn), 2-hydroxyquinoline (Hhq), and 2-mercaptoquinoline (Hmq) to afford hydridorhenium(V) and chlororhenium(III) complexes are summarized in Schemes I and II. When quinoline is reacted with $ReH_7(PPh_3)_2$ in refluxing tetrahydrofuran (ethanol is an equally effective solvent), the compound $ReH_5(PPh_3)_2(qn)$ is formed; this is of a type commonly encountered in the thermal reactions of $ReH_7(PPh_3)_2$ with neutral monodentate donors (e.g. py, $C_6H_{11}NH_2$, *t*-$BuNH_2$, pyrazine) in which loss of H_2 and concomitant coordination of one 2-electron-donor ligand molecule occurs.[4,6,11]

Scheme II. Reactions of $ReH_7(PPh_3)_2$ with 2-Hydroxyquinoline (Hhq) and 2-Mercaptoquinoline (Hmq)



The corresponding reactions with 2-hydroxyquinoline (Hhq) and 2-mercaptoquinoline (Hmq) proceed in this same general fashion, except that a second step occurs involving protonation by the ligand and loss of a further equivalent of H_2. The resultant diamagnetic tetrahydrido complexes $ReH_4(hq)(PPh_3)_2$ and $ReH_4(mq)(PPh_3)_2$ are formally derivatives of Re(V) since they also contain the monoanionic chelating hq^- and mq^- ligands. All three polyhydride compounds are moderately soluble in dichloromethane and acetonitrile, and their solutions in acetonitrile (ca. 1×10^{-3} M) are essentially nonconducting, with Λ_m values in the range 1–5 Ω^{-1} cm^2 mol^{-1}. They show characteristic ν(Re–H) modes in their IR spectra; these spectra are very similar for $ReH_4(hq)(PPh_3)_2$ and $ReH_4(mq)(PPh_3)_2$, with bands at 2064 (m–w), 2029 (m), 2020 (sh), and 1996 (m) cm^{-1} for the former and 2062 (w), 2021 (m), and 1990 (m) cm^{-1} for the latter complex. The pentahydride $ReH_5(PPh_3)_2(qn)$ has two broad bands centered at ca. 1980 (m–w) and ca. 1830 (m–w) cm^{-1} which we assign to ν(Re–H). The important NMR spectral data and electrochemical properties of these complexes are given in Table VI.

The structural identity of the tetrahydrido complex $ReH_4(hq)(PPh_3)_2$ (**1**) was established by X-ray crystallography. An ORTEP representation of the structure is shown in Figure 1, while important details of the crystallographic and structural parameters are given in Tables I, II, and IV.

The protonation of $ReH_5(PPh_3)_2(qn)$ with the use of $HBF_4{\cdot}Et_2O$ and HPF_6(aq) in acetonitrile leads to the evolution of H_2 and the formation of the salts $[ReH(NCCH_3)_3(PPh_3)_2(qn)](BF_4)_2$ and $[ReH(NCCH_3)_3(PPh_3)_2(qn)](PF_6)_2$. The reaction course is exactly the same as that encountered previously with other pentahydrides of the type $ReH_5(PPh_3)_2L$ (L = py, $C_6H_{11}NH_2$, *t*-$BuNH_2$).[6] The NMR spectra of these complexes (recorded in CD_2Cl_2) are in accord with a rigid seven-coordinate geometry for the cation; the Re–*H* resonance appears as a doublet of doublets at δ –4.50 (J_{H-P} = 63 and 67 Hz) in the ^1H NMR spectrum, while the $^{31}P\{^1H\}$ NMR spectrum shows singlets at δ +26.4 and +23.5 for the chemically inequivalent PPh_3 ligands. The $^{31}P\{^1H\}$ NMR spectrum of the $[PF_6]^-$ salt also shows a septet at δ –143.9 due to this anion. The IR spectra of the two salts differ only in the bands that are assigned to the different anions; ν(P–F) at 840 (vs) cm^{-1} for $[PF_6]^-$ and ν(B–F) at 1060 (vs) cm^{-1} for $[BF_4]^-$. The cyclic voltammograms of the salts of $[ReH(NCCH_3)_3(PPh_3)_2(qn)]^{2+}$ (recorded in 0.1 TBAH-CH_2Cl_2) show a reversible oxidation with $E_{1/2}(ox) = +1.03$ V vs Ag/AgCl ($E_{p,a} - E_{p,c}$ = 70 mV at v = 200 mV s^{-1}) and an irreversible reduction at $E_{p,c}$ = –1.51 V. This behavior is very similar to that reported[6] for other species of the type $[ReH(NCCH_3)_3(PPh_3)_2L]^{2+}$. A conductivity measurement on a solution of $[ReH(NCCH_3)_2(PPh_3)_3(qn)](PF_6)_2$ ($c_m = 1 \times 10^{-3}$M) confirmed it to be a 1:2 electrolyte (Λ_m = 232 Ω^{-1} cm^2 mol^{-1}).[12]

The treatment of a mixture of $ReH_4(hq)(PPh_3)_2$ and acetonitrile with HPF_6(aq) leads to a reaction course similar to that described above, except that both H_2 and the Hhq ligand are released in this reaction. The reaction product, $[ReH(NCCH_3)_4(PPh_3)_2]$-

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[11] Moehring, G. A.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 2910.

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

Table VI. Selected Electrochemical and NMR Spectral Data for Rhenium(V) Polyhydride Complexes

	chem shift, δ				
	^{1}H NMR[a]			CV half-wave potentials, V[d]	
complex	Re–H[b]	L[c]	^{31}P{^{1}H} NMR[a]	$E_{1/2}$(ox)[e]	$E_{p,a}$
$ReH_5(PPh_3)_2(qn)$	–4.50[f]	+6.49 (d, 6.4) +8.07 (d, 6.8)	+45.3 (s)	+0.19 (95)	ca. +0.8
$ReH_4(hq)(PPh_3)_2$	–4.48 (t, 20)	+5.47 (d, 9.4)	+33.0 (s)	+0.29 (60)	ca. +1.1
$ReH_4(mq)(PPh_3)_2$	–5.22 (t, 22)	+5.78 (d, 8.6)	+29.7 (s)	+0.30 (80)	ca. +1.0

[a] Spectra recorded in CD_2Cl_2. [b] J_{P-H} in hertz given in parentheses. Abbreviation: t = triplet. [c] The doublets quoted are for resonances that are characteristic of the ligands (L = qn, hq, mq) in these complexes. J_{H-H} in hertz given in parentheses. [d] Measured on 0.1 M TBAH–CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode, with scan rate (v) of 200 mV s^{-1} at a Pt-bead electrode. [e] Numbers in parentheses are the values of $E_{p,a} - E_{p,c}$ (in mV) for this process with a switching potential of ca. +0.5 V. [f] Broad resonance.

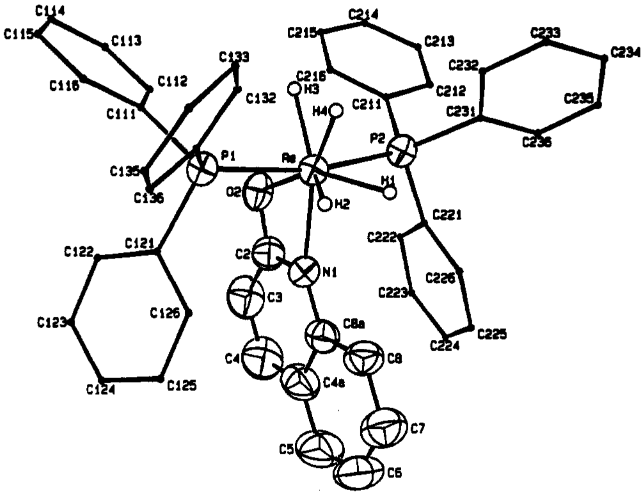

Figure 1. ORTEP representation of the structure of the eight-coordinate complex $ReH_4(hq)(PPh_3)_2$ (**1**). The thermal ellipsoids are drawn at the 50% probability level, and the carbon atoms of the phenyl rings of the PPh_3 ligands and the four hydrido ligands are represented as circles of arbitrary radius.

$(PF_6)_2$, has spectroscopic and electrochemical properties essentially identical to those of the analogous $[BF_4]^-$ salt that has been prepared[6] by the reaction of $ReH_7(PPh_3)_2$ with $HBF_4{\cdot}Et_2O$ in acetonitrile. Accordingly, details of its properties are not presented here. The corresponding reaction of $ReH_4(mq)(PPh_3)_2$ with HPF_6(aq) in acetonitrile did not give an isolable product, in spite of the similarity of the properties of this tetrahydrido complex to those of its hq analogue (Table VI). The reason for this is unclear.

Attempts were made to protonate $ReH_5(PPh_3)_2(qn)$, $ReH_4(hq)(PPh_3)_2$, and $ReH_4(mq)(PPh_3)_2$ in "noncoordinating" solvents such as dichloromethane in order to generate the species $[ReH_6(PPh_3)_2(qn)]^+$, $[ReH_5(hq)(PPh_3)_2]^+$, and $[ReH_5(mq)(PPh_3)_2]^+$, respectively, as has been done previously[13] in the conversion of $ReH_5(PPh_3)_3$ to $[ReH_6(PPh_3)_3]BF_4$. However, we were unable to isolate the desired product in any of these reactions. In all instances, decomposition occurred.

The hydrido complexes $ReH_5(PPh_3)_2(qn)$, $ReH_4(hq)(PPh_3)_2$, and $ReH_4(mq)(PPh_3)_2$ react with refluxing 1,2-dichloroethane to produce the chlororhenium(III) complexes $ReCl_3(qn)_2(PPh_3)$, $ReCl_2(hq)(PPh_3)_2$, and $ReCl_2(mq)(PPh_3)_2$, respectively, as major reaction products (see Schemes I and II). These same compounds are formed when $ReH_7(PPh_3)_2$ is reacted with qn, Hhq, and Hmq in refluxing 1,2-dichloroethane. Yields from these reactions are quite variable and in some instances relatively low, ranging from ca. 20 to 80%. The low yields, particularly for the mq derivative, were due in part to the tendency of the product to oil as it precipitated from the reaction mixture, thus causing difficulties of its isolation and purification. Furthermore, a small portion of the $ReH_7(PPh_3)_2$ does not react with the ligand, but instead undergoes loss of H_2 and dimerizes under these thermal conditions to form the well-known complex $Re_2H_8(PPh_3)_4$.[14] The quinoline complex $ReCl_3(qn)_2(PPh_3)$ is also produced quite easily when the preformed rhenium(III) compound $ReCl_3(PPh_3)_2(NCCH_3)$[5] is reacted with an excess of qn. However, attempts to prepare $ReCl_2(hq)(PPh_3)_2$ and $ReCl_2(mq)(PPh_3)_2$ by such a procedure were unsuccessful; the Re–Cl bonds of $ReCl_3(PPh_3)_2(NCCH_3)$ are apparently not susceptible to solvolysis by the hydroxy and hydrosulfido groups of the Hhq and Hmq ligands under these conditions.

All three compounds $ReCl_3(qn)_2(PPh_3)$, $ReCl_2(hq)(PPh_3)_2$, and $ReCl_2(mq)(PPh_3)_2$ dissolve in acetonitrile to give nonconducting solutions (Λ_m = 1–2 Ω^{-1} cm^2 mol^{-1}). They have properties typical of paramagnetic mononuclear rhenium(III) species. Each possesses characteristically sharp, well-defined, Knight-shifted ^{1}H NMR spectra.[15-18] The chemical shift data for the PPh_3, qn, hq, and mq ligands are listed in Table S12 (supplementary material). While the resonances for the different ligands in each complex were readily assigned, we made no attempt to make detailed assignments of the individual resonances for the qn, hq, and mq ligands. However, the observation of 14 separate quinoline resonances in the ^{1}H NMR spectrum of $ReCl_3(qn)_2(PPh_3)$ (see Table S12) accords with the presence of two inequivalent qn ligands.

The electrochemical properties of these complexes resemble those of similar mononuclear chlororhenium(III) complexes such as $ReCl_3(PMe_2Ph)_3$.[19] Cyclic voltammetric (CV) measurements on solutions of $ReCl_3(qn)_2(PPh_3)$ in 0.1 M TBAH–CH_2Cl_2 show a reversible Re(IV)/Re(III) couple at $E_{1/2}$ = +0.48 V vs Ag/AgCl and a reversible process at $E_{1/2}$ = –0.96 V vs Ag/AgCl that is due to the corresponding Re(III)/Re(II) couple. The cyclic voltammograms of the hq and mq derivatives also consist of these two types of reversible processes, at approximately the same potentials, *viz.*, $E_{1/2}$(ox) = +0.46 V and $E_{1/2}$(red) = –1.08 V for $ReCl_2(hq)(PPh_3)_2$ and $E_{1/2}$(ox) = +0.47 V and $E_{1/2}$(red) = –0.98 V for $ReCl_2(mq)(PPh_3)_2$. The ΔE_p values ($E_{p,a} - E_{p,c}$) for these processes were in the range 60–100 mV. The oxidations at ca. +0.50 V were accessible through controlled potential electrolysis carried out at ca. +0.75 V with the use of a Pt-gauze electrode. These solutions were characterized electrochemically by the CV technique. In the cases of $ReCl_3(qn)_2(PPh_3)$ and $ReCl_2(hq)(PPh_3)_2$, the same oxidation process was accessible through the use of $NOPF_6$. The red-purple oxidation products $[ReCl_3(qn)_2(PPh_3)]PF_6$ and $[ReCl_2(hq)(PPh_3)_2]PF_6$ were characterized by IR spectroscopy (ν(P–F) at 840 cm^{-1}), by electrochemistry (CV

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(14) Identification of this dinuclear complex was based upon its spectroscopic and electrochemical properties: Fanwick, P. E.; Root, D. R.; Walton, R. A. *Inorg. Chem.* **1989**, *28*, 3203.

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(17) Rossi, R.; Duatti, A.; Magon, L.; Casellato, U.; Craziani, R.; Toniolo, L. *J. Chem. Soc., Dalton Trans.* **1982**, 1949.

(18) Cameron, C. J.; Tetrick, S. M.; Walton, R. A. *Organometallics* **1984**, *3*, 240.

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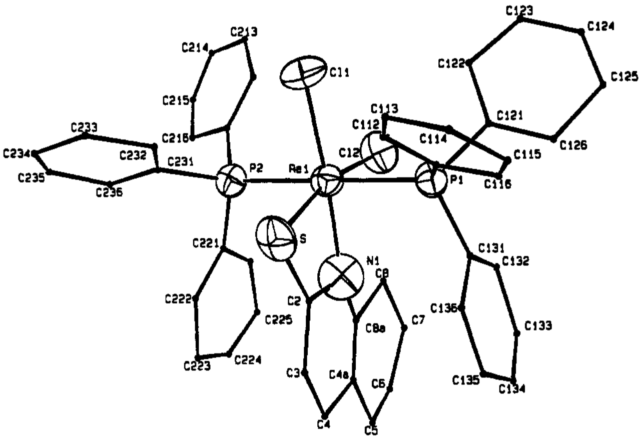

Figure 2. ORTEP representation of the structure of the $ReCl_2(mq)(PPh_3)_2$ molecule (**2**). The thermal ellipsoids are drawn at the 50% probability level, and the carbon atoms of the phenyl rings of the PPh_3 ligands and the mq ligand are represented as filled circles of arbitrary radius.

technique), and by conductivity measurements on acetonitrile solutions (Λ_m = 122 Ω^{-1} cm^2 mol^{-1} for $[ReCl_3(qn)_2(PPh_3)]PF_6$ and Λ_m = 102 Ω^{-1} cm^2 mol^{-1} for $[ReCl_2(hq)(PPh_3)_2]PF_6$).

The structural identity of $ReCl_2(mq)(PPh_3)_2$ (**2**) was confirmed by X-ray crystallography. An ORTEP representation of the structure is shown in Figure 2, while key details of the crystallographic and structural parameters are given in Tables I, III, and V.

Discussion

The reactions of $ReH_7(PPh_3)_2$ with quinoline (qn), 2-hydroxyquinoline (Hhq), and 2-mercaptoquinoline (Hmq) proceed in a similar fashion to afford hydridorhenium(V) species (eqs 1 and 2). This behavior contrasts with the analogous reactions of $ReH_7(PPh_3)_2$ with 2-hydroxypyridine (Hhp) and 2-mercaptopyridine (Hmp), which proceed further with the coordination of a second monoanionic ligand molecule (hp or mp), evolution of a further 2 equiv of H_2, and reduction to rhenium(III) (eq 3).[1] The termination of the reactions with Hhq and Hmq at the rhenium(V) stage can be attributed to the increased steric bulk of these ligands compared to Hhp and Hmp.

$$ReH_7(PPh_3)_2 + qn \rightarrow ReH_5(PPh_3)_2(qn) + H_2 \quad (1)$$

$$ReH_7(PPh_3)_2 + HA \rightarrow ReH_4(A)(PPh_3)_2 + 2\,H_2 \quad (2)$$

$$HA = Hhq \text{ or } Hmq$$

$$ReH_7(PPh_3)_2 + 2HA' \rightarrow ReH(A')_2(PPh_3)_2 + 4H_2 \quad (3)$$

$$HA' = Hhp \text{ or } Hmp$$

The electrochemical properties of $ReH_5(PPh_3)_2(qn)$, $ReH_4(hq)(PPh_3)_2$, and $ReH_4(mq)(PPh_3)_2$ (Table VI) are typical of other rhenium(V) polyhydrides, such as various $ReH_5(PPh_3)_2L$ compounds (L = PPh_3, PEt_2Ph, py, piperidine, $C_6H_{11}NH_2$).[20,21] CV measurements on solutions of these complexes in 0.1 M TBAH–CH_2Cl_2 (Table VI) show a couple at $E_{1/2}$ = ca. +0.25 V vs Ag/AgCl and an irreversible oxidation with an $E_{p,a}$ value between +0.8 and +1.1 V. A characteristic of the oxidation process at ca. +0.25 V is that with use of a switching potential of ca. +0.5 V (i.e. cathodic of the irreversible oxidation) the $i_{p,c}/i_{p,a}$ ratio for the couple becomes unity at a sweep rate of 200 mV s^{-1}. However, this oxidation is not chemically reversible.

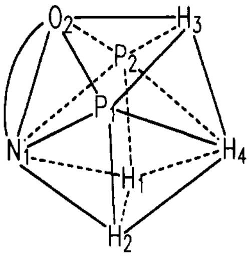

Figure 3. Idealized representation of the structure of $ReH_4(hq)(PPh_3)_2$ in terms of a dodecahedral geometry.

All three complexes show a well-defined Re–*H* resonance in their ^1H NMR spectra at room temperature (Table VI). However, in the case of $ReH_5(PPh_3)_2(qn)$ it consists of a broad band at δ −4.5 displaying no resolvable P–H coupling, the lack of which we attribute to a slow exchange of the hydride ligands on the NMR time scale. When a CD_2Cl_2 solution of this complex is cooled to −78 °C, the hydride resonance collapses (coalescence at ca. −25 °C) and then splits into a four signal pattern (δ −1.1 (t), −2.5 (d), −8.2 (br t), −9.5 (br s)), which is typical of the behavior of other pentahydridorhenium(V) species.[11,22] The appearance of the ^1H NMR spectra of $ReH_4(hq)(PPh_3)_2$ and $ReH_4(mq)(PPh_3)_2$ as binomial triplets at room temperature (Table VI) signifies the presence of highly fluxional molecules in solution. Accordingly, a temperature-range study was carried out on a CD_2Cl_2 solution of $ReH_4(mq)(PPh_3)_2$. Coalescence was achieved at ca. −60 °C, and by −80 °C three broad peaks were observed (δ ca. −4.1, ca. −5.5, ca. −7.2; intensity ratio of ca. 1:2:1) although these did not display resolvable P–H coupling. This is consistent with the solid-state structure of the analogous hq complex $ReH_4(hq)(PPh_3)_2$ as established by a single-crystal X-ray structure determination at +20 °C (Figure 1).

The X-ray structure determination of $ReH_4(hq)(PPh_3)_2$ confirmed an eight-coordinate structure which is best represented in terms of a dodecahedral geometry (Figure 3). The chelating hq ligand was found to be in the same plane as two of the hydrogen atoms, while the other two hydride ligands are essentially coplanar with the two phosphorus atoms. Least-squares calculations on the Re–N(1)–O(2)–H(3)–H(4) plane show the largest displacement of any of the five atoms that form the plane is 0.05(6) Å for H(4). Least-squares calculations on the Re–P(1)–P(2)–H(1)–H(2) plane show that Re is 0.073(0) Å from the plane. Significant distortions from the idealized dodecahedral geometry are present in the structure. These are mainly due to the variety of different ligands that are present, as well as the geometric constraints imposed by the relatively small bite of the chelating hq ligand. When compared to the atoms of a regular MA_4B_4 dodecahedron, the H(1), H(2), H(3), and O(2) atoms occupy the A sites while the P(1), P(2), N(1), and H(4) atoms occupy the B sites.

In an earlier report[3] we described the structural characterization of two geometric isomers of the eight-coordinate complex $[ReH_2(mhp)_2(PPh_3)_2]PF_6$ (mhp = the anion of 2-hydroxy-6-methylpyridine). They were designated as the "cis" and "trans" isomers on the basis of the P–Re–P bond angles, which were ca. 129 and 169°, respectively. The P(1)–Re–P(2) bond angle in $ReH_4(hq)(PPh_3)_2$ is 164.47(5)°; this value along with other structural features suggests that it most closely resembles *trans*-$[ReH_2(mhp)_2(PPh_3)_2]PF_6$.

On the basis of the crystallographic data, $ReH_4(hq)(PPh_3)_2$ appears to be a classical hydride. The shortest H··· H contact is 1.53(8) Å for H(1)···H(2), while the H(1)–Re–H(2) bond angle is 53(3)°, values which are similar to those reported[3] for the dihydrido complex *trans*-$[ReH_2(mhp)_2(PPh_3)_2]PF_6$.

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Although we were unable to isolate stable protonated species $[ReH_6(PPh_3)_2(qn)]^+$, $[ReH_5(hq)(PPh_3)_2]^+$, and $[ReH_5(mq)(PPh_3)_2]^+$, treatment of the neutral precursor complexes with the strong acids $HBF_4{\cdot}Et_2O$ and $HPF_6(aq)$ in acetonitrile afforded salts of the monohydrido complex species $[ReH(NCCH_3)_3(PPh_3)_2(qn)]^+$ and $[ReH(NCCH_3)_4(PPh_3)_2]^+$. These complexes are of a type that have been prepared and characterized previously.[6,23]

The formation of chloro complexes of rhenium when $ReH_5(PPh_3)_2(qn)$, $ReH_4(hq)(PPh_3)_2$, and $ReH_4(mq)(PPh_3)_2$ are reacted directly with 1,2-dichloroethane, or when $ReH_7(PPh_3)_2$ is reacted with qn, Hhq, or Hmq in this same chlorocarbon solvent, has plenty of precedent. For example, $ReH_7(PPh_3)_2$ and $ReH_5(PPh_3)_2(L)$ (L = piperidine, $C_6H_{11}NH_2$) have been found[24] to react with a variety of chlorocarbons with the resulting evolution of H_2 and formation of several types of rhenium chloride complexes. The mononuclear chlororhenium(III) complexes $ReCl_3(qn)_2(PPh_3)$, $ReCl_2(hq)(PPh_3)_2$, and $ReCl_2(mq)(PPh_3)_2$ that were isolated in the present study (see Schemes I and II) are new compounds. The conversion of $ReH_5(PPh_3)_2(qn)$ to $ReCl_3(qn)_2(PPh_3)$ in refluxing 1,2-dichloroethane must involve the sacrifice of half of the starting rhenium complex to provide the extra molecule of qn that is necessary to replace one of the PPh_3 ligands. As expected, the addition of a quantity of free qn to the initial reaction mixture results in the isolation of $ReCl_3(qn)_2(PPh_3)$ in much higher yield. The lability of one or both of the PPh_3 ligands is not surprising, given the previous observation[5] that the reaction of $ReCl_3(PPh_3)_2(NCR)$ with pyridine forms $ReCl_3(py)_2(PPh_3)$ and $ReCl_3(py)_3$.

The single crystal X-ray structure determination of $ReCl_2(mq)(PPh_3)_2$ (Figure 2) shows the presence of a trans pair of PPh_3 ligands and a chelating mq ligand. The distorted octahedral geometry resembles closely that of the structurally characterized complex $ReCl_2[(p\text{-tol})_2N_3](PPh_3)_2$,[17] which also contains a pair of trans PPh_3 ligands. The Re–P and Re–Cl bond distances in $ReCl_2(mq)(PPh_3)_2$ (the average values are 2.470(4) and 2.393(4) Å, respectively) are essentially the same as those reported[17] for $ReCl_2[(p\text{-tol})_2N_3](PPh_3)_2$. While the dirhenium complex $[Re_2Cl_3(\mu\text{-mq})(\mu\text{-dppm})_2]PF_6$ has been structurally characterized previously,[25] the compound $ReCl_2(mq)(PPh_3)_2$ represents the first example of a mononuclear mq complex of rhenium.

Further investigations into the reactivity of $ReH_4(hq)(PPh_3)_2$ and $ReH_4(mq)(PPh_3)_2$ are underway. Preliminary studies have shown[26] that the mercaptoquinoline complex activates alkynes in the presence of electrophiles to afford a class of novel hydrido–alkylidyne complexes. These complexes hold promise for developing some interesting organometallic chemistry.

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Supplementary Material Available: For compounds **1** and **2** Tables S1–S11, giving full details of the crystal data and data collection parameters, positional parameters, thermal parameters, and complete bond distances and bond angles, and for mononuclear chlororhenium(III) complexes Table S12, giving ^1H NMR spectral data (31 pages). Ordering information is given on any current masthead page.

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