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REACTIONS OF THE POLYHYDRIDE COMPLEX ReH_7(dppe) (dppe = $Ph_2PCH_2CH_2PPh_2$) WITH PYRIDINE-2-CARBOXYLIC ACID, 1-ISOQUINOLINECARBOXYLIC ACID, 2-HYDROXY-6-METHYLPYRIDINE AND 2-MERCAPTOQUINOLINE. SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF SEVEN-COORDINATE MONOHYDRIDO COMPLEXES OF RHENIUM(III)

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Abstract—The thermal reactions of ReH_7(dppe) (dppe = $Ph_2PCH_2CH_2PPh_2$) with pyridine-2-carboxylic acid (Hpic), 1-isoquinolinecarboxylic acid (Hisoquin), 2-hydroxy-6-methylpyridine (Hmhp) and 2-mercaptoquinoline (Hmq) in refluxing benzene afforded the monohydridorhenium(III) species $ReH(L)_2$(dppe) [L = pic (**1a**), isoquin (**1b**), mhp (**1c**), mq (**1d**)]. While analogous complexes have been prepared previously from $ReH_7(PPh_3)_2$ in the case of L = pic, isoquin and mhp, the reactions between $ReH_7(PPh_3)_2$ and the ligands 2-hydroxyquinoline and 2-mercaptoquinoline are dependent on the choice of reaction solvent; the rhenium hydride complexes $ReH_4(L)(PPh_3)_2$ (L = hq or mq) and $ReH(hq)_2(PPh_3)_2$ have been isolated in a pure state. ^1H and ^{31}P NMR spectral measurements on the seven-coordinate species **1a–d** show that these compounds are stereochemically rigid at room temperature. The solution structures are in accord with the solid state structures of **1c** and **1d**, as determined by X-ray crystallography. Copyright © 1996 Elsevier Science Ltd

The reactions of the polyhydride complex $ReH_7(PPh_3)_2$ with organic acids HL (where L represents a chelating monoanionic ligand) can proceed in two steps, as represented in eqs (1) and (2). In the case of the reactions with the ligands pyridine-2-carboxylic acid (Hpic),

$$ReH_7(PPh_3)_2 + HL \rightarrow ReH_4(L)(PPh_3)_2 + 2H_2 \quad (1)$$

$$ReH_4(L)(PPh_3)_2 + HL \rightarrow ReH(L)_2(PPh_3)_2 + 2H_2 \quad (2)$$

pyridine-2,3-dicarboxylic acid (Hquin), 1-isoquinolinecarboxylic acid (Hisoquin), 2-hydroxypyridine (Hhp), 2-hydroxy-6-methylpyridine (Hmhp) and 2-mercaptopyridine (Hmp), the seven-coordinate monohydridorhenium(III) complexes $ReH(L)_2(PPh_3)_2$, where L = pic, quin, isoquin, hp, mhp or mp, are obtained [eq. (2)],[1,2] whereas the analogous reactions with 2-hydroxyquinoline (Hhq) and 2-mercaptoquinoline (Hmq) have been found to produce the tetrahydrido complexes $ReH_4(L)(PPh_3)_2$ [eq. (1)].[3] We attributed[3] the termination of these particular reactions at the first step [eq. (1)] to the increased steric bulk of the chelating hq and mq ligands. The 2-mercaptoquinoline complex $ReH_4(mq)(PPh_3)_2$ has in turn proven to be a very useful synthon for the preparation of a new class of hydrido-alkylidyne complexes of rhenium,[4,5] a reaction course which can also involve the isomerization of internal to terminal alkynes.[5]

An aspect of the aforementioned chemistry that

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has not yet been examined is the effect of changing the phosphine ligand in complexes of the type $ReH_7(PR_3)_2$ upon the reactions with organic acids and the dependence of the phosphine ligand on the chemistry of the complexes that are formed. In the present report we examine the reactions of the complex ReH_7(dppe), where dppe is the chelating phosphine $Ph_2PCH_2CH_2PPh_2$, with a representative set of organic ligands of the above type, *viz.* pyridine-2-carboxylic acid, 1-isoquinolinecarboxylic acid, 2-hydroxy-6-methylpyridine and 2-mercaptoquinoline. These results have in turn led us to re-examine the reactions of $ReH_7(PPh_3)_2$ with 2-hydroxyquinoline and 2-mercaptoquinoline from which we have established that the reaction course is solvent dependent.

EXPERIMENTAL

Starting materials

The compound ReH_7(dppe) (dppe = $Ph_2PCH_2CH_2PPh_2$) and $ReH_7(PPh_3)_2$ were synthesized by the use of a procedure similar to that described by Chatt and Coffey.[6] The tetrahydrido complexes ReH_4(hq)$(PPh_3)_2$ and ReH_4(mq)$(PPh_3)_2$ were obtained from the reactions between $ReH_7(PPh_3)_2$ and Hhq or Hmq with the use of ethanol as the reaction solvent.[3] The ligands pyridine-2-carboxylic (Hpic), 1-isoquinolinecarboxylic acid (Hisoquin), 2-hydroxy-6-methylpyridine (Hmhp), 2-hydroxyquinoline (Hhq) and 2-mercaptoquinoline (Hmq) were obtained from the Aldrich Chemical Co. The other reagents and solvents were also purchased from commercial sources and were deoxygenated by purging with dinitrogen prior to use.

Reaction procedures

All reactions were performed under dry dinitrogen.

(a) *Reactions of* ReH_7(dppe). (i) ReH(pic)(dppe) (**1a**). A mixture of ReH_7(dppe) (0.25 g, 0.42 mmol) and pyridine-2-carboxylic acid (0.22 g, 1.8 mmol) was refluxed in benzene (10 cm^3) for 3 days. The reaction mixture was allowed to cool to room temperature and a small quantity of a solid material was filtered off and washed with benzene. The combined filtrates were evaporated to dryness and the resulting residue was dissolved in a small amount of dichloromethane (5 cm^3) followed by the addition of an excess of hexanes (30 cm^3). The red solid which precipitated was filtered off, washed with hexanes and dried *in vacuo*: yield 0.325 g (93%). Found: C, 53.7; H, 4.0. Calc. for $C_{38}H_{33}N_2O_4P_2Re$: C, 55.0; H, 4.0%.

(ii) ReH(isoquin)$_2$(dppe) (**1b**). A mixture of ReH_7(dppe) (0.20 g, 0.34 mmol) and 1-isoquinolinecarboxylic acid (0.18 g, 1.04 mmol) was refluxed in benzene (20 cm^3) for 3 days. The reaction mixture was allowed to cool slowly to room temperature, whereupon a purple solid precipitated. This was filtered off, washed with benzene and dried under vacuum; yield 0.140 g (45%). Further purification can be accomplished by recrystallization from benzene/diethyl ether mixtures. Found: C, 57.9; H, 3.9; N, 2.9. Calc. for $C_{46}H_{37}N_2O_4P_2Re$: C, 59.4; H, 4.0; N, 3.0%.

(iii) ReH(mhp)$_2$(dppe) (**1c**). A mixture of ReH_7(dppe) (0.25 g, 0.42 mmol) and 2-hydroxy-6-methylpyridine (0.19 g, 1.7 mmol) was refluxed in benzene (10 cm^3) for 3 days. The reaction mixture was allowed to cool to room temperature, concentrated to low volume and then treated with an excess of heptane (30 cm^3) to precipitate any remaining starting material along with some Re_2H_8(dppe)$_2$ contaminant. This mixture was filtered off, the filtrate evaporated to dryness and the residue extracted with diethyl ether (5 × 20 cm^3). The extract was collected and evaporated to dryness. The resulting orange product was then crystallized from benzene/heptane, washed with heptane and dried *in vacuo*; yield 0.083 g (24%). Found: 57.3; H, 4.6. Calc. for $C_{38}H_{37}N_2O_2P_2Re$. C, 56.9; H, 4.6%.

(iv) ReH(mq)$_2$(dppe) (**1d**). A mixture of ReH_7(dppe) (0.20 g, 0.34 mmol) and 2-mercaptoquinoline (0.22 g, 1.36 mmol) was refluxed in benzene (10 cm^3) for 3 days. As the reaction mixture slowly cooled, a small amount of yellow solid precipitated. This was filtered off and the filtrate was evaporated to dryness. The residue that resulted was dissolved in acetone and the solution concentrated to *ca* 3 cm^3. Any excess 2-mercaptoquinoline, along with an unidentified yellow product, precipitated upon the addition of hexanes (30 cm^3) and was filtered off. Again the filtrate was evaporated to dryness. The bright red solid was washed with a small amount of hexanes and dried *in vacuo*; yield 0.092 g (30%). If necessary, further purification can be achieved by recrystallization of the complex from benzene/hexane mixtures. Found: C, 56.9; H, 4.1; N, 3.0. Calc. for $C_{44}H_{37}N_2P_2S_2Re$: C, 58.3; H, 4.1; N, 3.1%.

(b) *Reactions of* $ReH_7(PPh_3)_2$. (i) ReH(hq)$_2$$(PPh_3)_2$ (**2a**). A mixture of $ReH_7(PPh_3)_2$ (0.15 g, 0.21 mmol) and 2-hydroxyquinoline (0.075 g, 0.52 mmol) was refluxed in acetone (20 cm^3) for 3 h. The reaction mixture was allowed to cool to room temperature and a red–orange solid (0.115 g) was filtered off and dried *in vacuo*. The filtrate was evaporated to about one-half of its original volume and placed in a refrigerator overnight. A further quantity of **2a** (0.035 g) was obtained as red crystals. The combined yield of the product was 0.150 g (72%). Found: C, 64.1; H, 4.3. Calc. for $C_{54}H_{43}H_2O_2P_2Re$: C, 64.8; H, 4.3%.

(ii) Attempted synthesis of $ReH(mq)_2(PPh_3)_2$ (**2b**). The reactions of $ReH_7(PPh_3)_2$ with Hmq in refluxing ethanol afforded only $ReH_4(mq)(PPh_3)_2$ as reported previously.[3] Reactions in refluxing acetone (3 h) and benzene (30 min) also afford $ReH_4(mq)(PPh_3)_2$. Longer reaction times in benzene (> 2 h) led to decomposition of the $ReH_4(mq)$ $(PPh_3)_2$ complex, but no other hydrido species were detected under these reaction conditions.

(c) *Reactions of* $ReH_4(hq)(PPh_3)_2$. $ReH(hq)_2$ $(PPh_3)_2$ (**2a**). A quantity of $ReH_4(hq)(PPh_3)_2$ (0.05 g, 0.058 mmol) was refluxed in acetone (2 cm^3) for 3 h. The reaction mixture was then allowed to cool to room temperature and filtered. The filtrate was reduced to about one-half of its original volume under a stream of dinitrogen. The flask and its contents were cooled to 0°C overnight to afford a crop of red crystals of **2a**; yield 0.020 g (34%).

When a mixture of $ReH_4(hq)(PPh_3)_2$ (0.100 g, 0.116 mmol) and Hhq (0.017 g, 0.117 mmol) was refluxed in acetone (4 cm^3) for 3 h and then cooled to room temperature, the red–orange insoluble product **2a** precipitated; yield 0.088 g (76%).

The spectroscopic and electrochemical properties of these samples of **2a** were identical with those of the same compound prepared by the use of procedure b(i).

(d) *Reactions of* $ReH_4(mq)(PPh_3)_2$. A mixture of $ReH_4(mq)(PPh_3)_2$ (0.050 g, 0.052 mmol) and 2-mercaptoquinoline (0.010 g, 0.062 mmol) was refluxed in benzene (5 cm^3) for 1 h. The reaction mixture was filtered and the filtrate evaporated to dryness. The ^1H NMR spectrum (in $CDCl_3$) of the residue showed a very weak Re—H resonance at $\delta -4.72$ (t, $^2J_{P\text{–}H} = 69$ Hz), which is tentatively assigned to the presence of a small amount of $ReH(mq)_2(PPh_3)_2$, in addition to a much more intense feature at δ -5.26 (t, $^2J_{P\text{–}H} = 22$ Hz) due to unreacted $ReH_4(mq)(PPh_3)_2$. Longer reaction times (> 1 h) resulted in decomposition of the $ReH_4(mq)$ $(PPh_3)_2$ starting materials and loss of the resonance at $\delta -4.72$; no other hydrido species were formed as monitored by ^1H NMR spectroscopy. The $^{31}P[^1H]$ spectrum of the final reaction residue showed weak singlets at $\delta + 43.8$ (unassigned) and $\delta + 29.5$ (free Ph_3PO), and an intense singlet at $\delta -4.9$ (free Ph_3P).

No reaction was observed when mixtures of $ReH_4(mq)(PPh_3)_2$ and Hmq were heated in ethanol or methylethyl ketone.

When solutions of $ReH_4(mq)(PPh_3)_2$ in acetone were refluxed for periods of up to 7 h, the starting material was recovered unchanged.

X-ray crystallography for $ReH(mhp)_2$(dppe) (**1c**) *and* $ReH(mq)_2$(dppe) (**1d**)

Single crystals of $ReH(mhp)_2$(dppe) (**1c**) were obtained by the slow evaporation of a solution of this complex in acetone/hexanes (5 : 1 by volume) under a nitrogen atmosphere at 25°C. Single crystals of the compound $ReH(mq)_2$(dppe) (**1d**) were grown by the use of a similar procedure to that described for **1c**. The crystals used for data collection were mounted on glass fibers and the data collection was performed on an Enraf–Nonius CAD-4 computer-controlled diffractometer with graphite-monochromatized Mo-K_α radiation at 20°C. The cell contents were based on 25 reflections obtained in the range $16 < \theta < 20°$ for **1c** and $17 < \theta < 21°$ for **1d**, measured by the computer-controlled diagonal slit method of centering. Calculations were performed on a VAX computer using the Enraf–Nonius structure determination package MolEN. Lorentz and polarization corrections were applied to the data sets and an empirical absorption correction[7] was also applied.

Both compounds **1c** and **1d** crystallized in the monoclinic crystal system. The space groups, $P2_1/n$ for **1c** and $P2_1/c$ for **1d**, were determined on the basis of systematic absences observed in the data and subsequently confirmed by the successful solutions and refinements of the structures. The structures were solved by the use of the Patterson heavy-atom method, which revealed the position of the Re atoms. The remaining atoms were located in succeeding difference-Fourier syntheses. All non-hydrogen atoms in these structures were refined with anisotropic thermal parameters. The atomic position of the single hydrido ligand was obtained from the difference-Fourier syntheses for **1c** and was calculated by using the energy minimizing program HYDEX[8] for **1d**. These hydrido ligands were refined isotropically in both structures. All other hydrogen atoms were located from the difference Fourier maps and added to the structure factor calculations, but their positions were not refined. The structures were refined in full-matrix least-squares, where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(|F_o|)$. Corrections for anomalous scattering were applied to the anisotropically refined atoms.[9] The final residuals for **1c** were $R = 0.035$ ($R_w = 0.044$) and GOF = 1.01. The highest remaining peak in the final difference-Fourier map of **1c** was 0.80 e $Å^3$. The final residuals for **1d** were $R = 0.033$ ($R_w = 0.040$) and GOF = 0.90. The

Table 1. Crystallographic data for ReH(mhp)$_2$(dppe) (**1c**) and ReH(mq)$_2$(dppe) (**1d**)

	1c	**1d**
Chemical formula	$ReP_2O_2N_2C_{38}H_{37}$	$ReS_2P_2N_2C_{44}H_{37}$
fw	801.88	906.07
Space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	12.412(5)	18.841(5)
b (Å)	18.660(4)	11.966(3)
c (Å)	15.728(5)	18.211(5)
β (°)	112.18(3)	108.81(2)
V (Å^3)	3373(4)	3886(4)
Z	4	4
T (°C)	20	20
λ(Mo-K_α) (Å)	0.71073	0.71073
ρ_{calc} (cm^3)	1.579	1.548
μ(Mo-K_α) (cm^{-1})	37.79	33.86
Transmission coefficient: max, min	1.00–0.62	0.67–0.42
R^a	0.035	0.033
$R_w{}^b$	0.044	0.040
GOF	1.011	0.903

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

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

highest remaining peak in the final difference-Fourier map of **1d** was 0.85 e Å^3. The basic crystallographic parameters for compounds **1c** and **d** are listed in Table 1. Important intramolecular bond distances and angles for these two complexes are given in Table 2. Full details of the crystal data, data collection parameters and all structural parameters are available as supplementary material.

Physical measurements

IR spectra were recorded as Nujol mulls between NaCl or KBr plates on a Perkin–Elmer 1800 FT–IR spectrometer. ^1H NMR spectra were obtained with the use of either a Varian Gemini-200 or a GE QE-300 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. $^{31}P[^1H]$ and ^{31}P NMR spectra were recorded with the use of a Varian XL-200A spectrometer. Resonances were referenced externally to a sample of H_3PO_4. An internal lock was used. Electrochemical measurements were carried out with use of a BAS Inc. Model CV-27 instrument in conjunction with a BAS Model RXY recorder and were recorded 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 25°C and were uncorrected for junction potentials. Under our experimental conditions $E_{1/2} = 0.47$ V versus Ag/AgCl for the ferrocenium/ferrocene couple. Conductivity measurements were obtained on acetone solutions of the complexes (*ca* 1×10^{-3} M) by the use of a YSI Model 35 conductance meter.

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

RESULTS AND DISCUSSION

The reactions of ReH$_7$(dppe) with benzene solutions of various organic acids (HL) proceed as shown in eq. (3) to afford mononuclear, seven-coordinate, monohydridorhenium(III) complexes of stoichiometry ReH(L)$_2$(dppe) (**1**)

$$\mathrm{ReH_7(dppe) + 2HL \xrightarrow[\text{reflux, 3 days}]{C_6H_6} ReH(L)_2(dppe) + 4H_2} \quad (3)$$

$$\mathrm{L = pic\ (\mathbf{1a})}$$
$$\mathrm{= isoquin\ (\mathbf{1b})}$$
$$\mathrm{= mhp\ (\mathbf{1c})}$$
$$\mathrm{= mq\ (\mathbf{1d}).}$$

In contrast to the analogous reactions of ReH$_7$(PPh$_3$)$_2$ with these same organic ligands, which proceed quite rapidly (30 min or less) in ethanol, acetone or THF solvents,[1,2] the reactions of ReH$_7$(dppe) are much more sluggish and the

Table 2. Comparison of selected important bond distances (Å) and angles (°) for **1c** and **d**[a,b]

1c		**1d**	
Re—P(1)	2.293(2)	Re—P(2)	2.337(2)
Re—P(2)	2.328(2)	Re—P(1)	2.332(2)
Re—O(42)	2.164(6)	Re—S(1)	2.533(2)
Re—O(32)	2.120(6)	Re—S(2)	2.455(2)
Re—N(41)	2.126(6)	Re—N(11)	2.166(6)
Re—N(31)	2.155(7)	Re—N(21)	2.191(6)
Re—H	1.50(6)	Re—H	1.57(6)
P(1)—Re—P(2)	80.55(8)	P(2)—Re—P(1)	79.76(7)
P(1)—Re—O(32)	110.3(2)	P(2)—Re—S(2)	110.05(7)
P(1)—Re—O(42)	96.6(2)	P(2)—Re—S(1)	92.93(7)
P(1)—Re—N(31)	171.8(2)	P(2)—Re—N(21)	173.1(2)
P(1)—Te—N(41)	90.5(2)	P(2)—Re—N(11)	85.9(2)
P(1)—Re—H	103(2)	P(2)—Re—H	109(2)
P(2)—Re—O(32)	83.5(2)	P(7)—Re—S(2)	85.47(7)
P(2)—Re—O(42)	162.5(2)	P(1)—Re—S(1)	163.93(7)
P(2)—Re—N(31)	95.0(2)	P(1)—Re—N(21)	103.7(2)
P(2)—Re—N(41)	135.6(2)	P(1)—Re—N(11)	128.2(2)
P(2)—Re—H	60(2)	P(1)—Re—H	71(2)
O(32)—Re—O(42)	81.3(2)	S(2)—Re—S(1)	83.63(7)
O(32)—Re—N(31)	62.1(3)	S(2)—Re—N(21)	64.7(2)
O(32)—Re—N(41)	139.3(2)	S(2)—Re—N(11)	145.6(2)
O(32)—Re—H	125(2)	S(2)—Re—H	129(2)
O(42)—Re—N(31)	85.6(3)	S(1)—Re—N(21)	82.2(2)
O(42)—Re—N(41)	61.3(2)	S(1)—Re—N(11)	64.8(2)
O(42)—Re—H	137(2)	S(1)—Re—H	125(2)
N(31)—Re—N(41)	97.4(3)	N(21)—Re—N(11)	96.3(2)
N(31)—Re—N	80(2)	N(21)—Re—H	78(2)
N(41)—Re—H	81(2)	N(11)—Re—H	67(2)

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

[b] The analogous bond distances and angles for **1c** and **d** are compared (see Figs 1 and 2).

yields quite varied. This difference reflects the much greater stability of ReH$_7$(dppe) compared with ReH$_7$(PPh$_3$)$_2$, both to the loss of H$_2$ upon protonation by the acidic function of HL and reductive elimination of H$_2$ upon coordination of the neutral N donor atom of HL. The relative inertness of ReH$_7$(dppe) compared with ReH$_7$(PPh$_3$)$_2$ under thermal reaction conditions has been noted previously.[6,10,11]

The highly coloured (orange–purple) complexes **1a–d** are soluble in a range of solvents (e.g. dichloromethane, acetone and benzene) and solutions of **1a** and **1c** in acetone (*ca* 1×10^{-3} M) were found to be essentially non-conducting, with Λ_m values close to 1 $\Omega^{-1}\,\mathrm{cm}^2\,\mathrm{mol}^{-1}$. The IR spectra of Nujol mulls of **1a–d** showed a well-defined ν(Re—H) mode only in the cases of **1a** (2044 m, cm^{-1}) and **c** (2016 m-w, cm^{-1}); the variability in the intensity of this ν(Re—H) band has been documented in similar systems.[1] All four complexes have electrochemical properties very similar to those previously reported for the corresponding triphenylphosphine complexes ReH(L)$_2$(PPh$_3$)$_2$.[1,2] Cyclic voltammetric measurements on solutions of the complexes in TBAH/CH$_2$Cl$_2$ (0.1 M) revealed the existence of two accessible oxidations (Table 3), the first of which approached reversibility in the case of **1c** and **d**, but the second one was irreversible in all cases.

Single-crystal X-ray structure determinations on two of the four complexes of the type ReH(L)$_2$(dppe) were carried out. The ORTEP representations of the structures of **1c** (L = mhp) and **d** (L = mq) are shown in Figs 1 and 2. The crystallographic data and important structural parameters are given in Tables 1 and 2.

Table 3. Electrochemical properties of ReH(L)$_2$(dppe)

	CV half-wave potentials[a] (V)		
Complex	$E_{p,a}$	$E_{1/2}$(ox)	$E_{p,c}$
ReH(pic)$_2$(dppe) (**1a**)	+1.39	+0.38[b]	
ReH(isoquin)$_2$(dppe) (**1b**)	+1.30	+0.33[b]	−1.59[c]
ReH(mhp)$_2$(dppe) (**1c**)	+1.28	+0.07(70)	
ReH(mq)$_2$(dppe) (**1d**)	+1.06[d]	+0.05(140)	

[a] Measured on 0.1 M TBAH/CH$_2$Cl$_2$ solutions and referenced to the Ag/AgCl electrode, with a scan rate of 200 mV s^{-1} at a Pt-bead electrode. Numbers in parentheses are the $E_{p,a}-E_{p,c}$ values in mV for those processes which are reversible or approach reversibility ($i_{p,a} \approx i_{p,c}$).

[b] $E_{p,a}$ value; this process has a coupled reduction process at $E_{p,c} = 0.00$ V ($i_{p,a} > i_{p,c}$).

[c] This reduction has a coupled oxidation at $E_{p,a} = -1.51$ ($i_{p,a} < i_{p,c}$).

[d] This oxidation is followed by a process at $E_{p,a} = +1.26$ V, which is in turn coupled to a reduction at $E_{p,c} \approx +1.12$ V.

The structures of **1c** and **d** are very similar to one another and in turn resemble the previously determined structures of the neutral monohydride ReH(acac)$_2$(PPh$_3$)$_2$(acac = acetylacetonate) and the 17-electron species [ReH(acac)$_2$(PPh$_3$)$_2$]PF$_6$ and [ReH(pic)$_2$(PPh$_3$)$_2$]PF$_6$.[1] The structures of **1c**, **d** and ReH(acac)$_2$(PPh$_3$)$_2$ can be represented in terms of the "idealized" distorted pentagonal-bipyramidal geometries shown in **I** and **II**. These structures differ primarily in terms of whether both P donor atoms

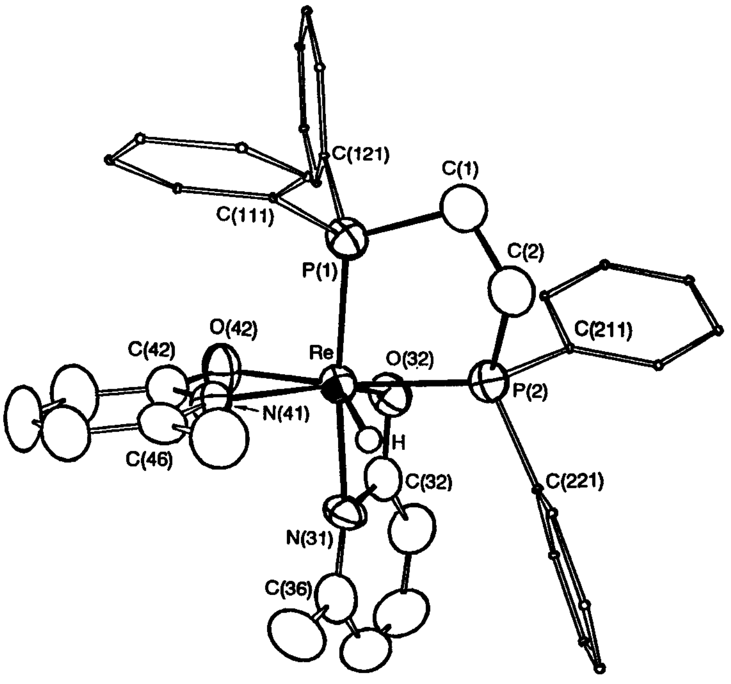
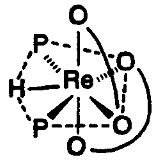


Fig. 1. ORTEP representation of the structure of the ReH(mhp)$_2$(dppe) molecule (**1c**). The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppe ligand and the hydrido ligand atom, which are circles of arbitrary radius.



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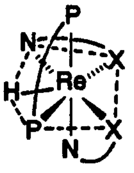

II

O - O = acac; P = PPh$_3$

X = O or S; P - P = dppe

are in the "pentagonal plane" (**I**) or one is in the plane and one occupies an axial site (**II**). This structural description is an approximation since with such disparate sets of ligands there is an appreciable deviation from any ideal geometry. While the axial N—Re—P ligand unit approaches linearity [171.8(2)° for **1c** and 173.1(2)° for **1d**], there are quite large distortions within the pentagonal plane. Least-squares planes calculations for **1c** and **d** show that the displacements (in Å) from this plane are as follows:

1c Re 0.160(0), P(2) 0.359(2), O(32) −0.277(6), O(42) 0.178(6), N(41) 0.022(6), H −0.44(6);

1d Re 0.149(0), P(1) 0.472(2), S(2) −0.309(2), S(1) 0.219(2), N(11) 0.074(6), H −0.66(6).

In the two structures of type **II** it is the P atom of the non-hydrido ligand atom set which shows the largest deviation from the plane; this is presumably a consequence of the bite of the chelating dppe ligand (the P—Re—P angle is close to 80° in both structures). Angular disparities within the plane are in part a result of the relatively small bite of the chelating mhp and mq ligands, which lie entirely within the pentagonal plane; the angles are 61.3(2)° [for O(42)—Re—N(41) of **1c**] and 64.8(2)° [for S(1)—Re—N(11) of **1d**]. The other angles

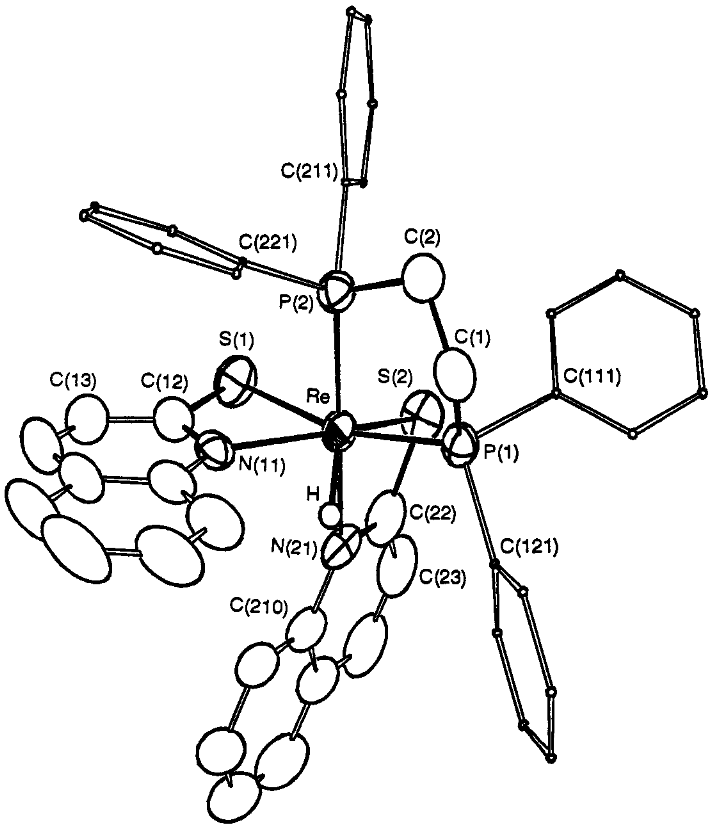

Fig. 2. ORTEP representation of the structure of the ReH(mq)$_2$(dppe) (**1d**). The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms of the dppe ligand and the hydrido ligand atom, which are circles of arbitrary radius.

within this plane which do not involve the hydrido ligand are in the range 81.3–85.5° (Table 2).

The sets of Re—P distances for **1c**, **d** and $ReH(acac)_2(PPh_3)_2$[1] occur within the relatively narrow range 2.29–2.34 Å, while the Re—O and Re—N distances for the chelating mhp ligands of **1c** are on average a little longer (2.12–2.16 Å) than the comparable distances found in the structures of the two eight-coordinate geometrical isomers of $[ReH_2(mhp)_2(PPh_3)_2]PF_6$ (2.10–2.13 Å).[2] We also note that in the structure of **1d** (Fig. 2) there is a rather close contact between the hydrogen atom which is bound to the carbon atom C(19) of one of the mq rings and the single hydrido ligand. Within the unit C(19)—H(191) ··· H—Re, the distance H(191) ··· H is *ca* 2.00 Å; the angles C(19)—H(191) ··· H and Re—H ··· H(191) are 120 and 132°, respectively. These parameters may signal the presence of an unconventional intramolecular three-centre M—H ··· H—C hydrogen bond similar to the type of M—H ··· H—X interaction (X = O, N or C) reported by Crabtree[12] and Morris.[13]†

The ^1H, $^{31}P[^1H]$ and ^{31}P NMR spectra of **1a**–**d** closely resemble one another and are in accord with all four complexes possessing very similar structures. The important ^1H and $^{31}P[^1H]$ NMR spectroscopic data are presented in Table 4. A major difference between the properties of $ReH(L)_2(dppe)$ (**1**) and the analogous triphenylphosphine complexes $ReH(L)_2(PPh_3)_2$ is the stereochemical rigidity of the former and fluxional nature of the latter as probed by ^1H and ^{31}P NMR spectroscopy. In the case of **1a**–**d** this is reflected by a doublet-of-doublets for the Re—*H* resonance, compared with a binomial triplet in the ^1H NMR spectra of $ReH(L)_2(PPh_3)_2$.[1,2] In the $^{31}P[^1H]$ NMR spectra of **1a**–**d**, there are two separate resonances for the chemically inequivalent P atoms, while the corresponding spectra of $ReH(L)_2(PPh_3)_2$ show only a singlet at room temperature. The NMR spectral results for the four complexes of type **1** are fully in accord with the solid-state structures of **1c** and **d** as determined by X-ray crystallography. The corresponding ^{31}P spectra of the four complexes show that the most upfield resonance of the two broadens upon proton coupling, but reveals no observable splitting, while the downfield resonance (that between $\delta +66$ and $+51$) splits into a doublet (J_{P-H} = 91, 92, 86 and 89 Hz for **1a**, **b**, **c** and **d**, respectively). This result is consistent with the largest P—H coupling involving the P atom that is in the "axial" position in the approximately pentagonal bipyramidal structures, i.e. that showing the largest P—Re—H angle [P(1) of **1c** (Fig. 1) and P(2) of **1d** (Fig. 2)].

Although the complexes $ReH(pic)_2(dppe)$ (**1a**), $ReH(isoquin)_2(dppe)$ (**1b**) and $ReH(mhp)_2(dppe)$ (**1c**) resemble those of the type $ReH(L)_2(PPh_3)_2$, which have been prepared previously from $ReH_7(PPh_3)_2$,[1] the reaction of $ReH_7(dppe)$ with Hmq to afford $ReH(mq)_2(dppe)$ (**1d**) can be contrasted with the formation of $ReH_4(mq)(PPh_3)_2$ from the reaction of the Hmq ligand with $ReH_7(PPh_3)_2$.[3,4] We had originally proposed[3] that the latter reaction might terminate at the "intermediate" stage of $ReH_4(mq)(PPh_3)_2$ [see eq. (1)] because of steric factors, but the formation of $ReH(mq)_2(dppe)$ calls this conclusion into question. Accordingly, we have reinvestigated the reactions of $ReH_7(PPh_3)_2$ with both 2-hydroxyquinoline (Hhq) and 2-mercaptoquinoline (Hmq).

Our previous procedure for preparing $ReH_4(hq)(PPh_3)_2$ and $ReH_4(mq)(PPh_3)_2$ involved the reactions of $ReH_7(PPh_3)_2$ with Hhq and Hmq, respectively, in refluxing ethanol or THF.[3] We have confirmed that under these reaction conditions $ReH(hq)_2(PPh_3)_2$ and $ReH(mq)_2(PPh_3)_2$ are not formed. However, when acetone (or methylethyl ketone) is used as the reaction solvent $ReH_7(PPh_3)_2$ reacts with an excess of Hhq under reflux conditions (3 h) to afford $ReH(hq)_2(PPh_3)_2$ (**2a**) in good yield via the intermediacy of $ReH_4(hq)(PPh_3)_2$. Under these same conditions the reaction of $ReH_7(PPh_3)_2$ with Hmq in refluxing acetone led only to the formation of $ReH_4(mq)(PPh_3)_2$. Similar results were obtained when the latter reaction was carried out in refluxing benzene for 30 min, but longer reaction times led to the decomposition of $ReH_4(mq)(PPh_3)_2$ to give non-hydrido species.

The 2-hydroxyquinoline complex **2a** is also formed in good yield when $ReH_4(hq)(PPh_3)_2$ is reacted with an equivalent of Hhq in refluxing acetone and, surprisingly, when $ReH_4(hq)(PPh_3)_2$ is refluxed in acetone *in the absence of Hhq*. The latter reaction course must involve the sacrifice of one-half of the $ReH_4(hq)(PPh_3)_2$ starting complex to provide the additional 2-hydroxyquinoline ligand, since we have shown that disproportionation of $ReH_4(hq)(PPh_3)_2$ to give a mixture of $ReH(hq)_2(PPh_3)_2$ and $ReH_7(PPh_3)_2$ does not occur. Evidence for the decomposition of a portion of the $ReH_4(hq)(PPh_3)_2$ under these conditions is provided by the IR spectrum of the reaction residue which is formed following the isolation of **2a** (ν(Re—O) at 910 cm^{-1} due to $[ReO_4]^-$) and by its ^1H NMR spectrum (which showed the presence of free PPh_3).

All attempts to prepare a pure sample of

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† We thank one of the reviewers for drawing our attention to the short intramolecular H(191) ··· H contact.

Table 4. NMR spectral data for $ReH(L)_2(dppe)$

	Chemical shift, δ			
	^1H NMR[a]			
Complex	Re—H[b]	—CH_2CH_2— of dppe[c]	L[d]	$^{31}P[^1H]$NMR[a]
1a	-2.91 (dd, 91, 6)	$+3.00$ to $+2.22$ (m, 4H)[e]	[f]	$+62.4$(s), $+38.2$(s)
1b	-2.75 (dd, 92, 6)	$+3.10$ to $+2.40$ (m, 4H)[e]	[g]	$+59.6$(s), $+36.2$(s)
1c	-3.46 (dd, 86, 8)	$+3.47$ (dm, 1H), $+2.88$ (dm, 1H), $+2.37$ (m 1H), ~ 1.80 (m, 1H)	$+6.29$ (d, 1H), $+5.84$ (d, 1H), $+5.75$ (d, 1H), $+5.59$ (d, 1H), $+1.84$ (s, 3H), $+1.36$ (s, 3H)[h]	$+66.1$(s), $+36.2$(s)
1d	-5.45 (dd, 89, 9)	$+3.30$ (dm, 1H), $+2.88$ (m, 1H), $+2.80$ (m, 1H), $+2.12$ (m, 1H)	[i]	$+51.0$ (d),[j] $+45.9$ (d)[j]

[a] Spectra recorded in CD_2Cl_2.

[b] $J_{P\text{-}H}$ (Hz) given in parentheses. Abbreviation: dd = doublet-of-doublets.

[c] Abbreviations: m = multiplet, dm = doublet-of-multiplets.

[d] Resonances for L = mhp only are given. Those for pic, isoquin and mq overlap with the phenyl resonances of dppe; see footnotes *f*, *g* and *i*.

[e] Overlapping multiplets.

[f] Overlapping multiplets in the range $\delta +8.7$ to $+6.4$ for the aromatic ring Hs of pic and dppe.

[g] Overlapping multiplets in the range $\delta +9.7$ to $+6.4$ for the aromatic ring Hs of isoquin and dppe.

[h] The resonance for the H atom at the 4-position of the pyridyl ring of each of the two mhp ligands is overlapped by the phenyl ring resonances of the dppe ligands ($\delta +8.0$ to $+6.7$).

[i] Overlapping multiplets in the range $\delta +8.0$ to $+6.2$ for the aromatic ring Hs of mq and dppe.

[j] These resonances have the appearance of doublets ($J_{P\text{-}P'}$ *ca* 8–9 Hz).

$ReH(mq)_2(PPh_3)_2$ (**2b**) starting from $ReH_7(PPh_3)_2$ and $ReH_4(mq)(PPh_3)_2$ were unsuccessful. It seems to be a rather unstable compound. The only evidence we have for the formation of **2b** is as a minor component of the mixture of products which is formed upon reacting $ReH_4(mq)(PPh_3)_2$ with Hmq in refluxing benzene (see Experimental). Its NMR spectral properties appear to be similar to those of **2a** (*vide infra*) with a Re—*H* resonance at $\delta -4.72$ (t, $^2J_{P\text{-}H} = 69$ Hz).

The properties of the hq complex **2a** are similar to those of other complexes of the type $ReH(L)_2(PPh_3)_2$.[1] It forms a non-conducting solution in acetone and displays a well-defined ν(Re—H) mode at 2084 cm^{-1} in its Nujol mull IR spectrum. Cyclic voltammetric measurements on solutions of this complex in 0.1 M $Bu_4{}^nNPF_6/CH_2Cl_2$ revealed the existence of two accessible oxidations with $E_{1/2}(ox) = -0.03$ V and $E_p \approx +1.20$ V versus Ag/AgCl; for the first process $\Delta E_{p,a}$ (i.e. $E_{p,a}-E_{p,c}$) = 160 mV at a scan rate of 200 mV s^{-1}. The ^1H NMR spectrum of **2a** (recorded in $CDCl_3$) showed a Re—*H* resonance at $\delta -3.23$ (t, $^2J_{P\text{-}H} = 66$ Hz), while the $^{31}P[^1H]$ displayed a singlet at $\delta +29.5$; the latter resonance splits into a doublet ($^2J_{P\text{-}H} = 66$ Hz) in the ^{31}P spectrum.

The reason for the dependence of the course of reactions between $ReH_7(PPh_3)_2$ and Hhq or Hmq upon the choice of reaction solvent is not entirely clear. We find no evidence that the solvents themselves react with any of the hydrido starting materials or products. it may be that the extent of reaction [eq. (1) or (2)] is influenced by a combination of factors such as reflux temperature and solvent polarity.

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