Protonation Reactions of the Mononuclear Rhenium Polyhydride Complexes $[ReH_7(PPh_3)_2]$, $[ReH_5(PPh_3)_2L]$ (L = Unidentate Ligand), and $[ReH_4I(PPh_3)_3]$

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Protonation of the rhenium polyhydride complexes $[ReH_7(PPh_3)_2]$, $[ReH_5(PPh_3)_2L]$ [L = pyridine (py), $NH_2(C_6H_{11})$, or NH_2Bu^t], or $[ReH_4I(PPh_3)_3]$ with $HBF_4{\cdot}Et_2O$ in acetonitrile or propionitrile leads to the seven-co-ordinate complexes $[ReH(NCR)_3(PPh_3)_2L][BF_4]_2$ [R = Me or Et; L = RCN, PPh_3, py, $NH_2(C_6H_{11})$, or NH_2Bu^t]. Their ^1H and ^{31}P-$\{^1H\}$ n.m.r. spectral properties are consistent with pentagonal-bipyramidal or face-capped octahedral geometries in solution. These complexes show a reversible one-electron oxidation in the potential range +1.0 to +1.6 V (*vs.* Ag–AgCl) in 0.1 mol dm^{-3} NBu_4PF_6–CH_2Cl_2, and an irreversible reduction below −1.4 V. The substitution chemistry of $[ReH(NCR)_4(PPh_3)_2][BF_4]_2$ has been investigated and the mixed-phosphine complexes $[ReH(NCR)_3(PPh_3)(dppe)][BF_4]_2$ (R = Me or Et; dppe = $Ph_2PCH_2CH_2PPh_2$) isolated as the initial reaction products. These species have been characterized by i.r. and n.m.r. spectroscopy and by cyclic voltammetry. Further reaction with dppe leads to reductive substitution and the formation of $[Re(NCR)_2(dppe)_2]BF_4$.

Recently we investigated the reactivity of the dirhenium polyhydride complex $[Re_2(\mu\text{-}H)_4H_4(PPh_3)_4]$ towards HBF_4, CPh_3PF_6 (used here as an oxidizing agent and as a hydride-ion abstractor), alkyl isocyanides, and halogenocarbons.[1–3] This work was initiated with the object of devising procedures for the activation of this relatively inert compound and led, amongst other things, to the discovery of various compounds that contain the novel paramagnetic $[Re_2H_8]^+$, $[Re_2H_7]^{2+}$, and $[Re_2H_5]^{2+}$ cores.[1–3] During the course of these studies we also examined the reactions of mononuclear $[ReH_7(PR_3)_2]$ (PR_3 = PPh_3 or $PEtPh_2$) and complexes of the type $[ReH_5(PPh_3)_2L]$[L = PPh_3, PEt_2Ph, pyridine (py), piperidine, or cyclohexylamine] with halogenocarbons[3] and with isocyanide ligands,[4,5] and explored their electrochemical redox properties.[4] In the present report, we describe the behaviour of $[ReH_5(PPh_3)_2L]$ upon protonation (using $HBF_4{\cdot}Et_2O$) which affords a route to cationic seven-co-ordinate monohydrido-complexes of rhenium(III). For a preliminary report of some of these results see ref. 1.

Results and Discussion

Monohydrido-complexes of the Type $[ReH(NCR)_3(PPh_3)_2L][BF_4]_2$ [L = RCN, PPh_3, py, $NH_2(C_6H_{11})$, *or* NH_2Bu^t].—The addition of $HBF_4{\cdot}Et_2O$ to acetonitrile or propionitrile slurries of the mononuclear rhenium polyhydride complexes $[ReH_7(PPh_3)_2]$ and $[ReH_5(PPh_3)_2L]$ [L = py, $NH_2(C_6H_{11})$, or NH_2Bu^t] leads to the formation of monohydridorhenium(III) complexes $[ReH(NCR)_3(PPh_3)_2L][BF_4]_2$ [R = Me or Et; L = RCN, py, $NH_2(C_6H_{11})$, or NH_2Bu^t] in good yield (usually >65%) with the concomitant loss of H_2 gas (g.c. analysis). The usual sluggish thermal chemistry of the rhenium pentahydrides[4–8] is in marked contrast to these facile protonation reactions [equations (1) and (2)], which show a resemblance to the behaviour of other transition-metal polyhydrides. Thus, acetonitrile slurries of $[MoH_4(PR_3)_4]$ (PR_3 = PMe_2Ph or $PMePh_2$)[9] and $[WH_6(PMe_2Ph)_3]$[10] give $[MoH_2(NCMe)_2(PMe_2Ph)_4][BF_4]_2$ and $[MH_2(NCMe)_3(PMe_2Ph)_3][BF_4]_2$ (M = Mo or W) upon acidolysis with $HBF_4{\cdot}Et_2O$.[9,10] Related behaviour is seen in the acidolysis of osmium and iridium polyhydrides.[10,11] Our isolation of the complexes $[ReH(NCR)_3(PPh_3)_2L][BF_4]_2$ [L = RCN, py, $NH_2(C_6H_{11})$, or NH_2Bu^t] expands considerably the range of seven-co-ordinate, *cationic* monohydrido-complexes of rhenium(III) that are known. An interesting example of a slightly different type has recently been described by Wilkinson and co-workers,[12] *viz.* the monocationic species $[ReH(Cl)(PMe_3)_5]BF_4$ prepared by the interaction of $[ReCl(PMe_3)_5]$ with HBF_4 or CPh_3BF_4.

$$[ReH_7(PPh_3)_2] + 2HBF_4 + 4RCN \longrightarrow [ReH(NCR)_4(PPh_3)_2][BF_4]_2 + 4H_2 \quad (1)$$

$$[ReH_5(PPh_3)_2L] + 2HBF_4 + 3RCN \longrightarrow [ReH(NCR)_3(PPh_3)_2L][BF_4]_2 + 3H_2 \quad (2)$$

Since our preliminary report describing the formation of the acetonitrile complexes $[ReH(NCMe)_3(PPh_3)_2L][BF_4]_2$ [L = MeCN, py, or $NH_2(C_6H_{11})$],[1] Crabtree *et al.*[10] have reported the preparation of $[ReH(NCMe)_4(PPh_3)_2][BF_4]_2$ (the same complex as that isolated by ourselves), and the dimethylphenylphosphine derivative $[ReH(NCMe)_3(PMe_2Ph)_3][BF_4]_2$, the PPh_3 analogue of which has been prepared in this study. Thus, the reaction of $[ReH_4I(PPh_3)_3]$ with $HBF_4{\cdot}Et_2O$ in a solution of the appropriate nitrile affords $[ReH(NCR)_3(PPh_3)_3][BF_4]_2$ (R = Me or Et; 80—90% yield) according to equation (3).

$$[ReH_4I(PPh_3)_3] + 2HBF_4 + 3RCN \longrightarrow [ReH(NCR)_3(PPh_3)_3][BF_4]_2 + 2H_2 + HI \quad (3)$$

Surprisingly, the use of $[ReH_5(PPh_3)_3]$ in place of $[ReH_4I(PPh_3)_3]$ failed to give $[ReH(NCR)_3(PPh_3)_3]^{2+}$.

The substitutional lability of one of the nitrile ligands of $[ReH(NCR)_4(PPh_3)_2][BF_4]_2$ was demonstrated by the conversion of $[ReH(NCMe)_4(PPh_3)_2][BF_4]_2$ into $[ReH(NCMe)_3(PPh_3)_2L][BF_4]_2$ (L = py or PPh_3). The opposite behaviour was shown by the reaction of $[ReH(NCEt)_3(PPh_3)_3][BF_4]_2$ with propionitrile to give $[ReH(NCEt)_4(PPh_3)_2][BF_4]_2$.

The Nujol-mull i.r. spectra of the monohydrides $[ReH(NCR)_3(PPh_3)_2L][BF_4]_2$ [L = RCN, PPh_3, py, $NH_2(C_6H_{11})$, or NH_2Bu^t] show weak bands due to ν(C≡N) of the nitrile ligands (Table 1), but we were unable to locate the ν(Re–H) modes. Additionally, ν(B–F) of the BF_4^- anions was observed at *ca.* 1 060 cm^{-1} for all complexes, and certain other characteristic modes were clearly discernible [*e.g.* ν(N–H) of the $NH_2(C_6H_{11})$ and NH_2Bu^t complexes at 3 285—3 281w and 3 253—3 239w cm^{-1}].

The ^1H n.m.r. spectra (in CD_2Cl_2 or $CDCl_3$) showed resonances for the co-ordinated organic ligands that had the correct relative intensities. In the case of $[ReH(NCR)_4(PPh_3)_2][BF_4]_2$ and $[ReH(NCR)_3(PPh_3)_2L][BF_4]_2$ [L = py, $NH_2(C_6H_{11})$, or NH_2Bu^t] the presence of chemically and magnetically inequivalent nitrile ligands was evident (see Table 1). The intensity ratios were 1 : 1 and 2 : 1, respectively, for these two groups of complexes. This observation is consistent with the presence of rigid seven-co-ordinate structures in solution, at least insofar as the RCN ligands are concerned. For $[ReH(NCMe)_4(PPh_3)_2][BF_4]_2$ this result is at variance with ^1H n.m.r. data reported previously,[10] where only one singlet (at δ 2.36 p.p.m.) was attributed to the co-ordinated acetonitrile. However, the consistency of the n.m.r. data for a range of such complexes (Table 1) gives us confidence that our observations are correct. The Re–H resonances of $[ReH(NCR)_3(PPh_3)_2L][BF_4]_2$ [L = RCN, py, $NH_2(C_6H_{11})$, or NH_2Bu^t] appeared as triplets or doublets of doublets [*J*(P–H) *ca.* 65 Hz]. Representative ^1H n.m.r. studies over different temperature ranges, carried out on samples of $[ReH(NCMe)_4(PPh_3)_2][BF_4]_2$ (25 to −55 °C), $[ReH(NCEt)_3(PPh_3)_2(py)][BF_4]_2$ (25 to −55 °C), and $[ReH(NCEt)_3(PPh_3)_2(NH_2Bu^t)][BF_4]_2$ (25 to −74 °C), revealed no significant temperature dependence of the spectra other than of some minor chemical shifts. The room-temperature ^{31}P-{^1H} n.m.r. spectra (in $CDCl_3$) consist of singlets in the case of $[ReH(NCR)_4(PPh_3)_2][BF_4]_2$ and $[ReH(NCR)_3(PPh_3)_2(NH_2Bu^t)][BF_4]_2$, and two doublets [*J*(P–P) *ca.* 4—5 Hz] for the py and $NH_2(C_6H_{11})$ complexes of the type $[ReH(NCR)_3(PPh_3)_2L][BF_4]_2$ (see Table 1).

The tris(triphenylphosphine) complexes $[ReH(NCR)_3(PPh_3)_3][BF_4]_2$ have simpler n.m.r. spectra than those of the aforementioned types, with a quartet for the Re–H resonance in each case, equivalent RCN ligands, and a singlet in the ^{31}P-{^1H} n.m.r. spectra (Table 1). The spectrum of $[ReH(NCEt)_3(PPh_3)_3][BF_4]_2$ is essentially unchanged over the range 25 to −55 °C, with the exception of the splitting of the CH_2 quartet of the propionitrile ligands into an ABX_3 pattern due to restricted rotation about the C–C bond as the temperature is lowered. The spectral properties imply either that these two complexes are fluxional on the n.m.r. time-scale or that they possess a rigid capped-octahedral structure in solution, with the hydride ligand capping a trigonal face comprising the three PPh_3 ligands. While we are confident of these structural possibilities for $[ReH(NCR)_3(PPh_3)_3][BF_4]_2$, we are somewhat less so in the

Table 1. I.r. and ^1H and ^{31}P-{^1H} n.m.r. spectroscopic properties of monohydridorhenium(III) complexes

	^1H n.m.r. (δ[a])			
Complex	Re–H[b]	RCN	^{31}P-{^1H} N.m.r. (δ[c,d])	I.r. (cm^{-1}),[e] ν(C≡N)
$[ReH(NCMe)_4(PPh_3)_2][BF_4]_2$	−4.53 (t, 64.8)	2.17 (s, CH_3, 6 H) 2.47 (s, CH_3, 6 H)	23.12 (s)	2 265w, 2 294vw, 2 322vw
$[ReH(NCEt)_4(PPh_3)_2][BF_4]_2$	−4.44 (t, 63.0)	0.71 (t, CH_3, 6 H), 2.91 (q, CH_2, 4 H) 1.01 (t, CH_3, 6 H), 2.45 (q, CH_2, 4 H)	23.42 (s)	2 249w, 2 290vw
$[ReH(NCPh)_4(PPh_3)_2][BF_4]_2$	−4.09 (t, 62.4)[c]			2 197m, 2 251w
$[ReH(NCMe)_3(PPh_3)_2(py)][BF_4]_2$	−4.48 (t, 64.8)[c]	2.02 (s, CH_3, 3 H)[c] 2.53 (s, CH_3, 6 H)	25.45 (d, 4.1), 23.20 (d, 4.1)	2 253m–w
$[ReH(NCEt)_3(PPh_3)_2(py)][BF_4]_2$	−4.35 (dd, 62.8, 65.5)	0.57 (t, CH_3, 6 H), 2.96 (m,[f] CH_2, 4 H) 0.76 (t, CH_3, 3 H), 2.34 (q, CH_2, 2 H)	25.53 (d, 4.1), 23.38 (d, 4.1)	2 232w
$[ReH(NCMe)_3(PPh_3)_2\{NH_2(C_6H_{11})\}][BF_4]_2$	−5.26 (dd, 62.4, 66.8)	2.15 (s, CH_3, 3 H) 2.52 (s, CH_3, 6 H)	23.50 (d, 4.3), 21.09 (d, 4.3)	2 253w
$[ReH(NCEt)_3(PPh_3)_2\{NH_2(C_6H_{11})\}][BF_4]_2$	−5.20 (dd, 62.0, 67.2)	0.77 (t, CH_3, 6 H), 2.95 (q, CH_2, 4 H) 1.05 (t, CH_3, 3 H), 2.56 (q, CH_2, 2 H)	23.44 (d, 5.0), 21.22 (d, 5.0)	2 244w
$[ReH(NCMe)_3(PPh_3)_2(NH_2Bu^t)][BF_4]_2$	−4.50 (t, 64.4)	2.20 (s, CH_3, 3 H) 2.46 (s, CH_3, 6 H)	22.53 (s)	2 254w
$[ReH(NCEt)_3(PPh_3)_2(NH_2Bu^t)][BF_4]_2$	−4.96 (t, 73.2)[c]	0.75 (t, CH_3, 6 H), 2.78 (q, CH_2, 4 H)[c] 1.04 (t, CH_3, 3 H), 2.49 (q, CH_2, 2 H)	22.60 (s)	2 236w
$[ReH(NCMe)_3(PPh_3)_3][BF_4]_2$	−2.08 (q, 63.2)[c]	1.99 (s, CH_3, 9 H)[c]	15.56 (s)	2 288vw
$[ReH(NCEt)_3(PPh_3)_3][BF_4]_2$	−2.00 (q, 54.6)	0.65 (t, CH_3, 9 H), 2.49 (q, CH_2, 6 H)	15.31 (s)	2 278w
$[ReH(NCMe)_3(PPh_3)(dppe)][BF_4]_2$	−5.99 (td, 8.0, 51.6)	1.77 (s, CH_3, 3 H) 1.92 (s, CH_3, 6 H)	54.00 (dd, 8.5, 33.3), 37.04 (dd, 33.3, 134.3), 18.10 (dd, 8.5, 134.3)	2 255m–w
$[ReH(NCEt)_3(PPh_3)(dppe)][BF_4]_2$	−5.98 (td, 7.3, 53.1)	0.40 (t, CH_3, 6 H), 2.40 (q, CH_2, 4 H) 0.55 (t, CH_3, 3 H), 2.23 (q, CH_2, 2 H)	53.90 (dd, 8.5, 33.0), 36.21 (dd, 33.0, 135.4), 17.54 (dd, 8.5, 135.4)	2 244w

[a] Spectra recorded in CD_2Cl_2 unless otherwise stated. s = Singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, and td = triplet of doublets. [b] Figures in parentheses are *J*(P–H) in Hz. [c] Spectra recorded in $CDCl_3$. [d] Figures in parentheses are *J*(P–P) in Hz. [e] Nujol mulls. [f] ABX_3 pattern.

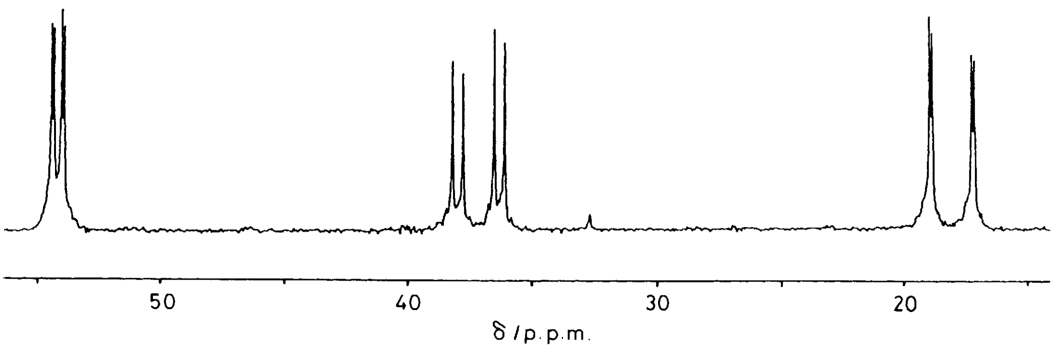

Figure 1. $^{31}P-\{^1H\}$ N.m.r. spectrum of $[ReH(NCMe)_3(PPh_3)(dppe)][BF_4]_2$ recorded in $CDCl_3$ (with 85% H_3PO_4 as an external standard). Positive chemical shifts are downfield from H_3PO_4

case of $[ReH(NCR)_3(PPh_3)_2L][BF_4]_2$ [L = RNC, py, $NH_2(C_6H_{11})$, or NH_2Bu^t]. While the $^{31}P-\{^1H\}$ and ^1H n.m.r. spectral results for the RCN groups imply that the skeleton containing these sets of ligands is rigid, the Re–H triplet observed in the case of L = RCN or NH_2Bu^t does raise the possibility of a hydride-ligand fluxionality. In any event, our data for these complexes are in accord with (although do not prove) a face-capped octahedral geometry, with the hydride ligand in the capping positions associated with the two trigonal faces that share the PPh_3 ligands, or a pentagonal-bipyramidal geometry, with the hydride ligand in an equatorial position adjacent to the phosphine ligands. These are the preponderant geometries in the case of other seven-co-ordinate monohydrido-complexes.[13–21]

Reactions of $[ReH(NCR)_4(PPh_3)_2][BF_4]_2$ (R = Me, Et, *or* Ph) *with* $Ph_2PCH_2CH_2PPh_2$ (*dppe*).—Reaction for 5 h in refluxing dichloromethane gives the seven-co-ordinate hydrido-species $[ReH(NCR)_3(PPh_3)(dppe)][BF_4]_2$ (R = Me or Et), while in refluxing 1,2-dichloroethane longer reaction times (8—11 h) lead to reductive substitution and the formation of $[Re(NCR)_2(dppe)_2]BF_4$. The latter rhenium(I) species are apparently similar to the benzonitrile complex of stoicheiometry $[Re(NCPh)_2(dppe)_2]BF_4$ prepared previously by Leigh *et al.*[22] by the reaction of $[ReCl(N_2)(dppe)_2]$ with $TlBF_4$ in benzonitrile. The complexes $[Re(NCR)_2(dppe)_2]BF_4$ dissolve in acetonitrile to give solutions (*ca.* 1×10^{-3} mol dm^{-3}) that exhibit conductivities (Λ *ca.* 140 ohm^{-1} cm^2 mol^{-1}) characteristic of 1:1 electrolytes. Their Nujol-mull i.r. spectra show a single ν(C≡N) mode (at 2 220m, 2 203m, and 2 149w–m cm^{-1} for R = Me, Et, and Ph, respectively), and ^1H n.m.r. spectra which display the expected nitrile and dppe ligand resonances with the correct integrated intensities. The $^{31}P-\{^1H\}$ n.m.r. spectra of $CDCl_3$ solutions of $[Re(NCR)_2(dppe)_2]BF_4$ (R = Me or Et) each show a singlet (δ +30.59 p.p.m. for R = Me, +30.18 p.p.m. for R = Et), in accord with a *trans*-octahedral geometry. We were unable to isolate the benzonitrile derivative in sufficient purity to justify the reporting of its n.m.r. spectrum. The electrochemical properties of solutions of $[Re(NCR)_2(dppe)_2]BF_4$ in 0.1 mol dm^{-3} NBu_4PF_6–CH_2Cl_2, as measured by the cyclic voltammetric technique using a platinum-bead electrode, show that each complex exhibits a reversible one-electron couple at $E_{\frac{1}{2}} = +0.20$ to $+0.25$ V *vs.* Ag–AgCl (with $E_{p,a} - E_{p,c}$ *ca.* 100 mV at $v = 200$ mV s^{-1}) which corresponds to an oxidation process. The peak-current ratios were close to unity, and values of $i_{p,a}:v^{\frac{1}{2}}$ were constant for scan rates (v) from 50 to 400 mV s^{-1}. A second, albeit less well defined, oxidation process was found at $E_{p,a}$ *ca.* + 1.4 V *vs.* Ag–AgCl.

The monohydridorhenium(III) species $[ReH(NCR)_3(PPh_3)(dppe)][BF_4]_2$, which are formed prior to the reductive substitution step, exhibit well defined spectroscopic properties (Table 1). The derivatives with R = Me or Et show a very well defined triplet of doublets pattern for the Re–H resonance (δ *ca.* −6.0 p.p.m.) in the ^1H n.m.r. spectra, together with resonances for the three nitrile ligands which indicate that inequivalent sets are present in a 2:1 ratio. The $^{31}P-\{^1H\}$ n.m.r. spectra of these two complexes are very similar; three doublets of doublets signify the inequivalence of the three phosphorus-donor atoms. The spectrum of $[ReH(NCMe)_3(PPh_3)(dppe)][BF_4]_2$ is shown in Figure 1. Selective-decoupling experiments involving the phenyl protons showed that the upfield resonance (δ *ca.* +18 p.p.m.) is due to the PPh_3 ligand. From the ^1H and ^{31}P n.m.r. results and the values of the P–P coupling constants given in Table 1, and with the assumption that $J(P-P)_{trans} > J(P-P)_{cis}$, we have two possible structures. One of these is a pentagonal bipyramid with a pair of axial RCN ligands and the Re–H bond located in the equatorial plane between the PPh_3 ligand and one of the phosphorus atoms of the dppe ligand; P–H coupling is the same for these two P-donor atoms. Alternatively, we could have a capped octahedron with the hydride capping a trigonal face comprising two phosphine donors (one being the PPh_3 ligand, the other a dppe phosphorus atom) and a nitrile. In this structure the other dppe phosphorus atom must be *trans* to the PPh_3. These structures resemble those which best fit the available data for the other monohydrido-complexes listed in Table 1.

Redox Properties of Monohydrido-complexes of Rhenium(III).—Cyclic voltammograms of the monohydrides were recorded on solutions in 0.1 mol dm^{-3} NBu_4PF_6–CH_2Cl_2 using a platinum-bead electrode. All complexes show a reversible couple with an associated $E_{\frac{1}{2}}$ value between +1.0 and +1.6 V *vs.* Ag–AgCl (Table 2),* and an irreversible reduction process which occurs at quite negative potentials. Representative cyclic voltammograms are shown in Figure 2. We believe that the oxidation corresponds to the processes (4) and (5). The peak-

$$[ReH(NCR)_3(PPh_3)_2L]^{2+} \xrightarrow{-e^-} [ReH(NCR)_3(PPh_3)_2L]^{3+} \quad (4)$$

R = Me or Et; L = RCN, PPh_3, py, $NH_2(C_6H_{11})$, or NH_2Bu^t

$$[ReH(NCR)_3(PPh_3)(dppe)]^{2+} \xrightarrow{-e^-} [ReH(NCR)_3(PPh_3)(dppe)]^{3+} \quad (5)$$

R = Me or Et

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* Under the same experimental conditions the ferrocenium–ferrocene couple has $E_{\frac{1}{2}} = +0.47$ V *vs.* Ag–AgCl.

Table 2. Cyclic voltammetric and conductivity data for solutions of monohydridorhenium(III) complexes

Complex	Half-wave potentials[a] $E_{\frac{1}{2}}$	$E_{p,c}$	Λ^{b}/ohm^{-1} cm^2 mol^{-1}
$[ReH(NCMe)_4(PPh_3)_2][BF_4]_2$	+1.06	−1.82	235
$[ReH(NCEt)_4(PPh_3)_2][BF_4]_2$	+1.06	−1.81	
$[ReH(NCPh)_4(PPh_3)_2][BF_4]_2$	+1.11	−1.25, 1.42[c]	
$[ReH(NCMe)_3(PPh_3)_2(py)][BF_4]_2$	+1.04	−1.66	230
$[ReH(NCEt)_3(PPh_3)_2(py)][BF_4]_2$	+1.03	−1.67	
$[ReH(NCMe)_3(PPh_3)_2\{NH_2(C_6H_{11})\}][BF_4]_2$	+1.02	−1.86	225
$[ReH(NCEt)_3(PPh_3)_2\{NH_2(C_6H_{11})\}][BF_4]_2$	+1.04	−1.88	
$[ReH(NCMe)_3(PPh_3)_2(NH_2Bu^t)][BF_4]_2$	+1.08	−1.80	237
$[ReH(NCEt)_3(PPh_3)_2(NH_2Bu^t)][BF_4]_2$	+1.07	−1.88	
$[ReH(NCMe)_3(PPh_3)_3][BF_4]_2$	+1.57	*ca.* −1.95	250
$[ReH(NCEt)_3(PPh_3)_3][BF_4]_2$	+1.56	*ca.* −2.0	
$[ReH(NCMe)_3(PPh_3)(dppe)][BF_4]_2$	+1.13	−1.85	270
$[ReH(NCEt)_3(PPh_3)(dppe)][BF_4]_2$	+1.13	−1.75	

[a] Measured on 0.1 mol dm^{-3} NBu_4PF_6–CH_2Cl_2 solutions, $E_{\frac{1}{2}}$ for oxidation step. Data given in V *vs.* Ag–AgCl; scan rate v = 200 mV s^{-1}. [b] Measured on acetonitrile solutions (*ca.* 1 × 10^{-3} mol dm^{-3} complex); values are typical of 1:2 electrolytes (see W. J. Geary, *Coord. Chem. Rev.*, 1971, 7, 81). [c] Two sequential reduction processes occurring at quite similar potentials.

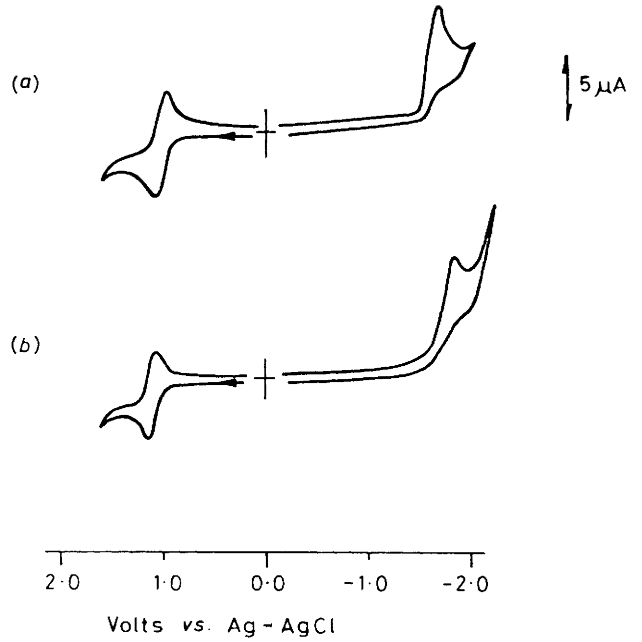

Figure 2. Cyclic voltammograms (scan rate 200 mV s^{-1} at a platinum-bead electrode) in 0.1 mol dm^{-3} tetra-n-butylammonium hexafluorophosphate–dichloromethane: (*a*) $[ReH(NCMe)_3(PPh_3)_2(py)][BF_4]_2$, (*b*) $[ReH(NCMe)_3(PPh_3)(dppe)][BF_4]_2$

current ratios $i_{p,a}:i_{p,c}$ were very close to unity (1.0—1.1), and values of $i_{p,c}:v^{\frac{1}{2}}$ were constant for scan rates (v) in the range 50—400 mV s^{-1}. This is in accord with diffusion control. Values of $E_{p,a} - E_{p,c}$ were in the range 90—130 mV at v = 200 mV s^{-1}, and increased slightly with increasing scan rates. These properties are, with our experimental set-up,[23] consistent with this being a reversible electron-transfer process, or a process which approaches reversibility. While bulk electrolysis of solutions of $[ReH(NCMe)_3(PPh_3)_2(py)]^{2+}$ at +1.3 V leads to the production of a violet solution {presumably containing $[ReH(NCMe)_3(PPh_3)_2(py)]^{3+}$}, this oxidation is accompanied by appreciable decomposition of the complex as a consequence of the chemical instability of the rhenium(IV) species. *X*-Band e.s.r. spectral measurements on frozen CH_2Cl_2 solutions at −160 °C (formed 10 s following completion of the bulk electrolysis) do not show any signal. Attempts at the isolation of the trications using chemical oxidations failed.

Experimental

Starting Materials.—The polyhydride complexes $[ReH_7(PPh_3)_2]$[5,6] and $[ReH_5(PPh_3)_2L][L = py$ or $NH_2(C_6H_{11})]$[6] were prepared by standard literature methods. The t-butylamine derivative $[ReH_5(PPh_3)_2(NH_2Bu^t)]$ was prepared by a method similar to that described for its cyclohexylamine analogue.[6] A solution of $[ReH_7(PPh_3)_2]$ (0.365 g) in tetrahydrofuran (thf, 5 cm^3) was treated with NH_2Bu^t (1.0 cm^3) and the mixture refluxed for 10 min. The solvent was removed under vacuum and the dried solid residue crystallized from benzene–ethanol; yield 0.32 g, 79% (Found: C, 60.7; H, 6.4. $C_{40}H_{46}NP_2Re$ requires C, 60.9; H, 5.9%).

The previously reported complex $[ReH_4I(PPh_3)_3]$[24] was prepared by a new, high-yield method. A quantity of $[ReH_5(PPh_3)_3]$ (0.41 g) was added to benzene (8 cm^3) and methyl iodide (1.5 cm^3) and the mixture stirred for 15 min. The dark green mixture was filtered into ethanol (100 cm^3) whereupon green plates of $[ReH_4I(PPh_3)_3]$ separated; yield 0.38 g, 82% (Found: C, 59.0; H, 4.7. $C_{54}H_{49}IP_3Re$ requires C, 58.7; H, 4.5%). The spectroscopic properties of this complex (i.r. and n.m.r.) agree with those reported.[24]

All other reagents and solvents were obtained from commercial sources. Solvents were thoroughly deoxygenated and/or distilled prior to use. All reactions were carried out under an atmosphere of nitrogen.

(*a*) *Reactions of* $[ReH_7(PPh_3)_2]$.—(*i*) $[ReH(NCMe)_4(PPh_3)_2][BF_4]_2$. A suspension of $[ReH_7(PPh_3)_2]$ (0.58 g) in acetonitrile (8 cm^3) was treated with $HBF_4 \cdot Et_2O$* (0.1 cm^3). Effervescence occurred immediately due to H_2 evolution (as shown by g.c. analysis). The mixture was stirred for 5 min and then added to diethyl ether (100 cm^3). Yellow platelets formed and were recrystallized from CH_2Cl_2–Et_2O; yield 0.77 g, 88%. Spectroscopic and microanalytical data were in accord with the product being the hemi-solvate $[ReH(NCMe)_4(PPh_3)_2][BF_4]_2 \cdot 0.5CH_2Cl_2$ (Found: C, 48.4; H, 4.1; N, 5.1. $C_{44.5}H_{44}B_2ClF_8N_4P_2Re$ requires C, 48.9; H, 4.0; N, 5.1%).

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* $HBF_4 \cdot Et_2O$ is a solution of HBF_4 (54%) in diethyl ether.

Proton n.m.r. spectroscopy (in $CDCl_3$) showed the CH_2Cl_2 resonance at δ 5.35 p.p.m.

(*ii*) $[ReH(NCEt)_4(PPh_3)_2][BF_4]_2$. This complex was prepared from a mixture of $[ReH_7(PPh_3)_2]$ (0.50 g), propionitrile (5 cm^3), and $HBF_4{\cdot}Et_2O$ (0.15 cm^3) by using a procedure similar to that described above; yield 0.61 g, 78% (Found: C, 50.9; H, 4.8. $C_{48}H_{51}B_2F_8N_4P_2Re$ requires C, 52.1; H, 4.65%).

(*iii*) $[ReH(NCPh)_4(PPh_3)_2][BF_4]_2$. This complex was prepared from a mixture comprising $[ReH_7(PPh_3)_2]$ (0.305 g), acetone (8 cm^3), benzonitrile (1 cm^3), and $HBF_4{\cdot}Et_2O$ (0.15 cm^3). The orange powder obtained upon addition of diethyl ether (100 cm^3) was filtered off and dried; yield 0.37 g, 67% (Found: C, 58.9; H, 4.3. $C_{64}H_{51}B_2F_8N_4P_2Re$ requires C, 59.2; H, 4.0%).

(*b*) *Reactions of* $[ReH_5(PPh_3)_2(py)]$.—(*i*) $[ReH(NCMe)_3(PPh_3)_2(py)][BF_4]_2$. A mixture containing $[ReH_5(PPh_3)_2(py)]$ (0.22 g), acetonitrile (5 cm^3) and $HBF_4{\cdot}Et_2O$ (0.12 cm^3) was allowed to react as described in (*a*)(*i*); yield 0.13 g (44%) (Found: C, 52.3; H, 4.7. $C_{47}H_{45}B_2F_8N_4P_2Re$ requires C, 51.9; H, 4.2%).

(*ii*) $[ReH(NCEt)_3(PPh_3)_2(py)][BF_4]_2$. A yellow powder was isolated from the reaction between $[ReH_5(PPh_3)_2(py)]$ (0.32 g), propionitrile (5 cm^3), and $HBF_4{\cdot}Et_2O$ (0.50 cm^3) using a procedure similar to (*a*)(*i*), and purified by chromatography on a silica gel column. Elution with dichloromethane gave a yellow fraction which was evaporated and the residue crystallized by the addition of Et_2O; yield 0.40 g (85%). Based upon spectroscopic and microanalytical data this product appeared to be the dihydrate (Found: C, 51.5; H, 4.5. $C_{50}H_{55}B_2F_8N_4O_2P_2Re$ requires C, 51.5; H, 4.8%). Proton n.m.r. spectroscopy (in CD_2Cl_2) showed an H_2O resonance at δ 1.84 p.p.m. (with the correct integration), while the i.r. spectrum (Nujol mull) had ν(O–H) at *ca.* 3 350w,br and δ(O–H) at *ca.* 1 640w,br cm^{-1}.

(*c*) *Reactions of* $[ReH_5(PPh_3)_2\{NH_2(C_6H_{11})\}]$.—(*i*) $[ReH(NCMe)_3(PPh_3)_2\{NH_2(C_6H_{11})\}][BF_4]_2$. The reaction of $[ReH_5(PPh_3)_2\{NH_2(C_6H_{11})\}]$ (0.14 g) with acetonitrile (5 cm^3) and $HBF_4{\cdot}Et_2O$ (0.10 cm^3) afforded yellow microcrystals of the title complex using a procedure similar to that described in (*a*)(*i*); yield 0.13 g, 65% (Found: C, 51.6; H, 4.8. $C_{48}H_{53}B_2F_8N_4P_2Re$ requires C, 52.0; H, 4.8%).

(*ii*) $[ReH(NCEt)_3(PPh_3)_2\{NH_2(C_6H_{11})\}][BF_4]_2$. This complex was prepared using a procedure similar to that of (*a*)(*i*) from $[ReH_5(PPh_3)_2\{NH_2(C_6H_{11})\}]$ (0.15 g), propionitrile (5 cm^3), and $HBF_4{\cdot}Et_2O$ (0.10 cm^3); yield 0.11 g, 52% (Found: C, 53.0; H, 5.0; N, 4.65. $C_{51}H_{59}B_2F_8N_4P_2Re$ requires C, 53.3; H, 5.2; N, 4.9%).

(*d*) *Reactions of* $[ReH_5(PPh_3)_2(NH_2Bu^t)]$.—(*i*) $[ReH(NCMe)_3(PPh_3)_2(NH_2Bu^t)][BF_4]_2$. A suspension of $[ReH_5(PPh_3)_2(NH_2Bu^t)]$ (0.110 g) in acetonitrile (5 cm^3) was acidified with $HBF_4{\cdot}Et_2O$ (0.10 cm^3). The mixture effervesced while the suspended solid dissolved. Following dissolution, diethyl ether (100 cm^3) was added and the yellow powder was collected. This product was then recrystallized from CH_2Cl_2–Et_2O in the presence of an excess of PPh_3 (0.05 g). The resulting yellow microcrystals were collected and washed with diethyl ether to remove any excess of PPh_3; yield 0.11 g, 70% (Found: C, 51.3; H, 5.2; N, 4.95. $C_{46}H_{51}B_2F_8N_4P_2Re$ requires C, 51.1; H, 4.75; N, 5.2%).

(*ii*) $[ReH(NCEt)_3(PPh_3)_2(NH_2Bu^t)][BF_4]_2$. A suspension of $[ReH_5(PPh_3)_2(NH_2Bu^t)]$ (0.15 g) in propionitrile (5 cm^3) was treated with $HBF_4{\cdot}Et_2O$ (0.12 cm^3). Treatment of the reaction solution with diethyl ether (40 cm^3) gave a yellow powder which was recrystallized from EtCN–Et_2O. Spectroscopic and microanalytical data supported its formulation as the dihydrate $[ReH(NCEt)_3(PPh_3)_2(NH_2Bu^t)][BF_4]_2{\cdot}2H_2O$; yield 0.16 g, 72% (Found: C, 50.1; H, 4.9. $C_{49}H_{61}B_2F_8N_4O_2P_2Re$ requires C, 50.7; H, 5.3%). I.r. spectroscopy (Nujol mull) showed a broad ν(O–H) band at *ca.* 3 400 cm^{-1}.

(*e*) *Reactions of* $[ReH_4I(PPh_3)_3]$.—(*i*) $[ReH(NCMe)_3(PPh_3)_3][BF_4]_2$. A quantity of $[ReH_4I(PPh_3)_3]$ (0.38 g) in acetonitrile (10 cm^3) was acidified with $HBF_4{\cdot}Et_2O$ (0.15 cm^3). The suspension dissolved with effervescence and the resulting solution was treated with diethyl ether (100 cm^3), followed by hexane (50 cm^3). The pale yellow insoluble product was recrystallized from CH_2Cl_2–Et_2O; yield 0.37 g, 84% (Found: C, 55.5; H, 4.5. $C_{60}H_{55}B_2F_8N_3P_3Re$ requires C, 56.7; H, 4.4%).

(*ii*) $[ReH(NCEt)_3(PPh_3)_3][BF_4]_2$. The reaction of $[ReH_4I(PPh_3)_3]$ (0.16 g) in propionitrile (5 cm^3) with $HBF_4{\cdot}Et_2O$ (0.10 cm^3) was carried out similarly to that described in (*a*)(*i*). The title complex was obtained as its hemi-CH_2Cl_2 solvate upon recrystallization from CH_2Cl_2–Et_2O; yield 0.17 g, 89% (Found: C, 55.8; H, 4.6. $C_{63.5}H_{62}B_2ClF_8N_3P_3Re$ requires C, 56.3; H, 4.6%). Proton n.m.r. spectroscopy (in $CDCl_3$) showed the CH_2Cl_2 resonance (with the correct integration) at δ 5.35 p.p.m.

(*f*) *Reactions of* $[ReH(NCMe)_4(PPh_3)_2][BF_4]_2$ *with* $Ph_2PCH_2CH_2PPh_2$ (*dppe*).—(*i*) $[ReH(NCMe)_3(PPh_3)(dppe)][BF_4]_2$. A solution containing $[ReH(NCMe)_4(PPh_3)_2][BF_4]_2$ (0.14 g) and dppe (0.50 g) in dichloromethane (5 cm^3) was refluxed for 5 h. The solution was cooled, diethyl ether (25 cm^3) was added, and the resulting flocculent pale yellow precipitate (0.116 g) was filtered off and dried. This material was extracted with diethyl ether for 40 h in a Soxhlet extractor. The pale yellow insoluble residue which remained was then recrystallized from CH_2Cl_2–Et_2O; yield 0.10 g, 67% (Found: C, 52.9; H, 4.6; N, 3.4. $C_{50}H_{49}B_2F_8N_3P_3Re$ requires C, 52.3; H, 4.3; N, 3.7%).

(*ii*) $[Re(NCMe)_2(dppe)_2]BF_4$. A mixture of $[ReH(NCMe)_4(PPh_3)_2][BF_4]_2$ (0.09 g) and dppe (0.495 g) in 1,2-dichloroethane (5 cm^3) was refluxed for 8 h and the reaction mixture allowed to cool to room temperature. The insoluble white precipitate of $(Hdppe)BF_4$ (identified by i.r. spectroscopy) was filtered off, and the reaction filtrate treated with diethyl ether (100 cm^3). The yellow powder was recrystallized from CH_2Cl_2–Et_2O to give the CH_2Cl_2 solvate $[Re(NCMe)_2(dppe)_2]BF_4{\cdot}CH_2Cl_2$; yield 0.045 g, 43% (Found: C, 55.1; H, 4.6. $C_{57}H_{56}BCl_2F_4N_2P_4Re$ requires C, 55.35; H, 4.6%). Proton n.m.r. spectroscopy (in $CDCl_3$) showed the CH_2Cl_2 resonance (with the correct integration) at δ 5.35 p.p.m.

(*g*) *Reactions of* $[ReH(NCEt)_4(PPh_3)_2][BF_4]_2$ *with dppe*.—(*i*) $[ReH(NCEt)_3(PPh_3)(dppe)][BF_4]_2$. The reaction between $[ReH(NCEt)_4(PPh_3)_2][BF_4]_2$ (0.16 g) and dppe (0.57 g) in refluxing dichloromethane (15 cm^3) was carried out similarly to that in (*f*)(*i*) except that extraction of the product with diethyl ether was unnecessary; yield 0.035 g, 21% (Found: C, 52.6; H, 4.6. $C_{53}H_{55}B_2F_8N_3P_3Re$ requires C, 53.5; H, 4.7%).

(*ii*) $[Re(NCEt)_2(dppe)_2]BF_4$. This complex was obtained as yellow needles from the reaction between $[ReH(NCEt)_4(PPh_3)_2][BF_4]_2$ (0.15 g) and dppe (0.51 g) in refluxing 1,2-dichloroethane (5 cm^3). A procedure similar to that in (*f*)(*ii*) was used; yield 0.045 g, 28% (Found: C, 58.7; H, 5.0. $C_{58}H_{58}BF_4N_2P_4Re$ requires C, 59.0; H, 4.95%).

(*h*) *Reaction of* $[ReH(NCPh)_4(PPh_3)_2][BF_4]_2$ *with dppe*.—$[Re(NCPh)_2(dppe)_2]BF_4$. A mixture of $[ReH(NCPh)_4(PPh_3)_2][BF_4]_2$ (0.37 g) and dppe (0.34 g) was refluxed in 1,2-dichloroethane (5 cm^3) for 11 h. A work-up procedure similar to that in (*f*)(*ii*) gave an orange powder which was filtered off, washed with diethyl ether and pentane, and dried; yield 0.28 g, 84%. Although the spectroscopic and electrochemical properties of this product were in accord with this formulation we were unable to obtain an analytically pure sample.

(*i*) *Interconversions of Monohydrido-species.*—(*i*) [ReH(NCMe)$_4$(PPh$_3$)$_2$][BF$_4$]$_2$ *into* [ReH(NCMe)$_3$(PPh$_3$)$_3$][BF$_4$]$_2$. A dichloromethane solution (15 cm^3) containing [ReH(NCMe)$_4$(PPh$_3$)$_2$][BF$_4$]$_2$ (0.12 g) and PPh$_3$ (0.37 g) was refluxed for 16 h. Diethyl ether (100 cm^3) was added and the reaction mixture cooled to afford crystals of [ReH(NCMe)$_3$(PPh$_3$)$_3$][BF$_4$]$_2$; yield 0.075 g, 53%.

(*ii*) [ReH(NCMe)$_4$(PPh$_3$)$_2$][BF$_4$]$_2$ *into* [ReH(NCMe)$_3$(PPh$_3$)$_2$(py)][BF$_4$]$_2$. The reaction between [ReH(NCMe)$_4$(PPh$_3$)$_2$][BF$_4$]$_2$ (0.06 g) and pyridine (8 µl) in chloroform (1 cm^3) for 24 h at room temperature gave orange crystals of [ReH(NCMe)$_3$(PPh$_3$)$_2$(py)][BF$_4$]$_2$; yield 0.025 g, 41%.

(*iii*) [ReH(NCEt)$_3$(PPh$_3$)$_3$][BF$_4$]$_2$ *into* [ReH(NCEt)$_4$(PPh$_3$)$_2$][BF$_4$]$_2$. A solution of [ReH(NCEt)$_3$(PPh$_3$)$_3$][BF$_4$]$_2$ (0.05 g) in propionitrile (3 cm^3) was stirred for 12 h. Following the addition of diethyl ether (50 cm^3), a quantity of [ReH(NCEt)$_4$(PPh$_3$)$_2$][BF$_4$]$_2$ precipitated; yield 0.03 g, 57%.

The products isolated in these reactions were identified on the basis of their spectral and electrochemical properties which were the same as those found for authentic samples.

Physical Measurements.—Infrared spectra were recorded for Nujol mulls (in the region 4 800—400 cm^{-1}) on an IBM IR/32 spectrometer. Proton n.m.r. spectra were recorded at 90 MHz using a Perkin-Elmer R-32 spectrometer or at 200 MHz with a Varian XL-200 spectrometer. Resonances were referenced internally to residual protons in CD$_2$Cl$_2$ (δ 5.35 p.p.m.) or to SiMe$_4$ in CDCl$_3$ solutions. The ^{31}P n.m.r. spectra were recorded on a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock and aqueous 85% H$_3$PO$_4$ as an external standard. Positive chemical shifts are downfield from H$_3$PO$_4$. Conductivities were measured on an Industrial Instruments model RC 16B2 conductivity bridge. Cyclic voltammetry experiments were performed on CH$_2$Cl$_2$ solutions containing 0.1 mol dm^{-3} tetra-n-butylammonium hexafluorophosphate as the supporting electrolyte. The $E_{\frac{1}{2}}$ values [taken as $(E_{\mathrm{p,a}} + E_{\mathrm{p,c}})/2$] were referenced to the Ag–AgCl reference electrode at room temperature and are uncorrected for junction potentials. Voltammetric measurements were obtained with a Bioanalytical Systems model CV-1A instrument in conjunction with a Hewlett-Packard model 7035B *x-y* recorder. *X*-Band e.s.r. spectra of dichloromethane solutions were recorded at *ca.* −160 °C on a Varian E-109 spectrometer.

Microanalyses were performed by Dr. H. D. Lee of the Purdue University microanalytical laboratory.

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