Reactivity of the Polyhydride Complexes $[ReH_5(PPh_3)_3]$, $[ReH_3(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$), $[ReH_3(PPh_3)_3L]$, and $[ReH_4(PPh_3)_3L]PF_6$ (L = MeCN or Bu^{t}NC) towards Electrophiles and Nucleophiles

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Protonation of $[ReH_5(PPh_3)_3]$ with HBF_4 in CH_2Cl_2 gives yellow $[ReH_6(PPh_3)_3]BF_4$, whereas its treatment with $C_7H_7^+PF_6^-$ in the presence of various ligands leads to formation of the compounds $[ReH_4(PPh_3)_3L]PF_6$, where L = MeCN, PPh_3, Bu^{t}NC, or 2,6-$Me_2C_6H_3NC$. Deprotonation of the complexes where L = MeCN or Bu^{t}NC was accomplished using NEt_3 to form the neutral trihydrides $[ReH_3(PPh_3)_3(NCMe)]$ and $[ReH_3(PPh_3)_3(CNBu^t)]$. Protonation of $[ReH_3(PPh_3)_3(NCMe)]$ with HBF_4 in MeCN reforms $[ReH_4(PPh_3)_3(NCMe)]^+$, whereas with $C_7H_7^+PF_6^-$ in MeCN the dihydride $[ReH_2(PPh_3)_3(NCMe)_2]PF_6$ is produced; a second equivalent of $C_7H_7^+PF_6^-$ (in MeCN) results in the formation of $[ReH(PPh_3)_3(NCMe)_3][PF_6]_2$. The complex $[ReH_3(PPh_3)_3(CNBu^t)]$ reacts with $C_7H_7^+PF_6^-$ and MeCN in a similar fashion to $[ReH_3(PPh_3)_3(NCMe)]$ to produce $[ReH_2(PPh_3)_3(NCMe)(CNBu^t)]PF_6$, but when it is treated with HBF_4 and MeCN the protonated isocyanide complex $[ReH_2(PPh_3)_3\{CN(H)Bu^t\}(NCMe)][BF_4]_2$ is isolated. Furthermore, $[ReH_3(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) reacts with $C_7H_7^+PF_6^-$ in the presence of MeCN, Bu^{t}NC, or 2,6-$Me_2C_6H_3NC$ to produce complexes of the type $[ReH_2(dppe)_2L]PF_6$.

One focus of our studies on mononuclear and dinuclear polyhydride complexes of rhenium[1—7] has been in the activation of rather inert species such as $[Re_2(\mu\text{-}H)_4H_4(PPh_3)_4]$ and $[ReH_5(PPh_3)_2L]$ (L = pyridine, cyclohexylamine, or t-butylamine). One of the findings of this previous work was that Lewis acids such as HBF_4, $Ph_3C^+PF_6^-$, or $C_7H_7^+PF_6^-$ serve as effective activating agents either by behaving as electron-transfer reagents or as hydride-ion abstractors. In this report we investigate the interactions of these reagents with two other rhenium hydride complexes, $[ReH_5(PPh_3)_3]$ and $[ReH_3(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$). While these complexes have been activated photochemically,[8,9] reports of their thermal chemistry are very limited.

Results and Discussion

(*a*) *Reactions of* $[ReH_5(PPh_3)_3]$ *with* $C_7H_7^+PF_6^-$.—In a previous report[3] we noted that a slurry of $[ReH_5(PPh_3)_3]$ in acetonitrile did not form $[ReH(NCMe)_3(PPh_3)_3][BF_4]_2$ when treated with $HBF_4{\cdot}Et_2O$. This was surprising in view of our preparation of the latter monohydride complex from $[ReH_4I(PPh_3)_3]$,[3] and the formation of $[ReH(NCMe)_3(PMe_2Ph)_3][BF_4]_2$ from the acidolysis of $[ReH_5(PMe_2Ph)_3]$.[10] Because $[ReH_5(PPh_3)_3]$ reacts with MeI to produce $[ReH_4I(PPh_3)_3]$, a reaction that we believe proceeds through hydride abstraction to form CH_4 (g.c. analysis) and I^-, we investigated the reaction of $[ReH_5(PPh_3)_3]$ with $C_7H_7^+PF_6^-$, a hydride-abstracting agent, in the presence of co-ordinating ligands. These reactions afford the rhenium tetrahydride cations $[ReH_4(PPh_3)_3L]PF_6$ (L = MeCN, PPh_3, Bu^{t}NC, or 2,6-$Me_2C_6H_3NC$) in high yield [equation (1)]. An attempt to prepare the complex $[ReH_4(PPh_3)_3(N_2)]PF_6$ in a similar manner produced only a moderate yield of $[ReH_4(PPh_3)_4]PF_6$, the fourth phosphine ligand apparently arising from some decomposition of the starting complex.

$$[ReH_5(PPh_3)_3] + C_7H_7^+PF_6^- + L \longrightarrow [ReH_4(PPh_3)_3L]PF_6 \quad (1)$$

These complexes dissolve in acetonitrile to give solutions (*ca.* 1×10^{-3} mol dm^{-3}) that exhibit conductivities (Λ = 100—125 ohm^{-1} cm^2 mol^{-1}) characteristic of 1 : 1 electrolytes. The spectroscopic properties of these four complexes are summarized in the Table. The ^1H n.m.r. spectra integrate in accord with the proposed formulations. Only a single Re–H resonance, a binomial multiplet due to equivalent coupling to the phosphorus nuclei, is observed in the range δ -1.8 to -2.7 p.p.m. This implies that the hydride ligands are fluxional at room temperature, at least in the cases where L = MeCN, Bu^{t}NC, and 2,6-$Me_2C_6H_3NC$. Triphenylphosphine protons are observed as broad multiplets around δ $+7.3$ p.p.m. in the ^1H n.m.r.; resonances for the other organic ligands are given in the Table. A study of the ^1H n.m.r. spectrum of $[ReH_4(PPh_3)_3(NCMe)]PF_6$ at different temperatures (35 to -80 °C) revealed no significant temperature dependence other than a broadening of the Re–H resonance. A single phosphorus resonance for the phosphine ligands (Table) as well as a multiplet due to PF_6^- is seen in the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of these four compounds. The presence of the PF_6^- anion is further demonstrated by i.r. spectroscopy which showed ν(P–F) at *ca.* 841 cm^{-1} (Nujol mull). Additionally, weak bands assignable to ν(Re–H) are found for all four compounds between *ca.* 1 900 and 2 030 cm^{-1}. The ν(C≡N) modes for the isocyanide complexes $[ReH_4(PPh_3)_3(CNR)]PF_6$ (R = Bu^t or 2,6-$Me_2C_6H_3$) occur at 2 184 and 2 132 cm^{-1}, respectively. These relatively high frequencies are consistent with isocyanides bound to a metal in a high formal oxidation state (*i.e.* Re^V in this case).

The electrochemical properties of solutions of $[ReH_4(PPh_3)_3L]PF_6$ in 0.1 mol dm^{-3} NBu_4PF_6–CH_2Cl_2, as measured by the cyclic voltammetric technique (c.v.) using a platinum-bead electrode, show that each complex exhibits an irreversible oxidation above +1.20 V *vs.* Ag–AgCl, *viz.* $E_{p,a}$ = +1.25, +1.60, +1.60, and +1.55 V for L = MeCN, PPh_3, Bu^{t}NC, and 2,6-$Me_2C_6H_3NC$, respectively.† In the case of the acetonitrile complex this oxidation process is followed by the appearance of a product wave at $E_{p,a}$ *ca.* +1.4 V *vs.* Ag–AgCl [Figure 1(*a*)]. The preceding behaviour contrasts with the much more accessible oxidation of $[ReH_5(PPh_3)_3]$; its c.v. (measured

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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. I.r. and ^{1}H and ^{31}P-{^{1}H} n.m.r. spectroscopic properties of polyhydridorhenium complexes

	^{1}H N.m.r. (δ)^{a}		^{31}P-{^{1}H} N.m.r.	I.r. (cm^{-1})^{d}	
Complex	Re–H^{b}	L^{c}	(δ)^{a}	ν(Re–H)	ν(C≡N)
$[ReH_4(PPh_3)_3(NCMe)]PF_6$	-1.85 (q, 23.8)^{e}	1.16 (s, CH_3, 3 H)	+32.80 (s)^{f}	1 898w	2 249vw
$[ReH_4(PPh_3)_4]PF_6$	-2.43 (qnt, 25.2)		+17.77 (s)^{f}	2 029w	
$[ReH_4(PPh_3)_3(CNBu^t)]PF_6$	-2.67 (q, 20.0)^{g}	0.84 (s, CH_3, 9 H)^{g}	+23.68 (s)	1 945w	2 184s
$[ReH_4(PPh_3)_3(CNC_6H_3Me_2\text{-}2,6)]PF_6$	-2.26 (q, 22.4)^{g}	1.83 (s, CH_3, 6 H)^{g}	+27.55 (s)	1 941vw	2 132s
$[ReH_3(PPh_3)_3(NCMe)]$	-6.27 (q, 15.7)^{h}	1.44 (s, CH_3, 3 H)^{h}	+33.03 (s)^{h}	2 066vw, 1 980w, 1 950m	2 249m
$[ReH_3(PPh_3)_3(CNBu^t)]$	-5.00 (q, 22.0)^{g,i}	0.67 (s, CH_3, 9 H)^{g}	+31.02 (s)^{h}	1 890w, 1 806m	2 010s
$[ReH_2(PPh_3)_3(NCMe)_2]PF_6$	-1.91 (q, 53.5)	2.10 (s, CH_3, 6 H)	+16.84 (s)	1 908vw	2 261vw
$[ReH_2(PPh_3)_3(NCMe)(CNBu^t)]PF_6$	-3.20 (q, 31.2)^{e,g}	1.85 (s, CH_3, 3 H), 1.28 (s, CH_3, 9 H)^{g}	+23.97 (s)	1 945w	2 272vw, 2 085w, 2 033s
$[ReH_2(PPh_3)_3(CNBu^t)_2]PF_6$	-4.10 (q, 33.6)^{g}	0.75 (s, CH_3, 18 H)^{g}	+26.73 (s)	1 943w	2 126w, 2 076s, 2 047s
$[ReH_2(dppe)_2(NCMe)]PF_6$	-9.37 (qnt, 13.8)^{e,g}	1.40 (s, CH_3, 3 H)^{g}	+43.47 (s)^{f}		2 265w
$[ReH_2(dppe)_2(CNBu^t)]PF_6$	-5.97 (m)^{g}	0.65 (s, CH_3, 9 H)^{g}	+41.11 (s)	1 914w (sh)	2 097s, 2 064s^{j,k}
$[ReH_2(dppe)_2(CNC_6H_3Me_2\text{-}2,6)]PF_6$	-5.24 (qnt, 18.5)	1.22 (s, CH_3, 6 H)	+43.27 (s)	1 914w (sh)	2 035s, 2 002s^{k}
$[ReH_2(PPh_3)_3\{CN(H)Bu^t\}(NCMe)][BF_4]_2$	-1.99 (qd, 53.2)^{l,m}	3.26 (t, N–H, 1 H) 2.11 (s, CH_3, 3 H) 1.01 (s, CH_3, 9 H)^{l}	+19.82 (s) +18.03 (s)		1 559m^{n}

[a] Spectra recorded in $(CD_3)_2CO$ unless otherwise stated. s = Singlet, t = triplet, q = quartet, m = multiplet, qnt = quintet, qd = quartet of doublets. [b] Figures in parentheses are J(P–H) in Hz. [c] Non-phenyl ring resonances only. [d] Nujol mull spectra. Assignments for ν(Re–H) are tentative. [e] Proton n.m.r. spectra show very little temperature dependence between 35 and −80 °C. [f] Spectra recorded in CD_3CN. [g] Spectra recorded in CD_2Cl_2. [h] Spectra recorded in C_6D_6. [i] Some change observed in the Re–H resonance at low temperatures (see text). [j] Spectrum essentially the same as in CH_2Cl_2 and MeCN. [k] Isomers may be present. [l] Spectra recorded in $CDCl_3$. [m] J(H–H) = 6.7 Hz (see text). [n] ν(C≡N) of the CN(H)Bu^t ligand.

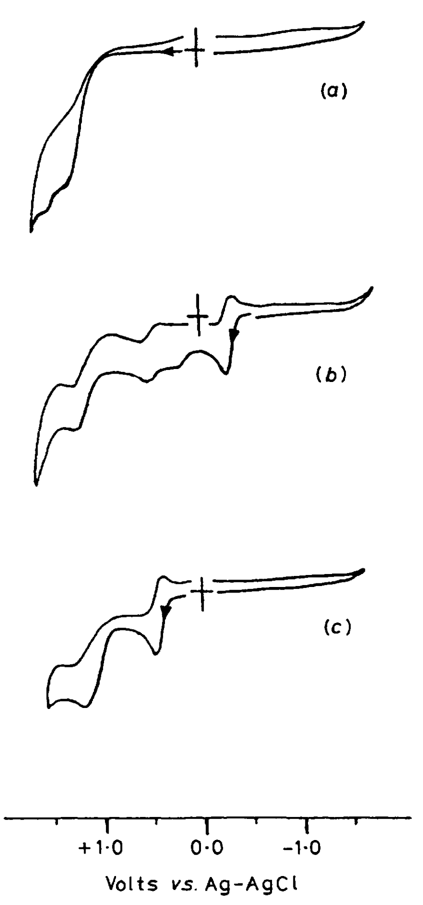

Figure 1. Cyclic voltammograms (scan rate 200 mV s^{-1} at a platinum-bead electrode) in 0.1 mol dm^{-3} tetra-n-butylammonium hexafluorophosphate–dichloromethane: (*a*) $[ReH_4(PPh_3)_3(NCMe)]PF_6$, (*b*) $[ReH_3(PPh_3)_3(NCMe)]$, and (*c*) $[ReH_2(PPh_3)_3(NCMe)_2]PF_6$

in 0.2 mol dm^{-3} NBu_4PF_6–CH_2Cl_2) has $E_{\frac{1}{2}} = +0.37$ V *vs.* saturated calomel electrode (s.c.e.).[6] The shift in the oxidation potential between the $[ReH_5(PPh_3)_3]$ starting material and the rhenium(V) products implies that substitution of a single hydride ligand by a less nucleophilic neutral σ donor, while maintaining the formal oxidation state of the metal, results in a significant decrease in the electron density at the metal centre.

These new complexes, $[ReH_4(PPh_3)_3L]PF_6$ (L = MeCN, PPh_3, Bu^{t}NC, or $2,6\text{-}Me_2C_6H_3NC$), increase significantly the number of known mononuclear rhenium tetrahydride cations. Previously, $[ReH_4(dppe)_2]^+$,[11] $[ReH_4(PPh_3)_2(dppe)]^+$,[11] $[ReH_4(PMe_3)_4]^+$,[12] $[ReH_4(PPh_3)_2\{P(OPh)_3\}_2]^+$,[13] and $[ReH_4(PPh_3)\{P(OPh)_3\}_3]^+$ [13] were prepared by protonation of the corresponding neutral rhenium trihydride compounds. Our use of $C_7H_7^+PF_6^-$ affords a new synthetic route to this class of compounds. It should also be noted that the complexes $[ReH_4(PPh_3)_3L]PF_6$ (L = MeCN, Bu^{t}NC, or $2,6\text{-}Me_2C_6H_3NC$) are the first members of this class that are stabilized by ligands other than phosphines or phosphites. The isocyanide-containing complexes are of special significance since previous attempts to isolate a rhenium(V) polyhydride complex stabilized by isocyanide, through the reactions of $[ReH_7(PPh_3)_2]$ with RNC ligands were unsuccessful.[7] In the present report, however, we have demonstrated that the method used previously to prepare bimetallic mixed polyhydride–isocyanide complexes[4] is also applicable to monomeric systems.

As mentioned at the beginning of this section, we had observed in an earlier study[3] that $[ReH_5(PPh_3)_3]$ does not react with $HBF_4{\cdot}Et_2O$ in acetonitrile to give the expected product $[ReH(NCMe)_3(PPh_3)_3][BF_4]_2$. In the present work we find that the product is in fact $[ReH_4(PPh_3)_3(NCMe)]^+$ (isolated as its PF_6^- salt). Accordingly, the course of this reaction resembles that between $[ReH_5(PPh_3)_3]$ and $C_7H_7^+PF_6^-$. We also find that when the reaction between $[ReH_5(PPh_3)_3]$ and $HBF_4{\cdot}Et_2O$ is carried out in the non-co-ordinating solvent CH_2Cl_2 the yellow salt $[ReH_6(PPh_3)_3]BF_4$ can be isolated. This reaction is quite similar to that recently reported by Crabtree and Lavin[14] where $[IrH_2(H_2)_2\{P(C_6H_{11})_3\}_2]^+$ was generated by protonation of $[IrH_5$-

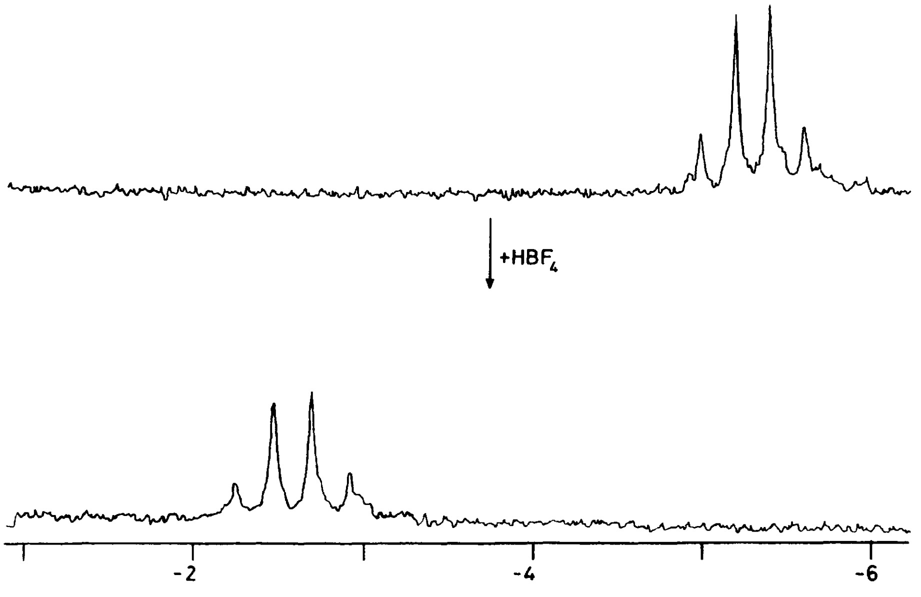

Figure 2. Proton n.m.r. spectrum (recorded in CD_2Cl_2) of the Re–H resonance of $[ReH_5(PPh_3)_3]$ showing the effect of adding $HBF_4{\cdot}Et_2O$

$\{P(C_6H_{11})_3\}_2]$. Unlike the iridium cation, however, no evidence for co-ordinated H_2 is observed in the room-temperature ^1H n.m.r. spectrum of the rhenium cation. The formation of $[ReH_6(PPh_3)_3]^+$ was initially identified through a ^1H n.m.r. experiment (Figure 2). Further evidence for this stoicheiometry includes the reaction of the solid with MeCN which produces $[ReH_4(PPh_3)_3(NCMe)]^+$ quantitatively (n.m.r.) along with H_2 (g.c. analysis). An earlier conductimetric study had suggested the formation of the analogous PMe_2Ph compound, $[ReH_6(PMe_2Ph)_3]Cl$, as the product from the reaction of $[ReH_5(PMe_2Ph)_3]$ with HCl.[15] This is an interesting species for it becomes the fourth member of the nine-co-ordinate polyhydride–phosphine series $[ReH_9]^{2-}$, $[ReH_8(PR_3)]^-$, $[ReH_7(PR_3)_2]$, and $[ReH_6(PR_3)_3]^+$.[16,17] It is noteworthy that such a plethora of isoelectronic polyhydride complexes of a single metal oxidation state (in this case formally Re^{VII}) can be isolated. Their remarkable stability may reflect the co-ordinative saturation of the metal centre in each case.

(*b*) *Reactions of* $[ReH_4(PPh_3)_3L]PF_6$ (L = MeCN, PPh_3, *or* Bu^{t}NC) *with Triethylamine*.—Deprotonation of rhenium tetrahydride cations is a known reaction.[11] We were able to isolate the neutral rhenium trihydride complexes $[ReH_3(PPh_3)_3(NCMe)]$ and $[ReH_3(PPh_3)_3(CNBu^t)]$ by treating their corresponding rhenium tetrahydride cations with NEt_3 in polar solvents such as acetone or acetonitrile [equation (2)] (L =

$$[ReH_4(PPh_3)_3L]PF_6 + NEt_3 \longrightarrow [ReH_3(PPh_3)_3L] \quad (2)$$

MeCN or Bu^{t}NC). We were, however, unable to isolate pure samples of the previously reported compound $[ReH_3(PPh_3)_4]$[8,11] by such a method using CH_2Cl_2, acetone, tetrahydrofuran (thf), or methanol as reaction solvents, although we have spectroscopic[8] and electrochemical evidence that it is formed. When acetonitrile is used as the solvent in the reaction between $[ReH_4(PPh_3)_4]PF_6$ and NEt_3 then deprotonation occurs but the product is $[ReH_3(PPh_3)_3(NCMe)]$. From measurements of the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of $[ReH_4(PPh_3)_4]PF_6$ in CD_3CN we have been able to show that this salt reacts slowly to give $[ReH_4(PPh_3)_3(NCMe)]^+$ and free PPh_3. Accordingly, we believe that this latter reaction precedes that of deprotonation in the conversion of $[ReH_4(PPh_3)_4]PF_6$ into $[ReH_3(PPh_3)_3(NCMe)]$ in acetonitrile–NEt_3.

A simple quartet is observed for the Re–H resonances in the ^1H n.m.r. spectra of $[ReH_3(PPh_3)_3L]$; resonances due to the PPh_3 protons and the other organic ligands show correct integrated intensities (Table). Over the temperature range 35 to −50 °C the Re–H resonance of the fluxional molecule $[ReH_3(PPh_3)_3(CNBu^t)]$ changed to a broad unresolved multiplet and by −80 °C (the lower limit of our measurements) had split into three very broad unstructured features (at −5.0, −5.7, and −6.1 p.p.m.); the remainder of the ^1H n.m.r. spectrum remained essentially unaffected over the temperature range. This spectral change, which is not structurally enlightening, was reversed upon warming the CD_2Cl_2 solution to 35 °C. Only one resonance is observed for each complex in their $^{31}P\text{-}\{^1H\}$ n.m.r. spectra. The complex $[ReH_3(PPh_3)_3(CNBu^t)]$ exhibits an i.r.-active ν(C≡N) mode at 2 010 cm^{-1}. This is a shift of more than 170 cm^{-1} to lower energy compared to $[ReH_4(PPh_3)_3(CNBu^t)]PF_6$, and is indicative of increased Re-to-π*(CNR) back bonding in the case of the more electron-rich metal centre in the trihydride. Tentative assignments for the ν(Re–H) modes in the i.r. spectra of these complexes are given in the Table.

The electrochemistry of these neutral trihydride complexes and also of $[ReH_3(dppe)_2]$ are very similar and apparently characteristic of this class of compounds as a whole. Solutions of $[ReH_3(PPh_3)_3(NCMe)]$, $[ReH_3(PPh_3)_3(CNBu^t)]$, and $[ReH_3(dppe)_2]$ in 0.1 mol dm^{-3} NBu_4PF_6–CH_2Cl_2 show c.v.s which display a couple (corresponding to a one-electron oxidation of the bulk complex) at $E_{\frac{1}{2}} = -0.29$, -0.10, and $+0.19$ V *vs.* Ag–AgCl, respectively. The very low potential for the oxidation in the case of the acetonitrile complex reflects its instability towards oxidation. These couples are characterized by peak separations ($\Delta E_p = E_{p,a} - E_{p,c}$) of 90, 190, and 120 mV at a scan rate v = 200 mV s^{-1}, respectively, and current ratios $i_{p,a}/i_{p,c}$ very close to unity. Single-scan c.v.s of these complexes show that following the oxidation step, weak product waves are encountered if the sweeps are carried out to +1.5 V, *e.g.* $E_{p,a}$ at *ca.* +0.3, *ca.* +0.5, and *ca.* + 1.25 V in the case of $[ReH_3(PPh_3)_3(NCMe)]$ [Figure 1(*b*)]. The electron-rich nature of the metal centre in these trihydrides contrasts with the situation for the analogous cationic tetrahydride species for which the first oxidation process occurs at a potential up to 1.7 V more positive; $E_{p,a}$ values for $[ReH_4(PPh_3)_3(NCMe)]^+$, $[ReH_4(PPh_3)_3(CNBu^t)]^+$, and $[ReH_4(dppe)_2]^+$ are + 1.25, + 1.60, and + 1.61 V *vs.* Ag–AgCl, respectively.

(*c*) *Reactions of* $[ReH_3(PPh_3)_3(NCMe)]$, $[ReH_3(PPh_3)_3(CNBu^t)]$, *and* $[ReH_3(dppe)_2]$ *with* $C_7H_7^+PF_6^-$ *and* HBF_4.—Since neutral rhenium trihydride compounds are known to undergo reversible protonation,[11,13] it is not surprising that $[ReH_4(PPh_3)_3(NCMe)]^+$ and $[ReH_4(dppe)_2]^+$ are formed by treating $[ReH_3(PPh_3)_3(NCMe)]$ and $[ReH_3(dppe)_2]$, respectively, with $HBF_4{\cdot}Et_2O$ in acetonitrile. However, when $[ReH_3(PPh_3)_3(CNBu^t)]$ was treated in a similar fashion, the complex $[ReH_2(PPh_3)_3\{CN(H)Bu^t\}(NCMe)][BF_4]_2$ was isolated following H_2 evolution. Protonation at the nitrogen atom of the co-ordinated Bu^tNC ligand was not entirely unexpected in view of the rather low ν(C≡N) frequency (2 010 cm^{-1}) of the parent compound. Low C≡N stretching frequencies are often diagnostic of relatively electron-rich isocyanide ligands which are susceptible to electrophilic attack at the nitrogen atom.[18–22]

While the cations $[ReH_4(PPh_3)_3(NCMe)]^+$ and $[ReH_4(dppe)_2]^+$ were identified on the basis of a comparison of their properties with those of authentic samples (see Table and ref. 11), $[ReH_2(PPh_3)_3\{CN(H)Bu^t\}(NCMe)][BF_4]_2$ was identified through measurement of its cyclic voltammogram ($E_{p,a}$ = + 1.55 V *vs.* Ag–AgCl in 0.1 mol dm^{-3} NBu_4PF_6–CH_2Cl_2), its conductivity (Λ = 232 ohm^{-1} cm^2 mol^{-1} for a 1 × 10^{-3} mol dm^{-3} solution in acetonitrile), and its spectroscopic properties (Table). In addition to a ν(N$\overset{\dots}{=}$C) mode at 1 559m cm^{-1} in the i.r. spectrum, other characteristic features are observed at 3 289w [ν(N–H)] and 1 065s cm^{-1} [ν(B–F)]. The ^1H n.m.r. spectrum displayed a quartet of doublets for the Re–H resonance; this may be explained by *J*(P–H) = 53.2 Hz with further coupling to the unique hydrogen on the carbyne-like ligand [*J*(H–H) = 6.7 Hz]. In accord with this we see the N–H resonance as a triplet at δ +3.26 p.p.m. [*J*(H–H) = 6.7 Hz].

Like $[ReH_5(PPh_3)_3]$, the neutral trihydride complexes $[ReH_3(PPh_3)_3L]$ (L = MeCN or Bu^tNC) and $[ReH_3(dppe)_2]$ react with $C_7H_7^+PF_6^-$ in the presence of ligand L *via* hydride abstraction. The acetonitrile-substituted complexes $[ReH_2(PPh_3)_3(NCMe)_2]PF_6$, $[ReH_2(PPh_3)_3(NCMe)(CNBu^t)]PF_6$, and $[ReH_2(dppe)_2(NCMe)]PF_6$ are prepared from slurries of $[ReH_3(PPh_3)_3(NCMe)]$, $[ReH_3(PPh_3)_3(CNBu^t)]$, and $[ReH_3(dppe)_2]$, respectively, in the presence of acetonitrile and $C_7H_7^+PF_6^-$ [equations (3), L = MeCN or Bu^tNC, and (4)].

$$[ReH_3(PPh_3)_3L] + C_7H_7^+PF_6^- \xrightarrow{MeCN} [ReH_2(PPh_3)_3(NCMe)L]PF_6 \quad (3)$$

$$[ReH_3(dppe)_2] + C_7H_7^+PF_6^- \xrightarrow{MeCN} [ReH_2(dppe)_2(NCMe)]PF_6 \quad (4)$$

The formation of $[ReH_2(dppe)_2(NCMe)]PF_6$ by the action of $C_7H_7^+PF_6^-$ on $[ReH_3(dppe)_2]$ [equation (4)] illustrates an important point, namely the difference in reactivity between the Lewis acids HBF_4 and $C_7H_7^+PF_6^-$. The protic acid HBF_4 co-ordinates to the metal centre while the non-protic acid abstracts a hydride ligand.

By the use of the reactions (5) and (6) (L = Bu^tNC or 2,6-$Me_2C_6H_3NC$) the related isocyanide complexes could be

$$[ReH_3(PPh_3)_3(CNBu^t)] + C_7H_7^+PF_6^- + Bu^tNC \longrightarrow [ReH_2(PPh_3)_3(CNBu^t)_2]PF_6 \quad (5)$$

$$[ReH_3(dppe)_2] + C_7H_7^+PF_6^- + L \longrightarrow [ReH_2(dppe)_2L]PF_6 \quad (6)$$

obtained. Of the three such species isolated, only $[ReH_3(dppe)_2(CNC_6H_3Me_2\text{-}2,6)]PF_6$ was not obtained in an analytically pure form; thus, its formulation is based primarily on its spectroscopic properties (Table). Conductivity measurements on the six dihydride complexes show that they behave as 1:1 electrolytes (Λ = 110—144 ohm^{-1} cm^2 mol^{-1} for 1 × 10^{-3} mol dm^{-3} solutions in acetonitrile). As far as their electrochemical properties are concerned, c.v. measurements (in 0.1 mol dm^{-3} NBu_4PF_6–CH_2Cl_2 *vs.* Ag–AgCl) show that the acetonitrile complexes are, as expected, much easier to oxidize than their isocyanide analogues. Voltammetric data for $[ReH_2(PPh_3)_3(NCMe)_2]PF_6$ [see Figure 1(*c*)], $[ReH_2(PPh_3)_3(NCMe)(CNBu^t)]PF_6$, and $[ReH_2(PPh_3)_3(CNBu^t)_2]PF_6$ are $E_{\frac{1}{2}}$ = +0.43 V (with a second irreversible process at $E_{p,a}$ = + 1.2 V), $E_{p,a}$ = +0.88 V, and $E_{p,a}$ = + 1.04 V, respectively, whereas for $[ReH_2(dppe)_2(NCMe)]PF_6$, $[ReH_2(dppe)_2(CNBu^t)]PF_6$, and $[ReH_2(dppe)_2(CNC_6H_3Me_2\text{-}2,6)]PF_6$ we find $E_{\frac{1}{2}}$ = +0.70 V (with a second irreversible process at $E_{p,a}$ = + 1.30 V), $E_{p,a}$ = + 1.00 V, and $E_{\frac{1}{2}}$ = + 1.01 V, respectively. As confirmation of the identity of $[ReH_2(PPh_3)_3(NCMe)_2]PF_6$, we find that it can be converted into the monohydride $[ReH(PPh_3)_3(NCMe)_3][PF_6]_2$[3] by treatment with further $C_7H_7^+PF_6^-$ in acetonitrile [equation (7)]. Thus, the dihydride

$$[ReH_2(PPh_3)_3(NCMe)_2]PF_6 + C_7H_7^+PF_6^- \xrightarrow{MeCN} [ReH(PPh_3)_3(NCMe)_3][PF_6]_2 \quad (7)$$

can be considered as an intermediate in the conversion of $[ReH_5(PPh_3)_3]$ into $[ReH(PPh_3)_3(NCMe)_3][PF_6]_2$. It is probable that a similar intermediate is involved in the conversion of $[ReH_5(PMe_2Ph)_3]$ into $[ReH(PMe_2Ph)_3(NCMe)_3][BF_4]_2$.[10]

(*d*) *Concluding Remarks*.—Based upon the results presented herein and those described in our earlier report[3] we can represent those reactions of $[ReH_5(PPh_3)_3]$ with H^+ or $C_7H_7^+$ which give rise to tetra-, tri-, di-, and mono-hydride species in terms of the following reaction sequence (in which L and L′ are ligands such as MeCN and Bu^tNC): $[ReH_5(PPh_3)_3] \xrightarrow{H^+} [ReH_6(PPh_3)_3]^+ \xrightarrow[+L]{-H_2} [ReH_4(PPh_3)_3L]^+ \xrightarrow{-H^+} [ReH_3(PPh_3)_3L] \xrightarrow[+L']{-H^-} [ReH_2(PPh_3)_3L(L')]^+ \xrightarrow[+L']{-H^-} [ReH(PPh_3)_3LL'_2]^{2+}$. This scheme, in which L may or may not be the same as L′, can equally well explain the related behaviour of complexes of the type $[ReH_5(PPh_3)_2L]$ (L = py, $C_6H_{11}NH_2$, or Bu^tNH_2)[3] in which protonation in nitrile solvents gives $[ReH(PPh_3)_2(NCR)_3L]^{2+}$ (R = Me or Et). The tetra-, tri-, di-, and mono-hydride complexes that we have isolated are isoelectronic with various $[ReH_xL_2]$ (*x* = 1—4; L = phosphine ligand) species complexed by unsaturated organic molecules, *e.g.* those of the type $[ReH_3(PPh_3)_2(diene)]$.[23–29] Several such molecules have been of special interest in the chemistry of C–H bond activation. The present work provides analogues where the use of better σ donors affords complexes where the metal centres are demonstrably more electron-rich.

Experimental

Starting Materials.—The complexes $[ReH_7(PPh_3)_2]$,[7,16] $[ReH_5(PPh_3)_3]$,[16] and $[ReH_3(dppe)_2]$[11] were prepared by standard literature methods. t-Butyl isocyanide was prepared by the method of Weber *et al.*[30] 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.

Preparations.—(*a*) $[ReH_6(PPh_3)_3]BF_4$. A solution of $[ReH_5(PPh_3)_3]$ (0.10 g, 0.10 mmol) in CH_2Cl_2 (5 cm^3) was treated with $HBF_4 \cdot Et_2O$* (0.1 cm^3). The reaction mixture was stirred for 10 min, mixed with diethyl ether (30 cm^3), and then stirred for an additional 20 min. The pale yellow precipitate of $[ReH_6(PPh_3)_3]BF_4 \cdot 3H_2O$ was filtered off and washed with diethyl ether; yield 0.04 g (36%) (Found: C, 57.65; H, 5.05. $C_{54}H_{57}BF_4O_3P_3Re$ requires C, 57.9; H, 5.1%). The H_2O of crystallization was identified by ^1H n.m.r. spectroscopy in $(CD_3)_2CO$ (δ 3.08 p.p.m. with correct integration), and i.r. spectroscopy (Nujol mull) with ν(O–H) at 3 614w and 3 514m–w cm^{-1} and δ(O–H) at 1 632m cm^{-1}.

(*b*) $[ReH_4(PPh_3)_3(NCMe)]PF_6$. (*i*) A mixture of $[ReH_5(PPh_3)_3]$ (0.12 g, 0.12 mmol) and $C_7H_7^+PF_6^-$ (0.03 g, 0.13 mmol) was treated with acetonitrile (5 cm^3). Upon stirring this reaction mixture for 30 min the suspension dissolved. The mixture was filtered into diethyl ether (100 cm^3). The addition of pentane (100 cm^3) followed by agitation of the solution induced precipitation of a white powder. This was filtered off and washed twice with diethyl ether; yield 0.125 g (88%) (Found: C, 57.8; H, 4.6. $C_{56}H_{52}F_6NP_4Re$ requires C, 57.8; H, 4.5%).

(*ii*) A suspension of $[ReH_3(PPh_3)_3(NCMe)]$ (0.18 g, 0.18 mmol) in a solution of KPF_6 (0.04 g, 0.21 mmol) in acetone (5 cm^3) was treated with $HBF_4 \cdot Et_2O$ (0.10 cm^3). The reaction mixture was stirred for 5 min, and diethyl ether (50 cm^3) and pentane (50 cm^3) were added to induce precipitation. The white precipitate was recrystallized from dichloromethane–diethyl ether–pentane; yield 0.155 g (76%).

(*iii*) The reaction between $[ReH_5(PPh_3)_3]$ and $HBF_4 \cdot Et_2O$ in a solution of KPF_6 in acetonitrile was carried out using a procedure similar to (*b*)(*ii*). Hydrogen evolution was monitored by g.c.; yield 0.078 g (64%).

(*iv*) The addition of acetonitrile (5 cm^3) to a mixture of $[ReH_6(PPh_3)_3]BF_4$ (0.06 g, 0.06 mmol) and KPF_6 (0.015 g, 0.08 mmol) led to H_2 evolution (g.c.) and the formation of the required complex. Work-up and recrystallization was as described in (*b*)(*ii*); yield 0.04 g (62%).

(*c*) $[ReH_4(PPh_3)_4]PF_6$. A dichloromethane solution (10 cm^3) containing $[ReH_5(PPh_3)_3]$ (0.15 g, 0.15 mmol), $C_7H_7^+PF_6^-$ (0.04 g, 0.16 mmol), and PPh_3 (0.31 g, 1.1 mmol) was stirred for 30 min and filtered into an excess of diethyl ether (100 cm^3). The same volume of pentane was added and the mixture stirred until white microcrystalline $[ReH_4(PPh_3)_4]PF_6$ had precipitated. The product was filtered off and washed with diethyl ether; yield 0.175 g (83%) (Found: C, 62.4; H, 4.75. $C_{72}H_{64}F_6P_5Re$ requires C, 62.5; H, 4.7%).

(*d*) $[ReH_4(PPh_3)_3(CNBu^t)]PF_6$. This complex was isolated as its monohydrate using a preparative procedure similar to (*c*), but with Bu^tNC (40 µl, 0.38 mmol) in place of PPh_3 and a reaction time of only 5 min; yield 0.12 g (66%) (Found: C, 56.9; H, 5.1. $C_{59}H_{60}F_6NOP_4Re$ requires C, 57.9; H, 4.8%). The presence of H_2O was confirmed by ^1H n.m.r. spectroscopy in CD_3CN (δ 2.10 p.p.m. with correct integration), and the i.r. spectrum (Nujol mull) showed ν(O–H) at *ca.* 3 300w,br and δ(O–H) at *ca.* 1 627w,br cm^{-1}.

(*e*) $[ReH_4(PPh_3)_3(CNC_6H_3Me_2\text{-}2,6)]PF_6$. This complex was formed in a 15-min reaction at −78 °C by use of a procedure similar to that described in (*c*); yield 0.10 g (52%) (Found: C, 59.3; H, 4.9. $C_{63}H_{58}F_6NP_4Re$ requires C, 60.4; H, 4.7%).

(*f*) $[ReH_3(PPh_3)_3(NCMe)]$. (*i*) A solution of $[ReH_4(PPh_3)_3(NCMe)]PF_6$ (0.44 g) in acetonitrile (5 cm^3) and triethylamine (1 cm^3) was stirred for 30 min, and the resulting bright yellow precipitate filtered off and washed with acetonitrile; yield 0.34 g, (89%) (Found: C, 65.9; H, 5.1. $C_{56}H_{51}NP_3Re$ requires C, 66.1; H, 5.1%).

(*ii*) The use of $[ReH_4(PPh_3)_4]PF_6$ (0.31 g) in place of $[ReH_4(PPh_3)_3(NCMe)]PF_6$ gave the same product after reaction for 3 h; yield 0.14 g (52%).

(*iii*) The reaction between $[ReH_5(PPh_3)_3]$ (0.415 g, 0.42 mmol) and $C_7H_7^+PF_6^-$ (0.10 g, 0.43 mmol) in acetonitrile (5 cm^3) for 5 min, followed by the addition of triethylamine (1 cm^3) and stirring for 30 min, gave the bright yellow complex which was filtered off and washed with acetonitrile; yield 0.33 g (76%).

(*g*) $[ReH_3(PPh_3)_3(CNBu^t)]$. This bright yellow complex can be prepared from $[ReH_4(PPh_3)_3(CNBu^t)]PF_6$ (0.20 g) and NEt_3 using acetone (5 cm^3) as the solvent; yield 0.13 g (75%) (Found: C, 66.3; H, 5.5. $C_{59}H_{57}NP_3Re$ requires C, 66.9; H, 5.4%).

(*h*) *Reactions of* $[ReH_3(PPh_3)_3L]$ (L = MeCN *or* Bu^tNC) *with* $C_7H_7^+PF_6^-$.—(*i*) $[ReH_2(PPh_3)_3(NCMe)_2]PF_6$. A mixture of $[ReH_3(PPh_3)_3(NCMe)]$ (0.32 g, 0.31 mmol) and $C_7H_7^+PF_6^-$ (0.075 g, 0.32 mmol) was added to diethyl ether (10 cm^3) which contained a small quantity of acetonitrile (16 µl, 0.50 mmol). The reaction mixture was stirred for 45 min and the insoluble off-white product filtered off and washed several times with diethyl ether; yield 0.30 g (78%) (Found: C, 56.75; H, 4.8. $C_{58}H_{53}F_6N_2P_4Re$ requires C, 57.95; H, 4.4%). The microanalytical data reflect the difficulty of freeing this complex from contamination by $[ReH(PPh_3)_3(NCMe)_3][PF_6]_2$ [see (*k*)].

(*ii*) $[ReH_2(PPh_3)_3(NCMe)(CNBu^t)]PF_6$. This complex was prepared by the reaction between $[ReH_3(PPh_3)_3(CNBu^t)]$ (0.13 g, 0.135 mmol) and $C_7H_7^+PF_6^-$ (0.03 g, 0.13 mmol) in acetonitrile (5 cm^3); yield 0.07 g (47%) (Found: C, 58.9; H, 5.25. $C_{61}H_{60}F_6N_2P_4Re$ requires C, 58.8; H, 4.9%).

(*iii*) $[ReH_2(PPh_3)_3(CNBu^t)_2]PF_6$. The reaction between $[ReH_3(PPh_3)_3(CNBu^t)]$ (0.135 g, 0.13 mmol), $C_7H_7^+PF_6^-$ (0.03 g, 0.13 mmol), and Bu^tNC (40 µl, 0.38 mmol) in CH_2Cl_2 (5 cm^3) for 10 min gave this complex as very pale yellow microcrystals; yield 0.10 g (60%). Identification was based upon electrochemical and spectroscopic measurements as an analytically pure sample could not be prepared.

(*i*) *Protonation of* $[ReH_3(PPh_3)_3(CNBu^t)]$.—A quantity of $[ReH_3(PPh_3)_3(CNBu^t)]$ (0.16 g, 0.15 mmol) was treated with $HBF_4 \cdot Et_2O$ (100 µl) in acetonitrile (5 cm^3) and the mixture stirred for 5 min, treated with diethyl ether (50 cm^3) and pentane (50 cm^3), and then filtered. The yellow trihydrate $[ReH_2(PPh_3)_3\{CN(H)Bu^t\}(NCMe)][BF_4]_2 \cdot 3H_2O$ was filtered off and dried; yield 0.12 g (60%) (Found: C, 55.2; H, 5.2. $C_{61}H_{66}B_2F_8N_2O_3P_3Re$ requires C, 55.2; H, 5.0%). The H_2O of crystallization was identified by ^1H n.m.r. spectroscopy in $CDCl_3$ (δ 1.69 with correct integration), and by i.r. spectroscopy (Nujol mull) with ν(O–H) at *ca.* 3 550m,br cm^{-1} and δ(O–H) at 1 632m cm^{-1}.

(*j*) *Reactions of* $[ReH_3(dppe)_2]$ *with* $C_7H_7^+PF_6^-$.—(*i*) $[ReH_2(dppe)_2(NCMe)]PF_6$. The reaction between $[ReH_3(dppe)_2]$ (0.09 g, 0.095 mmol) and $C_7H_7^+PF_6^-$ (0.025 g, 0.11 mmol) in acetonitrile (5 cm^3) was carried out using a procedure similar to (*b*)(*i*) to give the complex as off-white crystals; yield 0.06 g, 51% (Found: C, 55.3; H, 4.7. $C_{54}H_{53}F_6NP_5Re$ requires C, 55.4; H, 4.6%).

(*ii*) $[ReH_2(dppe)_2(CNBu^t)]PF_6$. A reaction similar to (*j*)(*i*) but with CH_2Cl_2 (5 cm^3) as the reaction solvent and a threefold excess of Bu^tNC in place of acetonitrile gave the desired complex; yield 70% (Found: C, 55.5; H, 4.8. $C_{57}H_{59}F_6NP_5Re$ requires C, 56.4; H, 4.9%).

(*iii*) $[ReH_2(dppe)_2(CNC_6H_3Me_2\text{-}2,6)]PF_6$. The use of 2,6-$Me_2C_6H_3NC$ in place of Bu^tNC gave the required complex as a white powder; yield 67%.

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* A solution of HBF_4 (54%) in diethyl ether.

(*k*) *The Conversion of* $[ReH_2(PPh_3)_3(NCMe)_2]PF_6$ *into* $[ReH(PPh_3)_3(NCMe)_3][PF_6]_2$.—A small quantity of $[ReH_2(PPh_3)_3(NCMe)_2]PF_6$ (0.09 g, 0.08 mmol) was mixed with 1 equivalent of $C_7H_7^+PF_6^-$ (0.02 g, 0.08 mmol) in acetonitrile (5 cm^3), the mixture stirred for 30 min, and then treated with a large excess of diethyl ether (100 cm^3). The precipitate was filtered off and identified on the basis of a comparison of its i.r. and n.m.r. spectra and cyclic voltammogram with literature data;[3] yield 0.06 g (58%).

Physical Measurements.—Infrared spectra were recorded as 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_2Cl_2 (δ 5.35 p.p.m.), $(CD_3)_2CO$ (δ 2.05 p.p.m.), or to $SiMe_4$ in $CDCl_3$ solutions. The ^{31}P n.m.r. spectra were recorded with a Varian XL-200 spectrometer operated at 80.98 MHz with an internal deuterium lock and aqueous 85% H_3PO_4 as an external standard. Positive chemical shifts are downfield from H_3PO_4. Conductivities were measured on an Industrial Instruments Inc. model RC 16B2 conductivity bridge. Cyclic voltammetry experiments were performed on CH_2Cl_2 solutions containing 0.1 mol dm^{-3} tetra-n-butylammonium hexafluorophosphate as the supporting electrolyte. The $E_{\frac{1}{2}}$ values [taken as $(E_{p,a} + E_{p,c})/2$] and $E_{p,a}$ values were referenced to the Ag–AgCl electrode at room temperature and are uncorrected for junction potentials. Voltammetric measurements were obtained with a Bioanalytical Systems Inc. model CV-1A instrument in conjunction with a Hewlett-Packard model 7035B x-y recorder.

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

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