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^tNC) towards Electrophiles and Nucleophiles

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Protonation of $[ReH_5(PPh_3)_3]$ with HBF₄ in CH₂Cl₂ 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, PPh₃, Bu^tNC, or 2,6-Me₂C₆H₃NC. Deprotonation of the complexes where L = MeCN or Bu^tNC was accomplished using NEt₃ 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 HBF₄ 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 HBF₄ 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^tNC, 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 $[\text{Re}_2(\mu-\text{H})_4\text{H}_4(\text{PPh}_3)_4]$ and $[\text{ReH}_5-(\text{PPh}_3)_2\text{L}]$ (L = pyridine, cyclohexylamine, or t-butylamine). One of the findings of this previous work was that Lewis acids such as HBF₄, Ph₃C⁺PF₆⁻, or C₇H₇⁺PF₆⁻ 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, $[\text{ReH}_5(\text{PPh}_3)_3]$ and $[\text{ReH}_3-(\text{dppe})_2]$ (dppe = Ph₂PCH₂CH₂PPh₂). 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 HBF₄·Et₂O. 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 $[ReH_4(PPh_3)_3L]PF_6$ $(L = MeCN, PPh_3, Bu'NC, or 2,6-Me_2C_6H_3NC)$ in high yield [equation (1)]. An attempt to prepare the complex $[ReH_4-Ph_3]$

$$[\operatorname{ReH}_{5}(\operatorname{PPh}_{3})_{3}] + \operatorname{C}_{7}\operatorname{H}_{7}^{+}\operatorname{PF}_{6}^{-} + \operatorname{L} \longrightarrow \\ [\operatorname{ReH}_{4}(\operatorname{PPh}_{3})_{3}\operatorname{L}]\operatorname{PF}_{6} \quad (1)$$

 $(PPh_3)_3(N_2)]PF_6$ 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.

These complexes dissolve in acetonitrile to give solutions (ca. $1 \times 10^{-3} \text{ mol dm}^{-3}$) that exhibit conductivities ($\Lambda = 100-125$

ohm⁻¹ cm² 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 $\delta - 1.8$ 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^tNC , and 2,6-Me₂C₆H₃NC. 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 $[\text{ReH}_4(\text{PPh}_3)_3]$ -(NCMe)]PF₆ 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 ${}^{31}P-{}^{1}H$ n.m.r. spectra of these four compounds. The presence of the PF_6^- anion is further demonstrated by i.r. spectroscopy which showed v(P-F) at ca. 841 cm⁻¹ (Nujol mull). Additionally, weak bands assignable to v(Re-H) are found for all four compounds between ca. 1 900 and 2 030 cm^{-1} . The v(C=N) modes for the isocyanide complexes $[\text{ReH}_4(\text{PPh}_3)_3(\text{CNR})]\text{PF}_6 (\text{R} = \text{Bu}^t \text{ or } 2,6-\text{Me}_2\text{C}_6\text{H}_3) \text{ occur}$ 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 [ReH₄-(PPh₃)₃L]PF₆ in 0.1 mol dm⁻³ NBu₄PF₆-CH₂Cl₂, 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, PPh₃, Bu'NC, and 2,6-Me₂C₆H₃NC, 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 [ReH₅(PPh₃)₃]; its c.v. (measured

[†] Under the same experimental conditions the ferrocenium-ferrocene couple has $E_{\pm} = +0.47$ V vs. Ag-AgCl.

	¹ H N.m.r. $(\delta)^{a}$		31D (111) N	I.r. $(cm^{-1})^{d}$	
Complex	Re-H ^b	L°	$(\delta)^a$	v(Re-H)	v(C≡N)
$[\text{ReH}_4(\text{PPh}_3)_3(\text{NCMe})]\text{PF}_6$	-1.85 (q, 23.8) ^e	1.16 (s, CH ₃ , 3 H)	+32.80 (s) ^f	1 898w	2 249vw
$[\text{ReH}_4(\text{PPh}_3)_4]\text{PF}_6$	-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
$[\operatorname{ReH}_4(\operatorname{PPh}_3)_3(\operatorname{CNC}_6\operatorname{H}_3\operatorname{Me}_2-2,6)]\operatorname{PF}_6$	$-2.26 (q, 22.4)^{g}$	1.83 (s, CH ₃ , 6 H) ^g	+27.55 (s)	1 941vw	2 132s
$[\text{ReH}_3(\text{PPh}_3)_3(\text{NCMe})]$	-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
$[\text{ReH}_{3}(\text{PPh}_{3})_{3}(\text{CNBu}^{i})]$	$-5.00 (q, 22.0)^{g,i}$	0.67 (s, CH ₃ , 9 H) ^{<i>g</i>}	+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),	+23.97 (s)	1 945w	2 272vw, 2 085w,
		1.28 (s, CH ₃ , 9 H) ^g			2 033s
$[\text{ReH}_2(\text{PPh}_3)_3(\text{CNBu}')_2]\text{PF}_6$	-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}
$[\text{ReH}_2(\text{dppe})_2(\text{CNC}_6\text{H}_3\text{Me}_2-2,6)]\text{PF}_6$	- 5.24 (qnt, 18.5)	1.22 (s, CH ₃ , 6 H)	+43.27 (s)	1 914w (sh)	2 035s, 2 002s*
$[\text{ReH}_2(\text{PPh}_3)_3\{\text{CN}(\text{H})\text{Bu}^t\}(\text{NCMe})]$ -	-1.99 (qd, 53.2) ^{1,m}	3.26 (t, N-H, 1 H)	+ 19.82 (s)		1 559m"
$[BF_4]_2$		2.11 (s, CH ₃ , 3 H)	+ 18.03 (s)		
		1.01 (s, CH ₃ , 9 H) ¹			

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

^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 v(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 v(C=N) of the CN(H)Bu' ligand.



Figure 1. Cyclic voltammograms (scan rate 200 mV s⁻¹ at a platinumbead electrode) in 0.1 mol dm⁻³ tetra-n-butylammonium hexafluorophosphate-dichloromethane: (a) [ReH₄(PPh₃)₃(NCMe)]PF₆, (b) [ReH₃(PPh₃)₃(NCMe)], and (c) [ReH₂(PPh₃)₃(NCMe)₂]PF₆

in 0.2 mol dm⁻³ NBu₄PF₆-CH₂Cl₂) has $E_{\frac{1}{2}} = +0.37$ V vs. saturated calomel electrode (s.c.e.).⁶ The shift in the oxidation potential between the [ReH₅(PPh₃)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, PPh₃, Bu'NC, or 2,6-Me₂C₆H₃NC), increase significantly the number of known mononuclear rhenium tetrahydride cations. Previously, $[\text{ReH}_4(\text{dppe})_2]^+$,¹¹ $[\text{ReH}_4(\text{PPh}_3)_2(\text{dppe})]^+$,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 $C_7 H_7^+ PF_6^-$ affords a new synthetic route to this class of compounds. It should also be noted that the complexes $[\text{ReH}_4(\text{PPh}_3)_3\text{L}]\text{PF}_6$ (L = MeCN, Bu^tNC, or 2,6-Me₂C₆- H_3NC) are the first members of this class that are stabilized by ligands other than phosphines or phosphites. The isocyanidecontaining 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 complexes⁴ is also applicable to monomeric systems.

As mentioned at the beginning of this section, we had observed in an earlier study³ that $[ReH_5(PPh_3)_3]$ does not react with HBF₄·Et₂O 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 PF₆⁻ 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 HBF₄·Et₂O is carried out in the nonco-ordinating solvent CH₂Cl₂ the yellow salt $[ReH_6(PPh_3)_3]$ -BF₄ can be isolated. This reaction is quite similar to that recently reported by Crabtree and Lavin¹⁴ 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 CD₂Cl₂) of the Re-H resonance of [ReH₅(PPh₃)₃] showing the effect of adding HBF₄·Et₂O

 $\{P(C_6H_{11})_3\}_2$]. Unlike the iridium cation, however, no evidence for co-ordinated H₂ 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 H₂ (g.c. analysis). An earlier conductimetric study had suggested the formation of the analogous PMe₂Ph compound, [ReH₆- $(PMe_2Ph)_3$]Cl, as the product from the reaction of [ReH₅-(PMe₂Ph)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 coordinative saturation of the metal centre in each case.

(b) Reactions of $[ReH_4(PPh_3)_3L]PF_6$ (L = MeCN, PPh₃, or Bu'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 $[ReH_3(PPh_3)_3(CNBu')]$ by treating their corresponding rhenium tetrahydride cations with NEt₃ in polar solvents such as acetone or acetonitrile [equation (2)] (L =

$$[\operatorname{ReH}_4(\operatorname{PPh}_3)_3 L]\operatorname{PF}_6 + \operatorname{NEt}_3 \longrightarrow [\operatorname{ReH}_3(\operatorname{PPh}_3)_3 L] \quad (2)$$

MeCN or Bu^tNC). We were, however, unable to isolate pure samples of the previously reported compound $[\text{ReH}_3(\text{PPh}_3)_4]^{8.11}$ by such a method using CH₂Cl₂, acetone, tetrahydrofuran (thf), or methanol as reaction solvents, although we have spectroscopic⁸ 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 NEt₃ then deprotonation occurs but the product is [ReH₃(PPh₃)₃(NCMe)]. From measurements of the ³¹P-{¹H} n.m.r. spectrum of $[ReH_4(PPh_3)_4]PF_6$ in CD₃CN we have been able to show that this salt reacts slowly to give [ReH₄(PPh₃)₃(NCMe)]⁺ and free PPh₃. 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-NEt₃.

A simple quartet is observed for the Re-H resonances in the ¹H n.m.r. spectra of [ReH₃(PPh₃)₃L]; resonances due to the PPh₃ 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 [ReH₃(PPh₃)₃(CNBu^t)] changed to a broad unresolved multiplet and by $-80 \degree C$ (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 CD₂Cl₂ solution to 35 °C. Only one resonance is observed for each complex in $^{31}P-{^{1}H}$ n.m.r. spectra. The complex [Retheir $H_3(PPh_3)_3(CNBu^1)$ exhibits an i.r.-active v(C=N) mode at 2010 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- $\pi^*(CNR)$ back bonding in the case of the more electron-rich metal centre in the trihydride. Tentative assignments for the v(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 $[\text{ReH}_3(\text{dppe})_2]$ are very similar and apparently characteristic of this class of compounds as a whole. Solutions of $[\text{ReH}_3(\text{PPh}_3)_3(\text{NCMe})]$, $[\text{ReH}_3(\text{PPh}_3)_3(\text{CNBu}^{\text{I}})]$, and $[\text{ReH}_3(\text{dppe})_2]$ in 0.1 mol dm⁻³ NBu₄PF₆-CH₂Cl₂ 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 [ReH₃(PPh₃)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 $[\text{ReH}_4(\text{PPh}_3)_3(\text{NCMe})]^+$, $[\text{ReH}_4(\text{PPh}_3)_3(\text{CNBu}')]^+$, and $[\text{ReH}_4(\text{dppe})_2]^+$ are + 1.25, +1.60, and +1.61 V vs. Ag-AgCl, respectively.

(c) Reactions of [ReH₃(PPh₃)₃(NCMe)], [ReH₃- $(PPh_3)_3(CNBu^t)]$, and $[ReH_3(dppe)_2]$ with $C_7H_7^+PF_6^-$ and HBF₄.—Since neutral rhenium trihydride compounds are known to undergo reversible protonation,^{11,13} it is not surprising that $[\text{ReH}_4(\text{PPh}_3)_3(\text{NCMe})]^+$ and $[\text{ReH}_4(\text{dppe})_2]^+$ are formed by treating [ReH₃(PPh₃)₃(NCMe)] and [ReH₃-(dppe)₂], respectively, with HBF₄·Et₂O in acetonitrile. However, when [ReH₃(PPh₃)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 H₂ evolution. Protonation at the nitrogen atom of the co-ordinated Bu'NC ligand was not entirely unexpected in view of the rather low v(C=N) frequency (2010 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 $[\text{ReH}_4(\text{PPh}_3)_3(\text{NCMe})]^+$ and $[\text{ReH}_4(\text{dpp})_2]^+$ were identified on the basis of a comparison of their properties with those of authentic samples (see Table and ref. 11), $[\text{ReH}_2(\text{PPh}_3)_3(\text{CN(H)Bu}^1)(\text{NCMe})][\text{BF}_4]_2$ was identified through measurement of its cyclic voltammogram ($E_{p,a} = +1.55 \text{ V}$ vs. Ag-AgCl in 0.1 mol dm⁻³ NBu₄PF₆-CH₂Cl₂), its conductivity ($\Lambda = 232 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$ for a 1 × 10⁻³ mol dm⁻³ solution in acetonitrile), and its spectroscopic properties (Table). In addition to a v(N:=C) mode at 1 559m cm⁻¹ in the i.r. spectrum, other characteristic features are observed at 3 289w [v(N-H)] and 1 065s cm⁻¹ [v(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 $\delta + 3.26 \text{ p.p.m.}$ [J(H-H) = 6.7 Hz].

Like $[\text{ReH}_{5}(\text{PPh}_{3})_{3}]$, the neutral trihydride complexes $[\text{ReH}_{3}(\text{PPh}_{3})_{3}L]$ (L = MeCN or Bu'NC) and $[\text{ReH}_{3}(\text{dppe})_{2}]$ react with $C_{7}H_{7}^{+}\text{PF}_{6}^{-}$ in the presence of ligand L via hydride abstraction. The acetonitrile-substituted complexes $[\text{ReH}_{2}(\text{PPh}_{3})_{3}(\text{NCMe})_{2}]\text{PF}_{6}$, $[\text{ReH}_{2}(\text{PPh}_{3})_{3}(\text{NCMe})(\text{CNBu'})]\text{PF}_{6}$, and $[\text{ReH}_{2}(\text{dppe})_{2}(\text{NCMe})]\text{PF}_{6}$ are prepared from slurries of $[\text{ReH}_{3}(\text{PPh}_{3})_{3}(\text{NCMe})]$, $[\text{ReH}_{3}(\text{PPh}_{3})_{3}(\text{CNBu'})]$, and $[\text{ReH}_{3}(\text{dppe})_{2}]$, respectively, in the presence of acetonitrile and $C_{7}H_{7}^{+}\text{PF}_{6}^{-}$ [equations (3), L = MeCN or Bu'NC, and (4)].

$$[\operatorname{ReH}_{3}(\operatorname{PPh}_{3})_{3}L] + \operatorname{C}_{7}\operatorname{H}_{7}^{+}\operatorname{PF}_{6}^{-} \xrightarrow{\operatorname{MeCN}} [\operatorname{ReH}_{2}(\operatorname{PPh}_{3})_{3}(\operatorname{NCMe})L]\operatorname{PF}_{6} (3)$$

$$[\operatorname{ReH}_{3}(\operatorname{dppe})_{2}] + \operatorname{C}_{7}\operatorname{H}_{7}^{+}\operatorname{PF}_{6}^{-} \xrightarrow{\operatorname{MeCN}} [\operatorname{ReH}_{2}(\operatorname{dppe})_{2}(\operatorname{NCMe})]\operatorname{PF}_{6} \quad (4)$$

The formation of $[\text{ReH}_2(\text{dppe})_2(\text{NCMe})]\text{PF}_6$ by the action of $C_7\text{H}_7^+\text{PF}_6^-$ on $[\text{ReH}_3(\text{dppe})_2]$ [equation (4)] illustrates an important point, namely the difference in reactivity between the Lewis acids HBF₄ and $C_7\text{H}_7^+\text{PF}_6^-$. The protic acid HBF₄ coordinates to the metal centre while the non-protic acid abstracts a hydride ligand.

By the use of the reactions (5) and (6) ($L = Bu^{t}NC$ or 2,6-Me₂C₆H₃NC) the related isocyanide complexes could be

$$[\operatorname{ReH}_{3}(\operatorname{PPh}_{3})_{3}(\operatorname{CNBu}^{t})] + \operatorname{C}_{7}\operatorname{H}_{7}^{+}\operatorname{PF}_{6}^{-} + \operatorname{Bu}^{t}\operatorname{NC} \longrightarrow \\ [\operatorname{ReH}_{2}(\operatorname{PPh}_{3})_{3}(\operatorname{CNBu}^{t})_{2}]\operatorname{PF}_{6} \quad (5)$$

$$[\operatorname{ReH}_{3}(\operatorname{dppe})_{2}] + \operatorname{C}_{7}\operatorname{H}_{7}^{+}\operatorname{PF}_{6}^{-} + \operatorname{L} \longrightarrow \\ [\operatorname{ReH}_{2}(\operatorname{dppe})_{2}\operatorname{L}]\operatorname{PF}_{6} \quad (6)$$

obtained. Of the three such species isolated, only [ReH₃- $(dppe)_2(CNC_6H_3Me_2-2,6)]PF_6$ 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 ($\Lambda = 110$ —144 ohm⁻¹ cm² 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 -CH₂Cl₂ vs. Ag-AgCl) show that the acetonitrile complexes are, as expected, much easier to oxidize than their isocyanide analogues. Voltammetric data for [ReH₂(PPh₃)₃- $(NCMe)_2]PF_6$ [see Figure 1(c)], $[ReH_2(PPh_3)_3(NCMe) (CNBu')]PF_6$, and $[ReH_2(PPh_3)_3(CNBu')_2]PF_6$ 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 $[\text{ReH}_2(\text{dppe})_2(\text{NCMe})]$ PF₆, $[\text{ReH}_2(\text{dppe})_2(\text{CNBu}^i)]$ PF₆, and $[\text{ReH}_2(\text{dppe})_2(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)]\text{PF}_6 \text{ we find } E_{\frac{1}{2}} = +0.70 \text{ V}$ (with a second irreversible process at $E_{\text{p,a}} = +1.30 \text{ V}$), $E_{p,a} = +1.00$ 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

$$[\operatorname{ReH}_{2}(\operatorname{PPh}_{3})_{3}(\operatorname{NCMe})_{2}]\operatorname{PF}_{6} + \operatorname{C}_{7}\operatorname{H}_{7}^{+}\operatorname{PF}_{6}^{-} \xrightarrow{\operatorname{MeCN}} [\operatorname{ReH}(\operatorname{PPh}_{3})_{3}(\operatorname{NCMe})_{3}][\operatorname{PF}_{6}]_{2} \quad (7)$$

can be considered as an intermediate in the conversion of $[\text{ReH}_5(\text{PPh}_3)_3]$ into $[\text{ReH}(\text{PPh}_3)_3(\text{NCMe})_3][\text{PF}_6]_2$. It is probable that a similar intermediate is involved in the conversion of $[\text{ReH}_5(\text{PMe}_2\text{Ph})_3]$ into $[\text{ReH}(\text{PMe}_2\text{Ph})_3](\text{NCMe})_3][\text{BF}_4]_2$.¹⁰

(d) Concluding Remarks.--Based upon the results presented herein and those described in our earlier report³ we can represent those reactions of $[\text{ReH}_5(\text{PPh}_3)_3]$ with H⁺ or C₇H₇⁺ 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'NC): $[\text{ReH}_5(\text{PPh}_3)_3] \xrightarrow{H^+} [\text{ReH}_6(\text{PPh}_3)_3]^+ \xrightarrow{-H_2} [\text{ReH}_4(\text{PPh}_3)_3L]^+ \xrightarrow{-H^+} [\text{ReH}_3]_3L] \xrightarrow{-H^-} [\text{ReH}_2(\text{PPh}_3)_3L(L')]^+ \xrightarrow{-H^-} [\text{ReH}_4(\text{PPh}_3)_3L(L')]^+ \xrightarrow{-H^-} [\text{ReH}_4(\text{PPh}_3)_3]_3$ LL'_{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 $[\text{ReH}_5(\text{PPh}_3)_2\text{L}]$ (L = py, C₆H₁₁NH₂, or $Bu^{t}NH_{2})^{3}$ 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_xL₂] (x = 1-4; L = phosphine ligand) species complexed by unsaturated organic molecules, *e.g.* those of the type $[\text{ReH}_3(\text{PPh}_3)_2(\text{diene})]^{23-29}$ 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 $[\text{ReH}_7(\text{PPh}_3)_2]$,^{7,16} $[\text{ReH}_5(\text{PPh}_3)_3]$,¹⁶ and $[\text{ReH}_3(\text{dppe})_2]^{11}$ 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*) [ReH₆(PPh₃)₃]BF₄. A solution of [ReH₅-(PPh₃)₃] (0.10 g, 0.10 mmol) in CH₂Cl₂ (5 cm³) was treated with HBF₄·Et₂O* (0.1 cm³). The reaction mixture was stirred for 10 min, mixed with diethyl ether (30 cm³), and then stirred for an additional 20 min. The pale yellow precipitate of [ReH₆(PPh₃)₃]BF₄·3H₂O was filtered off and washed with diethyl ether; yield 0.04 g (36%) (Found: C, 57.65; H, 5.05. C₅₄H₅₇BF₄O₃P₃Re requires C, 57.9; H, 5.1%). The H₂O of crystallization was identified by ¹H n.m.r. spectroscopy in (CD₃)₂CO (δ 3.08 p.p.m. with correct integration), and i.r. spectroscopy (Nujol mull) with v(O–H) at 3 614w and 3 514m–w cm⁻¹ and δ(O–H) at 1 632m cm⁻¹.

(b) $[\text{ReH}_4(\text{PPh}_3)_3(\text{NCMe})]\text{PF}_6$. (i) A mixture of $[\text{ReH}_5-(\text{PPh}_3)_3]$ (0.12 g, 0.12 mmol) and $C_7\text{H}_7^+\text{PF}_6^-$ (0.03 g, 0.13 mmol) was treated with acetonitrile (5 cm³). Upon stirring this reaction mixture for 30 min the suspension dissolved. The mixture was filtered into diethyl ether (100 cm³). The addition of pentane (100 cm³) 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. $C_{56}\text{H}_{52}\text{F}_6\text{NP}_4\text{Re}$ requires C, 57.8; H, 4.5%).

(*ii*) A suspension of $[\text{ReH}_3(\text{PPh}_3)_3(\text{NCMe})]$ (0.18 g, 0.18 mmol) in a solution of KPF₆ (0.04 g, 0.21 mmol) in acetone (5 cm³) was treated with HBF₄·Et₂O (0.10 cm³). The reaction mixture was stirred for 5 min, and diethyl ether (50 cm³) and pentane (50 cm³) were added to induce precipitation. The white precipitate was recrystallized from dichloromethane-diethyl ether-pentane; yield 0.155 g (76%).

(*iii*) The reaction between [ReH₅(PPh₃)₃] and HBF₄·Et₂O in a solution of KPF₆ 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 cm³) to a mixture of $[\text{ReH}_6(\text{PPh}_3)_3]\text{BF}_4$ (0.06 g, 0.06 mmol) and KPF_6 (0.015 g, 0.08 mmol) led to H₂ 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) $[\text{ReH}_4(\text{PPh}_3)_4]\text{PF}_6$. A dichloromethane solution (10 cm³) containing $[\text{ReH}_5(\text{PPh}_3)_3]$ (0.15 g, 0.15 mmol), $C_7\text{H}_7^+$ - PF_6^- (0.04 g, 0.16 mmol), and PPh₃ (0.31 g, 1.1 mmol) was stirred for 30 min and filtered into an excess of diethyl ether (100 cm³). The same volume of pentane was added and the mixture stirred until white microcrystalline $[\text{ReH}_4(\text{PPh}_3)_4]\text{PF}_6$ had precipitated. The product was filtered off and washed with diethyl ether; yield 0.175 g (83%) (Found: C, 62.4; H, 4.75. $C_{72}\text{H}_6\text{P}_5\text{Re}$ requires C, 62.5; H, 4.7%).

(d) [ReH₄(PPh₃)₃(CNBu')]PF₆. This complex was isolated as its monohydrate using a preparative procedure similar to (c), but with Bu'NC (40 µl, 0.38 mmol) in place of PPh₃ 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 H₂O was confirmed by ¹H n.m.r. spectroscopy in CD₃CN (δ 2.10 p.p.m. with correct integration), and the i.r. spectrum (Nujol mull) showed v(O-H) at *ca.* 3 300w,br and δ (O-H) at *ca.* 1 627w,br cm⁻¹.

(e) $[\text{ReH}_4(\text{PPh}_3)_3(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)]\text{PF}_6$. 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. C₆₃H₅₈F₆NP₄Re requires C, 60.4; H, 4.7%).

(f) [ReH₃(PPh₃)₃(NCMe)]. (i) A solution of [ReH₄(PPh₃)₃-(NCMe)]PF₆ (0.44 g) in acetonitrile (5 cm³) and triethylamine (1 cm³) 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. C₅₆H₅₁NP₃Re requires C, 66.1; H, 5.1%). (*ii*) The use of $[\text{ReH}_4(\text{PPh}_3)_4]\text{PF}_6$ (0.31 g) in place of $[\text{ReH}_4(\text{PPh}_3)_3(\text{NCMe})]\text{PF}_6$ gave the same product after reaction for 3 h; yield 0.14 g (52%).

(*iii*) The reaction between $[\text{ReH}_5(\text{PPh}_3)_3]$ (0.415 g, 0.42 mmol) and $C_7H_7^+\text{PF}_6^-$ (0.10 g, 0.43 mmol) in acetonitrile (5 cm³) for 5 min, followed by the addition of triethylamine (1 cm³) and stirring for 30 min, gave the bright yellow complex which was filtered off and washed with acetonitrile; yield 0.33 g (76%).

(g) $[\text{ReH}_3(\text{PPh}_3)_3(\text{CNBu}^1)]$. This bright yellow complex can be prepared from $[\text{ReH}_4(\text{PPh}_3)_3(\text{CNBu}^1)]\text{PF}_6$ (0.20 g) and NEt₃ using acetone (5 cm³) as the solvent; yield 0.13 g (75%) (Found: C, 66.3; H, 5.5. C₅₉H₅₇NP₃Re requires C, 66.9; H, 5.4%).

(h) Reactions of $[\text{ReH}_3(\text{PPh}_3)_3\text{L}]$ (L = MeCN or Bu'NC) with $C_7H_7^+\text{PF}_6^-$.—(i) $[\text{ReH}_2(\text{PPh}_3)_3(\text{NCMe})_2]\text{PF}_6$. A mixture of $[\text{ReH}_3(\text{PPh}_3)_3(\text{NCMe})]$ (0.32 g, 0.31 mmol) and $C_7H_7^+\text{PF}_6^-$ (0.075 g, 0.32 mmol) was added to diethyl ether (10 cm³) 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 $[\text{ReH}(\text{PPh}_3)_3(\text{NCMe})_3][\text{PF}_6]_2$ [see (k)].

(*ii*) [ReH₂(PPh₃)₃(NCMe)(CNBu^t)]PF₆. This complex was prepared by the reaction between [ReH₃(PPh₃)₃(CNBu^t)] (0.13 g, 0.135 mmol) and $C_7H_7^+PF_6^-$ (0.03 g, 0.13 mmol) in acetonitrile (5 cm³); 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*) $[\text{ReH}_2(\text{PPh}_3)_3(\text{CNBu'})_2]\text{PF}_6$. The reaction between $[\text{ReH}_3(\text{PPh}_3)_3(\text{CNBu'})]$ (0.135 g, 0.13 mmol), $C_7H_7^+\text{PF}_6^-$ (0.03 g, 0.13 mmol), and Bu'NC (40 µl, 0.38 mmol) in CH₂Cl₂ (5 cm³) 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 $[ReH_3(PPh_3)_3(CNBu^{\dagger})]$.—A quantity of $[ReH_3(PPh_3)_3(CNBu^{\dagger})]$ (0.16 g, 0.15 mmol) was treated with HBF₄·Et₂O (100 µl) in acetonitrile (5 cm³) and the mixture stirred for 5 min, treated with diethyl ether (50 cm³) and pentane (50 cm³), and then filtered. The yellow trihydrate $[ReH_2-(PPh_3)_3\{CN(H)Bu^{\dagger}\}(NCMe)][BF_4]_2\cdot3H_2O$ was filtered off and dried; yield 0.12 g (60%) (Found: C, 55.2; H, 5.2. C₆₁H₆₆B₂F₈N₂O₃P₃Re requires C, 55.2; H, 5.0%). The H₂O of crystallization was identified by ¹H n.m.r. spectroscopy in CDCl₃ (δ 1.69 with correct integration), and by i.r. spectroscopy (Nujol mull) with v(O–H) at *ca.* 3 550m, br cm⁻¹ and δ (O–H) at 1 632m cm⁻¹.

(*j*) Reactions of $[\text{ReH}_3(\text{dppe})_2]$ with $C_7H_7^+\text{PF}_6^-$.—(*i*) $[\text{ReH}_2(\text{dppe})_2(\text{NCMe})]\text{PF}_6$. The reaction between $[\text{ReH}_3^-(\text{dppe})_2]$ (0.09 g, 0.095 mmol) and $C_7H_7^+\text{PF}_6^-$ (0.025 g, 0.11 mmol) in acetonitrile (5 cm³) 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. $C_{54}H_{53}F_6\text{NP}_5\text{Re}$ requires C, 55.4; H, 4.6%).

(*ii*) $[\text{ReH}_2(\text{dppe})_2(\text{CNBu}^1)]\text{PF}_6$. A reaction similar to (*j*)(*i*) but with CH_2Cl_2 (5 cm³) as the reaction solvent and a three-fold excess of Bu'NC in place of acetonitrile gave the desired complex; yield 70% (Found: C, 55.5; H, 4.8. $C_{57}\text{H}_{59}\text{F}_6\text{NP}_5\text{Re}$ requires C, 56.4; H, 4.9%).

(*iii*) $[\text{ReH}_2(\text{dppe})_2(\text{CNC}_6\text{H}_3\text{Me}_2\text{-}2,6)]\text{PF}_6$. The use of 2,6-Me₂C₆H₃NC in place of Bu¹NC gave the required complex as a white powder; yield 67%.

^{*} A solution of HBF₄ (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 cm³), the mixture stirred for 30 min, and then treated with a large excess of diethyl ether (100 cm³). 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 Nuiol 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 SiMe₄ in CDCl₃ solutions. The ³¹P 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% H₃PO₄ as an external standard. Positive chemical shifts are downfield from H₃PO₄. Conductivities were measured on an Industrial Instruments Inc. model RC 16B2 conductivity bridge. Cyclic voltammetry experiments were performed on CH₂Cl₂ solutions containing 0.1 mol dm⁻³ tetran-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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