# Activation of Mono- and Di-nuclear Polyhydrides of Rhenium: Protonation, Solvation, and Oxidation

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Activation of the rhenium polyhydrides $ReH_5(PPh_3)_2L$ (L = monodentate ligand) and $Re_2H_8(PPh_3)_4$ has been achieved through their protonation (using $HBF_4$), the formation of solvento-complexes, and their oxidation to reactive paramagnetic cations, strategies which have led to a range of novel species, including $[ReH(NCMe)_3(PPh_3)_2L]^{2+}$, $[Re_2H_7(PPh_3)_4L]^+$, and $[Re_2H_5(PPh_3)_4(CNBu^t)_2]^+$ together with their '17-electron' paramagnetic congeners.

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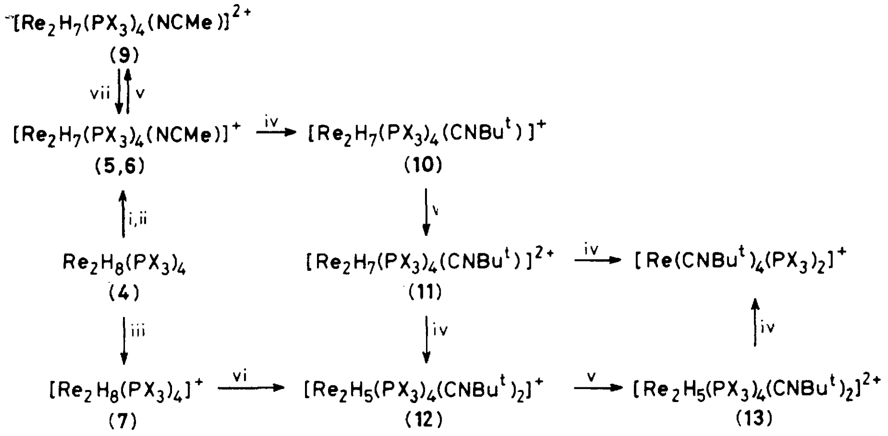
Rhenium polyhydride complexes have attracted renewed attention because of the reactivity of diolefins with $ReH_7(PX_3)_2$[1,2] ($PX_3$ = tertiary phosphine) and the ability of $ReH_7(PX_3)_2$ to activate C–H bonds.[3,4] Following our recent studies on the thermal reactions of rhenium polyhydrides,[5–7] we have sought means of activating the less reactive poly-



**Scheme 1.** X = Ph; (i) $HBF_4$, MeCN; (ii) $Ph_3C^+PF_6^-$, MeCN; (iii) $Ph_3C^+PF_6^-$, $CH_2Cl_2$; (iv) $Bu^tNC$, $CH_2Cl_2$, room temperature; (v) $NOPF_6$, acetone; (vi) $Bu^tNC$, $CH_2Cl_2$, 0 °C; (vii) Zn, $CH_2Cl_2$.

hydrides $[ReH_5(PX_3)_2L$, where L = monodentate ligand, and $Re_2H_8(PX_3)_4]$ through their protonation, the formation of solvento-complexes, and their oxidation to paramagnetic cations.

The addition of $HBF_4$ to a slurry of $ReH_5(PPh_3)_2(py)$ (py = $C_5H_5N$) in MeCN produces a yellow solution from which yellow crystals of $[ReH(NCMe)_3(PPh_3)_2(py)](BF_4)_2$ (**1**), can be isolated in quantitative yield. Starting with $ReH_5(PPh_3)_2(cy)$ (cy = $C_6H_{11}NH_2$), an analogous reaction gives $[ReH(NCMe)_3(PPh_3)_2(cy)](BF_4)_2$ (**2**). These ready protonation reactions are in sharp contrast to the usual sluggish thermal chemistry of the rhenium pentahydrides.[5,6,8,9]

$$[ReH(NCMe)_3(PPh_3)_2(py)](BF_4)_2$$
**(1)**

$$[ReH(NCMe)_3(PPh_3)_2(cy)](BF_4)_2$$
**(2)**

$$[ReH(NCMe)_4(PPh_3)_2](BF_4)_2$$
**(3)**

Extending this reaction with $HBF_4$ to the heptahydride $ReH_7(PPh_3)_2$ affords the analogous complex $[ReH(NCMe)_4(PPh_3)_2](BF_4)_2$ (**3**),† which is isoelectronic with the recently prepared $[WH_2(NCMe)_3(PMe_2Ph)_3](BF_4)_2$.[10]

We have sought to check the generality of this reaction insofar as it might be used to enhance the reactivity of $Re_2(\mu\text{-}H)_4H_4(PPh_3)_4$ (**4**) (see Scheme 1), a complex containing a formal Re–Re triple bond.[11,12] Compound (**4**) reacts with $HBF_4$ in MeCN to give deep violet $[Re_2H_7(PPh_3)_4(NCMe)]BF_4$ (**5**). Alternatively, this cation can be generated by the reaction of $Ph_3C^+PF_6^-$ with a suspension of (**4**) in MeCN, a procedure which gives a quantitative yield of $[Re_2H_7(PPh_3)_4(NCMe)]PF_6$ (**6**).‡ However, reaction of $Ph_3C^+PF_6^-$ with (**4**) in a *non-coordinating solvent* (*e.g.* $CH_2Cl_2$) leads to oxidation of the octahydride to the air-sensitive, paramagnetic, salt $[Re_2H_8(PPh_3)_4]PF_6$ (**7**).

The cyclic voltammogram (c.v.) of (**1**) in 0.2 M tetra-n-butylammonium hexafluorophosphate (TBAH)–$CH_2Cl_2$ consists of a reversible one-electron oxidation at an $E_{1/2}$ of +1.03 V and an irreversible two-electron reduction at −1.71 V *vs.* S.C.E. (standard calomel electrode); analogous c.v.s were obtained for (**2**) and (**3**). The oxidation corresponds to the process shown in equation (1). The peak current ratio $i_{p,a}:i_{p,c}$

$$[ReH(NCMe)_3(PPh_3)_2L]^{2+} \xrightarrow{-e} \underset{\textbf{(8)}}{[ReH(NCMe)_3(PPh_3)_2L]^{3+}} \quad (1)$$

*ca.* = 1, and values of $i_{p,c}:\nu^{1/2}$ were constant for scan rates (ν) from 50 to 400mV/s. Values of $E_{p,a} - E_{p,c}$ (90mV at 200 mV/s for L = py) increased with increasing scan rates. These properties are consistent with a quasi-reversible electron transfer process. Bulk electrolysis at +1.30 V ($n$ = 1.0 ± 0.1) leads to violet $[ReH(NCMe)_3(PPh_3)_2L]^{3+}$ (**8**); reduction of this solution at +0.70 V regenerates yellow $[ReH(NCMe)_3(PPh_3)_2L]^{2+}$.

The c.v. of (**6**) exhibits two reversible one-electron oxidations with associated $E_{1/2}$ values of +0.01 and +0.75 V *vs.* S.C.E. The position of the oxidation at +0.01 V is indicative of the ease of oxidation of (**6**); its treatment with $NOPF_6$ in acetone leads to complete conversion into the paramagnetic $[Re_2H_7(PPh_3)_4(NCMe)](PF_6)_2$ (**9**), a process which can be reversed by zinc metal.§

To test the enhanced reactivity of these new cationic species, we have carried out some preliminary reactions with t-butyl isocyanide. Refluxing a solution of (**1**) in EtOH with $Bu^tNC$ for 3 h leads to the stable rhenium(I) complex $[Re(CNBu^t)_4(PPh_3)_2]BF_4$, whereas addition of $Bu^tNC$ to a solution of (**6**) in $CH_2Cl_2$ proceeds smoothly in 1 h at room temperature to give the mixed hydride–isocyanide $[Re_2H_7(PPh_3)_4(CNBu^t)]PF_6$ (**10**). The oxidation of an acetone solution of (**10**) with $NOPF_6$ gives a colour change from green to turquoise and produces $[Re_2H_7(PPh_3)_4(CNBu^t)](PF_6)_2$ (**11**). This paramagnetic salt reacts with additional $Bu^tNC$ in $CH_2Cl_2$ to form $[Re_2H_5(PPh_3)_4(CNBu^t)_2]PF_6$ (**12**) and $[Re(CNBu^t)_4(PPh_3)_2]PF_6$ (in *ca.* 3 : 1 proportions by c.v.), demonstrating the enhanced reactivity of the electron-deficient dication.

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† Microanalytical data and spectroscopic properties for (**1**)—(**3**) are fully in accord with the proposed formulations, *e.g.*, for $[ReH(NCMe)_3(PPh_3)_2(py)](BF_4)_2$ $^1H$ n.m.r. ($CDCl_3$) δ −4.2 [t, $J$(P–H) 66.6 Hz, Re–H], 2.45 and 1.90 (each s, 2 : 1 intensity ratio, $CH_3CN$), and 7.60 (m, $PPh_3$ and $C_5H_5N$).

‡ $^1H$ N.m.r. ($CD_2Cl_2$): δ −5.15 (br. s, Re–H), 1.15 (s, $CH_3CN$), and 7.10 (m, $PPh_3$).

§ The e.s.r. spectrum of this complex and those of (**7**) and (**8**), and other paramagnetic complexes described herein were recorded for dichloromethane glasses at −160 °C. Full details will be provided at a later date.

In contrast to the very sluggish reaction between (**4**) and Bu$^t$NC in refluxing tetrahydrofuran, leading eventually to a low yield of $[Re(CNBu^t)_4(PPh_3)_2]^+$, the salt $[Re_2H_8(PPh_3)_4]PF_6$ (**7**) reacts very rapidly with Bu$^t$NC (in *ca.* 30 s at 0 °C) to afford the complex (**12**) as maroon prisms. To satisfy the effective atomic number rule we formulate this complex so as to contain a Re–Re triple bond.¶ The c.v. of (**12**) in 0.2 M TBAH–$CH_2Cl_2$ shows two one-electron oxidations ($E_{1/2}$ = +0.36 and +1.13 V *vs.* S.C.E.). In acetone (**12**) is oxidized to $[Re_2H_5(PPh_3)_4(CNBu^t)_2](PF_6)_2$ (**13**) by $NOPF_6$, which upon reaction with Bu$^t$NC in $CH_2Cl_2$ produces $[Re(CNBu^t)_4(PPh_3)_2]PF_6$ together with significant amounts of re-reduced (**12**). Having established that (**12**) is not reactive towards an excess of Bu$^t$NC, it is clear that the reactive species is the electron-deficient salt (**13**). This was confirmed by the reaction of (**13**) with an excess of Bu$^t$NC in 0.2 M TBAH–$CH_2Cl_2$ in a c.v. cell at a potential of +0.70 V [thereby preventing reduction back to (**12**)]; this led to the quantitative conversion of (**13**) into $[Re(CNBu^t)_4(PPh_3)_2]PF_6$.

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¶ Based upon its spectroscopic properties we believe that this complex contains an Re≡Re bond supported by three $\mu$-H bridges, *viz.* i.r. (Nujol) 2095sh and 2040s cm$^{-1}$ (*i.e.* terminal Bu$^t$NC ligands only); $^1$H n.m.r. ($CD_2Cl_2$, −40 °C) δ −5.5 [br. s, Re($\mu$-H)Re] and −6.65 p.p.m. [br. t, *J*(P–H) 49.5 Hz, Re–H]; $^{31}$P n.m.r. [$(CD_3)_2CO$, +22 °C] δ 29.9 p.p.m. [d, *J*(P–H) 49 Hz]; $^{31}$P{$^1$H} n.m.r. δ 29.9 p.p.m. (s). This structure is related to that found for $[Re_2H_5(PMe_2Ph)_4\{P(OCH_2)_3CEt\}_2]^+$; see M. A. Green, J. C. Huffman, and K. G. Caulton, *J. Am. Chem. Soc.*, 1982, **104**, 2319.