Synthesis and Characterization of Some Rhenium Complexes with the New Mixed Phosphorus–Nitrogen Donor Ligand $NPh(CH_2CH_2PPh_2)_2$

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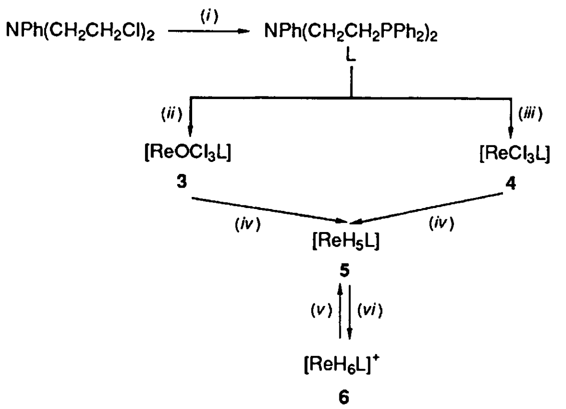
Reaction of $NPh(CH_2CH_2Cl)_2$ with $LiPPh_2$ at 0 °C yields the new mixed nitrogen–phosphorus donor ligand $NPh(CH_2CH_2PPh_2)_2$ (L). Reaction of $[ReOCl_3(AsPh_3)_2]$ with L in CH_2Cl_2 at room temperature gives $[ReOCl_3L]$ **3**. Reaction of $[ReCl_3(MeCN)(PPh_3)_2]$ with L in refluxing benzene gives $[ReCl_3L]$ **4**. Treatment of **3** or **4** with $LiAlH_4$ at 0 °C in Et_2O affords $[ReH_5L]$ **5**. Protonation of **5** with $HBF_4{\cdot}OEt_2$ in CD_2Cl_2 at 193 K gives $[ReH_6L]^+$ **6**. Deprotonation of **6** with NEt_3 regenerates **5** quantitatively. Compound **5** shows a ^1H NMR T_1 (minimum) value of 78 ms at 250 MHz, consistent with a classical structure having only terminal hydride ligands, while **6** shows a T_1 (minimum) value of 10 ms, suggesting a non-classical structure containing one or more η^2-H_2 ligands.

Transition-metal dihydrogen (η^2-H_2) complexes have received much recent attention.[1] The electronic and steric factors which favour η^2-H_2 co-ordination are not yet completely understood. The great majority of the known η^2-H_2 complexes are six-co-ordinate with a d^6 configuration. Examples of d^2 and d^4 η^2-H_2 complexes are very rare.

Brammer *et al.*[2] have characterized the important d^2 species $[ReH_5(\eta^2\text{-}H_2)\{P(C_6H_4Me\text{-}p)_3\}_2]$ by neutron diffraction. It contains an elongated η^2-H_2 ligand with an H $\cdots$ H distance of 1.357 Å. Such a long H $\cdots$ H distance is unprecedented, but the authenticity of the η^2-H_2 formulation is shown by the adoption of the eight-co-ordinate dodecahedral rather than a nine-co-ordinate tricapped trigonal-prismatic geometry and by the free rotation of the η^2-H_2 ligand which is needed to account quantitatively for the T_1 data.[3] Relatively long H $\cdots$ H bond distances have been suggested for the d^2 species $[ReH_4(\eta^2\text{-}H_2)\{PPh[CH_2CH_2CH_2P(C_6H_{11})_2]_2\}]^+$ **1** [r(H $\cdots$ H) = 1.08 Å][4a] and $[ReH_4(\eta^2\text{-}H_2)\{PPh(CH_2CH_2PPh_2)_2\}]^+$ **2** [r(H $\cdots$ H) = 1.17 Å],[4b] based on X-ray diffraction and solution ^1H NMR T_1 studies. The d^4 species $[ReH_2(\eta^2\text{-}H_2)(CO)(PMe_2Ph)_3]^+$ appears to be a normal η^2-H_2 complex, but it is in tautomeric equilibrium with the classical tautomer $[ReH_4(CO)(PMe_2Ph)_3]^+$.[5]

Polyhydride complexes, such as **1** and **2**, containing polydentate phosphines as supporting ligands are relatively rare in contrast to those supported by mono- and bi-dentate phosphines. Motivated by the unusual behaviour of **1** and **2**, we attempted to replace the triphosphine ligands by the new mixed phosphorus–nitrogen donor ligand $NPh(CH_2CH_2PPh_2)_2$ that contains a hard nitrogen donor flanked by two soft phosphorus donors. Hydride ligands are considered soft according to the HSAB (hard–soft acid–base) theory. While soft phosphine ligands are ubiquitous in polyhydride complexes, hard nitrogen-donor ligands are rarely present as coligands.[6] This is probably due to the symbiotic effect,[7] *i.e.* the tendency of soft ligands to congregate in metal complexes. Soft ligands generally render a metal centre more polarizable and so more ready to bind other soft ligands. The 'hybrid' ligand $NPh(CH_2CH_2PPh_2)_2$ gives us the opportunity to study the properties of polyhydride complexes in a mixed nitrogen–phosphorus donor environment and compare them with the known phosphine analogues. In this paper we describe the preparation of $NPh(CH_2CH_2PPh_2)_2$ and its co-ordination chemistry with rhenium.



Scheme 1 (*i*) $LiPPh_2$; (*ii*) $[ReOCl_3(AsPh_3)_2]$; (*iii*) $[ReCl_3(MeCN)(PPh_3)_2]$; (*iv*) $LiAlH_4$; (*v*) NEt_3; (*vi*) H^+

Results and Discussion

The preparations and reactions of the compounds described in this paper are summarized in Scheme 1. All the new compounds were identified from microanalytical and spectroscopic data. These are presented in the Experimental section and in Table 1. The new ligand $NPh(CH_2CH_2PPh_2)_2$ (L) is readily prepared from the reaction of $NPh(CH_2CH_2Cl)_2$ with 2 equivalents of $LiPPh_2$ in tetrahydrofuran (thf) and isolated as an air-stable white solid.

Preparation of $[ReOCl_3L]$ **3**.—The ligand-replacement reaction of the readily available $[ReOCl_3(AsPh_3)_2]$[8] with 1 equivalent of $NPh(CH_2CH_2Ph_2)_2$ in CH_2Cl_2 at room temperature gives a grey complex for which the microanalytical data were consistent with the formulation $[ReOCl_3L]$ **3**. The IR spectrum in Nujol mull shows a characteristic ν(Re=O) stretching band at 976 cm^{-1}. The ^{31}P-$\{^1H\}$ NMR spectrum shows two singlet resonances in a 1:1 ratio, and the ^1H NMR spectrum shows four resonances due to the methylene groups of the ligand. The NMR data are consistent with an octahedral structure in which the three chloride ligands occupy three facial positions and L acts as a bidentate ligand with one phosphorus donor unbound. Similar *fac*-octahedral structures have been

Table 1 Variable-temperature ^1H NMR T_1 measurements on the hydride resonances of $[ReH_5L]$ **5** and $[ReH_6L]^+$ **6** in CD_2Cl_2 at 250 MHz

	T_1/ms	
T/K	5	6
233	93	
223	89	13
213	85	12
203	78	10
193	84	11
183	94	13
173	122	15

observed for $[ReOCl_3(bpm)]$ [bpm = bis(pyrazolyl)methane],[6a] $[ReOCl_3(PEt_3)_2]$[9] and $[ReOCl_3L']$ (L′ = a chelating bidentate phosphine).[10]

It is noteworthy that the alternative product, in which L acts as a bidentate ligand *via* the two phosphorus donors and with one nitrogen donor unbound, is not formed from the reaction. Nor does complex **3** rearrange to this alternative product upon standing. Compound **3** is thus thermodynamically favoured probably because: (1) the five-membered chelating ring is more stable than the eight-membered chelating ring; (2) the hard nature of the oxo ligand encourages the binding of the hard nitrogen donor.

Preparation of $[ReCl_3L]$ **4**.—The reaction of $[ReCl_3(MeCN)(PPh_3)_2]$[11a] with one equivalent of $NPh(CH_2CH_2PPh_2)_2$ in refluxing benzene results in the formation of $[ReCl_3L]$ **4**, which was isolated as an air-stable reddish brown solid. The microanalytical data are in accord with the formulation shown, although no interpretable ^1H and ^{31}P NMR spectra can be obtained owing to the paramagnetism of this d^4 octahedral complex. The compound probably adopts a meridional configuration as found for $[ReCl_3(PMePh_2)_3]$[11b] and $[ReCl_3\{P(OCH_2)_3CEt\}_3]$.[11c]

Preparation of $[ReH_5L]$ **5**.—Treatment of complex **3** or **4** with an excess of $LiAlH_4$ in Et_2O followed by hydrolysis in thf yields the pentahydride complex $[ReH_5L]$ **5**, which was isolated as an off-white solid. The ^1H NMR spectrum in CD_2Cl_2 at 298 K shows a triplet hydride resonance [δ −5.55, ^2J(PH) = 19.0 Hz] integrating as five protons. The five hydride ligands are equivalent at this temperature due to rapid fluxionality, as is commonly found for rhenium polyhydride complexes. Upon cooling to 183 K the hydride resonance becomes a broad feature suggesting the onset of decoalescence, but the slow-exchange-limit spectrum could not be observed. The $^{31}P-\{^1H\}$ NMR spectrum shows a singlet resonance, indicating that both phosphorus donors of the ligand L are bound. The IR spectrum in Nujol mull shows ν(Re–H) stretching bands at 1971, 1923 and 1878 cm^{-1}.

The variable-temperature ^1H NMR T_1 data for the hydride resonance of complex **5** in CD_2Cl_2 at 250 MHz are listed in Table 1. The minimum T_1 value of 78 ms at 203 K is very close to 83 ms found for the closely related species $[ReH_5\{PPh(CH_2CH_2PPh_2)_2\}]$.[4b] The T_1 data are consistent with a classical structure similar to those found for $[ReH_5(PPh_3)_3]$[12] and $[ReH_5(PMePh_2)_3]$[13] by X-ray and neutron diffraction studies.

Preparation of $[ReH_6L]^+$ **6**.—Protonation of complex **5** with $HBF_4 \cdot OEt_2$ in CD_2Cl_2 at 193 K occurs rapidly without hydrogen evolution and gives the hexahydride complex $[ReH_6L]^+$ **6**. The protonation is reversible, and addition of NEt_3 leads to immediate deprotonation and quantitative recovery of **5**.

Complex **6** is unstable above 243 K, decomposing with irreversible loss of H_2 to give products that we cannot characterize. This is in sharp contrast with the behaviour of the all-phosphorus analogues **1** and **2** which are remarkably stable toward hydrogen loss even *in vacuo* at room temperature.[4] The decomposition rate of **6** is highly temperature dependent. A solution of **6** prepared *in situ* in CD_2Cl_2 can be stored at 193 K for several days without significant decomposition. Complex **6** was therefore characterized spectroscopically at low temperature.

At 193 K complex **6** shows a very broad hydride resonance (δ −5.30, $w_{\frac{1}{2}}$ = 86 Hz) in the ^1H NMR spectrum. No decoalescence or other change was observed at any accessible temperature. The plot of lnT_1 *vs.* $1/T$ for **6** has a well defined V shape, suggesting that **6** exists as a single tautomer in solution. The low T_1(minimum) value of 10 ms at 203 K (Table 1) indicates a non-classical structure. This value is lower than the values of 27 and 32 ms, respectively, for **1** and **2**,[4] suggesting that the r(H–H) distance of the η^2-H_2 ligand in **6** is shorter than those in **1** and **2**. These data suggest that the electron-donating ability of $NPh(CH_2CH_2PPh_2)_2$ is lower than that of the triphosphines, which is expected to reduce the Re(d_π) to $H_2(\sigma^*)$ back donation, leading to a shorter r(H–H) distance and a lower T_1(minimum) value for **6**. Probably, the soft phosphorus donors and hydride ligands render the rhenium centre in **6** rather soft. The electron-donating ability of the hard nitrogen donor to the soft rhenium centre is accordingly lower compared with that of the soft phosphorus donor in **1** and **2**. Alternatively, the lone pair on the nitrogen of $NPh(CH_2CH_2PPh_2)_2$ may be more delocalized into the phenyl ring than the lone pair on the central phosphorus of $PPh(CH_2CH_2PPh_2)_2$ because the valence orbitals of nitrogen and carbon atoms have relatively similar energies. This may also lower the electron-donating ability of $NPh(CH_2CH_2PPh_2)_2$.

Assuming that complex **6** adopts the same structure as that of **1** except for the r(H–H) distance of the η^2-H_2 ligand, it is possible to obtain a crude estimate of the r(H–H) in **6** by using the X-ray data obtained for **1** and altering the r(H–H) until a good fit is obtained with the observed T_1(minimum) value. We need to consider both H–H and Re–H dipole–dipole contributions to T_1 relaxation.[3,14] Morris and co-workers[15] have shown that the rotation rate of the η^2-H_2 ligand around the M–(η^2-H_2) axis relative to the tumbling rate of the molecule as a whole has to be taken into account. The relaxation rate of rapidly rotating η^2-H_2 ligand is only 0.25 of the value expected for a non-rotating η^2-H_2 ligand with the same r(H–H) distance. Since the Re–H distances in **1** are poorly determined by X-ray diffraction, we have assumed that they are all 1.70 Å. We find that the r(H–H) distance in **6** is 0.92 Å, assuming no H_2 rotation about the Re–(η^2-H_2) bond. Slow rotation is unusual for dihydrogen complexes, and only in the case of **1** has it previously been necessary to invoke it.[3a,4a] The fact that an X-ray rather than a neutron diffraction structure is available for **1** means we must be cautious in this interpretation. Fast rotation of H_2 in **6** would require an r(H–H) distance of 0.73 Å, very little different from that in free H_2 and therefore probably unreasonable for the complex.

Another way to account for the low T_1(minimum) value of complex **6** is to increase the number of η^2-H_2 ligands. The T_1(minimum) value is also consistent with the formulation $[ReH_{6-2x}(\eta^2\text{-}H_2)_xL]^+$, where x is 2 or 3. For example, if x = 2 and the structure is assumed to be monocapped octahedral with a terminal hydride as the capping atom, the r(H–H) distance is calculated to be 0.82 Å with fast rotation of H_2 and 1.03 Å with no rotation.

Conclusion

We have prepared the new mixed phosphorus–nitrogen donor ligand $NPh(CH_2CH_2PPh_2)_2$ and explored its co-ordination chemistry with rhenium. In particular, we have used it as a supporting ligand in rhenium polyhydride complexes. It is demonstrated that the nitrogen atom in $NPh(CH_2CH_2PPh_2)_2$ is not such a good donor as a phosphorus atom, so that the replacement of the triphosphine ligands in $[ReH_4(\eta^2\text{-}H_2)\{PPh[CH_2CH_2CH_2P(C_6H_{11})_2]_2\}]^+$ **1** and $[ReH_4(\eta^2\text{-}H_2)\{PPh(CH_2CH_2PPh_2)_2\}]^+$ **2** by $NPh(CH_2CH_2PPh_2)_2$ has two effects: (*a*) the stability toward hydrogen loss is sharply lowered in $[ReH_6L]^+$ **6**, and (*b*) based on the T_1(minimum) data the structural features of **6**, such as the H–H distance of the η^2-H_2 ligand and perhaps even the number of the η^2-H_2 ligands, seem to be changed from those of the analogous triphosphine complexes **1** and **2**.

Experimental

General.—All manipulations were performed under a dry nitrogen atmosphere by standard Schlenk-tube techniques. Proton and ^{31}P NMR spectra were recorded on Bruker WM 250 or WM 500 spectrometers in CD_2Cl_2; ^1H chemical shifts were measured with the residual solvent resonance as reference, ^{31}P chemical shifts with external 85% H_3PO_4 as reference. Infrared spectra were recorded on a Nicolet 5-SX FT-IR spectrometer. Proton NMR T_1 measurements were carried out at 250 MHz by the inversion-recovery method using a standard 180°–τ–90° pulse sequence. Diethyl ether, hexane and tetrahydrofuran were distilled from Na–Ph_2CO. Dichloromethane was distilled from CaH_2. All solvents were stored under N_2. The compound $NPh(CH_2CH_2Cl)_2$ was purchased from Alfa; other chemicals were purchased from Aldrich. The complexes $[ReOCl_3(AsPh_3)_2]$[8] and $[ReCl_3(MeCN)(PPh_3)_2]$[11a] were prepared according to the literature methods.

Bis(2-diphenylphosphinoethyl)phenylamine L.—Lithium diphenylphosphide was prepared by dropwise addition of $LiBu^n$ (1.6 mol dm^{-3} in hexane) (9.5 cm^3, 15.2 mmol) to a solution of $PHPh_2$ (2.82 g, 15.1 mmol) in hexane (20 cm^3) cooled to 0 °C. The solvent was removed *in vacuo*. The residue was washed with hexane (2 × 5 cm^3), dried, and redissolved in thf (20 cm^3). This thf solution was then added dropwise to a solution of $NPh(CH_2CH_2Cl_2)_2$ (1.65 g, 7.56 mmol) in thf (30 cm^3) cooled in a solid CO_2–acetone bath. The solution was then slowly warmed to 0 °C and maintained at this temperature for 1 h. A small excess of $LiPPh_2$ was quenched with ethanol. The solvent was then removed, and CH_2Cl_2 (60 cm^3) added. The white suspension was transferred to a separatory funnel and distilled water (30 cm^3) added. The clear organic layer was collected, dried with Na_2SO_4 (5 g), and filtered through Celite. The filtrate was concentrated to *ca.* 2 cm^3 and MeOH (50 cm^3) added. The resulting white solid was collected on a frit, washed with MeOH (3 × 10 cm^3) and dried *in vacuo* (3.52 g, 90%) (Found: C, 78.5; H, 6.2; N, 2.8. $C_{34}H_{33}NP_2$ requires C, 78.9; H, 6.3; N, 2.7%); $\delta_H(CDCl_3)$ 7.6–7.3 (25 H, m, Ph), 3.37 (4 H, br q, PCH_2) and 2.20 (4 H, br t, NCH_2); $\delta_P(CDCl_3)$ −21.29 (s).

[Bis(2-diphenylphosphinoethyl)phenylamine]trichlorooxorhenium(V) **3**.—The complex $[ReOCl_3(AsPh_3)_2]$ (0.15 g, 0.16 mmol) and $NPh(CH_2CH_2PPh_2)_2$ (0.093 g, 0.18 mmol) were stirred in CH_2Cl_2 (20 cm^3) for 3 h at room temperature. The solvent volume was reduced to *ca.* 0.5 cm^3 *in vacuo*. Addition of Et_2O (10 cm^3) and hexane (20 cm^3) resulted in the precipitation of a grey solid, which was filtered off, washed with Et_2O (3 × 10 cm^3) and dried *in vacuo*. Yield 0.13 g (98%) (Found: C, 49.4; H, 4.1. $C_{34}H_{33}Cl_3NOP_2Re$ requires C, 49.4; H, 4.0%); ν_{max}/cm^{-1}(Re=O) (Nujol) 976; $\delta_H(CD_2Cl_2$, 298 K) 7.9–7.3 (25 H, m, Ph), 3.7 (2 H, m, CH_2), 3.5 (2 H, m, CH_2), 3.3 (2 H, m, CH_2) and 3.1 (2 H, m, CH_2); $\delta_P(CD_2Cl_2$, 298 K) −24.80 (1 P, s) and −30.35 (1 P, s).

[Bis(2-diphenylphosphinoethyl)phenylamine]trichlororhenium(III) **4**.—A solution of $[ReCl_3(MeCN)(PPh_3)_2]$ (0.40 g, 0.47 mmol) and $NPh(CH_2CH_2PPh_2)_2$ (0.267 g, 0.52 mmol) in benzene (20 cm^3) was refluxed for 4 h. The solvent was removed under vacuum. The residue was extracted in CH_2Cl_2 (2 × 20 cm^3). A small amount of insoluble impurity was filtered off. The filtrate was concentrated to *ca.* 0.2 cm^3. Addition of Et_2O (10 cm^3) and hexane (20 cm^3) resulted in the precipitation of a reddish brown solid, which was filtered off, washed with hexane (2 × 10 cm^3) and Et_2O (2 × 10 cm^3) and dried *in vacuo*. Yield 0.26 g (69%) (Found: C, 50.1; H, 3.9; N, 2.0. $C_{34}H_{33}Cl_3NP_2Re$ requires C, 50.1; H, 3.9; N, 2.0%).

[Bis(2-diphenylphosphinoethyl)phenylamine]pentahydridorhenium(V) **5**.—(*a*) A suspension of $[ReCl_3L]$ (0.3 g, 0.37 mmol) and $LiAlH_4$ (0.14 g, 3.7 mmol) in Et_2O (20 cm^3) was vigorously stirred at 0 °C for 1 h. The mixture was filtered through Celite and the yellow filtrate evaporated to dryness under vacuum. The residue was dissolved in thf (20 cm^3), cooled to 0 °C and hydrolysed by dropwise addition of a solution of water (0.3 cm^3) in thf (20 cm^3). The mixture was dried with anhydrous Na_2SO_4 (5 g) and filtered through Celite. The filtrate was concentrated to *ca.* 0.2 cm^3. Addition of hexane (30 cm^3) gave an off-white solid. After cooling to 0 °C, the solid was filtered off, washed with hexane (3 × 10 cm^3) and dried *in vacuo*. Yield 0.21 g (80%) (Found: C, 57.4; H, 5.4; N, 2.1. $C_{34}H_{38}NP_2Re$ requires C, 57.6; H, 5.4; N, 2.0%); ν_{max}/cm^{-1}(Re–H) (Nujol) 1971, 1923 and 1878; $\delta_H(CD_2Cl_2$, 298 K) 7.9–7.2 (25 H, m, Ph), 3.41 (4 H, br s, PCH_2), 2.72 (4 H, br s, NCH_2) and −5.55 [5 H, t, *J*(PH) 19.00 Hz, Re–H]; $\delta_P(CD_2Cl_2$, 298 K) 11.79 (s); $\delta_H(CD_2Cl_2$, 213 K) 7.8–7.1 (25 H, m, Ph), 3.38 (4 H, br s, PCH_2), 2.64 (4 H, br s, NCH_2) and −5.70 [5 H, br t, *J*(PH) 18.62 Hz, Re–H].

(*b*) An alternative preparation was similarly carried out with $[ReOCl_3L]$ **3** as the starting material. Yield: 82%.

Observation of $[ReH_6L]^+$ **6**.—The complex $[ReH_5L]$ (0.05 g, 0.07 mmol) was dissolved in CD_2Cl_2 (0.4 cm^3) in a 5 mm NMR tube. The solution was cooled to −80 °C (solid CO_2–acetone), and $HBF_4\cdot OEt_2$ (85%, 9 mm^3, 0.07 mmol) was added *via* a microsyringe. The sample was shaken and then quickly introduced into a precooled NMR probe: $\delta_H(CD_2Cl_2$, 193 K) 7.7–7.1 (25 H, m, Ph), 2.94 (4 H, br s, PCH_2), 2.46 (4 H, br s, NCH_2) and −5.30 (6 H, br s, $w_{\frac{1}{2}}$ = 86 Hz, Re–H).

Deprotonation of $[ReH_6L]^+$ **6**.—The above NMR tube was quickly removed from the NMR probe and submerged in a solid CO_2–acetone bath. Triethylamine (10 mm^3, 0.07 mmol) was added *via* a microsyringe. The sample was shaken and transferred back to the precooled NMR probe. The ^1H NMR spectrum showed that the hydride resonance of complex **6** had been replaced by that of **5**.

Calculation of T_1.—The positional parameters from the X-ray crystallographic study[4a] of complex **1** were obtained from Professor A. Wojcicki. The terminal hydride atom positions were held constant, but the H–H distance of the η^2-H_2 ligand was altered until a match was obtained with the observed T_1(minimum) value. The method has been described in detail elsewhere.[3,10]

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References

1 G. J. Kubas, *Acc. Chem. Res.*, 1988, **21**, 120; R. H. Crabtree and D. G. Hamilton, *Adv. Organomet. Chem.*, 1988, **28**, 299; R. H. Crabtree, *Acc. Chem. Res.*, 1990, **23**, 95; R. H. Crabtree, X.-L. Luo and D. Michos, *Chemtracts Inorg. Chem.*, 1991, **3**, 245.

2 L. Brammer, J. A. K. Howard, O. Johnson, T. F. Koetzle, J. L. Spencer and A. M. Stringer, *J. Chem. Soc., Chem. Commun.*, 1991, 241.

3 (*a*) X.-L. Luo, J. A. K. Howard and R. H. Crabtree, *Magn. Reson.*

Chem., 1991, **29**, S89; (*b*) X.-L. Luo and R. H. Crabtree, *Inorg. Chem.*, 1990, **29**, 2788.

4 (*a*) Y. Kim, H. Deng, D. W. Meek and A. Wojcicki, *J. Am. Chem. Soc.*, 1990, **112**, 2798; (*b*) X.-L. Luo and R. H. Crabtree, *J. Chem. Soc., Dalton Trans.*, 1991, 587.

5 X.-L. Luo and R. H. Crabtree, *J. Chem. Soc., Chem. Commun.*, 1990, 189; *J. Am. Chem. Soc.*, 1990, **112**, 6912.

6 (*a*) D. G. Hamilton, X.-L. Luo and R. H. Crabtree, *Inorg. Chem.*, 1989, **28**, 3198; (*b*) U. E. Bucher, T. Lengweiler, D. Nanz, W. v. Philipsborn and L. M. Vananzi, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 548.

7 C. K. Jorgensen, *Inorg. Chem.*, 1964, **3**, 1201; R. H. Crabtree, M. W. Davis, M. F. Mellea and J. M. Mihelcic, *Inorg. Chim. Acta*, 1983, **72**, 223.

8 N. P. Johnson, C. J. L. Lock and G. Wilkinson, *J. Chem. Soc.*, 1964, 1054.

9 J. E. Fergusson and P. F. Heveldt, *J. Inorg. Nucl. Chem.*, 1976, **38**, 223.

10 X.-L. Luo and R. H. Crabtree, *Inorg. Chem.*, 1989, **28**, 3775; *J. Am. Chem. Soc.*, 1990, **112**, 4813.

11 (*a*) G. Rouschias and G. Wilkinson, *J. Chem. Soc.*, 1967, 993; (*b*) F. A. Cotton and R. L. Luck, *Inorg. Chem.*, 1989, **28**, 2181; (*c*) X.-L. Luo, D. Michos and R. H. Crabtree, *Inorg. Chem.*, 1991, **30**, 4286.

12 F. A. Cotton and R. L. Luck, *J. Am. Chem. Soc.*, 1989, **111**, 5757.

13 T. J. Emge, T. F. Koetzle, J. W. Bruno and K. G. Caulton, *Inorg. Chem.*, 1984, **23**, 4012.

14 P. J. Desrosiers, L. Cai, Z. Lin, R. Richards and J. Halpern, *J. Am. Chem. Soc.*, 1991, **113**, 4173; D. G. Gusev, A. B. Vymentis and V. I. Bakhmutov, *Inorg. Chem.*, 1991, **30**, 3116; X.-L. Luo, H. Liu and R. H. Crabtree, *Inorg. Chem.*, 1991, **30**, 4740.

15 M. T. Bautista, K. A. Earl, P. A. Maltby, R. H. Morris, C. T. Schweitzer and A. Sella, *J. Am. Chem. Soc.*, 1988, **110**, 7031.

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