# Mono- and Dinuclear Rhenium Polyhydride Complexes Bearing the Chelating Ligand 1,2-Bis(dicyclohexylphosphanyloxy)ethane

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*Dedicated to the memory of Dr. Juan Carlos del Amo[‡]*

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Variable-temperature NMR spectroscopic studies of new rhenium polyhydride compounds of the type [$ReH_7$(dcype)] (**1**), [$Re_2H_8$(dcype)$_2$] (**3**) and [$ReH_5$(dcype)L] (**5a–f**) [dcype = $Cy_2PO(CH_2)_2OPCy_2$; L = $PPh_n(OR)_{3-n}$, $n$ = 0–2, R = Me, Et] show them to be highly fluxional classical hydride complexes. In the case of the ethoxy compounds **5b**, **5d** and **5f**, three hydride interchange processes were observed in the temperature range 283–173 K and their activation parameters were determined by NMR line-shape analysis. A mechanism is proposed for each. Protonation of **1** and **5** with $HBF_4{\cdot}OMe_2$ gave the nonclassical hydrides [$ReH_8$(dcype)]$BF_4$ (**2**) and [$ReH_6$(dcype)L]$BF_4$ (**6**) which are relatively stable. Compound **2** decomposes at 273 K in solution releasing $H_2$,whereas compound **6** can be stored at room temperature for more than 24 h without decomposition. Protonation of **3** with $HBF_4{\cdot}OMe_2$ gave the classical dinuclear hydride [$Re_2H_9$(dcype)$_2$]$BF_4$.

## Introduction

Transition metal polyhydride complexes are notable for exhibiting H−H distances that range from 1.6 Å or more in the case of “classical” hydrides to 0.8−1.0 Å in “nonclassical” hydrides,[1] with intermediate distances having been observed in “elongated dihydrogen” or “stretched dihydride” complexes[2] such as [$ReH_7\{P(p\text{-tolyl})_3\}_2$], in which there is an H−H distance of 1.35 Å.[3] The exact length of the H−H bond in such elongated $\eta^2$-$H_2$ ligands appears to depend heavily on the nature of the non-hydrogen ligand {e.g. the phosphane ligand in the [$ReH_7\{P(C_6H_4\text{-}p\text{-}X)_3\}_2$] family to which the above compound belongs and in other [$ReH_7(PR_3)_2$] compounds[4]} which can also have a marked influence on the stability of the complex[5] and on properties such as the susceptibility to protonation of the hydride ion in [$ReH_2(CO)(NO)(PR_3)_2$].[6] Structures with elongated dihydrogen have been regarded as the result of a process of oxidative addition of dihydrogen that has been arrested at an intermediate stage but theoretical calculations have suggested, alternatively, that two of their hydrogen atoms move freely in a large region of the coordination sphere of the metal atom.[7]

Transition metal polyhydrides are also notable for their fluxionality. Because of their intermediate electronegativity, the nondirectionality of the 1s orbital and the absence of steric hindrance, the hydrogen ligands readily switch positions. The nature of these exchange processes and their thermodynamics can be explored by means of variable-temperature NMR spectroscopy.

Complexes of rhenium polyhydrides have proved useful in organometallic chemistry for the activation of C−H bonds by various routes.[8] They can also undergo a variety of thermal, photochemical or oxidative substitution reactions in which $H_2$ is replaced by a two-electron donor.[9] Although many rhenium polyhydride complexes of phosphanes are known, less attention has been given to complexes of phosphites [$P(OR)_3$], phosphonites [$PR_1(OR)_2$] and phosphinites [$PR_2(OR)_1$]. These ligands are all weaker σ-donors and stronger π-acceptors than phosphanes[10] and can therefore be expected to have different influences on the above-mentioned ligand-sensitive properties of the complex. Further control over these properties might come from the use of chelating ligands which afford two or more conformers, if it can be proved possible to favour one or another of these different forms.[11]

In previous work we synthesised, characterised and investigated the protonation of rhenium polyhydride complexes of the chelating ligand 1,2-bis(diphenylphosphanyloxy)-

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ethane.[12] Here we describe the ligand dependence of the properties of an analogous series in which the ligand is 1,2-bis(dicyclohexylphosphanyloxy)ethane (dcype), with or without a monodentate phosphorus ligand (a methyl or ethyl phosphite, phosphonite or phosphinite).

## Results and Discussion

### Synthesis and Properties of [ReH$_7$(dcype)] (1) and [ReH$_8$(dcype)]BF$_4$ (2)

Treatment of the complex [ReOCl$_2$(OMe)(dcype)] (prepared as previously reported[13]) with a 30-fold excess of NaBH$_4$ in absolute ethanol produced the violet complex **1** which is stable in air at room temperature in both the solid state and solution. Its IR spectrum shows two medium bands at 1933 and 1956 cm$^{-1}$ which are attributable to ν(Re−H) vibrations.[14]

$[ReH_7\{Cy_2PO(CH_2)_2OPCy_2\}]$ **1**
$[ReH_8\{Cy_2PO(CH_2)_2OPCy_2\}](BF_4)$ **2**

$[Re_2H_8\{Cy_2PO(CH_2)_2OPCy_2\}_2]$ **3**
$[Re_2H_9\{Cy_2PO(CH_2)_2OPCy_2\}_2](BF_4)$ **4**

$[ReH_5\{Cy_2PO(CH_2)_2OPCy_2\}\{PPh_n(OR)_{3-n}\}]$

**5**
R = Me $n = 0$ **5a**; $n = 1$ **5c**; $n = 2$ **5e**
R = Et $n = 0$ **5b**; $n = 1$ **5d**; $n = 2$ **5f**

$[ReH_6\{Cy_2PO(CH_2)_2OPCy_2\}\{PPh_n(OR)_{3-n}\}](BF_4)$

**6**
R = Me $n = 0$ **6a**; $n = 1$ **6c**; $n = 2$ **6e**
R = Et $n = 0$ **6b**; $n = 1$ **6d**; $n = 2$ **6f**

At room temperature, the $^1$H NMR spectrum of **1** in C$_6$D$_6$ shows the hydride resonance as a seven-proton triplet at $\delta = -6.55$ ppm ($J_{PH} = 17$ Hz), while the $^{31}P\{^1H\}$ NMR spectrum displays a singlet at $\delta = 157.0$ ppm which becomes an octuplet when an off-resonance experiment is performed [$J_{PH(residual)} = 15$ Hz]. These results confirm the number of hydride ions coordinated to the rhenium atom and show the magnetic equivalence of the two phosphorus atoms in the bidentate ligand. When the NMR experiments were performed at 183 K in CD$_2$Cl$_2$, both the $^1$H and the $^{31}$P signals broadened slightly which can be seen as reflecting a step towards resolution of a very fast fluxional process which renders the hydrido ligands equivalent. The value of $T_1$(min) at 400 MHz as measured by the standard inversion-recovery method is 88 ms at 217 K, confirming the classical nature of this complex.[1c]

Treatment of a solution of compound **1** in CD$_2$Cl$_2$ with 2 equiv. of HBF$_4$·OMe$_2$ in an NMR tube at 183 K yielded the nonclassical polyhydride complex [ReH$_8$(dcype)]BF$_4$ (**2**).[15] At that temperature its $^{31}P\{^1H\}$ NMR spectrum shows a single very broad signal at $\delta = 144.7$ ppm, while a broad signal at $\delta = -5.38$ ppm in its $^1$H NMR spectrum corresponds to the hydrido ligands. This cationic complex is therefore, like compound **1**, stereochemically nonrigid on the NMR time scale. The value of $T_1$(min) of this signal at 400 MHz is 13 ms at 226 K (Figure 1), denoting the presence of at least one dihydrogen ligand.

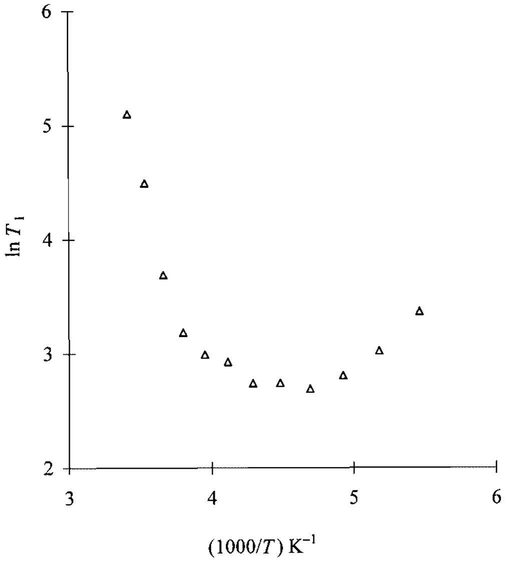


Figure 1. Plot of ln $T_1$ (CD$_2$Cl$_2$, 400 MHz) versus 1000/$T$ for **2**

Between 183 and 273 K, the $^1$H NMR spectrum of **2** shows just a slight sharpening of its signals, but between 273 and 293 K the hydride signal becomes a broad quintuplet integrating to nine protons ($J_{PH} = 8$ Hz) and a new singlet appears at $\delta = 4.6$ ppm which is attributable to H$_2$ (Figure 2).

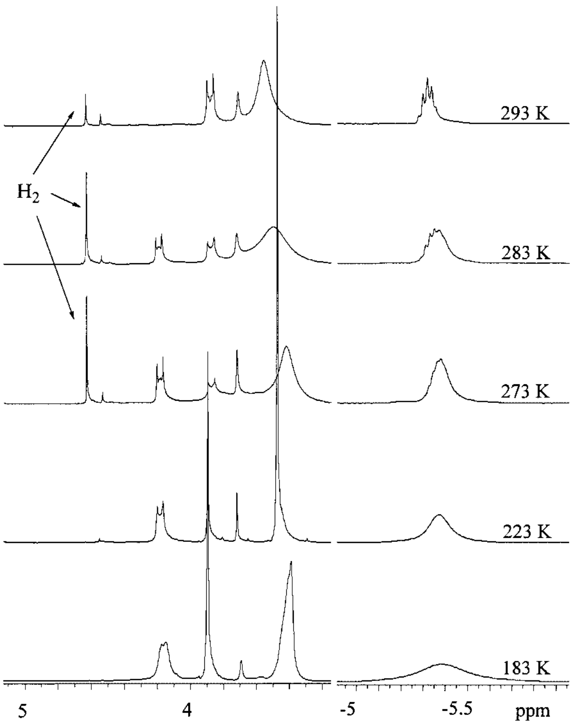


Figure 2. Selected regions of the $^1$H NMR spectra obtained at various temperatures following protonation of [ReH$_7$(dcype)] **(1)** with HBF$_4$·OMe$_2$ in CD$_2$Cl$_2$

In the $^{31}P\{^1H\}$ NMR spectrum, the broad signal at $\delta$ = 144.7 ppm sharpens when the temperature is raised and between 273 and 293 K is progressively replaced by a new singlet at $\delta$ = 151.3 ppm (Figure 3). This signal remains unaltered when the sample is maintained at 293 K for 24 h.

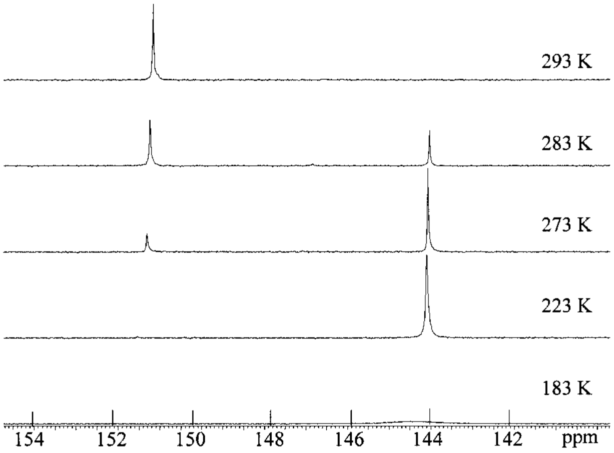
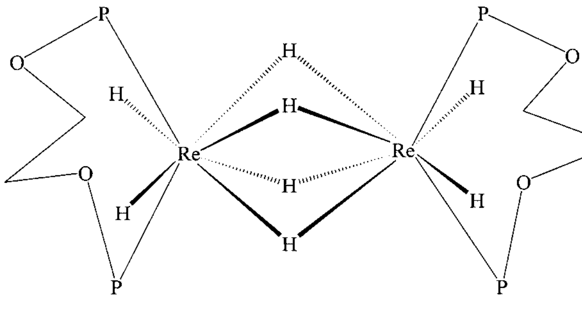


Figure 3. $^{31}P\{^1H\}$ NMR spectra obtained at various temperatures following protonation of $[ReH_7(dcype)]$ **(1)** with an excess of $HBF_4{\cdot}OMe_2$ in $CD_2Cl_2$

The spectroscopic features observed at room temperature coincide with those of $[Re_2H_9(dcype)_2]BF_4$ (**4**) (see next subsection). It seems likely that at temperatures above 273 K the dinuclear compound $[Re_2H_8(dcype)_2]$ (**3**) is formed from the nonclassical compound **2** with release of $H_2$ and immediately reacts with the excess $HBF_4{\cdot}OMe_2$ which is present in solution, thus yielding compound **4**.

### Synthesis and Properties of $[Re_2H_8(dcype)_2]$ (3) and $[Re_2H_9(dcype)_2]BF_4$ (4)

Heating of a solution of the heptahydride **1** to reflux in toluene for 24 h[14] resulted in the precipitation of a yellow solid with analytical and spectroscopic data in accordance with the formulation $[Re_2H_8(dcype)_2]$ (**3**). The $^{31}P\{^1H\}$ NMR spectrum of a solution of **3** in $CD_2Cl_2$ exhibits a single singlet at $\delta$ = 162.4 ppm showing the magnetic equivalence of the four P nuclei, while the $^1H$ NMR spectrum shows an eight-proton quintuplet at $\delta$ = −7.37 ppm ($^2J_{PH}$ = 9 Hz). The postulated structure of this compound (Scheme 1) has four bridging and four terminal H atoms as has been described for similar systems.[10a,16]



Scheme 1

Unfortunately, the poor solubility of compound **3** in dichloromethane prevented variable-temperature (VT) NMR spectroscopy. However, treatment of a suspension of **3** in $CD_2Cl_2$ in an NMR tube at 174 K with an excess of $HBF_4{\cdot}OMe_2$ resulted in the disappearance of the precipitate and the appearance of new NMR signals [$^{31}P\{^1H\}$ NMR: $\delta$ = 151.9 ppm (s); $^1H$ NMR: δ = −5.61 ppm (br. s)] corresponding to a protonated compound, **4**, which was amenable to a VT NMR study. Raising of the temperature from 174 to 293 K converted the broad singlet in the hydride region into a quintuplet ($J_{PH}$ = 8 Hz) which remained unaltered for several days. There was no evidence of evolution of $H_2$ gas. The $T_1$(min) value for the hydride signal at 400 MHz was 94 ms at 239 K showing the classical nature of this compound. These findings suggest the formulation ($\mu$-$H_3$) $[Re_2H_9(dcype)_2]BF_4$ indicating protonation of a hydride bridge as proposed for a similar system.[10a]

### Syntheses and Properties of $[ReH_5(dcype)L]$ (5a−f) and $[ReH_6(dcype)L]BF_4$ (6a−f) (L = $PPh_n(OR)_{3-n}$, $n$ = 0−2, R = Me, Et)

Treatment of compound **1** with the monodentate ligands L = $PPh_n(OR)_{3-n}$ ($n$ = 0−2, R = Me, Et) yielded the pentahydrides $[ReH_5(dcype)L]$ as solids which are stable in air. Their IR spectra exhibit 3−4 bands between 1895 and 2000 $cm^{-1}$ which correspond to Re−H stretching vibrations. Room-temperature $^1H$ NMR spectra of $CD_2Cl_2$ solutions of these compounds display, at high field (δ = −7 to −8 ppm), a double triplet which integrates to five protons. $^{31}P\{^1H\}$ NMR spectra show a doublet and a triplet in a 2:1 intensity ratio which are attributable to the dcype and L ligands, respectively, and form an $AX_2$ system. These spectroscopic features reflect fluxional processes which make the hydride nuclei equivalent. When the $^1H$ NMR spectra were recorded with decoupling of the $^{31}P$ nuclei, the hydride signals became singlets, showing the absence of coupling among the hydrido ligands. As the number of OR groups in the monodentate ligand L increased, the hydride signal shifted upfield in response to the increased electron-withdrawing character of L.

As representative examples of the VT NMR spectra of compounds **5**, Figures 4 and 5 (a) show the $^{31}P\{^1H\}$ spectrum and the hydride region of the $^1H\{^{31}P\}$ spectrum of $[ReH_5(dcype)\{P(OEt)_3\}]$ (**5b**). As was mentioned above, at 298 K this compound like other transition metal polyhydrides[17] shows marked fluxionality. As the temperature is lowered from 298 K to 198 K, the triplet observed at $\delta$ = 145 ppm in the $^{31}P\{^1H\}$ NMR spectrum becomes a double doublet in which the outer peaks are less intense than the inner ones, indicating that the coupling constants between the P nucleus of the monodentate ligand and the two dcype P nuclei have different signs.[18] At the same time, the doublet at $\delta$ = 157.5 ppm first becomes a single broad hump (at 228 K) and then a broad singlet and a broad doublet which narrows progressively, showing the transition from an $AX_2$ to an AMX system. Lowering of the temperature below 198 K broadens all these signals which probably reflects the initial stages of the freezing of the interconversion equilib-

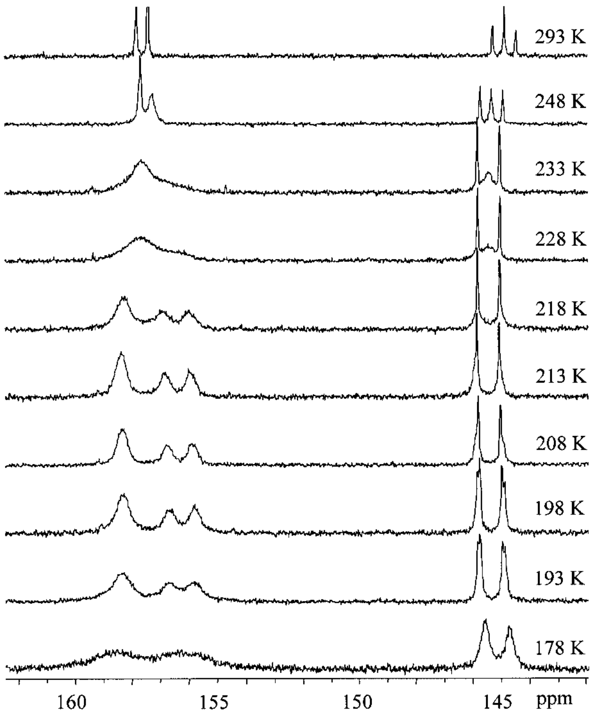


Figure 4. $^{31}P\{^{1}H\}$ NMR spectra of compound **5b** at various temperatures

rium between the conformers of the chelate ring of the bidentate ligand.

Their VT $^{1}H\{^{31}P\}$ NMR spectra [Figure 5, a) shows that of **5b**] show compounds **5** to be more rigid than the analogous complexes of 1,2-bis(diphenylphosphanyloxy)ethane,[12] since in most cases there is a separate signal for each hydrido ligand at the lowest temperature attainable. This afforded an opportunity to investigate the interchange processes in which the hydrido ligands are involved. From 198 to 173 K the five signals become slightly broader (for example, the signal of **5b** at $\delta = -8.40$ ppm broadens from $W_{1/2} = 16$ Hz to $W_{1/2} = 38$ Hz) which is in keeping with the behaviour of the $^{31}P$ NMR signals and is likewise attributable to the initial stages of the freezing of the chelate ring conformer interconversion. As the temperature is progressively increased above 198 K, three signals ($\delta = -6.50$, $-8.09$ and $-10.19$ ppm in the spectrum of **5b**) coalesce to form a signal so broad that at 218 K it disappears into the baseline. Meanwhile, at 213 K the two remaining signals (located at $\delta = -8.40$ and $-6.80$ ppm in the case of **5b**) also begin to coalesce, suggesting the existence of a second interchange process involving the other two hydrido ligands. Finally, a third process which makes all five protons equivalent, appears at 233 K and results in the room-temperature spectrum showing a single signal which for **5b** is located at $\delta = -8.00$ ppm.

Plausible mechanisms for the above processes are indicated in Scheme 2. Cyclic interchange of three hydride ions defining one of the triangular faces of a distorted dodecahedral coordination polyhedron, as proposed by Crabtree et al.[19] for $[ReH_5(PPh_3)_2(py)]$, may account for the lowest-temperature process. The second process, which was not observed in the case of Crabtree's complex, may be the interchange of the other two protons. Finally, the equivalence of all five protons at high temperature may be due to the pseudorotation illustrated in Scheme 2 (b).

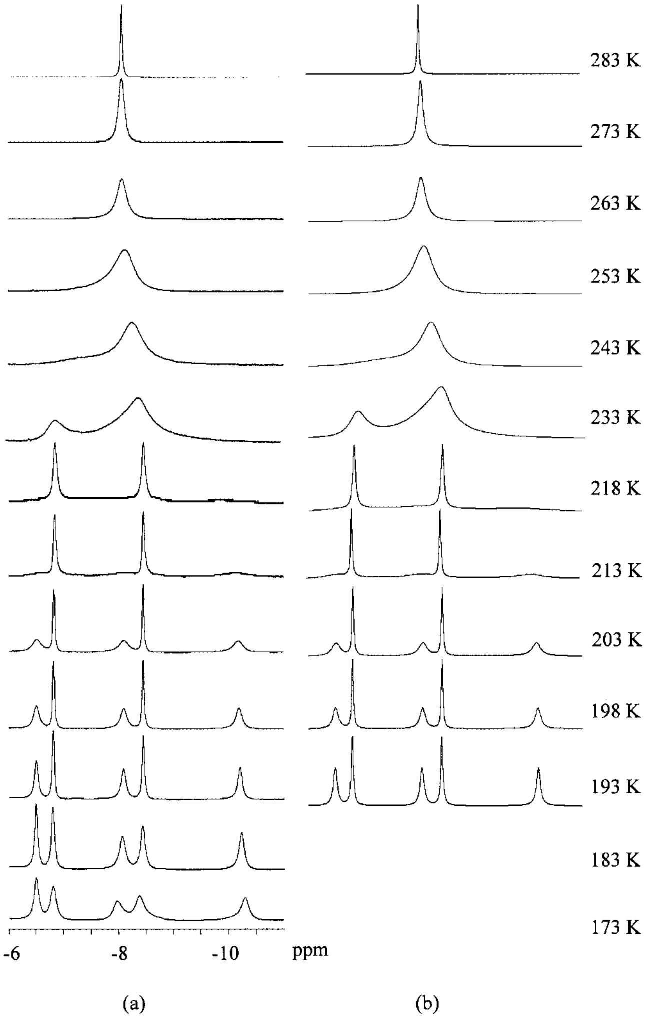
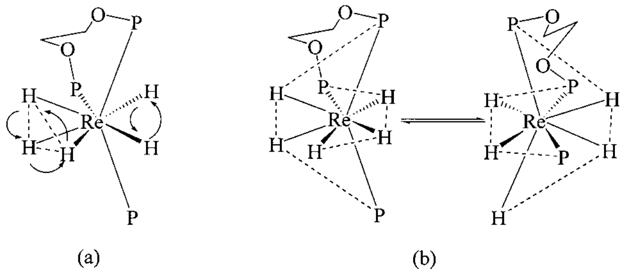


Figure 5. The observed (a) and simulated (b) hydride region of the $^{1}H\{^{31}P\}$ NMR spectra of compound **5b** at various temperatures



Scheme 2

Line-shape analysis performed using g NMR software[20] [Figure 5, b) shows the hydride region of the simulated VT $^{1}H$ NMR spectrum of **5b**] allowed us to calculate the thermodynamic parameters of the above interchange processes from the Eyring plots shown in Figure 6. Table 1 lists the results for the series of ethoxy compounds **5b**, **5d** and

Table 1. Activation parameters obtained by Eyring analysis for **5b**, **5d** and **5f**

| Compound | | Activation parameters[a] | |
|---|---|---|---|
| | Low-temperature process | Medium-temperature process | High-temperature process |
| [ReH$_5$(dcype){P(OEt)$_3$}] (**5b**) | $\Delta H^{\ddagger}$ = 11.4±0.2 | $\Delta H^{\ddagger}$ = 13.6±0.4 | $\Delta H^{\ddagger}$ = 14.1±0.8 |
| | $\Delta S^{\ddagger}$ = 8.9±0.1 | $\Delta S^{\ddagger}$ = 12.0±0.4 | $\Delta S^{\ddagger}$ = 12.5±0.7 |
| [ReH$_5$(dcype){PPh(OEt)$_2$}] (**5d**) | $\Delta H^{\ddagger}$ = 10.6±0.6 | $\Delta H^{\ddagger}$ = 12.5±0.3 | $\Delta H^{\ddagger}$ = 13.1±0.5 |
| | $\Delta S^{\ddagger}$ = 5.7±0.3 | $\Delta S^{\ddagger}$ = 8.9±0.2 | $\Delta S^{\ddagger}$ = 8.9±0.3 |
| [ReH$_5$(dcype){PPh$_2$(OEt)}] (**5f**) | $\Delta H^{\ddagger}$ = 10.3±0.5 | $\Delta H^{\ddagger}$ = 12.2±1.6 | $\Delta H^{\ddagger}$ = 12.3±1.2 |
| | $\Delta S^{\ddagger}$ = 4.9±0.2 | $\Delta S^{\ddagger}$ = 9.6±1.3 | $\Delta S^{\ddagger}$ = 9.3±0.9 |

[a] $\Delta H^{\ddagger}$ [kcal/mol], $\Delta S^{\ddagger}$ [cal/mol].

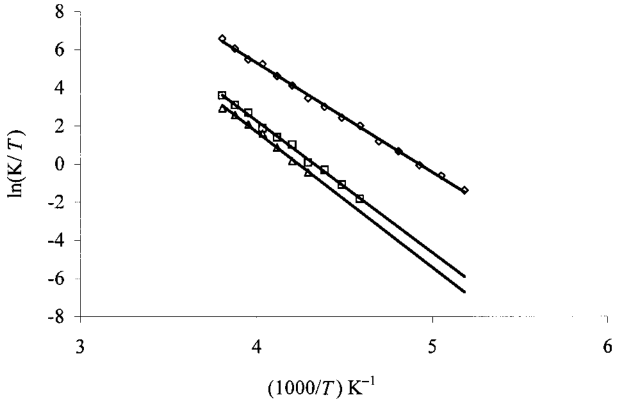


Figure 6. Eyring plots for the low- (open diamonds), medium- (open squares) and high-temperature (open triangles) interchange processes

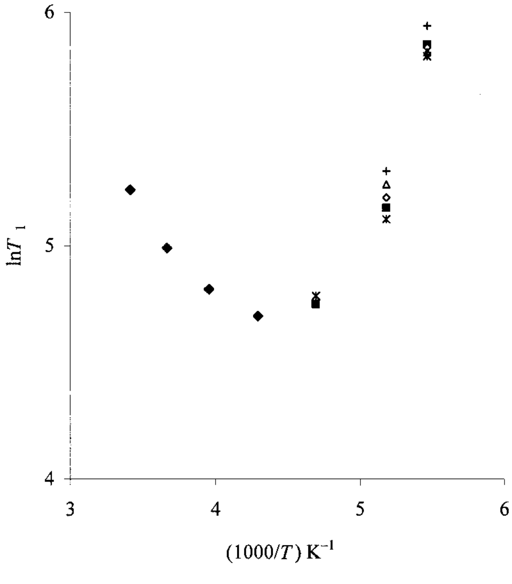


Figure 7. Plots of ln$T_1$ values vs. temperature for the hydride signals of compound **5b** in $CD_2Cl_2$, at 400 MHz; solid diamonds indicate the signal at $\delta = -8.15$ ppm (fast-exchange motion), solid squares the signal at $\delta = -6.82$ ppm; * the signal at $\delta = -8.45$ ppm, triangles the signal at $\delta = -6.51$ ppm, open diamonds the signal at $\delta = -8.09$ ppm; **+** the signal at $\delta = -10.19$ ppm

**5f**. The activation energy of each process shows a clear trend, falling as the donor capacity of L increases.

Figure 7 shows plots of ln$T_1$ against the temperature for the hydride signals of **5b** in $CD_2Cl_2$ at 400 MHz. At about the lowest coalescence temperature, all five signals have similar $T_1$ values of about 110 ms, values which increase as the temperature is lowered further. Similar behaviour is exhibited by the rest of compounds **5**, with the minimum $T_1$ values listed in Table 2. These compounds can, accordingly, all be regarded as classical in nature.

Table 2. $T_1$(min.) data at 400 MHz for compounds **5a−f** and **6a−f**

| Compound | $T$ [K] | $T_1$ [ms] |
|---|---|---|
| [ReH$_5$(dcype){P(OMe)$_3$}] (**5a**) | 227 | 114 |
| [ReH$_5$(dcype){P(OEt)$_3$}] (**5b**) | 215 | 116 |
| [ReH$_5$(dcype){PPh(OMe)$_2$}] (**5c**) | 229 | 115 |
| [ReH$_5$(dcype){PPh(OEt)$_2$}] (**5d**) | 226 | 113 |
| [ReH$_5$(dcype){PPh$_2$(OMe)}] (**5e**) | 212 | 103 |
| [ReH$_5$(dcype){PPh$_2$(OEt)}] (**5f**) | 230 | 108 |
| [ReH$_4$(η$^2$-H$_2$)(dcype){P(OMe)$_3$}]$^+$ (**6a**) | 226 | 25 |
| [ReH$_4$(η$^2$-H$_2$)(dcype){P(OEt)$_3$}]$^+$ (**6b**) | 225 | 24 |
| [ReH$_4$(η$^2$-H$_2$)(dcype){PPh(OMe)$_2$}]$^+$ (**6c**) | 226 | 26 |
| [ReH$_4$(η$^2$-H$_2$)(dcype){PPh(OEt)$_2$}]$^+$ (**6d**) | 226 | 21 |
| [ReH$_4$(η$^2$-H$_2$)(dcype){PPh$_2$(OMe)}]$^+$ (**6e**) | 225 | 42 |
| [ReH$_4$(η$^2$-H$_2$)(dcype){PPh$_2$(OEt)}]$^+$ (**6f**) | 226 | 32 |

Protonation of compounds **5a−f** with $HBF_4 \cdot O_2Me$ at 183 K in $CD_2Cl_2$ yielded the cationic complexes [ReH$_6$(dcype)L]$^+$ (**6a−f**) which in view of their $T_1$(min.) values (24−42 ms at 400 MHz) (Table 2) must each contain at least one dihydrogen ligand.[21] As a result of their marked fluxionality, their $^1$H NMR spectra show single broad hydride resonances between δ = −5 ppm and −6 ppm (Table 3) at 183 K. As the temperature is raised to 293 K, these signals become broad quadruplets (**6a−d**) or double triplets (**6e**,**f**). These compounds are fairly stable, showing the first sign of decomposition [loss of $H_2$(g)] only when kept at room temperature for more than 24 h. As reported for the related compound [ReH$_6${Ph$_2$PO(CH$_2$)$_2$OPPh$_2$}]BF$_4$,[12] their thermal stability increases with the electron-withdrawing character of the monodentate phosphorus ligand L. When they were treated with $Et_3N$, the starting pentahydrides **5a−f** were obtained. At 183 K the $^{31}$P{$^1$H} NMR spectra of the compounds show two broad signals which resolve into a typical $AX_2$ system when the temperature is raised (see Table 3).

## Conclusions

The new rhenium polyhydride compounds [ReH$_7$(dcype)] (**1**), [Re$_2$H$_8$(dcype)$_2$] (**3**) and [ReH$_5$(dcype)L] (**5a−f**) [dcype =

Table 3. Selected VT NMR spectroscopic data for the cationic complexes **6a−f**

| Compound[a] | $^1H$ NMR[b] $T$ = 183 K δ [ppm]; $J$ [Hz] | $T$ = 293 K δ [ppm]; $J$ [Hz] | Assignment | $^{31}P\{^1H\}$ NMR $T$ = 183 K δ [ppm]; $J$ [Hz] | $T$ = 293 K δ [ppm]; $J$ [Hz] |
|---|---|---|---|---|---|
| **6a** | −5.98 (br)[c] | −5.71 (q); $J_{P,H}$ = 14 | H/$\eta^2$-$H_2$ | 126.48 (t)[c] | 145.54 (d) |
| | | 3.62 (d); $J_{P,H}$ = 12 | $CH_3$ (L) | 142.66 (br) | 123.69 (t) |
| | | 4.09 (m) | $-(CH_2)_2-$ (dcype) | 150.22 (br) | $J$ = 36 |
| | | | | $J$ = 39 | |
| **6b** | −5.87 (br) | −5.66 (q); $J_{P,H}$ = 14 | H/$\eta^2$-$H_2$ | 117.59 (t) | 145.84 (d) |
| | | 1.34 (t); $J_{H,H}$ = 7 | $CH_3$ (L) | 146.4 (br) | 115.20 (t) |
| | | 3.97 (quin); $J_{P,H}$ = 7 | $CH_2$ (L) | $J$ = 38 | $J$ = 34 |
| | | 4.09 (m) | $-(CH_2)_2-$ (dcype) | | |
| **6c** | −5.58 (br) | −5.31 (q); $J_{P,H}$ = 15 | H/$\eta^2$-$H_2$ | 141.88 (s) | 145.20 (d) |
| | | 3.56 (d); $J_{P,H}$ = 13 | $CH_3$ (L) | 144.12 (br) | 139.73 (t) |
| | | 4.06 (m) | $-(CH_2)_2-$ (dcype) | | $J$ = 23 |
| **6d** | −5.55 (br)[c] | −5.30 (q); $J_{P,H}$ = 15 | H/$\eta^2$-$H_2$ | 133.54 (vbr)[c] | 145.40 (d) |
| | | 1.36 (t); $J_{P,H}$ = 7 | $CH_3$ (L) | 151.13 (vbr) | 131.39 (t) |
| | | 3.80 (m) | $CH_2$ (L) | | $J$ = 23 |
| | | 4.00 (m); 4.07 (m) | $-(CH_2)_2-$ (dcype) | | |
| **6e** | −5.19 (br) | −4.89 (dt); $J_{PB,H}$ = 19; | | 111.07 (s) | 144.91 (d) |
| | | $J_{PA,H}$ = 17 | H/$\eta^2$-$H_2$ | 145.79 (br) | 144.91 (d) |
| | | 3.44 (d); $J_{P,H}$ = 14 | $CH_3$ (L) | 113.70 (t) | 113.70 (t) |
| | | 4.12 (m) | $-(CH_2)_2-$ (dcype) | | $J$ = 9 |
| **6f** | −5.30 (br) | −4.89 (dt); $J_{PB,H}$ = 19; | | 106.09 (t)[d] | |
| | | $J_{PA,H}$ = 17 | H/$\eta^2$-$H_2$ | 146.31 (d) | |
| | | 1.33 (t); $J_{H,H}$ = 7 | $CH_3$ (L) | $J$ = 13 | |
| | | 3.67 (quin); $J_{P,H}$ = 7 | $CH_2$ (L) | | |
| | | 4.11 (m) | $-(CH_2)_2-$ (dcype) | | |

[a] In $CD_2Cl_2$ at 400 MHz. [b] Cyclohexyl and phenyl proton resonances are omitted. [c] Temperature 174 K. [d] Temperature 233 K.

$Cy_2PO(CH_2)_2OPCy_2$; L = $PPh_n(OR)_{3-n}$, $n$ = 0−2, R = Me, Et] are all highly fluxional classical hydride complexes but the combination of both the chelating ligand dcype and the monodentate ligand L in compounds **5** results in pentahydrides that are rigid enough to allow investigation of the various hydride interchange processes and calculation of the corresponding energy barriers. In contrast to other rhenium pentahydride systems, for which two interchange processes have been proposed (cyclic permutation of three hydride ions and a pseudorotation),[19] compounds **5** show signs of three processes, the third being the interchange of two hydride ions. Protonation of pentahydrides **5** with $HBF_4$·$OMe_2$ provided the relatively stable dihydrogen complexes $[ReH_6(dcype)L]BF_4$ (**6**) which can be stored at room temperature for more than 24 h without decomposition.

## Experimental Section

**General Methods:** All operations were carried out under argon using standard Schlenk techniques. Solvents were purified by distillation from the appropriate drying agents and degassed before use.[22] All other reagents and chemicals were reagent grade and, unless otherwise stated, were used as received from commercial suppliers. The ligand $Cy_2PO(CH_2)_2OPCy_2$ (dcype) and the complex $[ReOCl_2(OMe)(dcype)]$ were prepared as described in the literature.[13] Deuterated solvents for NMR measurements (Merck and Aldrich) were dried with molecular sieves (4 Å). Combustion C,H analyses were performed with a Fisons EA-1108 apparatus. NMR spectra were recorded with a Bruker AMX 400 spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane and were calibrated against the residual solvent resonance for $^1H$. Peak positions in $^{31}P\{^1H\}$ spectra were measured relative to external $H_3PO_4$ (85%) with downfield shifts considered positive. Variable-temperature spin-lattice relaxation times $T_1$ were determined in deuterated dichloromethane by the inversion-recovery method using a standard 180°−τ−90° pulse sequence and 16 different values of τ at each temperature. Infrared spectra (IR) of samples in KBr pellets were recorded with a Bruker Vector IFS28 FT spectrometer.

**$[ReH_7(dcype)]$ (1):** An excess of $NaBH_4$ (0.30 g, 7.91 mmol) in ethanol (20 mL) was added to a suspension of $[ReOCl_2(OMe)(dcype)]$ (0.20 g, 0.26 mmol) in ethanol (10 mL). After 6 h of vigorous stirring, the solvent was removed under vacuum and the product was extracted with benzene (30 mL). This solution was concentrated in vacuo and the oil obtained was treated with ethanol (5 mL) giving a tan solid which was filtered, washed with ethanol and dried under vacuum (0.127 g, 75% yield). $C_{26}H_{55}O_2P_2Re$ (648.32): calcd. C 48.12, H 8.5; found C 47.70, H 8.6. IR (KBr pellets): $\tilde{\nu}_{(Re-H)}$ = 1933 (m), 1956 (m) $cm^{-1}$. $^1H$ NMR ($C_6D_6$, 400 MHz): $\delta$ = −6.55 (t, $J_{P,H}$ = 17 Hz, 7 H, Re$H$), 1.10−2.20 (m, 44 H, Cy), 3.8 [m, 4 H, $-(CH_2)_2-$] ppm. $^{31}P\{^1H\}$ NMR ($C_6D_6$, 161 MHz): $\delta$ = 157.0 (s) ppm.

**$[Re_2H_8(dcype)_2]$ (3):** When compound **1** (0.10 g, 0.10 mmol) was dissolved in toluene (10 mL) and heated to reflux for 24 h, a yellow solid was obtained. This solid was filtered and dried under vacuum (0.08 g, 80% yield). $C_{52}H_{104}O_4P_4Re_2$ (1289.70): calcd. C 48.43, H 8.13; found C 48.01, H 7.98. IR (KBr pellets): $\tilde{\nu}_{(Re-H)}$ = 2012 (w), 2028 (w) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): $\delta$ = −7.37 (quint, $J_{P,H}$ = 9 Hz, 8 H, Re$H$), 0.70−1.94 (m, 88 H, Cy), 3.77 [m, 8 H, $-(CH_2)_2-$] ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 161 MHz): $\delta$ = 162.4 (s) ppm.

**[$ReH_5$(dcype)L] (5) [L = $P(OMe)_3$ (5a), $P(OEt)_3$ (5b), $PPh(OMe)_2$ (5c), $PPh(OEt)_2$ (5d), $PPh_2(OMe)$ (5e), $PPh_2(OEt)$ (5f)]:** The appropriate phosphinite, phosphonite or phosphite (L) was added in a 1:3 mol ratio to a solution of **1** (0.10 g, 0.15 mmol) in benzene (20 mL). The mixture was heated to reflux for 7 h. The solution obtained was vacuum concentrated and the resultant oil was treated with ethanol or methanol, as required, affording a solid which was filtered, washed with the same alcohol as had been used for its precipitation and dried under vacuum.

**5a:** 0.081 g, 68% yield. $C_{29}H_{62}O_5P_3Re$ (770.34): calcd. C 45.18, H 8.11; found C 45.40, H 8.42. IR (KBr pellets): $\tilde{\nu}_{(Re-H)}$ = 1901 (vw), 1928 (w), 1943 (w), 1987 (vw) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): $\delta = -8.05$ (dt, $J_{P(A),H} = 16$, $J_{P(B),H} = 20$ Hz, 5 H, Re*H*), 1.25−2.02 (m, 44 H, Cy), 3.45 (d, $J_{H,P} = 12$ Hz, 9 H, $-CH_3$), 3.87 [m, 4 H, $-(CH_2)_2-$] ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 161 MHz): $\delta = 152.9$ (t, $P_B$), 157.5 (d, $P_A$) ppm; $J_{P,P} = 51$ Hz.

**5b:** 0.093 g, 75% yield. $C_{32}H_{68}O_5P_3Re$ (812.38): calcd. C 47.27, H 8.44; found C 46.95, H 8.73. IR (KBr pellets): $\tilde{\nu}_{(Re-H)}$ = 1923 (w), 1943 (w), 1963 (vw) $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): $\delta = -8.01$ (dt, $J_{P(A),H} = 16$, $J_{P(B),H} = 19$ Hz, 5 H, Re*H*), 1.22 (t, $J_{H,H} = 7$ Hz, 9 H, $-CH_3$), 1.25−2.11 (m, 44 H, Cy), 3.89 (quint, $J_{H,H} = J_{H,P} = 7$ Hz, 6 H, $-O-CH_2-CH_3$), 3.86 [m, 4 H, $-(CH_2)_2-$] ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 161 MHz): $\delta = 144.8$ (t, $P_B$), 157.7 (d, $P_A$) ppm; $J_{P,P} = 49$ Hz.

**5c:** 0.075 g, 60% yield. $C_{34}H_{64}O_4P_3Re$ (816.01): calcd. C 50.05, H 7.91; found C 49.60, H 7.71. IR (KBr pellets): $\tilde{\nu}_{(Re-H)}$ = 1896 (w), 1943 (vw), 1968 (vw), 1990 (vw), $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): $\delta = -7.63$ (dt, $J_{P(A),H} = 15$, $J_{P(B),H} = 20$ Hz, 5 H, Re*H*], 1.21−1.88 (m, 44 H, Cy), 3.43 (d, $J_{P,H} = 12$ Hz, 9 H, $-CH_3$), 3.88 [m, 4 H, $-(CH_2)_2-$], 7.30−7.66 (m, 5 H, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 161 MHz): $\delta = 157.4$ (d, $P_A$), 160.8 (t, $P_B$) ppm; $J_{P,P} = 40$ Hz.

**5d:** 0.075 g, 58% yield. $C_{36}H_{68}O_4P_3Re$ (844.06): calcd. C 51.23, H 8.12; found C 50.81, H 8.33. IR (KBr pellets): $\tilde{\nu}_{(Re-H)}$ = 1920 (w), 1943 (w), 1962 (vw), $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): $\delta = -7.63$ (dt, $J_{P(A),H} = 16$, $J_{P(B),H} = 20$ Hz, 5 H, Re*H*), 1.24 (t, $J_{H,H} = 7$ Hz, 6 H, $-CH_3$), 1.28−2.05 (m, 44 H, Cy), 3.67 (m, 2 H, $O-CH_2-CH_3$), 3.86 [m, 4 H, $-(CH_2)_2-$], 3.99 (m, 2 H, $O-CH_2-CH_3$), 7.26−7.69 (m, 5 H, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 161 MHz): $\delta = 152.6$ (t, $P_B$), 157.8 (d, $P_A$) ppm; $J_{P,P} = 37$ Hz.

**5e:** 0.087 g, 65% yield. $C_{39}H_{66}O_3P_3Re$ (862.08): calcd. C 54.34, H 7.72; found C 53.90, H 8.04. IR (KBr pellets): $\tilde{\nu}_{(Re-H)}$ = 1910 (w), 1945 (w), 1964 (vw), $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): $\delta = -7.33$ (dt, $J_{P(A),H} = 16$, $J_{P(B),H} = 21$ Hz, 5 H, Re*H*), 1.18−2.07 (m, 44 H, Cy), 3.36 (d, $J_{P,H} = 13$ Hz, 3 H, $-CH_3$), 3.91 [m, 4 H, $-(CH_2)_2-$], 7.23−7.76 (m, 10 H, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 161 MHz): $\delta = 133.2$ (t, $P_B$), 156.9 (d, $P_A$) ppm; $J_{P,P} = 34$ Hz.

**5f:** 0.054 g, 40.% yield. $C_{40}H_{68}O_3P_3Re$ (876.11): calcd. C 54.84, H 7.82; found C 54.75, H 7.92. IR (KBr pellets): $\tilde{\nu}_{(Re-H)}$ = 1903 (w), 1943 (w), 1983 (vw), $cm^{-1}$. $^1H$ NMR ($CD_2Cl_2$, 400 MHz): $\delta = -7.31$ (dt, $J_{P(A),H} = 16$, $J_{P(B),H} = 21$ Hz, 5 H, Re*H*), 1.28 (t, $J_{H,H} = 7$ Hz, 3 H, $-CH_3$), 1.34−1.80 (m, 44 H, Cy), 3.71 (quint, $J_{H,H} = J_{H,P} = 7$ Hz, 2 H, $O-CH_2-CH_3$), 3.91 [m, 4 H, $-(CH_2)_2-$], 7.22−7.80 (m, 10 H, Ph) ppm. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$, 161 MHz): $\delta = 126.6$ (t, $P_B$), 157.1 (d, $P_A$) ppm; $J_{P,P} = 32$ Hz.

**Protonation Reactions** Polyhydrides **1**, **3** and **5a−f** were protonated according to a procedure reported in the literature for similar compounds.[10a]

**Supporting Information:** Plot of ln$T_1$ vs. temperature for compounds **5a−f** and **6a−f** in $[D_2]CH_2Cl_2$ at 400 MHz (see also footnote on the first page of this article).

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