Unusual Fluxional and T_1 Properties for $[ReH_4(CO)(PMe_2Ph)_3]^+$: a Polyhydride with Classical and Nonclassical Tautomers

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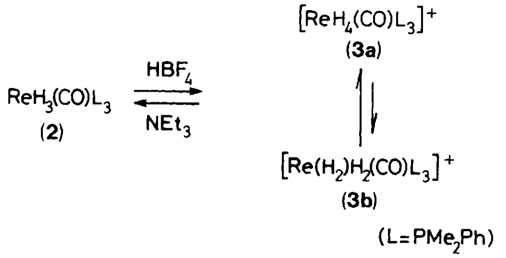
NMR studies show that $[ReH_4(CO)(PMe_2Ph)_3]BF_4$ exists as a tautomeric mixture (ΔH 1.1 kcal mol^{-1}) (1 cal = 4.184 J) of the classical tetrahydride [T_1(min., 250 MHz) 80 ms] **(3a)** (major) and the nonclassical d^4 tautomer [T_1(min., 250 MHz) 8 ms for the (H_2) peak] **(3b)** $[Re(H_2)H_2(CO)(PMe_2Ph)_3]^+$ (minor), the HD analogue of which has $J_{H,D}$ 34 Hz; the fluxional processes in the system lead to an unusual temperature dependence of the T_1 values.

Polyhydrides[1] L_nMH_x ($x > 3$) may have a classical (*e.g.*, WH_4L_4) or a nonclassical (*e.g.*, $[IrH_2(H_2)_2L_2]^+$) structure,[2] but up until now, no case is known in which both tautomeric forms exist. In contrast, such an equilibrium has been seen for several dihydrides.[3] We have been looking for such a tautomeric polyhydride in part to test our T_1 method,[4] in which a short T_1(min.)† is associated with the presence of short $H \cdots H$ distances in the structure.

Caulton *et al.*[5] have recently found that $[ReH_3(PMe_2Ph)_4]$ can be protonated to give the classical $[ReH_4(PMe_2Ph)_4]^+$ **(1)**. We have prepared $[ReH_3(CO)(PMe_2Ph)_3]$ **(2)** in high yield from $[ReCl_3(CO)(PMe_2Ph)_3]$ by reflux with $LiAlH_4$ in Et_2O for 40 h. We protonated it with $HBF_4 \cdot Et_2O$ in CD_2Cl_2 at 193 K. The ^1H and ^{31}P NMR spectra indicate that the major product is a classical tetrahydride, $[ReH_4(CO)(PMe_2Ph)_3]^+$ **(3a)**. Also present is the minor nonclassical tautomer, $[ReH_2(H_2)(CO)(PMe_2Ph)_3]^+$ **(3b)**. Addition of NEt_3 leads to deprotonation and quantitative recovery of the NMR resonances of **(2)**.

As shown in Figure 1, at 193 K **(3a)** gives an apparent binomial quartet hydride resonance at δ −3.91 with $^2J_{P,H}$ of 18 Hz, indicating that intramolecular fluxional exchange of the hydrides is taking place, not unexpected in an eight-co-ordinate complex. The relatively large $^2J_{P,H}$ value suggests the classical formulation. In the ^{31}P NMR, in contrast, an AB_2 pattern is seen, indicating that the phosphorus nuclei remain inequivalent. This inequivalence is insufficient to perturb the quartet seen in the ^1H NMR spectrum, however. The cation **(1)** has a dodecahedral structure with the PMe_2Ph ligands in the B sites; an analogous structure with a CO replacing PMe_2Ph would explain the NMR spectra if the hydrides (A sites) are exchanging and the other ligands (B sites) are fixed.

At 188—198 K, the classical and nonclassical sites in the nonclassical tautomer **(3b)** are distinguishable by ^1H NMR spectroscopy. We assign the multiplet at δ −4.90 to the classical hydrides, because of their apparent $J_{P,H}$ of 55 Hz, appropriate for a terminal hydride. A broad feature ($w_{1/2}$ 100 Hz) at δ −5.35 is assigned to the H_2 ligand. No significant coupling to phosphorus is apparent. The HD analogue shows a well defined 1 : 1 : 1 triplet at δ −5.35 with $J_{H,D}$ of 34 Hz at the high end of the range of values observed for dihydrogen complexes. This is the first time this coupling has been observed for a polyhydride. On warming to 212 K, the classical and non-classical resonances coalesce into a single broad peak.



(1)

On further warming to 278 K, the intermolecular exchange between **(3a)** and **(3b)** is fast so that only an average hydride resonance is observed. Finally, on warming above 280 K, H_2 is lost, although only slowly, and **(3)** can still be observed at 298 K if the NMR spectrum is obtained quickly. Hydrogen loss is irreversible, because the deuterium label is not incorporated in the presence of D_2. The decomposition product resulting from H_2 loss has not yet been characterized.

The activation energies for the two fluxional processes were estimated from the coalescence temperatures as $\Delta G^{\ddagger}$ 9.9 kcal mol^{-1} at 208 K (1 cal = 4.184 J) for the low temperature intramolecular process and $\Delta G^{\ddagger}$ 12.3 kcal mol^{-1} at 278 K for the high temperature intermolecular process **(3b)** to **(3a)**.[6] The fact that intramolecular scrambling within complex **(3b)** seems to be faster than exchange with **(3a)** suggests that the mechanism for the exchange between the classical and nonclassical sites in **(3b)** does not involve oxidative addition of the (η^2-H_2) ligand to give **(3a)**.‡ An alternative mechanism may operate: we propose the transfer of a proton from the (η^2-H_2) ligand to an adjacent terminal hydride with an $H \cdots H \cdots H$ structure as an intermediate or transition state. Such H_3 complexes have been studied theoretically by Burdett.[7]

Over the temperature range 188—258 K, the ln K *vs.* $1/T$ plot gave the following thermodynamic parameters for the conversion of **(3a)** to **(3b)**: ΔH +1.1 kcal mol^{-1}; ΔS 2.4 cal mol^{-1} K.

The coexistence of **(3a)** and **(3b)** in the temperature range 193—253 K, together with our ability to see the distinct resonances (Figure 1) for each species, allows us to measure the T_1 for each resonance. These are shown in Figure 2. As can be seen, the data do not conform to the usual[4,8] V-shaped curve. This is to be expected in the case of a fluxional system, because exchange at a rate too slow to bring about full coalescence can still lead to averaging of the T_1 values. There is a clear difference between the T_1 values for the two tautomers. For example, at 193 K, the T_1 value for **(3a)**, 92 ms, is much longer than 9 ms for the (η^2-H_2) ligand in **(3b)**. The true minimum for both species probably occurs near 200 K. As the sample is warmed from 188 K, the T_1 of **(3a)** and the (η^2-H_2) resonance of **(3b)** decrease gradually, as is observed for other polyhydrides.[4] The T_1 for the classical site in **(3b)**

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† We have recently found that T_1(min., 250 MHz) values of 55—80 ms can be associated with classical hydrides,[4b] as a result of multiple close but nonbonding $H \cdots H$ contacts in polyhydrides of co-ordination number greater than six.

‡ This argument fails if the H_2 ligand in **(3b)** undergoes oxidative addition to give a nonfluxional classical isomer, different from and not exchanging with **(3a)**, or if the H positions in **(3a)** did not scramble rapidly. Since **(3a)** is fluxional even at 193 K, scrambling in the classical isomer would be fast and the existence of a second classical isomer not exchanging with **(3a)** is unlikely.

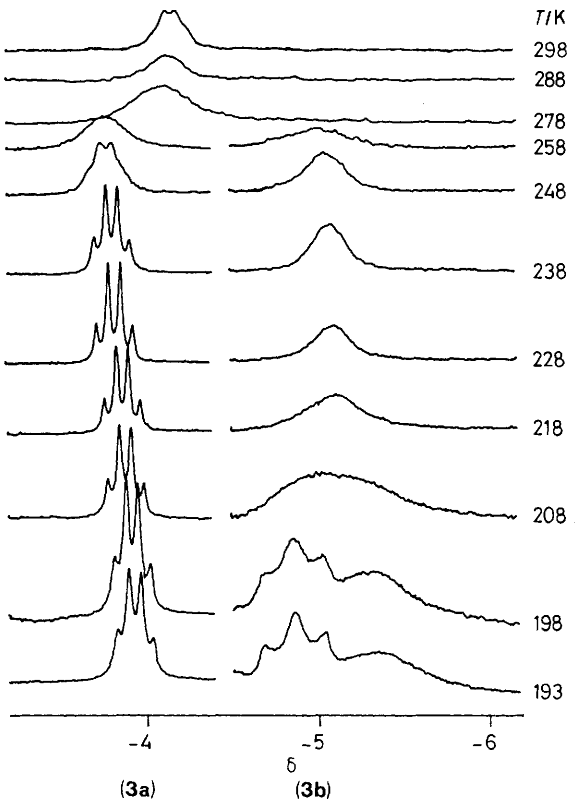

Figure 1. The fluxional behaviour of $[ReH_4(CO)(PMe_2Ph)_3]^+$ (**3a**) and $[Re(H_2)H_2(CO)(PMe_2Ph)_3]^+$ (**3b**). The peak intensities for (**3b**) have been increased eight times.

shows a sharp decrease until, at 208 K, the T_1 values coalesce. The T_1 value for (**3a**) is essentially constant with temperature as a result of the intermolecular exchange process. This confirms that the intramolecular exchange of the classical or nonclassical sites for (**3b**) is faster than intermolecular exchange of (**3a**) with (**3b**).

Rather than adopt a structure with an H · · · H distance intermediate between that of an H_2 complex and a classical hydride, (**3**) prefers to exist as an equilibrating mixture of isomers. Further studies on polyhydrides may reveal more examples which are near the classical/nonclassical borderline. Most H_2 complexes discovered to date have a six-co-ordinate d^6 configuration. Compound (**3b**) is one of the rare seven-co-ordinate d^4 examples.[4a] The large difference in T_1(min.) for (**3a**) and (**3b**) supports the proposed T_1 method.[4]

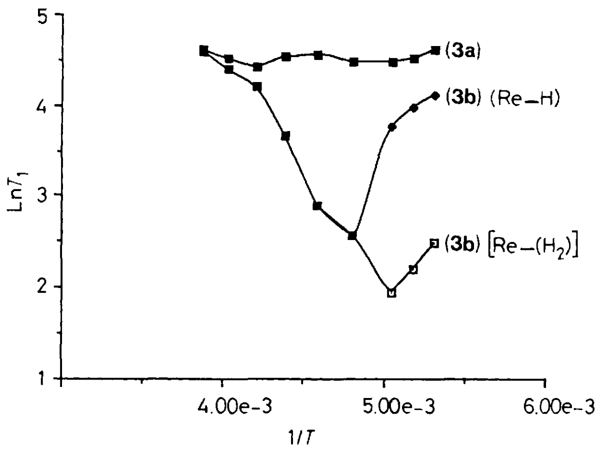

Figure 2. The T_1 behaviour of the tautomeric mixture of (**3a**) and (**3b**). The plot shows ln (T_1) *vs.* inverse absolute temperature. The T_1 (min.) value for the H_2 site of (**3b**) is 8 ms. Higher temperatures are to the left.

We thank the NSF for support.

Received, 21st August 1989; Com. 9/03574E

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