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Communications

Rhenium Phosphine Heptahydride Complexes: ^{1}H NMR Evidence for Classical Structures in Solution

The structural characterization of transition-metal polyhydrides is a particularly challenging problem that has attracted much recent attention.[1] We previously developed a ^{1}H NMR T_1 method for the characterization of η^2-H_2 complexes,[2,3] based on the fast dipole–dipole relaxation expected for dihydrides in which two of the protons are close together. The T_1 goes through a minimum with temperature, and short values of T_1(min) (viz. <30 ms *at 250 MHz*) seem to be associated with nonclassical hydrides, containing only η^2-H_2 ligands with r(H–H) < 1 Å.

In polyhydrides such as $FeH_2(\eta^2\text{-}H_2)L_3$ (L = tertiary phosphine), fluxionality rapidly permutes protons between classical and nonclassical sites, so lengthening the observed T_1. Even so, T_1(obs) is still less than 35 ms and so there is little ambiguity. For ReH_7L_2, on the basis of T_1(min) values of 55–67 ms at 250 MHz, we[3b] proposed the nonclassical structure $ReH_5(\eta^2\text{-}H_2)L_2$. Although this assignment seemed to be supported by subsequent studies,[4a] we felt that the solution structure was not yet settled. Other work on these complexes has appeared recently.[4b] Close but nonbonding H···H contacts enforced by the high coordination number might be sufficient to give T_1 values below 100 ms. We found T_1(min) values in the range of 55–80 ms at 250 MHz for a number of classical polyhydride complexes, such as $[HB(pz)_3]ReH_6$, $[HB(pz)_3]Re(PPh_3)H_4$, and $[CH_2(pz)_2]ReH_7$ (pz = pyrazolyl)[5a] and $ReH_6(SiPh_3)(PPh_3)_2$.[5b] Cotton et al.[6] and Albertin et al.[7] have also reported rather low T_1 values in classical hydrides, but the measurements were not made at 250 MHz, so the data are not strictly comparable.[7b] A neutron diffraction study[8a] of ReH_7(dppe) (dppe = $Ph_2CH_2CH_2PPh_2$) indicates a classical tricapped trigonal prismatic (TTP) structure[8b] of type **1a** in the solid state. This does not define the solution structure, because cases are known in which the solution and solid-state structures of metal hydrides are not the same.[1]

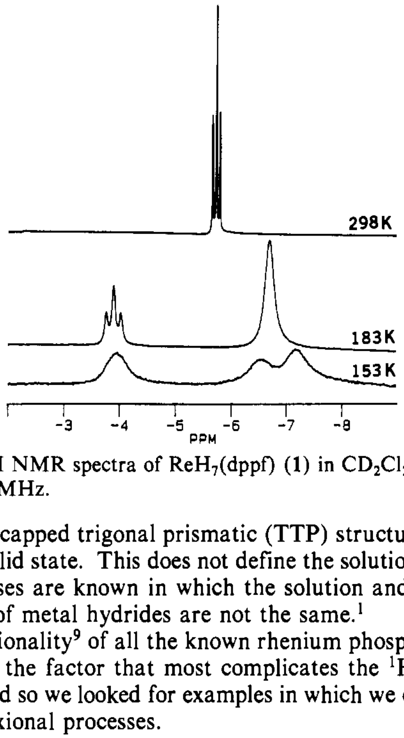

Figure 1. ^{1}H NMR spectra of ReH_7(dppf) (**1**) in CD_2Cl_2/CF_3Cl (3:2 v/v) at 250 MHz.

The fluxionality[9] of all the known rhenium phosphine heptahydrides is the factor that most complicates the ^{1}H NMR T_1 analysis, and so we looked for examples in which we could freeze out the fluxional processes.

The new heptahydride complexes ReH_7(dppf) (**2**, dppf = 1,1′-bis(diphenylphosphino)ferrocene) and ReH_7(dppb) (**3**, dppb = 1,4-bis(diphenylphosphino)butane) were prepared from $LiAlH_4$ treatment of the compounds $ReOCl_3L_2$ (L = $^1/_2$ dppf or $^1/_2$ dppb), which were readily available from $ReOCl_3(AsPh_3)_2$[10] by substitution of $AsPh_3$ with L_2. **2** and **3** were fully characterized by elemental analyses and IR and ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy. The minimum T_1 values observed for the hydride resonances of **2** and **3** (Table I) are 54 and 56 ms, respectively, in CD_2Cl_2 at 250 MHz. These numbers fall into the range reported[3b] for ReH_7L_2 (L = PPh_3, PCy_3, or $^1/_2$ $Ph_2PCH_2CH_2PPh_2$), which have been formulated as nonclassical.

Fortunately, the steric constraints of the chelating ligands are such that the fluxionality can be frozen out. Figure 1 displays the ^{1}H NMR spectra of **2** at three temperatures in $CD_2Cl_2/CFCl_3$ (3:2 v/v). At 298 K the spectrum shows a triplet hydride resonance at δ −5.75 ($^2J_{PH}$ = 16.9 Hz). When the sample is cooled

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[7] (a) Antoniutti, S.; Albertin, G.; Amendola, P.; Bordignon, E. *J. Chem. Soc., Chem. Commun.* **1989**, 229. (b) These authors measured their T_1 data at 80 MHz and did not adjust their data on the basis that T_1(min) scales with the magnetic field. When the data are adjusted to 250 MHz, the compounds of ref 7a have T_1 values greater than ca. 150 ms, and $ReH_5(PPh_3)_3$[6] has a T_1(min) value (57 ms) comparable to those observed in the present paper.

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[9] We recently reported the case of $[CH_2(pz)_2]ReH_7$ (pz = pyrazolyl),[5a] which appears to be classical and shows decoalescence at 178 K.

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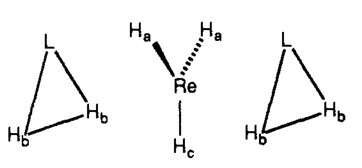
Table I. ^{1}H NMR T_1 and Isotope Shift Data for the ReH_7L_2 Complexes Studied[a]

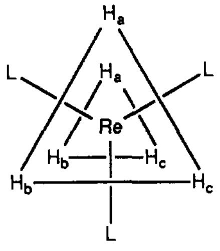
compd	L_2[b]	T, K	δ_{Ir-H}[c]	T_1, ms[d]	IS, ppm/D[e]
2	$Fe(C_5H_4PPh_2)_2$	153	−3.93, 2 H, br t (32)	351	−0.002[f]
			−6.52, 1 H,[g] br	301	
			−7.12, 4 H,[g] br	301	
		183	−3.89, 2 H, t (32)	112	
			−6.70, 5 H, br	95	
		233	−5.98, 7 H, br	**54**	
		298	−5.75, 7 H, t (16.9)	132	
3	$Ph_2P(CH_2)_4PPh_2$	163	−4.73, 2 H, br t (32)	211	−0.0062[f]
			−7.02, 5 H, br	186	
		219	−6.30, 7 H, br	**56**	
		298	−6.18, 7 H, t (16.2)	125	
4	$(PPh_3)_2$	193	−5.12, 7 H, t (19)	**55**[h]	−0.0088[j]
5	$(PCy_3)_2$	200	−7.07, 7 H, t (19)	**60**[h]	−0.0083[j]
6	$Ph_2P(CH_2)_2PPh_2$	222	−6.79, 7 H, t (13)	**67**[h]	−0.0071[j]

[a] All NMR studies were carried out at 250 MHz in either CD_2Cl_2 or, for measurements carried out below 183 K, CD_2Cl_2/CF_3Cl (ca. 3:2 v/v) as solvent. [b] L_2 in ReH_7L_2. [c] Hydride resonances reported as chemical shift (ppm), intensity, multiplicity (t = triplet, br = broad singlet) (coupling constant $^2J_{PH}$ (Hz)). [d] Minimum T_1 values observed are given in bold type. For a complex that does not undergo decoalescence, only the minimum T_1 value is listed. [e] The isotope shift in ppm/D is defined as IS = $\delta(ReH_{6-x}D_{x+1}) - \delta(ReH_{7-x}D_x)$, an upfield isotope shift having a negative sign. In the cases of **1** and **2** where decoalescence occurs, the IS can be measured only in the fast-exchange-limit spectra. [f] In the range 273–298 K. [g] The intensity ratio could not be unambiguously determined in this case, because decoalescence was not complete. [h] From ref 3b. [j] In the range 253–298 K.

to 183 K, decoalescence of the hydride resonance takes place to give a triplet resonance at δ −3.89 ($^2J_{PH}$ = 32 Hz) of intensity 2 and a broad resonance at δ −6.70 of intensity 5. The resonance at δ −3.89 obviously arises from classical hydrides, because $^2J_{PH}$ is far too large for an η^2-H_2 ligand. When the sample is further cooled to 153 K, the resonance at δ −6.70 due to five hydrides collapses into two broad features at δ −6.52 and −7.12. It is difficult to measure the relative intensity of these two resonances because the lines are broad. A 1:4 intensity ratio is more likely than a 2:3 ratio because a 1:4 weighted average of the two chemical shifts best fits the observed average chemical shift at 183 K, after allowing for the temperature dependence of the chemical shifts. A 2:1:4 intensity ratio in the low-temperature limiting spectrum would be exactly the ratio expected from either of the two classical nine-coordinate TTP structures **1a** and **1b**.



1a



1b

Of the two structures, **1a** should be favored by a ligand with a bite angle of 90° and **1b** by one with an angle of 120°. **1a** is therefore likely to be adopted in the case of dppe, dppb, and dppf because they prefer bite angles of 85–103°.[8a,11] The dppe complex adopts structure **1a** in the solid state.[8a]

The ^{1}H NMR spectra of **3** in $CD_2Cl_2/CFCl_3$ (3:2 v/v) at 298 and 163 K are given in Figure 2. Like **2**, **3** shows a triplet hydride resonance at δ −6.18 ($^2J_{PH}$ = 16.2 Hz) at 298 K. The complex is more fluxional than **2** and shows only the first decoalescence upon cooling, the spectrum at 163 K consisting of one broad triplet at δ −4.73 with a $^2J_{PH}$ value of 32 Hz and a broad singlet at δ −7.02 in an intensity ratio 2:5. At this temperature, the H_b and H_c protons are still exchanging and so are unresolved. This low-temperature hydride pattern again suggests one of the classical structures **1a** or **1b**.

Confirmatory evidence for the classical structure has been obtained from ^{1}H NMR deuterium isotope shift data. If the complexes contained both classical and nonclassical sites, then partial deuteration would lead to a temperature-dependent isotopic fractionation between the two sites and thus an isotopic perturbation of the resonance position (IPR)[12] in the fast-exchange-limit spectrum. The IPR method has been successfully used for the study of agostic C–H interactions,[13] a situation closely resembling this one. The IPR shift is expected to be large for a nonclassical polyhydride because of the large changes in vibrational frequencies for H_2 vs HD and M–H vs M–D, assuming that the chemical shift difference ($\Delta\delta$) between the two sites is significant. We observed[14] an IPR shift of 0.1 ppm/D for $[IrH(\eta^2\text{-}H_2)(bq)(PPh_3)_2]^+$ (bq = 7,8-benzoquinolinate) but the breadth of the ^{1}H NMR hydride resonances for most dihydrogen hydride complexes makes the effect difficult to observe.

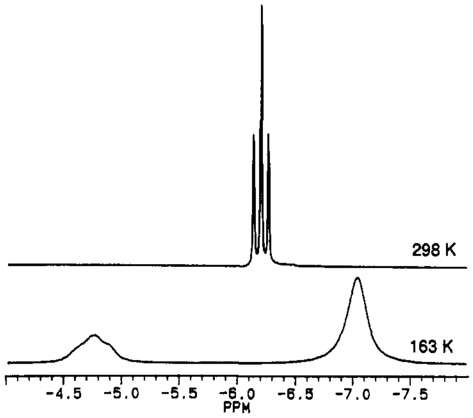


Figure 2. ^{1}H NMR spectra of $ReH_7(dppb)$ (**2**) in CD_2Cl_2/CF_3Cl (3:2 v/v) at 250 MHz.

The isotopomeric mixtures of $ReH_{7-x}D_xL_2$ (x = 0–7) were prepared by treatment of $ReOCl_3L_2$ with $LiAlD_4$ followed by hydrolysis with H_2O/D_2O. As shown in Table I, the isotope shifts observed for all the heptahydrides studied are very small, even though the decoalescence data shows that $\Delta\delta$ would be substantial if one of the resonances in the low-temperature limiting spectrum arises from an η^2-H_2 ligand. In addition, the observed isotope shifts (ppm/D) are temperature independent and are the same upon successive deuterium substitution. These are more likely caused by secondary isotope effects on nuclear magnetic shielding[15a,b] than

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by true IPR.[15c] Geminal deuterium substitution of H by D in a second-row main-group element usually gives rise to upfield isotope shifts of −0.01 to −0.03 ppm/D in the ^{1}H NMR.[16]

Furthermore, the value of $^2J_{PH}$ in the fast-exchange spectrum remains the same for all the isotopomers. This, too, is inconsistent with a nonclassical structure, which should also show isotopic perturbation of the coupling constant because $^2J_{PH}$ is much larger than $^2J_{PH_2}$ and so upon deuterium substitution the observed $^2J_{PH}$ should change significantly due to the isotopic fractionation between classical and nonclassical sites.

Although we were not able to observe decoalescence for the known complexes **4**–**6**,[17] they show similar isotope shifts and minimum T_1 values. We believe that these complexes, too, adopt a classical structure in solution, because of the close analogy of spectroscopic properties for all the complexes **2**–**6**.

The upper limiting value of T_1(min) that we previously suggested[3b] could be associated with a nonclassical structure is clearly too high. Rather than having a fixed limiting value, it is perhaps better to calculate[3b,18] values of T_1(min) to be expected on the basis of plausible classical and nonclassical structures for a given compound, and to compare these with the observed numbers. Only if the theoretical numbers are sufficiently different, will the T_1 method be suitable for making a distinction.

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Note Added in Proof. Cotton and Luck (Cotton, F. A.; Luck, R. *J. Am. Chem. Soc.* **1989**, *111*, 5757) have suggested that non dipole–dipole (DD) mechanisms are important for ReH$_5$(PPh$_3$)$_3$ (**7**). Applying the DD calculation[3b,11] to their crystallographic H···H distances for **7** leads to a T_1(min) value of 148 ms at 400 MHz, in excellent agreement with their observed T_1(min) value in toluene of 138 ms. We conclude that the DD mechanism is dominant, at least in this case.

Supplementary Material Available: Experimental data including synthetic details for the complexes and their partially deuteriated species, details for the calculations and a table of theoretical T_1(min) values (6 pages). Ordering information is given on any current masthead page.

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A High-Potential Mononuclear Manganese(IV) Complex. Synthesis, Structure, and Properties, Including EPR Spectroscopy and Electrochemistry, of [Mn(HB(3,5-Me$_2$pz)$_3$)$_2$](ClO$_4$)$_2$ (pz = Pyrazolyl)

A resurgence of interest in higher valent manganese chemistry in recent years stems from the realization of its importance in biological processes such as photosynthetic water oxidation,[1] superoxide dismutation,[2] and peroxide disproportionation.[3] The S$_2$ state of the oxygen-evolving complex of photosystem II displays a multiline EPR[4] signal centered at g = 2.0 as well as a prominent g = 4.1 signal, both of which are associated with the manganese center.[5] Although it is generally agreed that the multiline signal originates from a multinuclear manganese center, the source of the g = 4.1 signal is not well understood. Recently, Hansson, Aasa, and Vänngård (HAV)[6] postulated that the g = 4.1 signal arises from a mononuclear Mn(IV) center that is in redox equilibrium with a separate polynuclear site. If one assumes that (i) water oxidation occurs at the multiline site and (ii) there is a relatively small separation between the Mn^{IV}/Mn^{III} reduction potential of the putative mononuclear g = 4.1 site and that of the multiline site, then the g = 4.1 site is required to have a rather high reduction potential, perhaps in the vicinity of ~1 V vs NHE. While several Mn(IV) species have been characterized,[7] very few have reduction potentials of ≥1.0 V. Here we report the synthesis, structure, and properties of a novel Mn(IV) complex that is noteworthy in the

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(4) Abbreviations used: EPR, electron paramagnetic resonance; cp, cyclopentadienyl; SCE, saturated calomel electrode; SSCE, sodium saturated calomel electrode; pz, pyrazolyl; H$_2$saladhp, 1,3-dihydroxy-2-methyl-2-(salicylideneamino)propane; H$_2$sal, salicylic acid; dtbc, 3,5-di-*tert*-butylcatecholato; py, pyridine; TPP, 5,10,15,20-tetraphenylporphinato; bpy, 2,2′-bipyridine; phen, 1,10-phenanthroline; tren, 2,2′,2″-triaminotriethylamine; terpyO, 2,2′:6′,2″-terpyridine 1,1′,1″-trioxide; H$_2$Salahp, 1-hydroxy-3-(salicylideneamino)propane; H$_3$hps, *N*-(2-hydroxyphenyl)salicylamide; PS II, photosystem II.

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