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# Testing the $T_1$ Method: A Comparison of $T_1$(min) and Structural Data

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For a series of mononuclear polyhydrides for which both structural and relaxation data are available, there is good agreement between the calculated and observed $T_1$(min) values. This substantiates the two assumptions made in the calculations, that the solid-state structure is maintained in solution and that dipole–dipole (DD) relaxation is dominant. There do not seem to be significant contributions from the spin rotation (SR), chemical shift anisotropy (CSA), or scalar (SC) mechanisms in the cases studied. The effects of thermal excursions from the equilibrium positions and DD relaxation from the $^{31}$P nuclei of the ligands are shown to be relatively small. The implications for the interpretation of $T_1$ data are discussed. The binuclear complexes $Re_2H_8L_4$ relax significantly faster than predicted from the structure by the DD equations. Further study is needed to identify the origin of the discrepancy.

We recently suggested an NMR method for obtaining qualitative structural information about metal hydride complexes.[1,2] This involves measuring the $T_1$ value [$T_1$(min)] for the $^1$H NMR hydride resonance(s) at the minimum of the ln $T_1$ vs inverse temperature curve for the sample. In particular, if an $H_2$ ligand is present, then the large contribution from dipole–dipole (DD) relaxation as a result of the short H···H separation will lead to a relatively short $T_1$(min). In this paper we test the basis of the method by a quantitative comparison of the $T_1$(min) data observed for a variety of hydride complexes with the values calculated from the respective crystal structures. The dipole–dipole relaxation equations can be used to calculate a $T_1$(min) value; for mononuclear complexes, these closely match the observed values, as expected if DD relaxation is dominant.

## Results and Discussion

**Approach and Assumptions.** The growing use of the $T_1$ method and discussion of the validity of the assumptions made[3-5] prompted us to carry out a more quantitative and rigorous test of the method than has been the case to date. In this paper we assume that (a) the structure of the hydrides studied is the same in the crystal as in solution and (b) the DD mechanism dominates the relaxation. By doing so, we can predict the $T_1$(min) value of a given hydride from the crystal structural data. The agreement between experiment and theory, described here, validates the assumptions.

With the assumptions mentioned above, we can use the DD equations to calculate the contribution to the relaxation from all the H···H vectors in the molecule. We neglect contributions from the phosphine protons, since, in a study using perdeuterated phosphines, the effect of these has been shown by Morris et al.[3b] to be negligible in a typical nonclassical case; these, however, could become more significant for a classical hydride with a long $T_1$(min). For the moment we neglect contributions from the phosphine P nuclei, but we later show that these contributions are also very small. We also neglect contributions from the solvent, since the effect should be small for the deuterated solvents used. We prefer neutron diffraction data to X-ray data, because the hydride positions are better defined in the neutron experiment, but have also used high-quality X-ray work, where neutron data are not available.

**Table I.** Observed $T_1$(min) Values Matching Those Calculated from Crystallographic and Other Structural Methods[a]

| compd | structural method | $T_1$(min) calcd | $T_1$(min) found | field | ref |
|---|---|---|---|---|---|
| $FeH_2(H_2)(PEtPh_2)_3$ | n-diff | 3.8–14.6[b] | 24[c] | 250 | 11 |
| $ReH_7(dppe)$ | n-diff | 77 | 67 | 250 | 12 |
| $ReH_5(PPh_3)_3$ | X-ray | 148 | 138 | 400 | 5 |
| $ReH_5(PMePh_2)_3$ | n-diff | 156, 157 | | 400 | 15 |
| $W(H_2)(CO)_3(P(i\text{-}Pr)_3)_2$ | n-diff | 3.5–14.5[b] | 4[d] | 200 | 6 |
| $W(H_2)(CO)_3(PCy_3)_2$ | sd st NMR | 2.5–10.1[b] | 4[d,e] | 200 | 18 |
| $[FeH(H_2)(dppe)_2]^+$ | X-ray | 1.7–7.5[b] | 8.5[f] | 200 | 3e |
| $[IrH(H_2)bq(PPh_3)_2]^+$ | sd st NMR | 4–15.5[b] | 8[g] | 250 | 18b |
| $WH_6(PMePh_3)_3$ | n-diff | 201 | 181 | 250 | 16 |
| $[CpIr(PMe_3)H_3]^+$ | n-diff | 189[d] | 300[h] | 500 | 17 |
| $[CpIr(PPh_3)H_3]^+$ | | (189)[i] | 200[h] | 500 | 17 |
| $[CpIr(AsPh_3)H_3]^+$ | | (189)[i] | 210[h] | 500 | 17 |
| $[CpRu(H_2)CO(PCy_3)]^+$ | sd st NMR | 5.3–21.2[b] | 4 | 250 | 17c, 18b |
| $Re_2H_8(PEt_2Ph)_4$ | n-diff | 302 | 140 | 400 | 19 |

[a] All $T_1$ values in ms. n-diff = neutron diffraction; X-ray = X-ray diffraction; sd st NMR = direct observation of dipole–dipole coupling by solid-state NMR spectroscopy. [b] The first figure cited assumes no rotation of the $H_2$ ligand; i.e., $C = 1$. The second assumes fast $H_2$ rotation ($C = 0.79$). [c] At 203 K; minimum not observed. [d] At 193 K; minimum not observed. [e] Assuming the $T_1$ is essentially the same as the P($i$-Pr)$_3$ analogue at the same $\tau_c$. Cy = cyclohexyl. [f] At minimum by curve fitting. [g] Of the $H_2$ resonance. [h] At 210 K; minimum not observed. [i] Assuming the structure is essentially the same as the $PMe_3$ analogue.

When the $T_1$ data refer to the minimum at 250 MHz, the usual DD equations reduce to eq 1, which shows how each H···H vector should contribute to the overall $T_1$(min). Equation 2 shows how

$$R(\mathrm{DD}) = [T_1(\mathrm{min}, 250)]^{-1} = 157.2r^{-6} \qquad (1)$$

($r$ = H···H distance, Å; $R$(DD) = relaxation rate, s$^{-1}$)

$$T_1(\mathrm{min}, B) = [T_1(\mathrm{min}, 250)B]/250 \qquad (2)$$

($T_1$(min, $B$) is the $T_1$ at $B$ MHz)

the $T_1$(min) scales with spectrometer field $B$. Since each H···H distance contributes twice to the overall relaxation (for example, $H_a$···$H_b$ contributes to the relaxation of both $H_a$ and $H_b$), then if we only need the overall relaxation and not the relaxation of each H in the structure, we can simply double the calculated relaxation rate $R$(DD) for each distinct $H_n$···$H_m$ vector for all n and m (n ≠ m).

In the case of $H_2$ complexes, Morris et al.[3b] have shown that if the $H_2$ rotates about the M–($H_2$) bond, relaxation will be slower.

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For fast $H_2$ rotation, the relaxation is 0.25 of the value expected for no rotation. Intermediate rotation rates lead to intermediate reductions in relaxation rate. Equation 3 shows how this situation

$$R(\mathrm{DD}) = [T_1(\mathrm{min}, 250)]^{-1} = C^6(157.2r^{-6}) \qquad (3)$$

is covered by the use of a constant $C$, which takes the value 0.7937 in the fast-rotation regime and unity in the slow-rotation limit. For simplicity, we have calculated a $T_1$ range for $H_2$ complexes. The smaller $T_1$ (faster rate) refers to the relaxation expected if the $H_2$ ligand does not rotate ($C = 1$), and the larger $T_1$ refers to the fast-rotation case ($C$ = ca. 0.79). We have only applied this 0.25 ($=0.7937^6$) factor to the H···H vector of the $H_2$ ligand itself. For the fast-rotation case, we have ignored the slight modification in the contribution to the overall relaxation from the $H_n \cdots H_m$ vectors, where $H_n$ is a proton of the $H_2$ ligand and $H_m$ is any classical M–H proton; this should be small but is not easily calculable.

Table I shows the results for all the cases in which we could find both structural and $T_1$ data. For mononuclear complexes, there is good agreement between the calculated and observed figures. The solid-state structure is therefore probably preserved in solution in each case. The calculated relaxation rate is never significantly smaller than the observed value. This suggests that relaxation mechanisms other than DD probably do not contribute significantly to the relaxation in these cases.

**Solution versus Solid-State Structures.** We certainly did not expect to find such good quantitative agreement, and only when a wider range of compounds have been studied by both methods, will we be able to say how general these conclusions are. Exceptions will almost certainly be found, but it will require some further experiments for any given case to determine which of the two assumptions is not valid. Assumption a is the most likely candidate because cases are known[6,7a] where there is a difference between the solution- and solid-state structures.

**Other Relaxation Mechanisms.** Cases where assumption b fails would be of particular interest because none of the other relaxation mechanisms[8] have yet been proved to be significant for proton relaxation in metal hydrides. Other possible mechanisms do not seem to apply to the particular cases we have studied.

Spin rotation seems the most likely of the alternative mechanisms because the SR contribution is known to be important in the relaxation of free $H_2$.[8] In cases where spin rotation (SR) has been shown to be important,[9] the $T_{1\mathrm{SR}}$ contribution decreases monotonically with rising temperature. If the SR mechanism were dominant, no $T_1$(min) would be observed. If SR were a significant contributor, the usual V-shaped curve due to DD relaxation should be skewed; this is not observed for the metal hydrides studied here.

Scalar (SC) relaxation, especially "of the second kind",[10] is often responsible for broad lines in nuclei such as $^1$H when they are bound to a quadrupolar nucleus. Although SC contributions to $T_2$ are not uncommon (these affect line width), the SC mechanism, whether of the first or of the second kind, only very rarely contributes to $T_1$ because theory indicates that the Larmor frequencies of the quadrupolar nucleus and the relaxing dipolar nucleus have to be very close for a significant contribution to $T_1$. This is not the case for any of the transition-metal nuclei when $^1$H is the dipolar nucleus. In the case of elements, such as ruthenium, containing both quadrupolar ($^{99}$Ru and $^{101}$Ru, $I = {}^5/_2$, abundance 35.3%) and dipolar or $I = 0$ nuclei ($^{98}$Ru, $^{100}$Ru, $^{102}$Ru, and $^{104}$Ru, $I = 0$, abundance 64.7%), each with significant abundances, the observed relaxation of the nuclear magnetization should not be described by a single rate constant if scalar relaxation of the second kind were significant. This effect is not observed in any of the cases we have studied. Even if seen, however, nonexponential decay of the magnetization is not a criterion for scalar relaxation because fluxionality can also lead to similar nonsimple behavior.

Chemical shift anisotropy (CSA) is the least likely mechanism for protons because of the small $\Delta\sigma$ anisotropies involved, but it would immediately be detected if present because the $T_1$ values at different fields to the high-temperature side of the minimum should differ, since $T_{1\mathrm{CSA}}$ scales with the square of the spectrometer field strength. CSA relaxation is absent in the case of $ReH_7(PPh_3)_2$ because the $T_1$ is independent of field in the fast-motion regime.[2] The same observation also rules out SC relaxation, for which a field dependence is also expected.

**Details for Individual Complexes.** We now look in detail at the results from some of the hydrides studied. $[FeH_2(H_2)(PEtPh_2)_3]$ (**1**) is an important example because, thanks to the neutron diffraction data of Koetzle, Caulton, et al.,[11] **1** is now known to have a nonclassical structure in the solid state; we had earlier suggested that this was the solution structure on $T_1$ grounds. Unfortunately, a minimum was not obtained in the $T_1$ study, but the value at the lowest temperature is only slightly longer than the range calculated.

The calculation also allows us to dissect the averaged $T_1$ into its components. For example, between 95 and 98.6% of the relaxation for the averaged hydride resonance comes from the DD contribution of the H···H of the dihydrogen ligand ($r$ = 0.82 Å). The higher figure applies to the fast-rotation situation; the lower, to a nonrotating $H_2$.

For $ReH_7$(dppe) (**2**), both the neutron diffraction structure[12] and the $T_1$(min) are known. In addition, isotope shift[13] data have been obtained. The agreement between the calculated and observed $T_1$(min) values, 77 and 67 ms, respectively, is satisfactory: theory accounts for 87% of the observed relaxation. Different hydride positions in the molecule show large differences in calculated relaxation rate. The most rapidly relaxing proton is H(1), with a calculated relaxation rate of 20.36 s$^{-1}$. The most slowly relaxing protons, H(2) and H(2a), have a $T_1$(min, calc) of 115 ms. The H···H vectors of <2 Å contribute most of the DD relaxation in this structure.

**2** was originally but wrongly assigned a nonclassical structure by Hamilton and Crabtree[2] from the relatively short $T_1$. We now see that this short $T_1$ arises from the cumulation of relatively short nonbonding contacts. At the time they made their suggestion, the only model that existed was the pure tricapped trigonal prism (TTP) of $[ReH_9]^{2-}$,[14] from which calculated $T_1$(min) values of 94 and 107 ms are obtained for $ReH_7L_2$, depending on whether the two phosphines are assigned equatorial or eclipsing axial sites (the latter now turns out to be the better description for **2**). The difference between the $T_1$(min) calculated on the pure TTP model and that calculated for the crystal structure is a result of the distortion of the real H positions from those of a pure TTP structure, presumably as a result of the steric size of the phosphorus atoms.

The DD equations applied to the X-ray structural data of Cotton and Luck[5e] for $ReH_5(PPh_3)_3$ give excellent agreement with the $T_1$(min) observed by the same authors. A neutron diffraction study of the $PMePh_2$ analogue, also classical, is available.[15] This leads to a calculated $T_1$(min) only slightly longer than that from the X-ray data for the $PPh_3$ complex. A feature of interest in

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the neutron work is that two independent molecules of the pentahydride are present in the crystal. Even though each has different H···H distances, carrying out the calculation on both forms leads to essentially identical $T_1$(min) values of 156 and 157 ms, giving us confidence in the approach.

The structure of $WH_6(PMe_2Ph)_3$ (**3**), determined by neutron diffraction,[16] is TTP with two phosphines at eclipsing axial sites and the third at the nonadjacent equatorial site. There are only two H···H vectors <2 Å, and the averaged relaxation is only 4.95 $s^{-1}$, corresponding to a $T_1$(min) of 201 ms at 250 MHz. The observed value of 181 ms indicates a relaxation rate 12% faster than the calculated rate. This is the largest disparity that we have found for any mononuclear polyhydride studied. Even so, the extra relaxation rate is only 0.57 $s^{-1}$.

$[CpIr(PMe_3)H_3]^+$ has also been studied by neutron diffraction.[17] The $T_1$(min, calc) is 189 ms at 250 mHz,[17c] but the small moment of inertia means that the molecule is far from the $T_1$ minimum at the lowest accessible temperatures; the heavier $PPh_3$ and $AsPh_3$ derivatives, however, show $T_1$'s of 200 and 210 ms at 193 K,[17c] which must be near the minimum.

Calculations are less easy for the $H_2$ complexes because of the uncertainty in the $H_2$ rotation rate and therefore in the value of $C$. Morris et al.[3b] consider fast rotation to be more probable, and if we take $C = 0.79$, we see good agreement between the calculated and observed $T_1$ values. For $[IrH(H_2)bq(PPh_3)_2]^+$, the H···H distance has been determined by Zilm[18] using solid-state NMR spectroscopy. This is probably a better method for determining $r$(H–H) than n-diffraction. The $T_1$(min) for the $H_2$ ligand falls in the middle of the range calculated, confirming the approach.

**Further Sources of Relaxation.** Thermal excursions from the equilibrium positions of the hydrides in a polyhydride will cause some H···H vectors to lengthen and others to decrease in length, but the net result will be to shorten $T_1$(obs). The reason is that we are averaging $r^{-6}$, and so the increase in relaxation due to the shorter distances outweighs the decrease due to those that are longer. We use a simple quantitative model to examine this question. Consider a linear array of three protons $H_a$–$H_c$ with $H_b$, the central H, flanked by two other hydrogens at a distance, $r$(H–H), of 2 Å. The central H, $H_b$, will experience relaxation due to $H_a$ and $H_c$. The $T_1$(min) for $H_b$ corresponding to this static situation is 204 ms. If $H_b$ is allowed to oscillate in a sinusoidal way about the equilibrium position, the change in the relaxation can be calculated. For simplicity we take the case in which only $H_b$ moves, and we consider the motion as having sinusoidal components along the $H_a$–$H_c$ vector. If the amplitude of the oscillation is only ±0.1 Å, then the relaxation rate only increases 2.6% (i.e., the new value of $T_1$(min) is 198 ms). If the amplitude is set at ±0.2 Å, then the relaxation increases by a substantial 11.1%, leading to a $T_1$(min) of 181 ms for $H_b$. We conclude that thermal excursions of ±0.2 Å are sufficient to account for $T_1$(obs) exceeding $T_1$(calc) by about 10% in the way observed for **2** and related polyhydrides.

Another source of extra DD relaxation, the presence of $^{31}P$ nuclei close to the hydride protons, can also be calculated. In the case of **2**, the additional relaxation is 0.394 $s^{-1}$, which is only 0.4% of the calculated H···H relaxation. For **3**, where the H···H contributions are smaller and there are three phosphorus nuclei, the P···H relaxation is 0.792 $s^{-1}$, or 2.6% of the calculated H···H relaxation; this is not significant.

Ligand protons will also contribute; Morris has shown by using perdeuterated phosphines that this effect is small for nonclassical protons but could contribute for classical hydrides. The DD relaxation effects due to the solvent should be small because perdeuterated solvents were used.

**Table II.** Values of $r$(H–H) in Å as a Function of $T_1$(min) at 250 MHz for $C = 1$ and 0.79

| $T_1$(min), ms | $r(C = 0.79)$ | $r(C = 1)$ | $T_1$(min), ms | $r(C = 0.79)$ | $r(C = 1)$ |
|---|---|---|---|---|---|
| 5 | 0.76 | 0.96 | 75 | 1.19 | 1.51 |
| 10 | 0.85 | 1.08 | 100 | 1.25 | 1.58 |
| 15 | 0.91 | 1.15 | 150 | 1.34 | 1.69 |
| 20 | 0.96 | 1.21 | 200 | 1.40 | 1.78 |
| 25 | 0.99 | 1.26 | 500 | 1.63 | 2.07 |
| 30 | 1.02 | 1.29 | 750 | 1.75 | 2.21 |
| 35 | 1.05 | 1.33 | 1000 | 1.83 | 2.32 |
| 50 | 1.11 | 1.41 | | | |

**Table III.** $T_1$ Averaging in Fluxional Polyhydrides[a]

| | | $T_1$ | | |
|---|---|---|---|---|
| $n_c/n_{nc}$ | type | 50[b] | 100[b] | 200[b] |
| | For $r$(H–H) = 0.82 Å | | | |
| 0 | $M(H_2)$ | 7.7 | 7.7 | 7.7 |
| 0.5 | $MH(H_2)$ | 10.7 | 11.1 | 11.3 |
| 1.0 | $MH_2(H_2)$ | 13.3 | 14.3 | 14.8 |
| 2.0 | $MH_4(H_2)$ | 17.7 | 20.0 | 21.4 |
| | For $r$(H–H) = 0.92 Å | | | |
| 0 | $M(H_2)$ | 15.4 | 15.4 | 15.4 |
| 0.5 | $MH(H_2)$ | 20.1 | 21.5 | 22.3 |
| 1.0 | $MH_2(H_2)$ | 23.6 | 26.7 | 28.7 |
| 2.0 | $MH_4(H_2)$ | 28.6 | 35.4 | 40.1 |

[a] The figures are $T_1$(min, av) in ms and assume free rotation about the M–$H_2$ bond. [b] The $T_1$(min, c) value assumed for the relaxation of the classical sites.

**Accuracy of the Data.** The agreement between calculated and experimental $T_1$(min) values might seem to be *too* good. Errors in experimental $T_1$ determinations are often quoted to be 10–20%. It is therefore important to emphasize that we believe we have better accuracy from cutting and weighing the spectra than by allowing the spectrometer's computer to process the data. Unconscious bias is avoided by plotting the data only after completing the cutting and weighing. In addition, when a variable-temperature study is carried out, the accuracy of the measurements can be assessed by looking at how closely the data points fit the linear part of the ln $T_1$ vs temperature curve in the high-temperature regime. Our accuracy appears to be at least ±5% in such cases.

**Implications for Analysis of $T_1$ Data.** For a complex $L_nM(\eta^2\text{-}H_2)$, $T_1$(min) is dominated by the short H···H distance of the $H_2$ ligand. Table II lists some calculated relaxation times corresponding to H···H distances for fast and slow rotation. The H···H distances observed to date in $H_2$ complexes (0.82–0.92 Å) lead to ranges of $T_1$(min) of 2–4 ms (slow $H_2$ rotation) and 8–15.4 ms (fast $H_2$ rotation) at 250 MHz. These values are much shorter than any yet seen for a classical hydride, and so the interpretation is unambiguous. Longer H···H distances may well be found for $H_2$ complexes in the future, however.

For tri- and polyhydrides, either (i) the hydrides are fluxional at all accessible temperatures or (ii) fluxionality is slow at some accessible temperature. For the second group, the analysis is again relatively easy. The ratio of peak intensities gives the ratio of different types of hydride, and the $T_1$(min) data show which, if any, of the peaks corresponds to an $H_2$ ligand (e.g.,[7b] $[Re(H_2)H_2(CO)L_3]^+$).

For the more common fluxional tri- and polyhydrides (case i), the relaxation will be averaged over all the exchanging sites by eq 4.[2] In this case, the observed average will be higher than the

$$(n_c + n_{nc})/T_1(\text{min, av}) = n_c/T_1(\text{min, c}) + n_{nc}/T_1(\text{min, nc}) \tag{4}$$

(av = averaged; c = classical; nc = nonclassical;
n = no. of protons of a given type)

8–15.4-ms range cited above, even if $r$(H–H) is still in the range 0.82–0.92 Å. Even so, if $n_c/n_{nc}$ is not too large, the dilution effect will still produce a short average. In $FeH_2(H_2)(PEtPh_2)_3$ ($n_c/n_{nc}$

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= 1), we were still able to correctly assign the structure on the basis of the short (but nonminimum) $T_1$ of 24 ms. No classical hydride yet reported has been shown to have a $T_1$ this short at 250 MHz.

For high-coordinate (CN > 6) polyhydrides, the H⋯H contacts will be relatively short. In **2**, H(1) has four nearest neighbors with H⋯H distances of <1.8 Å. The overall relaxation rate is correspondingly high: 50 ms at 250 MHz for H(1) in **2**, for example. Table III shows calculated $T_1$(min, av) values for various ratios of $n_c/n_{nc}$, assuming that there is free rotation of $H_2$, that $r$(H–H) is 0.82 and 0.92 Å, and that $T_1$(min, c) is 50, 100, and 200 ms. All of these values are still shorter than any observed for classical hydrides.

This is only true if $r$(H–H) for $H_2$ complexes is always in the range observed for complexes studied to date. If substantially longer $H_2$ distances, e.g. 1.1 Å, prove to be possible, then the $T_1$(min) even for $L_nM(H_2)$ becomes 11 ms (no rotation) or 45 ms (free rotation). The observed $T_1$ now approaches the classical range, and the $T_1$ method cannot reliably detect the $H_2$.

**Dinuclear Complex.** In one dinuclear polyhydride, $Re_2H_4(\mu\text{-}H)_4(PEt_2Ph)_4$, both the neutron diffraction structure and the $T_1$ data are available.[19] The observed $T_1$(min) of 140 ms at 400 MHz is substantially shorter than predicted from the structure by the DD equations (302 ms). This interesting molecule clearly needs further study to identify the origin of the discrepancy. The $T_1$(min) does scale with field, as expected for the DD mechanism, however. The motion may be anisotropic, which invalidates eq 1.

## Conclusion

When we developed the $T_1$ method, we thought of it as purely qualitative, but the work of Morris et al.[3b] has encouraged us to carry out a quantitative study. We have now found that for a series of mononuclear polyhydrides for which both structural and relaxation data are available, there is good agreement between the calculated and observed $T_1$(min) values. This substantiates the two assumptions made in the calculations: that the solid-state structure is maintained in solution and that DD relaxation is dominant. We also look at the effect of thermal excursions of the hydrides from the equilibrium positions and DD relaxation from the $^{31}P$ nuclei of the ligands and show that these are relatively small. In one case, the observed relaxation is substantially faster than predicted, but further work is needed to understand the discrepancy.

## Experimental Section

The structural data were obtained from the original papers or directly from the crystallographers. We report below either the H⋯H distances calculated in the structural study or the crystal and positional data that we used to derive the required distances. In the case of **3**, we recalculated all the distances because there appear to be some minor errors in the derived data given. We also report the net relaxation rate ($s^{-1}$) calculated for 250 MHz. We did not artificially increase the M–H bond lengths obtained by X-ray methods to account for the difference between the centroids of the electron and nuclear density distributions because the observed M–H distances seemed reasonable and the appropriate adjustment is less well established for M–H than it is for C–H bonds.

$FeH_4(PEtPh_2)_3$: $a = 21.527$ Å; $b = 11.753$ Å; $c = 31.034$ Å; $\beta = 112.09°$; H(1) 0.7835, 0.9991, 0.6855; H(2) 0.8107, 0.9638, 0.6780; H(3) 0.8644, 0.0584, 0.6584; H(4) 0.7897, 0.1456, 0.6030 (data of Koetzle, Caulton, et al.[11]).

$[CpIr(PMe_3)H_3]^+$: H(1)⋯H(2) 1.67 Å; H(2)⋯H(3) 1.70 Å; H(1)⋯H(3) 2.66 Å (data of Koetzle, Heinekey, et al.[17]).

$ReH_7(dppe)$: $a = 17.262$ Å; $b = 11.408$ Å; $c = 17.609$ Å; $\beta = 107.79°$; H(1) 0, 0.128 89, 0.25; H(2) 0.054 21, 0.326 42, 0.192 12; H(3) −0.0203, 0.212 33, 0.160 05; H(4) −0.091 68, 0.211 07, 0.225 25; H(2a) −0.0203, 0.212 33, 0.307 88; H(3a) −0.0203, 0.212 33, 0.339 95; H(4a) 0.091 68, 0.211 07, 0.274 75 (data of Howard et al.[12]).

**Thermal Excursions.** We consider a linear system $H_a \cdots H_b \cdots H_c$, in which $H_b$ undergoes a sinusoidal oscillation and in which the equilibrium H⋯H distances are 2 Å. The relaxation of $H_b$ is studied. Only the H⋯H distances change during the vibration, and the relaxation rate depends upon $r^{-6}$, so we only need to evaluate the average of $r^{-6}$. If $H_b$ begins by moving toward $H_a$, then $H_a \cdots H_b$ decreases and $H_b \cdots H_c$ increases. The ratio $\rho$ of the averaged $T_1$(min) including thermal excursions to the $T_1$(min) for the static structure is therefore $\rho = [(2 - dr \sin \theta)^{-6} + (2 + dr \sin \theta)^{-6}]/2(2)^{-6}$. $\rho$ was evaluated every 10° from 0 to 90° and averaged over 90° by weighting the values at 0 and 90° by a factor of $^1/_2$. The amplitude of oscillation, d$r$, took the values 0.1 and 0.2 Å. The results are reported in the text.

**Phosphorus Proton Relaxation.** To account for P⋯H relaxation, we calculated the P⋯H distances, entered the value into the usual H⋯H equation, and multiplied the result by the required conversion factor, $2\gamma_P^2/3\gamma_H^2$ or 0.109.

**Note Added in Proof.** Wojcicki et al. (Kim, Y.; Deng, H.; Meek, D. W.; Wojcicki, A. *J. Am. Chem. Soc.* **1990**, *112*, 2798) have also found good agreement between calculated and observed $T_1$(min) values.

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