will have to await more detailed work on boron sulfide structures.

In conclusion, gas-phase boron oxide ions are formed by particle-induced desorption from condensed-phase (vitreous) boron trioxide by random B–O bond breaking at any site along the $(B_2O_3)_n$ network. The relative abundances of boron oxide ions are directly related to the relative stabilities of the desorbed ions. Relatively less stable boron oxide ions are more likely to undergo dissociation during the ca. 23×10^{-6} s flight time from ion source to detector (ZAB-2F mass spectrometer, ion of m/z 100, 8-kV accelerating voltage[39]). The relative stability of a desorbed boron oxide ion is also related to the ability of its structure to satisfy the +3 oxidation state of boron; there is no indication that boron exists in other than the +3 oxidation state in the boron oxide cations reported here. Accordingly, boron oxide structures incorporate integral BO_3 units and terminal –B═O units. Stability is enhanced by resonance forms and electron sharing that achieve delocalization of the charge on the cation.

Finally, it is important to note the structural differences between the new boron oxide cations reported here and the large (and growing) body of known, condensed-phase, borate anions.[40] Borate anions typically contain both three-coordinated BO_3 units and four-coordinated (tetrahedral) BO_4^- units in association with metal cations. The insular boron oxide cations, however, are unable to accommodate the negative charge and contain only three-coordinated BO_3 units and two-coordinated –B═O units.

Acknowledgment. The author expresses his gratitude to E.B.D.

Registry No. B_2O_3, 1303-86-2.

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An NMR Method for Distinguishing Classical from Nonclassical Structures in Transition-Metal Polyhydrides

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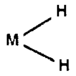
Abstract: A T_1 method is described for distinguishing classical hydrides with terminal M–H bonds from nonclassical hydrides with H–H as well as M–H bonds. The method can still be used even where the hydrides are fluxional as is the case for transition-metal polyhydrides. The temperature dependence of the T_1 shows a minimum for several cases studied. This allows the H–H distance in the H_2 ligand to be estimated and the structural type determined. $ReH_7(PPh_3)_2$ is shown to be nonclassical with the probable structure $Re(H_2)H_5(PPh_3)_2$. $[ReH_8PPh_3]^-$ is shown to be classical and $[ReH_9]^{2-}$ seems to be classical, however. Other hydrides shown to be nonclassical are $Re(H_2)H_5(dpe)$, $FeH_2(H_2)L_3$, $RuH_2(H_2)L_3$, and $[Os(H_2)H_3(PPh_3)_3]^+$; the Re examples are the first d^2 and the Os example the first d^4 dihydrogen complex. Complexes shown to be classical are the following: $IrH_5(PCy_3)_2$, $ReH_5(PPh_3)_3$, $OsH_4(P\{p\text{-tolyl}\}_3)_3$ $MoH_4(PMePh_2)_4$, and, more surprisingly, $[WH_5(PMePh_2)_4]^+$, $H_2Fe(CO)_4$, $[IrH_2(CO)_2(PPh_3)_2]^+$, and $WH_6(PMe_2Ph)_3$. Typical distance estimates (r_{eff}) obtained are the following: $[IrH(H_2)(bq)(PPh_3)_2]^+$, 1.04$C$ Å; $ReH_5(H_2)(PPh_3)_2$, 1.20C Å; $ReH_5(H_2)(dpe)$, 1.25C Å; $MoH_4(PMePh_2)_4$, 1.72C Å, where C is a calibration constant (as yet undetermined but ~0.9). The ordering of the r_{eff} values observed seems to parallel the relative lability order of the complexes studied, the more labile species being associated with shorter r_{eff} values.

We describe in detail a T_1 method for determining whether a given transition-metal hydride has a classical structure, with all terminal M–H bonds (**1**) or a nonclassical structure, with one or more H–H bonds. An example of such a structure is dihydrogen complex **2**. In 1984 Kubas et al.[1] first showed that structures



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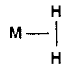

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of type **2** could exist. Since that time several other examples have been discovered both by ourselves[2] and by others.[3] Kubas et al.[1] used neutron diffraction, IR, and the $^1J(H,D)$ in the ^1H NMR spectrum of the HD complex to characterize their complex. Morris[3a,f] has used IR, NMR, and X-ray methods. Neutron diffraction is more reliable than X-ray but requires large crystals. IR data can be unreliable because the $\nu(MH_2)$ absorption is often too weak to be seen. $^1J(H,D)$ can only be observed if fluxionality does not interfere. It is precisely for the most interesting group of candidate structures, metal polyhydrides,[4] that rapid fluxionality is most common.

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We developed the T_1 NMR method, described below, in response to the problem[2b] of characterizing $[IrH_2(H_2)_2(PCy_3)_2]^+$ (Cy = cyclohexyl). This complex gives no useful IR bands and is too fluxional to allow determination of ^1J(H,D). These findings led us to speculate that well-known polyhydrides might also have nonclassical structures in which H_2 or even H_3 or H_4 ligands might be present. We now report the full details of the T_1 method including variable-temperature studies, which allow the H–H distance in the dihydrogen ligand to be estimated and a distinction made between classical and nonclassical structures.

Results and Discussion

The T_1 of any resonance can be measured by a standard inversion–recovery pulse sequence (180°–t–90°). This reveals how rapidly the inverted spins recover their equilibrium magnetization along the direction of the applied magnetic field. The dipole–dipole mechanism is usually the major contributor to this relaxation for protons less than 2 Å apart.[5] By this mechanism a given dipolar nucleus, say a proton, is relaxed by other nearby dipolar nuclei. As the molecule rotates under the influence of collisions with the solvent molecules (Brownian motion), the magnetic field felt by the first proton fluctuates as the direction of the internuclear vector changes with respect to the applied field direction. If the fluctuations happen to include components at the Larmor frequency, then a transition may occur. This has the effect of dispersing the excess energy of the inverted spins to the thermal sink of the solvent, and so reestablishing the normal thermal spin equilibrium which was originally present before the 180° inversion pulse was applied. Relaxation by this mechanism becomes more efficient with the inverse sixth power of the distance, r, between the dipolar nuclei and the fourth power of γ.[5]

The H–H distance in H_2 being the shortest in chemistry, and γ_H being one of the largest known, the corresponding relaxation rate is potentially very large, and essentially the whole of the relaxation may arise from the dipole–dipole mechanism. The equation governing the rate of relaxation R(DD) for the homonuclear proton case is shown in eq 1.[5] The characteristic relaxation time, T_1(DD), is simply the inverse of R(DD) and is of the order of a second for simple organic molecules or classical metal hydrides in solution. For dihydrogen complexes, on the other hand, we find that the observed T_1 often lies in the range of 4–100 ms.

$$R(\mathrm{DD}) = \{T_1(\mathrm{DD})\}^{-1} = 0.3\gamma^4\hbar^2 r^{-6}\{\tau_c/(1+\omega^2\tau_c^2) + 4\tau_c/(1+4\omega^2\tau_c^2)\} \quad (1)$$

(γ = gyromagnetic ratio, $\hbar$ = Planck's constant/2π,
r = internuclear distance,
τ_c = rotational correlation time (s/rad),
ω = Larmor frequency (rad/s))

The simplest way of applying this method is to measure T_1 for a given hydride in solution and to compare the value with those found for a range of hydrides having known T_1 values (see Table I). Since the T_1 depends on τ_c and therefore on temperature, a suitable temperature must be chosen; −80 °C was used for the earliest work.[2] A nonclassical structure should have one or more H–H distances of 0.8–1.2 Å as opposed to a classical hydride which would have only nonbonded H···H distances of at least 1.5 Å, if not more. The relaxation rates in the two cases should differ by several orders of magnitude. This analysis ignores the influence of τ_c on the observed T_1. This omission is not too serious if we restrict ourselves to the study of molecules of similar moments of inertia in solvents of similar viscosity, but we will return to this problem later.

Our attention was drawn to the group 8 tetrahydrides, MH_4L_3, by Dr. G. Hlatky of Exxon Corp. These species show a number of features, which suggested that further study might be useful.

Table I. The T_1 Values for Some Hydrides

complex[g]	T_1[a]	T_1(n)[b]	conditions
H_2	1600		toluene-d_8, 203 K
$IrH_5(PCy_3)_2$	820		CD_2Cl_2, 193 K
$[IrH_2(H_2)_2(PCy_3)_2]^+$	48[c], 76[d]	37	CD_2Cl_2, 193 K
$IrH(H_2)(bq)(PPh_3)_2]^+$	30[c], 390[d]	30	CD_2Cl_2, 193 K
$Fe(H_2)H_2(PEtPh_2)_3$	24	12	toluene-d_8, 203 K
$Ru(H_2)H_2(PPh_3)_3$	38	20	toluene-d_8, 203 K
$OsH_4\{P(p\text{-tolyl})_3\}_3$	820		toluene-d_8, 203 K
$ReH_5(H_2)(PPh_3)_2$	79[e]	25	toluene-d_8, 203 K
$ReH_5(H_2)(dpe)$	78[e]	25	CD_2Cl_2, 203 K
$ReH_5(H_2)(PPh_3)_2$	110	33	CD_2Cl_2, 203 K
$ReH_5(PPh_3)_3$	540		toluene-d_8, 203 K
Cp^*ReH_6	290 (ax) 618 (eq)		toluene-d_8, 203 K
$MoH_4(PMePh_2)_4$	485		toluene-d_8, 203 K
$[WH_5(PMePh_2)_4]^+$	205[f]		CD_2Cl_2, 203 K
$WH_6(PMe_2Ph)_3$	166[f]		toluene-d_8, 203 K
$H_2Fe(CO)_4$	3000		toluene-d_8, 203 K
ReH_9^{2-}	2500		methanol-d_4, 205 K
$WH_4(PMe_2Ph)_4$	524		toluene-d_8, 203 K

[a] By inversion/recovery ±10% in ms. [b] Calculated as shown in the text (eq 5) based on the formulation shown. [c] For the nonclasical hydrides. [d] For the classical hydrides. [e] Unpublished neutron diffraction data[31] are interpreted in terms of a disordered but classical structure for the $PPrPh_2$ complex. Since the least soluble tautomer will crystallize, this result does not tell us what structure is adopted in solution. [f] Intermediate values not interpretable in terms of a structure (but see Table II). [g] bq = 7,8-benzoquinolinate; dpe = $Ph_2PCH_2CH_2PPh_2$; Cy = C_6H_{11}. For references, see Experimental Section.

The Fe and Ru complexes readily undergo substitution with loss of H_2, but the Os complex does not. The broad ^{1}H NMR resonance of the Ru complex had previously been attributed to reversible H_2 loss. On the other hand, Ashworth and Singleton[6] speculated as early as 1976 that the complex "might be effectively considered as a Ru(II) complex containing neutral dihydrogen".

Aresta et al.[7] made the iron complex (L = PEt_2Ph, **3**) in 1971. The molecule shows a hydridic ^{1}H NMR resonance at δ −11.5 with ^2J(P,H) of 27 Hz. We have now measured the T_1 of this resonance (toluene-d_8, 205 K). The resulting value, 24 ms, indicates a nonclassical structure. This assignment provides an explanation for the IR band at 2380–2400 cm^{-1} noted by Aresta et al. for **3**. This band is not present in the spectrum of the corresponding 16e dihydride $FeH_2(PR_3)_3$, nor of $FeH_2(N_2)(PR_3)_3$. IR bands in the range 2300–2700 cm^{-1} have been found in a number of dihydrogen complexes and assigned to $\nu(MH_2)$.[1,5b]

The hydride resonance for **3** broadens on cooling and this is probably due to a very short T_2 in the slow-motion regime (see below). Terminal Fe–H stretching bands at 1860–1922 cm^{-1} are observed in the IR, suggesting the structure $FeH_2(H_2)(PR_3)_3$ rather than $Fe(H_2)_2(PR_3)_3$. Only two hydrogens are substituted by N_2 to give $FeH_2(N_2)(PR_3)_3$, which is a classical dihydride by IR and NMR. The structure $FeH(H_3)(PR_3)_3$ cannot be eliminated.[3i,j]

$RuH_4(PPh_3)_3$ (**4**)[8] is a particularly important and extensively studied polyhydride which has useful catalytic properties.[8a] It has a broad Ru–H resonance at δ −7.06 (toluene-d_8, 25 °C). The previous attribution of the broadening to reversible dissociation of H_2 is not entirely convincing because the line width should vary as the partial pressure of H_2 is changed. On the other hand no $\nu(MH_2)$ is observed in the IR spectrum, only ν(Ru–H) at 1942 cm^{-1}. We have now measured the T_1 for **4** (toluene-d_8, 205 K) and find a value of 38 ms, entirely consistent with a nonclassical structure. The formulation $RuH_2(H_2)(PPh_3)_3$ is preferred on the same grounds as discussed for **3**.

$OsH_4(PPh_3)_3$ was too insoluble to be studied by our method but the o-tolylphosphine analogue **5** gives a value of 820 ms

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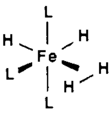
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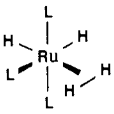
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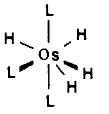
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(toluene-d_8, 205 K), indicating a classical structure.

The difference in structure between the 1st and 2nd row hydrides on the one hand and the 3rd row hydride on the other raises the questions as to what factors control the relative stability of the classical and nonclassical forms. The bonding scheme[9] we favor is shown in Figure 1. The $H_2(\sigma)$ bonding electrons are donated to an empty metal (d_σ) orbital and the $M(d_\pi)$ electrons engage in back donation to the $H_2(\sigma^*)$. While the $H_2(\sigma)$ to $M(d_\sigma)$ electron donation weakens the H–H bond, it probably does not break it, since the resulting 2e, 3-center orbital is bonding over all three centers. The back donation populates the σ^* orbital of the H_2 molecule and so can break the H–H bond if the back bonding is sufficiently strong. Since the sites that bind H_2 in **3** and **4** also bind N_2, a ligand which requires a significant degree of back donation, we imagine that there is also significant back donation to H_2 in **3** and **4**. On this picture, **5** is classical because Os is a better π-donor than Fe or Ru. Another way of looking at the question is to say that most of the H–H bond energy is retained in **2** but is completely lost in **1**. The M–H bonds formed


2 1 (2)

have to be stable enough to drive the equilibrium of eq 2 to the right. First and second row M–H bonds are probably less strong than those in the third row.

The same method was applied to a number of other hydrides (Table I), and although clear-cut structural distinctions could be made in many cases, doubt remained in others[3g] because T_1 values were found which are intermediate between the 4–100 ms usually observed for nonclassical species and values >350 ms found for some classical hydrides.

In particular $ReH_7(PPh_3)_2$ gives a T_1 of 78 ms at 205 K in toluene-d_8. This is at the high end of the range for nonclassical complexes. The values for $[WH_5(PMePh_2)_4]^+$ and $WH_6(PMe_2Ph)_3$ of 205 ms (CD_2Cl_2, 205K) and 166 ms (toluene-d_8, 205 K), respectively, are so high that they might seem to constitute an intermediate group.

The method as described above relies on τ_c, the rotational correlation time, being comparable for all the molecules studied. This in turn requires the moments of inertia of the complexes studied, and the viscosities of the solvents used, to be comparable. The group 8 tetrahydrides chosen for the experiments described above do indeed have comparable moments of inertia and therefore comparable T_1's, and all measurements were carried out in the same solvent, toluene-d_8. A tris triphenylphosphine complex such as $MH_4(PPh_3)_3$ is not expected to have a moment of inertia comparable with a bis PPh_3 complex such as $ReH_7(PPh_3)_2$ or a tetrakis phosphine complex such as $MoH_4(PMe_2Ph)_4$. To take the extreme example of a molecule with a low moment of inertia, we find that the T_1 for free H_2 in toluene solution at −80 °C and 250 MHz is 1600 ms. The reason for the long T_1 is the rapid rotation of the H_2 molecule. In the case of H_2 the magnetic field fluctuations felt by each proton during the molecular rotation tend to be more rapid than the Larmor frequency, and relaxation is inefficient. [The long T_1 for free H_2 also rules out rapid exchange with free H_2 as the source of the short T_1 values observed for nonclassical hydrides.]

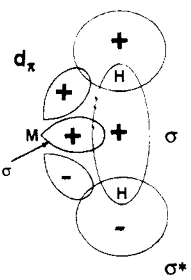

Figure 1. The bonding picture shown here[9] shows how H_2 resembles other π-acid ligands, such as CO, but the acceptor orbital on the ligand has σ^*, rather than π^*, character. Electron donation from $H_2(\sigma)$ into $M(d_\sigma)$ weakens but does not break the H–H bond, because the resulting 3-center bond has bonding character over all three nuclei. Since H_2 does not bind significantly to pure Lewis acids, some back-donation from $M(d_\pi)$ into $H_2(\sigma^*)$ may be required for stability; too much back-donation, however, is expected to break the H–H bond by filling the antibonding orbital, and a classical hydride will result. Weakly π-basic metals are therefore expected to be most suited for forming dihydrogen complexes.

Table II. Variable-Temperature T_1 Data

compound^{a,w}	temp (K)^b	T_1 (min)^c	r (Å)^d	r (Å)	structure^e
$CpRu(PPh_3)_2H^f$	238	300	$1.90C$		c
$[IrH_2(CO)_2(PPh_3)_2]^{+g}$	210	245	$1.81C$		c
$IrH_5(PCy_3)_2$	<193	<820	$<2.22C$		c
$ReH_5(H_2)(PPh_3)_2{}^h$	200^i	110^j	$1.20C$		nc
$ReH_5(H_2)(dpe)$	222	67	$1.25C$		nc
$ReH_5(H_2)\{P(p\text{-}C_6H_4F)_3\}_2{}^k$	200	55	$1.20C$		nc
$ReH_5(H_2)(PCy_3)_2$	<200	<60	$<1.22C$		nc
$[ReH_8(PPh_3)]^{-l}$	200	245	$1.83C$		c
$Ru(H_2)H_2(PPh_3)_3$	266	30	$1.16C$		nc
$[Os(H_2)H_3(PPh_3)_3]^{+m}$	220	35	$1.16C$		nc
$MoH_4(PMePh_2)_4$	250	165	$1.72C$		c
$WH_6(PMe_2Ph)_3$	235	181	$1.74C$		c
$WH_5(PMePh_2)_4{}^+$	240	179	$1.74C$		c
$W(H_2)(CO)_3(P\text{-}i\text{-}Pr_3)_2{}^n$	193	<5^p	$<0.96C$	0.84^q	nc
$[FeH(H_2)(dppe)_2]^{+r}$	210	<8.5^{s,t}	$<1.05C$	0.89^u	nc
$[IrH(H_2)(bq)(PPh_3)_2]^+$	200	8^t	$1.04C$	0.92^v	nc

[a] Solvents as in Table I and at 250 MHz. Unless stated. [b] Of the turning point. [c] At the turning point. [d] ±0.02 Å, calculated as described in the text. C is a calibration constant to be determined but which seems to be ca. 0.9 for nonclassical and 1 for classical hydrides (see text). [e] Classical, c; nonclassical, nc. [f] In toluene-d_8. [g] In CD_2Cl_2. [h] In toluene-d_8. [i] At 500 MHz. [j] By eq 1, this value is equivalent to a T_1 (min) of 55 ms at 250 MHz. At the lowest temperature, the observed T_1 at 250 MHz was indeed 55 ms, and so we were very close to the minimum. [k] In toluene-d_8. [l] In ethanol-d_6. [m] In CD_2Cl_2. [n] In toluene-d_8. [p] From ref 1; original measurement at 200 MHz, but T_1 value shown here calculated for 250 MHz. [q] By neutron diffraction.[1] [r] In CD_2Cl_2. [s] From ref 3f; original measurement at 200 MHz, but T_1 value shown here calculated for 250 MHz. [t] Of the dihydrogen resonance. [u] By X-ray diffraction.[3] [v] By solid-state NMR.[15b] [w] Abbreviations as in Table I.

Observations made on molecules having different moments of inertia and in different solvents are therefore not comparable. The key to making the T_1 criterion quantitative is the study of its temperature dependence. Equation 1 predicts that the T_1 will go through a minimum when the Brownian motion (measured by a rotational correlation time, τ_c) is best matched with the Larmor frequency, ω. By differentiation of eq 1, this should happen when

$$\tau_c = 0.63/2\pi\nu \qquad (3)$$

and so if we can observe the T_1 minimum experimentally we will know τ_c at that temperature, and therefore, as described in more detail in a later section, we can estimate an effective H–H distance, r_{eff}, assuming all the observed relaxation can be ascribed to dipole–dipole interaction with the second proton of the H_2 ligand. Ferrar and Quinting[10] used very similar arguments to estimate r(Mn–H) in $HMn(CO)_5$. They also estimated the rate of re-

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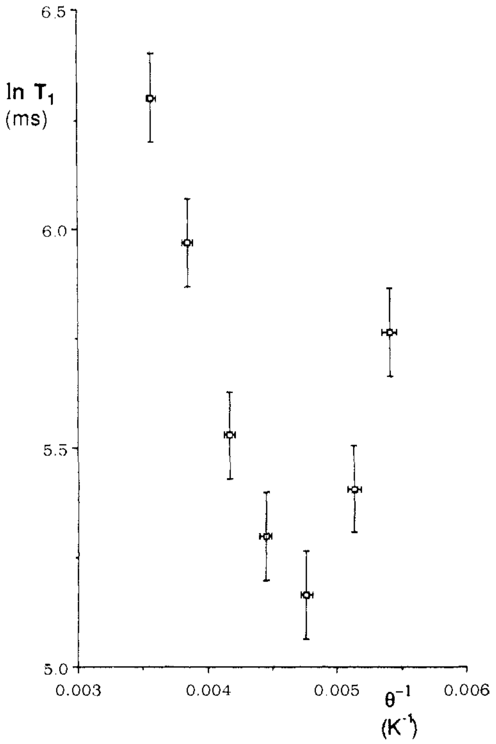

Figure 2. This plot of ln T_1 versus inverse temperature for $[WH_6(PMe_2Ph)_3]$ in toluene-d_8 shows the sharp T_1 minimum found on varying the temperature of the sample.

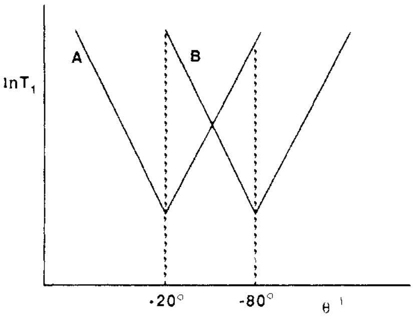

Figure 3. Two complexes A and B might have exactly the same H–H distance yet show very different T_1 values if measurements are only obtained at one temperature. For example, in the case shown above, A might appear to be classical at −80 °C but nonclassical at −20 °C.

laxation due to solvent deuterons to be ca. 0.076 s^{-1} in 5% CD_2Cl_2: 95% thf-d_8; a contribution of this magnitude is negligable in our case in view of the very short T_1's observed for the nonclassical hydrides. Solubility limitations prevented us from measuring the rate of relaxation due to the solvent deuterons in our cases.

We had already obtained an indication that $[Ir(H_2)H(bq)(PPh_3)_2]^+$ is in the slow motion regime ($2\pi\nu\tau_c < 1$) at 205 K and 500 MHz.[2c] We have now verified this postulate experimentally for this and a number of other hydrides.

The measurements are reported in Table II and a typical experimental curve is shown in Figure 2. As expected on the basis of eq 1, the T_1 value generally goes through a minimum, which we will call T_1(min), at a temperature θ(min). If this happens, then the observed values of T_1(min) should be comparable even for molecules of different moments of inertia, and so constitute a reliable structural criterion.

The table shows how the T_1(min) values observed for the hydrides studied fall into two groups which we identify as follows: classical hydrides, $T_1 > 150$ ms; nonclassical hydrides, $T_1 < 80$ ms.

Figure 3 shows schematically the behavior of two hypothetical nonclassical hydrides A and B having the same T_1(min) but θ(min) values of −20 °C (A) and −80 °C (B). A single T_1 measurement carried out at −80 °C would show B is nonclassical, but T_1 for species A would appear to be anomalously long. Conversely, at −20 °C, a short T_1 would be observed for A and a long T_1 for B. We therefore recommend that the T_1(min) be determined if possible when using the T_1 method. Failing that, the moment of inertia of the complex can be estimated by comparison with the complexes shown in the table (or otherwise), and then the appropriate temperature for measuring the T_1 can be estimated.

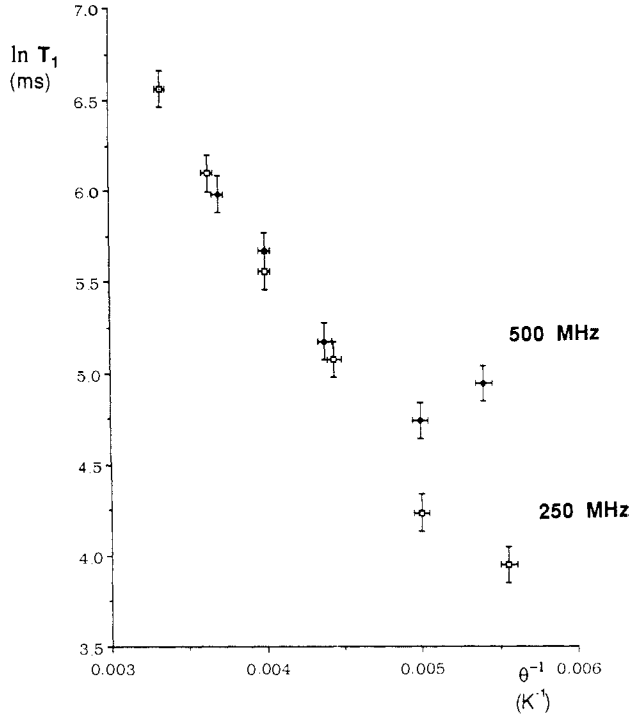

Figure 4. The two T_1 curves shown above were both obtained for $ReH_7(PPh_3)_2$, but at different magnetic fields: 250 and 500 MHz. Note how at high temperature the two data sets are essentially identical, confirming the reprodubility of our measurements (±3% in this case) and strengthening our proposal that dipole–dipole relaxation is the dominant mechanism. although at 250 MHz the minimum is not clearly defined, it is at 500 MHz.

The temperature of the minimum (θ(min)) in a given solvent is a measure of the moment of inertia of the complex under study. From eq 3, τ_c is 400 ps/rad at θ(min) at 250 MHz (200 ps/rad at 500 MHz).

By eq 1 the temperature of the minimum will be higher at higher field. Figure 4 shows the case of $ReH_7(PPh_3)_2$. This complex does not exhibit a minimum at 250 MHz down to 180 K where the solvent freezes. By running the experiment at 500 MHz the minimum is clearly defined. By eq 1, the T_1(min) value of 110 ms so obtained is equivalent to a T_1(min) of 55 ms at 250 MHz. Note the excellent agreement between the values obtained at the two fields in the fast-motion regime. This suggests that the dipole–dipole mechanism is indeed the main contributor to relaxation.

The Rhenium Polyhydrides

The rhenium polyhydrides ReH_7L_2, $[ReH_8L]^-$, and $[ReH_9]^{2-}$ are of very great interest. The heptahydride is an important catalyst for alkane conversions[11a] and the nonahydride was not only the first polyhydride but is one of the very few homoleptic hydrides known. The neutron structure of $[ReH_9]^{2-}$ dates from 1964 and shows a classical tricapped trigonal prismatic structure.[11b]

The data reported in the table suggest that $ReH_7(PPh_3)_2$ is nonclassical. Unfortunately the T_1 data do not distinguish between $ReH_5(H_2)L_2$ and $ReH_3(H_2)_2L_2$ or a trihydrogen structure $ReH_4(H_3)L_2$. We cannot be sure which formulation is correct but believe that $ReH_5(H_2)L_2$ is the most likely. In recent unpublished

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(11) (a) Baudry, D.; Ephritikine, D.; Felkin, H. *Chem. Commun.* **1982**, 606. (b) Abrahams, S. C.; Ginsberg, A. P.; Knox, K. *Inorg. Chem.* **1964**, *3*, 558.

data from our laboratory, we find that the bis(pyrazolyl)methane analogue shows two hydride NMR resonances of relative intensity 2:5 at 180 K in CD_2Cl_2, supporting the proposed formulation. A variety of ligands L′ displace H_2 from ReH_7L_2 to give ReH_5L_2L'. The T_1 of $ReH_5(PPh_3)_3$ at 200 K is 540 ms, an unambiguously classical value.

$$ReH_5(H_2)L_2 \xrightarrow{L'} ReH_5(L')L_2 \qquad (4)$$

Moving to $ReH_7\{(p\text{-}C_6H_4F)_3P\}_2$ leads to an increase in the moment of inertia of the complex so that the minimum can now be observed at 200 K without going to 500 MHz. The net electronic effect of the *p*-fluoro group is very small because the electron-withdrawing inductive effect is almost exactly balanced by the electron-releasing mesomeric effect. The Tolman electronic parameters of PPh_3 and $P(p\text{-}C_6H_4F)_3$ are very similar (2069 and 2071 cm^{-1}, respectively). Accordingly, the T_1 observed, 55 ms, is exactly what would have been expected for $ReH_7(PPh_3)_2$ had it been possible to reach θ(min) at 250 MHz. On the other hand, the complex ReH_7(dpe) is noticeably more stable toward loss of H_2 than the PPh_3 analogue. This could be due to the electron-releasing character of dpe relative to PPh_3; $M(d_\pi)$ to $H_2(\sigma^*)$ back donation should be more important in ReH_7(dpe) and so the H–H distance if the H_2 ligand would be expected to rise. Alternatively, the change in stereochemistry on moving to the chelating ligand might force the H_2 to occupy a more π-basic site at the metal. The T_1(min) for the ReH_7(dpe) is 67 ms. This difference, although small, may be significant, since it is reasonable to suppose that the H- -H distance is longer in the dpe compound than in $ReH_7(PPh_3)_2$ and $ReH_7(P\{p\text{-}C_6H_4F\}_3)_2$, because of the greater lability of the H_2 in the complexes containing monodentate phosphines.

ReH_7(dpe) is soluble in ethanol, a solvent that is more viscous than toluene. Even though this Re complex should have a lower moment of inertia then the PPh_3 analogue, the use of the more viscous solvent more than makes up for this, and θ(min) is 222 K.

For $[ReH_8(PPh_3)]^-$, we were able to observe a T_1(min) of 245 ms at 200 K by using ethanol as solvent. This large increase in T_1(min) compared to the ReH_7L_2 species is consistent with a structural changeover to the classical form. The reason for this change seems to be the presence of the net negative charge on the complex. Replacing PPh_3 by H^- gives a more π-basic metal. The $H_2(\sigma^*)$ orbital is therefore filled by back bonding and the H–H bond is cleaved. By extrapolation, $[ReH_9]^{2-}$ should also be classical.

Although we were not able to observe a minimum for $[ReH_9]^{2-}$, the long T_1 (2500 ms at 205 K in methanol-d_4) suggests a classical structure. Since ReH_9^{2-} must have a substantially larger moment of inertia than H_2 and since the Re complex was studied in the more viscous solvent, the turning point (θ(min)) for ReH_9^{2-} must come at a considerably higher temperature than for H_2. If $[ReH_9]^{2-}$ were nonclassical it would therefore have to have a considerably shorter T_1 than H_2 at 205 K, given the similar slopes of the T_1–temperature curves which we observed even in different solvents. In fact, H_2 has a substantially lower T_1 (1600 ms) than $[ReH_9]^{2-}$ (2500 ms), and so a classical structure is strongly indicated. The classical structure determined by neutron diffraction in the solid is therefore probably the same as is adopted in solution. Solid-state studies are not definitive in this area, however. Kubas et al.[1] found that crystals of the dihydrogen complex $W(H_2)(CO)_3(PCy_3)_2$ form a solution which contained both the H_2 complex and its classical tautomer. Similarly Chinn and Heinekey[12a] find that $[CpRu(dmpe)(H_2)]^+$ crystallizes from a solution of this complex as its classical tautomer, which is a minor constituent of the equilibrium mixture in solution.

Herrmann and Okuda[12b] kindly sent us a sample of their unusual polyhydride, Cp^*ReH_6, formally obtained by replacing a hydride and two PPh_3 groups in $ReH_7(PPh_3)_2$ by the strongly electron-releasing Cp* group. The two hydride resonances observed for this species have an intensity ratio of 1:5, and so Herrmann and Okuda assigned a C_{5v} structure with a single axial and five equatorial hydrogens. We were unable to observe a turning point for this complex at 200 K owing to its low moment of inertia. The observed T_1 values at 200 K (axial, 290 ms; equatorial, 618 ms) are sufficient to characterize the complex as a classical polyhydride. Since there is only one axial hydride it must be classical, and the T_1 for the equatorial hydrides are substantially longer. The extra electron density at the metal compared to the case of $ReH_7(PPh_3)_2$ is therefore enough to give the classical structure.

For the axial H to be so efficiently relaxed relative to the equatorial H's, it is possible that the equatorial Re–H bonds are distorted so as to lower the H(ax)···H(eq) nonbonded distances. This would bring five H's within relatively close range of H(ax). If we assume that all the Re–H distances are the same, that the molecule has C_{5v} symmetry, and that the dipolar mechanism is operating with random molecular tumbling, then simple geometrical arguments (see supplementary data) suggest that the H(ax)–Re–H(eq) angle is 50°. This seems a rather small angle, and further structural studies would be valuable.

The Structure of Caulton's $[OsH_5L_3]^+$

Bruno, Huffman, and Caulton[12c] showed that $OsH_4(PMe_2Ph)_3$ is protonated by $HBF_4{\cdot}Et_2O$ in CD_2Cl_2 at low temperature to give $[OsH_5(PMe_2Ph)_3]^+$. The addition of base led to the quantitative regeneration of the tetrahydride. The pentahydride cation has a rather small $^2J(P,H)$ of 4 Hz. We studied the analogous PPh_3 complex, which is insoluble in CD_2Cl_2, and find that protonation takes place to give $[OsH_5(PPh_3)_3]^+$, which is very soluble in the medium. The turning point was observed in the ^1H NMR, and the T_1(min) of 35 ms leads to the conclusion that the structure is nonclassical. The most probable structure is $[Os(H_2)H_3(PPh_3)_3]^+$, and this choice leads to a reasonable value for *r* (1.16C Å, see below), but the octahedral structures $[Os(H_3)H_2(PPh_3)_3]^+$ and $[OsH(H_2)_2(PPh_3)_3]^+$ cannot be excluded.

d^n Configurations and Hydride Structures

Nearly all the known H_2 complexes are d^6; $ReH_5(H_2)L_2$ are the first d^2 examples and $[Os(H_2)H_3(PPh_3)_3]^+$ is the first d^4 example. d^0 species would only be expected to give labile H_2 complexes because of the lack of back donation. d^0 species may still form H_2 adducts as intermediates in such reactions as hydrogenolysis, but the H_2 is not expected to be strongly bound. Some d^{10} examples (e.g., $Ni(CO)_3(H_2)$) are known from matrix work only.[13] 16e, d^8 species tend to oxidatively add H_2 rather than form H_2 complexes, perhaps because the favorable octahedral d^6 state is achieved by oxidative addition. Nevertheless we thought it would be useful to examine a dihydride which would be d^8 if it were nonclassical. We chose $[IrH_2(CO)_2(PPh_3)_2]^+$[14] because H_2 loss is facile, and because the presence of both the electron-withdrawing CO ligands and a positive charge should limit back donation and encourage the formation of a dihydrogen adduct. Our observations, reported in Table II, show a T_1(min) of 245 ms, an unambiguously classical value.

We therefore suggest that the facility with which different d^n configurations form nonclassical hydrides is $d^6 > d^2, d^4, d^{10} > d^8, d^0$.

Group 6 Polyhydrides

$MoH_4(PMePh_2)_4$, $[WH_5(PMePh_2)_4]^+$, and $WH_6(PMe_2Ph)_3$ were each studied and gave T_1(min) values of 165, 179, and 181 ms, respectively. These values are consistent with classical structures. The θ(min) values of 235, 240, and 250 K show the high moments of inertia of these species.

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(12) (a) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865–7 and personal communication, 1987. (b) Herrmann, W. A.; Okuda, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1092–3. (c) Bruno, J. W.; Huffman, J. C.; Caulton, K. G. *J. Am. Chem. Soc.* **1984**, *106*, 1663–9.

(13) Sweaney, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374. Gadd, G. E.; Upmacis, R. K.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 2547. Ozin, G. A.; Garcia-Prieto, J. *J. Am. Chem. Soc.* **1986**, *108*, 2547.

(14) Church, M. J.; Mays, M. J., Simpson, R. N. F., Stefanini, F. P. *J. Chem. Soc. A* **1970**, 2909.

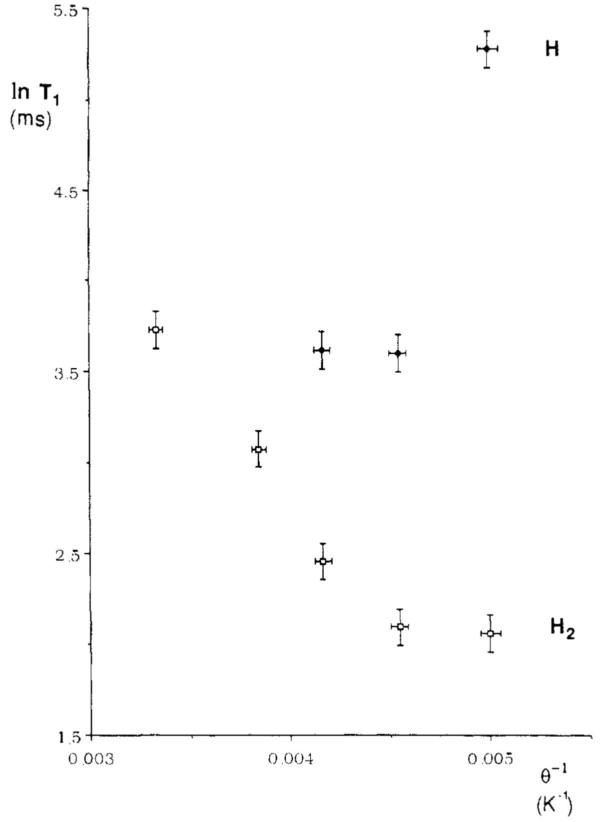

Figure 5. This plot shows the T_1 behavior of $[IrH(H_2)(bq)(PPh_3)_2]^+$ with temperature. On the high-temperature side, only one resonance is seen because of fluxionality. As we lower the temperature, the H and H_2 resonances can be distinguished. Although the H_2 site behaves as it should, the slowly relaxing H site shows nonstandard behavior. We ascribe this to exchange.

Fluxional Systems

$[IrH(H_2)(bq)L_2]^+$ (bq = 7,8-benzoquinolinate; L = PPh_3) undergoes exchange between the classical and nonclassical sites at a rate that leads to coalescence of the two resonances at 285 K. This system therefore provides a case in which we were able to study the effect of fluxionality on the T_1 values. The observed T_1 values (Figure 5) do not follow the usual V-shaped curve. This non-ideal behavior is a result of exchange. If the lifetime of the H nuclei at each site is comparable with the T_1's involved then the effective T_1 observed for, say, the classical proton signal will reflect not only the relaxation of the classical but also that of the nonclassical site. The T_1 of the single peak at the high-temperature limit is short because two of three sites are nonclassical. As we cool the sample, the T_1 decreases because we are approaching T_1(min). Below the coalescence temperature, the two broad signals have distinctly different T_1's, the classical signal having the longer T_1. As we cool further the classical signal goes through a broad minimum and then starts rising sharply. We interpret this to mean that on cooling the T_1 of the classical signal reflects a smaller and smaller contribution from the nonclassical protons and T_1 therefore lengthens dramatically. The T_1 for the nonclassical signal goes through a broad minimum. In this case cooling depresses the T_1 because of the lower and lower contribution of the classical proton to the observed T_1 of this resonance.

Effective H-H Distances

If we assume that τ_c at the minimum is $0.63/2\pi\nu$, we can in principle calculate an effective H-H distance, r_{eff} for any polyhydride from eq 1 if we know the value of T_1(min) for the classical site, which we will call T_1(c, min).

Our first problem is to establish the way in which the T_1 values average when the protons involved permute between n_c classical sites and n_n nonclassical sites (e.g., for $Re(H_2)H_5L_2$ $n_c = 5$ and $n_n = 2$). Since it is the rates of relaxation which average, and these rates are proportional to $\{T_1\}^{-1}$, we can write

$$(n_c + n_n)\{T_1(\text{obsd, min})\}^{-1} = n_c\{T_1(\text{c, min})\}^{-1} + n_n\{T_1(\text{n, min})\}^{-1} \quad (5)$$

Unfortunately we have several unknowns in this equation. The sum of n_c and n_n is known from the stoichiometry of the complex and n_c is chosen based on chemical and spectroscopic evidence as discussed above. T_1(c, min) is the T_1 to be assigned to the classical sites. If the exchange could be frozen out, T_1(c, min) could be measured directly, but this is not possible in the cases studied here. Since the values of T_1(c, min) that we observe for undoubtedly classical hydrides having two or more H ligands range from 165 to 245 ms, we have taken T_1(c, min) to be 200 ms for all the complexes studied. The T_1(n, min) obtained from eq 5 leads to an estimate of the H-H distance r from eq 1. The r values so obtained are systematically slightly longer than the ones found by other methods. This may be due to a failure in the assumption of isotropic rotation of the H_2 group used in the derivation of eq 1. As the data set of known H-H distances and observed T_1(min) increases it should be possible to calibrate the theoretical values with the observed values by adjustment of the calibration constant C. Only in the case of $Ir(H)(H_2)(bq)(PPh_3)_2^+$ have the r(H-H) (0.92 Å by solid-state NMR[15]) and T_1(min) (8 ms) been determined. This indicates that C may be in the region of 0.90. The low-temperature T_1 values reported for $W(H_2)(CO)_3(PR_3)_2$ (4 ms)[1] and $Fe(H_2)H(H_2)(dppe)_2^+$ (8.5 ms)[3f] lead to values of r (0.96C and 1.05C Å, respectively) which should be regarded as upper bounds on the true r(H-H). The most labile H_2 complexes should have the least amount of back bonding to the H_2 ligand and the shortest H-H distance. The rate of substitution reactions of the polyhydrides $RuH_4(PPh_3)_3 > ReH_7(PPh_3)_2 > ReH_7(dpe)$ is indeed the reverse of the order found for r_{eff} in these complexes by the T_1 method described above. This gives cause for optimism that differences in r_{eff} will prove to be real. A C value of 0.9 gives the best empirical fit with the data in Table II. Theoretical work by Morris et al.[3h] shows that when H_2 rotation around the M-H_2 bond is considered, C varies from 1.0 (no rotation) to 0.79 (fast rotation). If the rotation rate cannot be estimated,[3h] the use of the value $C = 0.9$ is expected to introduce an error of no more than 10%.

Since r_{eff} relies on our estimate of T_1(c, min) we looked at the sensitivity of the distance to a change in T_1(c, min). We find that for $RuH_2(H_2)L_3$, a change in T_1(c, min) of 10 ms alters r_{eff} by less than 0.001 Å. A change in T_1(obsd) of 10% leads to change in r of 0.018 Å, and we believe that this is an important source of error in the method; the calculated error is very close to ±0.02 Å for all the cases studied. A different choice of n_n and n_c has a larger effect on the result. For example, $n_n = 4$ and $n_c = 0$ leads to an increase of 0.1 Å in the r value in the ruthenium case. When we know more about what r_{eff} values to expect, it will probably be possible to rule out certain choices of n_n and n_c as giving unreasonable values of r_{eff}. There should also be a correlation of r_{eff} values with the ^1J(H,D) coupling constants, but of all the complexes we have studied, it is only for $[IrH(H_2)(bq)(PPh_3)_2]^+$ that both values are known (^1J(H,D) = 29.5 Hz, r_{eff} = 1.04C Å). Further minor approximations are involved; for example, the zero-point energy leads to a certain vibrational amplitude, so that the observed dipole-dipole coupling is an average value. Zilm et al.[15] have described an important new method of determining r(H--H) from the value of the dipole-dipole coupling determined by direct measurement in the solid-state NMR experiment. They point out that since T_1 depends on r^6, the averaging favors the shorter distances. r_{eff} is therefore expected to be shorter than the true internuclear distance, but their estimate of the error involved suggests it will be less than 0.01 Å.[15]

The presence of quadrupolar nuclei should not significantly affect the results. Although such nuclei can broaden the resonances of attached protons, this is normally a T_2 effect. In addition, only a fraction of the metal isotopes are quadrupolar and if these did have any effects on the T_1's, we would see nonexpo-

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[15] (a) Zilm, K. W.; Merrill, R. A.; Kummer, M. W.; Kubas, G. J. *J. Am. Chem. Soc.* **1986**, *108*, 7837. (b) Zilm, K. W., personal communication.

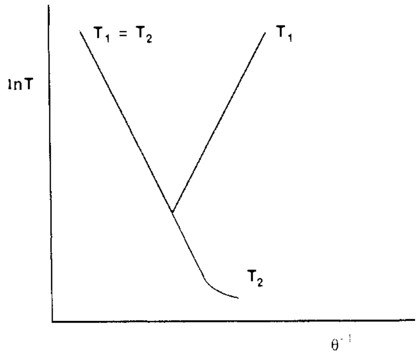

Figure 6. A schematic representation of the behavior of the T_2 (which governs the line width) with temperature. At high temperature, $T_1 = T_2$ is expected. Below the T_1 minimum, T_2 is expected to become much shorter and the line width is expected to increase.

nential behavior of the relaxation; this is not observed.

Other Effects of the T_1 Minimum and Anomalous Broadening

It was a surprise to us that the T_1(min) for these species occurs at such a relatively high temperature. Other than our own earlier paper,[2c] the literature gives no suggestion that unexceptional metal complexes, such as the ones we have studied, should have a θ(min) above −80 °C. In the so-called extreme narrowing regime above θ(min) T_1 should equal T_2 and line widths ($W_{1/2}$) should be limited by T_2 as given by

$$W_{1/2} = (\pi T_2)^{-1} \tag{6}$$

Below θ(min) T_2 becomes very much shorter than T_1 (Figure 6) and broad lines are often seen (slow motion regime). This is an accepted phenomenon in NMR spectroscopy of polymers and of biological samples but it has not been considered up to now for unexceptional metal complexes. Our work suggests that unexplained line broadening in the spectra of metal complexes at low temperatures may have its origin in a changeover of the rotational behavior of the molecule from the extreme narrowing to the slow-motion regimes.

From the argument given above it is clear that nonclassical hydrides should show line broadening of the M–H resonances at low temperature. This is indeed the case; $FeH_4(PEtPh_2)_3$ shows a quartet at room temperature but a broad resonance at low temperature. Above θ(min) T_1 should equal T_2 and the line width should depend on T_1. For example, T_1 values of 10, 50, and 100 ms lead to line widths of 32, 6, and 3 Hz, respectively. Line widths close to the predicted T_1-limited values are found for $FeH_4(PEtPh_2)_3$ and $ReH_7(PPh_3)_2$. On the other hand, some complexes have line widths greatly exceeding this value. $[IrH(H_2)bq(PPh_3)_2]^+$ has $W_{1/2}$ = 150 Hz[2] and $W(H_2)(CO)_3(PCy_3)_2$ has $W_{1/2}$ = 300 Hz.[1] Up to now we have not been able to account for this anomalous broadening. An exchange phenomenon should give rise to changes in the line width with temperature; only small changes are in fact seen. A nuclear interaction should change with a change of the nucleus involved. Indeed, partially deuteriated samples do show reduced line widths. Further study of the phenomenon of anomalous broadening is in progress.

In a fluxional system $MH_x(H_2)_yL_z$, partial deuterium substitution should lead to isotopic fractionation between the classical and nonclassical sites so that if the chemical shifts, δ_c and δ_n, for the two sites differ, a shift in the averaged chemical shift should be seen.[16] Many nonclassical polyhydrides have rather broad resonances, so that this effect might not always be seen. The effect is just perceptible[2b] in $[IrH(H_2)(bq)(PPh_3)_2]^+$, because even though the resonances are rather broad, δ_c and δ_n differ considerably. $ReH_5(H_2)(PPh_3)_2$ has relatively sharp resonances and distinct resonances can be seen for each of the isotopomers separated by 0.009 ppm per substitution. We cannot identify this as being due entirely to the population effect mentioned above because the separation of the peaks does not show the expected temperature dependence. There may be other effects at work, or δ_c and δ_n may differ by a small amount, or δ_c and δ_n may show an unusual temperature dependence. In the two known series of complexes for which both tautomers can be detected in the NMR, δ_c and δ_n are very similar: $WH_2(CO)_3(P\text{-}i\text{-}Pr_3)_2$, δ_n = −4.2 and δ_c = −3.2; $[CpRuH_2(dmpe)H_2]^+$,[3e] δ_c = −8.6, and δ_n = −9. Isotopomers of the unambiguously classical hydride $MoH_4(PMePh_2)_4$ do not show distinct resonances. Further work is in progress to understand these effects.

Structural Trends

Because we have studied a wide range of complexes, we are able to say something about the factors that predispose a hydride toward one or other of the possible structures. The most important factors are listed below:

(i) Position in the periodic table. Early transition metals are more likely to form classical hydrides, for example, WH_6L_3 is classical but ReH_7L_2 is not (L = 3° phosphine). Third-row metals are more likely to form classical hydrides, e.g., OsH_4L_3 is classical but the Fe and Ru analogues are not. This is probably because the d_π orbitals of the metals are relatively less stabilized for the earlier metals and the third row, and so these metals act as better π-donors and the H–H bond is cleaved.

(ii) Effects of the d^n configuration and the coordination geometry. Octahedral and d^6 systems are favored, so that $OsH_5L_3^+$ attains this configuration by being nonclassical and $H_2Fe(CO)_4$ or $IrH_2(CO)_2L_2^+$ attains it by being classical.

(iii) Charge on the metal. Anionic complexes are more likely to be classical (e.g., classical ReH_8L^- versus nonclassical ReH_7L_2) and cationic complexes are more likely to be nonclassical (e.g., nonclassical $OsH_5L_3^+$ versus classical OsH_4L_3). Complexes with more electron donating ligands are more likely to be classical (e.g., nonclassical ReH_7L_2 versus classical Cp^*ReH_6). In general, a metal in a low oxidation state is more likely to form a classical hydride (e.g., nonclassical FeH_4L_3 versus classical $H_2Fe(CO)_4$). Once again, factors that make the metal a better π-donor tend to give classical hydrides.

Conclusion

We previously showed that the T_1 of the M–H resonance at low temperature constitutes a qualitative test for structure in transition-metal hydride chemistry. Further study has revealed some ambiguous cases, and this has induced us to look at the T_1 at variable-temperature. This has allowed us to make our method quantitative so that we can now obtain an estimate of the H–H distance. The qualitative T_1 method should be used with due caution and the variable-temperature experiment used whenever possible.

We also describe the first identification of dihydrogen complexation to metals of d^2 and d^4 configurations and discuss the general trends that emerge from the data.

Experimental Section

The T_1 experiments were performed on 250- or 500-MHz Brucker instruments with a standard 180°–τ–90° pulse sequence. The temperature was monitored on a Brucker VT-1000 unit. Several experimental problems arose in determining reliable T_1 values. Changes in the resistance of the probe windings with temperature led to changes in the length of the 180° pulse and so we had to determine the required pulse length at each temperature. We used peak area rather than height as being a better measure of signal intensity. We also found that the computer estimate of the signal intensity gave poorer reproducibility than cutting and weighing the peaks. With these precautions, we found that our results were reproducible to ±10% at each temperature. The T_1 was found by plotting ln ($A_\infty - A_\tau$) versus τ. The complexes were prepared by literature methods: $ReH_7(PPh_3)_2$,[17] $ReH_7(dpe)$,[17] $ReH_7(PCy_3)_2$,[18] $OsH_5(PPh_3)_3^+$,[12c] $H_2Fe(CO)_4$,[19] $FeH_4(PEtPh_2)_3$,[7] $OsH_4(P(p\text{-tol})_3)_3$,[20]

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RuH$_4$(PPh$_3$)$_3$,[21] MoH$_4$(PMePh$_2$)$_4$,[22] WH$_4$(PMePh$_2$)$_4$,[23] WH$_5$(PMePh$_2$)$_4$$^+BF_4$$^-$,[24] WH$_6$(PMe$_2$Ph)$_3$,[25] Na$_2ReH_9$,[26] (Et$_4$N)ReH$_8$(PPh$_3$),[27] ReH$_5$(PPh$_3$)$_3$,[28] Ir(CO)$_2$(PPh$_3$)$_2H_2$$^+$,[29] Ir(H$_2$)H(bq)(PPh$_3$)$_2$$^+SbF_6$$^-$,[2c] and CpRu(PPh$_3$)$_2$H.[30]

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Supplementary Material Available: A sample calculation and a calculation on Cp*ReH$_6$ estimating the H$_{ax}$–Re–H$_{eq}$ angle (4 pages). Ordering information is given on any current masthead page.

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Vibrational Circular Dichroism of Optically Active Allenes. Experimental Results

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Abstract: Vibrational circular dichroism (VCD) spectra of several substituted allenes have been measured for various characteristic fundamental vibrations. For all of the allenes studied, the VCD of the C=C=C asymmetric stretch ($\sim$1950 cm^{-1}) correlates directly to the absolute configuration of the molecule, being positive for the *S* configuration. In addition, for 1-halo-3-*tert*-butylallenes, the VCD of the C(X)–H stretch ($\sim$3050 cm^{-1}) was also found to correlate to configuration but the available data set was limited. Additional VCD data for di-*tert*-butyl- and diphenylallene and a phenylallenecarboxylic acid are discussed with respect to individual bands for the sake of comparison.

Vibrational circular dichroism (VCD) has shown great potential as a new tool of use for conformational analysis.[1,2] In the past, VCD on a variety of structurally related molecules, such as substituted cyclopropanes,[3] polypeptides,[4] amino acids,[5] cyclohexyl derivatives,[6] and chiral phosphates,[7] have been measured; and empirical correlations were drawn between the respective stereochemistries and the spectra obtained. In other instances, VCD intensities have been calculated with use of various ad hoc models,[1,2,8,9] which were then compared to experimental results. These approaches parallel those traditionally used over the last 2–3 decades in the interpretation of electronic CD.

Both approaches have advantages but also corresponding limitations. For drawing empirical correlations, detailed understanding of the spectral phenomenon is not required; but a reasonable number of molecules must be studied to avoid ambiguous interpretation. Furthermore, that set should encompass a systematic variation of substituents. On the other hand, calculations can be performed on a single species at different levels of rigor. Unfortunately, the value of these various ad hoc models is far from established. For small molecules having a known geometry and an established force field, this approach appears to be attractive,[10,12] but as larger molecules are studied, more severe approximations become inevitable, and the feasibility of such calculations becomes doubtful.

Substituted allenes constitute an interesting series of molecules for chiroptical studies.[13] These molecules can be made chiral by lowering the D_{2d} allene symmetry to C_2 or C_1. Yet the structure remains small and conformationally restricted if the substituents are simple in nature.

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