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found that these polymers also adhere very well to the alumina on aluminum surfaces,[10] and have used the lower oligomers as a component of hybrid polymers, which allows compatibility with a variety of organic polymers from polyesters to polyolefins.[26]

In conclusion, we have found that metal coordination polymers that behave similar to organic polymers can be synthesized by a careful consideration of the intermolecular forces that have typically limited the size of many metal coordination polymers in the past. The additional complication of interface interactions between the ends of metal coordination polymers and oxide surfaces is both a concern for synthesis and characterization and an opportunity for the preparation of improved surface coatings.

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Variable-Temperature ^{1}H NMR Spectra and T_1 Measurements on the Dinuclear Octahydride Complexes $Re_2H_8(PR_3)_4$ (PR_3 = PPh_3, PEt_2Ph, PMe_2Ph, PMe_3) and the Monohydride Complexes Cp_2ReH and $Re_2HCl_3(CO)_2(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$)

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The variable-temperature spectra and T_1 ^{1}H NMR data for the dinuclear complexes $Re_2H_8(PR_3)_4$ (PR_3 = PPh_3, PEt_2Ph, PMe_2Ph, PMe_3) are reported in CD_2Cl_2. The room-temperature spectra consist of a quintet in the hydride region. In all cases, at very low temperatures, it was possible to obtain spectra indicative of a frozen-out species; the quintet for the metal-bonded hydrogen atoms resolved into two distinct resonances of equal intensity. Definitive assignments as to which peak was due to the terminal and which to the bridging hydrogen atoms were made on the basis of an isotopic perturbation of resonance experiment, and thus the peak at higher field was assigned as due to the terminal hydrogen atoms. Furthermore, all of the $Re_2H_8(PR_3)_4$ complexes exhibited minimum T_1 times around ca. 140 ms at 400 MHz. A minimum T_1 value of 280 ms at 400 MHz was found for Cp_2ReH in toluene-d_8. In the case of $Re_2HCl_3(CO)_2(dppm)_2$, the value of ca. 85 ms was obtained at 200 MHz and −80 °C in CD_2Cl_2. These results suggest, at least in the case of $Re_2HCl_3(CO)_2(dppm)_2$, that other relaxation mechanisms, in addition to the H–H dipolar one, can operate in these rhenium complexes.

Introduction

Complexes of the general form $[ReH_x(PR_3)_2]_n$ (PR_3 = tertiary phosphine) were discovered in seminal work by Chatt and Coffey in 1969.[2] However, it remained until there was a neutron diffraction study on $Re_2H_8(PEt_2Ph)_4$ for the exact structural nature of these complexes to be unambiguously established as containing four bridging and four terminal metal-bonded hydrogen atoms.[3] More recently, work in this area has involved protonation and oxidation reactions,[4] auration substitution reactions on these dimers,[5] reactions with *tert*-butyl isocyanide,[6] and studies of different synthetic routes to these complexes.[7]

We were interested in the variable-temperature (VT) ^{1}H NMR spectra and T_1 values for the metal-bonded hydrogen ligands in these complexes as the molecules were completely fluxional down to temperatures of ca. −80 °C.[7b] The VT spectra reported herein reveal that at low enough temperatures it is possible to freeze out the fluxional process responsible for the interconversion of the terminal and bridging hydrogen atoms. Our previous studies on other fluxional rhenium hydride complexes, such as $ReH_3(PMePh_2)_4$ and $ReH_5(PPh_3)_3$, revealed that low T_1 values (<160 ms at 400 MHz) are not always indicative of molecular dihydrogen ligands.[8] In fact, T_1 minimum values for the metal-bonded hydrogen atoms in complexes $Re_2H_8(PR_3)_4$ (PR_3 = PPh_3, (**1**), PEt_2Ph (**2**), PMe_2Ph (**3**), PMe_3 (**4**)) of around 140 ms at 400 MHz were obtained. We have also measured the variable-temperature T_1 values for the monohydride complexes Cp_2ReH (**5**)[9] and $Re_2HCl_3(CO)_2(dppm)_2$ (**6**).[10] A minimum value of 280 ms was obtained for complex **5**, which is consistent with the relaxation of the hydrogen atom by the Re atom via a dipole–dipole mechanism. In the case of the dimer **6**, the data show a decrease in T_1 with temperature to ca. 85 ms at 200 MHz and −50 °C but no increase or decrease as the temperature was lowered further. This result cannot be attributed to a dipole–dipole relaxation mechanism and indicates that some other mechanism, such as scalar coupling, might also contribute to the low T_1 values in this complex and possibly in other rhenium hydrides. Moreover, the T_1 minimum values for the $Re_2H_8(PR_3)_4$ species need not be taken to suggest that η^2-H_2 ligands are present in these complexes. The importance of these results is that they contribute to defining the limits of applicability of the T_1 NMR criterion for detecting η^2-H_2 ligands in rhenium polyhydride complexes.

Experimental Section

The NMR spectra were recorded in CD_2Cl_2 and toluene-d_8 by using Varian XL-200 and XL-400 NMR spectrometers. The inversion-recovery method was used to measure the T_1 values with prior determination of the 180° pulse for some samples. The Carr–Purcell–Meiboom–Gill sequence was employed to evaluate T_2 in $Re_2H_8(PEt_2Ph)_4$ (**2**).[11] Complexes $Re_2H_8(PR_3)_4$ (PR_3 = PEt_2Ph (**2**), PMe_2Ph (**3**), PMe_3 (**4**)) were prepared as described previously,[7b] and $Re_2HCl_3(CO)_2(dppm)_2$ was generously supplied by Professor K. R. Dunbar and S.-J. Chen of Michigan State University. $Re_2H_8(PPh_3)_4$ (**1**) and Cp_2ReH (**5**) were prepared according to procedures in ref 2 and 9, respectively. Complexes of the form $Re_2H_nD_{8-n}(PR_3)_4$ (PR_3 = PEt_2Ph, PMe_2Ph) were prepared by adding mixtures of $LiAlH_4$ and $LiAlD_4$ to the chloride precursors,

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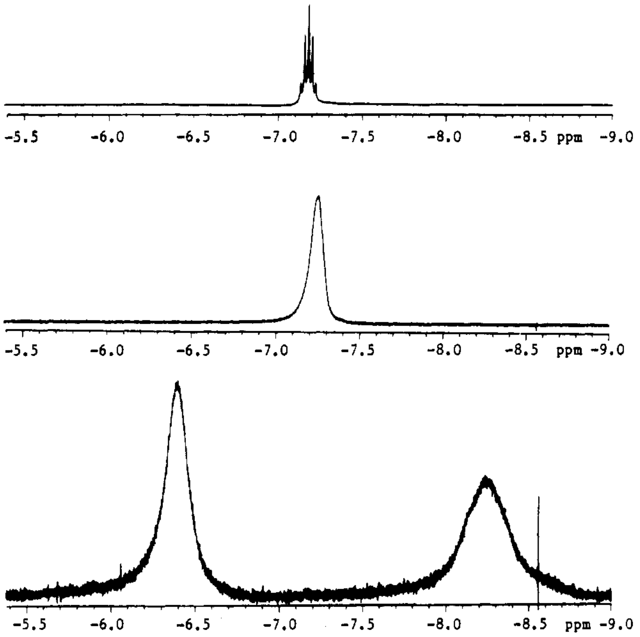

Figure 1. ^1H NMR spectra of complex **2** in the hydride region only at 400 MHz in CD_2Cl_2 at temperatures of +22 (top), −60 (middle) and −120 °C (bottom). The temperature reading was obtained from the digital gauge on the spectrometer and is obviously not accurate at low temperatures; i.e. −120 °C is probably equivalent to −110 °C.

Table I. ^1H NMR Data for Complexes **1–4** in CD_2Cl_2 at 400 MHz in the Hydride Region[a]

	Re_2H_8-(PPh_3) (**1**)	Re_2H_8-$(PEt_2Ph)_4$ (**2**)	Re_2H_8-$(PMe_2Ph)_4$ (**3**)	Re_2H_8-$(PMe_3)_4$ (**4**)
δ, ppm	−5.6	−7.2	−7.0	−7.4
J_{HP}, Hz	9.4	8.9	9.1	9.6
ν, cm^{-1}[b]	2068.9	2063.7	2065.3	2064.1
T, °C[c]	−115	−100	−115	−115
δ, ppm[d]	−5.3, −6.3	−6.5, −8.2	−6.5, −7.8	−7.2, −8.1

[a] ^1H NMR data were previously reported for **2** in C_6D_6,[3] and **3**[7c] and **4**[7b,12] in C_6D_6. [b] This is the Tolman electronic parameter ν.[13] [c] This is the temperature where two resonances are clearly discernible. The temperatures reported are obtained from the instrument and are probably off on the low side at this reading by ca. 10 °C. The peak at lower field can be assigned to the four bridging metal-bonded hydrogen atoms and that upfield to the four terminal ones. This assignment is based on an isotopic perturbation of resonance experiment; see Discussion. [d] These are the positions of the resonances at the temperatures listed immediately above in the table.

$Re_2Cl_4(PR_3)_4$, as discussed for the preparation of the $Re_2H_8(PR_3)_4$ complexes in ref 7b.

Table II. T_1 Data Obtained at Variable Temperatures for Complexes **1–4** and the T_2 Data for Complex **2**

$Re_2H_8(PPh_3)_4$ (**1**)[a]

T, °C	T_1, ms[b]	T_1, ms[b,c]	δ, ppm
25	189 [3]		−5.6 (q, *J* = 10 Hz)
19		147 [9]	
0	152 [2]	101 [4]	−5.6 (q, *J* = 9 Hz)
−20	139 [1]	76 [2]	−5.6 (q, *J* = 8 Hz)
−40	137 [1]	65 [2]	−5.6 (br)
−60	151 [1]	70 [4]	−5.7 (br)
−80	192 [2]	70 [1]	−5.7 (br)
−90		83 [4]	
−100	245 [3]		−5.7 (br)

$Re_2H_8(PEt_2Ph)$ (**2**)[a]

T, °C	T_1, ms[b]	T_2, ms[b]	δ, ppm
22	255 [2]	201 [1]	−7.2 (q, *J* = 9 Hz)
0	206 [2]	164 [3]	−7.2 (q, *J* = 9 Hz]
−20	171 [1]	113 [1]	−7.2 (q, *J* = 9 Hz)
−40	150 [0]	57 [4]	−7.2 (br q, *J* = 8 Hz)
−60	140 [0]	22 [1]	−7.3 (br)
−80	161 [0]	4.9 [2]	−7.3 (v br)
−100	333 [7]	*d*	−6.5 (br)
	340 [10]		−8.1 (br)
−115	551 [6]		−6.4 (br)
	540 [5]		−8.3 (br)
−120	610 [4]	9.3 [1]	−6.4 (br)
	634 [8]	9.5 [2]	−8.2 (br)

$Re_2H_8(PMe_2Ph)_4$ (**3**)[a]

T, °C	T_1, ms[b]	δ, ppm
22	389 [1]	−7.0 (q, *J* = 9 Hz)
0	308 [2]	−7.0 (q, *J* = 9 Hz)
−20	241 [2]	−7.0 (q, *J* = 9 Hz)
−40	190 [2]	−7.0 (q, *J* = 9 Hz)
−60	160 [0]	−7.1 (q, *J* = 8 Hz)
−80	157 [1]	−7.1 (br)
−100	205 [1]	−7.1 (br)
−115	418 [3]	−6.5 (br)
	439 [4]	−7.8 (br)
−120	540 [2]	−6.5 (br)
	548 [5]	−7.9 (br)

$Re_2H_8(PMe_3)_4$ (**4**)[a]

T, °C	T_1, ms[b]	δ, ppm
22	796 [4]	−7.4 (q, *J* = 10 Hz)
0	599 [9]	−7.4 (q, *J* = 10 Hz)
−20	459 [3]	−7.4 (q, *J* = 10 Hz)
−40	331 [2]	−7.4 (q, *J* = 10 Hz)
−60	236 [9]	−7.5 (q, *J* = 9 Hz)
−80	172	−7.5 (br)
−100	163 [1]	−7.6 (br)
−110	197 [1]	−7.6 (br)
−115	281 [23]	−7.2 (br)
	277 [21]	−8.1 (br)

[a] Measurement in CD_2Cl_2 and at 400 MHz. [b] Numbers in square brackets indicate the variance obtained in the calculation of the mean T_1 values, viz. $[(\sum\Delta_i^2)/n(n-1)]^{1/2}$. [c] Data obtained at 200 MHz. [d] Solutions to T_2 not found.

Results and Discussion

Variable-Temperature NMR Studies. The variable-temperature ^1H NMR spectra, in the hydride region only, of complex **2** are presented in Figure 1. Those for complexes **1**, **3**, and **4** are available as supplementary material. Quintet patterns for the metal-bonded hydrogen atoms of these complexes (**1–4**), due to H coupling to four equivalent P atoms, are obtained at room temperature with a coupling constant of ca. 9 Hz, which agrees (see Table I) with what was reported previously.[2,3,7b,12] There is a rough correlation between the electronic parameters (ν) of the tertiary phosphine ligands[13] and the chemical shift of the hydride ligands to the extent that the more electron-donating phosphine results in a more upfield shift, probably indicating an increase in the hydridic nature of these hydrogen atoms.

One interesting aspect to these dinuclear complexes is that, despite the neutron data on complex **2** that clearly indicated two types of metal-bonded hydrogen atoms were present, previous studies provided no ^1H NMR evidence for this.[2,3,7b,12] The reason is simply that the low temperatures (<−95 °C) required to freeze out the fluxional process into the two broad resonances were not attained; see Figure 1. The assignment of these resonances was somewhat more challenging. Previous studies on $Re_2H_4(PMe_2Ph)_4[P(OCH_2)_3CEt]_2$[14] and $Re_2H_6(PMe_2Ph)_5$[15] had shown that the most upfield resonance could be assigned to the terminal metal-bonded hydrogen atoms in those complexes. However, with these complexes the assignments are greatly simplified because of the differing intensities in the resonances of the unequal number of bridging and terminal hydrogen atoms. In the case of complexes

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1–4, the areas of the resolved resonances were roughly equal, which indicates a clean separation into bridging and terminal hydrogen atoms, and were of different shape (the resonance at lower field was narrower; see Figure 1).

A T_2 study on these two resonances in complex **2** at −120 °C revealed that both had the same values; see Table II. This suggested that the shape of the broader resonance was probably due to coupling to the phosphorus atoms. It might be reasonable to conclude that the narrower peak at lower field was due to the terminal hydrogen atoms, as they were cis to the P atoms, whereas the bridging ones that were trans to these P atoms should show larger coupling constants and thus give the broader resonance at higher fields. However, the bridging hydrogen atoms might still be fluxional among themselves, and thus the trans H–P coupling may be reduced or not observed.

A relatively simple way to resolve this problem of assignment is to do the isotopic perturbation of resonance experiment.[16] Thus, complexes of the form $Re_2H_n/D_{8-n}(PR_3)_4$ (PR_3 = PEt_2Ph, PMe_2Ph) were synthesized. It was not necessary to obtain complexes containing exactly equal amounts of hydrogen and deuterium atoms, for a change in the areas of the resonances was all that was needed to assign the peaks unambiguously. In the resolved spectra at the required low temperatures, increases of the ^1H resonance at lower field relative to the one at higher fields were observed, for the molecules mentioned above (see the supplementary material). Since we expect the bridging sites to have the lower zero-point energy, and thus to be preferred by H over D, this provides conclusive evidence that the resonance at lower field is due to the bridging hydrogen atoms.

T_1 Studies. The results of variable-temperature longitudinal relaxation (T_1) measurements on complexes **1–4** are given in Table II. For comparison purposes, the measurement at 200 MHz for complex **1** in CD_2Cl_2 has been included. The minimum time of 137 ms is obtained at −40 °C and 400 MHz and is roughly twice that of 65 ms at −40 °C obtained at 200 Mz. This provides experimental evidence that the minimum T_1 time is related directly to the field strength of the NMR instrument for these molecules, and more importantly, because the T_1 values go through a minimum, it suggests that a dipole–dipole mechanism for the relaxation is operative.[17,18]

The minimum T_1 time occurs at different temperatures for these complexes in the following order **1** (137 ms, −40 °C) > **2** (140 ms, −60 °C) > **3** (157 ms, −80 °C) > **4** (163 ms, −100 °C). The variation with temperature correlates with the decrease of the size of the tertiary phosphine ligands as this leads to smaller rotational correlation times τ_c for the complexes. The increase in the minimum T_1 values from complex **1** to complex **4** is also consistent with an increasing hydridic component to the metal-bonded hydrogen atoms.

One of the more interesting attributes of the use of T_1(min) values in assessing whether or not a given polyhydride metal complex contains a molecular dihydrogen ligand was its presumed simplicity.[17] A value below a certain limit could supposedly be taken to indicate the presence of a molecular dihydrogen ligand. Of much greater significance was the idea that the T_1 method could be applied to fluxional hydride systems, where the T_1(min) value for all the magnetically equivalent metal-bonded H atoms in the complex, e.g. $ReH_7(PPh_3)_2$, could be used in the assessment. For $ReH_7(PPh_3)_2$, it is not possible to freeze out (at least on the NMR time scale) a distinct $ReH_5(\eta^2\text{-}H_2)(PPh_3)_2$ species, and thus eq 1 (where n_c and n_n are the number of classical, i.e., separate,

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

hydridic protons, and nonclassical, i.e., η^2-H_2 type protons) was applied to calculate the "true" T_1 min for the supposed "η^2-H_2" ligand associated with this structure and that of other rhenium polyhydrides.[17] The T_1(c,min) value was arbitrarily assigned as 200 ms in the calculations using eq 1.[17]

Table III. Analysis of the T_1 Data on Complexes **1–4**

	Re_2H_8-(PPh_3) (**1**)	Re_2H_8-$(PEt_2Ph)_4$ (**2**)	Re_2H_8-$(PMe_2Ph)_4$ (**3**)	Re_2H_8-$(PMe_3)_4$ (**4**)
min T_1, ms[a]	68.5	70.0	78.5	81.5
H–H (rapid rotation), Å[b]	1.22	1.22	1.25	1.25
H–H (no rotation), Å[b]	1.53	1.54	1.57	1.58
$T_1(n_n)$, ms[c]	23	24	28	29
H–H (rapid rotation), Å	1.02	1.02	1.05	1.06
H–H (no rotation), Å	1.28	1.29	1.32	1.32

[a] Value given for spectra at 200 MHz. [b] Calculated as suggested in ref 19. [c] Calculated as suggested in ref 17a with n_c = 6, n_n = 2 and T_1(c, min) = 200 ms. If we use the T_1(c, min) value of 280 ms at 400 MHz obtained for Cp_2ReH (**5**) (see Table IV), slightly larger values are obtained for $T_1(n_n)$, e.g. 27 ms for **1**.

This equation[17] (with n_c = 6 and n_n = 2) and the equations[19] for calculating effective H–H distances by assuming either rapid rotation of the H–H bond or no rotation for the H–H bond were used to calculate the various T_1 (n_n) times and H–H distances listed in Table III.

On the basis of the values in Table III obtained by published procedures[17] using eq 1, we could conclude that there was involvement of molecular dihydrogen ligands in these complexes. However, there are several points to the contrary. For instance, the fact that upon further cooling separate resonances were obtained for the bridging and terminal metal-bonded hydrogen atoms argues in favor of a classical formulation of these complexes, which is, in turn, more consistent with the results of the neutron structure analysis of **2**.[3] The similar T_1 values for the resonances associated with the bridging and terminal metal-bonded hydrogen atoms indicate that these atoms are still fluxional, at least on the T_1 time scale. One could argue that the reason the T_1 values were similar, in the slow-exchange spectra obtained at low temperatures, is because of an η^2-H_2 ligand that is fluxional between bridging and terminal sites and is responsible for the equivalent values. However, additional ^1H NMR evidence, such as a separate resonance due to the η^2-H_2 ligand, should have been discerned in the low-temperature decoalescence pattern as there should be some thermodynamic preference for this η^2-H_2 ligand to reside in one of the two sites. Furthermore, the T_2 values for complex **2** are also affected by the fluxional processes involved with the metal-bonded hydrogen ligands. At similar temperatures they are less than the T_1 values obtained for **2** (see Table III), and they decrease with temperature as predicted by theory[18] up to the coalescence temperature. At lower temperatures, there was a slight increase in T_2 values as those values pertain to the almost frozen-out species (slow exchange), bridging and terminal hydrides, and not the fluxional average hydride species (rapid exchange). The results of this NMR work provide further evidence that highly fluxional polyhydride molecules can have short T_1 values, which agrees with our previous studies on mononuclear polyhydride rhenium complexes.[8]

Structural assignments have been made regarding the presence of η^2-H_2 ligands solely on this T_1 basis for two other dinuclear molecules, namely $Ru_2H_4Cl_2(P(tol)_3)_4$[20] and $Ru_2H_6(PCy_3)_4$.[21] There are, however, nonrelated T_1 data that substantiate these assignments. For example, the latter complex reacts with dinitrogen to form the complex $Ru_2H_4(N_2)(PCy_3)_4$, with ν(NN) = 2145 cm^{-1}.[21] This is within the range (ν(NN) = 2060–2150

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Table IV. T_1 NMR Data for Complexes Cp_2ReH (**5**) and $Re_2HCl_3(CO)_2(dppm)_2$ (**6**)

Cp_2ReH (**5**)[a]

toluene-d^8		CD_2Cl_2
T, °C	T_1, s	T_1, s
22	10.0 (4)	10.0 (5)
0	7.7 (6)	7.8 (1.3)
−20	5.2 (5)	5.0 (1)
−40	2.8 (2)	3.3 (1)
−60	1.7 (1)	2.2 (1)
−80	0.75 (9)	−1.3 (1)
−90	0.60 (3)	
−95	0.38 (7)	
−100	0.33 (7)	0.60 (4)
−105	0.35 (4)	
−110	0.28 (6)	
−115	0.28 (2)	
−117.5	0.36 (8)	
−120	0.52 (9)	0.37 (3)
−122		0.29 (2)

$Re_2HCl_3(CO)_2(dppm)_2$ (**6**)[b]

T, °C	T_1, ms	*T*, °C	T_1, ms
22	343 (62)	−50	87.4 (16)
0	279 (99)	−60	99.6 (22)
−20	257 (33)	−80	83.9 (2)
−30	139 (15)	−100	80.9 (15)
−40	107 (9)		

[a] Data at 400 MHz on the 11-line resonance obtained at δ −13.4 (*J* = 1.2 Hz) for the hydride ligand. The 10 hydrogen atoms on the two cyclopentadienyl rings resonate at δ 4.4 (*J* = 1.2 Hz). Line broadening was used to broaden out the resonance into one broad peak, and so the error given is from the T_1 calculation. [b] Data at 200 MHz in CD_2Cl_2. The bridging hydride for complex **6** resonates as a quintet at 12.75 ppm with J_{HP} = 3 Hz.[10]

cm^{-1}) usually found for dinitrogen complexes where the corresponding dihydrogen analogues are of the η^2-H_2 form and are stable at room temperature.[22] Furthermore, the results of an X-ray structure determination of the dinuclear $Fe(\eta^5\text{-}C_5H_3\text{-}(CHMeNMe_2)P(i\text{-}Pr)_2\text{-}1,2)(\eta^5\text{-}C_5H_5)(\eta^2\text{-}H_2)Ru(\mu\text{-}Cl)_2(\mu\text{-}H)\text{-}Ru(H)(PPh_3)_2$, which has a core geometry similar to that of $Ru_2H_4Cl_2(P(tol)_3)_4$,[20] contained a short H–H interaction (0.80 (6) Å).[23]

More recently, work on the tetrahydride bridged complex $(\eta^5\text{-}C_5Me_5)Ru(\mu\text{-}H_4)Ru(\eta^5\text{-}C_5Me_5)$ revealed a T_1 value for the bridging hydrogen atoms at 193 K and 500 MHz of 2.28 s.[24] Although this value was not reported as a minimum T_1, it appears that a fairly wide range of values can be obtained for similar μ-H_4 bridged species ranging from ca. 70 ms at 200 MHz for the rhenium complexes reported here to 2.28 s at 500 MHz for the above-mentioned ruthenium species.

In order to further understand the variation of the T_1 values for metal-bonded hydrogen atoms attached to rhenium, we obtained this datum for Cp_2ReH (**5**) and $Re_2HCl_3(CO)_2(dppm)_2$ (**6**), a dimer containing one bridging hydrogen atom. These are listed in Table IV.

No minimum T_1 was detected for **5** in CD_2Cl_2, but the more viscous toluene-d_8 allows us to conclude that a value of 280 ms at 400 MHz is a reasonable estimate, which represents a 36-fold decrease from the value at room temperature of 10.0 s. That a minimum was observed with decreasing temperature is in keeping with the theoretically expected dependence for dipole–dipole interactions. It is interesting to compare our T_1(min) value for the monohydride **5** (280 ms at 400 MHz) to that reported for $HMn(CO)_5$ in 95% THF-d_8/5% CD_2Cl_2 of 337 ms at 500 MHz,[25] (equivalent to 270 ms at 400 MHz). The relaxation mechanism in the case of $HMn(CO)_5$ was shown via a series of complicated experiments to be 85% due to the H–Mn dipole–dipole relaxation in deuterated solvents.[25] The similarity in the T_1(min) values for **5** and $HMn(CO)_5$ and the fact that the magnetic moments of the elements Mn and Re are almost equal imply that the T_1(min) value of 280 ms for **5** is a good measure of the minimum value to be expected in the case of a monohydride on Re, where a H–Re dipole–dipole interaction contributes significantly to the T_1 relaxation time. However, this does not mean that all monohydride complexes *will* have T_1(min) values for the hydride of 270–280 ms at 400 MHz. For example, the much lower T_1 value of 110 ms at 203 K and 300 MHz was reported recently for the metal-bonded hydrogen atom in the complex $[(PP)_3CoH]$ (PP = $P(CH_2CH_2PPh_2)_3$).[26] In this case, the hydrogen atoms on the ligands may contribute significantly to the relaxation rate of the metal-bonded H atoms.

The T_1 values obtained for the dinuclear **6** in CD_2Cl_2 are more difficult to rationalize, for the structure[10] does not permit close H–H contacts between the H atom bridging the two Re atoms and those H atoms on the dppm ligand. In this case a value of 343 ms is obtained at room temperature, and this decrease to ca. 85 ms; see Table IV. The data do not indicate a T_1 minimum for complex **6**, which is contrary to expected dipole–dipole relaxation behavior, and it is possible that contributions from the scalar relaxation mechanism are at work in this molecule. These contributions are not expected to be large, as the magnitude of this effect is very dependent on the resonant frequencies of the two nuclei being very close, which is not the case with Re and H. Indeed, one of the few cases where this has been observed is with CH_3HgI, where relaxation of ^{199}Hg by ^{127}I is shown to occur.[27] Nonetheless, the value of ca. 85 ms for this dinuclear bridging monohydride is similar to that for the $Re_2H_8(PR_3)_4$ complexes also reported in this paper and other mononuclear rhenium species.[8,17] Therefore, armed with this information, it would not be reasonable to suggest that the T_1 values for those complexes (including $ReH_7(PPh_3)_2$[17]) indicate that molecular dihydrogen ligands are present.

Conclusions. The results presented in this paper show that the manipulation of T_1 values by use of eq 1 is not accurate in determining whether or not rhenium polydride complexes (those in which the number of metal-bonded hydrogen atoms is greater than or equal to three), dimeric or monomeric, contain molecular dihydrogen ligands. The recently published neutron structure[28] of $ReH_7(dppe)$ (dppe = $Ph_2PCH_2CH_2PPh_2$) a complex for which the T_1 technique augmented by use of eq 1[17] suggested a nonclassical structure, revealed no short H–H interactions. As a consequence of this structure and the work reported herein, the assignment of $[ReH_8(PR_3)_2]^+$ as nonclassical on the basis of T_1 values of 30 ms may also be questioned.[29] The complex $Re(\eta^2\text{-}H_2)Cl(PMePh_2)_4$, where the number of metal-bonded hydrogen atoms was shown to be two and where a minimum T_1 value of 25 ms at 200 MHz was obtained, appears to be the only unambiguous η^2-H_2 rhenium complex to date.[30]

Note Added in Proof. Luo and Crabtree (*Inorg. Chem.* **1989**, *28*, 3775) have recently employed the X-ray crystallographic H⋯H distances for $ReH_5(PPh_3)_3$[8c] to calculate a T_1(min) value for that complex. They give 148 ms at 400 MHz, which is close to the value of 138 ms that we measure at 400 MHz in toluene.[8c] To be meaningful, such a calculation must employ *proton–proton* distances, whereas an X-ray structure determination gives the centroids of *electron density*. As is well-known, and recently reemphasized by us (Cotton, F. A.; Luck, R. L. *Inorg. Chem.*

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1989, *28*, 3210), the position of a proton and the centroid of electron density associated with it for a hydrogen atom bound to another atom do *not* coincide; a disparity of 0.15 Å is typical for a M–H bond. The average Re–H distance in the X-ray structure determination of ReH$_5$(PPh$_3$)$_3$ was 1.54 [5] Å,[8c] and this can be compared to the average Re–H distance of 1.688 [5] Å determined by neutron diffraction in ReH$_5$(PMePh$_2$)$_3$ (Emge, T. J.; Koetzle, T. F.; Bruno, J. W.; Caulton, K. G. *Inorg. Chem.* **1984**, *23*, 4012). Correcting for the X-ray-determined H···H distances for ReH$_5$(PPh$_3$)$_3$ and applying the DD calculation[17] lead to the significantly larger T_1(min) value of 259 ms at 400 MHz. Thus, with T_1^{-1} depending on r_{HH}^{-6}, such discrepancies introduce serious errors.

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Supplementary Material Available: Figures containing the variable-temperature spectra of complexes **1**, **3**, and **4** and variable-temperature spectra for Re$_2$H/D$_{8-n}$(PR$_3$)$_4$ (PR$_3$ = PEt$_2$Ph, PMe$_2$Ph) (5 pages). Ordering information is given on any current masthead page.

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Bonding in Clusters. 11.[†] Gas-Phase Photoelectron Spectra of the 12-Apex Closo Systems 1,12-B$_{12}$H$_{10}$(CO)$_2$, 1,2- and 1,7-C$_2$B$_{10}$H$_{12}$, and Related Main Group V and VI Heteroboranes and -carboranes. The Electronic Structure of B$_{12}$H$_{12}{}^{2-}$

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The He I and He II photoelectron spectra of 1,12-B$_{12}$H$_{10}$(CO)$_2$ and 1,2- and 1,7-C$_2$B$_{10}$H$_{12}$ are assigned in terms of correspondence of bands to BH bonding or cluster-localized orbitals. The experimental assignments are found to agree excellently with MNDO calculations on the molecules, which allows assignment of the cluster orbitals and ionizations in terms of Stone's theory of *closo*-boranes. Spectra of the related *closo*-heteroboranes 1,2-X(CH)B$_{10}$H$_{10}$ (X = P, As, Sb), X$_2$B$_{10}$H$_{10}$ (X = As, Sb), and SeB$_{11}$H$_{11}$ are found to be very similar, also agreeing with calculated results. The lone pairs of the heteroatoms are found to be localized in the valence s atomic orbital. An orbital diagram for B$_{12}$H$_{12}{}^{2-}$ is extrapolated from these results, which shows it to be distinctly different from the smaller *closo*-borane anions.

The electronic structure and bonding of boranes have attracted an enormous amount of attention since the basic set of chemical/geometric types became established by structural techniques. The interest stemmed initially from a general appreciation that the molecules presented a "soluble problem" in molecular bonding whose solution involved "nonclassical" bonding ideas. It received more purpose when equivalent structural types of molecules were identified in heteroborane, metallaborane, and all-metal clusters. The vast majority of this interest is represented by theoretical considerations of the nature of the bonding ranging in sophistication from the powerful, largely heuristic, approaches of Lipscomb's *styx* rules[1] and Wade's rules[2] to full ab initio calculations on individual molecules. In recent years Stone has presented[3,4] a general theory of the electronic structure of the *closo*-borane anions, which may be considered as the parent molecules for all the structural types,[4,5] which has been extensively adopted as the framework for the discussion of the properties of all related molecules. There is, in comparison with all this theoretical work, a distinct paucity of experimental data on the molecules, other than structure determinations.

One of the most useful experimental techniques applied to these compounds is photoelectron (pe) spectroscopy. The available studies are distributed widely across the various types of clusters, and as much of the work was performed before the advent of Stone's theory, they lack the organization provided by a consistent framework. Further, very few of the studies are on the closo compounds, which are the most tractable theoretically, and those that are usually involve the introduction of heteroatoms into the cage to compensate for the anionic charge of the parent *closo*-B$_n$H$_n{}^{2-}$ systems. The only study of a volatile compound with an intact *closo*-borane cage is an earlier paper in this series[6] on 1,10-B$_{10}$H$_8$(N$_2$)$_2$.

In this paper we report the pe spectra of a number of 12-apex closo compounds and are able to provide a consistent assignment of all features observed. The assignment is found to agree remarkably well with the results of MNDO calculations[7] of the electronic structure of the molecules. We also compare the MNDO-optimized geometries with structural data where available, again finding very good agreement. In general, the MNDO calculations appear to provide a very accurate description of these molecules. We extrapolate from the experimental data an energy level diagram for the parent B$_{12}$H$_{12}{}^{2-}$ anion, which again agrees with calculation and which provides an explanation for the remarkable thermal and hydrolytic stability of the anion.

The discussion and assignments use Stone's theory labeling. The theory shows that the molecular orbitals of the near-spherical systems B$_n$H$_n{}^{2-}$ have distributions and degeneracies (as close as molecular symmetry permits) that are characterizable by atomic orbital labels. Thus, in B$_{12}$H$_{12}{}^{2-}$, the 13 cluster orbitals are labeled $S^\sigma(a_{1g})$, $P^\sigma(t_{1u})$, $D^\pi(h_g)$, and $F^\pi(t_{2u})$, the σ and π superscripts indicating predominantly B 2s and B 2p (tangential to the surface of the sphere) composition, respectively. Similarly the 12 BH bonding orbitals can be labeled $S^x(a_{1g})$, $P^x(t_{1u})$, $D^x(h_g)$, and $F^x(g_u)$, these having large percentage B 2p (radial to the sphere) composition. In a recent paper[8] we have shown that the σ/x orbitals

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