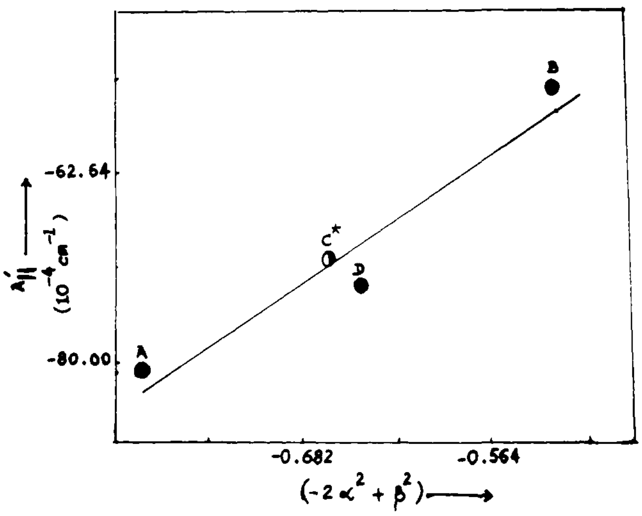

Figure 14. A correlation of experimental anisotropic hyperfine splitting due to ^{63,65}Cu ($A_{\parallel} = A - A_{av}$) and calculated molecular orbital coefficients from $3d_{xy}$ and $4p_z$ of Cu: A = planar $(n\text{-}Bu_4N)_2Cu(mnt)_2$; B = bent $(n\text{-}Bu_4N)_2Cu(dcmdtcroc)_2$; C = bent $(Me_4N)_2Cu(mnt)_2$; (* indicates unavailability of experimental data on $A'_{\parallel}$); D = $(MB^+)_2Cu(mnt)_2$.

as calculated from point charge model yields 168 G with the observed Cu–Cu bond distance in the dimeric unit. However, it is expected to decrease with increased covalency. Hence, the estimated $\mathbf{D}^{dip}$ term will only be about 80–90 G in this complex. Furthermore, $\mathbf{D}^{ex}$ can be calculated by the equation[23]

$$\mathbf{D}^{ex} = \tfrac{1}{8}(2J)\,[0.25(g_{zz} - 2.0023)^2 - 0.5\{(g_{xx} - 2.0023)^2 + (g_{yy} - 2.0023)^2\}] \quad (15)$$

and it turns out to be 28 G with the observed $2J$ of 12 cm^{-1}. The total observed **D** of 102 G at room temperature compares very favorably with the calculated value of about 108–118 G though the model may be simple.

Conclusion

The lattice of $(n\text{-}Bu_4)_2Cu(dcmdtcroc)_2$ is an interesting example of ferromagnetically coupled dimer with an antiferromagnetic interdimer coupling. The $2J$ value calculated from susceptibility, powder simulations of EPR using an appropriate Hamiltonian, and temperature variation of intensity all lead to an identical conclusion revealing an interesting method of deriving $2J$. The interdimer coupling and its manifestations on EPR spectra are not correctly identifiable at this stage.

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Supplementary Material Available: Tables containing the anisotropic temperature factors for the non-hydrogen atoms and the positional parameters for the hydrogen atoms (4 pages); table of observed and calculated structure factors for $(n\text{-}Bu_4)_2[Cu(dcmdtcroc)_2]$ (20 pages). Ordering information is given on any current masthead page.

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X-ray Crystal Structure of $ReH_5(PPh_3)_3$ and Variable-Temperature T_1 Studies on $ReH_5(PPh_3)_3$ and $ReH_5(PMe_2Ph)_3$ in Various Solvents: Are T_1 Measurements Reliable in Predicting Whether Polyhydride Complexes Contain Molecular Hydrogen Ligands?

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Abstract: The variable-temperature ^{1}H NMR longitudinal relaxation times (T_1) and spectra of the complexes $ReH_5(PPh_3)_3$ in toluene-d_8 and CD_2Cl_2 and $ReH_5(PMe_2Ph)_3$ in CD_2Cl_2 are reported. The trends observed are in keeping with our previous assignment of $ReH_5(PPh_3)_3$ as containing a dihydrogen (η^2-H_2) ligand. However, the X-ray structure determination of this complex reveals no bonding H–H interactions and gives an average Re–H distance of 1.54 [5] Å. Crystal data for $ReH_5(PPh_3)_3$: monoclinic, space group $P2_1/n$, $a = 9.968$ (4) Å, $b = 33.237$ (9) Å, $c = 13.591$ (4) Å, $\beta = 92.27$ (3)°, $V = 4500$ (3) Å^3, $Z = 4$, $R = 0.0376$ ($R_w = 0.0482$) for 436 parameters and 4824 unique data having $F_o^2 > 3\sigma(F_o)^2$.

There has been renewed interest in the properties of rhenium polyhydride complexes[1] especially as to whether these complexes contain molecular hydrogen (η^2-H_2) ligands.[2-5] In a recent communication[2b] we pointed out that the classical formulation of $ReH_5(PPh_3)_3$,[5] **1**, based on a reported T_1 value of 540 ms, was incorrect. Our conclusion was based on the fact that we obtained much lower T_1 values than reported earlier for **1** (T_1 (min) = 46

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Table I. Crystal Data for Complex **1**

formula	$C_{54}H_{50}P_3Re$
formula wt	978.12
space group	$P2_1/n$
systematic absences	$0k0$; $k \neq 2n$ $h0l$; $h + l \neq 2n$
a, Å	9.968 (4)
b, Å	33.237 (9)
c, Å	13.591 (4)
α, deg	90
β, deg	92.27 (3)
γ, deg	90
V, Å^3	4500 (3)
Z	4
d_{calc}, g/cm^3	1.44
crystal size, mm	0.30 × 0.30 × 0.10
μ (Mo Kα), cm^{-1}	28.764
data collectn instrument	Nicolet R3m/E
radiatn (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)
orientatn reflcns, number, range (2θ)	25, 23 < 2θ < 44
temp, °C	19 ± 1
scan method	ω
data col. range, 2θ, deg	$0 \leq 2\omega \leq 50$
no. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	7922, 4824
no. of parameters refined	436
trans. factors, max., min.	99.77, 74.24
R^a	0.0376
$R_w{}^b$	0.0482
quality-of-fit indicator^c	1.045
largest shift/esd, final cycle	0.075
largest peak, e/Å^3	0.47

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1.2219/(\sigma^2(|F_o|) + 0.001F_o^2)$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{obsd} - N_{parameters})]^{1/2}$.

ms at 200 MHz and −80 °C in acetone-d_6) and by a comparison with the spectra and the T_1 values that we also obtained for ReH$_5$(PMePh$_2$)$_3$, **2**.[2b] The results of a variable-temperature ^{1}H NMR experiment[2b] and the previously reported neutron diffraction structure[6] suggested a classical formulation for complex **2** under those circumstances.

There are at least two problems evident with use of the T_1 method to determine whether or not a polyhydride molecule contains a molecular hydrogen ligand. The first is that with fluxional systems (e.g., ReH$_7$(PPh$_3$)[2b,5] ReH$_3$(PMePh$_2$)$_4$[2c]) it is necessary for the spectra with T_1 values at each temperature to be reported, and this is not often done in literature reports.[5,7] It is often possible to freeze out distinct hydride and molecular hydrogen components.[2b,c,8] The second problem is that there might be another mechanism, in addition to the dipole–dipole relaxation one, that operates in these fluxional systems and that results in short T_1 values.[9] These points were quite evident in our recent study of the variable temperature ^{1}H NMR T_1 times for ReH$_3$(PMePh$_2$)$_4$,[2c] where the results were ambiguous. The low T_1 times suggested a nonclassical formulation at −49 °C, while the single-crystal X-ray structure suggested a classical one.

In this paper we present the variable-temperature spectra and T_1 measurements for **1** in toluene-d_8 and CD$_2$Cl$_2$ and also for ReH$_5$(PMe$_2$Ph)$_3$, **3**, in CD$_2$Cl$_2$. In the case of complex **1** in CD$_2$Cl$_2$, better resolved low-temperature spectra were obtained than those reported previously with other solvent systems.[2b] The pattern of the lowest temperature spectrum is in keeping with our assignment of a nonclassical formulation for **1**. However, the X-ray crystal structure of **1** reveals a geometry similar to that determined in the neutron structure of **2** and contains no short H–H distances. This suggests that this complex is classical and provides further evidence that low T_1 values (35 < T_1(min) < 100 ms at 250 MHz)[5] are not always indicative of a molecular hydrogen ligand.

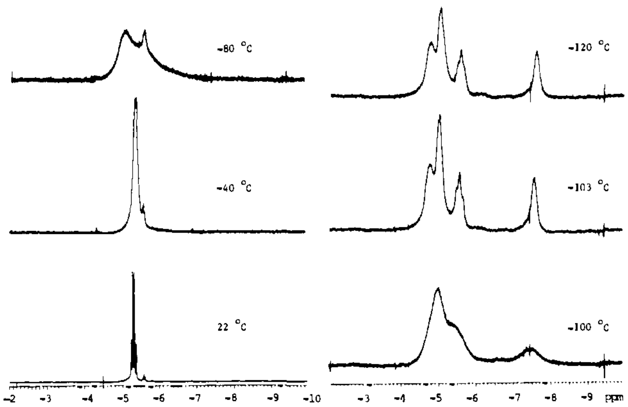

Figure 1. The variable temperature ^{1}H NMR spectra of **1** in CD$_2$Cl$_2$ at 400 MHz in the hydride region only. The small quintet at δ −5.6 is due to the hydride ligands in Re$_2$H$_8$(PPh$_3$)$_4$ which was produced during the synthesis of **1**.

Experimental Section

ReH$_5$(PPh$_3$)$_3$[10] and ReH$_5$(PMe$_2$Ph)$_3$[11] were prepared as described previously. The NMR spectra were recorded on a Varian XL-400 NMR spectrometer. X-ray quality crystals of **1** grew from the acetone solution in the NMR tube on standing. All relevant crystallographic information is given in Table I. A suitable crystal was coated with epoxy resin and mounted on top of a glass fiber. The X-ray data were collected and corrected as previously described.[2c] All of the non-hydrogen atoms were located from a three-dimensional Patterson function. These positions were refined first isotropically and then anisotropically to convergence with the Enraf-Nonius SDP software. At this point the difference map indicated several peaks, some at sites for phenyl hydrogen atoms and close to the rhenium atom. Subsequent refinement was performed with the SHELX-76 package of programs. Hydrogen atoms were put in at calculated positions for the phenyl rings. The phenyl groups were then refined as rigid bodies, and the thermal parameters on all of the hydrogen atoms attached to phenyl carbon atoms were constrained to the same value which was refined. After convergence, a difference map contained five peaks around the rhenium atom at reasonable hydride positions. These were entered without restriction as hydrogen atoms and this model refined. After several least-squares cycles the coordinates and, more importantly, the thermal parameter of one of the hydrogen atoms had refined to unacceptable values. This atom was deleted, and a difference map revealed a peak which was in a more reasonable position. The new peak was entered as a hydrogen atom, and this model again comprising five hydrogen atoms refined to give the final figures of merit listed in Table I. Tables listing the fractional atomic coordinates are available as Supplementary Material. Selected bond distances and angles are listed in Table II.

Results and Discussion

NMR Studies. As reported previously,[2b,10] a quartet is obtained for the hydride ligands in **1** at room temperature, Figure 1. This collapses at −80 °C and is resolved at −100 °C into three signals, one at δ −5.0, for three magnetically equivalent hydrogen atoms, and two others, at δ −5.4 and −7.5, for the remaining two magnetically inequivalent hydrogen atoms. This is similar to what we reported previously for **1** in acetone-d_6.[2b] However, in CD$_2$Cl$_2$, we were able to reach lower temperatures, and at −120 °C the spectrum is further resolved to reveal three magnetically inequivalent hydrogen atoms at δ −4.8, −5.6, and −7.6 and two magnetically equivalent hydrogen atoms at δ −5.1. Similar decoalescing patterns were observed in variable-temperature studies of ReH$_5$(AsEtPh$_2$)$_3$ and ReH$_5$(PEtPh$_2$)$_3$,[12] where, for both

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Table II. Selected Bond Distances and Angles for $ReH_5(PPh_3)_3$ (**1**)[a]

Bond Distances (Å)

atom1	atom2	distance	atom1	atom2	distance	atom1	atom2	distance	atom1	atom2	distance
Re	P(1)	2.378 (2)	P(1)	H(3)	2.70 (8)	P(3)	H(3)	3.81 (8)	H(3)	H(5)	1.60 (13)
Re	P(2)	2.397 (2)	P(1)	H(4)	3.89 (10)	P(3)	H(4)	2.53 (9)	H(4)	H(5)	1.85 (14)
Re	P(3)	2.403 (2)	P(1)	H(5)	2.34 (11)	P(3)	H(5)	2.80 (10)	P(1)	C(111)	1.848 (7)
Re	H(1)	1.48 (6)	P(2)	P(3)	3.893 (3)	H(1)	H(2)	1.70 (12)	P(1)	C(121)	1.844 (6)
Re	H(2)	1.49 (10)	P(2)	H(1)	2.31 (6)	H(1)	H(3)	1.78 (10)	P(1)	C(131)	1.850 (7)
Re	H(3)	1.56 (8)	P(2)	H(2)	2.44 (10)	H(1)	H(4)	2.99 (12)	P(2)	C(211)	1.841 (6)
Re	H(4)	1.73 (10)	P(2)	H(3)	2.66 (8)	H(1)	H(5)	2.52 (12)	P(2)	C(221)	1.844 (6)
Re	H(5)	1.43 (10)	P(2)	H(4)	2.63 (10)	H(2)	H(3)	2.86 (12)	P(2)	C(231)	1.854 (6)
P(1)	P(3)	3.853 (3)	P(2)	H(5)	3.58 (10)	H(2)	H(4)	2.83 (14)	P(3)	C(311)	1.872 (5)
P(1)	H(1)	2.20 (6)	P(3)	H(1)	3.66 (6)	H(2)	H(5)	2.81 (14)	P(3)	C(321)	1.854 (6)
P(1)	H(2)	2.82 (9)	P(3)	H(2)	2.38 (10)	H(3)	H(4)	2.10 (12)	P(3)	C(331)	1.837 (6)

Bond Angles (deg)

atom1	atom2	atom3	angle	atom1	atom2	atom3	angle	atom1	atom2	atom3	angle
P(1)	Re	P(2)	133.28 (7)	P(3)	Re	H(4)	74 (3)	C(111)	P(1)	C(121)	101.6 (3)
P(1)	Re	P(3)	107.43 (7)	P(3)	Re	H(5)	90 (4)	C(111)	P(1)	C(131)	101.3 (3)
P(1)	Re	H(1)	65 (2)	H(1)	Re	H(2)	70 (4)	C(121)	P(1)	C(131)	101.5 (3)
P(1)	Re	H(2)	91 (4)	H(1)	Re	H(3)	72 (4)	Re	P(2)	C(211)	113.8 (2)
P(1)	Re	H(3)	84 (3)	H(1)	Re	H(4)	138 (4)	Re	P(2)	C(221)	122.4 (2)
P(1)	Re	H(4)	142 (3)	H(1)	Re	H(5)	120 (5)	Re	P(2)	C(231)	114.8 (2)
P(1)	Re	H(5)	71 (4)	H(2)	Re	H(3)	140 (5)	C(211)	P(2)	C(221)	102.2 (3)
P(2)	Re	P(3)	108.38 (7)	H(2)	Re	H(4)	124 (5)	C(211)	P(2)	C(231)	102.0 (3)
P(2)	Re	H(1)	68 (2)	H(2)	Re	H(5)	149 (5)	C(221)	P(2)	C(231)	98.7 (3)
P(2)	Re	H(2)	74 (4)	H(3)	Re	H(4)	79 (4)	Re	P(3)	C(311)	117.6 (2)
P(2)	Re	H(3)	81 (3)	H(3)	Re	H(5)	65 (5)	Re	P(3)	C(321)	119.3 (2)
P(2)	Re	H(4)	77 (3)	H(4)	Re	H(5)	71 (5)	Re	P(3)	C(331)	116.3 (2)
P(2)	Re	H(5)	137 (4)	Re	P(1)	C(111)	111.6 (2)	C(311)	P(3)	C(321)	100.2 (2)
P(3)	Re	H(1)	140 (3)	Re	P(1)	C(121)	121.0 (2)	C(311)	P(3)	C(331)	102.1 (3)
P(3)	Re	H(2)	71 (4)	Re	P(1)	C(131)	117.0 (2)	C(321)	P(3)	C(331)	97.9 (3)
P(3)	Re	H(3)	148 (3)								

[a] Numbers in parentheses in the distance and angle columns are estimated standard deviations in the least significant digits.

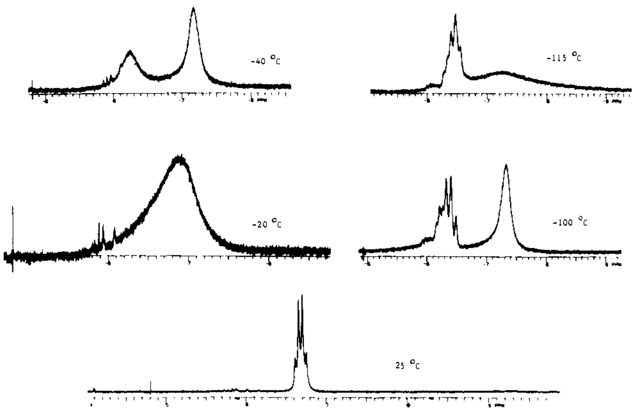

Figure 2. The variable temperature ^1H NMR spectra of **3** in CD_2Cl_2 at 400 MHz in the hydride region only.

molecules, it was found that the peak due to the two magnetically equivalent hydrogen atoms remained single down to temperatures of −155 °C.

The spectra obtained for **3** in CD_2Cl_2 at various temperatures are given in Figure 2. A quartet is observed for the resonance of the metal-bonded hydrogen atoms at room temperature which decoalesces at −20 °C and is resolved into two bumps of 2:3 intensity at δ −6.3 and −7.2, respectively, at −40 °C. The resonance at δ −6.3 is further resolved at −100 °C into what could be described as a quartet at δ −6.2 and a triplet at δ −6.4 with the single broad resonance at δ −7.3 remaining unchanged. At −115 °C the peak at δ −7.3 was beginning to decoalesce, but lower temperature spectra were unobtainable. This differs from the decoalescing pattern obtained for complex **1**, but it is similar to that obtained for complex **2**, probably, as explained below, for steric reasons.[2b]

The variable-temperature T_1 data for the metal-bonded hydrogen atoms in **1** in toluene-d_8 and CD_2Cl_2 and **3** in CD_2Cl_2 are listed in Table III. These results are also consistent with a nonclassical formulation for **1**. Although the minimum T_1, which is related to the correlation time τ_c, occurs, as expected, at different temperatures in the different solvents (ca. −20 °C in toluene-d_8 (138 ms) < −60 °C in CD_2Cl_2 (117 ms) ≤ −60 °C in acetone-d_6 (123 ms)[2b]), there is not a great deal of variation, and the average of 126 ms is well within the range (≤ 160 ms at 400 MHz) previously proposed[5] and generally accepted for a complex to be considered as containing a molecular hydrogen ligand.

The T_1 value obtained for **3** (552 ms) at room temperature is at least 350 ms greater than that obtained for **1** (196 ms). This is probably due to the difference in τ_c values between **1** and **3**, because this value for **3** with smaller tertiary phosphine ligands should be greater than that for **1**. A minimum T_1 value of 140 ms at 400 MHz is obtained for the resonance due to the three magnetically equivalent hydrogen atoms at −80 °C. This is within experimental error (generally believed to be 10–20% for these measurements) similar to the value obtained for **1** (126 ms) and for **2** (132 ms).[2b] It is interesting that a value of 70 ms at 250 MHz was used to classify $ReH_7(PPh_3)_2$ as containing nonclassical dihydrogen ligands.[5] Therefore, it would seem reasonable to conclude on this T_1 basis that these molecules, **1**, **2**, and **3**, all contain molecular hydrogen ligands.

X-ray Crystallography. An ORTEP drawing of **1** is given in Figure 3, and selected bond distances and angles are listed in Table II. Because the structure is rather irregular and thus difficult to visualize, a stereo pair representation is also given in Figure 4. The three Re–P distances for this complex are 0.13–0.17 Å shorter than those reported earlier in a partial structure determination of **1**,[12] although the unit cell parameters are similar, and the P–Re–P angles are equivalent within experimental error. The reason for the bond length differences is probably due to the fact that the positions of the atoms were not refined in the study reported earlier.

The ReP_3 group of atoms is not planar. The three PReP angles add up to only 349°, and the Re atom lies ca. 0.45 Å out of the plane defined by the three P atoms. Two of the metal-bonded hydrogen atoms are on the opposite side of this plane to the Re

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Table III. T_1 Measurements (ms) on $ReH_5(PPh_3)_3$, **1**, in Toluene-d_8 and CD_2Cl_2 and $ReH_5(PMe_2Ph)_3$, **3**, in CD_2Cl_2 at 400 MHz[a]

T (°C)	T_1 (ms)	δ (ppm)
	Complex **1** in Toluene-d_8	
25	173 [1]	−4.7, q (quartet), J = 18 H
0	144 [3]	−4.7, q, J = 18 Hz
−20	138 [3]	−4.7, q, J = 19 Hz
−40	152 [1]	−4.7, q, J = 18 Hz
−60	182 [1]	−4.7, br
−80	286 [7]	−4.7, br
−100	423 [15]	−4.5, br
	Complex **1** in CD_2Cl_2	
22	196 [1]	−5.3, q, J = 18 Hz
0	165 [2]	−5.3, q, J = 18 Hz
−20	136 [1]	−5.4, q, J = 16 Hz
−40	125 [0]	−5.4, br
−60	117 [1]	−5.0, br
−80	160 [1]	−5.1, br
−95	219 [2]	−5.0, br
	237 [4]	−7.3, br
−105	>300	−4.7, sh
	283 [0]	−4.9, br
	270 [0]	−5.4, br
	282 [1]	−7.4, br
	Complex **3** in CD_2Cl_2	
25	552 [9]	−6.7, q, J = 19 Hz
0	410 [2]	−6.7, br
−20	299 [3]	−6.9, br
−40	208 [8]	−6.3, br, 2 H
	218 [5]	−7.2, br, 3 H
−60	174 [3]	−6.3, br, 2 H
	171 [2]	−7.2, br, 3 H
−80	151 [2]	−6.3, br, 2 H
	140 [1]	−7.3, br, 3 H
−100	270 [3]	−6.2, q, J = 24 Hz, 1 H
	200 [5]	−6.4, t, J = 32 Hz, 1 H
	176 [9]	−7.3, br, 3 H
−110	334 [3]	−6.3, m, 1 H
	284 [6]	−6.4, m, 1 H
	257 [5]	−7.3, v br, 3 H
−115	460 [7]	−6.4, m, 1 H[b]
	476	−7.26, v br

[a] Numbers in [ ] indicate the variance obtained in the calculation of the mean T_1 values viz. $[(\sum\Delta_i^2)/n(n-1)]^{1/2}$. [b] The value for the multiplet on the left side of the peak at −6.4 was not determined, see Figure 2.

atom, and the remaining three are on the same side, which is less sterically hindered.

The overall core geometry of **1**, a distorted dodecahedron, is similar to that determined in the neutron study of **2**[6] and also to that of $ReH_5(PMe_2Ph)_3$, **3**, determined by X-ray diffraction, where unfortunately the metal-bonded hydrogen atoms were not found.[13] Furthermore, the relative orientations of the PPh_3 ligands in **1** are similar to those for the $PMePh_2$ groups in **2** which indicates similar crystal-packing forces. Previous X-ray studies on rhenium hydride complexes where such metal-bonded hydrogen atoms were located include $Re_2H_4(PMe_2Ph)_4[P(OCH_2)_3CEt]_2$[14] and $[Re_2(\mu\text{-}H)_3(PPh_3)_4(CN^tBu)_2]PF_6$.[15]

In the neutron structure of **2** two independent molecules constituted the asymmetric unit, and Table IV lists the values for various bonds and angles averaged for those two molecules along with the corresponding values obtained in the X-ray structure determination of **1**.

There is a much greater range of Re–H distances found in the X-ray structure of **1** as compared to those for **2** (1.43 (7)–1.73 (10) Å for **1** compared to 1.675 [3]–1.698 [3] Å in **2**). This is to be expected as X-ray estimations of metal–hydrogen distances are far less accurate than those determined via the neutron technique. However, the average Re–H distance in **1**, 1.54 [5] Å, is, after due allowance for the tendency of X-ray crystallography to give shortened X–H distances, similar to that in **2**, 1.688 [5] Å, as well as to those in K_2ReH_9, 1.68 (1) Å,[16] and also to the terminal ones in $Re_2H_8(PEt_2Ph)_4$, 1.669 (7) Å,[17] all of which were determined by neutron diffraction. The reasonable agreement between the values listed in Table IV provides a good measure of the accuracy of the structure of **1**, and thus we believe that the hydride positions are credible. The closest H–H distance of 1.60 (13) Å is too great to be associated with an H–H bond, and thus the $ReH_5(PPh_3)_3$ molecule in the crystal used in the structure determination is best described as containing only classical hydride ligands.

Table IV. Listing of Selected Distances and Angles in $ReH_5(PPh_3)_3$, **1**, and Corresponding Average Values in $ReH_5(PMePh_2)_3$, **2**[a]

	1	**2**
	Bond Distances	
H(1)–H(2)	1.70 (12)	1.99 [1]
H(1)–H(3)	1.78 (10)	1.852 [7]
H(3)–H(4)	2.10 (12)	2.03 [2]
H(3)–H(5)	1.60 (13)	2.053 [1]
H(4)–H(5)	1.85 (14)	1.827 [7]
H(1)–P(1)	2.20 (6)	2.496 [1]
H(1)–P(2)	2.31 (6)	2.493 [1]
H(2)–P(1)	2.82 (9)	2.648 [8]
H(2)–P(2)	2.44 (10)	2.824 [2]
H(2)–P(3)	2.38 (10)	2.444 [9]
H(3)–P(1)	2.70 (8)	2.90 [2]
H(3)–P(2)	2.66 (8)	2.72 [1]
H(4)–P(2)	2.63 (10)	2.47 [2]
H(4)–P(3)	2.53 (9)	2.670 [8]
H(5)–P(1)	2.34 (11)	2.409 [7]
H(5)–P(3)	2.80 (10)	2.71 [3]
P(1)–P(3)	3.853 (3)	3.65 [3]
P(2)–P(3)	3.893 (3)	3.73 [3]
	Bond Angles	
H(1)–Re–H(2)	70 (4)	72.0 [3]
H(1)–Re–H(3)	72 (4)	67.2 [4]
H(1)–Re–H(4)	138 (4)	130.6 [4]
H(1)–Re–H(5)	120 (5)	127.8 [6]
H(2)–Re–H(3)	140 (5)	139.1 [7]
H(2)–Re–H(4)	124 (5)	138.1 [5]
H(2)–Re–H(5)	149 (5)	135 [1]
H(3)–Re–H(4)	79 (4)	73.9 [6]
H(3)–Re–H(5)	65 (5)	75.4 [2]
H(4)–Re–H(5)	71 (5)	65.5 [5]
H(1)–Re–P(1)	65 (2)	74.2
H(1)–Re–P(2)	68 (2)	73.5 [7]
H(1)–Re–P(3)	140 (3)	142.8 [5]
H(2)–Re–P(1)	91 (4)	79.5 [1]
H(2)–Re–P(2)	74 (4)	85.7 [8]
H(2)–Re–P(3)	71 (4)	70.9 [3]
H(3)–Re–P(1)	84 (3)	90.1 [7]
H(3)–Re–P(2)	81 (3)	82.2 [6]
H(3)–Re–P(3)	148 (3)	150.1 [8]
H(4)–Re–P(1)	142 (3)	135.9 [5]
H(4)–Re–P(2)	77 (3)	72.2 [6]
H(4)–Re–P(3)	74 (3)	79.4 [2]
H(5)–Re–P(1)	71 (4)	70.9 [3]
H(5)–Re–P(2)	137 (4)	136.0 [3]
H(5)–Re–P(3)	90 (4)	81.3 [8]
P(1)–Re–P(2)	133.28 (7)	147.3 [8]
P(1)–Re–P(3)	107.43 (7)	100 [1]
P(2)–Re–P(3)	108.38 (7)	102.5 [9]

[a] Esd's of mean values are calculated as $\sigma = [(\sum\Delta_i^2)/n(n-1)]^{1/2}$.

The corresponding Re–P and P–P (see Table IV) distances in **1** are all significantly larger than those in **2** and **3**, and, there are

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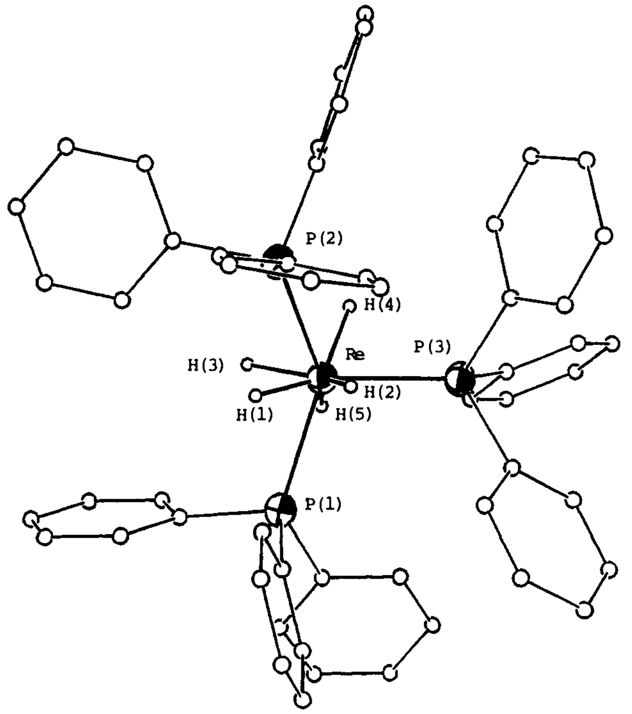

Figure 3. An ORTEP drawing of **1**. The ellipsoids represent thermal displacements and are drawn at the 50% probability level. Carbon atoms and the metal-bonded hydrogen atoms are represented by spheres of arbitrary size.

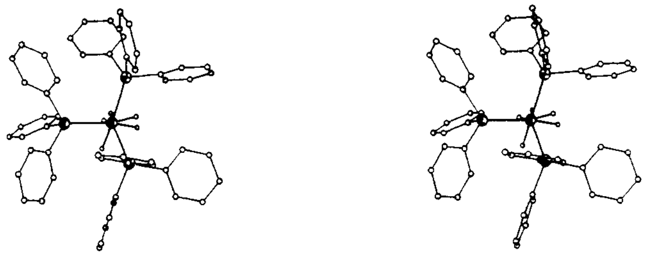

Figure 4. A stereopair representation of **1**.

important differences in their respective P–Re–P angles (107.43 (7)°, 108.38 (7)°, 133.28 (7)° in **1** to 100 [1]°, 102.5 [9]°, 147.3 [8]° in **2**, and 99.8(2)°, 101.9 (2)° and 149.5 (2)° in **3**). This may be attributed to steric interactions between the sterically bulkier pseudo-*cis*-PPh_3 ligands which would enlarge the P(1)ReP(3) and P(2)ReP(3) angles while making the P(1)ReP(2) angle smaller in **1** as compared to the other molecules.

Conclusions

The T_1 (min) values for **1**, **2**, and **3** are well within the generally accepted range used to suggest that a complex contains a molecular hydrogen ligand. These results are at variance with the structure of **1** determined by X-ray crystallography and the structure of **2** determined by neutron diffraction methods as containing only classical hydride ligands. Although, there is no way of proving that some crystals did not contain a molecular hydrogen ligand, we believe that the problem of classification resides with the vagaries of the T_1 analytical technique. Perhaps, in the case of these polyhydride complexes, where the number of metal-bonded hydrogen atoms is greater than two, the suggested upper limit (100 ms at 250 MHz) of the T_1 value used to predict η^2-H_2 ligands is too high. Furthermore, the fluxional process for the hydrogen atoms may involve temporary molecular hydrogen formation that would lower T_1 values. Thus, it remains for future experiments to determine if merely taking a lower value as the upper limit will maintain the validity of the T_1 criterion or whether the results of this technique, per se, should always be viewed skeptically. Our results, needless to say, raise questions about the correctness of the assignment of other rhenium polyhydride complexes, such as $ReH_7(PPh_3)_2$, as nonclassical by this technique.

It is interesting that the recently reported neutron structure[18] of ReH_7(dppe), dppe = $Ph_2PCH_2CH_2PPh_2$, assigned as Re(η^2-H_2)H_5(dppe) by the T_1 method,[5] contained no short H–H contacts that would justify the η^2-H_2 formulation.

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Supplementary Material Available: An ORTEP drawing of **1** showing the full atomic labeling scheme, a stereoview of the crystal packing of **1**, and tables listing the fractional atomic coordinates, bond distances and angles, and the anisotropic displacement parameters (18 pages); listings of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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Indole Diterpene Synthetic Studies. 5. Development of a Unified Synthetic Strategy; a Stereocontrolled, Second-Generation Synthesis of (–)-Paspaline

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Abstract: We record here a full account of a highly stereocontrolled, second-generation synthesis of (–)-paspaline (**1**). The synthesis proceeded via an initial nine-step conversion of (+)-Wieland–Miescher ketone to tricyclic cyclopentanone **5**, an intermediate that we anticipate will be useful for the construction of other members of this family of tremorgenic indole diterpene alkaloids. Completion of the synthetic scheme involved an eight-step transformation of **5** to **6**, the latter an advanced intermediate in our first total synthesis of paspaline (**1**).

In a recent paper,[1] we recorded a first-generation synthesis of (–)-paspaline (**1**),[2,3] the simplest member of a family of tremorgenic indole diterpenes. Notwithstanding the eventual success of this approach, considerable difficulty was encountered in

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