is possible (Figure 10) because in such complexes intramolecular S transfer following DMA insertion reactions cannot occur. This accounts for the stability and isolation of the cis–syn vinyl disulfide precursor of III (Figure 10; IIIb). The X-ray crystal structure of the latter has been reported.[30]

Additional support for the proposed vinyl disulfide intermediates in DMA insertion reactions is provided by detailed ^1H NMR studies of the reaction of the $[(Cp)(O)Mo^V(\mu\text{-}S)_2Mo^V(O)(S_2)]^-$ complex with DMA.[36] These reactions demonstrate that insertion into the coordinated S_2^{2-} ligand and formation of vinyl disulfide precedes the final formation of dithiolene. At elevated temperatures (~70 °C), in CH_3CN solution, the coordinated vinyl disulfide slowly converts to dithiolene. This conversion is rapid in the presence of catalytic amounts of elemental sulfur. Possible pathways for these transformations have been proposed previously.[36]

A similar pathway, involving vinyl disulfide intermediates, most likely is followed in reactions that lead to the synthesis of II and III (Figure 10). A particular pathway for the formation of I from the reaction of $[(S_4)_2Mo^{IV}(O)]^{2-}$ with DMA is not clear. It has not been possible to detect evidence for the dissociation of S_2 from the $[(S_4)_2Mo^{IV}(O)]^{2-}$ anion or for the presence of vinyl disulfide intermediates in the course of the reaction. At this stage other possible mechanisms such as cycloaddition to the coordinated S_4 ligand followed by elimination of S_2 cannot be ruled out.

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Supplementary Material Available: For I-III and V, Tables S1-S4, listing hydrogen coordinates, thermal parameters for all atoms, and detailed bond distances and angles (45 pages); listings of calculated and observed structure factors (52 pages). Ordering information is given on any current masthead page. The corresponding data for IV already have been deposited with the preliminary communication reporting on the structure of IV[24] and also can be found in ref 53.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure
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Solution and Solid-State Conformational Isomers of the Molecular Dihydrogen Complex $ReCl(H_2)(PMePh_2)_4$: Does It Contain an Asymmetric Molecular Dihydrogen Ligand?

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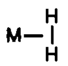
The complex $ReCl(H_2)(PMePh_2)_4$ with four $PMePh_2$ ligands in the equatorial plane and the Cl^- ligand trans to an $\eta^2\text{-}H_2$ ligand has been investigated by means of variable-temperature ^1H and $^{31}P(^1H)$ NMR spectroscopies in different solvents, namely, CD_2Cl_2, acetone-d_6, and toluene-d_8. In this crowded molecule metastable conformational isomers based on rotational orientations about the Re–P bonds can arise. The data obtained indicate that different percentages of conformational isomers are formed in the different solvents. The T_1(min) time of 92 ms at 400 MHz in CD_2Cl_2 is obtained for the metal-bonded H atoms in $ReCl(H_2)(PMePh_2)_4$. Structural data are reported for $ReCl(H_2)(PMePh_2)_4{\cdot}2C_4H_8O$ (**1a**) at 292 and 193 K, $ReCl(H_2)(PMePh_2)_4{\cdot}0.5(CH_3)_2CO$ (**1b**), and $ReCl(H_2)(PMePh_2)_4{\cdot}0.5(CH_3)_2CO$ (**1c**). These different crystalline forms were obtained under different crystallization conditions. Crystal data: compound **1a**, triclinic, space group $P\bar{1}$, $a = 12.287$ (3) Å, $b = 19.318$ (8) Å, $c = 12.275$ (3) Å, $\alpha = 101.06$ (3)°, $\beta = 104.42$ (2)°, $\gamma = 103.83$ (3)°, $V = 2640$ (4) Å^3, $Z = 2$, $T = 292$ K, $R = 0.055$ ($R_w = 0.073$) for 446 parameters and 5091 unique data having $F_o > 3\sigma(F_o)^2$; compound **1a**, triclinic, space group $P\bar{1}$, $a = 12.210$ (4) Å, $b = 19.269$ (9) Å, $c = 12.138$ (4) Å, $\alpha = 101.10$ (3)°, $\beta = 103.92$ (2)°, $\gamma = 104.13$ (3)°, $V = 2590$ (4) Å^3, $Z = 2$, $T = 193$ K, $R = 0.041$ ($R_w = 0.058$) for 449 parameters and 7334 unique data having $F_o > 3\sigma(F_o)^2$; compound **1b**, triclinic, space group $P\bar{1}$, $a = 13.044$ (3) Å, $b = 18.434$ (5) Å, $c = 11.701$ (4) Å, $\alpha = 94.12$ (3)°, $\beta = 113.44$ (2)°, $\gamma = 80.58$ (2)°, $V = 2547$ (2) Å^3, $Z = 2$, $T = 292$ K, $R = 0.046$ ($R_w = 0.063$) for 467 parameters and 6089 unique data having $F_o > 3\sigma(F_o)^2$; compound **1c**, triclinic, space group $P\bar{1}$, $a = 14.186$ (4) Å, $b = 17.317$ (4) Å, $c = 11.675$ (3) Å, $\alpha = 108.57$ (2)°, $\beta = 96.32$ (2)°, $\gamma = 76.39$ (2)°, $V = 2640$ (2) Å^3, $Z = 2$, $T = 292$ K, $R = 0.036$ ($R_w = 0.067$) for 487 parameters and 8763 unique data having $F_o > 3\sigma(F_o)^2$. In forms **1a** and **1b** the main molecule was ordered and the final difference maps revealed two electron density maxima near the Re atom and trans to the Cl^- ligand that could be representative of two H atoms bonded to the Re atom in an $\eta^1\text{-}H_2$ mode. For both data sets with form **1a** these H atoms failed to refine freely to reasonable parameters. However, the positions of these atoms from the difference maps are reported. In form **1b** the two H atoms were refined freely, which resulted in the following parameters: Re–H(1) = 1.49 (9) Å, Re–H(2) = 1.98 (9) Å, H(1)–H(2) = 1.17 (13) Å, Re–H(1)–H(2) = 95 (8)°, and Re–H(2)–H(1) = 48 (6)°. Form **1c** contains disorder between the trans Cl^- and $\eta\text{-}H_2$ ligands.

Introduction

Since the important discovery by Kubas[1] that the complex $W(\eta^2\text{-}H_2)(CO)_3(PCy_3)_2$, Cy = cyclohexyl, contains a molecular dihydrogen ligand, many other such complexes have been synthesized[2-15] and previously known complexes containing polyhydride ligands have been reassigned as containing molecular dihydrogen ligands.[16] Some of these latter reassignments have been based exclusively on the ^1H NMR longitudinal relaxation time (T_1)[16b] and we have since then pointed out several difficulties associated with this technique.[17] More recently, additional refinements to the interpretation of the T_1 results have been suggested.[18]

Previous structural results[8b,10,11b,12a,c] on the nature of the $\eta^2\text{-}H_2$ ligand have established so far a symmetrical arrangement with equal (within esd's) M–H distances. Theoretical calculations[19] do suggest that the symmetrical bonding mode $\eta^2\text{-}H_2$ (I) is



I

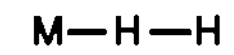


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Table I. Crystallographic Data for $ReCl(H_2)(PMePh_2)_4 \cdot 2C_4H_8O$ (**1a**) at 292 K and 193 K, $ReCl(H_2)(PMePh_2)_4 \cdot 0.5(CH_3)_2CO$ (**1b**), and $ReCl(H_2)(PMePh_2)_4 \cdot 0.5(CH_3)_2CO$ (**1c**)

	1a	**1a**	**1b**	**1c**
formula	$C_{52}H_{54}ClP_4Re \cdot 2C_4H_8O$	$C_{52}H_{54}ClP_4Re \cdot 2C_4H_8O$	$C_{52}H_{54}ClP_4Re \cdot 0.5(CH_3)_2CO$	$C_{52}H_{54}ClP_4Re \cdot 0.5(CH_3)_2CO$
fw	1168.8	1168.8	1053.60	1053.60
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	12.287 (3)	12.210 (4)	13.044 (3)	14.186 (4)
b, Å	19.318 (8)	19.269 (9)	18.434 (5)	17.317 (4)
c, Å	12.275 (3)	12.138 (4)	11.701 (4)	11.675 (3)
α, deg	101.06 (3)	101.10 (3)	94.12 (3)	108.57 (2)
β, deg	104.42 (2)	103.98 (2)	113.44 (2)	96.32 (2)
γ, deg	103.83 (3)	104.13 (3)	80.58 (2)	76.39 (2)
V, Å^3	2640 (4)	2590 (4)	2547 (2)	2640 (2)
Z	2	2	2	2
d_{calc}, g/cm^3	1.470	1.499	1.374	1.325
μ(Mo Kα), cm^{-1}	25.4	25.9	26.3	25.4
radiation monochromated/ in incident beam (λ, Å)	Mo Kα (λ_α = 0.71073 Å)		Mo Kα (λ_α = 0.71073 Å)	
temp, °C	19	−80	19	19
max, min transm factors, %	99.99, 50.00	99.99, 87.01	100.00, 84.52	99.90, 77.69
R^a	0.055	0.041	0.046	0.036
R_w	0.073^b	0.058^b	0.063^c	0.067^c

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/(\sigma^2\{|F_o| + 0.001|F_o|^2\}$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 0.4362/(\sigma^2\{|F_o| + 0.001|F_o|^2\}$ for **1b** and $w = 1/(\sigma^2\{|F_o| + 0.001|F_o|^2\}$ for **1c**.

preferable to the end-on or asymmetric bonding mode η^1-H_2 (II). It is only at very low temperatures on a Pd/H_2 system that IR evidence for η^1-H_2 was found, as indicated in various IR vibrational modes.[20]

In previous papers[5] we reported the preparation of $ReCl(H_2)(PMcPh_2)_4$ (**1**) and gave some preliminary results concerning its structure and NMR spectra. Since then we have been attempting to characterize **1** more thoroughly by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and X-ray and neutron diffraction. Since our preliminary results led to the conclusion that this compound contained a molecular dihydrogen ligand, that is, an η^2-H_2 complex, we were particularly interested in obtaining neutron diffraction data. Unfortunately, we were unable to do this because of technical problems and/or the unfortunate fact that form **1c** has the H_2 and Cl^- ligands disordered. However, we have obtained X-ray crystallographic data on three different forms (on one of them at two temperatures), and these together with more extensive NMR data give us further insight into the surprisingly complex behavior of this molecule, much of which appears to be due to the existence of metastable conformational isomers arising from different rotational orientations about the Re–P bonds. The X-ray results, especially for one crystal form (**1b**), support the presence of the η^2-H_2 ligand, albeit with an apparently unsymmetrical binding to the rhenium atom.

Experimental Section

General Data. All manipulations were carried out under an argon or dinitrogen atmosphere. The ^1H NMR spectra were recorded with a Varian XL-400 spectrometer. $^{31}P\{^1H\}$ NMR spectra, referenced externally to 85% H_3PO_4, were recorded at 162 MHz with a Varian XL-400 spectrometer. The complex $ReCl(H_2)(PMePh_2)_4$ (**1**) was synthesized according to the published procedure.[5b] The crystalline form **1a** was obtained by allowing methanol to diffuse into a THF solution of **1**.[5a] Form **1b** crystallized from a concentrated solution of **1** in acetone, and **1c** was obtained from diffusing hexanes into a solution of **1** in acetone. All crystals were obtained at ambient temperatures, and the different crystallizing conditions were employed in an attempt to get suitable crystals for neutron diffraction studies.

X-ray Crystallography. In all cases, crystals were mounted on top of glass fibers with 5-min epoxy resin. In the case of **1a**, two different crystals from the same batch were utilized. Accurate unit cell parameters were obtained by means of a least-squares analysis of 25 reflections. Intensity data on each compound were then collected by use of the general procedures for data collection as previously described.[21] All data sets were corrected for decay (except that for **1a**, which was collected at −80 °C), Lorentz, and polarization effects. In addition, absorption corrections were also made by using an empirical method based on nine ψ scans (χ = 0–360° every 10°) for χ values near 90°.[22] In all cases the heavy-atom positions were located from a three-dimensional Patterson function and then most of the non-H positions were revealed in a subsequent difference Fourier map. The positions of the remaining non-H atoms on the main molecule were found by alternating least-squares full-matrix cycles of refinement and difference Fourier maps for a cutoff ratio $F_o > 3\sigma(F_o)^2$ of 3. For this the Enraf-Nonius SDP software was employed.[23a]

The final refinements on all structures were carried out by using the SHELX-76 program with anisotropic thermal parameters for all the non-H atoms, excluding those that represented the various molecules of crystallization in forms **1a** at the two temperatures and **1b**. The disorder in **1c** was quite apparent, as there were significant amounts of electron density situated at the apical sites in the initial difference Fourier map. The exact amounts were determined by refining the site occupancies at

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Table II. Positional and Equivalent Isotropic Thermal Parameters and Their Esd's for $ReCl(H_2)(PMePh_2)_4 \cdot 2C_4H_8O$ (**1a**) at 292 K[a]

atom	*x*	*y*	*z*	*B*, Å^2
Re	0.20984 (4)	0.24691 (3)	0.39115 (4)	3.08 (1)
H(1)[b]	0.3536	0.3056	0.3992	2.0*
H(2)[b]	0.4286	0.3334	0.4413	2.0*
Cl	0.0092 (4)	0.1563 (2)	0.3556 (3)	6.0 (1)
P(1)	0.2757 (3)	0.2377 (2)	0.5882 (2)	3.50 (9)
P(2)	0.1146 (3)	0.3398 (2)	0.4442 (2)	3.50 (8)
P(3)	0.1843 (3)	0.2683 (2)	0.2003 (3)	3.9 (1)
P(4)	0.2498 (3)	0.1323 (2)	0.3104 (3)	4.3 (1)
C(11)	0.178 (1)	0.1655 (7)	0.6285 (9)	4.1 (4)
C(21)	−0.030 (1)	0.3248 (7)	0.3419 (9)	4.1 (4)
C(31)	0.311 (1)	0.2657 (8)	0.150 (1)	5.5 (5)
C(41)	0.144 (1)	0.0781 (7)	0.171 (1)	6.1 (5)
C(121)	0.3063 (7)	0.3164 (5)	0.7139 (6)	3.7 (3)
C(131)	0.4185 (8)	0.2206 (5)	0.6326 (9)	4.5 (4)
C(221)	0.1895 (7)	0.4377 (4)	0.4322 (8)	3.9 (4)
C(231)	0.0642 (7)	0.3445 (4)	0.5742 (7)	4.1 (4)
C(321)	0.1783 (6)	0.3602 (5)	0.1811 (7)	3.9 (4)
C(331)	0.0614 (8)	0.2128 (5)	0.0724 (6)	4.9 (4)
C(421)	0.2407 (6)	0.0576 (5)	0.3874 (7)	3.9 (4)
C(431)	0.390 (1)	0.1354 (6)	0.2808 (9)	2.9 (5)
O(1)	0.5786	0.3244	0.0660	24*
C(1)	0.6205	0.3242	−0.0498	24*
C(2)	0.7511	0.3712	0.0475	24*
C(3)	0.7495	0.3887	0.1468	24*
C(4)	0.7111	0.2943	0.0987	24*
O(2)	0.7887	0.9826	0.1731	29*
C(5)	0.7747	1.0189	0.1371	29*
C(6)	0.6058	0.9604	0.0948	29*
C(7)	0.6370	0.8726	0.0560	29*
C(8)	0.7841	0.9126	0.1266	29*

[a] *B* values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^*B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. Starred *B* values are those of atoms that were refined isotropically. [b] H atoms were inserted at positions determined in a difference Fourier map and were not refined. The isotropic thermal parameters for these H atoms were fixed at 2 Å^2.

Table III. Positional and Equivalent Isotropic Thermal Parameters and Their Esd's for $ReCl(H_2)(PMePh_2)_4 \cdot 2C_4H_8O$ (**1a**) at 193 K[a]

atom	*x*	*y*	*z*	*B*, Å^2
Re	0.20851 (2)	0.24658 (1)	0.38910 (2)	2.334 (7)
H(1)[b]	0.3447	0.3055	0.4096	2.0*
H(2)[b]	0.4253	0.3237	0.4271	2.0*
Cl	0.0061 (2)	0.1554 (1)	0.3545 (2)	4.42 (6)
P(1)	0.2747 (1)	0.23802 (9)	0.5881 (1)	2.53 (4)
P(2)	0.1136 (2)	0.3400 (1)	0.4432 (1)	2.54 (4)
P(3)	0.1821 (2)	0.2682 (1)	0.1978 (2)	3.04 (5)
P(4)	0.2484 (2)	0.1318 (1)	0.3083 (2)	3.27 (5)
C(11)	0.1772 (6)	0.1662 (4)	0.6297 (6)	3.1 (2)
C(21)	−0.0330 (6)	0.3250 (4)	0.3404 (6)	3.1 (2)
C(31)	0.3107 (8)	0.2659 (5)	0.1452 (7)	4.5 (3)
C(41)	0.1390 (9)	0.0757 (4)	0.1676 (7)	4.8 (3)
C(121)	0.3078 (4)	0.3188 (3)	0.7155 (4)	2.6 (2)
C(131)	0.4189 (4)	0.2210 (3)	0.6347 (5)	3.3 (2)
C(221)	0.1889 (4)	0.4392 (2)	0.4618 (4)	2.9 (2)
C(231)	0.0649 (4)	0.3463 (2)	0.5772 (4)	2.6 (2)
C(321)	0.1765 (3)	0.3608 (3)	0.1781 (4)	2.9 (2)
C(331)	0.0578 (5)	0.2099 (3)	0.0675 (3)	3.6 (2)
C(421)	0.2422 (3)	0.0578 (3)	0.3879 (4)	3.2 (2)
C(431)	0.3886 (6)	0.1352 (4)	0.2733 (6)	4.9 (3)
O(1)	−0.7417	−0.3837	−0.1400	17*
C(1)	−0.7692	−0.3639	−0.0388	17*
C(2)	−0.6427	−0.3389	0.0449	17*
C(3)	−0.5712	−0.3090	−0.0180	17*
C(4)	−0.6139	−0.3415	−0.1224	17*
O(2)	−0.7926	0.0292	−0.1760	17*
C(5)	−0.7440	0.1180	−0.1107	17*
C(6)	−0.6104	0.1168	−0.0684	17*
C(7)	−0.6405	0.0268	−0.0988	17*
C(8)	−0.7745	−0.0285	−0.1327	17*

[a] B values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. Starred *B* values are those of atoms that were refined isotropically. [b] H atoms were inserted at fixed positions determined in a difference Fourier map and were not refined. The isotropic thermal parameters for these H atoms were fixed at 2 Å^2.

Table IV. Positional and Equivalent Isotropic Thermal Parameters and Their Esd's for $ReCl(H_2)(PMePh_2)_4 \cdot 0.5(CH_3)_2CO$ (**1b**)[a]

atom	*x*	*y*	*z*	*B*, Å^2
Re	0.03604 (3)	0.22279 (2)	0.22092 (3)	2.258 (9)
H(1)	0.042 (7)	0.168 (5)	0.123 (8)	4 (2)*
H(2)	0.082 (8)	0.118 (5)	0.191 (8)	5 (2)*
Cl	0.0234 (2)	0.3103 (1)	0.3927 (2)	3.99 (7)
P(1)	−0.1406 (2)	0.1773 (1)	0.1513 (2)	2.68 (6)
P(2)	0.2199 (2)	0.2535 (1)	0.2612 (2)	3.16 (7)
P(3)	0.1129 (2)	0.1372 (1)	0.3961 (2)	2.68 (6)
P(4)	−0.0594 (2)	0.3304 (1)	0.0881 (2)	2.98 (7)
C(11)	−0.2131 (8)	0.1742 (5)	−0.0198 (8)	3.5 (3)
C(21)	0.234 (1)	0.2917 (7)	0.408 (1)	5.6 (4)
C(31)	0.0715 (8)	0.1350 (6)	0.4745 (8)	3.6 (3)
C(41)	−0.0034 (9)	0.4156 (5)	0.154 (1)	4.0 (3)
C(121)	−0.1398 (5)	0.0775 (3)	0.1709 (5)	2.8 (2)
C(131)	−0.2582 (4)	0.2170 (4)	0.1982 (5)	3.6 (3)
C(221)	0.2386 (6)	0.3181 (4)	0.1593 (7)	4.0 (3)
C(231)	0.3252 (6)	0.1759 (4)	0.2475 (5)	3.2 (3)
C(321)	0.2399 (6)	0.1514 (4)	0.5362 (7)	3.3 (3)
C(331)	0.1536 (5)	0.0395 (3)	0.3673 (5)	2.9 (2)
C(421)	−0.2093 (7)	0.3627 (5)	0.0543 (7)	4.4 (3)
C(431)	−0.0630 (7)	0.3305 (3)	−0.0711 (6)	3.2 (3)
C(1)	0.202 (3)	0.491 (2)	0.504 (3)	10.8 (5)*
C(2)	0.133 (2)	0.473 (2)	0.553 (3)	10.8 (5)*
C(3)	0.175 (3)	0.426 (2)	0.649 (3)	10.8 (5)*
C(4)	0.024 (3)	0.503 (3)	0.504 (5)	10.8 (5)*

[a] *B* values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. Starred *B* values are those for atoms that were refined isotropically.

both sites with the total sum constrained to unity. In all structures H atoms were calculated and inserted for the methyl and the phenyl C atoms. The methyl and phenyl groups were refined as rigid bodies, and the isotropic thermal parameters of the H atoms on all methyl groups and those on the phenyl groups were constrained to two different values, which were refined.

At this stage with form **1a** electron density that could be interpreted as two THF molecules was evident in the difference Fourier maps. In each case one atom was arbitrarily chosen to be an O atom. For **1a** at 19 °C the isotropic thermal parameters for each THF molecule were constrained to different values, which were refined. With **1a** at −80 °C the isotropic thermal parameters for both THF molecules were constrained to the same value, which was refined. Additionally, some constraints were added by using the DFIX program[23b] to maintain reasonable bond distances for the THF molecules. With **1b** and **1c** the difference Fourier maps revealed electron density maxima that could be interpreted as representing acetone molecules. These were arbitrarily represented by four C atoms in the case of **1b**, and for **1c** the different bond lengths justified an O atom assignment. These molecules had reasonable thermal parameters when their site occupancies were adjusted down to 50%, and thus in these cases the formulae consisted of $ReCl(H_2)(PMePh_2)_4 \cdot 0.5(CH_3)_2CO$.

The difference Fourier maps for both data sets of **1a** and that of **1b** at this stage revealed two electron density peaks that could be interpreted as two H atoms. For both data sets of **1a** these peaks did not refine to reasonable parameters as H atoms. In the final cycles of refinement to convergence they were simply inserted at fixed positions with fixed isotropic thermal parameters. However, with **1b** the two positions were refined freely as H atoms with isotropic thermal parameters. Some final crystallographic data are outlined in Table I. Positional parameters and selected bond distances and angles are given in Tables II–IX.

Results and Discussion

^1H and $^{31}P\{^1H\}$ NMR Results. We had previously published the variable-temperature ^1H NMR spectra for **1** in CD_2Cl_2 at 200 MHz and the variable-temperature $^{31}P\{^1H\}$ NMR spectra for **1** in CH_2Cl_2 at 81 MHz.[5b] The ^1H NMR spectra consisted of a quintet at room temperature, and this changed into a broad bump as the temperature was lowered. The $^{31}P\{^1H\}$ NMR spectra did suggest, due to the complex pattern observed at −90 °C, that there

Table V. Positional and Equivalent Isotropic Thermal Parameters and Their Esd's for $ReCl(H_2)(PMePh_2)_4{\cdot}0.5(CH_3)_2CO$ (**1c**)[a]

atom	x	y	z	B, Å^2
Re	0.26046 (1)	0.24371 (1)	0.24173 (2)	1.998 (6)
Cl(1)[b]	0.3767 (2)	0.1832 (2)	0.0659 (3)	3.05 (7)
Cl(2)[c]	0.1437 (2)	0.3050 (2)	0.4193 (3)	3.36 (7)
P(1)	0.14273 (9)	0.15701 (9)	0.1494 (1)	2.54 (3)
P(2)	0.3558 (1)	0.34206 (8)	0.3673 (1)	2.49 (3)
P(3)	0.3584 (1)	0.13265 (8)	0.3163 (1)	2.49 (3)
P(4)	0.1852 (1)	0.34232 (8)	0.1321 (1)	2.43 (3)
C(11)	0.0966 (4)	0.1192 (4)	0.2565 (5)	3.5 (2)
C(21)	0.2841 (4)	0.4463 (3)	0.4408 (5)	3.2 (1)
C(31)	0.4907 (4)	0.1168 (4)	0.2969 (5)	3.2 (1)
C(41)	0.1688 (4)	0.2931 (4)	−0.0316 (5)	3.1 (1)
C(121)	0.0235 (3)	0.2067 (2)	0.0968 (3)	3.0 (1)
C(131)	0.1720 (3)	0.0625 (2)	0.0184 (4)	3.1 (1)
C(221)	0.4548 (3)	0.3689 (2)	0.3060 (4)	2.8 (1)
C(231)	0.4187 (2)	0.3240 (2)	0.5076 (3)	3.0 (1)
C(321)	0.3480 (3)	0.0231 (2)	0.2387 (3)	2.9 (1)
C(331)	0.3538 (2)	0.1342 (2)	0.4758 (3)	2.8 (1)
C(421)	0.2529 (2)	0.4190 (2)	0.1184 (3)	2.9 (1)
C(431)	0.0658 (2)	0.4122 (3)	0.1722 (3)	2.6 (1)
O	0.1725 (9)	0.7523 (9)	0.359 (1)	7.1 (4)
C(1)	0.034 (2)	0.715 (1)	0.345 (2)	9.4 (8)
C(2)	0.128 (1)	0.728 (1)	0.408 (2)	6.3 (5)
C(3)	0.151 (2)	0.696 (1)	0.509 (2)	8.9 (8)

[a] B values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. [b] Atom refined at 51% occupancy. [c] Atom refined at 49% occupancy.

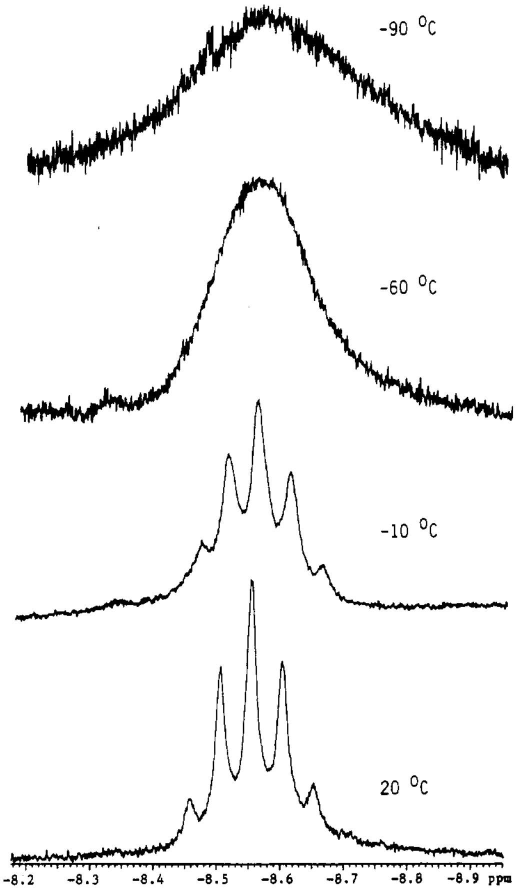

Figure 1. Variable-temperature ^1H NMR spectra in the hydride region only of $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$ (**1**) in toluene-d_8 at 400 MHz.

was magnetic inequivalence of the four P atoms at these temperatures which might be due to restricted rotation about the Re–P bond or the P–C(Ph) bonds.

Here, in an expanded study of these effects, the ^1H NMR variable-temperature spectra, in the hydride region only, for **1** at 400 MHz is presented in toluene-d_8, acetone-d_6, and CD_2Cl_2 as Figures 1–3, respectively. At ambient temperatures the spectra all consisted of a quintet due to coupling by the metal-bonded H atoms to the four P atoms. Subsequently, the spectra all coalesce

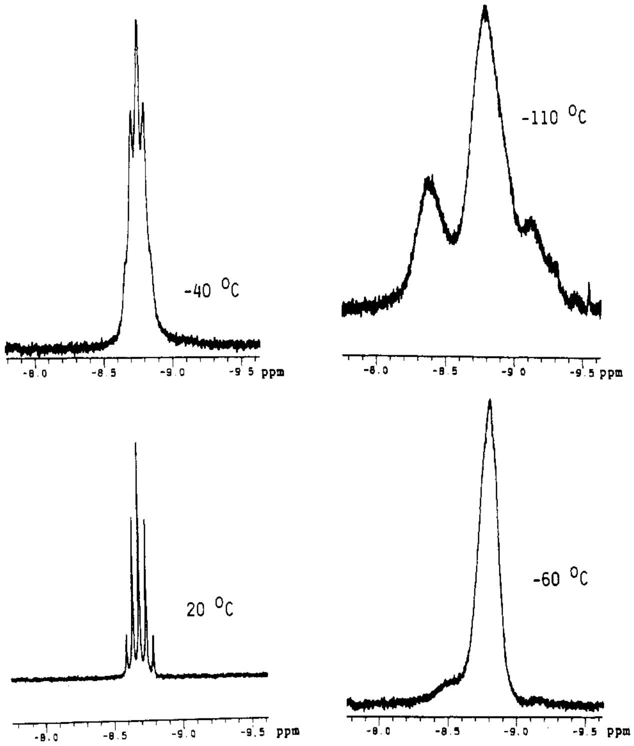

Figure 2. Variable-temperature ^1H NMR spectra in the hydride region only of $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$ (**1**) in acetone-d_6 at 400 MHz.

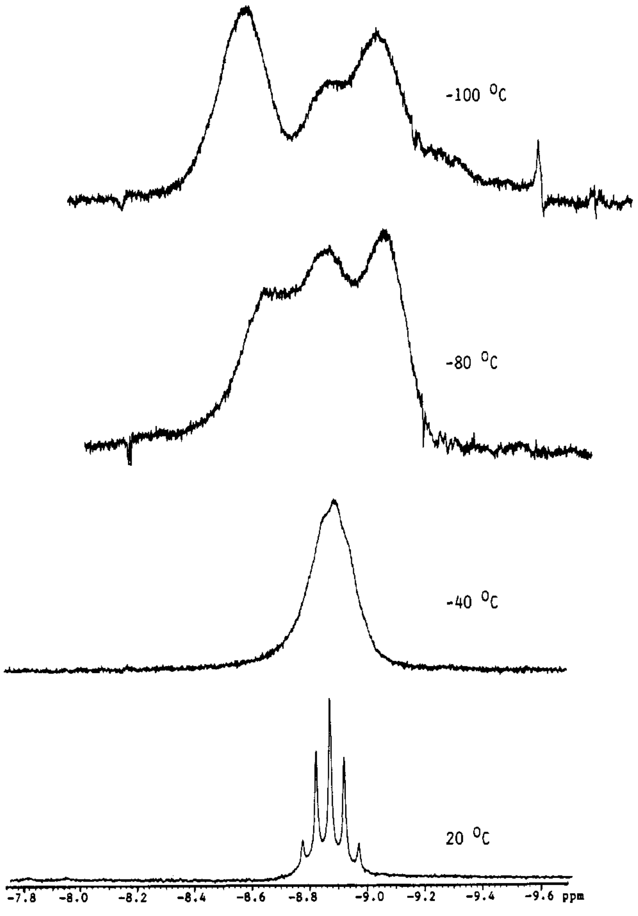

Figure 3. Variable-temperature ^1H NMR spectra in the hydride region only of $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$ (**1**) in CD_2Cl_2 at 400 MHz.

Table VI. Selected Bond Distances and Angles for $ReCl(H_2)(PMePh_2)_4{\cdot}2C_4H_8O$ (**1a**) at 292 K[a]

Bond Distances (Å)			
Re–H(1)	1.83	P(3)–C(321)	1.851 (11)
Re–H(2)	2.65	P(3)–C(331)	1.815 (7)
Re–Cl	2.538 (4)	P(4)–C(41)	1.807 (11)
Re–P(1)	2.407 (3)	P(4)–C(421)	1.867 (10)
Re–P(2)	2.439 (4)	P(4)–C(431)	1.837 (15)
Re–P(3)	2.414 (3)	O(1)–C(1)	1.629
Re–P(4)	2.459 (4)	O(1)–C(4)	1.835
H(1)–H(2)	0.91	C(1)–C(2)	1.661
P(1)–C(11)	1.841 (13)	C(2)–C(3)	1.207
P(1)–C(121)	1.837 (8)	C(3)–C(4)	1.712
P(1)–C(131)	1.831 (11)	O(2)–C(5)	0.925
P(2)–C(21)	1.818 (11)	O(2)–C(8)	1.345
P(2)–C(221)	1.838 (8)	C(5)–C(6)	1.993
P(2)–C(231)	1.844 (10)	C(6)–C(7)	1.828
P(3)–C(31)	1.83 (2)	C(7)–C(8)	1.706
Bond Angles (deg)			
H(1)–Re–Cl	172.94	Re–P(2)–C(21)	114.0 (4)
H(1)–Re–P(1)	93.69	Re–P(2)–C(221)	119.3 (3)
H(1)–Re–P(2)	100.93	Re–P(2)–C(231)	119.6 (3)
H(1)–Re–P(3)	75.09	C(21)–P(2)–C(221)	102.7 (5)
H(1)–Re–P(4)	93.29	C(21)–P(2)–C(231)	95.4 (5)
H(2)–Re–Cl	174.2	C(221)–P(2)–C(231)	101.9 (4)
H(2)–Re–P(1)	84.06	Re–P(3)–C(31)	112.2 (5)
H(2)–Re–P(2)	99.88	Re–P(3)–C(321)	119.6 (3)
H(2)–Re–P(3)	84.76	Re–P(3)–C(331)	123.5 (3)
H(2)–Re–P(4)	95.25	C(31)–P(3)–C(321)	97.4 (6)
Cl–Re–P(1)	91.3 (1)	C(31)–P(3)–C(331)	102.5 (5)
Cl–Re–P(2)	83.8 (1)	C(321)–P(3)–C(331)	97.3 (4)
Cl–Re–P(3)	99.8 (1)	Re–P(4)–C(41)	113.5 (6)
Cl–Re–P(4)	81.5 (1)	Re–P(4)–C(421)	120.1 (3)
P(1)–Re–P(2)	93.2 (1)	Re–P(4)–C(431)	120.7 (4)
P(1)–Re–P(3)	168.7 (1)	C(41)–P(4)–C(421)	97.8 (5)
P(1)–Re–P(4)	92.5 (1)	C(41)–P(4)–C(431)	101.5 (7)
P(2)–Re–P(3)	90.4 (1)	C(421)–P(4)–C(431)	99.3 (5)
P(2)–Re–P(4)	164.3 (1)	C(1)–C(1)–C(4)	76.28
P(3)–Re–P(4)	86.8 (1)	O(1)–C(1)–C(2)	83.09
Re–H(1)–H(2)	150.34	C(1)–C(2)–C(3)	114.67
Re–H(2)–H(1)	19.91	C(2)–C(3)–C(4)	70.45
Re–P(1)–C(11)	116.5 (3)	O(1)–C(4)–C(3)	70.29
Re–P(1)–C(121)	121.3 (3)	C(5)–O(2)–C(8)	130.00
Re–P(1)–C(131)	116.1 (4)	O(2)–C(5)–C(6)	84.27
C(11)–P(1)–C(121)	99.6 (5)	C(5)–C(6)–C(7)	92.58
C(11)–P(1)–C(131)	103.0 (6)	C(6)–C(7)–C(8)	92.09
C(121)–P(1)–C(131)	96.8 (4)	O(2)–C(8)–C(7)	101.78

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

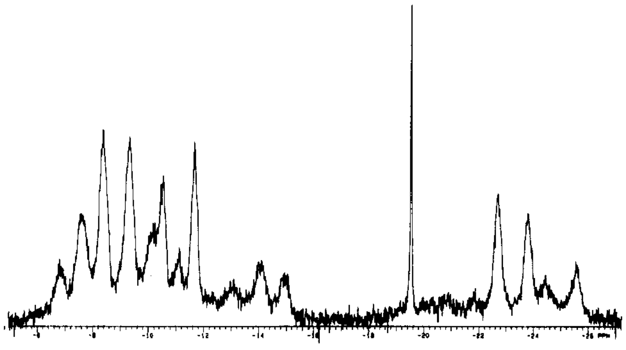

Figure 4. $^{31}P\{^1H\}$ NMR spectrum of $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$ (**1**) in toluene at −85 °C and at 162 MHz.

into a broad bump, which, in the case of toluene-d_8 (Figure 1), is maintained down to the lowest temperatures measured. However, in the case of acetone-d_6 and CD_2Cl_2, other resonances appear at the lowest temperatures. These we attribute to resonances from the molecular dihydrogen ligand that are bonded to different conformational forms of **1**. Furthermore, it is interesting that different solvents produce different amounts of these rotamers. This is not surprising, since these solvents would each have different viscosities at a given temperature and different steric approaches to the molecule of **1**.

Table VII. Selected Bond Distances and Angles for $ReCl(H_2)(PMePh_2)_4{\cdot}2C_4H_8O$ (**1a**) at 193 K[a]

Bond Distances (Å)			
Re–H(1)	1.697 (0)	P(3)–C(321)	1.857 (5)
Re–H(2)	2.577 (0)	P(3)–C(331)	1.840 (4)
Re–Cl	2.539 (2)	P(4)–C(41)	1.829 (7)
Re–P(1)	2.404 (2)	P(4)–C(421)	1.864 (6)
Re–P(2)	2.437 (2)	P(4)–C(431)	1.848 (8)
Re–P(3)	2.395 (2)	O(1)–C(1)	1.358 (0)
Re–P(4)	2.451 (2)	O(1)–C(4)	1.513 (0)
H(1)–H(2)	0.915 (0)	C(1)–C(2)	1.529 (0)
P(1)–C(11)	1.825 (8)	C(2)–C(3)	1.385 (0)
P(1)–C(121)	0.854 (4)	C(3)–C(4)	1.219 (0)
P(1)–C(131)	1.843 (6)	O(2)–C(5)	1.631 (0)
P(2)–C(21)	1.836 (7)	O(2)–C(8)	1.359 (0)
P(2)–C(221)	1.849 (5)	C(5)–C(6)	1.594 (0)
P(2)–C(231)	1.853 (5)	C(6)–C(7)	1.630 (0)
P(3)–C(31)	1.837 (10)	C(7)–C(8)	1.622 (0)
Bond Angles (deg)			
H(1)–Re–H(2)	6.84 (0)	Re–P(2)–C(21)	114.3 (3)
H(1)–Re–Cl	178.29 (5)	Re–P(2)–C(221)	120.1 (2)
H(1)–Re–P(1)	89.08 (4)	Re–P(2)–C(231)	119.7 (2)
H(1)–Re–P(2)	97.68 (4)	C(21)–P(2)–C(221)	102.4 (3)
H(1)–Re–P(3)	79.89 (4)	C(21)–P(2)–C(231)	95.8 (3)
H(1)–Re–P(4)	96.83 (5)	C(221)–P(2)–C(231)	100.5 (2)
H(2)–Re–Cl	171.97 (6)	Re–P(3)–C(31)	112.1 (3)
H(2)–Re–P(1)	85.25 (4)	Re–P(3)–C(321)	119.9 (2)
H(2)–Re–P(2)	103.52 (4)	Re–P(3)–C(331)	123.1 (2)
H(2)–Re–P(3)	83.62 (4)	C(31)–P(3)–C(321)	97.1 (4)
H(2)–Re–P(4)	91.32 (5)	C(31)–P(3)–C(331)	101.8 (3)
Cl–Re–P(1)	91.41 (6)	C(321)–P(3)–C(331)	98.4 (2)
Cl–Re–P(2)	83.93 (7)	Re–P(4)–C(41)	113.2 (3)
Cl–Re–P(3)	99.58 (6)	Re–P(4)–C(421)	120.3 (2)
Cl–Re–P(4)	81.51 (7)	Re–P(4)–C(431)	120.6 (2)
P(1)–Re–P(2)	93.08 (6)	C(41)–P(4)–C(421)	98.1 (3)
P(1)–Re–P(3)	168.86 (6)	C(41)–P(4)–C(431)	101.2 (4)
P(1)–Re–P(4)	92.44 (7)	C(421)–P(4)–C(431)	99.6 (3)
P(2)–Re–P(3)	89.90 (7)	C(1)–O(1)–C(4)	109.40 (0)
P(2)–Re–P(4)	164.54 (6)	O(1)–C(1)–C(2)	96.77 (0)
P(3)–Re–P(4)	87.44 (7)	C(1)–C(2)–C(3)	105.19 (0)
Re–H(1)–H(2)	160.40 (1)	C(2)–C(3)–C(4)	110.07 (0)
Re–H(2)–H(1)	12.76 (1)	O(1)–C(4)–C(3)	106.38 (0)
Re–P(1)–C(11)	116.5 (2)	C(5)–O(2)–C(8)	129.36 (0)
Re–P(1)–C(121)	121.1 (2)	O(2)–C(5)–C(6)	92.29 (0)
Re–P(1)–C(131)	117.0 (2)	C(5)–C(6)–C(7)	96.69 (0)
C(11)–P(1)–C(121)	100.3 (3)	C(6)–C(7)–C(8)	122.34 (0)
C(11)–P(1)–C(131)	102.4 (3)	O(2)–C(8)–C(7)	77.78 (0)
C(121)–P(1)–C(131)	95.8 (2)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

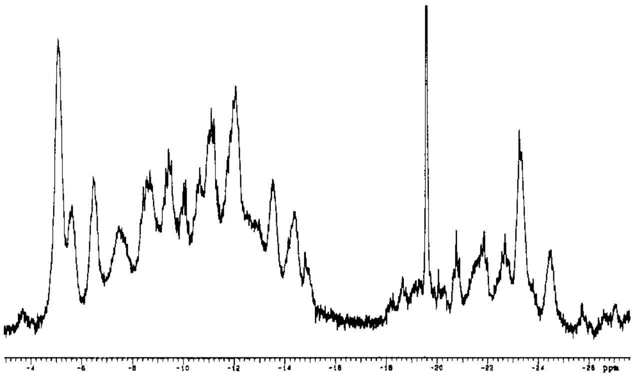

Figure 5. $^{31}P\{^1H\}$ NMR spectrum of $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$ (**1**) in acetone at −90 °C and at 162 MHz.

The low-temperature $^{31}P(^1H)$ NMR spectra displayed as Figure 4 for **1** in toluene at −85 °C and Figure 5 for **1** in acetone at −90 °C obtained at 162 MHz are also quite complex, and their patterns differ not only from each other but from the previously published $^{31}P\{^1H\}$ NMR spectra of **1** in CD_2Cl_2 at 81 MHz.[5b] Some of the differences from the latter may be related to the different field strengths used to obtain the spectra, but in general, these differences provide additional evidence that the different resonances

Table VIII. Selected Bond Distances and Angles for $ReCl(H_2)(PMePh_2)_4{\cdot}0.5(CH_3)_2CO$ (**1b**)[a]

Bond Distances (Å)			
Re–H(1)	1.49 (9)	P(2)–C(221)	1.851 (9)
Re–H(2)	1.98 (9)	P(2)–C(231)	1.859 (7)
Re–Cl	2.526 (3)	P(3)–C(31)	1.823 (12)
Re–P(1)	2.391 (2)	P(3)–C(321)	1.850 (6)
Re–P(2)	2.409 (3)	P(3)–C(331)	1.838 (6)
Re–P(3)	2.451 (2)	P(4)–C(41)	1.830 (10)
Re–P(4)	2.449 (2)	P(4)–C(421)	1.837 (9)
H(1)–H(2)	1.17 (13)	P(4)–C(431)	1.844 (8)
P(1)–C(11)	1.844 (8)	C(1)–C(2)	1.34 (6)
P(1)–C(121)	1.869 (7)	C(2)–C(3)	1.34 (5)
P(1)–C(131)	1.853 (7)	C(2)–C(4)	1.34 (5)
P(2)–C(21)	1.765 (11)		
Bond Angles (deg)			
H(1)–Re–H(2)	36 (4)	Re–P(1)–C(131)	124.2 (2)
H(1)–Re–Cl	177 (4)	C(11)–P(1)–C(121)	94.2 (4)
H(1)–Re–P(1)	77 (4)	C(11)–P(1)–C(131)	101.7 (4)
H(1)–Re–P(2)	93 (4)	C(121)–P(1)–C(131)	99.5 (3)
H(1)–Re–P(3)	97 (4)	Re–P(2)–C(21)	117.5 (5)
H(1)–Re–P(4)	99 (3)	Re–P(2)–C(221)	120.9 (2)
H(2)–Re–Cl	141 (3)	Re–P(2)–C(231)	115.4 (3)
H(2)–Re–P(1)	79 (3)	C(21)–P(2)–C(221)	99.9 (5)
H(2)–Re–P(2)	93 (3)	C(21)–P(2)–C(231)	102.8 (4)
H(2)–Re–P(3)	61 (3)	C(221)–P(2)–C(231)	96.8 (4)
H(2)–Re–P(4)	135 (3)	Re–P(3)–C(31)	113.3 (3)
Cl–Re–P(1)	101.38 (9)	Re–P(3)–C(321)	121.4 (3)
Cl–Re–P(2)	89.44 (9)	Re–P(3)–C(331)	118.9 (2)
Cl–Re–P(3)	80.35 (8)	C(31)–P(3)–C(321)	97.4 (4)
Cl–Re–P(4)	83.62 (8)	C(31)–P(3)–C(331)	103.4 (4)
P(1)–Re–P(2)	169.18 (9)	C(321)–P(3)–C(331)	98.7 (3)
P(1)–Re–P(3)	89.65 (8)	Re–P(4)–C(41)	114.0 (3)
P(1)–Re–P(4)	89.14 (8)	Re–P(4)–C(421)	119.2 (3)
P(2)–Re–P(3)	92.18 (8)	Re–P(4)–C(431)	119.9 (2)
P(2)–Re–P(4)	92.11 (9)	C(41)–P(4)–C(421)	98.6 (4)
P(3)–Re–P(4)	163.36 (9)	C(41)–P(4)–C(431)	102.3 (5)
Re–H(1)–H(2)	95 (8)	C(421)–P(4)–C(431)	99.4 (4)
Re–H(2)–H(1)	48 (6)	C(1)–C(2)–C(3)	119 (3)
Re–P(1)–C(11)	113.3 (4)	C(1)–C(2)–C(4)	118 (4)
Re–P(1)–C(121)	118.7 (2)	C(3)–C(2)–C(4)	123 (5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table IX. Selected Bond Distances and Angles for $ReCl(H_2)(PMePh_2)_4{\cdot}0.5(CH_3)_2CO$ (**1c**)[a]

Bond Distances (Å)			
Re–Cl(1)	2.568 (3)	P(2)–C(231)	1.858 (4)
Re–Cl(2)	2.587 (3)	P(3)–C(31)	1.860 (6)
Re–P(1)	2.441 (1)	P(3)–C(321)	1.857 (4)
Re–P(2)	2.436 (1)	P(3)–C(331)	1.862 (4)
Re–P(3)	2.435 (1)	P(4)–C(41)	1.842 (5)
Re–P(4)	2.435 (1)	P(4)–C(421)	1.865 (4)
P(1)–C(11)	1.823 (8)	P(4)–C(431)	1.845 (3)
P(1)–C(121)	1.845 (4)	O–C(2)	1.13 (3)
P(1)–C(131)	1.848 (3)	C(1)–C(2)	1.48 (3)
P(2)–C(21)	1.836 (5)	C(2)–C(3)	1.43 (3)
P(2)–C(221)	1.854 (5)		
Bond Angles (deg)			
Cl(1)–Re–Cl(2)	180.00 (0)	Re–P(2)–C(21)	114.5 (2)
Cl(1)–Re–P(1)	96.05 (7)	Re–P(2)–C(221)	122.1 (1)
Cl(1)–Re–P(2)	95.46 (7)	Re–P(2)–C(231)	119.1 (2)
Cl(1)–Re–P(3)	84.32 (8)	C(21)–P(2)–C(221)	100.9 (2)
Cl(1)–Re–P(4)	83.70 (7)	C(21)–P(2)–C(231)	96.2 (2)
Cl(2)–Re–P(1)	84.12 (7)	C(221)–P(2)–C(231)	99.5 (2)
Cl(2)–Re–P(2)	84.37 (8)	Re–P(3)–C(31)	113.3 (2)
Cl(2)–Re–P(3)	95.68 (8)	Re–P(3)–C(321)	119.5 (1)
Cl(2)–Re–P(4)	96.31 (8)	Re–P(3)–C(331)	121.5 (1)
P(1)–Re–P(2)	168.49 (5)	C(31)–P(3)–C(321)	96.8 (2)
P(1)–Re–P(3)	90.25 (5)	C(31)–P(3)–C(331)	102.6 (2)
P(1)–Re–P(4)	90.80 (5)	C(321)–P(3)–C(331)	99.0 (2)
P(2)–Re–P(3)	91.00 (5)	Re–P(4)–C(41)	113.6 (2)
P(2)–Re–P(4)	90.35 (5)	Re–P(4)–C(421)	119.6 (1)
P(3)–Re–P(4)	168.01 (5)	Re–P(4)–C(431)	121.5 (2)
Re–P(1)–C(11)	113.1 (2)	C(41)–P(4)–C(421)	95.9 (3)
Re–P(1)–C(121)	118.4 (2)	C(41)–P(4)–C(431)	102.5 (2)
Re–P(1)–C(131)	121.9 (2)	C(421)–P(4)–C(431)	99.4 (2)
C(11)–P(1)–C(121)	96.5 (2)	O–C(2)–C(1)	113 (2)
C(11)–P(1)–C(131)	103.0 (2)	O–C(2)–C(3)	132 (2)
C(121)–P(1)–C(131)	100.0 (2)	C(1)–C(2)–C(3)	114 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table X. T_1 Times for the Metal-Bonded Hydrogen Atoms in $ReCl(H_2)(PMePh_2)_4$ (**1**) at 200 and 400 MHz in CD_2Cl_2

temp, °C	T_1, ms[a] at 200 MHz[b]	T_1, ms[a] at 400 MHz[b]
20	77 (−8.6)	146 (−8.88)
0	56	120 (−8.88)
−20	46	106 (8.90)
−30	32	97 (8.92)
−40	24	95 (8.92)
−50	27	92 (8.90)
−60	23	96 (8.86)
−70	33	108 (8.90), 135 (9.5)
−80	37	177 (8.64), 123 (8.86), 168 (9.06)
−90	55	
−100		162 (8.58), 162 (9.08)

[a] The chemical shift in ppm is given in parentheses after the T_1 values. [b] Data obtained from ref 5b.

in the ^1H NMR spectra at low temperatures in Figures 1–3 for **1** arise because the molecular dihydrogen ligand is attached to different conformational forms of **1**.

These conformational effects influence the T_1 data listed in Table X. The T_1 data at the different field strengths at 20 °C are not equal. This can probably be attributed to the existence of different conformational forms of **1**, since a single sharp resonance for the P atoms in the $^{31}P\{^1H\}$ NMR spectrum is only obtained at 80 °C for these nuclei.[5b] Thus, the H_2 ligand in **1** at 20 °C is not in equivalent environments in the two different magnetic fields and the complex at 20 °C is not in the fast-motion regime for here the magnitude of the T_1 should be similar at different magnetic fields.

On the basis of theoretical considerations the T_1(min) value should scale directly with the field strength B, as is frequently mentioned.[18a] However, **1** provides a clear exception to this. The minimum T_1 value of $\simeq$ 24 ms in CD_2Cl_2 at 200 MHz is not a half of the minimum obtained, also in CD_2Cl_2, at 400 MHz $\simeq$ 92 ms. It is likely that these differences are caused by the different rotamers each having their own unique and different correlation times (they may in fact have the same T_1(min) value). Thus, the T_1 values we measure are a composite of these values, since the different correlation times would result in different T_1(min) temperatures.

The fact that the T_1(min) values for **1** do not scale with frequency shows that caution should be exercised in relating T_1(min) values from one field to another in cases where the actual measurements are not done. Obviously, with relatively small molecules this may still be an acceptable practice but with larger ones that may exhibit effects similar to those described above it may be unreliable. Another point of interest here is what would be the implications by itself of a T_1(min) value of 92 ms at 400 MHz for this dihydrogen complex?[18] The T_1(min) value of 25 ms at 200 MHz was the basis for assigning this complex as containing a molecular dihydrogen ligand.[5a]

Finally, it is interesting that the T_1 values for the different resonances obtained at the lower temperatures at 400 MHz differ little from each other. Large differences in magnitude might have indicated that we had equilibria involving dihydride(s) and the molecular dihydrogen species. On the contrary, the observed results are consistent with the idea that different conformers of this molecule exist and do not rapidly interconvert at the lowest temperatures.

Crystallographic Results. ORTEP[23b] drawings for form **1a** at the two temperatures, as well as for **1b** and **1c**, are displayed in Figures 6–9, and bond distances and angles are listed in Tables VI–IX. The complex, in all crystalline forms, can best be described as distorted octahedral, with one pair of trans P atoms lying a little above, and the other pair a little below, the equatorial plane. The

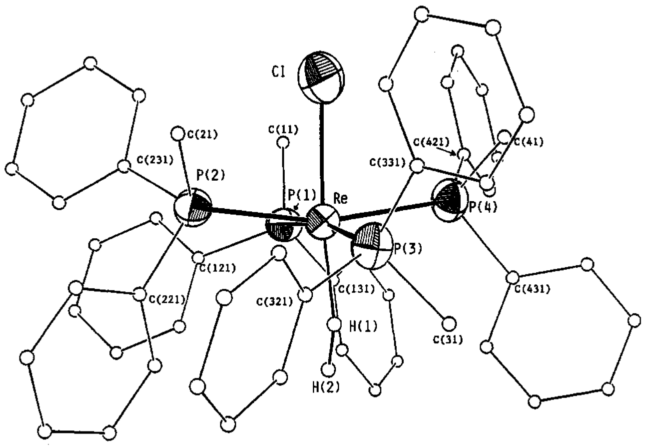

Figure 6. ORTEP[23c] drawing of **1a** without the molecules of solvation, from the data obtained at 292 K, with a partial listing of the atomic numbering scheme. The ellipsoids represent thermal displacements and are drawn at the 50% probability level. The carbon and hydrogen atoms are represented by circles of arbitrary radii.

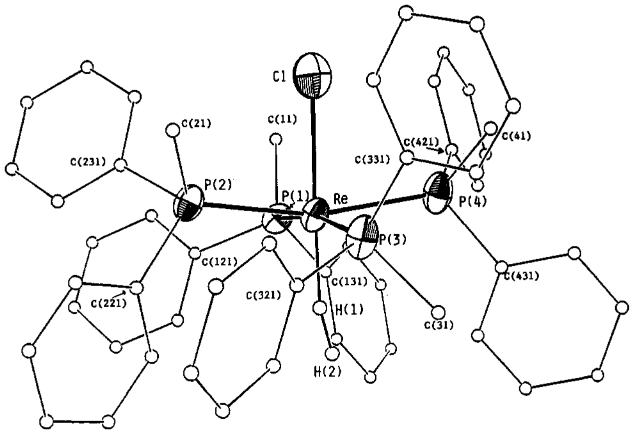

Figure 7. ORTEP[23c] drawing of **1a** without the molecules of solvation, from the data obtained at 193 K, with a partial listing of the atomic numbering scheme. The ellipsoids represent thermal displacements and are drawn at the 50% probability level. The carbon and hydrogen atoms are represented by circles of arbitrary radii.

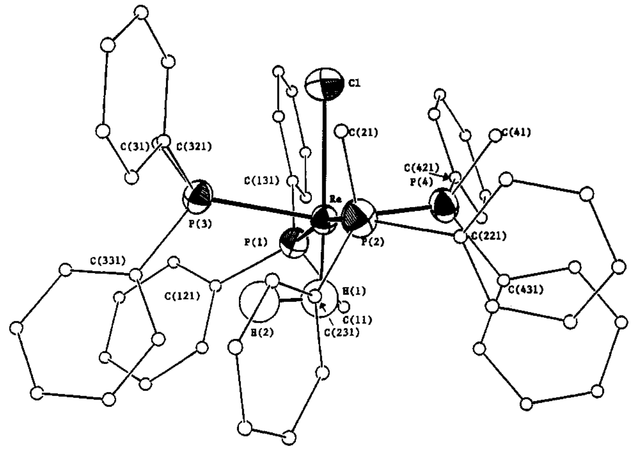

Figure 8. ORTEP[23c] drawing of **1b** without the molecule of solvation, with a partial listing of the atomic numbering scheme. The ellipsoids and the circles for the H atoms represent thermal displacements and are drawn at the 50% probability level. Carbon atoms are represented by circles of arbitrary radii.

Cl^- ligand is trans to the dihydrogen ligand.

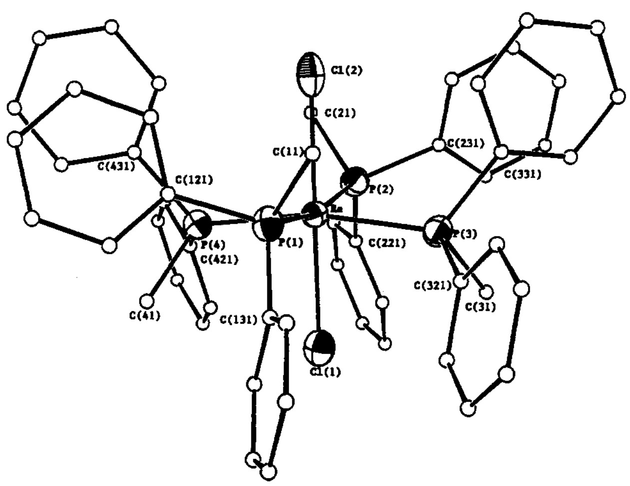

Figure 9. ORTEP[23c] drawing of **1c** without the molecule of solvation, with a partial listing of the atomic numbering scheme. The ellipsoids represent thermal displacements and are drawn at the 50‰ probability level. Carbon atoms are represented by circles of arbitrary radii.

Table XI. Comparison of Bond Distances (Å) and Angles (deg) for the Metal Core Geometry in $ReCl(H_2)(PMePh_2)_4 \cdot 2C_4H_8O$ (**1a**) at 292 K and 193 K, $ReCl(H_2)(PMePh_2)_4 \cdot 0.5(CH_3)_2CO$ (**1b**), and $ReCl(H_2)(PMePh_2)_4 \cdot 0.5(CH_3)_2CO$ (**1c**)

	1a, 292 K[a]	**1a**, 193 K[a]	**1b**[b]	**1c**[c]
Re–H(1)	1.83	1.70	1.49 (9)	
Re–H(2)	2.65	2.58	1.98 (9)	
H(1)–H(2)	0.91	0.92	1.17 (13)	
Re–Cl	2.538 (4)	2.539 (2)	2.526 (3)	2.568 (3)/ 2.587 (3)
Re–P(1)	2.407 (3)	2.404 (2)	2.409 (3)	2.441 (1)
Re–P(2)	2.439 (4)	2.437 (2)	2.449 (2)	2.435 (1)
Re–P(3)	2.414 (3)	2.395 (2)	2.391 (2)	2.436 (1)
Re–P(4)	2.459 (4)	2.451 (2)	2.451 (2)	2.435 (1)
P(1)–Re–P(3)	168.7 (1)	168.86 (6)	169.18 (9)	168.49 (5)
P(2)–Re–P(4)	164.3 (1)	164.54 (6)	163.36 (9)	168.01 (5)
H(1)–Re–Cl	172.94	178.29	177 (4)	
Cl–Re–P(1)	91.3 (1)	91.41 (6)	89.44 (9)	96.05 (7)/ 84.12 (7)
Cl–Re–P(2)	83.8 (1)	83.93 (7)	83.62 (8)	84.32 (8)/ 95.68 (8)
Cl–Re–P(3)	99.8 (1)	99.58 (6)	101.38 (9)	95.46 (7)/ 84.37 (8)
Cl–Re–P(4)	81.5 (1)	81.51 (7)	80.35 (8)	83.70 (7)/ 96.31 (8)

[a] H atoms inserted at positions revealed in the difference Fourier maps. These are not refined positions. [b] For the purposes of comparing data for **1b** the labels of the P atoms from the previous tables involving **1b** were changed as follows: P(1) → P(3), P(2) → P(1), P(3) → P(4), and P(4) → P(2). [c] With **1c** the following changes were made to the labels for the P atoms: P(1) → P(1), P(2) → P(3), P(3) → P(2), and P(4) → P(4). Furthermore, due to disorder in **1c**, two distances and angles are obtained for those measurements involving the Cl^- ligand.

A comparison between the ORTEP drawings in Figures 6 and 7 on the one hand with that in Figure 8 reveals that there are in fact different conformations in **1a** and **1b** with respect to the orientations of the hydrocarbon groups attached to the P atoms. Furthermore, forms **1a** and **1b** are clearly different from **1c** (Figure 9), where a more symmetrical arrangement of the $PMePh_2$ groups occurs. It is probably because of this symmetrical arrangement that **1** is able to crystallize with the ≃50% disorder between the Cl^- and H_2 ligands. This is reminiscent of the disorder reported for $ReCl(N_2)(PMe_2Ph)_4$,[24] where partial (12%) scrambling of the Cl^- and N_2 ligands was found.

A comparison of important bond distances and angles is provided in Table XI. Except for slight changes in the Re–P(3) distances, lowering the temperature from +19 to −80 °C did not produce any alteration in the core geometry for form **1a**. There are significant differences in the Re–Cl distances between forms **1a** and **1b** vs **1c**; Re–Cl in **1a**, 2.538 (4)/2.539 (2) Å, is equivalent within the usual 3σ esd criteria to Re–Cl in **1b**, 2.526 (3) Å, but these are all significantly shorter than the Re–Cl distances in **1c**,

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[24] Davis, B. R.; Ibers, J. A. *Inorg. Chem.* **1971**, *10*, 578.

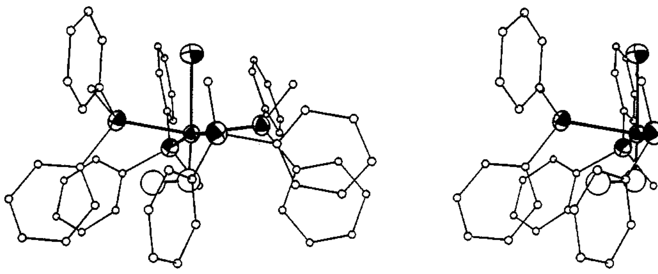

Figure 10. Stereoview of **1b** without the molecule of solvation.

2.568 (3)/2.587 (3) Å. These differences may well be steric in origin with the more symmetrical arrangement of the phosphine ligands in **1c** causing increased steric hindrance at the Cl^- ligand and thus an elongation of this bond. This symmetrical arrangement might also have important consequences for the H_2 ligand, and this will be further discussed below.

There are no significant differences between the Re–P bond lengths and the P–Re–P′ and Cl–Re–P′ angles obtained at either temperature for **1a** and those for **1b**. However, two different P–Re–P′ angles are obtained with, curiously, the smaller one being due to the trans P atoms that are closer to the chloride ligand. In the case of the more symmetrical form **1c** the Re–P bond lengths and the trans P–Re–P′ and related Cl–Re–P′ and Cl′–Re–P′ angles are equivalent within the esd's.

As mentioned previously, the hydrogen atom positions determined in the difference Fourier maps for the two data sets for form **1a** would not refine to acceptable parameters. The positions reported are therefore those obtained directly from the difference Fourier maps. However, it is interesting that two data sets on different crystals using different crystallographic instruments gave essentially the same two peaks. This means that these peaks are not likely to be artifacts due to data collection errors or crystal imperfections. They could, of course, be artifacts arising from other sources such as series termination errors. However, we think that they genuinely represent the presence of the η^2-H_2 ligand, albeit only with low accuracy.

The refinement of the H_2 ligand in **1b** proceeded satisfactorily without restraint, and thus these results merit more detailed discussion. A stereoview of **1b**, without the molecule of crystallization, is presented as Figure 10, as this more clearly demonstrates the environment surrounding the H_2 ligand. The H(1)–H(2) distance of 1.17 (13) Å is among the longest reported thus far (cf. 1.08 (5) Å for $d(\eta^2$-$H_2)$ in $[Re(H_2)H_4(Cyttp)]SbF_6$,[11b] Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$. The two Re–H distances, Re–H(1) = 1.49 (9) Å and Re–H(2) = 1.98 (9) Å, are not equivalent, even within the 3σ esd criteria. The two angles Re–H(1)–H(2) = 95 (8)° and Re–H(2)–H(1) = 48 (6)° also suggest an asymmetric location for the H_2 group. The plane described by ReH(1)H(2) is roughly coplanar with that described by P(3)ReP(4) (Figure 8) (dihedral angle = 17°), and there are significant differences between the Cl–Re–P(3) angle of 80.35 (8)° and that for Cl–Re–P(4) of 83.62 (8)°. This may be due to steric interactions between H(2) and the hydrocarbon groups on P(3). Furthermore, it is interesting that the location of the H_2 group is along the trans P–Re–P axis that has the trans P atoms closer to the Cl^- ligand. Obviously if the H_2 group were to turn 90°, there would be more steric interactions between the H_2 group and the groups on these P atoms, which are situated further from the Cl^- ligand.

While the indications that **1** may contain an unsymmetrically attached H_2 ligand are by no means conclusive, it is essentially certain that an H_2 ligand, however oriented, is present. As noted before,[5a] a curious feature of **1** is that its existence as a molecular H_2 complex is not predictable. A reasonable correlation had been developed showing that if $\nu(N_2)$ in $M(L)_n(N_2)$ is in the range 2060–2150 cm^{-1}, then it is likely that the analogous dihydrogen complex $M(L)_n(H_2)$ would contain an η^2-H_2 ligand.[25] On this basis the dihydride analogue of $ReCl(N_2)(PMePh_2)_4$[26] [$\nu(N_2)$ = 1925 cm^{-1}] would not be expected to contain a molecular dihydrogen ligand. A recently reported[15] $[Os(NH_3)_5(H_2)]^{2+}$ complex ($\nu(N_2)$ in $[Os(NH_3)_5(N_2)]^{2+}$ = 2010 cm^{-1}) is also an exception to the above correlation.

The synthesis of $ReCl(HD)(PMePh_2)_4$ was attempted by reducing $ReCl_5$ as described above but under an HD atomosphere and also by heating benzene solutions of **1** under an HD atmosphere. As in the D_2 case, this resulted in species of the form $ReCl(H_2)(PMe(C_6H_{5-n}D_n)_2)$.[5a] These species give complicated overlapping spectra in the hydride region, which obscures the HD coupling for the desired $ReCl(HD)(PMePh_2)_4$ complex. Under these circumstances (i.e., overlapping spectra) and knowing already the complex patterns obtained at lower temperatures for **1**, we did not attempt to obtain the spectra at lower temperatures. However, experiments designed to measure J_{HD} are worthy of more consideration. Furthermore, in light of the long H–H bond present in **1**, the HD coupling may not be as large (ca. 18–34 HZ) as that found for other well-characterized molecular dihydrogen complexes.[4] It is interesting that the complex $Os(OEP)(H_2)$, OEP = octaethylporphyrinato dianion, assigned as a molecular dihydrogen compound, had a T_1(min) time of 110 ms at 400 MHz indicative of a long H–H bond, and J(HD) for the HD analogue was 12 Hz.[4]

It is interesting to contemplate what geometric distortions would be needed in the structure of **1** if it were to become a dihydride. In order to accommodate two hydride ligands, a distorted pentagonal bipyramidal geometry, such as that found in the structure of $ReH_3(PMePh_2)_4$,[5b] is a reasonable probability. In the case of $ReH_3(PMePh_2)_4$, the metal-bonded H atoms were located in difference Fourier maps and refined without constraint. This structure contained an apical P–Re–P angle of 160.1 (1)° and an equatorial P–Re–P angle of 136.1 (1)°.[5b] The equivalent trans P–Re–P angles for the various forms of **1** are much larger than these angles, and thus we believe that a dihydride species is excluded from consideration on the basis of the heavier atom geometry alone.

Acknowledgment. We thank the National Science Foundation for financial support.

Supplementary Material Available: Figures of fully labeled ORTEP drawings and stereoviews of the unit cell packing and tables of full crystallographic data, full listings of atomic positions, bond distances and angles, and anisotropic displacement parameters for structures **1a** at 292 and 193 K, **1b**, and **1c** (60 pages); listings of observed and calculated structure factors for **1a** at 292 and 193 K, **1b**, and **1c** (118 pages). Ordering information is given on any current masthead page.

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