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Rhenium Dihydrogen Complexes and Long H–H Interactions: X-ray-Determined Single-Crystal Structures of $ReCl(\eta^2\text{-}H_2)(Ph_2PCH_2CH_2PPh_2)_2\cdot THF$ and $[ReO_2(Ph_2PCHCHPPh_2)_2][ReO_4]$

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Reduction of $ReCl_5$ in tetrahydrofuran under Ar with 4 equiv of Na in the presence of bidentate tertiary phosphines (L_2) yields complexes of the form $ReCl(\eta^2\text{-}H_2)(L_2)_2$, $L_2 = PPh_2CH_2CH_2PPh_2$ (**1**), and $L_2 = PPh_2CHCHPPh_2$ (**2**). A similar reduction of $ReCl_5$ in the presence of the monodentate ligand PMe_2Ph affords mixtures of $ReH_3(PMe_2Ph)_4$ and the cation $[ReH_4(PMe_2Ph)_4]^+$. The metal-bonded H atoms in complexes **1** and **2** display T_1(min) times of 43(5) and 29(4) ms, respectively, at 200 MHz. This suggests a long H–H interaction. The single-crystal X-ray structures of complexes **1**·THF and $[ReO_2(PPh_2CHCHPPh_2)_2][ReO_4]$ (**3**) are reported. Crystal data: compound **1**·THF, monoclinic, space group $P2_1/c$, $a = 11.472(4)$ Å, $b = 13.468(2)$ Å, $c = 17.339(5)$ Å, $\beta = 96.02(1)°$, $V = 2664.1(4)$ Å^3, $Z = 2$, $R = 0.041$ ($R_w = 0.058$) for 288 parameters and 2323 unique data having $F_o > 3\sigma(F_o^2)$; compound **3**, triclinic, space group, $P\bar{1}$, $a = 9.946(1)$ Å, $b = 11.744(3)$ Å, $c = 12.506(2)$ Å, $\alpha = 70.59(2)°$, $\beta = 73.46(1)°$, $\gamma = 65.72(1)°$, $V = 1237.0(3)$ Å^3, $Z = 1$, $R = 0.038$ ($R_w = 0.055$) for 310 parameters and 2582 unique data having $F_o > 3\sigma(F_o^2)$. The geometries of **1** and the cation in **3** are those of distorted octahedra with the Re atoms situated on inversion points. In **1**, there is 50% disorder between the trans Cl^- and the $\eta^2\text{-}H_2$ (not located) ligands. Important distances for **1**: Re–Cl at 2.574(6) Å and, Re–P(1) and Re–P(2) at 2.388(5) and 2.399(3) Å, respectively, with a P(1)–Re–P(2) angle of 80.3(1)°. Core distances for **3**: Re–O(101) at 1.788(6) Å and Re–P(1) and Re–P(2) at 2.476(2) and 2.473(2) Å, respectively, with a P(1)–Re–P(2) angle at 81.18(8)°. The tetrahedral anion in **3**, $[ReO_4]^-$, is located near an inversion point and was refined at 50% occupancy. Here Re–O bond distances range from 1.60(7) to 1.77(2) Å.

Introduction

There is a substantial amount of varied data to suggest that the $\eta^2\text{-}H_2$ ligand may adopt alternate geometries at least when coordinated to different transition metals.[2] For example, although the results of four neutron diffraction studies on different dihydrogen complexes[3] revealed that the H to H atom distance in $\eta^2\text{-}H_2$ is about 0.8 Å, there has been one study, i.e. the neutron diffraction determination of the structure of $ReH_7(P(p\text{-}tol)_3)_2$,[4] which revealed one H–H atom interaction at 1.357(7) Å. This long H–H interaction is suggested to occur when d(H–H) is between 1.0 and 1.6 Å.[2] Furthermore, there is solution-state evidence of this form of $\eta^2\text{-}H_2$ bond-stretch "ligand" isomerism as assessed by T_1(min) values for H_2 between 6 and 90 ms at 200 MHz and J_{HD} (in the η^2-HD analogues) on the order of 4–25 Hz.[2]

The complex $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$ has previously been shown to exhibit a long H–H interaction.[5] For this complex, the H–H distance has been assessed as 1.17(13) Å by single crystal X-ray techniques and the T_1(min) is 25 ms at 200 MHz.[5] We are interested in molecular complexes of the form $ReCl(\eta^2\text{-}H_2)(PR_3)_4$ (PR_3 = tertiary phosphine ligand other than $PMePh_2$) in order to assess the influence of the ancillary ligands on dihydrogen coordination. In this paper, we report on the syntheses and structural characteristics of $ReCl(\eta^2\text{-}H_2)(dppe)_2$ (**1**),[6] (dppe = $Ph_2PCH_2CH_2PPh_2$) and $ReCl(\eta^2\text{-}H_2)(dppee)_2$ (**2**) (dppee = $Ph_2PCHCHPPh_2$) two molecules that extend the number of complexes known to contain long H–H interactions. The X-ray single crystal structures of **1**·THF and $[ReO_2(PPh_2CHCHPPh_2)_2][ReO_4]$ (**3**) are also reported.

Experimental Section

General Data. All manipulations were carried out under either a dinitrogen or an argon atmosphere. Methanol was dried over magnesium methoxide, while other solvents were dried over sodium and distilled under nitrogen before use. $ReCl_5$ and the phosphine ligands were used as purchased from Strem Chemicals, Inc. The ^{1}H and ^{31}P NMR spectra were recorded using Varian XL-200 and XL-300 spectrometers, respectively. The ^{31}P NMR spectrum is reported referenced to H_3PO_4. The microanalyses were done by Galbraith Laboratories, Inc., Knoxville, TN.

Complexes **1**[6] and **2** were prepared in 60% yields by following routes similar to the published procedure for the synthesis of $ReCl(H_2)(PMePh_2)_4$,[5b] except that the appropriate phosphine ligand, dppe or dppee, respectively, was substituted for $PMePh_2$. ^{1}H NMR for **1** (C_6D_6): δ 6.6–8.8 (m, 40 H, C_6H_5P), 1.60, 1.92, 2.25, 2.60 (m, 8 H, H_2CP), −10.7 (q, 2 H, J = 21 Hz, H-Re). Anal. Calcd for $C_{52}H_{50}ClP_4Re\cdot C_4H_8O\cdot SiO_2$: C, 58.35; H, 5.07. Found: C, 58.10; H, 5.35. ^{1}H NMR for **2** (CD_2Cl_2): δ 6.6–8.2 (m, 40 H, C_6H_5P), −11.6 (q, 2 H, J = 19 Hz, H-Re). ^{31}P NMR for **2** (C_6H_6): δ 54.6 (s, 4 P). The positions for the resonances of the ethylenic H atoms were not apparent. Anal. Calcd for $C_{52}H_{46}ClP_4Re\cdot SiO_2$: C, 58.01; H, 4.31. Found: C, 57.74; H, 4.58.

The attempted synthesis of $ReCl(H_2)(PMe_2Ph)_4$ entailed reducing $ReCl_5$ with 4 equiv of Na/Hg in THF for 2 h under Ar in the presence of PMe_2Ph.[5b] Filtration of the reaction mixture, concentrating, and

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0020-1669/94/1333-0879$04.50/0

Table 1. Crystallographic Data for Complexes **1**·THF and **3**

	1·THF	**3**
formula	$C_{52}H_{50}ClP_4Re\cdot C_4H_8O$	$[C_{52}H_{44}O_2P_4Re][ReO_4]$
fw	1092.63	1261.22
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	11.472 (4)	9.946(1)
b, Å	13.468(2)	11.744(3)
c, Å	17.339(5)	12.506(2)
α, deg	90	70.59(2)
β, deg	96.02(1)	73.46(1)
γ, deg	90	65.72(1)
V, Å^3	2664.1(4)	1237.0(3)
Z	2	1
ρ_{calc}, g/cm^3	1.36	1.69
μ(Mo Kα), cm^{-1}	25.1	51.3
radiation monochromated in incident beam (λ_α, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
temp, °C	23	23
$R(F_o)^a$	0.041	0.038
$R_w(F_o)^b$	0.058	0.055

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

subsequent addition of MeOH did not yield a tractable precipitate. All solvents were removed under vacuum, leaving a brown/black precipitate. The ^{1}H NMR spectrum indicated that the known complexes $ReH_3(PMe_2Ph)_4$ and $[ReH_4(PMe_2Ph)_4]^+$ were produced.[7] It is possible that the presence of the more basic phosphine (PMe_2Ph) resulted in the tetrahydride species since the tetrahydride analogue was not produced when $PMePh_2$ was employed under similar reducing conditions.[5b] It is noteworthy that $ReH_3(PMe_2Ph)_4$ has been shown to be a stronger base than NEt_3.[7]

X-ray Crystallography. Suitable crystals of **1**·THF were obtained by the slow diffusion of methanol into a THF solution of **1**. The compound $[ReO_2(dppee)_2][ReO_4]$ (**3**) was obtained in an unsuccessful attempt at the synthesis of **2**. This involved reducing $K[ReO_4]$ with Na in the presence of dppee. The preparation of the closely related $[ReO_2(dppe)_2][ReO_4]$[8a] and the structure of this compound have been reported previously.[8b] Crystals were obtained by allowing the diffusion of methanol into a THF solution of **3**.

A suitable crystal of complex **1**·THF was mounted inside a glass capillary and a crystal of **3** was mounted on a glass fiber, both in random orientations. Accurate unit cell parameters were obtained by means of least-squares analyses of 25 reflections. Intensity data for each compound were then collected by utilizing the options specified in Table 1 and the general procedures for data collection as previously described.[9] All calculations were performed on a VAX computer using MolEN.[10] Lorentz and polarization corrections were applied to the data as well as an empirical absorption correction[11] based on two ψ scans.

The structure was solved in both cases using the Patterson heavy-atom method, which suggested that the Re atoms in **1** and the cation of **3** were located on inversion points. The remaining atoms were located by alternating least-squares full-matrix cycles of refinement and difference Fourier maps for a cutoff ratio of $F_o^2/\sigma(F_o^2) = 3$.

The fact that **1** contained a chloride ligand disorder was quite apparent as the Re atom was located on an inversion point and the distance from the center of the electron density assigned as the Cl^- ligand to the Re atom was 2.5 Å (thus ruling out a *trans* dioxo formulation). Five peaks indicative of a tetrahydrofuran (THF) molecule were also apparent in a difference Fourier map. One of these peaks was arbitrarily chosen to be the oxygen atom for the THF molecule. H atoms for the phenyl groups were placed at calculated positions, with isotropic thermal parameters fixed at 1.2 times the current converged isotropic equivalents of the C atoms to which they were attached. All of the non H and THF solvate atoms were refined with anisotropic thermal parameters.

Table 2. Positional and Equivalent Isotropic Thermal Parameters and Their Esd's for $ReCl(\eta^2\text{-}H_2)(dppe)_2\cdot C_4H_8O$ (**1**·THF)[a]

atom	x	y	z	B, Å^2
Re	0.000	0.000	0.000	2.63(1)
Cl	0.1813(5)	0.0569(4)	–0.0639(3)	3.2(1)
P(1)	–0.1068(3)	0.1069(2)	–0.0919(2)	3.20(7)
P(2)	–0.0223(3)	–0.1087(3)	–0.1102(3)	3.34(7)
C(11)	–0.059(1)	0.0768(9)	–0.1894(7)	3.6(3)
C(21)	–0.063(1)	–0.0357(8)	–0.2035(7)	4.0(3)
C(121)	–0.085(1)	0.2435(8)	–0.927(7)	3.6(3)
C(122)	0.025(1)	0.281(1)	–0.0752(8)	4.8(3)
C(123)	0.043(1)	0.383(1)	–0.0767(8)	5.9(4)
C(124)	–0.047(1)	0.447(1)	–0.0938(8)	5.7(4)
C(125)	–0.160(1)	0.410(1)	–0.1134(9)	6.7(4)
C(126)	–0.179(1)	0.307(1)	–0.1121(8)	6.1(4)
C(131)	–0.266(1)	0.0937(9)	–0.1012(7)	3.6(3)
C(132)	–0.332(1)	0.062(1)	–0.1715(8)	5.7(4)
C(133)	–0.453(1)	0.047(1)	–0.1730(9)	7.5(5)
C(134)	–0.512(1)	0.070(1)	–0.1077(9)	8.0(5)
C(135)	–0.447(1)	0.102(1)	–0.0450(9)	6.2(4)
C(136)	–0.327(1)	0.111(1)	–0.0392(8)	5.1(3)
C(221)	0.107(1)	–0.1795(9)	–0.1286(7)	3.8(3)
C(222)	0.125(1)	–0.272(1)	–0.0979(7)	5.5(4)
C(223)	0.228(1)	–0.328(1)	–0.1059(8)	7.4(4)
C(224)	0.311(1)	–0.287(1)	–0.1464(9)	8.1(5)
C(225)	0.295(1)	–0.194(1)	–0.1812(9)	7.6(5)
C(226)	0.193(1)	–0.141(1)	–0.1715(8)	6.1(4)
C(231)	–0.138(1)	–0.2028(9)	–0.1271(7)	4.0(3)
C(232)	–0.237(1)	–0.199(1)	–0.0915(8)	5.5(4)
C(233)	–0.333(2)	–0.261(1)	–0.1108(9)	8.9(5)
C(234)	–0.321(1)	–0.337(1)	–0.1634(9)	7.8(5)
C(235)	–0.223(1)	–0.342(1)	–0.205(1)	8.7(5)
C(236)	–0.135(1)	–0.273(1)	–0.1850(9)	6.8(4)
O(1)	0.529(2)	0.092(1)	0.337(1)	7.9(5)*
C(1)	0.509(2)	0.073(2)	0.408(2)	15.1(9)*
C(2)	0.387(3)	0.111(3)	0.423(2)	19(1)*
C(3)	0.348(2)	0.164(2)	0.359(1)	13.3(8)*
C(4)	0.449(2)	0.168(2)	0.312(2)	14.2(8)*

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

For complex **3**, the cation was located around an inversion point and the anion was located near an inversion point. Thus the anion $[ReO_4]^-$ was refined with atoms at 50% occupancy and with one O atom (O(1), poorly behaved) constrained to ride on Re(2) at a distance of 1.6067 Å. No attempt was made to include H atoms in this refinement, and all included atoms were refined with anisotropic thermal parameters. Some relevant crystallographic information is given in Table 1. Final positional parameters and their estimated standard deviations for non-H atoms are given in Tables 2 and 3 for **1**·THF and **3** respectively. Selected bond lengths and angles are given in Tables 4 and 5 for **1**·THF and **3**, respectively. ORTEP representations of **1**·THF and **3** are presented in Figures 1 and 2, respectively, and views of the unit cell crystal packing for both structures are available as supplementary material.

Results and Discussion

Synthesis and Reactivity. Complexes **1** and **2** were synthesized by following the procedure (with the appropriate phosphine ligand) established for the synthesis of $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$.[5b] This entailed the reduction of $ReCl_5$ with 4 equiv of Na in the presence of phosphine ligand in THF under Ar. The dihydrogen ligand presumably arises out of hydrogen abstraction from the THF solvent, but this has not been proven conclusively. Complexes **1** and **2** both display quintet resonances in the upfield region of the ^{1}H NMR spectrum at δ –10.7 and –11.6, respectively, and are thus easily identified. The magnitude of the $^2J_{HP}$ coupling, ca. 20 Hz, is similar to that of $^2J_{HP}$ in $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$,[5b] 19 Hz, and it should be noted that this coupling is very large for complexes suspected of containing η^2-H_2 ligands.[2] In itself, this

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Table 3. Positional and Equivalent Isotropic Thermal Parameters and Their Esd's for $[ReO_2(dppee)_2][ReO_4]$[a]

atom	*x*	*y*	*z*	*B*, $Å^2$
Re(1)	0.000	0.000	0.500	2.26(1)
P(1)	0.097(2)	–0.1283(2)	–.6813(2)	2.82(5)
P(2)	0.0903(2)	–0.2174(2)	0.4663(2)	2.97(5)
O(101)	0.1705(6)	0.0280(5)	0.4263(5)	3.0(1)
C(111)	0.145(1)	–0.2977(8)	0.6882(8)	3.7(2)
C(121)	–0.0389(9)	–0.1032(8)	0.8105(7)	3.0(2)
C(122)	–0.132(1)	–0.1756(9)	0.8578(8)	4.3(3)
C(123)	–0.243(1)	–0.147(1)	0.9531(9)	5.9(3)
C(124)	–0.258(1)	–0.052(1)	1.0007(9)	5.5(3)
C(125)	–0.162(1)	0.018(1)	0.9551(9)	5.0(3)
C(126)	–0.050(1)	–0.0099(9)	0.8592(8)	4.1(3)
C(131)	0.2653(9)	–0.1274(8)	0.7108(7)	3.2(2)
C(132)	0.3352(9)	–0.0430(9)	0.6366(9)	3.9(3)
C(133)	0.465(1)	–0.042(1)	0.6627(9)	5.0(3)
C(134)	0.523(1)	–0.126(1)	0.7580(9)	5.4(3)
C(135)	0.455(1)	–0.216(1)	0.8349(9)	5.7(3)
C(136)	0.324(1)	–0.214(1)	0.8082(8)	4.7(3)
C(211)	0.143(1)	–0.3343(8)	0.5986(8)	3.6(2)
C(221)	0.2538(9)	–0.2698(8)	0.3590(7)	3.5(2)
C(222)	0.334(1)	–0.1877(9)	0.2972(8)	4.3(3)
C(223)	0.461(1)	–0.230(1)	0.216(1)	5.8(3)
C(224)	0.509(1)	–0.352(1)	0.200(1)	6.2(4)
C(225)	0.429(2)	–0.434(1)	0.264(1)	8.5(5)
C(226)	0.297(1)	–0.389(1)	0.341(1)	6.5(4)
C(231)	–0.054(1)	–0.2616(8)	0.4455(8)	3.6(2)
C(232)	–0.169(1)	–0.2773(8)	0.5421(9)	4.0(3)
C(233)	–0.289(1)	–0.299(1)	0.527(1)	5.5(3)
C(234)	–0.299(1)	–0.3077(9)	0.421(1)	6.0(3)
C(235)	–0.182(1)	–0.295(1)	0.326(1)	5.9(3)
C(236)	–0.059(1)	–0.2697(9)	0.3365(8)	4.4(3)
Re(2)[b]	0.1046(1)	0.54833(7)	0.07992(7)	4.60(3)
O(1)[b]	0.168	0.527	–0.048	14.8(8)
O(2)[b]	0.194(2)	0.436(2)	0.176(2)	8.7(6)
O(3)[b]	–0.081(2)	0.551(2)	0.103(2)	7.4(6)
O(4)[b]	0.103(2)	0.687(1)	0.078(1)	6.8(5)

[a] *B* values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $^1/_3[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$. [b] Atom refined at 50% occupancy.

Table 4. Selected Bond Distances and Angles for $ReCl(\eta^2\text{-}H_2)(dppe)_2{\cdot}C_4H_8O$ (**1**·THF)[a]

Bond Distances (Å)			
Re–Cl	2.574(6)	P(2)–C(231)	1.83(1)
Re–P(1)	2.388(3)	C(11)–C(21)	1.53(2)
Re–P(2)	2.399(3)	O(1)–C(1)	1.30(3)
P(1)–C(11)	1.87(1)	O(1)–C(4)	1.41(3)
P(1)–C(121)	1.86(1)	C(1)–C(2)	1.55(5)
P(1)–C(131)	1.83(1)	C(2)–C(3)	1.35(4)
P(2)–C(21)	1.91(1)	C(3)–C(4)	1.48(4)
P(2)–C(221)	1.82(1)		
Bond Angles (deg)			
Cl–Re–Cl′	180(0)	C(121)–P(1)–C(131)	103.1(6)
Cl–Re–P(1)	85.1(1)	Re–P(2)–C(21)	110.9(4)
Cl–Re–P(1)′	94.9(1)	Re–P(2)–C(221)	116.0(4)
Cl–Re–P(2)	82.1(1)	Re–P(2)–C(231)	124.3(4)
Cl–Re–P(2)′	97.9(1)	C(21)–P(2)–C(221)	104.6(6)
P(1)–Re–P(1)′	180(0)	C(21)–P(2)–C(231)	96.4(5)
P(1)–Re–P(2)	80.3(1)	C(221)–P(2)–C(231)	101.4(6)
P(1)–Re–P(2)′	99.7(1)	P(1)–C(11)–C(21)	110.6(8)
P(2)–Re–P(2)′	180(0)	P(2)–C(21)–C(11)	111.9(8)
Re–P(1)–C(11)	107.1(4)	C(1)–O(1)–C(4)	105(2)
Re–P(1)–C(121)	122.9(4)	O(1)–C(1)–C(2)	110(2)
Re–P(1)–C(131)	116.1(4)	C(1)–C(2)–C(3)	105(3)
C(11)–P(1)–C(121)	99.0(5)	C(2)–C(3)–C(4)	105(2)
C(11)–P(1)–C(131)	106.4(5)	O(1)–C(4)–C(3)	109(2)

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

Table 5. Selected Bond Distances and Angles for $[ReO_2(dppee)_2][ReO_4]$ (**3**)[a]

Bond Distances (Å)			
Re(1)–P(1)	2.476(2)	P(2)–C(221)	1.818(8)
Re(1)–P(2)	2.473(2)	P(2)–C(231)	1.81(1)
Re(1)–O(101)	1.788(6)	C(111)–C(211)	1.33(2)
P(1)–C(111)	1.82(1)	Re(2)–O(1)	1.6067(9)
P(1)–C(121)	1.810(8)	Re(2)–O(2)	1.60(2)
P(1)C(131)	1.81(1)	Re(2)–O(3)	1.77(2)
P(2)–C(211)	1.814(8)	Re(2)–O(4)	1.62(2)
Bond Angles (deg)			
P(1)–Re(1)–P(1)′	180(0)	Re(1)–P(2)–C(211)	107.8(4)
P(1)–Re(1)–P(2)	81.18(8)	P(2)–C(211)–C(111)	121.3(7)
P(1)–Re(1)–P(2)′	98.82(8)	Re(1)–P(2)–C(221)	121.5(3)
P(1)–Re(1)–O(101)	94.1(2)	Re(1)–P(2)–C(231)	114.5(3)
P(1)–Re(1)–O(101)′	85.9(2)	C(211)–P(2)–C(221)	102.9(4)
P(2)–Re(1)–P(2)′	180(0)	C(211)–P(2)–C(231)	101.4(5)
P(2)–Re(1)–O(101)	93.8(2)	C(221)–P(2)–C(231)	106.4(5)
P(2)–Re(1)–O(101)′	86.2(2)	P(1)–C(111)–C(211)	121.2(6)
O(101)–Re(1)–O(101)′	180(0)	O(1)–Re(2)–O(2)	114.1(7)
Re(1)–P(1)–C(111)	107.4(4)	O(1)–Re(2)–O(3)	101.9(7)
Re(1)–P(1)–C(121)	114.4(3)	O(1)–Re(2)–O(4)	108.6(6)
Re(1)–P(1)–C(131)	122.4(3)	O(2)–Re(2)–O(3)	110.6(9)
C(111)–P(1)–C(121)	104.0(4)	O(2)–Re(2)–O(4)	111(1)
C(111)–P(1)–C(131)	102.6(4)	O(3)–Re(2)–O(4)	110.1(8)
C(121)–P(1)–C(131)	104.1(5)		

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

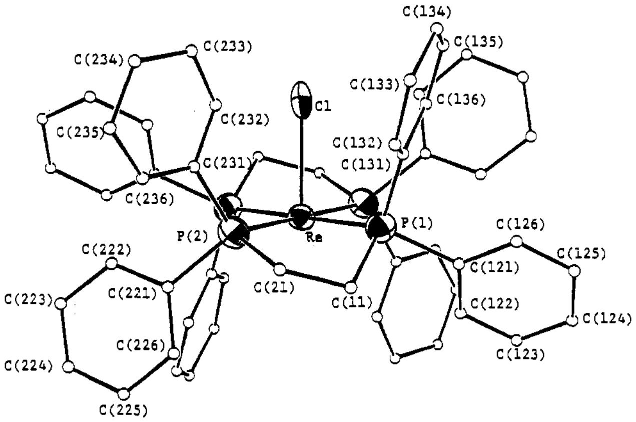

Figure 1. ORTEP drawing of **1**. The ellipsoids represent thermal displacements and are drawn at the 50% probability level. Carbon atoms are represented by spheres of arbitrary size. The THF molecule of solvation is not depicted, and the Cl atom depicted was refined at 50% occupancy.

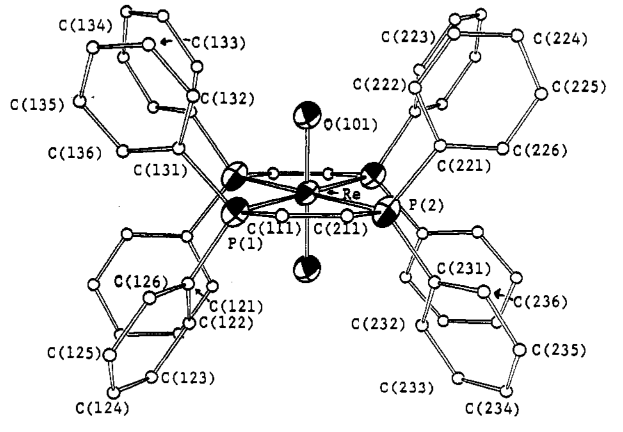

Figure 2. ORTEP drawing of the cation in **3**. The ellipsoids represent thermal displacements and are drawn at the 50% probability level. Carbon atoms are represented by spheres of arbitrary size.

suggests that complexes **1** and **2** may contain H_2 ligands having long H–H interactions.[2]

Interestingly enough, attempts to produce the complex $ReCl(\eta^2\text{-}H_2)(PMe_2Ph)_4$ by following a similar synthetic strategy were not successful. This reaction afforded mixtures of the known complexes $ReH_3(PMe_2Ph)_4$ and $[ReH_4(PMe_2Ph)_4]^+$, identified on the basis of their upfield ^1H NMR spectra.[7b] It is possible that both the lack of bulk and the enhanced electron donating properties of the PMe_2Ph ligand contribute to destabilize any

Table 6. Variable–Temperature T_1 Times for the Metal-Bonded Hydrogen Atoms in **1**, **2**, and $ReH_3(PMe_2Ph)_4$ and the Cation $[ReH_4(PMe_2Ph)_4]^+$ at 200 MHz in CD_2Cl_2

	$T_1{}^a$ ms			
temp, °C	**1**	**2**	$ReH_3(PMe_2Ph)_4$	$[ReH_4(PMe_2Ph)_4]^+$
35		42(13)		
26.4	96(3)	29(4)	529(14)	391(11)
11.4		40(5)		
0	78(8)	47(5)	385(16)	274(10)
–20	66(7)	53(3)	242(3)	184(5)
–40	43(5)	63(9)	148(2)	117(3)
–60	47(5)		81(4)	82(3)
–80	58(14)		100(6)	79(1)
–90			101(6)	90(1)
–95	79(28)			

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

η^2-H_2 complex intermediate (i.e. $ReCl(H_2)(PMe_2Ph)_4$) that may have been produced in this reduction. It should be noted that only the complex $ReH_3(PMePh_2)_4$ is produced if 5 equiv or more of Na is employed in reactions of $ReCl_5$, Na/Hg, and $PMePh_2$.[5b]

We find that complexes **1** and **2** are surprisingly unreactive. Reactions designed to substitute the metal-bonded H atoms with N_2 consisting of dissolving either **1** or **2** in benzene under N_2 atmospheres were not successful even under reflux conditions. This kind of substitution is usually found for η^2-H_2-containing compounds,[2] and furthermore, the closely related $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$ did readily exchange H_2 for N_2.[5b] Even more surprising was the resistance to substitution with CO. In fact, benzene solutions of **1** placed under CO only reacted to form the known complex $ReCl(CO)(dppe)_2$[12] (ν(CO) = 1818 cm^{-1} in $CHCl_3$) under reflux conditions. It should be noted that the complex $ReCl(dppe)_2$ was reported to react with CNMe to give *trans*-$[ReCl(CNMe)(dppe)_2]$ but not with N_2.[13] Therefore, even if the H_2 ligands in **1** and **2** were labile, the resulting 5-coordinate complexes could resist addition reactions with N_2. The compound $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$, which contains only monodentate phosphines, readily formed $ReCl(CO)_3(PMePh_2)_2$[5b] when benzene solutions of $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$ were placed under CO at ambient temperatures.

T_1(min) Studies. The results of variable temperature T_1 studies are depicted in Table 6. The T_1(min) for **1** of 43(5) ms is not significantly different from that in **2** of 29(4) ms. These values are also close to that of the 25 ms which was found for $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$.[5] This value suggests that the H_2 ligand in $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$ contains a long H–H interaction[2] on the order of 1.08 Å (fast rotation (FR)) to 1.37 Å (slow rotation (SR)) (observed T_1 of 25 ms corrected to 33 ms by assuming additional contributions to dipolar relaxation of η^2-H_2 by the Re and the ortho H atoms).[2,14] This range encompasses the value of 1.17(13) Å for d(H–H) obtained by X-ray diffraction.[5b] Therefore, based on the similarity of T_1 min values between $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$ (**1**) and (**2**), it is reasonable to suggest that **1** and **2** each contain a dihydrogen molecule possessing a long H–H interaction. These interactions would be on the order of 1.23 Å (FR) to 1.56 Å (SR) for **1** and 1.11 Å (FR) to 1.41 Å (SR) for **2**, making allowances for Re–H dipolar relaxation and the ortho H atoms as prescribed by Desrosiers et al.[14] and using a correction factor of 0.79 for the rotation suggested by Bautista et al.[15]

Of note is the fact that the T_1(min) occurred at –40 °C for **1** and 26 °C for **2**. It is possible that the effect of two rigid dppee ligands on **2** results in a longer correlation time as opposed to the case for the more flexible dppe ligand in **1**. However, this effect may require two dppee ligands ligated to the metal atom in order to manifest a slower correlation time since the minimum T_1 time for ReH_7dppee[16] occurs at –67 °C and that for ReH_7dppe[16] is at –51 °C, which is opposite to the trend noted above.

Also included in Table 6 are the variable temperature T_1 times for the metal-bonded H atoms in $ReH_3(PMe_2Ph)_4$ and $[ReH_4(PMe_2Ph)_4]^+$, where T_1(min) values of 81(4) and 79(1) ms, respectively, were obtained. The T_1(min) time for $[ReH_4(PMe_2Ph)_4]^+$ at 79(1) ms (200 MHz) agrees with the reported value of 97(18) ms (360 MHz), which had in part led to a classical formulation.[7] However data for the related $ReH_3(PMe_2Ph)_4$ have so far not been reported. The data in Table 6 are interesting, for they clearly indicate that the addition of an H atom to $ReH_3(PMe_2Ph)_4$ did not result in greater H to H atom dipolar contribution to the total relaxation rate. This suggests that the hydride–rhenium interaction and contributions from H atoms on the phosphine ligands account for a substantial amount of the relaxation rate as was pointed out recently.[14]

Crystallographic Results. Complex **1**, shown in Figure 1, has a distorted octahedral geometry. The Re atom is located at an inversion point, and thus there is disorder between the *trans* Cl^- ligand and the two metal-bonded H atoms. A similar sort of disorder was evident in the structures of *trans* $ReCl(N_2)(PMePh_2)_4$,[17] where partial (12%) scrambling of the Cl^- and N_2 ligands was found, and of $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$ which, with respect to the Cl^- and H_2 ligands, had been shown to crystallize in both completely ordered and disordered (≈50%) arrangements.[5c] It was not possible to locate the metal-bonded H atoms in complex **1**·THF, which is not surprising, given the limitations of the X-ray technique and the disorder in the packing of the molecules. However, the octahedral geometry argues in favor of a 6-coordinate complex containing a long H–H interaction (as also substantiated by the T_1 results) and not a 7-coordinate classical structure as was found in the structure of the classical $ReH_3(PMePh_2)_4$.[5b]

The Re–Cl(av) bond distance of 2.574(6) Å is within agreement with those of 2.568(3) and 2.583(3) Å found for the Re–Cl bond distances in the crystals of $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$ that exhibited a similar disorder.[5c] The Re–P bond distances in **1**·THF of 2.388(3) and 2.399(3) Å for Re–P(1) and Re–P(2), respectively, are shorter than those in disordered $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$[5c] (ranges from 2.435(1) to 2.444(1) Å). However they are similar to the lengths of two of the Re–P bonds in ordered $ReCl(\eta^2\text{-}H_2)(PMePh_2)_4$,[5c] where for three such structure determinations two of the Re–P bond distances were found to be shorter (average of 2.398 and 2.409 Å) than the others (average of 2.442 and 2.454 Å). Perhaps with the bidentate dppe ligand, less steric hindrance is encountered, resulting in a shorter Re–P bond.

Complex **2** crystallized in a triclinic crystal system with the Re atom in the cation $[ReO_2(dppee)_2]^+$ located on an inversion point and the atoms for the entire perrhenate anion $[ReO_4]^-$ located in general positions close to an inversion point. This implied that the anion contained 50% disorder, and indeed this was indicated early in the refinement process by abnormal temperature factors for the atoms describing the anion which at this stage were at 100% occupancy. This arrangement is similar to that reported for $[ReO_2(dppe)_2][ReO_4]$,[8b] which crystallized in a monoclinic system with the cation located around a point of inversion and the atoms of the anion situated on general positions. This crystal appeared to contain disorder of the anion, but this was not resolved.[8b] The Re–O distance in **2** of 1.788(6) Å is similar to that for $[ReO_2(dppe)_2]^+$[8b] of 1.781(6) Å. However, the Re–P distances of 2.476(2) and 2.473(2) Å in **2** are significantly shorter than those in $[ReO_2(dppe)_2]^+$[8b] of 2.497(3) and 2.485(3) Å.

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The bite angle of the dppee chelate of 81.18(8)°, i.e. the P(1)-ReP(2) angle, is significantly larger than that of 79.7(1)° for dppe in $[ReO_2(dppe)_2]^+$. This may be attributed to the requirements of the –CHCH– chain in the dppee ligand as opposed to the $-CH_2CH_2-$ chain in dppe.

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Supplementary Material Available: Figures depicting stereoviews of the unit cell packing for **1** and **3**, tables of full crystallographic data for **1** and **3**, a listing of H atom positions for **1**, and tables of bond distances, bond angles, and anisotropic displacement parameters for **1** and **3** (19 pages). Ordering information is given on any current masthead page.