carbons at 134.67 (t, J_{C-P} = 5.2 Hz), 133.38 (s), 129.59 (t, J_{C-P} = 6.0 Hz), 124.54 (dd, J_{C-P} = 71.9, 2.6 Hz), triflate carbon not observed, 95.62 (d, J_{C-P} = 2.7 Hz, C_5Me_5), 14.19 (d, J_{C-P} = 38.6, PMe_3), 9.46 (s, C_5*Me*$_5$); $^{31}P\{^1H\}$ NMR (ppm, CD_2Cl_2) 15.54 (s with ^{195}Pt satellites, J_{P-Pt} = 3774 Hz, 2 P–Pt), –16.00 (s, P–Ir); ^{19}F NMR (ppm, CD_2Cl_2) –78.97 (s). Anal. Calcd for $C_{51}H_{54}Cl_2F_6IrO_6P_3PtS_2$: C, 41.05; H, 3.65. Found: C, 40.36; H, 3.60.

Single-Crystal X-ray Diffraction Study of 10. Orange crystals of **10** were obtained by vapor diffusion of Et_2O into a CH_3NO_2 solution. A suitable crystal with a dimension of 0.30 × 0.20 × 0.12 mm was mounted on a glass fiber and was coated with epoxy cement for preliminary data collection on a Enraf-Nonius CAD-4 diffractometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using setting angles of 25 reflections in the range 20° < 2θ < 28°. The monoclinic cell parameters and calculated volume are as follows: a = 12.062 (1) Å, b = 20.776 (3) Å, c = 19.722 (2) Å, and V = 4922.56 Å^3. The space group was determined to be $P2_1/n$ (No. 1014).

The data were collected at a temperature of 16 (1) °C using a variable scan rate. A total of 9082 reflections were collected, of which 8366 were unique and not systematically absent. As a check on crystal and electronic stability, two representative reflections were measured every 200 reflections.

Lorentz and polarization corrections, and an empirical absorption correction based upon a series of ψ scans, were applied to the data. Inspection of the intensity standards revealed an overall reduction of 12.5% of the original intensity. The data were corrected for this decay. The structure was solved by the Patterson heavy-atom method. The structure was refined in full-matrix least squares, where the function minimized was $\sum w(|F_o| - |F_c|)^2$, with a weight of 1.0 for all observed reflections. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and were not refined. Scattering factors, and $\Delta f'$ and $\Delta f''$ values were taken from the literature.[10] Anomalous dispersion effects were included in F_c.[11] All calculations were performed on a VAX 8300 computer with the SDP/VAX package.[12]

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Registry No. 1, 80298-79-9; 2, 80298-81-3; 3, 137363-15-6; 4, 137363-16-7; 5, 137363-18-9; 6, 137363-20-3; 7, 59329-00-9; 8, 15604-36-1; 9, 137393-29-4; 10, 137363-26-9; 10·0.15CH_2Cl_2, 137363-27-0; 11, 137363-22-5; 12, 137363-24-7.

Supplementary Material Available: A table of anisotropic thermal parameters for **10** (3 pages); a listing of calculated and observed structure factors for **10** (23 pages). Ordering information is given on any current masthead page.

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$[ReH_2(CO)_2(PMe_2Ph)_3]^+$, a Dihydride Complex with Classical and Nonclassical Tautomeric Forms in Equilibrium

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Reactions of $[ReH_3(CO)(PMe_2Ph)_3]$ (**1**) with PMe_2Ph or CO in refluxing THF give the monohydride complexes *trans*-$ReH(CO)(PMe_2Ph)_4$ (**2**) and *cis,mer*-$[ReH(CO)_2(PMe_2Ph)_3]$ (**3**), respectively. Protonation of **2** with $HBF_4 \cdot OMe_2$ in CH_2Cl_2 at 298 K gives the classical dihydride complex $[ReH_2(CO)_2(PMe_2Ph)_3]^+$ (**4**), while protonation of **3** in CD_2Cl_2 at 193 K results in an equilibrium mixture of the classical dihydride complex $[ReH_2(CO)_2(PMe_2Ph)_3]^+$ (**5a**) and its nonclassical dihydrogen tautomer $[Re(\eta^2\text{-}H_2)(CO)_2(PMe_2Ph)_3]^+$ (**5b**). The η^2-HD isotopomer of **5b**, formed by protonation of the corresponding monodeuteride complex, shows a $^1J_{HD}$ value of 31 Hz in the ^{1}H NMR spectrum. Variable-temperature ^{1}H NMR equilibrium studies for the conversion of **5a** to **5b** produce the thermodynamic parameters ΔH = 1.7 ± 0.4 kcal mol^{-1} and ΔS = 8 ± 3 cal mol^{-1} K^{-1}. The lower limit of $\Delta G^{\neq}$ for the conversion of **5b** to **5a** at 223 K is estimated to be 11.5 ± 0.3 kcal mol^{-1}.

Introduction

Transition-metal η^2-dihydrogen complexes have received much recent attention.[1] Complexes on the borderline between classical, $M(H)_2$, and nonclassical, $M(\eta^2\text{-}H_2)$, behavior are of particular interest. In most cases, a pair of interconverting tautomers are found,[2-6] one of which is unambiguously classical, with $r(H \cdots H)$ > 1.65 Å, and the other nonclassical, with $r(H-H)$ < 1 Å.

Very recently Howard et al.[7] have shown by neutron diffraction that $ReH_7\{P(p\text{-tolyl})_3\}_2$ has an H···H distance of 1.357 Å, an intermediate value which lies between the

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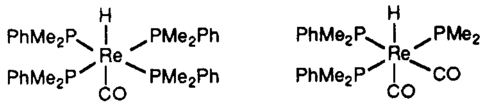
0276-7333/92/2311-0237$03.00/0

Chart I



2 3

two r(H–H) ranges previously ascribed to the two classes of complexes, whereas all other H···H distances in the molecule are larger than 1.74 Å. This complex can be regarded as an eight-coordinate dodecahedral dihydrogen complex with an elongated η^2-H_2 ligand occupying one coordination vertex, and there is no evidence for a tautomeric equilibrium in solution. The results of X-ray diffraction and solution ^{1}H NMR T_1 studies of $[ReH_6\{PPh(CH_2CH_2CH_2PCy_2)_2\}]^+$ [8a] and $[ReH_6\{PPh(CH_2CH_2PPh_2)_2\}]^+$ [8b] suggest that both exist as a single dihydrogen tautomer with a relatively long H–H bond distance.

This poses a question: why do some borderline hydride complexes, such as $ReH_7\{P(p\text{-tolyl})_3\}_2$, appear to adopt a single structure with an intermediate H–H distance but most others have two tautomeric forms in equilibrium? We have been looking for further examples of hydride complexes in the borderline region in order to try to answer this question. This paper describes the synthesis and characterization of $[ReH_2(CO)(PMe_2Ph)_4]^+$ and $[ReH_2(CO)_2(PMe_2Ph)_3]^+$. The first is a purely classical dihydride complex, but the latter exists as an equilibrium mixture of a classical dihydride complex and its nonclassical dihydrogen tautomer.

Results and Discussion

Synthesis and Characterization of *trans*-ReH(CO)(PMe$_2$Ph)$_4$ (2) and *cis,mer*-ReH(CO)$_2$(PMe$_2$Ph)$_3$ (3). In previous papers,[6] we described the synthesis and reactivity of $ReH_3(CO)(PMe_2Ph)_3$ (1), which is formed by treatment of $ReCl_3(CO)(PMe_2Ph)_3$ with $LiAlH_4$. Protonation of 1 with $HBF_4 \cdot OEt_2$ gives a tautomeric equilibrium mixture of $[ReH_4(CO)(PMe_2Ph)_3]^+$ and $[ReH_2(\eta^2\text{-}H_2)(CO)(PMe_2Ph)_3]^+$.[6] Reactions of 1 with Ph_3SiH and Ph_3SnH lead to the formation of the seven-coordinate complexes $ReH_2(EPh_3)(CO)(PMe_2Ph)_3$ (E = Si, Sn), which show unusual stereochemical rigidity.[9]

We now find that reactions of 1 with PMe_2Ph or CO in refluxing THF afford the monohydride complexes *trans*-$ReH(CO)(PMe_2Ph)_4$ (2) and *cis,mer*-$ReH(CO)_2(PMe_2Ph)_3$ (3) (eq 1). The new complexes were isolated in moderate

$$\underset{1}{ReH_3(CO)(PMe_2Ph)_3} + L \rightarrow$$
$$ReH(CO)L(PMe_2Ph)_3 + H_2 \quad (1)$$
$$L = PMe_2Ph\ (2),\ CO\ (3)$$

yields as air-stable white or off-white solids and were identified from their microanalytical and spectroscopic data. The corresponding isotopomers $ReD(CO)(PMe_2Ph)_4$ (2-*d*) and $ReD(CO)_2(PMe_2Ph)_3$ (3-*d*) were similarly prepared from $ReD_3(CO)(PMe_2Ph)_3$ (1-d_3).

The ^{1}H NMR spectrum of 2 in CD_2Cl_2 shows a binomial quintet hydride resonance at δ −5.34 with a $^2J_{HP}$ value of 23.3 Hz, indicating an octahedral configuration with the hydride ligand cis to four equivalent PMe_2Ph ligands and trans to the CO ligand, as shown in Chart I. The selectively hydride-coupled ^{31}P NMR spectrum shows a doublet ($^2J_{HP}$ = 22.4 Hz), confirming the presence of only one hydride ligand. The $^{13}C\{^1H\}$ spectrum displays a binomial quintet (δ 207.6, $^2J_{PC}$ = 8.3 Hz) for the CO ligand. The IR spectrum of 2 in Nujol mull shows a strong ν(CO) band at 1811 cm^{-1} and a weak ν(Re–H) band at 1957 cm^{-1}. The ν(Re–H) band is absent in the deuterated complex 2-*d*. No ν(Re–D) band is observed for 2-*d*, however, because it is buried under the aromatic ring C═C stretching bands.

Table I. Variable-Temperature ^{1}H NMR T_1 Data for the Hydride Resonance of $[ReH_2(CO)(PMe_2Ph)_4]^+$ (4) in CD_2Cl_2 at 250 MHz

temp, K	T_1, ms	temp, K	T_1, ms
158	164	200	136
170	153	210	140
180	144	220	150
190	138	230	158

The ^{1}H NMR spectrum of 3 in CD_2Cl_2 shows a triplet of doublets (δ −4.72, $^2J_{HP}$ = 28.1 and 21.7 Hz) in the hydride region. The lack of a large $^2J_{HP}$ coupling constant indicates that the hydride ligand is cis to all three PMe_2Ph ligands, which requires the *cis,mer*-octahedral structure shown in Chart I. The $^{31}P\{^1H\}$ NMR spectrum shows an AM_2 pattern ($^2J_{PP}$ = 26.9 Hz). The IR spectrum of 3 in Nujol mull shows a weak ν(Re–H) band at 1937 cm^{-1} and a pair of strong ν(CO) bands at 1824 and 1933 cm^{-1}, consistent with a *cis*-dicarbonyl structure.

Protonation of *trans*-ReH(CO)(PMe$_2$Ph)$_4$ (2). Protonation of 2 with $HBF_4 \cdot OMe_2$ in CH_2Cl_2 at 25 °C occurs rapidly without hydrogen evolution and yields the stable classical dihydride complex $[ReH_2(CO)(PMe_2Ph)_4]^+$ (4), which was isolated as the tetraphenylborate salt by counterion metathesis with $NaBPh_4$. Complex 4 is not deprotonated by NEt_3 but can be deprotonated by stronger bases such as KOH in CH_2Cl_2 to regenerate 2 quantitatively.

The hydride region of the ^{1}H NMR spectrum of 4 in CD_2Cl_2 at 158 K shows a complex pattern centered at δ −5.1 with two sharp outer lines flanking a broad central region which consists of many overlapping lines. Similar non-first-order hydride patterns have also been observed for $[ReH_4L_4]^+$ (L = PMe_2Ph,[10a] $PMePh_2$[10b]) and MH_4L_4 (M = Mo, W; L = PMe_2Ph, $PMePh_2$).[11] As the temperature is raised, the complex central region simplifies and becomes three broad lines at 298 K. On further warming to 310 K, the whole hydride pattern resembles a binomial quintet at δ −4.74 ($^2J_{HP}$ = 30.6 Hz) due to faster intramolecular rearrangements. The large $^2J_{HP}$ coupling constant is inconsistent with the presence of an η^2-H_2 ligand, which normally shows much smaller $^2J_{HP}$ values (<5 Hz).[1] The selectively hydride-coupled ^{31}P NMR spectrum of 4 at 298 K shows a triplet ($^2J_{HP}$ = 29.8 Hz), confirming the presence of two hydride ligands. The $^{13}C\{^1H\}$ spectrum at 298 K displays a multiplet at δ 197.6 for the CO ligand.

The IR spectrum of 4 in Nujol mull shows a strong ν(CO) band at 1881 cm^{-1} and a weak ν(Re–H) band at 1957 cm^{-1}. The other expected ν(Re–H) band is probably buried under the strong ν(CO) band or too weak to be observed. The ν(CO) stretching frequency of 4 is significantly higher than that of 2, which indicates the decreased Re to CO π-back-donation in 4 due to an increase in the formal oxidation state upon protonation.

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Solution ^1H NMR spin–lattice (T_1) relaxation time measurements have proven useful for distinguishing classical from nonclassical structures in hydride complexes.[12] The variable-temperature T_1 data for the hydride resonance of 4 in CD_2Cl_2 at 250 MHz are given in Table I. The minimum T_1 value of 136 ms found at 200 K is consistent with a classical dihydride structure.[1]

The HD isotopomer $[ReHD(CO)(PMe_2Ph)_4]^+$ (4-*d*) is formed from protonation of 2-*d* with $HBF_4{\cdot}OMe_2$. The $^1H\{^{31}P\}$ NMR spectrum of 4-*d* shows no significant H–D coupling for the hydride resonance, which also supports the classical formulation. The selectivity hydride-coupled ^{31}P NMR spectrum of 4-*d* shows a doublet ($^2J_{HP}$ = 29.4 Hz), confirming the presence of only one hydride ligand. The hydride region of the $^1H\{^{31}P\}$ NMR spectrum of an isotopomeric mixture of 4 and 4-*d* shows a small upfield isotope shift of −0.0074 ppm/D, as expected from the two-bond deuterium isotope effects.[13] We have observed similar isotope shifts in other rhenium hydride complexes.[6,8b,9,14]

Protonation of *cis,mer*-$ReH(CO)_2(PMe_2Ph)_3$ (3). Protonation of a neutral classical hydride can give a nonclassical η^2-H_2 complex,[1] because the net positive charge introduced onto the complex by protonation tends to reduce the $M(d_\pi)$ to $H_2(\sigma^*)$ π-back-donation, favoring a nonclassical structure. We find that although this strategy does not work for 2, it is successful for 3, in which a σ-donating PMe_2Ph ligand in 2 is replaced by a strongly π-accepting ligand CO.

Protonation of 3 with $HBF_4{\cdot}OMe_2$ in CD_2Cl_2 at 193 K results in an equilibrium mixture of the classical dihydride complex $[ReH_2(CO)_2(PMe_2Ph)_3]^+$ (**5a**) and its nonclassical dihydrogen tautomer $[Re(\eta^2\text{-}H_2)(CO)_2(PMe_2Ph)_3]^+$ (**5b**). The protonation is reversible, and addition of NEt_3 leads to immediate deprotonation and quantitative recovery of 3. Complex 3 therefore has a much lower Brønsted basicity than 2, reflecting the reduced electron density on the rhenium center in 3 versus that in 2.

Complexes **5a** and **5b** are not stable above 233 K. They lose hydrogen irreversibly to give products that we cannot characterize. The decomposition rate is highly temperature-dependent. A solution of **5a** and **5b** prepared in situ in CD_2Cl_2 was stored at 193 K for 1 week without significant decomposition. Both **5a** and **5b** were characterized at low temperatures by ^1H and ^{31}P NMR studies and T_1 measurements as described below.

Complex **5a** is clearly a classical dihydride complex, because the ^1H NMR hydride resonance at 193 K appears as a quartet at δ −4.87 with a large $^2J_{HP}$ coupling constant of 21 Hz. The $^{31}P\{^1H\}$ NMR spectrum at 193 K shows a broad resonance for **5a**. Both the ^1H NMR and ^{31}P NMR spectra indicate that **5a** is highly fluxional, as is commonly found for a seven-coordinate complex.[9] Consistent with the classical formulation, the HD isotopomer $[ReHD(CO)_2(PMe_2Ph)_3]^+$ (**5a**-*d*), formed from protonation of 3-*d* with $HBF_4{\cdot}OMe_2$, shows no significant H–D coupling for the hydride resonance (Figure 1).

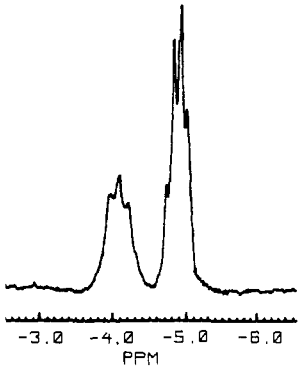

Figure 1. Hydride region of the 250-MHz ^1H NMR spectrum of an equilibrium mixture of $[ReHD(CO)_2(PMe_2Ph)_3]^+$ (**5a**-*d*) and $[Re(\eta^2\text{-}HD)(CO)_2(PMe_2Ph)_3]^+$ (**5b**-*d*) in CD_2Cl_2 at 193 K.

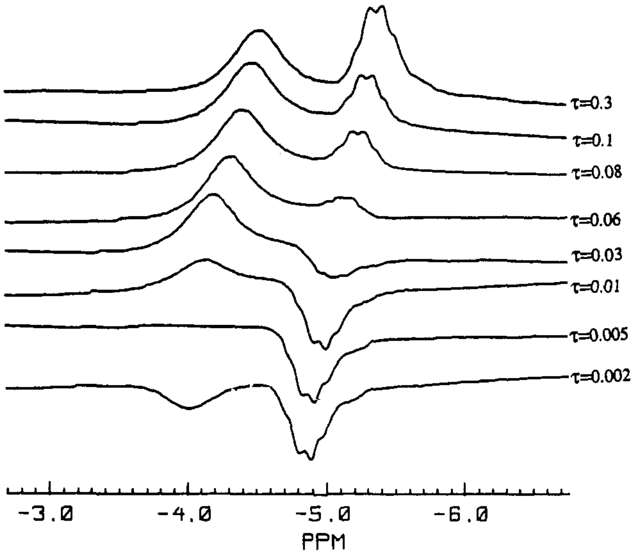

Figure 2. ^1H NMR (250 MHz) inversion-recovery spectra of an equilibrium mixture of $[ReH_2(CO)_2(PMe_2Ph)_3]^+$ (**5a**) and $[Re(\eta^2\text{-}H_2)(CO)_2(PMe_2Ph)_3]^+$ (**5b**) in CD_2Cl_2 at 213 K showing that the broad hydride resonance of **5b** clearly relaxes much faster than the quartet hydride resonance of **5a**.

Table II. Variable-Temperature ^1H NMR T_1 Data for the Hydride Resonances of $[ReH_2(CO)_2(PMe_2Ph)_3]^+$ (5a) and $[Re(\eta^2\text{-}H_2)(CO)_2(PMe_2Ph)_3]^+$ (5b) in CD_2Cl at 250 MHz

	T_1, ms			T_1, ms	
temp, K	**5a**	**5b**	temp, K	**5a**	**5b**
183	101	12	203	61	7
188	89	10	208	73	8
193	65	9	213	93	9
198	53	8			

At 193 K the dihydrogen tautomer **5b** shows a broad hydride resonance (δ −4.01, $w_{1/2} \approx 90$ Hz) typical of an η^2-H_2 complex, without resolvable coupling to the ^{31}P nuclei. The $^{31}P\{^1H\}$ NMR spectrum at 193 K shows an AM_2 pattern ($^2J_{PP}$ = 22 Hz) for **5b**. The complex probably adopts a *cis,mer* octahedral structure similar to that of 3 shown in Chart I and with the η^2-H_2 trans to one π-accepting CO ligand. As shown in Figure 1, the corresponding η^2-HD complex $[Re(\eta^2\text{-}HD)(CO)_2(PMe_2Ph)_3]^+$ (**5b**-*d*) shows a well-defined 1:1:1 triplet with a $^1J_{HD}$ coupling constant of 31 Hz. The $^1J_{HD}$ value lies at the upper end of the range commonly found for η^2-H_2 complexes.[1] This probably indicates a short *r*(H–H) value of 0.8–0.9 Å.

The variable-temperature ^1H NMR T_1 data for the hydride resonances of **5a** and **5b** in CD_2Cl_2 at 250 MHz are

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Table III. Thermodynamic Parameters for the Equilibrium between $[ReH_2(CO)_2(PMe_2Ph)_3]^+$ (5a) and $[Re(\eta^2\text{-}H_2)(CO)_2(PMe_2Ph)_3]^+$ (5b) in CD_2Cl_2

temp, K	K_{eq}[a]	ΔH, kcal mol^{-1} [b]	ΔS, cal mol^{-1} K^{-1} [c]
183	0.51	1.7 ± 0.4	8 ± 3
188	0.60		
193	0.66		
198	0.73		
203	0.82		
208	0.86		
213	1.00		
218	1.09		

[a] K_{eq} is defined as [**5b**]/[**5a**] and determined by ^1H NMR integration of the hydride resonances of **5a** and **5b**. [b] Calculated from the slope of the ln K_{eq} vs $1/T$ plot. [c] Calculated from the intercept of the ln K_{eq} vs $1/T$ plot.

listed in Table II. Figure 2 shows the differential relaxation behavior of the two tautomers at 203 K. The dihydrogen tautomer **5b** clearly relaxes much faster than the dihydride tautomer **5a**. The minimum T_1 values for **5a** and **5b** are 53 and 7 ms, respectively.

The T_1(min) value for **5a** is rather low for a classical dihydride complex. Cotton et al.[15a] suggested that contributions from Re–H dipole–dipole relaxation and scalar relaxation might be present in rhenium hydride complexes. Quantitative studies by Halpern et al.,[16] Bakhmutov et al.,[17] and ourselves[18] have shown that Re–H dipole–dipole relaxation can make a significant contribution to the T_1 relaxation, which can lead to T_1 values as short as 55 ms at 250 MHz for classical hydride complexes containing no η^2-H_2 ligand,[6,14,15] and that scalar relaxation is not important, however. It is also possible that the T_1 value of **5a** is partially lowered by exchange between **5a** and **5b** at a rate too slow to bring about the coalescence of chemical shifts but fast enough to give partial averaging of the T_1 values.[6,12c]

Thermodynamics and Kinetics of the Equilibrium between $[ReH_2(CO)_2(PMe_2Ph)_3]^+$ (5a) and $[Re(\eta^2\text{-}H_2)(CO)_2(PMe_2Ph)_3]^+$ (5b). The tautomeric equilibrium between **5a** and **5b** is very temperature-dependent and at higher temperature is shifted toward **5b**. The temperature dependence of the equilibrium constant was studied by integration of the ^1H NMR hydride resonances of the two tautomers in the temperature range 183–218 K. The data are summarized in Table III. The plot of ln K_{eq} vs $1/T$ is linear and gives the following thermodynamic parameters: $\Delta H = 1.7 \pm 0.4$ kcal mol^{-1} and $\Delta S = 8 \pm 3$ cal mol^{-1} K^{-1}, for the conversion of **5a** to **5b**. The ΔH and ΔS values are somewhat larger than those found for the equilibrium between $[ReH_4(CO)(PMe_2Ph)_3]^+$ and $[ReH_2(\eta^2\text{-}H_2)(CO)(PMe_2Ph)_3]^+$.[6] Both systems show a positive entropy change, which probably in part reflects the large rotational entropy of the η^2-H_2 ligand due to rapid rotation about the Re–H_2 bond.

The free energy of activation ($\Delta G^\ddagger$) for the interconversion of **5a** and **5b** cannot be derived from the NMR coalescence technique because the complexes decompose upon warming before reaching the coalescence temperature. Nor can it be determined with accuracy by ^1H NMR spin saturation transfer experiments because of the small separation between the two hydride resonances. Nevertheless, since the coalescence does not occur even at 223 K, the lower limit of $\Delta G^\ddagger$ for the conversion of **5b** to **5a** at this temperature is 11.5 ± 0.3 kcal mol^{-1} calculated from a method described by Shanan-Atidi and Bar-Eli for a two-site exchange process with unequal populations.[19] This barrier could simply be the barrier to the oxidative addition of the η^2-H_2 ligand of **5b**, but it could possibly have a significant contribution from the barrier to intramolecular rearrangements in an initially formed unstable dihydride intermediate that subsequently rearranges to the ground-state species **5a**. The latter situation is less likely because intramolecular rearrangements in seven-coordinate complexes normally have very low barriers,[9] as manifested by the rapid fluxionality that we observe for **5a** even at 183 K.

Conclusion

We have synthesized and characterized several new rhenium hydride complexes. We find that protonation of *trans*-$ReH(CO)(PMe_2Ph)_4$ (**2**) gives the unambiguously classical dihydride complex $[ReH_2(CO)(PMe_2Ph)_4]^+$ (**4**). The substitution of a σ-donating phosphine ligand by a π-accepting CO ligand reduces the electron density on the metal center sufficiently to induce a structural change, so that protonation of *cis,mer*-$ReH(CO)_2(PMe_2Ph)_3$ (**3**) results in the formation of a species on the classical/nonclassical borderline. This species, however, shows no sign of having an η^2-H_2 ligand with a long H–H bond but exists as an equilibrium mixture of the classical dihydride complex $[ReH_2(CO)_2(PMe_2Ph)_3]^+$ (**5a**) and its nonclassical dihydrogen tautomer $[Re(\eta^2\text{-}H_2)(CO)_2(PMe_2Ph)_3]^+$ (**5b**). So far, there are more examples of tautomeric equilibrium for hydride complexes in the classical/nonclassical borderline region than cases where an elongated η^2-H_2 ligand is found, as in $ReH_2\{P(p\text{-tolyl})_3\}_2$.

Experimental Section

General Procedures. All manipulations were performed under a dry N_2 atmosphere by standard Schlenk-tube techniques. Diethyl ether, hexane, heptane, toluene, and tetrahydrofuran were distilled from Na/Ph_2CO, and dichloromethane was distilled from CaH_2. All solvents were stored under N_2 over 4-Å molecular sieves. $ReH_3(CO)(PMe_2Ph)_3$ and $ReD_3(CO)(PMe_2Ph)_3$ were prepared according to the method previously described.[6] $HBF_4{\cdot}OMe_2$ was purchased from Columbia Organic Chemicals Co., Inc.

^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker WM 250 or WM 500 spectrometers; ^1H and ^{13}C chemical shifts were measured with the residual solvent resonance as reference; ^{31}P chemical shifts were measured with external 85% H_3PO_4 as reference. ^1H NMR T_1 measurements were carried out by the inversion-recovery method using a standard 180°–τ–90° pulse sequence. IR spectra were recorded on a Nicolet 5-SX FT-IR spectrometer. Microanalyses were carried out by Desert Analytic Co.

***trans*-Hydridocarbonyltetrakis(dimethylphenylphosphine)rhenium(I) (2).** A solution of $ReH_3(CO)(PMe_2Ph)_3$ (**1**; 0.50 g, 0.79 mmol) and PMe_2Ph (200 μL, 1.40 mmol) in 15 mL of tetrahydrofuran was heated at reflux for 20 min. The resulting yellow solution was concentrated in vacuo to ca. 0.5 mL and heptane (30 mL) added. The volume of the solution was reduced by half in vacuo. Cooling and stirring resulted in the precipitation of a white microcrystalline solid, which was filtered, washed with cold heptane (3 × 10 mL), and dried in vacuo; yield 0.43 g (74%).

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Anal. Calcd for $C_{33}H_{45}OP_4Re$: C, 51.62; H, 5.91. Found: C, 51.90; H, 6.03. IR (Nujol): ν_{Re-H} 1957 cm^{-1}; ν_{CO} 1811 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 7.2–7.7 (c, 20 H, Ph), 1.56 (br s, 24 H, Me), –5.34 (qnt, $^2J_{PH}$ = 22.8 Hz, 1 H, Re–H). Selectively hydride-coupled ^{31}P NMR (CD_2Cl_2, 298 K): δ –22.3 (d, $^2J_{PH}$ = 21.6 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 207.6 (q, $^2J_{PC}$ = 8.3 Hz, CO), 142.3 (c, C_1 of Ph), 132.2 (br s, C_2 of Ph), 128.6 (s, C_4 of Ph), 127.7 (s, C_3 of Ph), 25.8 (c, Me).

$ReD(CO)(PMe_2Ph)_4$ (**2**-*d*) was similarly prepared from the reaction of $ReD_3(CO)(PMe_2Ph)_3$ with PMe_2Ph.

***cis*,*mer*-Hydridodicarbonyltris(dimethylphenylphosphine)rhenium(I) (3).** A stream of CO was bubbled for 20 min through a refluxing solution of $ReH_3(CO)(PMe_2Ph)_3$ (0.30 g) in THF (20 mL). The resulting yellow solution was concentrated in vacuo to ca. 0.5 mL and heptane (20 mL) added. The volume of the solution was reduced by half in vacuo. Cooling the solution to –78 °C resulted in the precipitation of an off-white microcrystalline solid, which was filtered, washed with cold heptane (3 × 5 mL), and dried in vacuo; yield 0.12 g (40%). Anal. Calcd for $C_{26}H_{34}O_2P_3Re$: C, 47.48; H, 5.21. Found: C, 47.30; H, 5.09. IR (Nujol): ν_{Re-H} 1937 cm^{-1}; ν_{CO} 1933, 1824 cm^{-1}. ^1H NMR (CD_2Cl_2, 298 K): δ 7.2–7.8 (c, 15 H, Ph), 1.81 (t, $^2J_{PH}$ = 6.6 Hz, 12 H, Me), 1.17 (d, $^2J_{PH}$ = 7.3 Hz, 6 H, Me), –4.72 (dt, $^2J_{PH}$ = 28.1 and 21.7 Hz, 1 H, Re–H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ –24.3 (d, $^2J_{PP}$ = 26.9 Hz, 2 P), –30.2 (t, $^2J_{PP}$ = 26.9 Hz, 1 P).

$ReD(CO)_2(PMe_2Ph)_3$ (**3**-*d*) was similarly prepared from the reaction of $ReD_3(CO)(PMe_2Ph)_3$ with CO.

Dihydridocarbonyltetrakis(dimethylphenylphosphine)rhenium(III) Tetraphenylborate (4-BPh_4). To a solution of *trans*-$ReH(CO)(PMe_2Ph)_4$ (**2**; 0.20 g, 0.26 mmol) in CH_2Cl_2 (10 mL) was added HBF_4·OMe_2 (25 μL, ca. 0.26 mmol) via a microsyringe. The resulting yellow solution was stirred for 10 min and $NaBPh_4$ (0.40 g, 1.16 mmol) added. The mixture was stirred for 1.5 h and filtered through Celite. The filtrate was evaporated in vacuo to dryness, leaving a white fluffy solid, which was washed with Et_2O (3 × 15 mL) and dried in vacuo; yield 0.20 g (71%). Anal. Calcd for $C_{57}H_{66}BOP_4Re$: C, 62.92; H, 6.11. Found: C, 63.26; H, 6.25. IR (Nujol): ν_{Re-H} 1957 cm^{-1}; ν_{CO} 1881 cm^{-1}. ^1H NMR (CD_2Cl_2, 310 K): δ 6.8–7.7 (c, 40 H, Ph), 1.91 (d, $^2J_{PH}$ = 6.6 Hz, 24 H, Me), –4.74 (qnt, $^2J_{PH}$ = 30.6 Hz, 2 H, Re–H). Selectively hydride-coupled ^{31}P NMR (CD_2Cl_2, 298 K): δ –32.7 (t, $^2J_{PH}$ = 29.8 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 298 K): δ 197.6 (m, CO), 164.4 (q, $^1J_{BC}$ = 49.3 Hz, C_1 of BPh_4), 140.5 (d, $^1J_{PC}$ = 50.5 Hz, C_1 of PMe_2*Ph*), 136.3 (q, $^2J_{BC}$ = 1.9 Hz, C_2 of BPh_4), 130.7 (s, C_4 of PMe_2*Ph*), 129.4 (d, $^2J_{PC}$ = 5.7 Hz, C_2 of PMe_2*Ph*), 129.1 (d, $^2J_{PC}$ = 5.7 Hz, C_3 of PMe_2*Ph*), 125.9 (q, $^3J_{BC}$ = 3.1 Hz, C_3 of BPh_4), 122.1 (s, C_4 of BPh_4), 23.2 (d, $^1J_{PC}$ = 35.4 Hz, Me).

$[ReHD(CO)(PMe_2Ph)_4]BPh_4$ (4-BPh_4-*d*) was similarly prepared by protonation of $ReD(CO)(PMe_2Ph)_4$ (**2**-*d*).

Deprotonation of 4-BPh_4 with KOH. KOH (0.040 g, 0.71 mmol) was added to a solution of **4**-BPh_4 (0.16 g, 0.15 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at room temperature for 20 min and then filtered through Celite. The yellow filtrate was concentrated in vacuo to ca. 0.5 mL and heptane (30 mL) added. The volume of the solution was reduced by half in vacuo. Cooling and stirring resulted in the precipitation of **2** as a pale yellow microcrystalline solid, which was filtered, washed with cold heptane (3 × 5 mL), and dried in vacuo; yield 0.078 g (68%).

Dihydridodicarbonyltris(dimethylphenylphosphine)rhenium(III) Tetrafluoroborate (5a-BF_4) and (Dihydrogen)dicarbonyltris(dimethylphenylphosphine)rhenium(I) Tetrafluoroborate (5b-BF_4). $ReH(CO)_2(PMe_2Ph)_3$ (**3**; 25 mg, 0.038 mmol) was dissolved in CD_2Cl_2 (0.4 mL) in a 5-mm NMR tube. The solution was cooled to –80 °C (dry ice/acetone), and HBF_4·OMe_2 (4 μL, ca. 0.038 mmol) was added via a microsyringe. The sample was shaken and then quickly introduced into an NMR probe precooled to –80 °C. An equilibrium mixture of **5a** and **5b** was observed by ^1H and ^{31}P NMR spectroscopy. ^1H NMR (CD_2Cl_2, 193 K): δ 7.1–7.6 (c, Ph), 1.0–2.2 (c, Me), –4.01 (br, η^2-H_2, **5b**), –5.03 (br q, $^2J_{PH}$ = 21.3 Hz, Re–H, **5a**). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 193 K): δ –15.4 (d, $^2J_{PP}$ = 22 Hz, **5b**), –29.9 (br. s, **5a**), –30.4 (t, $^2J_{PP}$ = 22 Hz, **5b**). After the NMR experiments, an excess of NEt_3 was added and ^1H and ^{31}P NMR spectra were taken again to show that **3** was regenerated quantitatively.

$[ReHD(CO)_2(PMe_2Ph)_3]BF_4$ (**5a**-BF_4-*d*) and $[Re(\eta^2\text{-}HD)(CO)_2(PMe_2Ph)_3]BF_4$ (**5b**-BF_4-*d*) were similarly prepared by protonation of $ReD(CO)_2(PMe_2Ph)_3$ (**3**-*d*).

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