Stretched H_2 Complexes: Structural Control in $ReH_7\{P(C_6H_4\text{-}p\text{-}X)_3\}_2$ (X = CH_3, H, F, CF_3, OMe) Complexes by Electronic Ligand Effects

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A series of new or known $ReH_7\{P(C_6H_4\text{-}p\text{-}X)_3\}_2$ (X = CH_3 (**1**), H (**2**), F (**3**), CF_3 (**4**), OMe (**5**)) complexes which contain isosteric phosphine ligands are studied by ^{1}H NMR spin-lattice (T_1) hydride relaxation time measurements. The T_1(min) values are found to decrease as the electron-withdrawing ability of the aromatic para substituents X of the phosphines increases. A plot of log $\{T_{1X}(\text{min})/T_{1H}(\text{min})\}$ against the Hammett σ_p constants for the substituents gives a ρ value of -0.30. The results are consistent with the formulation of **1**-**5** in solution as containing an elongated η^2-H_2 ligand with different H···H distances (for compound **1**, r(H···H) = 1.357 Å by neutron diffraction) which depend primarily on the electronic character of the phosphine ligands and increase from 1.24 Å for the most electron-withdrawing phosphine $P(C_6H_4\text{-}p\text{-}CF_3)_3$ to 1.42 Å for the most electron-donating phosphine $P(C_6H_4\text{-}p\text{-}OMe)_3$.

Introduction

Some di- or polyhydride complexes are classical and have only terminal hydride ligands with long H···H distances (>1.7 Å); others are nonclassical and contain one or more η^2-H_2 ligands with short H···H distances (0.8-1.0 Å).[1] Borderline cases also exist in which an equilibrium mixture of classical and nonclassical tautomeric forms are found in solution.[2-6] The electronic and steric factors which favor η^2-H_2 coordination over dihydride formation are not yet fully understood.

The structural assignment of the heptahydrides ReH_7L_2 (L_2 = a chelating diphosphine or two monophosphines) as classical or nonclassical has been particularly controversial. Early ^{1}H NMR spin-lattice relaxation (T_1) data of these complexes were interpreted as indicating a nonclassical formulation, i.e., $ReH_5(\eta^2\text{-}H_2)L_2$, in solution,[7] which appeared to be supported by an electrochemical study.[8] A subsequent neutron diffraction study of ReH_7(dppe) (dppe = $Ph_2PCH_2CH_2PPh_2$) showed that it adopts a classical nine-coordinate tricapped trigonal prismatic (TTP) structure in the solid state,[9] which was supported by variable-temperature ^{1}H NMR studies of several other ReH_7L_2 complexes with diphosphine ligands that undergo decoalescence upon cooling to give low-temperature hydride patterns consistent with TTP structures.[10]

The structure of ReH_7L_2 complexes with monophosphine ligands might be different, however, since these species, in contrast to their diphosphine analogues, lose hydrogen easily.[10b,11] These complexes are too fluxional on the NMR time scale to give decoalescence even at the lowest accessible temperature. More recently, a neutron diffraction study of $ReH_7\{P(C_6H_4\text{-}p\text{-}CH_3)_3\}_2$ (**1**) found an H···H distance of 1.357 Å, intermediate between the 0.8-1.0 Å range typical for η^2-H_2 ligands in known H_2 complexes and >1.7 Å typical for classical polyhydrides.[12] This compound, although lying on the classical/nonclassical borderline, is best described as an eight-coordinate dodecahedral complex with an elongated η^2-H_2 ligand occupying one coordinate vertex. The presence of an elongated η^2-H_2 ligand was also suggested for $[ReH_6\{PPh(CH_2CH_2CH_2PCy_2)_2\}]^+$ [13a] and $[ReH_6\{PPh(CH_2CH_2PPh_2)_2\}]^+$.[13b]

Very recently, ab initio theoretical calculations[14] found that the classical form of $ReH_7(PH_3)_2$ is only 2-4 kcal/mol more stable than the nonclassical form $ReH_5(\eta^2\text{-}H_2)(PH_3)_2$, but as the authors noted, the small energy difference between these forms and the use of PH_3 instead of PR_3 in the model complex makes predictions of the most stable form of ReH_7L_2 with bulkier phosphine ligands difficult.

In this paper, we report the solution ^{1}H NMR T_1 studies on a series of $ReH_7\{P(C_6H_4\text{-}p\text{-}X)_3\}_2$ (X = CH_3 (**1**), H (**2**), F (**3**), CF_3 (**4**), OMe (**5**)) complexes containing isosteric phosphine ligands and present evidence that they adopt a structure containing an elongated η^2-H_2 ligand with a range of H···H distances which depend primarily on the electronic character of the phosphine ligands. These complexes can be considered as being frozen at

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various points on the reaction profile for the oxidative addition/reductive elimination of H$_2$ at the rhenium center.

Results and Discussion

The nonclassical character of a system poised at the classical/nonclassical borderline should be increased by electron-withdrawing ligands, which are expected to reduce M(d$_\pi$) to H$_2$(σ^*) back-donation. In the case of tautomeric equilibrium mixtures, this strategy may change the relative stabilities, and hence the ratio of classical and nonclassical tautomers, but not the H···H distance of the η^2-H$_2$ ligand. In analogues of **1**, in contrast, a continuum of structures with different H···H distances might be possible.

Compounds **1**–**5** have been chosen for study because they contain phosphine ligands of the type P(C$_6$H$_4$-*p*-X)$_3$ with the same cone angle,[15] which allows us to focus primarily on the electronic ligand effects by keeping the steric effects constant. The phosphines bear aromatic para substituents X with different electron-withdrawing or -donating ability, which can be measured by their Hammett σ_p constants.[16] Any changes in the structure of **1**–**5** can be attributed to the electronic ligand effects. Compounds **1**–**3** have been previously synthesized.[17–19]

Synthesis and Characterization of New ReH$_7$L$_2$ Complexes. The compound ReOCl$_3$(AsPh$_3$)$_2$ serves as a useful starting material in rhenium chemistry.[10,20] The literature procedure for the preparation of this compound involved reduction of HReO$_4$, generated in situ by oxidation of rhenium metal with hydrogen peroxide, with AsPh$_3$ in the presence of HCl in glacial acetic acid;[21] the yield was low, however, probably because insufficient amounts of HCl and AsPh$_3$ were used. We have prepared ReOCl$_3$(AsPh$_3$)$_2$ in 98% yield starting from the commercially available KReO$_4$ and using a modification of the literature procedure (see Experimental Section).

The ligand replacement reactions of ReOCl$_3$(AsPh$_3$)$_2$ with 2 equiv of P(C$_6$H$_4$-*p*-CF$_3$)$_3$ or P(C$_6$H$_4$-*p*-OCH$_3$)$_3$ at room temperature in CH$_2$Cl$_2$ led to the formation of ReOCl$_3$L$_2$ (L = P(C$_6$H$_4$-*p*-CF$_3$)$_3$, P(C$_6$H$_4$-*p*-OCH$_3$)$_3$). Treatment of the latter with an excess of LiAlH$_4$ at 0 °C in Et$_2$O followed by hydrolysis in THF gave ReH$_7$L$_2$ (L = P(C$_6$H$_4$-*p*-CF$_3$)$_3$ (**2**), P(C$_6$H$_4$-*p*-OCH$_3$)$_3$ (**3**)), which were isolated as off-white solids. The ^{1}H NMR spectra of these new complexes show a triplet hydride resonance integrated as seven proton at all accessible temperatures, which indicates rapid fluxionality as is commonly observed for other known ReH$_7$L$_2$ complexes containing monophosphine ligands.

Variable-Temperature ^{1}H NMR T_1 Measurements on ReH$_7${P(C$_6$H$_4$-*p*-X)$_3$}$_2$ Complexes. ^{1}H NMR T_1 values of the hydride resonances of **1**–**5** were measured in CD$_2$Cl$_2$ at 250 MHz by the inversion-recovery method using a standard 180°-τ-90° pulse sequence.[7] The minimum T_1 values (T_1(min)) observed on varying the temperature are listed in Table I, together with the Hammett σ_p constants of the para substituents of the phosphine ligands. It is notable that the T_1(min) values fall in a rather wide range and decrease as the electron-withdrawing ability of the substituents increases. A plot of log {T_{1X}(min)/T_{1H}(min)}[22] against the Hammett σ_p constants of the substituents yields a straight line with a good correlation (R = 0.97) and a ρ value of −0.30 (Figure 1). This is strong evidence that the ReH$_7${P(C$_6$H$_4$-*p*-X)$_3$}$_2$ series undergoes a systematic structural change in response to the electronic influence of the substituents.

Table I. ^{1}H NMR T_1(min) Values of [ReH$_7${P(C$_6$H$_4$-*p*-X)$_3$}$_2$] and Calculated H···H Distances of η^2-H$_2$ Ligands as a Function of Hammett σ_p Constants of Para Substituents

compd	substituent (X)	Hammett σ_p const[a]	T_1(min), ms[b]	r(H···H), Å[c]
4	CF$_3$	0.54	43	1.24
2	H	0.00	55	1.30
3	F	0.06	55	1.30
1	CH$_3$	−0.17	66	1.35
5	OMe	−0.27	75	1.42

[a] From ref 16. [b] All T_1 measurements were carried out at 250 MHz in CD$_2$Cl$_2$. [c] Estimated on the basis of the assumptions mentioned in the text.

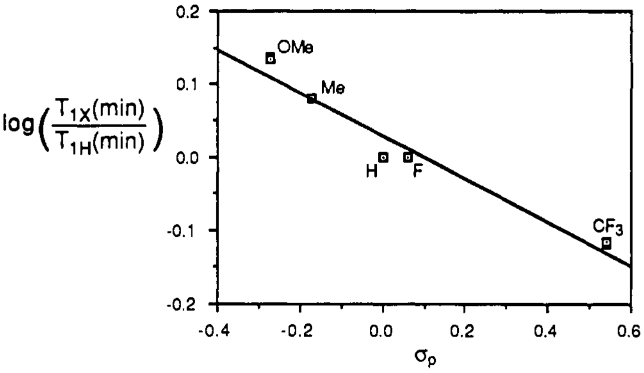

Figure 1. Plot of log {T_{1X}(min)/T_{1H}(min)} vs the Hammett σ_p constants of the substituents X for ReH$_7${P(C$_6$H$_4$-*p*-X)$_3$}$_2$ (X = CH$_3$, H, F, CF$_3$, OMe) complexes.

Are we seeing a true continuum of structures with different H···H distances for **1**–**5** in solution or do we have a rapid equilibration of classical and nonclassical tautomers? Several experimental observations appear to support the former. The ln T_1 vs 1/T plots for **1**–**5** have the usual V-shape and do not show any distortion that would be expected for a tautomeric equilibrium, where the ratio of the two tautomers should be temperature dependent.[2–6] In no case does the single hydride resonance in ^{1}H NMR or the single resonance in ^{31}P{^{1}H} NMR for any of the complexes undergo decoalescence at the lowest accessible temperature. Since the observed T_1(min) value of **1** is in excellent agreement with that we[23a] have calculated from the neutron diffraction coordinates assuming fast rotation of the η^2-H$_2$ ligand,[24] there is good reason to believe that the solid-state structure of **1** is preserved in solution. We therefore suggest that **1**–**5** all exist as a single tautomer with an elongated η^2-H$_2$ ligand in solution. Electron-withdrawing substituents on the phosphine ligands are expected to reduce the Re(d$_\pi$) to H$_2$(σ^*) back-donation, leading to shorter H···H distances and hence lower T_1(min) values. The wide range of observed T_1(min) values for **1**–**5** therefore indicates a smooth gradation of structures with different H···H distances for the η^2-H$_2$ ligand.

Estimation of the H···H Distances of the η^2-H$_2$ Ligands in ReH$_7${P(C$_6$H$_4$-*p*-X)}$_2$ from T_1(min) Data. The ^{1}H NMR T_1 relaxation of polyhydride complexes is usually dominated by proton–proton dipole–dipole contributions.[7] The T_1 values can be quantitatively predicted from neutron diffraction structures.[25] Cotton et al.,[26] Halpern et al.,[27] Bakhmutov et al.,[28a] and

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ourselves[23] find that contributions from Re–H dipole–dipole relaxation must be included to account for the discrepancies previously noted between calculated and observed T_1(min) values for rhenium hydride complexes, and so we include Re–H dipole–dipole relaxation in our calculations here.

Assuming that the solid-state structure of **1** is retained for all the ReH$_7${P(C$_6$H$_4$-*p*-X)}$_2$ complexes in solution and that all that changes is the H···H distance of the η^2-H$_2$ ligand, we can estimate the H···H distance for **1**–**5**. The positions of the terminal hydride ligands are held constant, but the H···H distance of the η^2-H$_2$ ligand is altered until a good match is obtained with the observed T_1(min) value. Morris et al.[24] have found that the rotation rate of the η^2-H$_2$ ligand around the M–(η^2-H$_2$) axis relative to the molecule as a whole has to be taken into account in the evaluation of T_1(min) data. The relaxation rate of a rapidly rotating η^2-H$_2$ ligand is only 0.25 of the rate expected for a nonrotating η^2-H$_2$ ligand with the same H···H distance. For **1**, we need to assume that the η^2-H$_2$ ligand is undergoing fast rotation in order to match the observed and predicted T_1(min) data,[23a] and we have therefore made the same assumption for **2**–**5** as well. The molecules are probably not tumbling isotropically, but Bakhmutov et al.[28b] have shown that neglect of this factor has very little effect on the interpretation of T_1(min) data in terms of H···H distances. We do not consider quantum mechanical exchange tunneling,[29] because this has not been shown to affect T_1 data and there is no evidence for its presence in **1**–**5**.

The H···H distances of the η^2-H$_2$ ligands in **1**–**5** estimated on the basis of the assumptions mentioned above are shown in Table I. The results show that the H···H distances seem to be controlled by the electronic nature of the para substituents of the phosphine ligands, increasing from 1.24 Å for the most electron-withdrawing substituent CF$_3$ to 1.42 Å for the most electron-donating substituent OMe.

We have not made allowance for the effect of possible variation of H$_2$ rotation rates on T_1(min) within the ReH$_7${P(C$_6$H$_4$-*p*-X)$_3$}$_2$ series. The barrier to H$_2$ rotation is normally rather low for η^2-H$_2$ complexes with short H···H distances. This is because M(d$_\pi$) to H$_2$(σ^*) back-donation that contributes to the barrier is usually weak, and H$_2$(σ) to M(d$_\sigma$) donation does not contribute to the barrier.[1,23] However, as M(d$_\pi$) to H$_2$(σ^*) back-donation increases and the η^2-H$_2$ ligand is increasingly elongated, the rotational barrier should increase. This probably introduces a small error in our calculations of H···H distances, especially for complex **5** with the longest H···H distance in the series.

Conclusion

We have made solution ^{1}H NMR T_1 measurements on a series of ReH$_7${P(C$_6$H$_4$-*p*-X)$_3$}$_2$ (X = CH$_3$ (**1**), H (**2**), F (**3**), CF$_3$ (**4**), OMe (**5**)) complexes which contain isosteric phosphine ligands. The T_1(min) value decreases as the electron-withdrawing ability of the aromatic para substituent X increases. These results, along with the neutron diffraction data of **1**,[12] suggest that these complexes, although lying on the classical/nonclassical borderline, adopt a structure containing an elongated η^2-H$_2$ ligand with a continuum of H···H distances, rather than exist as an equilibrium mixture of classical and nonclassical tautomers. These H···H distances model successive stages along the reaction coordinate for the oxidative addition/reductive elimination of H$_2$ at the rhenium center. Further studies are required on hydride complexes near the classical/nonclassical borderline to understand the electronic and steric factors that favor structures with elongated η^2-H$_2$ ligands over tautomeric equilibria or vice versa.

Experimental Section

General Procedures. All manipulations were performed under a dry N$_2$ atmosphere by standard Schlenk-tube techniques. Diethyl ether, heptane, toluene, and tetrahydrofuran were distilled from Na/Ph$_2$CO; dichloromethane was distilled from CaH$_2$. All solvents were stored under N$_2$ over 4-Å molecular sieves. The phosphines P(C$_6$H$_4$-*p*-X)$_3$ (X = CH$_3$, F, CF$_3$, OMe) were purchased from Strem Chemicals, Inc., and used as received without further purification.

^{1}H and ^{31}P NMR spectra were recorded on Bruker WM 250 or WM 500 spectrometers; ^{1}H chemical shifts were measured with the residual solvent resonance as reference; ^{31}P chemical shifts were measured with external 85% H$_3$PO$_4$ as reference. ^{1}H NMR T_1 measurements were carried out at 250 MHz 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 Analytics Co., Tucson, AZ.

Oxotrichlorobis(triphenylarsine)rhenium(V). AsPh$_3$ (6.40 g, 20.9 mmol) was added to a suspension of KReO$_4$ (2.00 g, 6.91 mmol) in glacial acetic acid (60 mL) and concentrated hydrochloric acid (2.3 mL, 28.0 mmol). The mixture was vigorously stirred at room temperature for 5 h. The resulting yellowish-green solid was filtered off, washed with glacial acetic acid (5 × 15 mL) and Et$_2$O (5 × 15 mL), and dried in vacuo. Yield: 6.24 g (98%). Anal. Calcd for C$_{36}$H$_{30}$As$_2$Cl$_3$ORe: C, 46.95; H, 3.28. Found: C, 46.72; H, 3.22. IR (Nujol): $\nu_{Re=O}$ 967 cm^{-1} (lit.[21] $\nu_{Re=O}$ 967 cm^{-1}).

Oxotrichlorobis(tris(*p*-(trifluoromethyl)phenyl)phosphine)rhenium(V). ReOCl$_3$(AsPPh$_3$) (0.30 g, 0.33 mmol) and P(C$_6$H$_4$-*p*-CF$_3$)$_3$ (0.30 g, 0.66 mmol) were stirred in CH$_2$Cl$_2$ (30 mL) at room temperature for 27 h. The solvent was concentrated in vacuo to ca. 0.2 mL. Addition of heptane (30 mL) resulted in the precipitation of a greenish solid, which was filtered off, washed with heptane (3 × 5 mL), and dried in vacuo. Yield: 0.38 g (95%). Anal. Calcd for C$_{42}$H$_{24}$Cl$_3$F$_{18}$OP$_2$Re: C, 40.64; H, 1.95. Found: C, 40.58; H, 1.86. IR (Nujol): $\nu_{Re=O}$ 970 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ 7.89–7.76 (m, Ph). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ −19.0 (s).

Oxotrichlorobis(tris(*p*-methoxyphenyl)phosphine)rhenium(V). This complex was similarly prepared by the above procedure by using P(C$_6$H$_4$-*p*-OMe)$_3$ (0.23 g, 0.66 mmol) and letting the solution stir for 8 h and was isolated as a green solid. Yield: 0.30 g (90%). Anal. Calcd for C$_{42}$H$_{42}$Cl$_3$O$_7$P$_2$Re: C, 49.78; H, 4.18. Found: C, 49.69; H, 4.09. IR (Nujol): $\nu_{Re=O}$ 972 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ 7.61–6.94 (m, 24 H, Ph), 3.83 (s, 18 H, OMe). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ −20.25 (s).

Heptahydridobis(tris(*p*-(trifluoromethyl)phenyl)phosphine)rhenium(VII) (4). LiAlH$_4$ (0.044 g, 1.16 mmol) was added to a suspension of ReOCl$_3${P(C$_6$H$_4$-*p*-CF$_3$)}$_2$ (0.12 g, 0.097 mmol) in Et$_2$O (50 mL) precooled to 0 °C. The mixture was stirred at 0 °C for 2 h. The resulting gray suspension was filtered through Celite and the filtrate evaporated to dryness in vacuo. The residue was dissolved in THF (20 mL), and the solution was cooled to 0 °C and hydrolyzed by dropwise addition of H$_2$O (0.1 mL) in 15 mL of THF. The mixture was dried with 5 g of anhydrous Na$_2$SO$_4$ for 15 min and filtered through Celite. The yellowish filtrate was concentrated to ca. 0.1 mL in vacuo. Addition of heptane (35 mL) resulted in the precipitation of an off-white solid. After the mixture was cooled to −20 °C, the solid was filtered out, washed with cooled heptane (2 × 4 mL), and dried in vacuo. Yield: 0.080 g (69%). Anal. Calcd for C$_{42}$H$_{31}$F$_{18}$P$_2$Re: C, 44.80; H, 2.78. Found: C, 44.77; H, 2.95. IR (Nujol): ν_{Re-H} 1964, 1933, 1885 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ 7.0–7.5 (m, 24 H, Ph), −5.00 (t, $^2J_{PH}$ = 17.3 Hz, 7 H, Re–H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ −2.34 (s).

Heptahydridobis(tris(*p*-methoxyphenyl)phosphine)rhenium(VII) (5). This compound was similarly prepared by the above procedure using ReOCl$_3${P(C$_6$H$_4$-*p*-OMe)$_3$}$_2$ (0.30 g, 0.30 mmol) and LiAlH$_4$ (0.13 g, 3.55 mmol) and was isolated as an off-white solid. Yield: 0.17 g (65%). Anal. Calcd for C$_{42}$H$_{49}$O$_6$P$_2$Re: C, 56.17; H, 5.50. Found: C, 56.01; H, 5.39. IR (Nujol): ν_{Re-H} 1971, 1943, 1906 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 298 K): δ 7.6–6.8 (m, 24 H, Ph), 3.81 (s, 18 H, OMe), −4.94 (t, $^2J_{PH}$ = 19.2 Hz, 7 H, Re–H). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 298 K): δ −23.51 (s).

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