

the quality of the crystal structure obtained for this complex is insufficient for publication due to twinning of crystals and possibly severe disorder in the CF_3 units, all indications are that the exo conformation prevails.³³ We conclude that apparently major changes in molecular conformation of these complexes arise from very minor differences in electronic distributions or overall energies. Detailed calculations with molecular orbital descriptions of the

(32) The $\text{HSC}_6\text{H}_4\text{CF}_3$ was prepared by the method given in the following: Wong, G. B.; Kurtz, D. M.; Holm, R. H.; Mortenson, L. E.; Upchurch, R. G. *J. Am. Chem. Soc.* 1979, 101, 3078. The $\text{Cp}_2\text{Nb}(\text{S-}p\text{-C}_6\text{H}_4\text{CF}_3)_2$ complex was synthesized by the same method as the other complexes. Elemental analysis: calcd C (49.92), H (3.14); found C (49.60), H (3.10).

(33) The molecular structure of $\text{Cp}_2\text{Nb}(\text{S-}p\text{-C}_6\text{H}_4\text{CF}_3)_2$ ($\text{C}_{24}\text{H}_{18}\text{F}_6\text{S}_2\text{Nb}$), $M_r = 577.4$, monoclinic, $P2_1/a$, $a = 26.001$ (11) Å, $b = 13.805$ (7) Å, $c = 13.715$ (6) Å, $\beta = 112.53$ (3)°, $V = 4547$ (4) Å³, $D_x = 1.687$ g cm⁻³, $\mu = 0.741$ mm⁻¹, $Z = 8$, $F(000) = 2312$ e⁻, $T = 193$ K. Two unique molecules were present in the unit cell. 6475 reflections were collected on a Nicolet R3m diffractometer employing the θ - 2θ scanning technique. A semiempirical absorption correction was applied (ellipsoid approximation; $\mu_{\text{xt}} = 0.15$, $T_{\text{max}} = 0.9855$, $T_{\text{min}} = 0.6477$). A total of 2349 unique reflections ($I \geq 4.0\sigma I$) were employed by full-matrix least-squares refinement on F^2 to refine 262 parameters to convergence. Final $R = 0.132$, $wR = 0.126$, $s = 3.55$. Poor crystal quality and disorder in the CF_3 groups prevented publication quality results. The conformation of the $\text{S-}p\text{-C}_6\text{H}_4\text{CF}_3$ groups was exo [$(\text{Nb-S})_{\text{av}} = 2.52$ (1) Å, $(\text{S-Nb-S})_{\text{av}} = 75.4$ (2)°].

electronic distribution and conformer preferences are presented in a subsequent paper.¹⁰

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Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic displacement coefficients, and hydrogen atom coordinates, thermal ellipsoid plots, and packing diagrams for **2**, **3**, **4** and **4**⁺ (42 pages); listing of structure factor amplitudes (33 pages). Ordering information is given on any current masthead page.

Solution Equilibrium between Classical and Nonclassical Polyhydride Tautomers $[\text{ReH}_4(\text{CO})\text{L}_3]^+$ and $[\text{ReH}_2(\eta^2\text{-H}_2)(\text{CO})\text{L}_3]^+$ ($\text{L} = \text{PMe}_2\text{Ph}$). Equilibrium Isotope Effects and an Intermediate Trihydrogen Complex in Intramolecular Site Exchange of Dihydrogen and Hydride Ligands

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Abstract: Treatment of $\text{ReCl}_3(\text{CO})(\text{PMe}_2\text{Ph})_3$ with LiAlH_4 in refluxing Et_2O gives $\text{ReH}_3(\text{CO})(\text{PMe}_2\text{Ph})_3$ (**1**). Protonation of **1** with $\text{HBF}_4\cdot\text{OEt}_2$ in CD_2Cl_2 at -78 °C results in an equilibrium mixture of $[\text{ReH}_4(\text{CO})(\text{PMe}_2\text{Ph})_3]^+$ (**2a**) and its nonclassical tautomer $[\text{ReH}_2(\eta^2\text{-H}_2)(\text{CO})(\text{PMe}_2\text{Ph})_3]^+$ (**2b**). The site exchange of dihydrogen and hydride ligands in **2b** and the interconversion of **2a** and **2b** lead to an unusual temperature dependence of the T_1 values. **2b-d**₃ shows a $^1J_{\text{HD}}$ value of 34 Hz. An isotope effect is observed for the equilibrium between **2a** and **2b**; deuteration shifts the equilibrium toward the nonclassical form. In addition, an isotope fractionation is found in partially deuterated **2b**, with a substantial preference for deuterium to occupy the nonclassical site. These two processes can lead to isotopic perturbation of resonance (IPR) effects of opposite sign and constitute a new case in which expected IPR shifts are not observed. The hydride site exchange in **2b** is much faster than the interconversion of **2b** and **2a**, indicating that **2a** is not an intermediate in the former process. The intermediacy of a trihydrogen complex is therefore proposed for the site exchange in **2b**.

Introduction

Transition-metal polyhydride complexes L_yMH_x ($x \geq 4$)¹ have attracted much interest, not only because they represent examples of the stabilization of high formal oxidation states and high coordination numbers by the uniquely small hydride ligand, but also because they offer a rich and fascinating chemistry including C-H activation.² Following the discovery of $\eta^2\text{-H}_2$ coordination,³ it is now well established⁴⁻⁷ that polyhydrides may adopt classical

structures having only terminal hydride ligands (e.g., WH_6L_3) or nonclassical structures with one or more $\eta^2\text{-H}_2$ ligands (e.g.,

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[IrH₂(η²-H₂)₂L₂]⁺). Up to now no example of a trihydride or polyhydride is known to exist as an equilibrium mixture of classical and nonclassical tautomers. In contrast, such a tautomeric equilibrium has been seen for several dihydrides.⁸

All nonclassical polyhydrides reported to date undergo facile exchange of dihydrogen and hydride ligands. As a result, the ¹J_{HD} coupling, which is considered diagnostic of η²-H₂ binding,³ cannot be observed even at the lowest accessible temperature. For reasons that are not fully understood, nearly all the known η²-H₂ complexes have a six-coordinate d⁶ configuration.³ The low T₁(min) and ²J_{HP} values of [OsH₃L₃]⁺ (L = PPh₃^{5b} and PMe₂Ph^{7c}) seemed to suggest the formulation of the complexes as [OsH₃(η²-H₂)L₃]⁺, i.e., η²-H₂ complexes of seven-coordinate d⁴ Os(IV); the alternative six-coordinate structure [OsH(η²-H₂)₂L₃]⁺ could not be excluded, however.

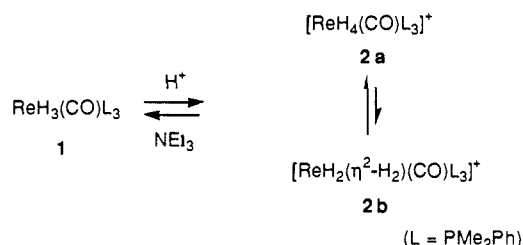
In this paper we describe the preparation and spectroscopic characterization of a tautomeric mixture of [ReH₄(CO)(PMe₂Ph)₃]⁺ (**2a**) and [ReH₂(η²-H₂)(CO)(PMe₂Ph)₃]⁺ (**2b**). This represents the first example of an equilibrium between a classical polyhydride and its nonclassical tautomer. The coexistence of **2a** and **2b** offers an opportunity to test the ¹H NMR T₁ method,^{4,5} in which short T₁(min) values are associated with the presence of the η²-H₂ ligand. To our knowledge, **2b** is the first unambiguous example of a seven-coordinate non-d⁶ η²-H₂ complex. A well-resolved ¹J_{HD} is observed for partially deuterated **2b**. The equilibrium isotope effects are examined. We also discuss the mechanism of the site exchange of dihydrogen and hydride ligands in nonclassical polyhydrides, and evidence is presented for the intermediacy of a trihydrogen complex in such a process. Part of this work has been communicated in a preliminary account.⁹

Results and Discussion

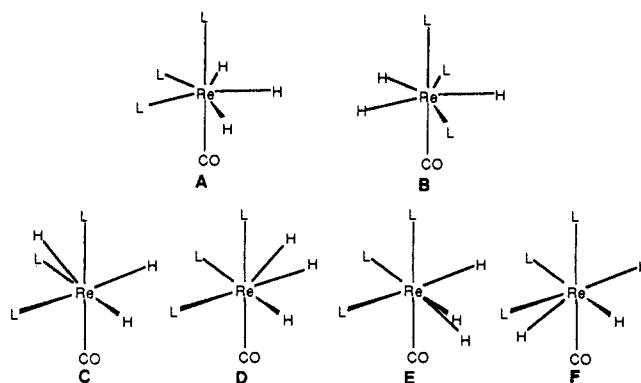
Synthesis and Characterization of ReH₃(CO)(PMe₂Ph)₃ (1). Treatment of ReCl₃(CO)(PMe₂Ph)₃¹⁰ with LiAlH₄ in refluxing Et₂O for 40 h followed by hydrolysis yields ReH₃(CO)(PMe₂Ph)₃ (**1**), which is isolated from THF/heptane as a pale-yellow solid. The ¹H NMR spectrum of **1** at 298 K shows a binomial quartet hydride resonance (δ -5.48, ²J_{PH} = 22.1 Hz, 3 H) and a doublet methyl resonance, indicating rapid fluxionality. Upon cooling to 193 K, the hydride resonance collapses into two overlapping multiplets, and three doublets are observed for the methyl groups. The ¹H{³¹P} NMR spectrum at 193 K shows an AB₂ hydride pattern with a ²J_{HH} of 7.4 Hz, which is similar to those observed for ReH₃(dppe)₂ (dppe = Ph₂P(CH₂)₂PPh₂) and ReH₃(dpae)₂ (dpae = Ph₂As(CH₂)₂AsPh₂).¹¹ The ³¹P{¹H} NMR spectrum shows a single resonance at 298 K, which decoalesces at 193 K to give an AB₂ pattern. The ¹³C{¹H} NMR spectrum at 298 K displays a quartet (²J_{PC} = 9.2 Hz) for the CO group, which becomes a doublet of triplets (²J_{PC} = 51.8, 10.1 Hz) at 193 K, indicating that the CO is trans to one PMe₂Ph and cis to the other two. The ¹H{³¹P} NMR spectrum of an isotopomeric mixture of ReH_{3-x}D_x(CO)(PMe₂Ph)₃ (1-d_x, x = 0-3) shows a small upfield isotope shift of -0.0089 ppm/D, which is in the range observed for classical rhenium polyhydrides.¹²

The spectroscopic data, especially the relatively large ²J_{HH} value for the AB₂ hydride pattern in the ¹H{³¹P} NMR spectrum at 193

Scheme I



K, are consistent with the formulation of **1** as a seven-coordinate classical trihydride complex. The coordination polyhedron is either a pentagonal bipyramid (A or B), in which the three hydrides and



two PMe₂Ph ligands lie in the pentagonal plane, and the CO and the third PMe₂Ph ligand occupy the two axial positions, or a monocapped octahedron with the three PMe₂Ph ligands in facial positions and a hydride capping any one of four of the triangular faces (C-F). We cannot distinguish between these possible structures from the spectroscopic data, but a structure similar to B has been found for ReH₃(dppe)₂ and ReH₃(PMePh₂)₄ by X-ray crystallography.¹³

Preparation and Spectroscopic Characterization of [ReH₄(CO)(PMe₂Ph)₃]⁺ (2a**) and [ReH₂(η²-H₂)(CO)(PMe₂Ph)₃]⁺ (**2b**).** Protonation of a neutral hydride complex is known to give an η²-H₂ complex in some cases.³ The net positive charge on the metal introduced by protonation tends to reduce the M(d_π) to H₂(σ*) back-donation and so favors a nonclassical structure in which the metal retains the same formal oxidation state as before protonation.

We find that protonation of **1** occurs rapidly with HBF₄·OEt₂ in CD₂Cl₂ at 193 K. The ¹H and ³¹P NMR studies described below indicate that an equilibrium mixture of a classical eight-coordinate tetrahydride [ReH₄(CO)(PMe₂Ph)₃]⁺ (**2a**) and its nonclassical seven-coordinate dihydrogen dihydride tautomer [ReH₂(η²-H₂)(CO)(PMe₂Ph)₃]⁺ (**2b**) is formed (Scheme I), with **2a** being the major species. The equilibrium is established too rapidly even at 193 K to allow the determination of the rate of approach to equilibrium by monitoring the change in the concentrations of **2a** and **2b**. Addition of NEt₃ leads to immediate deprotonation of **2a** and **2b** and quantitative recovery of **1**.

Caulton et al.¹⁴ have recently reported that ReH₃(PMe₂Ph)₄ can be protonated by [NH₄Et₃]⁺ to give a classical tetrahydride complex [ReH₄(PMe₂Ph)₄]⁺. Our results show that **1** is much less basic than ReH₃(PMe₂Ph)₄, which reflects the much lower electron density on rhenium in **1** resulting from the replacement of a σ-donor PMe₂Ph ligand in ReH₃(PMe₂Ph)₄ with a π-acceptor ligand CO.

The variable-temperature ¹H NMR spectra of **2a** and **2b** have already been presented in the preliminary account.⁹ At 193 K **2a** gives a quartet hydride resonance (δ -3.91, ²J_{HP} = 18 Hz), indicating rapid fluxionality of the hydride ligands, not unexpected

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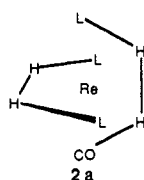
(13) (a) Albano, V. G.; Bellon, P. L. *J. Organomet. Chem.* **1972**, *37*, 151.

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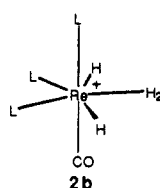
in an eight-coordinate complex.¹⁵ The relatively large $^2J_{\text{HP}}$ value is consistent with the classical formulation. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 193 K shows an AB₂ pattern ($^2J_{\text{PP}} = 15$ Hz) for **2a**, indicating that the chemically inequivalent phosphine ligands are not fluxional at this temperature. The coupling of the hydrides to two types of ^{31}P nuclei might be accidentally equal, however, leading to an apparent quartet hydride resonance. A small upfield isotope shift of -0.0072 ppm/D is observed for the hydride resonance of **2a** in the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum of the isotopomeric mixture generated by the protonation of $\text{ReH}_{3-x}\text{D}_x(\text{CO})(\text{PMe}_2\text{Ph})_3$ ($1-d_x$, $x = 0-3$).

According to Orgel's rule,¹⁶ eight-coordinate d^2 MX_4Y_4 complexes prefer a dodecahedral structure with the better π -acceptor ligands occupying the B positions to maximize overlap with the filled metal $d_{x^2-y^2}$ orbital. Consistent with this rule, $[\text{ReH}_4(\text{PMe}_2\text{Ph})_4]^+$ has been shown to have a dodecahedral structure with the PMe_2Ph ligands in the B sites.¹⁴ A similar dodecahedral structure for **2a**, shown below, with one PMe_2Ph replaced by a



CO would explain the ^1H and ^{31}P NMR spectra of **2a** if the hydrides (A sites) are exchanging and the other ligands (B sites) are fixed.

2b also shows an AB₂ pattern in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at 193 K. In the temperature range 183–203 K, the classical (Re–H) and nonclassical ($\text{Re}(\eta^2\text{-H}_2)$) sites of **2b** are distinguishable in the ^1H NMR spectrum. At 193 K, the multiplet hydride resonance at $\delta -4.90$, which collapses to a singlet upon decoupling ^{31}P , is assigned to the two classical hydride ligands, because of their large apparent $^2J_{\text{HP}}$ of 55 Hz, appropriate for terminal hydrides. A broad resonance ($\omega_{1/2} \approx 100$ Hz) at $\delta -5.40$ is assigned to the $\eta^2\text{-H}_2$ ligand; it shows no significant coupling to the phosphines because ^{31}P decoupling leads to no apparent change in the resonance. On warming to 213 K, the terminal hydride and $\eta^2\text{-H}_2$ resonances coalesce into a single broad peak due to the exchange of dihydrogen and hydride ligands. Three doublet resonances are observed at 193 K for the methyl groups of the phosphine ligands of **2b**. The spectroscopic data are consistent with the pentagonal-bipyramidal structure shown below.



On warming above 238 K, the resonances of **2a** and **2b** become broader due to the interconversion of the two tautomers. At 278 K the interconversion occurs so rapidly that only an average broad hydride resonance is observed. The loss of H_2 is rather facile above 283 K. Nevertheless, a broad quartet hydride resonance ($^2J_{\text{HP}} = 16$ Hz) is observable at 298 K if the ^1H NMR spectrum is obtained quickly. Hydrogen loss is irreversible, because deuterium is not incorporated into **2** if it is allowed to undergo partial decomposition in the presence of D_2 . Several decomposition products, which we cannot characterize, are formed from hydrogen loss. The decomposition rate is highly temperature-dependent. No significant decomposition had occurred when a CD_2Cl_2 solution

Table I. Thermodynamic Parameters for the Equilibrium between **2a** and **2b** in CD_2Cl_2

temp, K	K_{eq}^a	$\Delta H,^b$ kcal mol ⁻¹	$\Delta S,^c$ cal mol ⁻¹ K ⁻¹
188	0.17		
193	0.18		
198	0.21		
208	0.23		
218	0.27	1.1 ± 0.2	2.4 ± 0.8
228	0.30		
238	0.34		
248	0.36		
258	0.38		

^a K_{eq} is defined as $[\text{2b}]/[\text{2a}]$ and determined by ^1H NMR integration of the hydride resonances of **2a** and **2b**. ^bCalculated from the slope of the $\ln K_{\text{eq}}$ vs $1/T$ plot. ^cCalculated from the intercept of the $\ln K_{\text{eq}}$ vs $1/T$ plot.

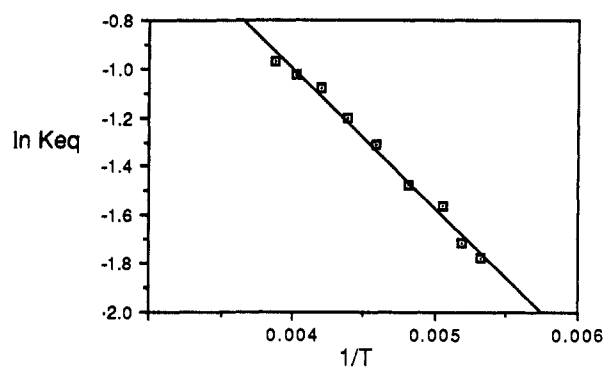


Figure 1. Plot of $\ln K_{\text{eq}}$ vs $1/T$ for the equilibrium between $[\text{ReH}_4(\text{CO})(\text{PMe}_2\text{Ph})_3]^+$ (**2a**) and $[\text{Re}(\eta^2\text{-H}_2)\text{H}_2(\text{CO})(\text{PMe}_2\text{Ph})_3]^+$ (**2b**).

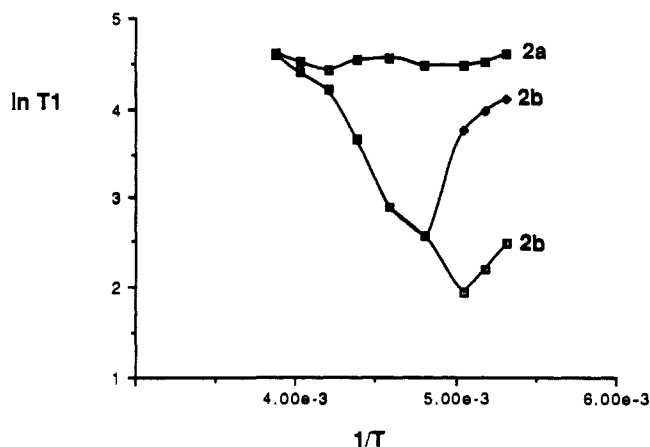


Figure 2. Plot of $\ln T_1$ vs $1/T$ for $[\text{ReH}_4(\text{CO})(\text{PMe}_2\text{Ph})_3]^+$ (**2a**) and $[\text{ReH}_2(\eta^2\text{-H}_2)(\text{CO})(\text{PMe}_2\text{Ph})_3]^+$ (**2b**).

of **2** was kept at 193 K for 1 week.

Temperature Dependence and Thermodynamics of the Tautomeric Equilibrium between 2a and 2b. The equilibrium between **2a** and **2b** is temperature-dependent and at high temperatures is driven toward **2b**. The values of the equilibrium constant, K_{eq} , were obtained by integration of the hydride resonances of the two tautomers in the temperature range 188–258 K. The data are summarized in Table I. The $\ln K_{\text{eq}}$ vs $1/T$ plot (Figure 1) is linear and gives the following thermodynamic parameters: $\Delta H = 1.1 \pm 0.2$ kcal mol⁻¹ and $\Delta S = 2.4 \pm 0.8$ cal mol⁻¹ K⁻¹, for the conversion of **2a** to **2b**. The small positive enthalpy change indicates that **2b** is only slightly less stable than **2a**. The positive entropy change of the process may be a result of the rotation of the $\eta^2\text{-H}_2$ ligand in **2b**.

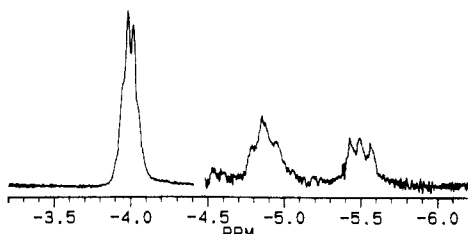
Variable-Temperature ^1H NMR T_1 Measurements on 2a and 2b. The coexistence of **2a** and **2b** provides a case in which we can test the viability of the ^1H NMR T_1 method for distinguishing classical from nonclassical polyhydrides.⁵ In addition, the presence of the exchange processes in the system offers an opportunity to

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Table II. Variable-Temperature ¹H NMR T₁ Data for a Tautomeric Mixture of [ReH₄(CO)(PMe₂Ph)₃]⁺ (**2a**) and [ReH₂(η²-H₂)(CO)(PMe₂Ph)₃]⁺ (**2b**)^a

temp, K	δ _{Re-H} ^b	assignment	T ₁ , ms
188	-3.94, q, 17.7	2a	101
	-4.86, m	2b (Re-H)	61
	-5.36, br	2b (Re-(H ₂))	12
193	-3.93, q, 17.7	2a	92
	-4.86, m	2b (Re-H)	53
	-5.34, br	2b (Re-(H ₂))	9
198	-3.90, q, 17.7	2a	88
	-4.86, m	2b (Re-H)	43
	-5.34, br	2b (Re-(H ₂))	7
208	-3.88, q, 17.7	2a	88
	-5.2, br	2b	13
218	-3.84, q, 17.7	2a	96
	-5.12, br	2b	18
228	-3.82, q, 17.7	2a	93
	-5.11, br	2b	39
238	-3.81, q, 17.7	2a	83
	-5.09, br	2b	67
248	-3.78, br q, 17.7	2a	91
	-5.07, br	2b	81
258	-3.76, br	2a	100
	-5.2, br	2b	98

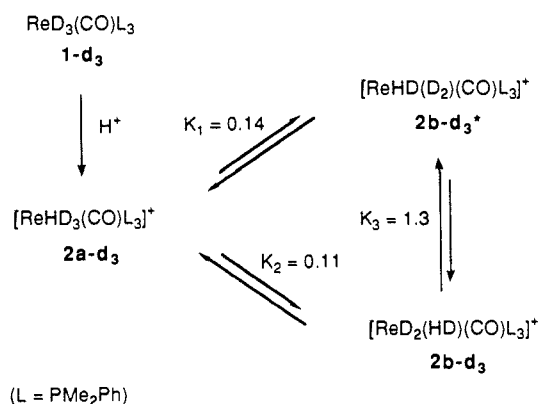
^aAll T₁ measurements were carried out at 250 MHz in CD₂Cl₂.^bHydride resonances reported as chemical shift (ppm), multiplicity (q = quartet, m = multiplet, br = broad singlet), and coupling constant (²J_{PH}) in hertz.**Figure 3.** Hydride region of the ¹H NMR (CD₂Cl₂, 193 K, 500 MHz) of an equilibrium mixture of [ReHD₃(CO)(PMe₂Ph)₃]⁺ (**2a-d₃**), left, [ReD₂(η²-HD)(CO)(PMe₂Ph)₃]⁺ (**2b-d₃**), right, and [ReHD(η²-D₂)(CO)(PMe₂Ph)₃]⁺ (**2b-d₃***), center.study the effects on the T₁ values.

¹H NMR T₁ measurements were carried out in the temperature range 188–258 K. The data are listed in Table II. There is a large difference between the T₁ values of the two tautomers; e.g., **2a** and **2b** show T₁ values of 88 and 13 ms, respectively, at 208 K. The T₁ values for the dihydrogen and hydride ligands of **2b** are also very different, being 7 and 43 ms, respectively, at 198 K.

As can be seen in the ln T₁ vs 1/T plot (Figure 2), the T₁ data do not conform to the usual V-shaped curve.^{5,17} This nonideal behavior is to be expected in a fluxional system because exchange at a rate too slow to bring about the coalescence of chemical shifts can still lead to averaging of the T₁'s. As the sample is warmed, **2b** shows a sharp decrease in the T₁ for the classical site and an increase in the T₁ for the nonclassical site just before reaching coalescence of the two sites. This is due to the exchange of dihydrogen and hydride ligands of **2b**. Similar behavior has been observed in [IrH(η²-H₂)(bq)(PPh₃)₂]⁺ (bq = 7,8-benzoquinolate).^{5b}

It is noteworthy that **2a** shows a relatively flat ln T₁ vs 1/T curve with two shallow minima, which is the result of the normal V-shaped curve being severely deformed by the exchange between **2a** and **2b**. The T₁ of **2a** decreases on warming from 188 K until a minimum is reached at 203 K. Interestingly, a second minimum is observed at 238 K due to the exchange process.

Observation of ¹J_{HD} and Equilibrium Isotope Effects. Treatment of ReCl₃(CO)(PMe₂Ph)₃ with LiAlD₄ followed by a D₂O quench

(17) Gutowsky, H. S.; Seike, A.; Takeda, T.; Woessner, D. E. *J. Chem. Phys.* **1957**, *27*, 534.**Scheme II**

yields ReD₃(CO)(PMe₂Ph)₃ (**1-d₃**). Protonation of **1-d₃** at 193 K in CD₂Cl₂ leads to the formation of an equilibrium mixture of **2a-d₃**, **2b-d₃**, and **2b-d₃*** (Scheme II and Figure 3). No intermolecular H/D scrambling occurs since only a single isotopomer can be observed for **2a**.

As shown in Figure 3, the η²-HD ligand in **2b-d₃** shows a well-defined 1:1:1 triplet (¹J_{HD} = 34 Hz) at δ = -5.48, unequivocal evidence for the nonclassical formulation. This is the first time that H-D coupling has been resolved for a nonclassical polyhydride. The ¹J_{HD} value lies at the high end of the range observed for η²-H₂ complexes, suggesting that the η²-H₂ ligand is only weakly bound to the cationic rhenium center of **2b**. This is consistent with the facile loss of H₂ above 280 K.

The values of the equilibrium constants K₁, K₂, and K₃ in Scheme II, determined at 193 K from the integration of the hydride resonances, are 0.14 ± 0.01, 0.11 ± 0.01, and 1.3 ± 0.1, respectively. It follows that ([**2b-d₃**] + [**2b-d₃***])/[**2a-d₃**] = K₁ + K₂ = 0.25 ± 0.02, which is significantly greater than the K_{eq} value (0.18 ± 0.01, Table I) for the perprotio species **2a** and **2b** at the same temperature. An isotope effect is clearly operative on the equilibrium between **2a** and **2b**, introduction of deuterium causing the equilibrium to shift toward **2b**.

It is noteworthy that the observed K₃ value of 1.3 ± 0.1 is greater than the statistical value of 1. This indicates that hydrogen and deuterium are not statistically distributed among the classical (Re-H) and nonclassical (Re(η²-H₂)) sites of **2b**, with deuterium preferentially occupying the nonclassical site, which can be interpreted as a consequence of a greater vibrational zero-point energy difference between Re(η²-HD) and Re(η²-D₂) relative to Re-H and Re-D. Although examples of deuterium isotope fractionation are well-known in systems that involve site exchange between M-H and M-CR₂H positions,¹⁸ the one reported here for site exchange between M-H and M(η²-H₂) has not been studied previously. A theoretical prediction of the magnitude and direction of the equilibrium isotope effect in this system is not yet possible, because a substantial number of vibrational modes are expected for the system and limited experimental data are available.

The experimental data presented above for deuterium isotope fractionation should be useful in the interpretation of isotopic perturbation of resonance (IPR)¹⁹ data in polyhydrides. Each isotopomer of a nonclassical polyhydride will show a distinctive hydride resonance in the fast-exchange-limit ¹H NMR spectrum

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on the conditions that M-H and M(η^2 -H₂) sites have significantly different chemical shifts and that there is a substantial deuterium isotope fractionation between the two sites.¹² Field et al.²⁰ have recently observed an IPR shift of ca. δ -0.020 at 298 K for [FeH(η^2 -H₂)(P(CH₂CH₂CH₂PMe₂)₃)⁺. In the case of **2b**, however, in spite of the isotope fractionation, we cannot observe any IPR shift in the temperature range 218–248 K where **2b** is in the fast-exchange limit. This is not so surprising because the classical and nonclassical sites in **2b** have very close chemical shifts and the average resonance after coalescence is still broad.

Precautions in the Use of the IPR Method for Tautomeric Polyhydrides. If a polyhydride exists as an equilibrium mixture of classical and nonclassical tautomers, the IPR shift is expected to arise from two contributions in the temperature range where the two tautomers undergo rapid exchange to give a single hydride resonance. We must consider the isotope effect on the equilibrium between the two tautomers as well as the isotope fractionation between classical and nonclassical sites of the nonclassical tautomer. Whether these two contributions reinforce or cancel each other depends on the relative chemical shifts of the two tautomers and of the two types of sites within the nonclassical tautomer.

In the case of **2**, we have been able to measure the appropriate chemical shifts and equilibrium isotope effects in the slow-exchange limit. On the one hand, deuteration increases the relative concentration of **2b**, whose hydride resonances are upfield from that of **2a**, leading to an upfield isotope shift. On the other hand, in **2b** deuterium prefers to occupy the nonclassical site, which is upfield from the classical site, leading to a downfield isotope shift. Thus, the two contributions turn out to have opposite signs. This, together with the instability of **2** above 280 K and the breadth of the average resonance, has made the IPR shift undetectable.

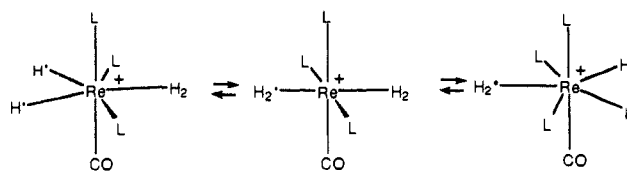
It has been generally recognized that no IPR shift will be seen if the zero-point energy difference is insufficient to induce any appreciable isotope fractionation between the sites or if the chemical shift difference between the sites is insignificant. Here we see a third general case in which no IPR effect can be seen for a tautomeric system, and this limitation of the method will need to be considered in interpreting a null result from an IPR experiment.

Mechanism of the Hydride Site Exchange Process in **2b.** Facile exchange of dihydrogen and hydride ligands is commonly observed for nonclassical polyhydrides.³ The mechanism for this process has not yet been defined. Since there are well-established examples of dynamic equilibria between dihydrogen and dihydride tautomers,⁸ it seems reasonable to postulate that the exchange involves oxidative addition of the dihydrogen ligand to form a classical tautomer as the intermediate. Direct evidence is lacking, however. Our system provides a unique opportunity to test this mechanism.

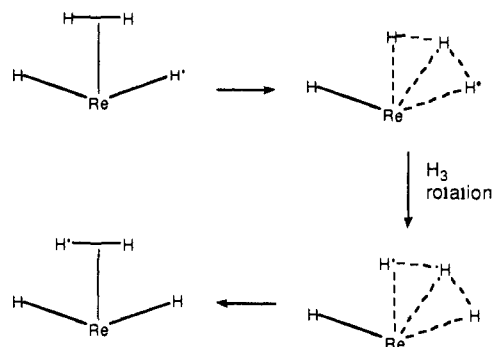
The free energies of activation for the two exchange processes can be derived by the NMR coalescence technique.²¹ The rate of the degenerate site exchange in **2b** (1:1 population ratio and $\Delta\nu = 125 \pm 10$ Hz) is calculated to be $k_1 = 278 \pm 22$ at 213 K. By use of the Eyring equation, $\Delta G_1^\ddagger(213 \text{ K}) = 9.9 \pm 0.2$ kcal mol⁻¹ is obtained. By a method²² described by Shanan-Atidi and Bar-Eli for a two-site exchange with unequal population, the rate of the conversion of **2b** to **2a** at 278 K (0.46:1.0 population ratio²³ and $\Delta\nu = 309 \pm 10$ Hz) is calculated to be $k_2 = 720 \pm 50$, which leads to $\Delta G_2^\ddagger(278 \text{ K}) = 12.6 \pm 0.2$ kcal mol⁻¹.

The large ΔG^\ddagger difference for the two exchange processes is an important clue that different mechanisms are involved. It could be argued, however, that the ΔG^\ddagger values for the two processes might be the same if measured at the same temperature. For this to happen would require ΔH^\ddagger and ΔS^\ddagger values of 1.0 ± 0.4 kcal

Scheme III



Scheme IV



mol⁻¹ and -42 ± 2 cal mol⁻¹ K⁻¹, respectively, which seem unreasonable. Kinetic studies on the bimolecular reaction of H₂ with *trans*-IrX(CO)(PPh₃)₂ gave ΔH^\ddagger and ΔS^\ddagger values in the range of 10–12 kcal mol⁻¹ and -20 to -24 cal mol⁻¹ K⁻¹, respectively.²⁴ In our case, the dihydrogen is pre-coordinated to the metal center and so ΔS^\ddagger for oxidative addition is expected to be smaller. Different mechanisms must therefore be operative for the two exchange processes of **2**.

To confirm this view, the rate of the conversion of **2b** to **2a** at 213 K was determined by a spin saturation transfer study.²⁵ Saturation of the hydride resonance of **2b** led to a ca. 11% decrease in the intensity of the hydride resonance of **2a**. This gives $\Delta G_2^\ddagger(213 \text{ K}) = 11.6 \pm 0.4$ kcal mol⁻¹, which is substantially higher than the $\Delta G_1^\ddagger(213 \text{ K})$ of 9.9 ± 0.2 kcal mol⁻¹ for the site exchange in **2b**. From the ΔG^\ddagger difference, the ratio of the rate constants for the two processes is calculated to be 55 at 213 K.

Since the site exchange in **2b** occurs much faster than the conversion of **2b** to **2a**, **2a** must be ruled out as a possible intermediate for the former process. This in turn suggests that the oxidative addition of the η^2 -H₂ ligand is *not* involved in the site exchange in **2b**. This argument would fail if the η^2 -H₂ ligand in **2b** could undergo oxidative addition to give a tetrahydride intermediate that is different from **2a**, the ground-state species, and does not rearrange to **2a** before returning to **2b**. Since the rearrangement barrier in an eight-coordinate complex is very low,¹⁵ as manifested by the rapid scrambling of the hydride ligands in **2a** even at 188 K, we feel that formation of such an intermediate is very unlikely.

The results require an associative pathway for site exchange in **2b**. Two such mechanisms can be envisaged. The first, shown in Scheme III, was suggested by Professor K. G. Caulton. It assumes a stereochemistry for **2b** slightly different from the one we prefer, but one that is also consistent with all the NMR data. The terminal hydride ligands associate to give an octahedral bis dihydrogen complex of d⁶ Re(I) as an intermediate or transition state, followed by scission of the original η^2 -H₂ ligand to give the mirror image of the original complex. According to this mechanism, the diastereotopic methyl groups of the equatorial phosphine ligands in **2b** should become equivalent when the exchange is rapid. Examination of the methyl region in the variable-temperature ¹H NMR spectra reveals that the diastereotopic methyl groups remain inequivalent up to 263 K at which the coalescence occurs. The

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(21) The hydride resonances of η^2 -H₂ complexes are broader than expected from their *T*₁ values. This "anomalous broadening" makes it difficult to obtain activation parameters ΔH^\ddagger and ΔS^\ddagger by full line-shape analysis of the variable-temperature ¹H NMR spectra. Nevertheless, the ΔG^\ddagger value at the coalescence temperature can be obtained with reliable accuracy.

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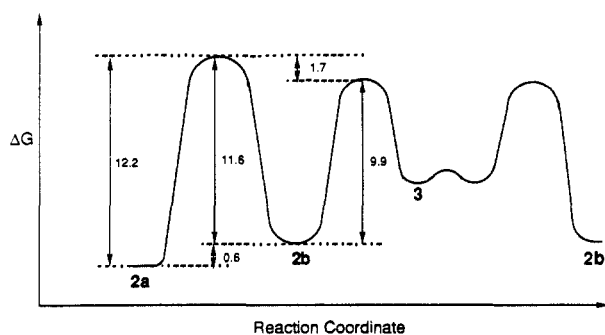
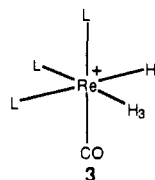


Figure 4. Free energy profile for the intramolecular exchange of dihydrogen and hydride ligands in **2b** and the interconversion of **2a** and **2b** at 213 K, with ΔG^\ddagger values in kilocalories per mole. **3** represents the proposed trihydrogen intermediate.

ΔG^\ddagger for methyl coalescence is 13.0 ± 0.4 kcal mol⁻¹, much higher than found for hydride site exchange in **2b**. The mechanism depicted in Scheme III can therefore be eliminated.

The second mechanism is shown in Scheme IV. It involves the association of a terminal hydride with the η²-H₂ ligand to give an η³-H₃ complex, [ReH(η³-H₃)(CO)(PMe₂Ph)₃]⁺, (**3**), as an



intermediate or transition state. **3** can be regarded as a pseudo-octahedral d⁶ Re(I) complex. The free energy profile constructed from the observed free energies of activation is shown in Figure 4. The position of **3** on the diagram cannot be determined because it was not directly observed; it may even be a transition state. The small barrier separating the potential wells for **3** is the barrier to the rotation of the η³-H₃ ligand, which is required for fluxional exchange to occur. This mechanism may be general for site exchange in nonclassical polyhydrides.

Trihydrogen and polyhydrogen complexes have been studied theoretically.^{26,27} The intermediacy of a trihydrogen complex was previously proposed for site exchange in ML_xH(η²-H₂) systems,^{4b,28} but an alternative classical trihydride intermediate could not be excluded. Several ground-state η³-H₃ complexes have been proposed,²⁹⁻³¹ but more recent studies³² have suggested that all these compounds are classical trihydrides. Our results show that even if an η³-H₃ species is not stable enough to observe directly, it can be accessible as an intermediate for site exchange of di-

hydrogen and hydride ligands. In our system, the η³-H₃ species **3** is no more than 10 kcal mol⁻¹ less stable than **2b**. This makes a ground-state η³-H₃ complex a reasonable goal for future work.

Conclusions

We have discovered the first example of a polyhydride with both classical and nonclassical tautomers. Rather than adopt a structure with H...H distances intermediate between that of an η²-H₂ ligand and that in a classical hydride, **2** prefers to exist as an equilibrium mixture of classical and nonclassical isomers. Further studies are needed on polyhydrides near the classical/nonclassical borderline to see if this is always the case or if intermediate H...H distances can also occur.

The interconversion of **2a** and **2b** is an interesting example of intramolecular redox isomerism. **2b** is an unequivocal seven-coordinate non-d⁶ η²-H₂ complex. The fluxionality in **2b** is frozen out at low temperature to allow the observation of the first resolved ¹J_{HD} coupling in a nonclassical polyhydride. An equilibrium isotope effect is observed for the interconversion of **2a** and **2b**; deuteration causes the equilibrium to shift toward the nonclassical form. Deuterium isotope fractionation is observed in partially deuterated **2b**, with a substantial preference for deuterium to occupy the nonclassical site.

The site exchange of dihydrogen and hydride ligands in **2b** is much faster than the conversion of **2b** to **2a**, which rules out the intermediacy of **2a** in the former process. This suggests that the ubiquitous site exchange process observed for nonclassical polyhydrides does not always involve the oxidative addition of the η²-H₂ ligand to give an intermediate classical tautomer. We find that a mechanism involving the formation of an intermediate η³-H₃ species can be preferred.

Experimental Section

General Procedures. All manipulations were performed under a dry N₂ atmosphere by standard Schlenk-tube techniques. ¹H, ¹³C, and ³¹P NMR spectra were recorded on Bruker WM 250 or WM 500 spectrometers with CD₂Cl₂ as the solvent; ¹H and ¹³C chemical shifts were measured with the residual solvent resonance as reference; ³¹P chemical shifts were measured with external 85% H₃PO₄ as reference. IR spectra were recorded on a Nicolet 5-SX FT-IR spectrometer. ¹H NMR T₁ measurements were carried out by the inversion-recovery method using a standard 180°-τ-90° pulse sequence.

Tetrahydrofuran, diethyl ether, hexane, and heptane were distilled from Na/Ph₂CO and stored under N₂ over 4-Å molecular sieves. ReCl₃(CO)(PMe₂Ph)₃ was prepared from the carbonylation of ReCl₃(PMe₂Ph)₃³³ by a modification of the literature method.¹⁰ Following the original procedure, we had difficulty in preparing the compound in pure form. Our method gives a highly pure product in essentially quantitative yield in comparison to 48% yield by the original procedure.

Trichlorocarbonyltris(dimethylphenylphosphine)rhenium(III). A solution of ReCl₃(PMe₂Ph)₃ (4.5 g, 6.4 mmol) in toluene (200 mL) was heated at reflux for 4 h with a stream of CO bubbled through the solution. The wine-red solution was evaporated to 10 mL and hexane (100 mL) added. The resulting yellow solid was washed with hexane (3 × 20 mL) and dried in vacuo. Yield: 4.7 g (100%). The spectroscopic data of the product are in agreement with those reported.¹⁰

Trihydridocarbonyltris(dimethylphenylphosphine)rhenium(III) (1). A mixture of ReCl₃(CO)(PMe₂Ph)₃ (2.0 g, 2.7 mmol) and LiAlH₄ (1.80 g, 47.4 mmol) in Et₂O (60 mL) was heated at reflux for 48 h. The resulting grey suspension was filtered through Celite and the filtrate evaporated to dryness in vacuo. The white residue was dissolved in THF (25 mL), cooled to 0 °C, and hydrolyzed by dropwise addition of H₂O (1.7 mL) in 10 mL of THF. The mixture was dried with 7 g of anhydrous Na₂SO₄ and filtered through Celite. The yellow filtrate was concentrated to 1 mL and heptane (40 mL) added. Upon cooling and stirring, a pale-yellow microcrystalline solid precipitated. This solid was filtered, washed with heptane (3 × 10 mL) and dried in vacuo. Yield: 1.1 g (65%). Anal. Calcd for C₂₅H₃₆OP₃Re: C, 47.53; H, 5.74. Found: C, 47.48; H, 5.83. IR (Nujol): ν_{Re-H} 1976, 1950, 1934 cm⁻¹; ν_{CO} 1831 cm⁻¹. ¹H NMR (298 K): δ 7.2-7.6 (c, 15 H, Ph), 1.66 (q, 8.1 Hz, 18 H, Me), -5.48 (q, 22.1 Hz, 3 H, Re-H). ¹H NMR (193 K): δ 7.2-7.6 (c, 15 H, Ph), 1.87 (d, 6.7 Hz, 6 H, Me), 1.84 (d, 6.7 Hz, 6 H, Me), 0.83 (d, 7.4 Hz, 6 H, Me), -5.3 to -5.8 (c, 3 H, Re-H). ¹H³¹P NMR (193

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K): δ 7.2-7.6 (c, 15 H, Ph), 1.87 (s, 6 H, Me), 1.84 (s, 6 H, Me), 0.83 (s, 6 H, Me), δ -5.40 (t, 7.4 Hz, 1 H, Re-H_A), -5.70 (d, 7.4 Hz, 2 H, Re-H_B). $^{31}\text{P}\{^1\text{H}\}$ NMR (298 K): δ -20.2. $^{31}\text{P}\{^1\text{H}\}$ NMR (193 K): δ -15.4 (d, 29 Hz, 2 P, P_B), -30.4 (t, 29 Hz, 1 P, P_A). $^{13}\text{C}\{^1\text{H}\}$ NMR (298 K): δ 203.2 (q, $^2J_{\text{PC}} = 9.2$ Hz, CO), 142.8 (d, $^1J_{\text{PC}} = 38.8$ Hz, C₁ of Ph), 130.5 (d, $^2J_{\text{PC}} = 11.1$ Hz, C₂ of Ph), 128.8 (s, C₄ of Ph), 128.0 (d, $^3J_{\text{PC}} = 7.4$ Hz, C₃ of Ph), 25.6 (d, $^1J_{\text{PC}} = 31.5$ Hz, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (193 K): δ 202.6 (dt, $^2J_{\text{PC}} = 51.8$, 10.1 Hz, CO), 141.7 (t, $^1J_{\text{PC}} = 42.5$ Hz, C₁ of P_BMe₂Ph), 140.3 (d, $^1J_{\text{PC}} = 35.1$ Hz, C₁ of P_AMe₂Ph), 130.1 (d, $^2J_{\text{PC}} = 9.0$ Hz, C₂ of P_AMe₂Ph), 129.3 (t, $^2J_{\text{PC}} = 11.0$ Hz, C₂ of P_BMe₂Ph), 128.1 (s, C₄ of P_BMe₂Ph), 127.9 (s, C₄ of P_AMe₂Ph), 127.4 (t, $^3J_{\text{PC}} = 8.4$ Hz, C₃ of P_BMe₂Ph), 127.1 (d, $^1J_{\text{PC}} = 7.4$ Hz, C₃ of P_AMe₂Ph), 25.7 (t, $^1J_{\text{PC}} = 37.0$ Hz, P_BMe₂Ph), 24.3 (t, $^1J_{\text{PC}} = 33.3$ Hz, P_AMe₂Ph), 21.4 (d, $^1J_{\text{PC}} = 25.9$ Hz, P_AMe₂Ph).

ReD₃(CO)(PMe₂Ph)₃ was prepared similarly by treatment of ReCl₃(CO)(PMe₂Ph)₂ with LiAlD₄ followed by hydrolysis with D₂O. The isotopomeric mixture of ReH_{3-x}D_x(CO)(PMe₂Ph)₃ (x = 0-3) was prepared by treatment of ReCl₃(CO)(PMe₂Ph)₂ with LiAlD₄ and hydrolysis with H₂O/D₂O (1:1 molar ratio).

Tetrahydridocarbonyltris(dimethylphenylphosphine)rhenium(V) Tetrafluoroborate (2a) and Dihydrido(dihydrogen)carbonyltris(dimethylphenylphosphine)rhenium(III) Tetrafluoroborate (2b). ReH₃(CO)(PMe₂Ph)₃ (**1**; 25 Mg) was dissolved in CD₂Cl₂ (0.4 mL) in a 5-mm NMR tube. The sample was cooled to -80 °C (dry ice/acetone). HBF₄·OEt₂ (6 μ L) was added via a microsyringe. The sample was shaken and then quickly introduced into an NMR probe precooled to -80 °C. ^1H NMR (193 K): δ 6.8-7.7 (c, Ph), 2.17 (d, $^2J_{\text{PH}} = 9$ Hz, Me, **2b**), 1.92 (d, $^2J_{\text{PH}} = 5$ Hz, Me, **2a**), 1.90 (d, $^2J_{\text{PH}} = 5$ Hz, Me, **2a**), 1.72 (d, $^2J_{\text{PH}} = 7$ Hz, Me, **2b**), 1.55 (d, $^2J_{\text{PH}} = 7$ Hz, Me, **2b**), 1.19 (d, $^2J_{\text{PH}} = 7$ Hz, Me, **2a**), -3.91 (q, $^2J_{\text{PH}} = 17.9$ Hz, Re-H, **2a**), -4.90 (pseudo t, $^2J_{\text{PH}} = 55$ Hz, Re-H, **2b**), -5.40 (br, η^2 -H₂, **2b**). $^{31}\text{P}\{^1\text{H}\}$ NMR (193 K): δ -26.6 (t, $^2J_{\text{PP}} = 15$ Hz, P_A, **2a**), -27.9 (d, $^2J_{\text{PP}} = 15$ Hz, P_B, **2a**), -27.6 (t, $^2J_{\text{PP}} = 11$ Hz, P_A, **2b**), -27.7 (d, $^2J_{\text{PP}} = 11$ Hz, P_B, **2b**). After the NMR experiments, excess NEt₃ was added and NMR spectra were taken again to show that **1** was regenerated quantitatively.

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Photo-Heterolysis and -Homolysis of Substituted Diphenylmethyl Halides, Acetates, and Phenyl Ethers in Acetonitrile: Characterization of Diphenylmethyl Cations and Radicals Generated by 248-nm Laser Flash Photolysis

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Abstract: Para-substituted diphenylmethyl halides, acetates, and ethers RPh(R'Ph)CH-X (R, R' = CF₃ to OCH₃), upon photolysis with ~250-nm light in acetonitrile solutions, undergo homolysis and heterolysis of the C-X bond to give the radicals, RPh(R'Ph)CH· (abbreviated as C·), and the cations, RPh(R'Ph)CH⁺ (C⁺). Whereas the quantum yields for homolysis (0.2-0.4) are rather independent of the nature of the substituent on the benzene ring, those for heterolysis increase with increasing electron-donor strength from ≤ 0.07 for CF₃ to 0.3 for OMe. The cation:radical ratios are also dependent on the nucleofugal properties of X. For the halides, the observed heterolysis:homolysis ratios correlate with the pK_a values of the conjugate acids HX and *not* with the electron affinities of X[·]. In acetonitrile, heterolysis is much less endothermic than homolysis. Homolysis and heterolysis can also be effected indirectly by reaction with triplet acetophenone (produced by 308-nm photolysis). Unless stabilized by one or more MeO, the cations decay predominantly by reaction with acetonitrile to give nitrilium ions. However, since this reaction is reversible (shown for the benzhydryl cation), the nitrilium ion contributes only to an insignificant degree to the formation of the final (cation-derived) products, which result from reaction with trace water (main product, benzhydryl alcohol; minor, benzhydrylacetamide). The rate constants for addition of C⁺ to CH₃CN are in the range 3.5×10^5 to 3.8×10^7 s⁻¹ for the cations with R = R' = Me to R = H, R' = CF₃. The rate constants for reaction of C⁺ with halides (ion recombination) are $\sim 2 \times 10^{10}$ M⁻¹ s⁻¹ (diffusion control). The radicals C· disappear by dimerization and disproportionation, for which a complete mass balance has been achieved by product analysis for the case of the benzhydryl system. At laser-pulse powers > 10 mJ electronically excited radicals, C^{*}, are additionally formed in many cases, via absorption of a light quantum by ground-state C·.

Introduction

Carbocationic structures exist as intermediates or transition states in nucleophilic substitutions, in elimination reactions, in electrophilic addition and substitution, in amide, ester, ortho ester, and acetal solvolyses, in (C-C and C-H) rearrangements, and in polymerization, to name some of the more important types of reaction.⁴ Carbocations can readily be generated in superacids

and studied by physical methods such as NMR, and an enormous wealth of information has thus been accumulated on the structures and also reactions of these species.^{5,6} With carbocations to some extent stabilized, production from appropriate precursors (C-X) is also possible in non-nucleophilic solvents, using Lewis acids⁶

(4) See, e.g., Ingold, C. K. *Structure and Mechanism in Organic Chemistry*, 2nd ed.; Cornell University Press: London, 1969. Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981.

(5) See, e.g., Olah, G. A. *Chem. Scr.* **1981**, *18*, 97.

(6) (a) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173. (b) Olah, G. A.; Schleyer, P. v. R. *Carbonium Ions*; Wiley: New York, 1968-1976; Vols. I-V.

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