Cu^{2+}, or O_2, then the chain is suppressed to the extent that the electrophilic pathway emerges, which was the method by which k_{14} was evaluated.

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82 and Argonne National Laboratory. We also acknowledge support from the U.S.-Israel Binational Science Foundation.

Registry No. 4-$CH_3C_6H_4CH_2CrL(H_2O)^{2+}$, 129834-70-4; 4-$BrC_6H_4CH_2CrL(H_2O)^{2+}$, 125329-98-8; $(CH_3)_2CHCrL(H_2O)^{2+}$, 70833-00-0; $C_2H_5CH_2CrL(H_2O)^{2+}$, 70832-98-3; $Br^{\bullet -}$, 12595-70-9; $(SCN)_2^{\bullet -}$, 34504-17-1; $I_2^{\bullet -}$, 12190-71-5.

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Kinetic and Thermodynamic Acidity of Hydrido Transition-Metal Complexes. 9.[1] A Sterically Hindered Cationic Hydride, $[H_4Re(PMe_2Ph)_4]^+$

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Received May 29, 1991

Cationic polyhydride complexes $MH_xL_y^+$ can adopt either a classical structure with individual hydride ligands or a nonclassical one, $M(\eta^2\text{-}H_2)H_{x-2}L_y^+$, with two hydrogens coordinated as a dihydrogen molecule.[2] While there has been considerable interest[3,4] in the relative acidity of dihydride cations and the corresponding η^2-H_2 complexes, only one dihydrogen complex, $CpRu(dmpe)(\eta^2\text{-}H_2)^+$,[3] has had its *thermodynamic* acidity measured in acetonitrile (the solvent we have found[1a,b] best suited for determining the thermodynamic acidity of transition-metal hydrides); no classical polyhydride cation has been examined in that solvent.[5] Furthermore, in no case has the *kinetic* acidity (k_{H^+} in eq 1) of a cationic polyhydride complex been measured

$$\mathrm{H{-}M} + \mathrm{PhNH_2} \underset{k_b}{\overset{k_{H^+}}{\rightleftharpoons}} \mathrm{M^-} + \mathrm{PhNH_3^+} \qquad (1)$$

in acetonitrile with aniline (the base we have used[1a,b,6] to compare the kinetic acidity of an extensive series of transition-metal hydrides). Finally, neither the thermodynamic nor the kinetic acidity of a *congested* hydride has ever been examined in acetonitrile; our previous studies[1,6] have involved relatively uncrowded complexes with carbonyl ligands.

Table I. Determination of the Acetonitrile pK_a of $[H_4Re(PMe_2Ph)_4][BF_4]$ (1)

base (B)	$pK_a(BH^+)$	K_{eq}	$pK_a(1)$
TMG	23.3[a]	5.66×10^{-3}	25.5
DBU	24.3[b]	7.54×10^{-2}	25.4
$K[OC_6H_5]$	26.6[c]	>0.4	<27

[a] Reference 10a,b,e. [b] Reference 11. [c] Reference 10d,e.

We have therefore quantified the thermodynamic and kinetic acidity of $[H_4Re(PMe_2Ph)_4]^+$ (**1**)[7] in acetonitrile solution. While the related rhenium hydride $[H_4Re(CO)(PMe_2Ph)_3]^+$ (**2**) exists in solution as a mixture of the classical tetrahydride and the nonclassical (η^2-H_2) dihydride tautomers[8] and the iridium analogue $[H_4Ir(PMe_2Ph)_3]^+$ (**3**) is entirely nonclassical, with two dihydride ligands and a labile dihydrogen ligand,[9] Caulton and co-workers have shown[7] **1** to exist in solution as the classical tetrahydride isomer only. Furthermore, while **2** and **3** are deprotonated by triethylamine in CH_2Cl_2,[8,9a] Caulton and co-workers have also found[7] that **1** is not deprotonated by triethylamine in that solvent.

Experimental Section

All manipulations were carried out using Schlenk, high-vacuum, or inert-atmosphere-box techniques. CD_3CN was dried over P_2O_5 and degassed by repeated freeze/pump/thaw cycles. Aniline-d_2 was generated by shaking aniline with D_2O 10 times, followed by fractional distillation from BaO and vacuum transfer prior to use; deuterium incorporation was 95%. $DNBu_2$ was prepared in the same way and dried and stored over 3-Å molecular sieves. The neutral parent complex of **1**, $H_3Re(PMe_2Ph)_3$ (**4**), was generously donated by Prof. K. G. Caulton, Indiana University, and converted to **1** by protonation with $HBF_4 \cdot OEt_2$.[7]

CD_3CN solutions of **1** and various bases were sealed under vacuum and their ^1H NMR spectra recorded on either an IBM WP-200-SY or an IBM WP-270-SY spectrometer. Concentrations of all species involved were determined by integration of ^1H peaks relative to $(Me_3Si)_2O$ as an internal standard. Since a very small amount of $(Me_3Si)_2O$ was needed, it was quantified by gas volume measurements (typically 1.05 mL at 30 mmHg and 23 °C, or 1.89×10^{-6} mol).

Results and Discussion

Thermodynamic Acidity. The inability of Et_3N to deprotonate **1** in CH_2Cl_2 suggested that a stronger base than Et_3N would be required to do so in acetonitrile. Preliminary experiments in CD_3CN showed no deprotonation of **1** with 8 equiv of tetramethylguanidine (TMG), a base whose conjugate acid has a CH_3CN pK_a of 23.3[10a,b,e] (the CH_3CN pK_a of Et_3NH^+ is 18.5[10c,e]). In contrast, potassium phenolate (the CH_3CN pK_a of PhOH is 26.6[10d,e]) completely deprotonated **1**. The use of conditions more basic than 8 equiv of TMG but less basic than phenolate was thus indicated, and the required partial deprotonation of **1** was effected by 60 equiv of TMG or 5 equiv of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) ($DBUH^+$ has a CH_3CN pK_a of 24.3[11]).

The concentrations of **1** and its conjugate base **4** in the presence of each base B (eq 2) were determined by integration of the

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0020-1669/91/1330-4470$02.50/0

$$\underset{\mathbf{1}}{H_4Re(PMe_2Ph)_4^+} + B \overset{K_{eq}}{\rightleftharpoons} \underset{\mathbf{4}}{H_3Re(PMe_2Ph)_4} + BH^+ \quad (2)$$

$$[BH^+]^2 + \left\{[B]_{tot} - 2[\mathbf{4}] + \frac{1}{K_f}\right\}[BH^+] - \frac{[\mathbf{4}]}{K_f} = 0 \quad (3)$$

$$pK_a^{MH} = pK_{eq} + pK_a^{BH^+} \quad (4)$$

hydride peaks in the ^1H NMR spectra. As both of these bases are known to associate with their conjugate acid BH^+, eq 3[1b] was used to calculate $[BH^+]$ from [**4**], the total amount of B added $[B]_{tot}$, and the B/BH^+ association equilibrium constant K_f (1.3 M^{-1} for TMG[10b,e] and 32 M^{-1} for DBU[12]). Charge balance was then used to calculate $[BHB^+]$ ($[\mathbf{4}] - [BH^+]$), and mass balance used to calculate [B] ($[B]_{tot} - 2[BHB^+] - [BH^+]$). The resulting values of K_{eq} (given in Table I) were substituted into eq 4[1a,b] to give the acetonitrile pK_a of **1** as 25.5 (1).

It is instructive to compare **1** with **2**, which, because it is deprotonated by Et_3N, must have a $pK_a < 18.5$; the neutral conjugate base of **1**, $H_3Re(PMe_2Ph)_4$ (**4**), must be at least 7 orders of magnitude more basic than the neutral conjugate base of **2**, $H_3Re(CO)(PMe_2Ph)_3$ (**5**). This increase with the substitution of PMe_2Ph for CO is about what we would expect from the effect of phosphine substitution on the pK_a of neutral carbonyl hydrides: PPh_3 substitution increases the pK_a of $HMn(CO)_5$ and $HCo(CO)_4$ by 6–7 units, and substitution by the stronger σ-donor phosphine PMe_3 increases the pK_a of $HW(CO)_3Cp$ by 10 units.[1b,13,14]

Kinetic Acidity. When **1** was allowed to react with a 300-fold excess of aniline-d_2 (0.78 M), no deuterium exchange was observed after 72 h at 40 °C or 12 h at 82 °C. We therefore used the stronger base $DNBu_2$ (the CH_3CN pK_a of $Bu_2NH_2^+$ is 18.3[10c]) to measure the kinetic acidity of **1**. In the presence of 0.1 M $DNBu_2$ in acetonitrile at 82 °C (conditions under which the pK_a values of **1** and $Bu_2NH_2^+$ indicate that no net deprotonation occurs), the hydride signal of **1** disappeared with a pseudo-first-order rate constant k_{obsd} of 1.5×10^{-5} s^{-1}. Application of the McKay equation for a species with four equivalent protons (eq 5)[6,15] gives k_{HD} (defined by eq 6) at 82 °C as 6.0×10^{-4} M^{-1}

$$k_{obsd} = k_{HD}\frac{[DNBu_2]}{4} \quad (5)$$

$$[H_{4-x}D_xReL_4]^+ + DNBu_2 \xrightarrow{k_{HD}} H_{3-x}D_xReL_4 + [HDNBu_2]^+ \quad (6)$$

s^{-1}. (We assume that k_{HD} is the rate constant for the removal of *any* H^+ by *any* molecule of dibutylamine and is independent of the isotopic nature of the remaining protons on rhenium (i.e., of the value of x) or on nitrogen and that H/D exchange among nitrogens is sufficiently fast that any H removed is replaced by D.[16])

The rate constant for proton transfer to *aniline* from **1** can be estimated from this measured k_{HD} for transfer to $DNBu_2$. Extrapolation from 82 to 25 °C with typical proton-transfer activation parameters ($\Delta H^\ddagger = 17.6$ kcal/mol and $\Delta S^\ddagger = -26.7$ eu)[6] gives 5×10^{-6} M^{-1} s^{-1}; the assumption that at least half of the decrease in thermodynamic driving force from $DNBu_2$ to $PhNH_2$ (ΔpK_a between $PhNH_3^+$ and $Bu_2NH_2^+$ is 7.75) will be reflected in the rate constant[17] allows estimation of the aniline second-order rate constant k_{H^+} (defined in eq 1) as $<10^{-9}$ M^{-1} s^{-1}. This estimate is *more than 5 orders of magnitude slower* than the rate constant (3×10^{-4} M^{-1} s^{-1} at 25 °C) predicted by the linear relationship between rate constant and pK_a^{MH} that we have found for aniline deprotonations of *uncrowded* mononuclear hydrides.[1b,6]

Little structural rearrangement is needed to deprotonate **1**: for steric reasons the structures of the $Re(PMe_2Ph)_4$ core must be very similar in **1** ($[H_4Re(PMe_2Ph)_4]^+$) and in its conjugate base **4**. The slow rate measured for proton transfer from **1** must therefore be due to steric factors—the ability of this $Re(PMe_2Ph)_4$ core to prevent close approach by aniline to Re from any direction.[18] A similar screening function must be performed by the $Mo(dppe)_2$ core in $[HMo(CO)_2(dppe)_2]^+$ (known to undergo very slow proton transfer to nitrogen bases)[19] and the $Cr(tripod)_2$ core in $HCr(tripod)_2^+$ (tripod = $MeC(CH_2PMe_2)_3$) (known to undergo slow proton transfer to its conjugate base)[20] but not by the $Ir(PMe_2Ph)_3$ core in **3** (for which fast transfer to Et_3N has been observed qualitatively at −80 °C).[9a]

Acknowledgment. This research was supported by NSF Grant CHE-8819760.

Registry No. **1**, 123674-40-8; TMG, 80-70-6; DBU, 6674-22-2; dibutylamine, 111-92-2; aniline, 62-53-3.

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Octahedral Metal Carbonyls. 78.[1] Mechanism of Alkane Displacement by 1-Hexene from (Alkane)W(CO)$_5$ Complexes (Alkane = Cyclohexane, *n*-Heptane). Estimates of the Alkane–W Bond Strengths in Condensed Media

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Received April 18, 1991

$(Solvent)M(CO)_5$ intermediates are produced in predominant concentration in solution after flash photolysis of $M(CO)_6$ complexes (M = Cr, Mo, W; eq 1); the solvation process has been

$$M(CO)_6 \xrightarrow{h\nu} [M(CO)_5] \xrightarrow{k[solv]} (solv)M(CO)_5 \quad (1)$$

studied intensively.[2-7] Where the solvent (=solv) is an alkane,

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