

Cu<sup>2+</sup>, or O<sub>2</sub>, then the chain is suppressed to the extent that the electrophilic pathway emerges, which was the method by which  $k_{14}$  was evaluated.

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**Registry No.** 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CrL(H<sub>2</sub>O)<sup>2+</sup>, 129834-70-4; 4-BrC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>CrL(H<sub>2</sub>O)<sup>2+</sup>, 125329-98-8; (CH<sub>3</sub>)<sub>2</sub>CHCrL(H<sub>2</sub>O)<sup>2+</sup>, 70833-00-0; C<sub>2</sub>H<sub>5</sub>CH<sub>2</sub>CrL(H<sub>2</sub>O)<sup>2+</sup>, 70832-98-3; Br<sup>-</sup>, 12595-70-9; (SCN)<sub>2</sub><sup>-</sup>, 34504-17-1; I<sub>2</sub><sup>-</sup>, 12190-71-5.

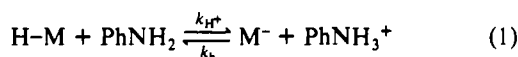
Contribution from the Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

### Kinetic and Thermodynamic Acidity of Hydrido Transition-Metal Complexes. 9.<sup>1</sup> A Sterically Hindered Cationic Hydride, [H<sub>4</sub>Re(PMe<sub>2</sub>Ph)<sub>4</sub>]<sup>+</sup>

S. Sóley Kristjánssdóttir, Amy J. Loendorf, and Jack R. Norton\*

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



in acetonitrile with aniline (the base we have used<sup>1a,b,6</sup> 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<sup>1,6</sup> have involved relatively uncrowded complexes with carbonyl ligands.

**Table I.** Determination of the Acetonitrile pK<sub>a</sub> of [H<sub>4</sub>Re(PMe<sub>2</sub>Ph)<sub>4</sub>][BF<sub>4</sub>] (1)

base (B)	pK <sub>a</sub> (BH <sup>+</sup> )	K <sub>eq</sub>	pK <sub>a</sub> (1)
TMG	23.3 <sup>a</sup>	5.66 × 10 <sup>-3</sup>	25.5
DBU	24.3 <sup>b</sup>	7.54 × 10 <sup>-2</sup>	25.4
K[OC <sub>6</sub> H <sub>5</sub> ]	26.6 <sup>c</sup>	>0.4	<27

<sup>a</sup> Reference 10a,b,e. <sup>b</sup> Reference 11. <sup>c</sup> Reference 10d,e.

We have therefore quantified the thermodynamic and kinetic acidity of [H<sub>4</sub>Re(PMe<sub>2</sub>Ph)<sub>4</sub>]<sup>+</sup> (1)<sup>7</sup> in acetonitrile solution. While the related rhenium hydride [H<sub>4</sub>Re(CO)(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>+</sup> (2) exists in solution as a mixture of the classical tetrahydride and the nonclassical (η<sup>2</sup>-H<sub>2</sub>) dihydride tautomers<sup>8</sup> and the iridium analogue [H<sub>4</sub>Ir(PMe<sub>2</sub>Ph)<sub>3</sub>]<sup>+</sup> (3) is entirely nonclassical, with two dihydride ligands and a labile dihydrogen ligand,<sup>9</sup> Caulton and co-workers have shown<sup>7</sup> 1 to exist in solution as the classical tetrahydride isomer only. Furthermore, while 2 and 3 are deprotonated by triethylamine in CH<sub>2</sub>Cl<sub>2</sub>,<sup>8,9a</sup> Caulton and co-workers have also found<sup>7</sup> 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<sub>3</sub>CN was dried over P<sub>2</sub>O<sub>5</sub> and degassed by repeated freeze/pump/thaw cycles. Aniline-*d*<sub>2</sub> was generated by shaking aniline with D<sub>2</sub>O 10 times, followed by fractional distillation from BaO and vacuum transfer prior to use; deuterium incorporation was 95%. DNBU<sub>2</sub> was prepared in the same way and dried and stored over 3-Å molecular sieves. The neutral parent complex of 1, H<sub>3</sub>Re(PMe<sub>2</sub>Ph)<sub>3</sub> (4), was generously donated by Prof. K. G. Caulton, Indiana University, and converted to 1 by protonation with HBF<sub>4</sub>·OEt<sub>2</sub>.<sup>7</sup>

CD<sub>3</sub>CN solutions of 1 and various bases were sealed under vacuum and their <sup>1</sup>H 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 <sup>1</sup>H peaks relative to (Me<sub>3</sub>Si)<sub>2</sub>O as an internal standard. Since a very small amount of (Me<sub>3</sub>Si)<sub>2</sub>O was needed, it was quantified by gas volume measurements (typically 1.05 mL at 30 mmHg and 23 °C, or 1.89 × 10<sup>-6</sup> mol).

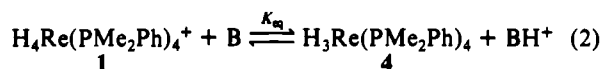
### Results and Discussion

**Thermodynamic Acidity.** The inability of Et<sub>3</sub>N to deprotonate 1 in CH<sub>2</sub>Cl<sub>2</sub> suggested that a stronger base than Et<sub>3</sub>N would be required to do so in acetonitrile. Preliminary experiments in CD<sub>3</sub>CN showed no deprotonation of 1 with 8 equiv of tetramethylguanidine (TMG), a base whose conjugate acid has a CH<sub>3</sub>CN pK<sub>a</sub> of 23.3<sup>10a,b,e</sup> (the CH<sub>3</sub>CN pK<sub>a</sub> of Et<sub>3</sub>NH<sup>+</sup> is 18.5<sup>10c,e</sup>). In contrast, potassium phenolate (the CH<sub>3</sub>CN pK<sub>a</sub> of PhOH is 26.6<sup>10d,e</sup>) 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<sup>+</sup> has a CH<sub>3</sub>CN pK<sub>a</sub> of 24.3<sup>11</sup>).

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

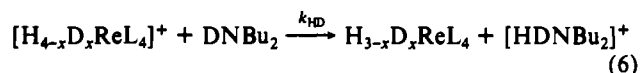
$$\text{p}K_{\text{a}}^{\text{MH}} = \text{p}K_{\text{eq}} + \text{p}K_{\text{a}}^{\text{BH}^+} \quad (4)$$

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

It is instructive to compare 1 with 2, which, because it is deprotonated by  $\text{Et}_3\text{N}$ , must have a  $\text{p}K_{\text{a}} < 18.5$ ; the neutral conjugate base of 1,  $\text{H}_3\text{Re}(\text{PMe}_2\text{Ph})_4$  (4), must be at least 7 orders of magnitude more basic than the neutral conjugate base of 2,  $\text{H}_3\text{Re}(\text{CO})(\text{PMe}_2\text{Ph})_3$  (5). This increase with the substitution of  $\text{PMe}_2\text{Ph}$  for CO is about what we would expect from the effect of phosphine substitution on the  $\text{p}K_{\text{a}}$  of neutral carbonyl hydrides:  $\text{PPh}_3$  substitution increases the  $\text{p}K_{\text{a}}$  of  $\text{HMn}(\text{CO})_5$  and  $\text{HCo}(\text{CO})_4$  by 6–7 units, and substitution by the stronger  $\sigma$ -donor phosphine  $\text{PMe}_3$  increases the  $\text{p}K_{\text{a}}$  of  $\text{HW}(\text{CO})_3\text{Cp}$  by 10 units.<sup>1b,13,14</sup>

**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  $\text{DNBu}_2$  (the  $\text{CH}_3\text{CN}$   $\text{p}K_{\text{a}}$  of  $\text{Bu}_2\text{NH}_2^+$  is 18.3<sup>10c</sup>) to measure the kinetic acidity of 1. In the presence of 0.1 M  $\text{DNBu}_2$  in acetonitrile at 82 °C (conditions under which the  $\text{p}K_{\text{a}}$  values of 1 and  $\text{Bu}_2\text{NH}_2^+$  indicate that no net deprotonation occurs), the hydride signal of 1 disappeared with a pseudo-first-order rate constant  $k_{\text{obsd}}$  of  $1.5 \times 10^{-5} \text{ s}^{-1}$ . Application of the McKay equation for a species with four equivalent protons (eq 5)<sup>6,15</sup> gives  $k_{\text{HD}}$  (defined by eq 6) at 82 °C as  $6.0 \times 10^{-4} \text{ M}^{-1}$

$$k_{\text{obsd}} = k_{\text{HD}} \frac{[\text{DNBu}_2]}{4} \quad (5)$$



$\text{s}^{-1}$ . (We assume that  $k_{\text{HD}}$  is the rate constant for the removal of any  $\text{H}^+$  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.<sup>16</sup>)

The rate constant for proton transfer to aniline from 1 can be estimated from this measured  $k_{\text{HD}}$  for transfer to  $\text{DNBu}_2$ . Extrapolation from 82 to 25 °C with typical proton-transfer activation parameters ( $\Delta H^\ddagger = 17.6 \text{ kcal/mol}$  and  $\Delta S^\ddagger = -26.7 \text{ eu}$ )<sup>6</sup> gives  $5 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$ ; the assumption that at least half of the decrease in thermodynamic driving force from  $\text{DNBu}_2$  to  $\text{PhNH}_2$  ( $\Delta\text{p}K_{\text{a}}$  between  $\text{PhNH}_3^+$  and  $\text{Bu}_2\text{NH}_2^+$  is 7.75) will be reflected in the rate constant<sup>17</sup> allows estimation of the aniline second-order rate constant  $k_{\text{H}^+}$  (defined in eq 1) as  $< 10^{-9} \text{ M}^{-1} \text{ s}^{-1}$ . This estimate

is more than 5 orders of magnitude slower than the rate constant ( $3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$  at 25 °C) predicted by the linear relationship between rate constant and  $\text{p}K_{\text{a}}^{\text{MH}}$  that we have found for aniline deprotonations of uncrowded mononuclear hydrides.<sup>1b,6</sup>

Little structural rearrangement is needed to deprotonate 1: for steric reasons the structures of the  $\text{Re}(\text{PMe}_2\text{Ph})_4$  core must be very similar in 1 ( $[\text{H}_4\text{Re}(\text{PMe}_2\text{Ph})_4]^+$ ) 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  $\text{Re}(\text{PMe}_2\text{Ph})_4$  core to prevent close approach by aniline to Re from any direction.<sup>18</sup> A similar screening function must be performed by the  $\text{Mo}(\text{dppe})_2$  core in  $[\text{HMo}(\text{CO})_2(\text{dppe})_2]^+$  (known to undergo very slow proton transfer to nitrogen bases)<sup>19</sup> and the  $\text{Cr}(\text{tripod})_2$  core in  $\text{HCr}(\text{tripod})_2^+$  (tripod =  $\text{MeC}(\text{CH}_2\text{PMe}_2)_3$ ) (known to undergo slow proton transfer to its conjugate base)<sup>20</sup> but not by the  $\text{Ir}(\text{PMe}_2\text{Ph})_3$  core in 3 (for which fast transfer to  $\text{Et}_3\text{N}$  has been observed qualitatively at  $-80$  °C).<sup>9a</sup>

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**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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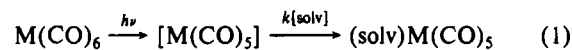
Contribution from the Department of Chemistry and Center for Organometallic Research, University of North Texas, Denton, Texas 76203-5068

### Octahedral Metal Carbonyls. 78.<sup>1</sup> Mechanism of Alkane Displacement by 1-Hexene from (Alkane)W(CO)<sub>6</sub> Complexes (Alkane = Cyclohexane, *n*-Heptane). Estimates of the Alkane–W Bond Strengths in Condensed Media

Gerard R. Dobson,\* Khalil J. Asali, Charles D. Cate, and Colin W. Cate

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(Solvent)M(CO)<sub>6</sub> intermediates are produced in predominant concentration in solution after flash photolysis of M(CO)<sub>6</sub> complexes (M = Cr, Mo, W; eq 1); the solvation process has been



studied intensively.<sup>2–7</sup> Where the solvent (=solv) is an alkane,

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