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Hydride Donor Abilities and Bond Dissociation Free Energies of Transition Metal Formyl Complexes

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Abstract: The hydride complex $[Pt(dmpe)_2H]^+$ (dmpe = 1,2-bis(dimethylphosphino)ethane) reversibly transfers H^- to the rhenium carbonyl complex $[CpRe(PMe_3)(NO)(CO)]^+$, giving the formyl $CpRe(PMe_3)(NO)(CHO)$. From the equilibrium constant for the hydride transfer (16.2), the $\Delta G°$ for the reaction was determined (−1.6 kcal/mol), as was the hydride-donating ability of the formyl (44.1 kcal/mol). The hydride-donating ability, $\Delta G°_{H^-}$, is defined as the energy required to release the hydride ion into solution by the formyl complex [i.e. $M(CHO) \rightarrow M(CO)^+ + H^-$]. Subsequently, the hydride-donating ability of a series of formyl complexes was determined, ranging from 44 to 55 kcal/mol. With use of this information, two rhenium carbonyl complexes, $[CpRe(NO)(CO)_2]^+$and $[Cp^*Re(NO)(CO)_2]^+$, were hydrogenated to formyls, employing $[Pt(dmpp)_2]^{2+}$ and Proton-Sponge. Finally, the $E_{1/2}(I/0)$ values for five rhenium carbonyl complexes were measured by cyclic voltammetry. Combined with the known $\Delta G°_{H^-}$ values for the complexes, the hydrogen atom donating abilities could be determined. These values were all found to be approximately 50 kcal/mol.

Introduction

Transition metal hydrides are important intermediates in a large range of catalytic reactions. Despite this importance, our knowledge of the energetics of the M−H bond is rudimentary. We recently reported the first solution measurements of the free energies for all three M−H bond cleavage modes ($M^- + H^+$, $M^\bullet + H^\bullet$, and $M^+ + H^-$) for a series of $[HM(diphosphine)_2]^+$ complexes.[1] These results provide an opportunity for a quantitative assessment of the potential of these metal complexes to undergo proton, hydrogen atom, and hydride transfer reactions. This type of quantitative information should be useful in understanding and designing stoichiometric and catalytic reactions. This paper describes our efforts to develop a quantitative thermodynamic understanding of the reduction of transition metal carbonyl complexes to formyl complexes.

We have previously reported studies on the reactions of nickel and platinum $[HM(diphosphine)_2]^+$ complexes with metal carbonyls, as shown in eq 1 .[2] In many instances, clean hydride

$$M_a{-}H^+ + M_b{-}CO^+ \rightleftharpoons M_a^{2+} + M_b{-}CHO \qquad (1)$$

transfer occurs to produce metal formyls. This reaction may represent a key step in the catalytic reduction of CO, as many others have noted.[3−14] However, the factors controlling the thermodynamics of this reaction are unknown. Our quantitative measurements of the hydride donor abilities of a series of nickel and platinum hydrides in acetonitrile, as defined in eq 2, also provide an opportunity for the measurement of the hydride acceptor abilities of a range of metal carbonyl complexes, as shown in eq 3. The free energy of reaction 3 can be calculated by subtracting the free energy of eq 2 from that of eq 1.

$$M_a{-}H^+ \rightleftharpoons M_a^{2+} + H^- \qquad (2)$$

$$M_b{-}CO^+ + H^- \rightleftharpoons M_b{-}CHO \qquad (3)$$

As discussed above, a better understanding of the thermodynamics of reaction 3 for a number of metal carbonyl complexes may facilitate the development of CO reduction catalysts. A model catalytic cycle for the reduction of CO to

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(1) Berning, D. E.; Noll, B. C.; DuBois, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 11432.
(2) Miedaner, A.; DuBois, D. L.; Curtis, C. J.; Haltiwanger, R. C. *Organometallics* **1993**, *12*, 299.
(3) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61.
(4) Olivé, G. H.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136.
(5) Rathke, J. W.; Feder, H. M. *J. Am. Chem. Soc.* **1978**, *100*, 3623.
(6) Casey, C. P.; Andrews, M. A.; McAlister, D. R.; Rinz, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 1927.
(7) Tam, W.; Lin, G.-Y.; Wong, W.-K.; Kiel, W. A.; Wong, V. K.; Gladysz, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 141.
(8) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 2811.
(9) Dombek, B. D.; Harrison, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 2485.
(10) Wayland, B. D.; Woods, B. A.; Pierce, R. *J. Am. Chem. Soc.* **1982**, *104*, 302.
(11) Cutler, A. R.; Hanna, P. K.; Vites, J. C. *Chem. Rev.* **1988**, *88*, 1363.
(12) Toyohara, K.; Tsuge, K.; Tanaka, K. *Organometallics* **1985**, *14*, 5099.
(13) Gibson, D. H.; Ding, Y.; Sleadd, B. A.; Franco, J. O.; Richardson, J. F.; Mashuta, M. S. *J. Am. Chem. Soc.* **1996**, *118*, 11984.
(14) Kubo, K.; Nakazawa, H.; Nakahara, S.; Yoshino, K.; Mizuta, T.; Miyoshi, K. *Organometallics* **2000**, *19*, 4932.

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Scheme 1

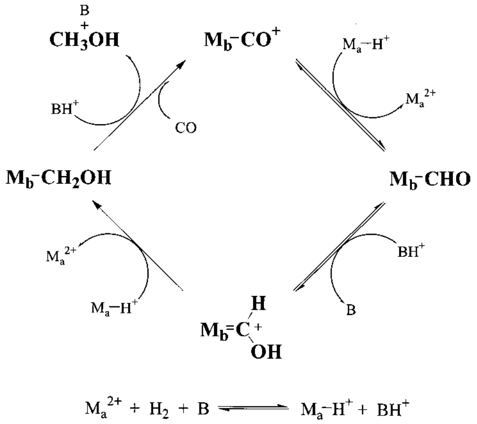

Table 1. Hydride-Donating Abilities of Selected Ni and Pt Complexes

hydride	$\Delta G°_{H^-}$ (kcal/mol)
$[Ni(dmpp)_2H]^+$	60.4[a]
$[Ni(depe)_2H]^+$	56.0[a]
$[Ni(dmpe)_2H]^+$	50.8[a]
$[Pt(dmpp)_2H]^+$	51.0[a]
$[Pt(depe)_2H]^+$	44.2[b]
$[Pt(dmpe)_2H]^+$	42.5[b]

[a] From ref 21. [b] From refs 1 and 21.

CH_3OH is shown in Scheme 1. There are many challenges in designing such a system. Most of the known formyl complexes are made by reacting carbonyl complexes with strong hydride donors, such as borohydride reagents.[6−8,15−19] Despite their convenience, these reagents are unsuitable for catalysis for two main reasons. As Scheme 1 shows, the first step of the catalytic reduction is a hydride transfer to generate a formyl, and the second step is protonation of the formyl to give a hydroxycarbene complex. To avoid quenching of the hydride by the proton source, the strength of both the acid and the hydride will have to be finely balanced, and it is likely that each of these steps will have to be reversible. Borohydride reagents would likely be quenched to H_2 by any acid of sufficient strength to protonate the formyl. Borohydride reagents are also undesirable because they are difficult to regenerate, and would have to be used as stoichiometric reductants. For these reasons, we and others have studied the reactions of transition metal hydrides with carbonyl complexes.[2,9,16,17,20] The nickel and platinum hydrides, $[HM(diphosphine)_2]^+$, can be generated in solution by reaction with H_2 and an appropriate base, as shown at the bottom of Scheme 1. The hydride donor abilities of these complexes cover a broad range, as shown in Table 1.[1,21] These hydride donor abilities can also be combined with the known pK_a data for the hydrides to predict the range of acid strengths over which the hydrides are stable. The ability to tune the hydride's acid stability and maintain the hydride donor ability required to reduce a particular carbonyl is essential for catalysis.

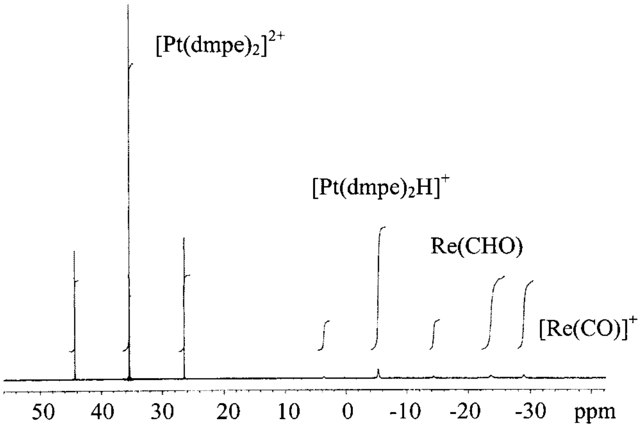

Figure 1. ^{31}P NMR of the reaction of $[Pt(dmpe)_2H]^+$ with $[CpRe(PMe_3)(NO)(CO)]^+$ in CD_3CN.

Results

Hydride-Donating Abilities of Selected Formyl Complexes. Previously, we observed nearly quantitative hydride transfer from $[Pt(dmpe)_2H]^+$ to $[CpRe(PPh_3)(NO)(CO)]^+$ to yield Gladysz's formyl $[CpRe(PPh_3)(NO)(CHO)]$ (**1**),[7] while there was only a slight hydride transfer when the weaker donor $[Pt(depe)_2H]^+$ was used (dmpe = 1,2-bis(dimethylphosphino)ethane; depe = 1,2-bis(diethylphosphino)ethane).[2] This suggested that we might be able to obtain the $\Delta G°_{H^-}$ for formyl **1** by observing hydride transfer from the formyl to $[Pt(depe)_2]^{2+}$, and measuring an equilibrium constant for reaction 4. However, we were unable to observe any hydride transfer from **1** to $[Pt(depe)_2]^{2+}$. Subsequently, we reacted **1** with the better hydride acceptor $[Pt(dmpp)_2]^{2+}$ (dmpp = 1,3-bis(dimethylphosphino)propane), and were able to observe a slow but quantitative reaction (1−2 days). It was unclear whether our failure to observe the reverse of eq 4 was due to unfavorable thermodynamics or if the reaction was just too slow to observe. The formyl **1** is relatively stable, but in acetonitrile it decomposes over several days.

$$[Pt(depe)_2H]^+ + [CpRe(PPh_3)(NO)(CO)]^+ \rightleftharpoons [Pt(depe)_2]^{2+} + CpRe(PPh_3)(NO)(CHO) \quad (4)$$

To remedy this problem, we prepared the formyl **2** (see the Experimental Section), with a trimethylphosphine donor. We anticipated that this would produce a stronger hydride donor, and that the smaller phosphine group on **2** might allow for faster hydride transfers. This proved to be the case. The equilibrium shown in eq 5 was established, starting from either side (see Figure 1). From the equilibrium constant, the platinum hydride was found to be a better donor than the rhenium formyl **2** by 1.6 kcal/mol (meaning that $\Delta G°_{H^-}$ for **2** is 44.1 kcal/mol).

$$[Pt(dmpe)_2H]^+ + [CpRe(PMe_3)(NO)(CO)]^+ \xrightleftharpoons{K_{eq} = 16.2 \pm 1.2} [Pt(dmpe)_2]^{2+} + CpRe(PMe_3)(NO)(CHO) \quad (5)$$

Formyl complex **2** is stable for months as a solid in a glovebox freezer kept at −40 °C. It is particularly useful for generating less-stable formyl complexes by "transformylation", a process first reported independently by Casey[22] and Glad-

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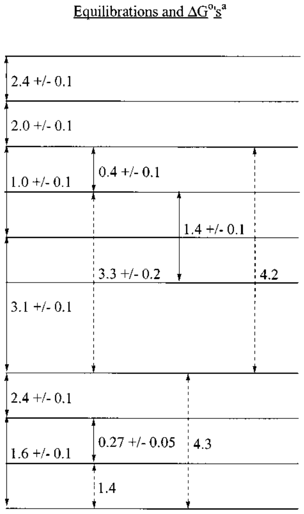
(15) Tam, W.; Marsi, M.; Gladysz, J. A. *Inorg. Chem.* **1983**, *22*, 1413.
(16) Nelson, G. O.; Sumner, C. E. *Organometallics* **1986**, *5*, 1983.
(17) Lapinte, C.; Catheline, D.; Astruc, D. *Organometallics* **1988**, *7*, 1683.
(18) Leoni, P.; Aquilini, E.; Pasquali, M.; Marchetti, F.; Sabat, M. *J. Chem. Soc., Dalton Trans.* **1988**, 329.
(19) Gibson, D. H.; Owens, K.; Mandal, S. K.; Sattich, W. E.; Franco, J. O. *Organometallics* **1989**, *8*, 498.
(20) Farnos, M. D.; Woods, B. A.; Wayland, B. B. *J. Am. Chem. Soc.* **1986**, *108*, 3659.
(21) Curtis, C. J.; Miedaner, A.; Ellis, W. W.; DuBois, D. L. *J. Am. Chem. Soc.* **2002**, *124*, 1918−1925.
(22) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544.

Table 2. Hydride-Donating Abilities of Metal Formyl Complexes

$\Delta G^\circ_{H^-}$ (kcal/mol)	Formyl
55.0	CpRe(NO)(CO)(CHO) (**5**)
52.6	Cp*Re(NO)(CO)(CHO) (**4**)
50.6	Cp*Ru(CO)$_2$(CHO) (**6**)
50.2	*cis*-Mn(PPh$_3$)(CO)$_4$(CHO) (*cis*-**7**)
49.6	[(bipy)$_2$Ru(CO)(CHO)]$^+$ (**8**)
48.8	*trans*-Mn(PPh$_3$)(CO)$_4$(CHO) (*trans*-**7**)
46.5	CpRe(PPh$_3$)(NO)(CHO) (**1**)
44.1	CpRe(PMe$_3$)(NO)(CHO) (**2**)
43.8	CpRe(PEt$_3$)(NO)(CHO) (**3**)
42.5	[Pt(dmpe)$_2$H]$^+$



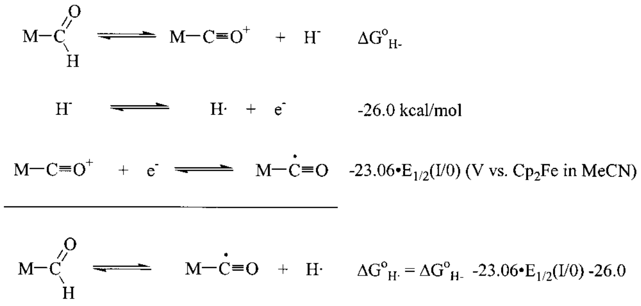
[a] Primary equlibration reactions used to generate the thermodynamics scale are denoted with solid arrows. Dotted arrows represent cross-checking experiments. ΔG° values without error estimates are for experiments that were run a single time.

ysz.[23,24] This has enabled us to measure the equilibria shown in eq 6. In the case where R = Ph, the equilibrium was found to lie to the right, with **2** being a better hydride donor than **1** by 2.4 kcal/mol. The equilibrium lies slightly to the left for R = Et, however. The triethylphosphine formyl complex **3**[2] was found to be a better donor than **2** by 0.3 kcal/mol. Formyls **1** and **3** could also be equilibrated with $[Pt(dmpe)_2]^{2+}$. These reactions gave values of $\Delta G^\circ_{H^-}$ that were consistent with those found in reaction 6.

$$\underset{\mathbf{2}}{CpRe(PMe_3)(NO)(CHO)} + [CpRe(PR_3)(NO)(CO)]^+ \xrightleftharpoons[=\ 0.63 \pm 0.03\ (R = Et)]{K_{eq} = 66 \pm 13\ (R = Ph)} [CpRe(PMe_3)(NO)(CO)]^+ + \underset{\substack{\mathbf{1}\ (R = Ph)\\ \mathbf{3}\ (R = Et)}}{CpRe(PR_3)(NO)(CHO)} \quad (6)$$

Subsequently, formyls **4**−**8**[6,8,12,16,19] were placed onto our thermochemical scale, as shown in Table 2. The hydride-donating abilities of these formyls are also relative to $[Pt(dmpe)_2H]^+$. The scale was built up by using a sequence of transformylation equilibria, as shown with arrows in the table. The free energy changes, with estimated errors, are given to the right of each arrow. Each of these equilibration reactions occurred rapidly relative to the decomposition of the formyls, needing typically from 15 min to 1 h to reach equilibrium. All of the reactions were run to equilibrium in both the forward and reverse directions for at least a total of three times. Reactions between formyl **2** and $[Cp^*Re(NO)(CO)_2]^+$, $[CpRe(NO)(CO)_2]^+$, $[Cp^*Ru(CO)_3]^+$, and $[(PPh_3)Mn(CO)_5]^+$ were all fast (<15 min) and quantitative by ^1H NMR. These reactions were used to generate formyls **4**−**7** in situ for the equilibration reactions shown in Table 2.

Scheme 2



As a cross-check to establish the validity of our scale, we attempted to equilibrate formyls **4**−**8** with $[Ni(dmpe)_2]^{2+}$ and $[Pt(dmpp)_2]^{2+}$. All of these reactions were much too slow to measure an equilibrium, with the exception of the reaction between formyl **4** and $[Ni(dmpe)_2]^{2+}$ (eq 7). Both the forward and the reverse reaction could be observed, although equilibrium could not be established prior to extensive decomposition of the formyl. Still, the equilibrium constant for eq 7 could be bracketed between 60 and 140, giving an estimated free energy change for the reaction of −2.6 kcal/mol, albeit with a large estimated error. By contrast, using the data in Tables 1 and 2 for the hydride-donating abilities of $[Ni(dmpe)_2H]^+$ and formyl **4**, the predicted free energy change for reaction 7 is −1.8 kcal/mol. These two values are certainly within the limits of combined experimental error.

$$[Ni(dmpe)_2H]^+ + [Cp^*Re(NO)(CO)_2]^+ \xrightleftharpoons{K_{eq} \sim 100} [Ni(dmpe)_2]^{2+} + Cp^*Re(NO)(CO)(CHO) \quad (7)$$

Bond Dissociation Free Energies of Selected Formyl Complexes. In addition to measuring the hydride donor abilities of these formyls, we were also able to measure the hydrogen atom donor abilities of several of them. The thermodynamic cycle shown in Scheme 2 was used to calculate these values. The free energies of the first step of the cycle are known for formyls **1**−**8**, as discussed above. The one-electron oxidation potential of the hydride ion in acetonitrile (step 2 of Scheme 2) has been calculated in the literature.[25,26] What remains is determining the $E_{1/2}(I/0)$ for each of the metal carbonyls corresponding to formyls **1**−**8**. This was not possible for the manganese and ruthenium carbonyls, $[Mn(PPh_3)(CO)_5]^+$, $[Cp^*Ru(CO)_3]^+$, and $[(bipy)_2Ru(CO)_2]^{2+}$, as each showed irreversible reduction waves by cyclic voltammetry. However, each of the rhenium carbonyl complexes showed reversible reductions (e.g. see Figure 2). The peak-to-peak separations for the set of five ranged from 60 to 70 mV, consistent with a one-electron reduction. In each case, plots of the peak current of the reduction wave vs the square root of the scan rate were linear, implying that the reductions operate under diffusion control. The $E_{1/2}(I/0)$ of each was determined relative to the Cp_2Fe^+/Cp_2Fe couple. Table 3 shows the results of these experiments. The $\Delta G^\circ_{H\cdot}$ values, calculated according to Scheme 2, are all approximately 50 kcal/mol. There is much less variation in this value than was found for the $\Delta G^\circ_{H^-}$ values for the same complexes. As a result, there is a linear relationship between the hydride-donating

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(23) Gladysz, J. A.; Tam, W. *J. Am. Chem. Soc.* **1978**, *100*, 2545.
(24) Tam, W.; Lin, G.-Y.; Gladysz, J. A. *Organometallics* **1982**, *1*, 525.
(25) Wayner, D. D. M.; Parker, V. D. *Acc. Chem. Res.* **1993**, *26*, 287.
(26) Zhang, X.-M.; Bruno, J. W.; Enyinnaya, E. *J. Org. Chem.* **1998**, *63*, 4671.

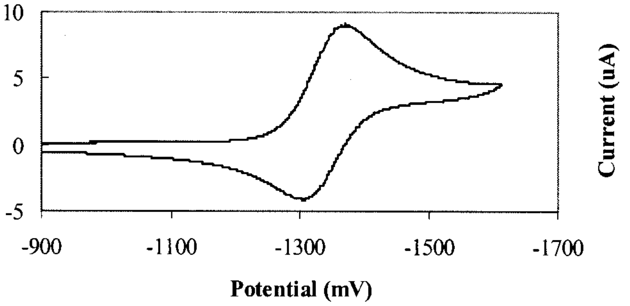


Figure 2. Cyclic voltammogram of a 2 mM solution of $[\mathrm{CpRe(PPh_3)(NO)(CO)}][\mathrm{BF_4}]$ in acetonitrile. The scan rate was 0.2 V/s, and the working electrode was a 2 mm glassy-carbon electrode. The potentials are referenced to the ferrocene/ferrocenium couple.

Table 3. $E_{1/2}$(I/0) Data and Hydrogen Atom Donating Abilities of Rhenium Formyl Complexes and Organic Aldehydes[a]

formyl	$E_{1/2}$(I/0) (V)[b]	$\Delta G°_{\mathrm{H}^\cdot}$[c](kcal/mol)
CpRe(NO)(CO)(CHO) (**5**)	−0.880[d]	49.3
Cp*Re(NO)(CO)(CHO) (**4**)	−0.970[e]	49.0
$\mathrm{CpRe(PPh_3)(NO)(CHO)}$ (**1**)	−1.339[e]	51.4
$\mathrm{CpRe(PMe_3)(NO)(CHO)}$ (**2**)	−1.458[d]	51.7
$\mathrm{CpRe(PEt_3)(NO)(CHO)}$ (**3**)	−1.456[f]	51.4
HCOH		84[g]
$\mathrm{H_3CCOH}$		85[h]
$\mathrm{F_3CCOH}$		87[g]
PhCOH		83[g]

[a] $\Delta G°_{\mathrm{H}^\cdot}$ values for the aldehydes have been calculated from bond dissociation energies by estimating that $T\Delta S$ is 4 kcal/mol, as found in ref 25. [b] Half-wave potentials vs $\mathrm{FeCp_2}$ couples in acetonitrile. [c] The estimated error is ±2.5 kcal/mol. [d] The scan rate was 0.5 V/s. [e] The scan rate was 0.1 V/s. [f] The scan rate was 0.2 V/s. [g] Bond dissociation energy found in: McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. [h] Bond dissociation energy found in: Niiranen, J. T.; Gutman, D.; Krasnoperov, L. N. *J. Phys. Chem.* **1992**, *96*, 5881.

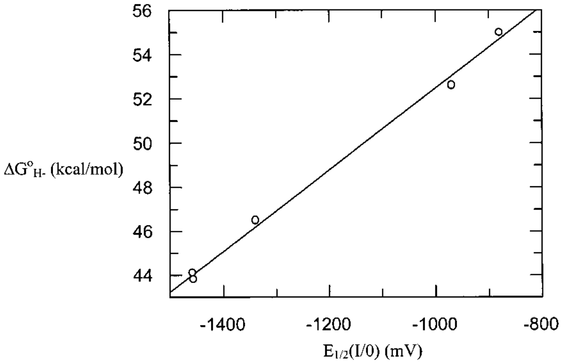
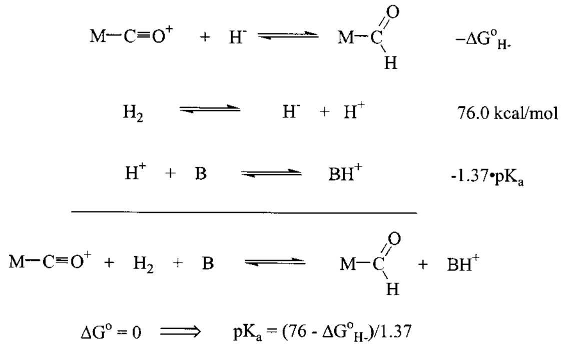


Figure 3. Plot showing the linear free energy relationship between the reduction potential of rhenium carbonyls and the hydride-donating abilities of corresponding formyls **1**−**5**. $\Delta G°_{\mathrm{H}^-} = 0.0185E_{1/2}(\mathrm{I/0}) + 70.957$ (r = 0.998).

abilities of formyls **1**−**5** and the $E_{1/2}$(I/0) values for their corresponding carbonyl complexes. A plot demonstrating this relationship is shown in Figure 3.

Hydrogenation of Coordinated CO. A long sought after reaction has been the direct reaction of a metal carbonyl complex with $\mathrm{H_2}$ to generate a formyl complex. Wayland has studied Rh(II) complexes which homolytically cleave $\mathrm{H_2}$ in the presence of CO to generate formyl complexes.[10,20,27−29] The cationic carbonyls that we have been studying require heterolytic activation of $\mathrm{H_2}$. A base must absorb the proton released by the cleavage of $\mathrm{H_2}$. The base strength necessary for this reaction to proceed can be calculated, given that the hydride-donating ability of the product formyl is known. The thermodynamic cycle needed to calculate the pK_a of the conjugate acid of the desired base is given in Scheme 3. In practice, we have not observed this reaction. For instance, the reaction of $[\mathrm{CpRe(NO)(CO)_2}]^+$ with $\mathrm{H_2}$ requires a base who's conjugate acid has a pK_a of 16.3 or greater in acetonitrile to give the formyl **5**. Both triethylamine (18.46)[30] and Proton-Sponge (1,8-bis(dimethylamino)naphthalene (18.19), see Experimental Section) are sufficiently strong bases for this reaction to proceed. However, the formyl is not an observable product. Instead, triethylamine quickly reacts with $[\mathrm{CpRe(NO)(CO)_2}]^+$ in acetonitrile to give a mixture of decomposition products. Proton-Sponge reacts much more slowly with $[\mathrm{CpRe(NO)(CO)_2}]^+$ to give a similar mixture of decomposition products.

Scheme 3



This hydrogenation reaction can be effected, however, by activating $\mathrm{H_2}$ with a platinum compound in the presence of an appropriate base. When $[\mathrm{CpRe(NO)(CO)_2}]^+$ is reacted with $\mathrm{H_2}$ and Proton-Sponge in the presence of $[\mathrm{Pt(dmpp)_2}]^{2+}$, the formyl **5** does form (see eq 8). The platinum complex is capable of

$$[\mathrm{LRe(NO)(CO)_2}]^+ + \mathrm{H_2} + [\mathrm{Pt(dmpp)_2}]^{2+} + \mathrm{B} \xrightarrow{\mathrm{CD_3CN}} \mathrm{LRe(NO)(CHO)} + \mathrm{BH^+} \quad (8)$$

4 (L = CP*)
5 (L = Cp)

B = Proton Sponge

activating $\mathrm{H_2}$, as shown in eq 9 , in the presence of Proton-

$$\mathrm{H_2} + [\mathrm{Pt(dmpp)_2}]^{2+} + \mathrm{B} \xrightarrow{\mathrm{CD_3CN}} [\mathrm{Pt(dmpp)_2H}]^+ + \mathrm{BH^+} \quad (9)$$

B = Proton Sponge

Sponge. Of the platinum complexes that we have studied, this one activates hydrogen the fastest,[21] which is essential for the success of the overall reaction. In addition, the resultant hydride, $[\mathrm{Pt(dmpp)_2H}]^+$, transfers its hydride ligand relatively quickly. The platinum hydride is a sufficiently strong donor to react with the carbonyl and give the formyl **5**. The reaction is still fairly slow, and as it proceeds, it is complicated by decomposition of the resultant formyl, as well as by the aforementioned reaction of the carbonyl complex with the base. Still, after 4 h of reaction,

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(27) Bunn, A. G.; Wei, M.; Wayland, B. B. *Organometallics* **1994**, *13*, 3390.
(28) Wei, M.; Wayland, B. B. *Organometallics* **1996**, *15*, 4681.
(29) Zhang, X.-X.; Parks, G. F.; Wayland, B. B. *J. Am. Chem. Soc.* **1997**, *119*, 7938.
(30) Kolthoff, I. M.; Thomas, F. G. *J. Phys. Chem.* **1965**, *69*, 3049.

5 is formed in approximately 9% yield (see Experimental Section). Likewise, formyl **4** can be made by reacting [Cp*Re(NO)(CO)$_2$]$^+$ with H$_2$ under the same conditions (see eq 8). Again, the reaction is fairly slow, and is complicated by ongoing decomposition. After 6 h, **4** is present in a maximum yield of ~9%.

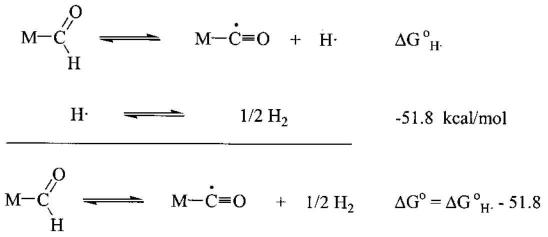
Discussion

We have found that these formyl complexes display a wide range of hydride-donating abilities. Formyls **3** and **5** differ by a single ligand, **3** having a strongly donating triethylphospine ligand, whereas **5** has a π-acidic carbonyl ligand. This single difference results in **3** being a stronger hydride donor than **5** by approximately 11 kcal/mol. Variation of the phosphine donor has a smaller, but still substantial effect (+2.7 kcal/mol on substituting PPh$_3$ for PEt$_3$). The effect of substituting a pentamethylcyclopentadienyl group for a cyclopentadienyl group is of similar magnitude (−2.5 kcal/mol). These results demonstrate that the hydride-donating ability of formyl complexes can be widely and easily tuned by variation of the ligand environment about the metal. By contrast, we found that the cationic ruthenium formyl **8** was indeed a stronger hydride donor than the neutral ruthenium formyl **6**. This was a surprising result, and may be accounted for by the presence of two carbonyl ligands on **6** compared to the single carbonyl ligand on **8**.

The variation in the hydride donor potentials of the formyls contrasts with the measurements of the hydrogen atom donor abilities of the five rhenium formyl complexes. These values were found to be relatively invariant, with an average value of ~50 kcal/mol. The substitution of a phosphine ligand for a carbonyl has little effect, as the $\Delta G°_{H•}$ values for the three phosphine complexes (**1**−**3**) are only ~2 kcal/mol higher than the values observed for the two carbonyl formyl complexes (**4** and **5**). In our previous studies of platinum and nickel hydrides, we made similar observations.[1,31] In that system, although the hydride-donating abilities of the complexes span almost a 30 kcal/mol range, the hydrogen atom donating abilities vary by only a few kilocalories per mole. We believe that this difference is a result of the change in charge that occurs when a hydride (or formyl) loses the hydride ion. The resultant cation is stabilized by donor ancillary ligands. By contrast, homolytic cleavage of the C−H bond results in a neutral radical, the stability of which is not so dependent on the donor ability of ancillary ligands.

Metal formyl complexes have long been known for their instability. It has generally been assumed that a weak C−H bond is the reason for this. Our results seem to indicate that this is indeed the case. As shown in Table 3, the C−H bond of the formyl complexes is ca. 30−35 kcal/mol weaker than the C−H bond of common organic aldehydes. In addition, each of the five rhenium formyls are unstable toward loss of H$_2$. The free energy of this reaction can be calculated, as shown in Scheme 4, using the $\Delta G°_{H•}$ values shown in Table 3. The driving force for this reaction is ca. −2.6 kcal/mol for the two carbonyl formyl complexes (**4** and **5**), and ca. −0.3 kcal/mol for the three phosphine substituted complexes (**1**−**3**). This is not necessarily the pathway for decomposition of these formyls. However, it has been shown by others that formyl complexes do decompose by a radical pathway, the first step of which is abstraction of the formyl hydrogen atom.[32−34] Consequently, the instability of these formyl complexes is likely due to their low $\Delta G°_{H•}$ values.

Scheme 4



The real value of the thermodynamic data we have obtained is the subsequent chemistry that it allows us to predict. Because we know the hydride-donating ability of a number of formyls, as well as many nickel and platinum hydride complexes, we have been able to design two hydrogenation reactions of rhenium carbonyls, to give the formyls **4** and **5** (eq 8). Accomplishing these reactions required balancing the hydride-donating ability of the hydride with that of the rhenium carbonyls, so that efficient hydride transfer could occur, as well as determining the base necessary to allow hydrogen activation to occur. Without the thermodynamic data, this would have been an arduous task.

Finally, albeit with only five data points, we have observed a correlation between the $E_{1/2}$(I/0) values for the rhenium carbonyls and the hydride donor abilities of their corresponding formyls (**1**−**5**). This correlation should allow us to predict the hydride donor ability of other rhenium formyl complexes based on the reduction potential of their corresponding carbonyl complexes. We have also reported previously a similar correlation between the $E_{1/2}$(II/I) values for a series of Ni(II) complexes and the hydride-donating abilities for their corresponding hydrides.[31] In both cases, these linear relationships are due to the fact that over each series of compounds, the $\Delta G°_{H•}$ values that we have determined are relatively invariant.

Conclusion

We have been able to measure the hydride-donating abilities of several neutral formyl complexes. The donating strength of these formyls varies over a range of 11 kcal/mol, and the strongest hydride donors are comparable to the best platinum hydride donor complexes that we have previously studied.[1] It is likely that we can expand the range as well, for example by preparing phosphine-substituted pentamethylcyclopentadienyl rhenium formyls such as Cp*Re(PEt$_3$)(NO)(CHO). We would expect this formyl to have a $\Delta G°_{H^-}$ value of 41.4 kcal/mol, based on the observed effects of substituting a Cp* ligand for a Cp ligand on the hydride-donating ability of a formyl. Such a hydride donor would be stronger than any of the Group VIII metal hydrides that we have characterized thus far. We have also determined that there is a linear free energy relationship between the hydride donor strength of the rhenium formyls and the reduction potential of their corresponding carbonyl com-

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(31) Berning, D. E.; Miedaner, A.; Curtis, C. J.; Noll, B. C.; Rakowski DuBois, M. C.; DuBois, D. C. *Organometallics* **2001**, *20*, 1832.

(32) Narayanan, B. A.; Amatore, C.; Casey, C. P.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 6351.

(33) Narayanan, B. A.; Amatore, C. A.; Kochi, J. K. *Organometallics* **1984**, *3*, 802.

(34) Narayanan, B. A.; Amatore, C.; Kochi, J. K. *Organometallics* **1986**, *5*, 926.

plexes. This relationship should allow us to predict $\Delta G°_{H^-}$ values for new rhenium formyls by making a simple electrochemical measurement.

Also, for the first time, the C−H bond dissociation free energies ($\Delta G°_{H^\bullet}$) of a series of rhenium formyls has been measured. These values were found to be fairly low (~50 kcal/mol).[35] The overall poor stability of these and other formyls is likely due to low $\Delta G°_{H^\bullet}$ values, as has long been suspected.

And finally, by studying the thermodynamics of hydride addition to carbonyl complexes, we have been able to design two systems which hydrogenate rhenium carbonyls to give formyl complexes. As such, this serves as a useful model for the catalytic cycle proposed for the hydrogenation of CO to CH_3OH shown in Scheme 1, by demonstrating both the activation of H_2 as well as a hydride transfer to give a formyl complex.

Experimental Section

Materials and Methods. NMR spectra were recorded on a Varian Unity 300 spectrometer. Proton chemical shifts are reported relative to residual protons in CD_3CN (1.93 ppm). ^{31}P chemical shifts are reported relative to an unlocked, external sample of H_3PO_4. All electrochemical measurements were carried out under an atmosphere of N_2 in 0.3 M $[Et_4N][BF_4]$ in acetonitrile with a Cypress Systems computer-aided electrolysis system. The working electrode was a glassy-carbon disk (2 mm diameter), and the counter electrode was a glassy-carbon rod. A platinum wire immersed in a permethylferrocene/permethylferrocenium solution was used as a pseudo-reference electrode to fix the potential. Ferrocene was used as an internal standard, and all potentials are referenced to the ferrocene/ferrocenium couple.

Solvents were reagent grade and were purchased from Aldrich. Hexanes and methylene chloride were degassed by using several freeze−pump−thaw cycles prior to use. Tetrahydrofuran was distilled from Na/benzophenone, and likewise degassed before use. CD_3CN was vacuum transferred from CaH_2 and stored in a glovebox.

The nickel and platinum complexes used in these studies were prepared by published methods. These include $[Ni(dmpe)_2][BF_4]_2$,[1] $[Ni(dmpe)_2H][PF_6]$,[2] $[Pt(dmpe)_2][PF_6]_2$,[1,36] $[Pt(dmpe)_2H][PF_6]$,[1] $[Pt(depe)_2][PF_6]_2$,[37−39] and $[Pt(dmpp)_2][PF_6]_2$.[1] The metal carbonyl complexes were also prepared by literature methods. These include $[CpRe(NO)(CO)_2][BF_4]$,[6−8] $[Cp^*Re(NO)(CO)_2][BF_4]$,[8] $[CpRe(PMe_3)(NO)(CO)][BF_4]$,[40] $[CpRe(PEt_3)(NO)(CO)][PF_6]$,[2] $[CpRe(PPh_3)(NO)(CO)][BF_4]$,[7] $[Cp^*Ru(CO)_3][BF_4]$,[16] $[(bipy)_2Ru(CO)_2][PF_6]_2$,[41] and $[(PPh_3)Mn(CO)_5][BF_4]$.[19] The following formyls were also prepared according to literature methods: $CpRe(PPh_3)(NO)(CHO)$[7] and $[(bipy)_2Ru(CO)(CHO)][PF_6]$.[12,13] Representative procedures used for the equilibration reactions of formyls follow in this section.

$CpRe(PMe_3)(NO)(CHO)$ (2). The following was performed under an atmosphere of N_2 on a Schlenck line. Sodium borohydride (0.435 g, 11.5 mmol) was added to a 0 °C solution of $[CpRe(PMe_3)(NO)(CO)](BF_4)$ (0.542 g, 1.15 mmol) in 1/1 THF/H_2O (70 mL). The yellow reaction mixture slowly became cloudy. After 1 h at 0 °C, the reaction mixture was extracted with three portions of CH_2Cl_2 (25, 15, and 10 mL). The combined extracts were cooled to 0 °C and dried over $MgSO_4$ for a few minutes. Upon filtration, and a small CH_2Cl_2 wash, the solution was concentrated in vacuo to give a yellow oil. The oil was extracted into THF (4 mL), filtered with two small washes (2 mL), and cooled to −25 °C. Hexane (45 mL) was added until clouding occurred. On sitting overnight, orange crystals formed. The product was collected by filtration and washed with hexanes. On drying, 302 mg (68% yield) of $CpRe(PMe_3)(NO)(CHO)$ was obtained as an orange solid. The material contained 1−2% of the starting $[CpRe(PMe_3)(NO)(CO)](BF_4)$. Due to this fact, and the its low thermal stability, it was not submitted for elemental analysis. ^1H NMR data (300 MHz, CD_3CN): δ 16.60 (s, 1 H, C(O)*H*), 5.49 (d, $J = 0.6$ Hz, 5 H, C_5H_5), 1.60 (d, $J = 10.8$ Hz, 9 H, $P(CH_3)_3$). ^{31}P NMR (121 MHz, CD_3CN): δ −24.27 (s).

Equilibration of $[CpRe(PMe_3)(NO)(CO)](PF_6)$ with $[Pt(dmpe)_2H](PF_6)$. $[CpRe(PMe_3)(NO)(CO)](PF_6)$ (10−15 mg, 0.02−0.03 mmol) and 1 equiv of $[Pt(dmpe)_2H](PF_6)$ were added to an NMR tube in the glovebox. The solids were dissolved in CD_3CN (0.6 mL). The reaction was monitored by ^1H and ^{31}P NMR for several hours. After approximately 5 h, the reaction had reached equilibrium. This experiment was performed two times.

The reverse reaction was performed as follows. The formyl **2** (12 mg, 0.03 mmol) and $[Pt(dmpe)_2](PF_6)_2$ (26 mg, 0.03 mmol) were dissolved in CD_3CN (0.6 mL). After reacting for several hours, equilibrium was established and concentrations were measured by ^1H and ^{31}P NMR. The free energy of the reaction was calculated from the equation $\Delta G° = -RT\ln K_{eq}$. The equilibrium constant, K_{eq}, was calculated according to eq 10.

$$PtH^+ + Re(CO)^+ \rightleftharpoons Pt^{2+} + Re(CHO) \qquad (10)$$

$$K_{eq} = [Pt^{2+}][Re(CHO)]/[PtH^+][Re(CO)^+]$$

Equilibration of $[CpRe(PMe_3)(NO)(CO)](PF_6)$ with $CpRe(PPh_3)(NO)(CHO)$. $[CpRe(PMe_3)(NO)(CO)](PF_6)$ (13 mg, 0.02 mmol) and $CpRe(PPh_3)(NO)(CHO)$ (5 mg, 0.01 mmol) were dissolved in CD_3CN (0.6 mL) in an NMR tube under inert atmosphere. The reaction was followed by ^1H and ^{31}P NMR over 2 h, during which time equilibrium was reached. The reverse reaction, between formyl **3** and $[CpRe(PMe_3)(NO)(CO)](PF_6)$ was performed two times.

Equilibration of $[CpRe(NO)(CO)_2](BF_4)$ with $Cp^*Re(NO)(CO)(CHO)$. Formyl **2**, $CpRe(PMe_3)(NO)(CHO)$ (11 mg, 0.03 mmol), and $[Cp^*Re(NO)(CO)_2](BF_4)$ (16 mg, 0.03 mmol) were dissolved in CD_3CN (0.6 mL). Quantitative hydride transfer to form $Cp^*Re(NO)(CO)(CHO)$ had occurred after 10 min, as seen in the ^1H NMR spectrum of the solution. Next, $[CpRe(NO)(CO)_2](BF_4)$ (13 mg, 0.03 mmol) was added, and the reaction was followed by ^1H NMR. The reaction was followed for 2 h, and had achieved equilibrium after 15 min. The reaction was repeated one more time in the forward direction. By reacting $[CpRe(NO)(CO)_2](BF_4)$ with formyl **3** first, and subsequently adding $[Cp^*Re(NO)(CO)_2](BF_4)$, the reaction was run one time in the reverse direction.

Other equilibria. pK_a of Proton Sponge. To three separate NMR tubes was added Proton Sponge (10−20 mg, 0.05−0.1 mmol) and $[Et_3NH][BF_4]$ (15−20 mg, 0.08−0.1 mmol). The solids were dissolved in CD_3CN (0.6 mL), and the reactions were monitored by ^1H NMR for at least an hour. Equilibration was rapid in all cases. The equilibrium constant for the protonation of Proton Sponge was found to be 0.536 ± 0.002, giving a pK_a value of 18.19 for the conjugate acid.

Hydrogenation of $[Cp^*Re(NO)(CO)_2](BF_4)$. A mixture of $[Cp^*Re(NO)(CO)_2](BF_4)$ (24 mg; 0.05 mmol), $[Pt(dmpp)_2](PF_6)$ (21 mg; 0.03 mmol), and Proton Sponge (25 mg; 0.12 mmol) was dissolved in CD_3CN (0.6 mL) in an NMR tube and sealed with a rubber septum. The septum was secured with a wire, and 5 mL of H_2 was added to the tube by syringe. The tube was mixed vigorously on a shaker when it was not being monitored by NMR. After 1 h, the formyl **4** could be observed in small conversion. After 6 h, it was present in 9% yield, as well as numerous decomposition products.

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(35) Griller, D.; Martinho Simoes, J. A.; Mulder, P.; Sim, B. A.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1989**, *111*, 7872.
(36) von Kozelka, J.; Ludwig, W. *Helv. Chim. Acta* **1983**, *66*, 902.
(37) Ittel, S. D. *Inorg. Synth.* **1990**, *28*, 98.
(38) Ittel, S. D. *Inorg. Synth.* **1977**, *17*, 117.
(39) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *J. Am. Chem. Soc.* **1974**, *96*, 53.
(40) Weiner, W. P.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7462.
(41) Kelly, J. M.; O'Connell, C. M. *J. Chem. Soc., Dalton Trans.* **1986**, 253.

Hydrogenation of [CpRe(NO)(CO)$_2$](BF$_4$). A mixture of [CpRe(NO)(CO)$_2$](BF$_4$) (19 mg; 0.05 mmol), [Pt(dmpp)$_2$](PF$_6$) (10 mg; 0.01 mmol), and Proton Sponge (25 mg; 0.12 mmol) was dissolved in CD$_3$CN (0.6 mL) in an NMR tube and sealed with a rubber septum. The septum was secured with a wire, and 5 mL of H$_2$ was added to the tube by syringe. The tube was mixed vigorously on a shaker when it was not being monitored by NMR. After 2 h, the formyl **5** could be observed in 4% conversion. After 4 h, it was present in 9% yield, as well as numerous decomposition products.

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