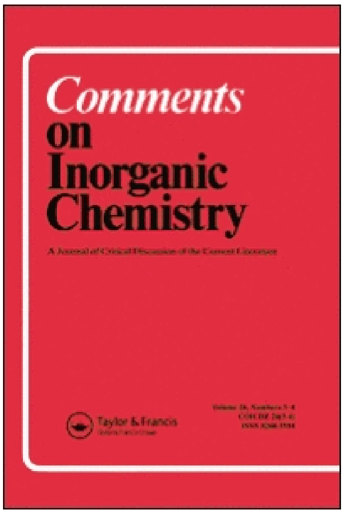

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The Brønsted Acidity of Transition Metal Hydrides

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The Brønsted Acidity of Transition Metal Hydrides

Recent work on measuring the Brønsted acidity of some transition metal carbonyl hydrides is reviewed. The basicity of low-valent transition metal complexes and the mechanism of addition of HX to planar ML_4 complexes is also discussed. Finally some further consequences of having a weak metal-hydrogen bond are presented.

INTRODUCTION

It has been known for some time that transition metal hydrides have Brønsted acid properties in polar solvents. There is a range of acid strengths from very strong (similar to HCl) to very weak (immeasurable). For example, cobalt hydrocarbonyl is a strong acid in aqueous solution:

$$HCo(CO)_4 \rightleftharpoons H^+ + Co(CO)_4^-. \quad (1)$$

The ionization of $H_2Fe(CO)_4$ is more difficult, but even the second hydrogen can be removed in strong base:

$$H_2Fe(CO)_4 \rightleftharpoons H^+ + HFe(CO)_4^-, \quad pK_1 = 4.4, \quad (2)$$

$$HFe(CO)_4^- \rightleftharpoons H^+ + Fe(CO)_4^{2-}, \quad pK_2 \simeq 14. \quad (3)$$

At another extreme, the hydride of Ir(III), $IrHCl_2(CO)(PhMe_2Ph)_2$, does not lose HCl even in boiling sodium methoxide, indicating that the proton is not removed even under these stringent conditions.[1] This is the case for an isomer with two chloride ligands *trans* to each other. The *cis* isomer is much more reactive towards loss of HCl.

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Transition metal hydrides are often formed by the addition of a proton (or a molecule HX) to a compound of the metal in a low oxidation state. These compounds are acting as Brønsted bases. For example,[2]

$$\mathrm{Ni[P(OEt)_3]_4 + H^+ \rightleftharpoons HNi[P(OEt)_3]_4^+}. \qquad (4)$$

In methanol the equilibrium constant for (4) is 33 M^{-1} at 0°C. Thus makes the nickel phosphite a base of the same strength as thiourea in methanol. Some metal complexes are much stronger bases. For example, $Pt(PEt_3)_3$ will abstract a proton from water[3]:

$$\mathrm{PtL_3 + H_2O \rightleftharpoons PtL_3H^+ + OH^-}. \qquad (5)$$

The basicity sequence $PtL_3 > PdL_3 > NiL_3$ is found.

Attempts to prepare ammine complexes of Rh(I) are often frustrated by the formation of hydrides of Rh(III). This probably occurs by way of reactions such as[4]

$$\mathrm{Rh\ en_2^+ + H_2O \rightleftharpoons Rh\ en_2H(OH)^+}, \qquad (6)$$

quite analogous to Reaction (5).

Recently Jordan and Norton have measured several pK_a's of metal hydrides in acetonitrile solvent.[5] They find

$HCr(Cp)(CO)_3$	pK_a = 13.3
$HMo(Cp)(CO)_3$	13.9
$HW(Cp)(CO)_3$	16.1
$H_2Os(CO)_4$	20.8.

For comparison, the pK_a of $W(Cp)(CO)_3H$ in 70:30 methanol–water is 8.0.[6a] The pK_a of $H_2Fe(CO)_4$ is 5.9 in the same solvent, and the pK_a of acetic acid is 6.15.[6b]

The acid dissociation of $HCo(CN)_5^{3-}$ in water has been studied kinetically, and a pK_a of about 20 inferred[7]:

$$\mathrm{HCo(CN)_5^{3-} \rightleftharpoons H^+ + CO(CN)_5^{4-}}. \qquad (7)$$

The similar complex $HRh(CN)_5^{3-}$ seems to be a somewhat weaker acid. Reference 8 compiles much of the remaining data available on the acidity of transition metal hydrides. The data are surprisingly sparse, considering that hundreds or perhaps thousands of transition metal hydrides have now been synthesized and that these hydrides play a major role in many important catalytic processes in industry, especially catalytic hydrogenation.

A modest amount of less quantitative data is available. For example, $(C_5H_5)_2MoH_2$ is more acidic than $(C_5H_5)_2WH_2$ by several pK_a units, in aqueous dioxane.[9] In dichloromethane solvent the order of increasing basicity is $C_5H_5Mn(CO)_2L < C_5H_5V(CO)_3L < C_6H_6Cr(CO)_2L < C_5H_5Re(CO)_2L < C_5H_5Nb(CO)_3L$, where L is a phosphine.[10] Protonation occurs at the metal in all cases, as judged by IR and NMR spectra.

One conclusion that can be drawn is that the heavier transition metals are more basic than the lighter ones. Conversely, their hydrides are less acidic. There is some evidence that acidity increases as one goes across the Periodic Table. We have the sequence $HCo(CO)_4 > H_2Fe(CO)_4 > HMn(CO)_5$, for example. However, the compounds are not strictly analogous. Analogs such as $HNi[P(OR)_3]_4^+$ and $HCo[P(OR)_3]_4$ show the expected effect of increased nuclear charge. The nickel complex is quite acidic, as already noted, but the cobalt analog is a very weak acid. Hydroxide ion will not remove the proton.[11]

There is a special feature in the protonation of transition metal complexes. Conventionally the hydrogen atom in the hydride is given an oxidation state of −1. Since the proton has a +1 oxidation state, an oxidation–reduction has occurred at least formally. For example, in the reaction

$$H^+ + Pt[P(C_2H_5)_3]_3 \rightarrow HPt[P(C_2H_5)_3]_3^+ \qquad (8)$$

the platinum changes from Pt(0) to Pt(II). This is more than a formal change since the properties of the product are just those of a square planar Pt(II) complex.[12] Also the H atom is in a hydride-like environment, as shown by NMR and other methods.

Actually protonation is the most elementary example of the oxidative-addition reaction. This important class of reactions is also of great value for both laboratory and industrial applications.[13] It is most common for d^8 and d^{10} metal atom complexes. There has been a great deal of work done in determining relative reactivity towards oxidative addition of various molecules. In regard to proton affinities, Reaction (9) may be the most straightforward way of accomplishing this:

$$ML_n + H^+ \rightleftharpoons ML_nH^+. \qquad (9)$$

Because protonation is also oxidation, a curious dilemma is found. One expects the basicity of a transition metal base to parallel its ease of oxidation, i.e., the more easily the molecule loses electrons, the more basic it will be. The order found for reactivity towards oxidative addition generally supports this for d^8 systems: Os(0) > Ru(0) > Fe(0) > Co(I) > Ir(I) > Rh(I) > Pt(II) > Pd(II) $\gg$ Ni(II).[13] However for d^{10} complexes the order of oxidative-addition reactivity towards methyl iodide is found to be Ni $\gg$ Pd > Pt, the opposite of the basicity sequence.[14]

It should be noted that for nontransition metal bases, pK_b and E^0 are independent parameters. In fact it is usually found that bases which are easily oxidized are not good proton bases. Compare iodide ion and fluoride ion, for example. Iodide ion is the more easily oxidized, but fluoride ion is the stronger base.

It is known that replacing a CO in $HCo(CO)_4$ by a phosphine or phosphite has a base strengthening effect, or acid weakening. This is not unexpected, since CO can remove electron density on the metal by π bonding. However, some other results are more surprising. The olefin complex $[Ir(COD)HCl_2]_2$, where COD is 1,5-cyclooctadiene, is acid enough to lower the pH on dissolving in water.[15] One would not expect this effect for an olefin ligand which is a good π donor and a poor π acceptor (other Ir(III) hydrides are much less acidic).

In this case the answer must lie in the fact that Ir(I) forms better olefin complexes than does Ir(III). Hence deprotonation and reduction are strongly favored by ligands such as olefins. This leads to a dilemma: soft bases normally stabilize low oxidation states of metals. But soft bases also put electron density on the metal and favor oxidative addition. Clearly there are opposing factors at work, and prediction is not straightforward.

Another unusual effect for transition metal hydrides shows up in their IR spectra.[1] Acidic hydrides, such as $[Ir(COD)HCl_2]$, have a high value for the Ir–H stretch frequency, suggesting a strong bond. Less acidic hydrides, such as *trans*-$Ir(CO)Cl_2H(PMe_2Ph)_2$, have a low Ir–H frequency, which suggests a weak bond. The interpretation is that a hydridic hydrogen is weakly bonded, but difficult to remove as a proton. A protonic hydrogen is strongly bonded, but easy to remove.[16]

Protonation and deprotonation reactions of metal complexes are by no means instantaneous.[2,7] This may be attributed to the structural reorganization that usually results. For example, $HMn(CO)_5$ has a square pyramidal arrangement of the carbonyl groups, whereas the anion $Mn(CO)_5^-$ has a trigonal bipyramidal arrangement consistent with the electronic configuration change from d^6[Mn(I)] to d^8[Mn(−I)]:

$$\underset{C_{4v}}{HMn(CO)_5} \rightleftharpoons H^+ + \underset{D_{3h}}{Mn(CO)_5^-}. \tag{10}$$

However, these proton transfer reactions are usually much more rapid (milliseconds to seconds) than other reations of the complexes involved. In fact, rates of proton transfer are additional valuable data in evaluating chemical behavior. If rates of proton transfer are studied, as well as equilibria, it may be possible to establish a relationship between them. This would be useful in estimating pK_a values of hydrides that are very weak acids, but which undergo hydrogen–deuterium exchange in the presence of bases.

The hydrogens of transition metal hydrides, in fact, are reminiscent of hydrogen that is bonded to carbon in organic molecules. These can act either as H^- or as H^+ depending on circumstances. Presumably, in the molecule the MH bond, like the CH bond, is relatively nonpolar. Rates of proton transfer involving CH bonds are also slow. The slowness has been correlated with the amount of electronic and structural rearrangement that accompanies the process. An example would be

$$CH_3NO_2 + OH^- \xrightarrow{\text{slow}} CH_2{=}NO_2^- + H_2O. \tag{11}$$

RATES AND EQUILIBRIA FOR METAL CARBONYL HYDRIDES

Taking advantage of the slow rates of deprotonation, we have developed a method for determining pK_a values of metal carbonyl hydrides by measuring rates of forward and reverse reactions[17]:

$$HML_n + CH_3O^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_n^- + CH_3OH. \tag{12}$$

The experiments are done in anhydrous methanol, with sodium or potassium methoxide as a base. The observed pseudo-first-order rate constants are given by

$$\begin{gathered} k_{\mathrm{obs}} = k_{-1} + k_1[\mathrm{OCH_3^-}], \\ k_1/k_{-1} = K_a/K_s. \end{gathered} \tag{13}$$

K_a is the desired acid dissociation constant of the hydride, and K_s is the ion product of methanol, equal to 2.0×10^{-17} at 25°C. Table I summarizes the most recent data obtained.[18] In some cases the equilibrium could also be checked by indicator methods.

Some of the figures in the table differ appreciably from those published earlier.[17] At that time we did not fully appreciate the instability of some of these compounds. Some of the polynuclear complexes readily declusterify and the simple metal carbonyls react very rapidly with methoxide ion. For example,[19]

$$\begin{gathered} \mathrm{Ru(CO)_5} + \mathrm{CH_3O^-} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Ru(CO)_4COOCH_3^-}, \\ k_2 = 8.2 \times 10^3\ \mathrm{M^{-1}\ s^{-1}}; \quad k_2/k_{-2} = K = 2.7 \times 10^3\ \mathrm{M^{-1}}. \end{gathered} \tag{14}$$

These reactions to form metallocarboxylic esters are as rapid as proton abstraction and have similar equilibrium constants. Furthermore they follow the rate and equilibrium equations of (13).

The pK_a value for $\mathrm{H_2Os(CO)_4}$ shows that it is 10^8 times weaker than $\mathrm{H_2Fe(CO)_4}$, in good agreement with an earlier estimate by Norton.[20] Unfortunately we have not yet succeeded in measuring the pK_a of $\mathrm{H_2Ru(CO)_4}$ owing to its apparent instability. The stable salt $\mathrm{[PPN][HRu(CO)_4]}$, when dissolved in methanol, rapidly trimerizes to $\mathrm{HRu_3(CO)_{11}^-}$.[18]

It appears from Table I that polynuclear hydrides are more acidic than their mononuclear analogs. This had been shown earlier by Hieber in a less quantitative study[21] which established the acidity order $\mathrm{H_2Fe_3(CO)_{11}} > \mathrm{H_2Fe_2(CO)_8} > \mathrm{H_2Fe(CO)_4}$. In fact the trimeric acid $\mathrm{H_2Fe_3(CO)_{11}}$ is completely ionized in solution.[22]

This increased acidity seems to be related to the fact that the hydride ligands are bridging normally in the polynuclear cases. Notice that $\mathrm{H_2Os_3(CO)_{12}}$ does not show enhanced acidity. It is believed that this complex has only terminal Os–H bonds.[23] While it seems anomalous that the bridging hydrogens are more acidic (held less strongly) than terminal hydrogens, this has also been observed for boron hydrides.[24]

TABLE I

Rates for reaction of metal carbonyl hydrides

Complex	$k_1(M^{-1}s^{-1})$	$k_1(s^{-1})$	pK_a
$H_4Ru_4(CO)_{12}$	8.7×10^3	0.08	11.7
$H_4Ru_4(CO)_{11}\{P(OCH_3)_3\}$	8.4×10^1	0.84	14.7
$H_4Os_4(CO)_{12}$	2.2×10^3	0.1	12.0
$H_4FeRu_3(CO)_{12}$	8.2×10^3	0.1	11.8
$H_2Ru_4(CO)_{13}$	8.0×10^3	0.02	11.1
$H_2FeRu_3(CO)_{13}$	1.6×10^4	0.05	11.2
$H_2Os_3(CO)_{12}$	2.2×10^3	25.	14.7
$H_2Os(CO)_4$	2.2×10^1	0.76	15.2
$H_2Fe(CO)_4$	$>1 \times 10$	. . .	6.9[a]

[a] W. Hieber and W. B. Hubel, Z. Electrochem. **57**, 235 (1953). In methanol $H_2Fe(CO)_4$ is 465 times more acid than acetic acid, which has a pK_a of 9.60 at 25°C.

In correlation to greater acidity, the rates of proton removal are large for bridging hydrides. However, for $H_2Os(CO)_4$ and $H_2Os_3(CO)_{12}$, which have only terminal hydrogens, the rate of reprotonation, k_{-1}, is anomalously large. This also leads to a lower acidity.

ADDITION OF HX TO PLANAR COMPLEXES

Protonation of planar d^8 ML_4 complexes usually, but not always, includes addition of a sixth group, X:

$$ML_4 + HX \rightleftharpoons HML_4X. \tag{15}$$

It is expected that the equilibrium constant for (15) will depend on the nature of X. This result has been found by Deeming and Shaw in their pioneering studies on the addition of HX to Vaska's compounds in benzene.[1,25] For example, HCl adds more completely than HNO_3. Strong carboxylic acids bind more than weak ones. However, these results are clouded by the unknown degree of dissociation of various HX molecules in benzene.

Recently we have found that in methanol it is possible to add the proton only to Vaska's compounds, using CF_3SO_3H[26]:

$$IrY(CO)L_2 + H^+ \xrightleftharpoons{K_{H'}} IrY(CO)L_2H^+. \tag{16}$$

It is assumed that the sixth coordination site of Ir(III) is occupied by a solvent molecule, *trans* to the added proton. If HCl is used instead of triflic acid, then it adds in a *trans* manner, as determined by NMR and IR studies:

$$\mathrm{IrY(CO)L_2 + HCl \overset{K_{HCl}}{\rightleftharpoons} IrY(CO)L_2HCl} \qquad (17)$$

A study of the equilibrium constants for (16) and (17) gave a surprising result: the values of K_{H^+} and K_{HCl} were very nearly the same. Table II shows some of the results obtained for different Y and L ligands. The similarity of the values for the addition of the proton alone and those for adding HCl must mean that the equilibrium constant for the solvolysis reaction is near unity:

$$\mathrm{IrY(CO)L_2HCl + CH_3OH \rightleftharpoons IrY(CO)L_2H(CH_3OH)^+ + Cl^-}. \qquad (18)$$

Addition of coligands more strongly bound than Cl^- does have a pronounced effect on the ability of Vaska's compound to add protons. For example, adding excess trimethyl phosphite to a reaction mixture of $IrCl(CO)(PPh_3)_2$ and CF_3SO_3H will increase the extent of formation of Ir(III) by a factor of 40 or so.[26] Presumably the product is now $IrHCl(CO)(PPh_3)_2(P[OMe]_3)^+$, with phosphite *trans* to hydrogen. An extreme example of the role of X was given in the Introduction. $IrHCl_2(CO)(PMe_2Ph)_2$ with H *trans* to CO cannot be deprotonated by $NaOCH_3$. This must be due to strong bonding of CO to the metal atom.

A stopped-flow kinetic study of the addition of H^+, or HCl, to Vaska's compounds also produced an unexpected result.[26] Figure 1

TABLE II

Equilibrium constants for the addition of H^+ and HCl to $MY(CO)L_2$ in methanol at 25°C

$MY(CO)L_2$	K_{H^+}, M^{-1}	K_{HCl}, M^{-1}
$IrCl(CO)(PPh_3)_2$	1.14×10^2	2.20×10^2
$IrBr(CO)(PPh_3)_2$	4.16×10^2	6.30×10^2
$IrI(CO)(PPh_3)_2$	7.04×10^2	. . .
$IrCl(CO)(PMe(Ph_2)_2$	3.02×10^2	6.17×10^2
$IrCl(CO)(PMe_2Ph)_2$	6.31×10^2	1.10×10^3
$IrCl(CO)(OsPh_3)_2$	2.03×10^2	. . .
$RhCl(CO)(PPh_3)_2$	6.3×10	. . .
$RhI(CO)(PPh_3)_2$	1.0×10^2	. . .
$RhCl(CO)(OsPH_3)_2$	9.9×10	. . .

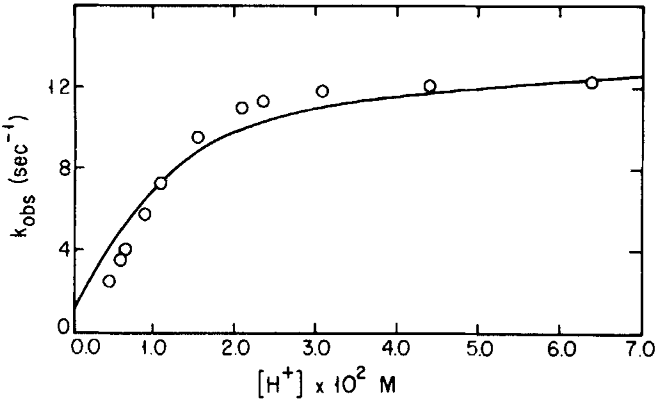


FIGURE 1 Circles are first-order rate constants observed for the addition of H^+ to $IrBr(CO)(PPh_3)_2$ in methanol at 25°C. The solid curve is the computed fit to Eq. (21).

shows a plot of the observed pseudo-first-order rate constant versus hydrogen ion concentration for the addition of H^+ to $IrBr(CO)(PPh_3)_2$. A limiting rate is reached at high $[H^+]$. Similar features are seen in the addition of HCl. Combining this result with the observed spectral changes leads to the following mechanism:

$$M + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MX^-, \tag{19}$$

$$MX^- + H^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} MHX, \tag{20}$$

where M stands for the complex, and X^- is either Cl^- or solvent. The observed rate constant is

$$k_{obs} = \frac{k_1 k_2[H^+] + k_{-1}k_{-2}}{k_{-1} + k_2[H^+]}. \tag{21}$$

The solid curve in Figure 1 is a computed least-squares fit of the data to Eq. (21).

The surprise is that apparently the expected mechanism of adding a proton first to the metal, followed by addition of X^-, is incorrect. Instead X^- adds first, increasing electron density at the metal, and perhaps distorting the geometry, so that the proton can add. This same mechanism has been found for the addition of HCl in methanol to $Ir(COD)L_2^+$ and IrCl(COD)L.[27] For these two iridium complexes HCl or HBr will add, but the proton alone will not add.

The kinetics of addition of HX to $IrY(CO)L_2$ in toluene has been studied by Walper and Kelm.[28] It was found that a concerted addition of HX took place. Such a result is reasonable in a nonpolar solvent where HX is undissociated. The product of addition has H and X in a *cis* configuration.

HYDRIDE MIGRATION AND LIGAND SUBSTITUTION

In addition to losing a proton, a transition metal hydride can also act as a source of hydrogen atoms and of hydride ions. The thermal decomposition of metal hydrides, with the production of hydrogen, depends on the homolytic M-H bond strength. A typical example is the decomposition of $H_2Fe(CO)_4$, which occurs even at 0°C:

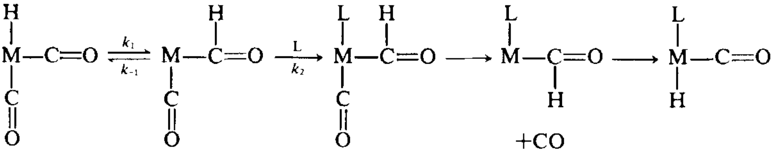
$$4H_2Fe(CO)_4 \rightarrow 3H_2\uparrow + H_2Fe_3(CO)_{11} + Fe(CO)_5. \qquad (22)$$

Such reactions can occur by several mechanisms.[29]

One interesting feature is that metal hydrides that are strong acids are also the least stable to hydrogen evolution; that is, the homolytic and heterolytic bond strengths parallel each other.[30] The first transition series hydrides are the strongest acids, and also the least stable.

It is also found that unstable carbonyl hydrides undergo very rapid ligand substitution reactions, much more rapid than H_2 elimination.[31] Examples include $H_2Fe(CO)_4$, $HCo(CO)_4$, $HFe(CO)_5^+$, $HMn(CO)_5$, $HCr(Cp)(CO)_3$ and $H_2Ru(CO)_4$. This suggests that a weak metal-hydrogen bond may allow for a novel hydride migration mechanism for ligand substitution[32]:

SCHEME I



If it is assumed that ligand substitution is essentially irreversible, Scheme I leads to the rate law

$$\text{rate} = \frac{k_1 k_2[\text{L}][\text{M}]}{k_{-1} + K[\text{L}]}. \tag{23}$$

Under second-order conditions, rate law (23) predicts a large inverse deuterium isotope effect because of the low frequency of M–H vibrations compared to C–H. Considering the importance of formyl complexes in various catalytic processes such as Fischer–Tropsch and the OXO process, it would be worthwhile to look for evidence bearing on the existence of the hydride migration mechanism.[33] Presumably compounds with a strong metal–hydrogen bond would not follow such a mechanism.

CONCLUSION

In the foregoing we have tried to show how the Brønsted acidity of transition metal hydrides, and the basicity of metal complexes where the metal atom is in low oxidation state, lead to a number of interesting chemical consequences. Clearly our knowledge of this chemistry is very incomplete and much remains to be done. Similarly, we need to know more about the factors which influence the acidity of metal hydrides. When new hydrides are synthesized, a simple measurement of their pK_a values would be a very useful parameter by which to characterize them.

Acknowledgments

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References

1. A. J. Deeming and B. L. Shaw, J. Chem. Soc. A **1968,** 1887 (1968).
2. C. A. Tolman, J. Am. Chem. Soc. **92,** 4217 (1970).
3. T. Yoshida, T. Matsuda, T. Okano, T. Kitani and S. Otsuka, J. Am. Chem. Soc. **101,** 2027 (1979).
4. R. D. Gillard, B. T. Heaton and D. H. Vaughan, J. Chem. Soc. A **1970,** 3126 (1970).
5. R. F. Jordan and J. R. Norton, private comunication.
6. (a) C. Amman, unpublished; (b) R. G. Pearson and H. Mauermann, J. Am. Chem. Soc., accepted for publication.
7. (a) G. D. Venerable II and J. Halpern, J. Am. Chem. Soc. **93,** 2176 (1971). (b) J. Halpern, R. Cozens and L. Y. Goh, Inorg. Chim. Acta **12,** 635 (1975).
8. R. A. Schunn, in *Transition Metal Hydrides,* edited by E. L. Muetterties (Dekker, New York, 1971), p. 239.
9. A. Nakamura and S. Otsuka, J. Mol. Catalysis **1,** 285 (1976).
10. B. V. Lokshin and A. A. Parinski, J. Organometal. Chem. **55,** 315 (1973).
11. E. L. Muetteries and F. J. Hirsekorn, J. Am. Chem. Soc. **96,** 7920 (1974).
12. P. Meakin, R. A. Schunn and J. P. Jesson, J. Am. Chem. Soc. **96,** 277 (1974).
13. J. P. Collman, Acc. Chem. Res. **1,** 136 (1968); L. Vaska, *ibid.* **1,** 335 (1968); J. Halpern, *ibid.* **3,** 386 (1970).
14. R. G. Pearson and P. E. Figdore, J. Am. Chem. Soc. **102,** 1541 (1980).
15. B. L. Shaw and R. E. Stainbank, J. Chem. Soc. A **1971,** 3716 (1971).
16. ESCA studies indicate that the hydrogen atoms in metal carbonyl hydrides are indeed negatively charged. H. W. Chen, W. L. Jolly, J. Kopf and T. H. Lee, J. Am. Chem Soc. **101,** 2607 (1979).
17. H. W. Walker, C. T. Kresge, P. C. Ford and R. G. Pearson, J. Am. Chem. Soc. **101,** 7428 (1979).
18. H. W. Walker, Ph.D. thesis, University of California, Santa Barbara, 1981.
19. D. C. Gross and P. C. Ford, submitted for publication.
20. J. Evans, S. J. Okrasinski, A. J. Pribula and J. R. Norton, J. Am. Chem. Soc. **98,** 4000 (1976).
21. W. Hieber and G. Brendel, Z. Anorg. Allgem. Chem. **289,** 324 (1957).
22. H. A Hodali, D. F. Shriver and C. A. Ammlung, J. Am. Chem. Soc. **100,** 5239 (1978).
23. M. Godwin and J. R. Moss, J. Organomet. Chem. **192,** 409 (1980).
24. E. L. Muetterties, *Boron Hydride Chemistry* (Academic, New York, 1975), pp. 82, 117, 356, 376.
25. A. J. Deeming and B. L. Shaw, J. Chem. Soc. A **1969,** 1802 (1969).
26. R. G. Pearson and C. T. Kresge, Inorg. Chem. **20,** 1878 (1981).
27. T. V. Askworth, D. J. A. DeWaal, W. Louw, E. Singleton and E. van der Stok, J. Chem. Soc. Dalton Trans. **1977,** 340 (1977); J. Chapman, D. J. A. de Waal and W. Louw, J. Chem. Soc. Chem. Commun. **1977,** 845 (1977).
28. W. Walper and H. Kelm, Z. Phys. Chem. (Frankfurt am Main) **113,** 207 (1978).
29. For a brief review see R. G. Pearson and H. Mauermann, Ref. 6(b).
30. For some metal-hydrogen bond strengths, see P. B. Armentrout and J. L. Beauchamp, J. Am. Chem. Soc. **103,** 784 (1981).
31. R. G. Pearson, H. W. Walker, H. Mauermann and P. C. Ford, Inorg. Chem. **20,** 2741 (1981).

32. Originally suggested in F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions* (Wiley, New York, 1967), Chap. 7.
33. A rapid, reversible hydrogen migration to a carbene ligand has recently been demonstrated. R. S. Threlkel and J. E. Bercaw, J. Am. Chem. Soc. **103,** 2650 (1981).