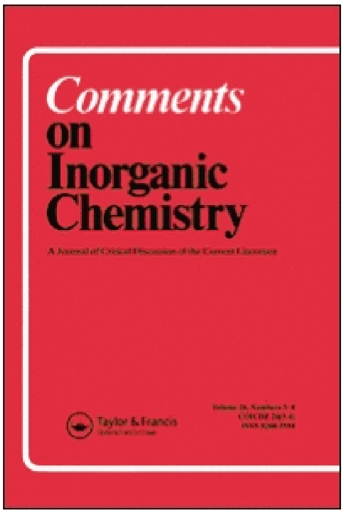


Comments on Inorganic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Metal-Hydrogen Bond Cleavage Reactions of Transition Metal Hydrides: Hydrogen Atom, Hydride, and Proton Transfer Reactions

R. Morris Bullock[a]
[a] Department of Chemistry, Brookhaven National Laboratory, Upton, New York

To cite this Article Bullock, R. Morris(1991) 'Metal-Hydrogen Bond Cleavage Reactions of Transition Metal Hydrides: Hydrogen Atom, Hydride, and Proton Transfer Reactions', Comments on Inorganic Chemistry, 12: 1, 1 — 33
To link to this Article: DOI: 10.1080/02603599108018617
URL: http://dx.doi.org/10.1080/02603599108018617

Metal–Hydrogen Bond Cleavage Reactions of Transition Metal Hydrides: Hydrogen Atom, Hydride, and Proton Transfer Reactions

R. MORRIS BULLOCK
Department of Chemistry,
Brookhaven National Laboratory,
Upton, New York 11973

Cleavage of the M–H bond of transition metal hydrides can result in delivery of a hydride (H^-), hydrogen atom ($H\cdot$), or proton (H^+) to an organic or organometallic substrate. Hydrogen atom transfer from a metal hydride to an olefin is an endothermic reaction; the rate at which different metal hydrides carry out this reaction is mainly dependent on the bond dissociation energy of the M–H bond. Hydrogen atom transfer from a metal hydride to a carbon-centered radical is an exothermic reaction in which the rate is largely determined by steric demands of the ligands of the metal hydride, with thermodynamics playing a less important role. Some neutral metal hydrides can function as hydride donors to carbocations. Anionic metal hydrides also exhibit hydridic reactivity, but in some cases the actual M–H bond cleavage step involves hydrogen atom transfer as a part of a radical chain reaction. Neutral metal hydrides can function as nucleophiles and as weakly coordinating ligands to coordinatively unsaturated metals.

Key Words: *metal hydrides, hydrogen atom transfer, proton transfer, hydride transfer, olefin hydrogenation*

Abbreviations Used: Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5, BDE = bond dissociation energy, bpy = 2,2′-bipyridine

Synthetic, structural and mechanistic studies of transition metal hydrides have been critically important to the development of con-

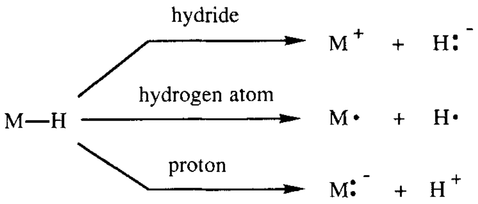
Comments Inorg. Chem.
1991, Vol. 12, No. 1, pp. 1–33
Reprints available directly from the publisher

Printed in the United Kingdom

temporary inorganic chemistry and homogeneous catalysis. Metal hydrides are involved in one or more steps of numerous homogeneous catalytic reactions,[1] including olefin hydrogenation, hydroformylation, hydrosilylation, hydrocyanation, polymerization, etc. Since cleavage of the M–H bond of metal hydrides is involved as an essential step in these reactions, it is important to obtain detailed mechanistic information about the factors governing such reactions. Careful mechanistic studies of stoichiometric reactions of metal hydrides can provide valuable insight into the details of similar reactions that occur under catalytic conditions. An understanding of the factors contributing to the diverse reactivity patterns of metal hydrides may eventually lead to more efficient uses of metal hydrides in applications to organic synthesis as well as catalytic reactions of industrial utility.

All complexes that have an M–H bond are called "hydrides." The electronegativity of hydrogen is larger than that of transition metals, so the assignment of formal oxidation state of the metal is also based on the presumed polarization ($M^{\delta+}$ and $H^{\delta-}$) of the M–H bond. Jolly and co-workers have studied the charge distribution in the M–H bond of several organometallic complexes, including metal carbonyl hydrides.[2] The results of their x-ray photoelectron spectroscopy data suggest that the approximate charges on hydrogen are -0.8 for $HMn(CO)_5$ and -0.75 for $HCo(CO)_4$. Sweany and Owens compared infrared data from matrix isolation experiments of metal hydrides and the corresponding metal radicals, and their conclusions also suggest a negative charge on the hydrogen of metal carbonyl complexes.[3] These experimental results and the formalisms of nomenclature and oxidation state assignment *do not*, however, mean that all metal hydrides will exhibit hydridic reactivity. This Comment will highlight the diversity of metal–hydrogen cleavage modes exhibited by organometallic hydrides in olefin hydrogenation and other reactions, with an emphasis on studies that provide comparisons of the relative reactivity of metal hydrides as the metal and ligands are systematically changed.

Scheme 1 shows the three elementary pathways for M–H bond cleavage. When the hydrogen leaves the metal and takes both of the electrons in the M–H bond, it obtains a negative charge, leaving the metal fragment as a cation. The second mode of M–H bond cleavage shown in Scheme 1 involves homolytic cleavage of

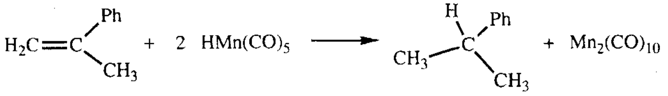


SCHEME 1 Modes of metal–hydrogen bond cleavage.

the M–H bond and results in delivery of a hydrogen atom (H·) to the organic or organometallic substrate. If the metal retains both of the electrons in the M–H bond, the hydrogen leaves as a proton, as shown in the last line of Scheme 1. The intent of these distinctions made for the various modes of M–H bond cleavage is to emphasize the formal differences in the three elementary steps in which the M–H bond is broken. It is *not* intended to imply that in an actual reaction, the bond between the metal and hydrogen is completely cleaved prior to any interaction with the reacting substrate. It is also recognized that some important reactions of metal hydrides, such as olefin insertion into the M–H bond, generally involve a more concerted pathway that may not fit unequivocally into any of the three reaction types above. Notwithstanding the simplifications implied by Scheme 1, the remarkable diversity of reactivity patterns of metal hydrides is attested to by the fact that some metal hydrides (e.g., $HW(CO)_3Cp$, $HMo(CO)_3Cp$, $HMn(CO)_5$, $HRe(CO)_5$, etc. have been observed to undergo *all* of these three reaction types, in reactions with different substrates.

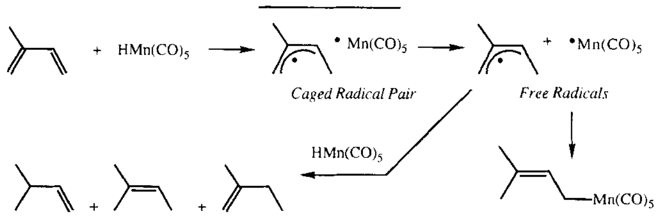
HYDROGEN ATOM TRANSFER REACTIONS OF METAL HYDRIDES

Hydrogen atom transfer reactions of metal hydrides are one of the most prominent examples of organometallic radical reactions.[4] The study by Sweany and Halpern of the hydrogenation of α-methylstyrene by $HMn(CO)_5$ (Eq. (1))



(1)

demonstrated that the reaction involved sequential hydrogen atom transfers from the metal hydride to the organic substrate.[5] An initial hydrogen atom transfer from $HMn(CO)_5$ to α-methylstyrene produces a carbon-centered radical which then forms the hydrogenated organic product by abstracting a hydrogen atom from a second equivalent of $HMn(CO)_5$. The organometallic product, $Mn_2(CO)_{10}$, forms by dimerization of two $[(CO)_5Mn\cdot]$ radicals. Analogous hydrogenation mechanisms involving sequential hydrogen atom transfers have been found for other substituted styrenes,[6] for anthracene,[7] and for substituted allenes.[8] Baird and co-workers examined the reaction of conjugated dienes with $HMn(CO)_5$[9] and with $HFe(CO)_2Cp$.[10] These reactions also proceed by a hydrogen atom transfer mechanism (Eq. (2)).

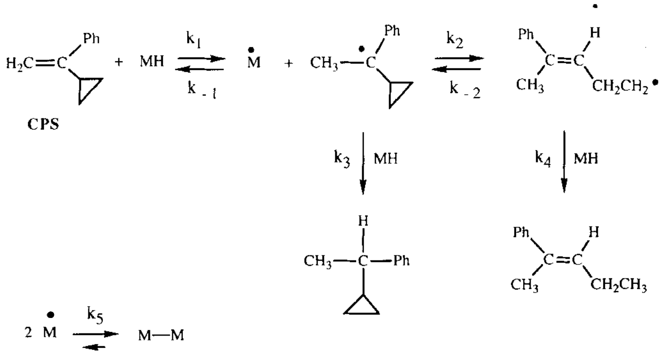


(2)

Following the first hydrogen atom transfer, the organic radical can either abstract a hydrogen atom from a second equivalent of metal hydride (leading to the hydrogenated organic product) or combine with the metal radical, leading to formation of the metal allyl complex.

While the generality of H· transfer to substituted anthracenes, allenes, dienes and styrenes had been established, several questions remained unanswered when we began our work in this area a few years ago. Although the variety of organic substrates employed in these studies had the benefit of giving some idea of the scope of C═C bond types that could be hydrogenated in this way, only limited kinetic data were available for the reaction of any single substrate with a systematically varied series of metal hydrides. The initial hydrogen atom transfer is generally rate-determining in these reactions. This means that the second hydrogen atom transfer, from the metal hydride to the carbon-centered radical, occurs after the rate-determining step. As a result, there was very little information about the relative rates at which different metal hydrides could donate a hydrogen atom to a carbon-centered radical. We were interested in finding out whether metal hydrides that were efficient at the first step would also be competent at the second hydrogen atom transfer. Another goal was to identify the steric and electronic factors that helped determine the relative reactivity of different hydrides toward an alkene, and toward carbon-centered radicals. The observation of an inverse isotope effect ($k_H/k_D < 1$, i.e., the metal deuteride reacting faster than the metal hydride) had been observed in many reactions of this type, so it was of interest to determine the isotope effect for the product-forming hydrogen atom transfer for comparison.

In an effort to address these questions, we carried out a study of the hydrogenation of α-cyclopropylstyrene by a series of metal carbonyl hydrides.[11] A substituted styrene was chosen since previous work[6] established them as prototypical substrates for hydrogenation by the free-radical pathway. The cyclopropyl substsituent was selected in order to utilize the radical ring-opening rearrangement in the evaluation of the relative rates of hydrogen atom transfer from the different metal hydrides to the same carbon-centered radical. By systematically changing the metal it was possible to evaluate the influence of the metal when the ligand set was kept the same (e.g., Cr vs. Mo vs. W in the $CpM(CO)_3H$ series). Information about the effect of changing a ligand (Cp vs. Cp*, or CO vs. phosphine) on a given metal is separately evaluated. The mechanism for the hydrogenation is shown in Scheme 2. The k_1 values obtained from the kinetic study ranked the dif-



SCHEME 2

ferent hydrides according to how efficient they were at donating a hydrogen atom to α-cyclopropylstyrene. Use of the radical ring-opening rearrangement enabled us to obtain information about the subsequent hydrogen atom transfer process (k_3), which occurred after the rate-determining step of the reaction. The competition between first-order rearrangement (k_2) and second-order trapping (k_3) predicts that the unrearranged/rearranged product ratio should increase linearly with [MH], and this was verified experimentally. (All of these experiments were carried out with excess metal hydride.) The results of this kinetic and mechanistic study allow a comparison of how the two hydrogen atom transfer steps, k_1 and k_3, vary among the different hydrides.

The second-order kinetics found in the hydrogenation of substituted styrenes, conjugated dienes and anthracenes discussed earlier was used as evidence for the free-radical pathway, as opposed to even-electron pathways that might be initiated by loss of CO, for example. The rate law for the hydrogenation reaction shown in Scheme 2 is $-d[\mathrm{CPS}]/dt = k_{obs}[\mathrm{CPS}]$, where α-cyclopropylstyrene is abbreviated as CPS and k_{obs} is defined as shown in Eq. (3).

$$k_{obs} = k_1[\mathrm{MH}]\frac{k_2 + k_3[\mathrm{MH}]}{k_{-1}[\mathrm{M}\cdot] + k_2 + k_3[\mathrm{MH}]} \qquad (3)$$

The crucial intermediate in the hydrogenation of CPS is the tertiary benzylic carbon-centered radical. The $k_1[\mathrm{MH}]$ term in Eq. (3) is the rate constant for generation of this intermediate. This term is multiplied by a partitioning ratio (productive pathways divided by all pathways) that has to do with how fast this intermediate is consumed. The k_2 and $k_3[\mathrm{MH}]$ terms in Eq. (3) are the productive pathways for the intermediate, the first of these leading to rearranged product and the latter leading to unrearranged product. The denominator in Eq. (3) includes contributions from *all* of the reaction pathways for the intermediate, the two productive pathways (k_2 and k_3) as well as the back hydrogen atom transfer (k_{-1}) that takes the metal radical and carbon-centered radical back to starting materials. The second-order kinetics observed in nearly all cases result from a further simplification which is appropriate in all cases studied to date, with the exception of $\mathrm{HCr(CO)_3Cp}$ (*vide infra*). When the $k_{-1}[\mathrm{M}\cdot]$ term in the denominator is small compared to the other terms in the denominator, then the partitioning ratio becomes equal to unity, and consequently $k_{obs} = k_1[MH]$. When this occurs, then substitution of this simplified k_{obs} back into the rate law gives $-d[CPS]/dt = k_1[MH][CPS]$, accounting for the straightforward second-order kinetics observed when MH = $HMo(CO)_3Cp$, $HW(CO)_3Cp$, $HMo(CO)_3Cp^*$, $HMo(CO)_2(PMe_3)Cp$, $HMn(CO)_5$, $HMn(CO)_4PPh_3$, $HFe(CO)_2Cp$, and $HFe(CO)_2Cp^*$.

We have found one exception to the commonly observed second-order kinetics. When α-cyclopropylstyrene is hydrogenated by $HCr(CO)_3Cp$, the rate of the hydrogenation slows down as it proceeds, due to inhibition by the $[Cp(CO)_3Cr\cdot]$ radical which builds up in solution. This is precisely the behavior predicted by Eq. (3): an increasing $[M\cdot]$ results in a decreasing value for k_{obs}. The metal–metal bond length of 3.281(1) Å in the Cr–Cr bonded dimer, $[Cp(CO)_3Cr]_2$, is surprisingly long (0.06 Å longer than in the analogous Mo–Mo dimer) and suggests a weak Cr–Cr bond.[12] McLain's quantitative study[13] of the temperature dependence of the equilibrium constant between the chromium radical and dimer indicated that $\Delta H° = 15.8\ (\pm 0.4)$ kcal/mol and $\Delta S° = 37.1\ (\pm 1.4)$ cal/K · mol for Eq. (4).

$$(C_5H_5)(CO)_3Cr{-}Cr(CO)_3(C_5H_5) \rightleftharpoons 2\ (C_5H_5)(CO)_3Cr\cdot \qquad (4)$$

When the hydrogenation of α-cyclopropylstyrene by $HCr(CO)_3Cp$ is carried out in a solution that is saturated with the chromium dimer $[Cp(CO)_3Cr]_2$, the rate of disappearance of α-cyclopropylstyrene is pseudo-first-order. The effect of carrying out these experiments in solutions saturated with the dimer is to maintain a constant concentration of the chromium radical. In toluene solutions at 22°C, the concentration of a saturated solution of $[Cp(CO)_3Cr]_2$ is 1.1×10^{-2} M, and under these conditions the concentration of the chromium radical is about $[Cp(CO)_3Cr\cdot] = 1.6 \times 10^{-3}$ M. The values of the forward ($k_1 = 3.4 \times 10^{-3}\ M^{-1}\ s^{-1}$) and reverse ($k_{-1} = 3.1 \times 10^9\ M^{-1}\ s^{-1}$) hydrogen atom transfers were determined for the reaction of $HCr(CO)_3Cp$ with α-cyclopropylstyrene. The resultant equilibrium constant ($K_{eq} \approx 1 \times 10^{-12}$) allows calculation of the free energy change ($\Delta G° = 16$ kcal/mol) for the first hydrogen atom transfer reaction (k_1) from

$HCr(CO)_3Cp$ to α-cyclopropylstyrene.

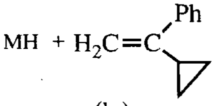
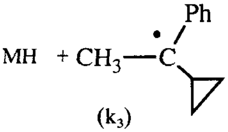
Accurate values of M–H bond dissociation energies (BDE) for metal hydrides are immensely important. They are, however, difficult to measure, and there has been no shortage of controversy over the reported results.[14] Tilset and Parker[15] reported the BDE's of the M–H bonds of many of the common metal carbonyl hydrides. Since their measurements provide the most comprehensive single source for M–H BDE's of metal carbonyl hydrides, their reported values will be utilized as a basis for the ensuing discussion. Experimental uncertainties stated by Tilset and Parker for their measurements are ± 1 kcal/mol. Comparisons of their measurements with other thermochemical data, and with kinetic data from hydrogen atom transfer reactions, will focus on several of the questions and controversies still surrounding M–H BDE values.

The reported BDE of the Cr–H bond of $HCr(CO)_3Cp$ (62 kcal/mol) is much lower than that of the W–H bond of $HW(CO)_3Cp$ (73 kcal/mol), providing support for the long-held belief that M–H bond dissociation energies increase significantly in moving from first row hydrides to their third row analogues. In agreement with this, we have found such a dramatic difference in the rate of hydrogenation of α-cyclopropylstyrene by these two hydrides that it was not possible to measure them at the same temperature—k_1 for $HCr(CO)_3Cp$ at 22°C is about 50 times larger than k_1 for $HW(CO)_3Cp$ at 100°C.

Informative comparisons can also be made when data are available for different hydrides at the same temperature. Table I summarizes the relative rate constants (k_1 and k_3) for four different metal hydrides at 60°C. The relative rates are normalized, with those for $HMo(CO)_3Cp^*$ being set equal to unity. The M–H bond dissociation energies reported by Tilset and Parker[15] are also listed in Table I. The relative k_1 values for the first three hydrides in Table I are quite similar. These hydrides have comparable M–H bond dissociation energies, but differing steric factors. We suggest that the BDE of the M–H bond is the predominant factor influencing how fast different metal hydrides can hydrogenate C=C bonds by a sequential hydrogen atom transfer mechanism. Our data support the results of Tilset and Parker[15] that the M–H BDE's are similar for $HMo(CO)_3Cp$, $HMo(CO)_3Cp^*$ and $HMn(CO)_4PPh_3$. Further demonstration of how differences in M–H bond dissocia-

TABLE I

Relative rates of hydrogen atom transfer at 60°C

MH	BDE, kcal/mol	 (k_1)	 (k_3)
$HMo(CO)_3Cp^*$	69	1	1
$HMo(CO)_3Cp$	70	1.3	23
$HMn(CO)_4PPh_3$	69	1.4	0.25
$HFe(CO)_2Cp^*$	~58	15	23

tion energies influence the rate of the first hydrogen atom transfer comes from a comparison (not shown in the Table) of the k_1 values of two metal hydrides with nearly identical structures, but different M–H BDE values. At 100°C, the k_1 for $HMo(CO)_3Cp$ (Mo–H BDE = 70 kcal/mol) is about 40 times higher than that for $HW(CO)_3Cp$ (W–H BDE = 73 kcal/mol). The $\Delta\Delta G^{\ddagger} = 2.8$ kcal/mol at this temperature is comparable to the $\Delta\Delta H^{\circ}$ of 3 kcal/mol determined from the differences in M–H BDE's.

In contrast to the good correlation between the M–H BDE values and the relative rates of hydrogen atom transfer (k_1) for the metal hydrides from groups 6 and 7, several questions arise when similar comparisons are made with the group 8 (Fe and Ru) hydrides. An anomaly regarding $HFe(CO)_2Cp$ comes from a comparison of its k_1 for hydrogenation of α-cyclopropylstyrene with that of $HCr(CO)_3Cp$ (both at 22°C). The fact that k_1 for $HFe(CO)_2Cp$ (reported[15] Fe–H BDE = 58 kcal/mol) is about ten times *smaller* than the k_1 for $HCr(CO)_3Cp$ (reported[15] Cr–H BDE = 62 kcal/mol) does not agree with our conclusion that M–H BDE's are the main influence on k_1. This raises the possibility that the actual Fe–H BDE of $HFe(CO)_2Cp$ is significantly higher than the reported value.

There is also uncertainty about the Fe–H BDE of the permethylcyclopentadienyl analog, $HFe(CO)_2Cp^*$. The Fe–H BDE of $HFe(CO)_2Cp^*$ was not reported by Tilset and Parker; the estimate of ~58 kcal/mol given in Table I is that reported[15] for $HFe(CO)_2Cp$. The assumption that changing Cp to Cp* has a negligible effect on the BDE is based on the lack of a significant change for

$HMo(CO)_3Cp^*$ (BDE = 69 kcal/mol) vs. $HMo(CO)_3Cp$ (BDE = 70 kcal/mol).[15] Qualitatively, the increased k_1 value for the iron hydride is expected from its lower M–H BDE compared to the other three hydrides in Table I. On the other hand, the fact that the increase in rate constant is only an order of magnitude for a ~10 kcal/mol difference in M–H BDE is difficult to rationalize. This is particularly true when we recall the striking difference in k_1 values for $HCr(CO)_3Cp$ vs. $HW(CO)_3Cp$ cited above, two metal hydrides that also differ in M–H BDE by ~10 kcal/mol. The surprisingly small increase in k_1 for $HFe(CO)_2Cp^*$ compared to such a large difference in BDE leads us to suggest the possibility that the Fe–H BDE of $HFe(CO)_2Cp^*$ may be significantly higher than 58 kcal/mol.

Another question concerns the related Ru hydride. We find little hydrogenation of α-cyclopropylstyrene by $HRu(CO)_2Cp$, even after a week at 100°C. The reported[15] Ru–H BDE of $HRu(CO)_2Cp$ is 65 kcal/mol, which is significantly lower than several other metal hydrides shown in Table I which hydrogenate α-cyclopropylstyrene at 60°C. This suggests to us that the Ru–H bond may also be significantly stronger than reported.

The conspicuous discrepancies between our kinetic data and the reported M–H BDE values for $HFe(CO)_2Cp$ and $HRu(CO)_2Cp$ (and that inferred for $HFe(CO)_2Cp^*$) do not disprove the validity of the reported M–H BDE values. Collectively, however, these points do raise some questions about the accuracy of the reported values for the group 8 metal hydrides. Based on the results and assumptions presented above, a rough estimate indicates that addition of as much as 7–9 kcal/mol to the reported[15] Fe–H and Ru–H BDE values might be needed to bring these BDE values into reasonable agreement with their relative k_1 values for reaction with α-cyclopropylstyrene.

Along with the questions about BDE's of individual metal hydrides, there is conflicting evidence regarding the more general question of whether substitution of a CO by a phosphine causes a significant increase in M–H BDE. Tilset and Parker reported[15] the W–H BDE of $HW(CO)_3Cp$ as 73 kcal/mol, and that of the phosphine-substituted hydride $HW(CO)_2(PMe_3)Cp$ as 70 kcal/mol. Accounting for the experimental error, however, it was concluded that their study detected "no effect of phosphine or phosphite substitution on M–H BDE's." Hoff and co-workers found[16] that the Cr–H BDE of the phosphine-substituted complex $HCr(CO)_2(PEt_3)Cp$ (59.9 kcal/mol) was similar to that of $HCr(CO)_3Cp$. The Cr–H BDE of $HCr(CO)_3Cp$ was reported by Hoff as 61.5 kcal/mol, in good agreement with the 62 kcal/mol reported by Tilset and Parker. The conclusion that phosphine substitution has a negligible effect on M–H BDE values is at odds with the evidence from Brown's classic radical chain mechanism for phosphine substitution of $HRe(CO)_5$, $HW(CO)_3Cp$, and other hydrides.[17] A key propagation step in this mechanism involves a hydrogen atom transfer between the two metals, as shown in Eq. (5).

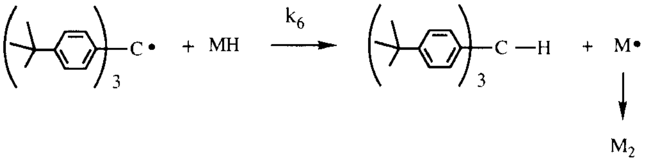
$$[CpW(CO)_2PBu_3]\cdot + CpW(CO)_3H \rightarrow CpW(CO)_2PBu_3H + [CpW(CO)_3]\cdot \qquad (5)$$

As discussed in detail by Brown,[4a] the implication is that the W–H BDE of the phosphine-substituted hydride is at least at large as that for $HW(CO)_3Cp$ (and probably larger). This conclusion conflicts with the results of the thermochemical experiments. A potential resolution to this enigma is the possibility that hydrogen atom transfer reactions (such as Eq. (5)) are thermoneutral but extremely fast; further kinetic and thermochemical experiments would be useful in resolving this problem.

Following this digression on the importance of reliable M–H BDE data, we now return to the discussion of how rates of hydrogen atom transfer reactions are influenced by thermochemical and steric factors. In contrast to the relationship between M–H BDE and k_1 in the hydrogenation of α-cyclopropylstyrene, there is little correlation of k_3 (Scheme 2) with M–H BDE. Indeed, an alternate explanation is required by the fact that k_3 varies widely among hydrides that have similar M–H BDE values. Consideration of the relative k_3 values and the steric properties of the ligands on the metal hydrides in Table I strongly supports the contention that steric factors are the dominant influence on the relative k_3 values. Substitution of the Cp ligand with the more sterically demanding Cp* ligand in the molybdenum hydride results in a k_3

value that is lower by more than an order of magnitude. Comparison of k_3 values for $HMo(CO)_3Cp$ and *cis*-$HMn(CO)_4PPh_3$ also supports this argument—although these two hydrides have nearly identical k_1 values, their relative k_3 values differ by about two orders of magnitude. This is consistent with the steric properties of the large PPh_3 ligand on the mangenese complex.

Norton and co-workers have been able to *directly* measure the rates of hydrogen atom transfer from metal hydrides to a carbon-centered radical.[4b,18] The substituted trityl radical shown in Eq. (6) abstracts a hydrogen atom from metal hydrides, and the resultant metal radicals combine with each other to give the metal dimer as the organometallic product.



(6)

The kinetics of this reaction were determined by stopped-flow measurements for a series of neutral metal hydrides. Table II lists the second-order rate constants k_6 at 25 °C for several metal carbonyl hydrides. As was found in the case of hydrogen atom transfer from metal hydrides to the tertiary benzylic radical discussed above (k_3 of Scheme 2), the rate constant k_6 is highly dependent on steric factors. Substitution of Cp* for Cp slowed the rate of hydrogen atom transfer from $HFe(CO)_2Cp$ by a factor of about 40; a similar effect on k_6 was found for $HMo(CO)_3Cp^*$ vs. $HMo(CO)_3Cp$.

TABLE II

Metal Hydride	k_6 (25°C), $M^{-1}\,s^{-1}$	Reported[15] M–H BDE, kcal/mol
$HFe(CO)_2Cp$	12000	58
$HRu(CO)_2Cp$	1020	65
$HMn(CO)_5$	640	68
$HMo(CO)_3Cp$	514	70
$HCr(CO)_3Cp$	335	62
$HFe(CO)_2Cp^*$	300	
$HW(CO)_3Cp$	91	73
$HMo(CO)_3Cp^*$	14	69

SIMILARITIES AND DIFFERENCES IN THE FIRST AND SECOND HYDROGEN ATOM TRANSFER STEPS IN OLEFIN HYDROGENATION BY METAL HYDRIDES

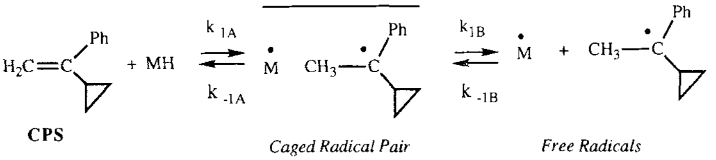
The data discussed above indicate that the rate at which a hydrogen atom is donated from a metal hydride to an olefin is largely influenced by the strength of the M–H bond. In contrast, the product-forming step of the hydrogenation, involving a hydrogen atom transfer from a metal hydride to a carbon-centered radical, is influenced more by steric factors than by enthalpic differences. This means that certain metal hydrides can be much more efficient at one step than the other. For example, although we find little reaction between $HRu(CO)_2Cp$ and α-cyclopropylstyrene, this same hydride was found by Norton and co-workers to be proficient at donating a hydrogen atom to the carbon-centered radical. On the other hand, metal hydrides such as $HMn(CO)_4PPh_3$, with bulky ligands but relatively weak M–H bonds, are able to convert an olefin to a carbon-centered radical fairly readily, but are less efficient at donating a hydrogen atom to the radical.

A similarity in the two steps of the olefin hydrogenation is that both the first (k_1) and subsequent hydrogen atom transfer (k_3 and k_4) steps involve rupture of a relatively weak M–H bond and formation of a comparatively strong C–H bond. Substantial differences in the thermodynamics of the two steps (endothermic for k_1 vs. exothermic for k_3 and k_4) are primarily due to the fact that the first step also involves conversion of a C═C double bond (~146 kcal/mol) to a C–C single bond (~84 kcal/mol). The strength of the M–M bond formed in the organometallic product will influence the ΔH° for the overall reaction, but the increase in thermodynamic driving force for the overall reaction that is provided by forming a stronger M–M bond is partly offset by the fact that the metals that form strong M–M bonds are generally the same as those that form relatively strong M–H bonds that must be cleaved in the rate-determining step.

Isotope effects for the hydrogenation of α-cyclopropylstyrene by $HW(CO)_3Cp$ (vs. $DW(CO)_3Cp$, at 100°C) give additional information about the differences in the first and second steps. The endothermic first step has an inverse isotope effect ($k_H/k_D = 0.55$) while the normal isotope effects observed for product-forming hydrogen atom transfer steps (k_H/k_D = 2.2 for k_3 and k_H/k_D = 1.8 for k_4) are interpreted in terms of an early transition state for this exothermic reaction.[19]

A CLOSER LOOK AT HYDROGEN ATOM TRANSFER FROM METAL HYDRIDES TO OLEFINS—THE INFLUENCE OF CAGED RADICAL PAIRS

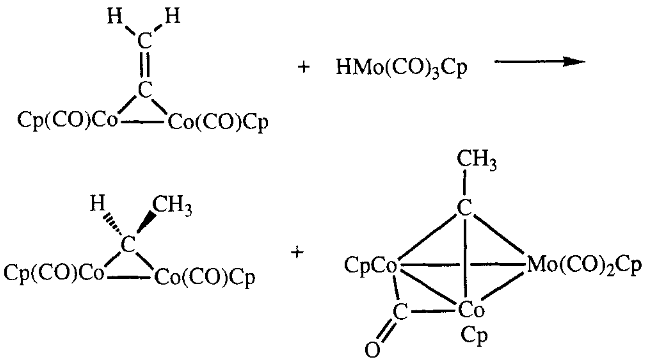
The first hydrogen atom transfer step, k_1 of Scheme 2, is written as if it were an elementary step, but definitive evidence in several closely related systems supports the assertion that caged radicals[20] are initially formed. The k_1 and k_{-1} steps (of Scheme 2) are separated in Eq. (7) to explicitly show the elementary steps, formation of the caged radical pair (k_{1A}) and diffusive cage escape (k_{1B}) to produce free radicals. The data obtained for the α-cyclopropylstyrene hydrogenation give k_1 (and k_{-1} in the case of $HCr(CO)_3Cp$) but do not provide values of the rate constants for the elementary steps shown in Eq. (7).



(7)

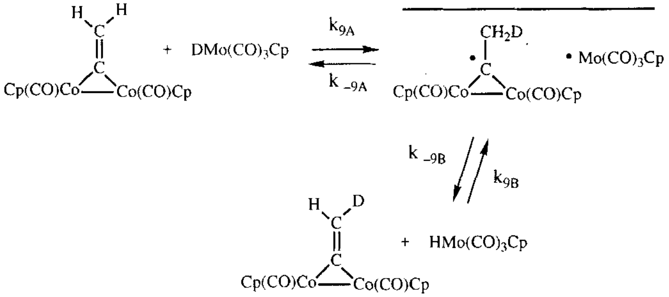
It is possible, however, to deduce useful comparative information about the kinetics and energetics of these elementary steps.

The reversibility of the initial hydrogen atom transfer has been verified by experiments using metal deuterides. In these experiments, deuterium is incorporated into the recovered starting material, and the metal deuteride is converted to a metal hydride. These H/D exchange experiments are commonly observed in hydrogenations of substituted styrenes.[6] A case of remarkably fast H/D exchange was reported by Jacobsen and Bergman in the hydrogenation of a Co_2-vinylidene complex by $HMo(CO)_3Cp$.[21] Their reaction (Eq. (8))



(8)

gives a mixture of the C═C bond hydrogenation product and the trinuclear cluster product, and was convincingly shown to proceed by a hydrogen atom transfer mechanism. The H/D exchange observed for this reaction (using $DMo(CO)_3Cp$) was found to occur at least two orders of magnitude faster than product formation, and it was suggested that the back hydrogen atom transfer (k_{-9} in Eq. (9)) had a rate constant of $k_{-9} > 10^{13}\ s^{-1}$.



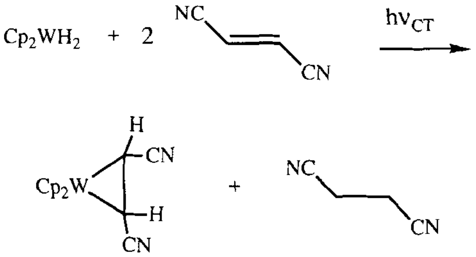
(9)

(Equation (9) separately shows two back hydrogen atom transfers, k_{-9A} which takes the caged radical pair back to isotopically identical starting material, and k_{-9B} which accomplishes the H/D exchange by hydrogen atom transfer following partial rotation of the CH_2D group.) This extraordinarily large first-order rate constant invites comparison to the second-order rate constant determined for the overall k_{-1} process in the reaction of α-cyclopropylstyrene with $HCr(CO)_3Cp$. The value of $k_{-1} = 3.1 \times 10^9\ M^{-1}\ s^{-1}$ determined for the latter process indicates that the reaction is essentially diffusion controlled. This large rate constant is not surprising, in view of the similar rate constants found for the combination of other metal- and carbon-centered radicals. For example, the rate constant for the combination of two $[Cp(CO)_3Mo\cdot]$ radicals to form $[Cp(CO)_3Mo]_2$ is $k = 3.1 \times 10^9\ M^{-1}\ s^{-1}$ at 22°C in cyclohexane,[22] and rate constants of the same order of magnitude are found for the combination of two organic radicals.[23] The remarkably large rate constant suggested for k_{-9} indicates that reactions of this type can have an even lower barrier than the small diffusional barrier to reactions such as k_{-1B} (Eq. (7)). The conclusion that $k_{-1A} >> k_{-1B}$ in Eq. (7) is interesting since it means that the reaction having the larger (albeit still small) barrier involves no bonds being broken or made but only bringing together the two radicals into the cage.

The large range of rate constants k_1 for the hydrogen atom transfer from metal hydrides to α-cyclopropylstyrene is therefore almost solely due to the differences in rate constants of the elementary step k_{1A}, since the rate constants for diffusive cage escape (k_{1B}) are expected to be similar for the different metal radicals. The slowest elementary step in the overall back reaction (k_{-1}) is formation of the caged radical pair (k_{-1B}) since the actual back hydrogen atom transfer step (k_{-1A}) involves an exothermic reaction between two radicals that have already overcome the entropic barriers to assembling themselves close enough for efficient reaction.

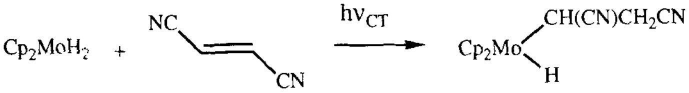
PHOTOCHEMICAL OLEFIN HYDROGENATION WITH METAL HYDRIDES

A recent report by Kochi and co-workers[24] documented a stoichiometric photochemical route to olefin hydrogenation and hydrometalation that accomplishes a similar transformation to those discussed above, but which exhibits some unique features not observed in the aforementioned systems. The electron-rich metal hydride complexes Cp_2MoH_2, Cp_2WH_2, and Cp_2ReH form electron donor–acceptor complexes with electron-deficient olefins such as fumaronitrile and maleic anhydride. The charge-transfer absorption band for the complex between Cp_2WH_2 and fumaronitrile has λ_{max} = 516 nm (ε = 140 M^{-1} cm^{-1}). A solution of Cp_2WH_2 and excess fumaronitrile showed no thermal reaction at 100°C, but photolysis led to hydrogenation of the fumaronitrile and formation of the fumaronitrile adduct of tungstenocene (Eq. (10)).



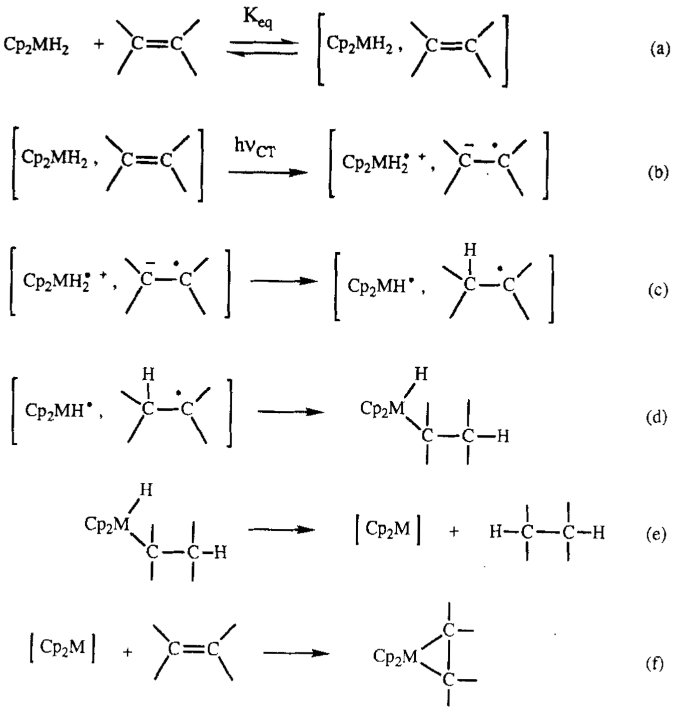
(10)

A similar photochemical reaction with Cp_2MoH_2 gave the hydrometalation product shown in Eq. (11).



(11)

As shown in the proposed mechanism (Scheme 3), the preequilibrium step (a) assembles the hydride and olefin together to form the electron donor–acceptor complex that gives rise to the charge transfer absorption. Photolysis into the charge transfer band (step (b)) produces the ion radical pair by electron transfer from the metal to the olefin. Step (c) is a proton transfer from the cation radical of the metal hydride to the anion radical of the olefin. This step will be discussed in more detail later, but first it is important to recognize that the intermediate that results from the proton transfer of step (c) is a caged radical pair containing a metal-centered radical and an organic radical, reminiscent of those produced in the olefin hydrogenations discussed earlier. The pathway for generation of this radical pair is clearly distinct from those formed earlier by hydrogen atom transfer processes, but the subsequent chemistry bears notable similarities. Step (d) of the mechanism shown in Scheme 3 involves geminate combination of the carbon- and metal-centered radicals, a step that parallels the formation of the manganese allyl complex in Eq. (2) and the cluster formation step in Eq. (8). In the case of the reaction of Cp_2MoH_2



SCHEME 3

with fumaronitrile (Eq. (11)), this is the final step, leading to the isolated molybdenocene alkyl hydride complex.

The analogous reaction with Cp_2WH_2, however, led to the hydrogenation of fumaronitrile and isolation of the olefin complex of tungstenocene (steps (e) and (f) in Scheme 3). It was suggested that the different stoichiometries and products for Mo vs. W resulted from further reaction of the initially formed alkyl hydride complex of W, which underwent reductive elimination and trapping of the reactive Cp_2W fragment by fumaronitrile. Mechanistic details of the thermal and photochemical reductive elimination of alkanes from alkyl hydride complexes such as $Cp_2W(CH_3)H$ have been reported,[25] so the elimination of alkane and subsequent trapping of the highly reactive $[Cp_2W]$ fragment have ample precedent. The fact that the alkyl hydride of Mo was isolable whereas the analogous tungsten species underwent further reaction is somewhat surprising in view of the higher stability expected for the third row compared to the second row metal complexes. The answer to this dilemma is most likely due to the fact that the molybdenum complex precipitated from solution during the reaction, thereby precluding further reaction.

PROTON TRANSFER FROM METAL HYDRIDES

Proton transfer reactions of metal hydrides[26] are a commonly encountered mode of M–H bond cleavage which can be compared to the hydrogen atom transfer reactivity discussed above. A substantial body of quantitative data on the kinetic and thermodynamic acidity of metal hydrides has been reported by Norton and co-workers.[26] The thermodynamic acidities of metal carbonyl hydrides decrease in going from first to second to third row metals, as exemplified by the pK_a data in CH_3CN for $HCr(CO)_3Cp$ ($pK_a = 13.3$), $HMo(CO)_3Cp$ ($pK_a = 13.9$), and $HW(CO)_3Cp$ ($pK_a = 16.1$). The pK_a of $HW(CO)_2(PMe_3)Cp$ is 26.6, indicating that substitution of a CO by the strongly electron-donating ligand PMe_3 dramatically decreases the acidity. This effect is understandable in terms of the lower stability of the metal anion containing the electron-donating phosphine ligand.

The acidity of Cp_2WH_2 or Cp_2MoH_2 is much lower than the acidity of the metal hydrides discussed above which contain electron-accepting carbonyls that can stabilize the negative charge of the metal anion resulting from deprotonation, although these more electron-rich metal hydrides can be deprotonated by strong bases such as BuLi. In the case of the proton transfer (step (c)) in Scheme 3, it is not a neutral metal hydride but the radical cation of the metal hydride that is the proton donor. In the reactions of Cp_2MoH_2 and Cp_2WH_2 with fumaronitrile, the higher overall reaction rate observed for the molybdenum hydride was attributed to the higher acidity of $[Cp_2MoH_2]^{\cdot +}$ compared to that of the tungsten analogue. More striking than the differences in acidity of second compared to third row hydrides is the huge enhancement in acidity of metal hydrides upon one-electron oxidation. Also related to the proposal of proton transfer from the $[Cp_2MH_2]^{\cdot +}$ complex in step (c) of Scheme 3 is the quantitative determination of pK_a data for radical cations of several metal carbonyl hydrides recently reported by Ryan, Tilset and Parker.[27] The radical cations formed by one-electron oxidation of metal hydrides are exceptionally strong acids. For example, the pK_a of $[HMo(CO)_3Cp]^{\cdot +}$ in CH_3CN is -6.0. Another intriguing result to emerge from this study is that the decrease in pK_a from MH to $[HM]^{\cdot +}$ is a relatively constant 20.6 ± 1.5 pK_a units for the Cr, Mo and W hydrides reported thus far [$HM(CO)_3Cp$ for M = Cr, Mo and W, along with $HMo(CO)_3Cp^*$ and $HW(CO)_2(PMe_3)Cp$].

The dramatic difference in acidity caused by a one-electron change has precedent in organic chemistry. For example, the pK_a of the radical cation of benzene[28] is estimated[29] to be -3.8 ± 2.0 in CH_3CN. Similar effects are also observed in the basicity of 2,2′-bipyridine[30] (abbreviated bpy). In aqueous solution, the pK_a of bpyH· is about 24. One-electron oxidation of bpyH· to give $bpyH^+$ produces a much strong acid: the pK_a of $bpyH^+$ in aqueous solution is 4.4.

HYDRIDE TRANSFER REACTIONS OF METAL HYDRIDES

Along with the hydrogen atom transfer and proton transfer reactivity discussed above, hydridic reactivity of metal hydrides is observed for many metal hydrides.[31] Labinger and Komadina reported the qualitative rates of the reduction of ketones by different metal hydrides, and they identified the position of the metal in the periodic table as one of the main factors influencing the tendency of metal hydrides to exhibit hydridic reactivity.[32] The group 4 hydride Cp_2ZrH_2 reacts quickly with acetone to produce $Cp_2Zr(OCHMe_2)_2$, which then gives isopropanol upon hydrolysis. The group 5 hydride Cp_2NbH_3 reacts more slowly with acetone, consistent with the general trend that metals on the left side of the periodic table exhibit enhanced hydridic character compared to similar compounds farther to the right side of the periodic table. The group 6 hydride Cp_2MoH_2 is reported to be unreactive towards acetone, but it does react with the more electrophilic ketone $CF_3(C{=}O)CH_3$. While these comparisons give useful information about the change in hydridic behavior for related hydrides from rows 4, 5 and 6 of the periodic table, these qualitative observations should not be interpreted as a direct measure of "inherent hydricity" since the ketones very likely coordinate to the metal prior to the actual hydride transfer step.

Along with the position in the periodic table, the ligands also have a profound influence on the hydridic behavior. For example, $HMo(CO)_3Cp$, which has electron-accepting carbonyl ligands, does not reduce $CF_3(C{=}O)CH_3$, and clearly has greatly diminished reactivity in terms of hydride donation compared to the electron-rich molybdenum hydride Cp_2MoH_2.

As would be expected based on their negative charge, anionic metal carbonyl hydrides[33] exhibit enhanced hydridic reactivity compared to neutral metal carbonyl hydrides. Nucleophilic transfer of hydride from many anionic metal hydrides has been used to convert alkyl halides to alkanes as generalized in Eq. (12).

$$MH^- + RBr \rightarrow MBr^- + RH \qquad (12)$$

In some cases, the mechanism of this reaction involves direct hydride transfer (H^-) by an S_N2 nucleophilic substitution mechanism. In many cases, however, a radical chain mechanism (S_H2, shown in Scheme 4) competes with the S_N2 mechanism. Kinney, Jones and Bergman[34] initially established the radical chain mechanism for conversion of organic halides to alkanes by the anionic vanadium hydride $CpV(CO)_3H^-$, but they also argued for the presence of a direct displacement S_N2 pathway for some substrates. More recently, Darensbourg and co-workers reported extensive studies using a series of anionic Cr, Mo and W hydrides.[35] A study utilizing

Chain Initiation

$$MH^- + \text{Initiator}\bullet \longrightarrow \overset{\bullet}{M}^- + \text{Initiator–H}$$

$$RBr + \text{Initiator}\bullet \longrightarrow R\bullet + \text{Initiator–Br}$$

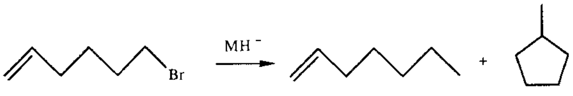
Chain Propagation

$$\overset{\bullet}{M}^- + RBr \longrightarrow MBr^- + R\bullet$$

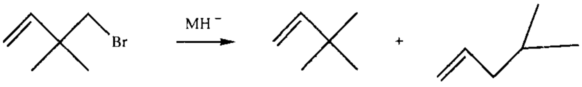
$$MH^- + R\bullet \longrightarrow \overset{\bullet}{M}^- + RH$$

SCHEME 4

two different radical rearrangements not only confirmed that both pathways are available, but also established the relative reactivity of a series of anionic metal carbonyl hydrides. The reaction of the 5-hexenyl bromide in Eq. (13) proceeds by both



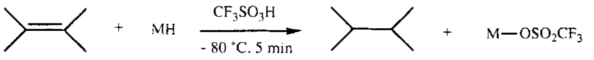
(13)



(14)

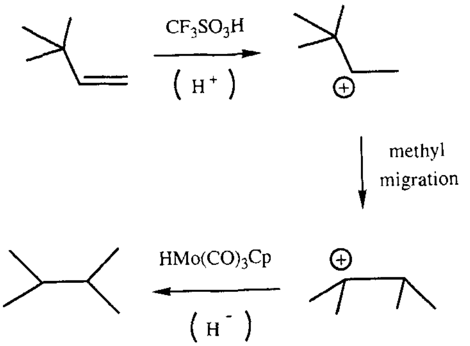
radical chain (S_H2) and direct hydride transfer (S_N2) pathways, but only the radical chain pathway was throught to occur in Eq. (14), since S_N2 reactivity of the neopentyl-like bromide was assumed to be precluded. One of the conclusions of this study was that the direct nucleophilic hydride transfer (S_N2) pathway was the predominant mechanism for the reaction of the primary bromide. The approximate percentage of the reaction proceeding by the radical chain (S_H2) pathway was 10% for $HCr(CO)_5^-$, 0.3% for $HW(CO)_5^-$, and only 0.03% for $HW(CO)_4P(OMe)_3^-$. The order of relative reactivity of several anionic metal hydrides with *n*-BuBr is $HW(CO)_4P(OMe)_3^- > HCr(CO)_4P(OMe)_3^- > HW(CO)_5^- > HV(CO)_3Cp^- > HCr(CO)_5^- > HRu(CO)_4^-$. The propensity for the direct hydride transfer (S_N2) pathway correlated with increasing tendency to form $Na^+ \cdots HM$ interaction in IR ion pairing studies. Conversely, the hydrides exhibiting greater radical chain reactivity were those which exhibited (in IR ion pairing studies) more interaction of Na^+ with the carbonyl oxygens, which was suggested to be indicative of greater delocalization of the negative charge. The iron hydride *trans*-$HFe(CO)_3P(OMe)_3^-$ was far less reactive with alkyl bromides, and it was suggested that a third mechanism (S_N2, metal site nucleophilicity, as opposed to hydride site nucleophilicity) involving an oxidative addition of the substrate to the metal was occurring.

Many of the *neutral* metal carbonyl hydrides that were shown to be efficient proton donors and hydrogen atom donors can also function as a source of hydride, H^-. A low-temperature ionic hydrogenation of substituted olefins which utilizes neutral metal carbonyl hydrides as the hydride source is shown in Eq. (15).[36]



(15)

Yields of hydrogenated products from 90–100% were found for Eq. (15) for MH = $HMo(CO)_3Cp$, $HW(CO)_3Cp$, and $HRe(CO)_5$. The mechanism involves protonation of the olefin to give a carbocation, which is subsequently converted to the alkane by a hydride transfer from the metal hydride.



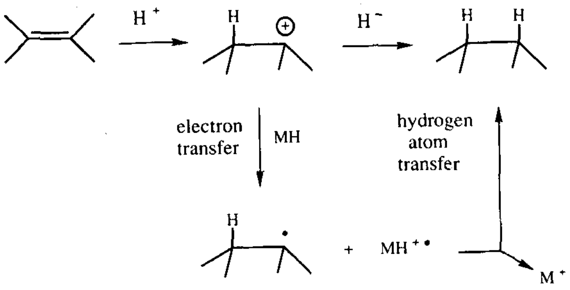
(16)

The intermediacy of a carbocation was demonstrated (Eq. (16)) by the rearrangement of a secondary to tertiary carbocation in the ionic hydrogenation of *t*-butylethylene, which gives the rearranged product, 2,3-dimethylbutane. The reaction proceeds rapidly at low temperature to give high yields of hydrogenation products for tetrasubstituted olefins, trisubstituted olefins, and 1,1-disubstituted olefins. We have not had any success in hydrogenation of 1,2-disubstituted olefins such as cyclohexene, so this olefin hydrogenation method is limited to cases where a tertiary carbocation can be formed, either by direct protonation or (as in Eq. (16)) by rearrangement following protonation. The rate of this reaction can be contrasted to a related ionic hydrogenation process developed by Kursanov and co-workers,[37] in which olefins are hydrogenated by $CF_3CO_2H/HSiEt_3$. Typical conditions quoted for hydrogenations using CF_3CO_2H and $HSiEt_3$ are a few hours at 50°C, compared to a few minutes at −80°C using CF_3SO_3H and transition metal hydrides. Since the acid (CF_3SO_3H vs. CF_3CO_2H) and the hydride (transition metal hydride vs. triethylsilane) are different in these two procedures, it was initially unclear which of these two changes resulted in the huge differences in hydrogenation rates. Our demonstration that use of $CF_3SO_3H/HSiEt_3$ gives rapid, high yield hydrogenations at $-80\,^{\circ}C$ is therefore important for synthetic and mechanistic reasons. For synthetic purposes, it means that commercially available $HSiEt_3$ can be used in conjunction with CF_3SO_3H for rapid olefin hydrogenations (subject to the limitation of being able to form a tertiary carbocation, a limitation also encountered in the more extensively studied $CF_3CO_2H/HSiEt_3$ method). The fact that similar results can be obtained whether the hydride source is $HSiEt_3$ or a transition metal hydride means that the profound increase in hydrogenation rate for $CF_3SO_3H/HSiEt_3$ over $CF_3CO_2H/HSiEt_3$ is clearly due to the much higher acid strength of CF_3SO_3H compared to CF_3CO_2H, leading to much faster carbocation formation with the stronger acid.

The success of the ionic hydrogenations using $CF_3SO_3H/HSiEt_3$ is surprising, since it had been stated in a review of the $CF_3CO_2H/HSiEt_3$ method that "stronger acids cannot be used in conjunction with silanes because they react with the latter."[37] The rapid reaction between CF_3SO_3H and $HSiEt_3$ *does not* preclude their utility in the ionic hydrogenations, but instead provides qualitative information about the reactivity of the carbocation. The success of the ionic hydrogenation is clearly dependent on the fact that under appropriate reaction conditions, the carbocation is converted to the product by hydride transfer (from either $HSiEt_3$ or transition metal hydride) faster than the carbocation can react with the olefin to begin polymerization.

Although it is clear that the overall hydrogenation sequence involves protonation followed by hydride transfer, further details of the mechanism are presently unanswered (but under investigation.) It is clear that the strong acid, CF_3SO_3H, is the source of the protons, but it has not been confirmed that the acid protonates the olefin directly. An interesting possibility is that the metal hydride is initially protonated to give a cationic dihydrogen complex, $Cp(CO)_3Mo(\eta^2\text{-}H_2)^+$, which then protonates the olefin. The possibility of high acidity of this complex is supported by quantitative measurements on the acidity of dihydrogen complexes that have been reported by Heinekey and co-workers.[38] They recently found that the cationic rhenium dihydrogen complex Cp*(NO)(CO)Re(η^2-H_2)$^+$ is a surprisingly strong acid ($pK_a \approx -2$ in CH_2Cl_2). The utility of cationic dihydrogen complexes of Os[39] and Ir[40] in olefin hydrogenation has been demonstrated by Caulton and co-workers. Their proposed mechanism involves loss of coordinated H_2, coordination of the olefin to the metal, etc., so the way in which hydrogen is delivered to the olefin is distinctly different from the mechanism involving protonation of the olefin that we consider here.

A second unanswered question concerns the details of the hydride transfer, which could occur by direct hydride transfer (as shown in the upper pathway of Scheme 5) or by a two-step pathway. The two-step pathway, shown in the lower part of Scheme 5, involves an initial electron transfer (oxidation of the metal hydride by the carbocation) followed by fast hydrogen atom transfer from the radical cation of the metal hydride. There is precedent for an electron transfer followed by hydrogen atom transfer in reactions of transition metal *alkyl* complexes with carbocations. Cooper and co-workers reported[41] that $Cp_2W(CH_3)_2$ and related complexes react with Ph_3C^+ by initial electron transfer followed by hydrogen atom transfer, to generate reactive cationic alkylidene complexes that undergo a variety of interesting insertion and trapping reactions. Reaction of Ph_3C^+ with rhenium alkyl complexes such as $Cp(PPh_3)(NO)ReCH_2Ph$ results in stereospecific α-hydride abstraction and produces isolable alkylidene complexes, $[Cp(PPh_3)(NO)Re{=}CHPh]^+$[42] Gladysz, Parker and co-workers



SCHEME 5

examined the details of this reaction using electrochemical techniques, and they suggested a two-step mechanism involving initial electron transfer followed by hydrogen atom transfer.[43] On the other hand, hydride abstraction from $Cp(PMe_3)(CO)_2MoH$ by Ph_3C^+ was studied by Ryan, Tilset and Parker, and was proposed to occur by direct hydride transfer rather than the two-step mechanism.[27] Literature precedents therefore indicate that either of the two pathways shown in Scheme 5 may be reasonable, and the data presently available are insufficient to distinguish between them.

Hydride transfer has also been proposed to occur from neutral metal hydrides to substrates less electrophilic than the carbocations discussed above. Sullivan and Meyer[44] reported the formation of $(CO)_3(bpy)ReOC(=O)H$ by insertion of CO_2 into the Re–H bond of $(CO)_3(bpy)ReH$. They suggested that this reaction involved a hydride transfer from Re to carbon in a highly polarized transition state or intermediate. An inverse kinetic isotope effect (k_H/k_D = 0.52 ± 0.05 in CH_3CN) was found when the metal deuteride, $(CO)_3(bpy)ReD$, was used. Further evidence for the hydride transfer mecahnism was provided by the observation of a large solvent effect in which the rate of the reaction increased with the dielectric constant of the solvent—the reaction was over two orders of magnitude faster in acetonitrile than in tetrahydrofuran.

HYDRIDIC VS. ACIDIC REACTIVITY[45]—EXPERIMENTAL AND THEORETICAL EVIDENCE

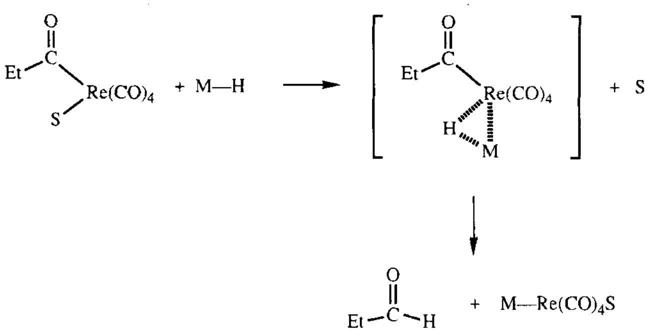
The kinetic (and thermodynamic) acidity of a metal carbonyl hydride decreases when a ligand on the metal is replaced by a more electron-donating ligand (e.g., Cp* vs. Cp, or phosphines vs. CO). In a qualitative sense, a metal hydride that produces hydrogen upon reaction with acids may be thought to exhibit hydridic character. We have found that the rate of reaction of $HMo(CO)_3Cp$ with CF_3SO_3H is much slower than that of the phosphine substituted hydride $HMo(CO)_2(PPh_3)Cp$, in agreement with the expected higher "hydricity" of the phosphine substituted hydride. The potential utility of the relative rates of reaction of metal hydrides with acid as an attempt to measure relative "hydricity" is compromised by the possible intermediacy of cationic dihydrogen complexes [$M(\eta^2-H_2)^+$] or dihydrides [MH_2^+] which could result from protonation of the neutral metal hydride. The relative rate of hydrogen evolution from reaction of metal hydrides with acids might be reflective of the stability of a dihydrogen complex or dihydride complex, rather than of the actual hydricity of the M–H bond.

Considerable differences in hydride transfer reactivity can result from supposedly similar complexes. Legzdins and Martin reported that $Cp(NO)_2WH$ exhibited hydridic behavior, since it produced $Cp(NO)_2WOSO_2C_6H_4CH_3$ upon reaction with *p*-toluenesulfonic acid.[46] The relatively acidic tungsten carbonyl hydride complex, $Cp(CO)_3WH$ (pK_a = 16.1 in CH_3CN) was unreactive with *p*-toluenesulfonic acid under identical conditions. Bursten and Gatter have utilized molecular orbital calculations to evaluate the reasons for the acidic vs. hydridic behavior of metal hydrides.[47] They found that the electronic stability of the organometallic fragment resulting from the loss of H^+ (or H^-) from the metal hydride was a key factor in determining the reactivity. Calculations on the $Cp(NO)_2CrH/Cp(CO)_3CrH$ species were carried out as a model for the related tungsten systems. The instability of the hypothetical anion $Cp(NO)_2Cr^-$ (which would result from deprotonation of $Cp(NO)_2CrH$) was suggested to account for the low acidity of $Cp(NO)_2WH$. In contrast, hydride donation from $Cp(NO)_2WH$ would produce $Cp(NO)_2W^+$, which would give $Cp(NO)_2W(solv)^+$ in a coordinating solvent. The stability of this cation was proposed to account for the hydridic behavior of $Cp(NO)_2WH$. It was also pointed out that this 18-electron cation has a d^6 three-legged piano stool structure similar to that observed for $Cp(CO)_3W^-$, which is the stable product resulting from proton loss from $Cp(CO)_3WH$.

Hydride donation to metal carbonyl complexes is another probe of hydride transfer reactivity. The formation of formyls by hydride transfer does not always indicate *direct* hydride transfer, however, since Kochi and co-workers have shown that metal formyls can be formed by electron transfer to metal carbonyls to give 19-electron radical anions which subsequently produce formyls by hydrogen atom abstraction from *n*-Bu_3SnH.[48] The neutral tungsten nitrosyl complex $Cp(NO)_2WH$ does not react with $Fe(CO)_5$,[46] but the anionic chromium complex $HCr(CO)_5^-$ does, forming the iron formyl complex $(CO)_4FeCHO^-$ as one of the products.[49] Curtis and DuBois recently reported that a nickel hydride complex, $(dmpe)_2NiH^+$, [dmpe = 1,2-bis(dimethylphosphino)ethane] donates H^- to cationic metal carbonyl complexes to generate metal formyls.[50] The observation that this cationic complex can donate a hydride is a compelling reminder that the overall charge on a hydride complex is only one of several factors that determine its reactivity towards a particular substrate. The hydridic reactivity of $(dmpe)_2NiH^+$ is most likely due to the very electron-rich nickel center (with 2 dmpe ligands) and the high stability of the Ni^{+2} product.

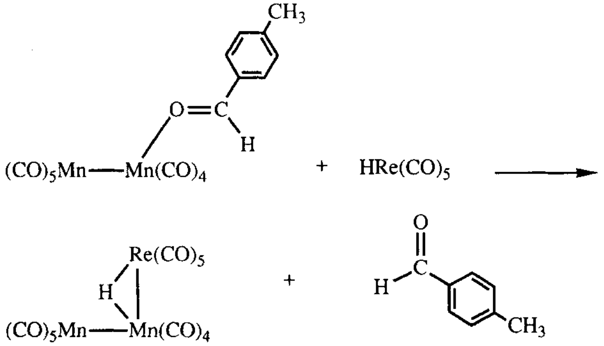
NEUTRAL METAL HYDRIDES AS NUCLEOPHILES AND LIGANDS

The hydridic reactivity discussed above involved cases where the M–H bond was (at least formally) cleaved to produce a hydride (H^-). Related to this hydridic reactivity of metal hydrides is the concept that the two electrons in the M–H bond can behave as a nucleophile towards some substrates, as in Darensbourg's results of hydride-site nucleophilicity of anionic metal hydrides.[33,35] A quantitative evaluation of the relative nucleophilicity of several *neutral* metal carbonyl hydrides was reported by Martin, Warner and Norton.[51] A solvated acyl complex, $Et(C{=}O)Re(CD_3CN)(CO)_4$, was directly observable from the reaction of $EtRe(CO)_5$ with CD_3CN. Metal hydrides react with this acyl complex to produce EtCHO in a reaction proposed to proceed through a hydride-bridged intermediate (or transition state) depicted in Scheme 6. The relative rate constants for this reaction were suggested to provide a measure of the relative nucleophilicity of the metal hydrides. The order of nucleophilicity established in this way was $HRe(CO)_5$ (k_{rel} = 139), $HMn(CO)_5$ (k_{rel} = 100), $H_2Os(CO)_4$ (k_{rel} = 58), $HW(CO)_3Cp$ (k_{rel} = 9), $HW(CO)_2(PMe_3)Cp$ (k_{rel} = 5), $HCr(CO)_3Cp$ (k_{rel} = 1). An intriguing observation made by Norton is that, to some extent, the order of nucleophilicity is the opposite of the order of the relative acidities of these metal hydrides. Note, however, that the range spanned by the nucleophilicity scale is only about two orders of magnitude, whereas the range in kinetic acidities of these complexes encompasses nearly eight orders of magnitude from $HRe(CO)_5$ to $HCr(CO)_3Cp$.



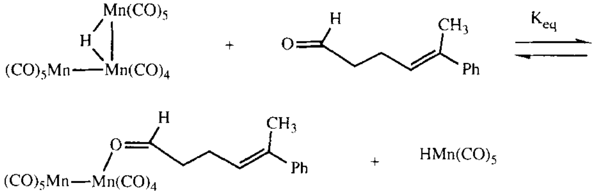
SCHEME 6

The bridging hydride intermediate shown in Scheme 6 has a 3-center, 2-electron interaction of the type found in numerous polynuclear hydride complexes. The use of metal hydrides as 2-electron donor ligands towards organometallic complexes with weakly coordinated ligands has been very successfully used in the preparation of a variety of M(μ-H)M′ complexes.[52] In contrast to the demonstrated synthetic utility of such reactions, less is known about the quantitative aspects of metal hydrides as ligands. Norton's data cited above indicated that $HRe(CO)_5$ was more reactive *kinetically* as a nucleophile than $HMn(CO)_5$.[51] Recent work demonstrates a considerable *thermodynamic* binding preference of the Re hydride compared to the analogous Mn hydride. The weakly bound aldehyde ligand in $Mn_2(CO)_9(\eta^1$-tolualdehyde) is readily displaced (Eq. (17)) by $HRe(CO)_5$, giving free tolualdehyde and $Mn_2(CO)_9(\mu$-H) $Re(CO)_5$.[53]



(17)

This established the preference of $HRe(CO)_5$ compared to tolualdehyde to bind to coordinatively unsaturated $Mn_2(CO)_9$. Thermodynamic data ($\Delta G° = -2.5$ kcal/mol) for the equilibrium shown in Eq. (18) indicates that $Mn_2(CO)_9$ binds the aldehyde more strongly than it binds $HMn(CO)_5$.[54] The combined results of these experiments reveal that the relative thermodynamics of binding to $Mn_2(CO)_9$ is $HRe(CO)_5 > \eta^1$-aldehyde $> HMn(CO)_5$.



(18)

SUMMARY

Transition metal hydrides are remarkably versatile in their reactions, functioning as donors of protons, hydrogen atoms, and hydride. Early metal hydrides with electron-donating ligands, such as Cp_2ZrH_2, tend to exhibit hydridic reactivity. Neutral metal carbonyl hydrides such as $HW(CO)_3Cp$ exhibit all three of the modes of metal–hydrogen bond cleavage listed in Scheme 1: several of them are moderately strong acids, they have been shown to readily donate a hydrogen atom to some substrates, and they can donate hydride to sufficiently electrophilic substrates such as carbocations. Anionic metal carbonyl hydrides often exhibit stoichiometric hydridic reactivity, but the actual mechanism is frequently a radical chain reaction in which the actual M–H bond cleavage step involves donation of a hydrogen atom from the anionic metal hydride.

The reactions of metal hydrides are influenced by numerous factors, including the position in the periodic table, the ligands (which influence both the electronic and steric properties of the metal hydride), the charge (negative, neutral, or cationic) and the stability of the resulting organometallic (and organic) products. The fascinating diversity of descriptive chemistry of metal hydrides which has been explored for over three decades has been complemented in recent years by an increasing number of quantitative kinetic studies which facilitate interpretation and understanding of some of the observed reactivity patterns. Along with new kinetic and mechanistic studies, recent thermochemical data, while not without controversy, have added an important component to our understanding (or lack thereof!) of metal hydride reactivity.

Acknowledgments

Research at Brookhaven National Laboratory is carried out under contract DE-AC02-76CH0016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. I thank Drs. Edward Samsel (who started our research in hydrogen atom transfer reactions), Carol Creutz, Mark Andrews, George Gould and Prof. Jack Norton for much helpful advice and discussions.

References

1. G. W. Parshall, *Homogeneous Catalysis* (John Wiley & Sons, New York, 1980).
2. H.-W. Chen, W. L. Jolly, J. Kopf and T. H. Lee, J. Am. Chem. Soc. **101**, 2607 (1979).
3. R. L. Sweany and J. W. Owens, J. Organomet. Chem. **255**, 327 (1983).
4. For reviews of hydrogen atom transfer reactions of metal hydrides, see: (a) T. L. Brown, in *Organometallic Radical Processes*, ed. W. Trogler (Elsevier, Lucerne, 1990). (b) D. C. Eisenberg and J. R. Norton, Isr. J. Chem., in press (1991). (c) J. Halpern, in *Transition Metal Hydrides: Recent Advances in Theory and Experiment*, ed. A. Dedieu (VCH, New York, 1991, in press).
5. R. L. Sweany and J. Halpern, J. Am. Chem. Soc. **99**, 8335 (1977).
6. References to hydrogenation of substituted styrenes by sequential hydrogen atom transfers from metal hydrides are listed in Footnote 3 of Ref. 11a.
7. (a) H. M. Feder and J. Halpern, J. Am. Chem. Soc. **97**, 7186 (1975). (b) R. Sweany, S. C. Butler and J. Halpern, J. Organomet. Chem. **213**, 487 (1981).
8. J. F. Garst, T. M. Bockman and R. Batlaw, J. Am. Chem. Soc. **108**, 1689 (1986).
9. B. Wassink, M. J. Thomas, S. C. Wright, D. J. Gillis and M. C. Baird, J. Am. Chem. Soc. **109**, 1995 (1987).
10. T. A. Shackleton and M. C. Baird, Organometallics **8**, 2225 (1989).
11. (a) R. M. Bullock and E. G. Samsel, J. Am. Chem. Soc. **112**, 6886 (1990). (b) R. M. Bullock and E. G. Samsel, J. Am. Chem. Soc. **109**, 6542 (1987).
12. R. D. Adams, D. E. Collins and F. A. Cotton, J. Am. Chem. Soc. **96**, 749 (1974).
13. S. J. McLain, J. Am. Chem. Soc. **110**, 643 (1988).
14. For a recent review of M–H bond dissociation energies, see: J. A. Martinho Simões and J. L. Beauchamp. Chem. Rev. **90**, 629 (1990).
15. M. Tilset and V. D. Parker, J. Am. Chem. Soc. **111**, 6711 (1989), as modified in J. Am. Chem. Soc. **112**, 2843 (1990).
16. G. Kiss, K. Zhang, S. L. Mukerjee, C. D. Hoff and G. C. Roper, J. Am. Chem. Soc. **112**, 5657 (1990).

17. (a) B. H. Byers and T. L. Brown, J. Am. Chem. Soc. **99**, 2527 (1977). (b) N. W. Hoffman and T. L. Brown, Inorg. Chem. **17**, 613 (1978).
18. D. C. Eisenberg, C. J. C. Lawrie, A. E. Moody and J. R. Norton, J. Am. Chem. Soc., in press.
19. For a review of isotope effects in reaction of metal hydrides, see R. M. Bullock, in *Transition Metal Hydrides: Recent Advances in Theory and Experiment*, ed. A. Dedieu (VCH, New York, 1991, in press).
20. For a review of radical cages in organometallic chemistry, see: T. W. Koenig, B. J. Hay and R. G. Finke, Polyhedron **7**, 1499 (1988).
21. E. N. Jacobsen and R. G. Bergman, J. Am. Chem. Soc. **107**, 2023 (1985).
22. For a review of the photochemistry of metal–metal dimers, including tables of recombination rate constants for metal radicals, see: T. J. Meyer and J. V. Caspar, Chem. Rev. **85**, 187 (1985).
23. For a comprehensive listing of kinetic data for the combination of carbon-centered radicals, see: *Radical Reaction Rates in Liquids*, ed. H. Fisher, Landolt-Börnstein, New Series, Group II, Volume 13, Subvolume a (Springer-Verlag, Berlin, 1984).
24. J. J. Ko, T. M. Bockman and J. K. Kochi, Organometallics **9**, 1833 (1990).
25. R. M. Bullock, C. E. L. Headford, K. M. Hennessy, S. E. Kegley and J. R. Norton, J. Am. Chem. Soc. **111**, 3897 (1989).
26. For a review of proton transfer reactions of metal hydrides, see: S. S. Kristjánsdóttir and J. R. Norton, in *Transition Metal Hydrides: Recent Advances in Theory and Experiment*, ed. A. Dedieu (VCH, New York, 1991, in press).
27. O. B. Ryan, M. Tilset and V. D. Parker, J. Am. Chem. Soc. **112**, 2618 (1990).
28. For a review of the kinetics and mechanism of reactions of aromatic radical cations, see: O. Hammerich and V. D. Parker, Adv. Phys. Org. Chem. **20**, 55 (1984).
29. A. M. de P. Nicholas and D. R. Arnold, Can. J. Chem. **60**, 2165 (1982).
30. C. V. Krishnan, C. Creutz, H. A. Schwarz and N. Sutin, J. Am. Chem. Soc. **105**, 5617 (1983).
31. For a review of nucleophilic reactions of metal hydrides, see: J. Labinger, in *Transition Metal Hydrides: Recent Advances in Theory and Experiment*, ed. A. Dedieu (VCH, New York, 1991, in press).
32. J. A. Labinger and K. H. Komadina, J. Organomet. Chem. **155**, C25 (1978).
33. For a review of anionic transition metal hydrides, see: M. Y. Darensbourg and C. E. Ash, Adv. Organomet. Chem. **27**, 1 (1987).
34. R. J. Kinney, W. D. Jones and R. G. Bergman, J. Am. Chem. Soc. **100**, 7902 (1978).
35. C. E. Ash, P. W. Hurd, M. Y. Darensbourg and M. Newcomb, J. Am. Chem. Soc. **109**, 3313 (1987).
36. R. M. Bullock and B. J. Rappoli, J. Chem. Soc., Chem. Commun. 1447 (1989).
37. D. N. Kursanov, Z. N. Parnes and N. M. Loim, Synthesis 633 (1974).
38. (a) M. S. Chinn, D. M. Heinekey, N. G. Payne and C. D. Sofield, Organometallics **8**, 1824 (1989). (b) M. S. Chinn and D. M. Heinekey, J. Am. Chem. Soc. **112**, 5166 (1990).
39. T. J. Johnson, J. C. Huffman, K. G. Caulton, S. A. Jackson and O. Eisenstein, Organometallics **8**, 2073 (1989).
40. E. G. Lundquist, K. Folting, W. E. Streib, J. C. Huffman, O. Eisenstein and K. G. Caulton, J. Am. Chem. Soc. **112**, 855 (1990).
41. (a) J. C. Hayes, G. D. N. Pearson and N. J. Cooper, J. Am. Chem. Soc. **103**, 4648 (1981). (b) J. C. Hayes and N. J. Cooper, J. Am. Chem. Soc. **104**, 5570 (1982). (c) P. Jernakoff and N. J. Cooper, J. Am. Chem. Soc. **106**, 3026 (1984).

42. W. A. Kiel, G.-Y. Lin, A. G. Constable, F. B. McCormick, C. E. Strouse, O. Eisenstein and J. A. Gladysz, J. Am. Chem. Soc. **104**, 4865 (1982).
43. G. Bodner, J. A. Gladysz, M. F. Nielsen and V. D. Parker, J. Am. Chem. Soc. **109**, 1757 (1987).
44. B. P. Sullivan and T. J. Meyer, Organometallics **5**, 1500 (1986).
45. For a discussion of the relevance of certain thermodynamic properties of metal hydrides to the hydridic or protic reactivity, see: R. G. Pearson, Chem. Rev. **85**, 41 (1985).
46. P. Legzdins and D. T. Martin, Inorg. Chem. **18**, 1250 (1979).
47. B. E. Bursten and M. G. Gatter, J. Am. Chem. Soc. **106**, 2554 (1984).
48. B. A. Narayanan, C. Amatore and J. K. Kochi, Organometallics **5**, 926 (1986).
49. M. Y. Darensbourg, C. E. Ash, L. W. Arndt, C. P. Janzen, K. A. Youngdahl and Y. K. Park, J. Organomet. Chem. **383**, 191 (1990).
50. C. J. Curtis, D. L. DuBois and A. Miedaner, *Abstracts of Papers*, 200th National Meeting of the American Chemical Society, Washington, D.C., 1990, INOR 426.
51. B. D. Martin, K. E. Warner and J. R. Norton, J. Am. Chem. Soc. **108**, 33 (1986).
52. L. M. Venanzi, Coord. Chem. Rev. **43**, 251 (1982).
53. A. Albinati, R. M. Bullock, B. J. Rappoli and T. F. Koetzle, Inorg. Chem., in press (1991).
54. R. M. Bullock and B. J. Rappoli, J. Am. Chem. Soc. **113**, 1659 (1991).