ORGANOMETALLICS

Volume 14, Number 9, September 1995

Communications

Kinetic Hydricity of Transition-Metal Hydrides toward Trityl Cation

Tan-Yun Cheng and R. Morris Bullock*

Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973-5000

Received July 5, 1995[⊗]

Summary: The kinetics of hydride transfer from a series of metal hydrides (MH) to $Ph_3C^+BF_4^-$ (producing Ph_3CH and $M\cdots FBF_3$) have been studied by stopped-flow methods in CH_2Cl_2 solution. Second-order rate constants at 25 °C span 5 orders of magnitude in kinetic hydricity, ranging from $k = 5.0 \times 10^1$ M^{-1} s^{-1} for $HMn(CO)_5$ to $k = 4.6 \times 10^6$ M^{-1} s^{-1} for trans-$HMo(CO)_2(PMe_3)Cp$.

Transition-metal hydrides are key reagents in many homogeneous catalytic reactions, and M–H bond cleavage is a requisite step in both catalytic and stoichiometric reactions of metal hydrides. A knowledge of the factors governing cleavage of the M–H bond may assist in the rational design of catalytic cycles employing metal hydrides. As might be expected due to their negative charge, anionic metal hydrides exhibit hydridic reactivity. Darensbourg and co-workers have reported extensive studies[1] demonstrating the utility of $HW(CO)_5^-$ and other anionic metal hydrides in the reduction of organic substrates. Neutral metal carbonyl hydrides such as $HW(CO)_3Cp$ ($Cp = \eta^5\text{-}C_5H_5$) undergo diverse reactivity patterns[2]—cleavage of the M–H bond can occur as a proton,[3] a hydrogen atom,[4] or a hydride.[5] In contrast to the detailed information available on the kinetics of *proton* transfer[3,6] and *hydrogen atom* transfer[4,7,8] reactions of these hydrides, little information is available on the kinetics of their *hydride* transfer reactions. The mechanism of ionic hydrogenation of olefins was shown to involve hydride transfer from metal hydrides to carbenium ions,[9] but a determination of the relative hydricity of the metal hydrides was not feasible from these reactions. We now report the kinetics of hydride transfer from a series of metal hydrides to a common carbenium ion, including kinetic hydricity data spanning 5 orders of magnitude.

The synthetic chemistry (eq 1) of organometallic complexes containing BF_4^- and other weakly coordinating ligands has been developed by Beck and others.[10]

$$\begin{aligned} &Ph_3C^+\ BF_4^- \ +\ MH \xrightarrow{k_{H^-}} \\ &Ph_3C{-}H \quad +\ M\cdots F{-}BF_3 \end{aligned} \qquad (1)$$

We determined the kinetics of these hydride transfer

[⊗] Abstract published in *Advance ACS Abstracts*, August 15, 1995.

[1] Darensbourg, M. Y.; Ash, C. E. *Adv. Organomet. Chem.* **1987**, *27*, 1–50.

[2] For a comparison of proton, hydrogen atom, and hydride transfer reactions of metal hydrides, see: Bullock, R. M. *Comments Inorg. Chem.* **1991**, *12*, 1–33.

[3] For a review of proton transfer reactions of metal hydrides, see: Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; Chapter 9.

[4] For a review of hydrogen atom transfer reactions of metal hydrides, see: Eisenberg, D. C.; Norton, J. R. *Isr. J. Chem.* **1991**, *31*, 55–66.

[5] For a review of nucleophilic reactivity of metal hydrides, see: Labinger, J. A. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; Chapter 10.

[6] (a) Edidin, R. T.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 3945–3953. (b) Kristjánsdóttir, S. S.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4366–4367.

[7] Bullock, R. M.; Samsel, E. G. *J. Am. Chem. Soc.* **1990**, *112*, 6886–6898.

[8] Eisenberg, D. C.; Lawrie, C. J. C.; Moody, A. E.; Norton, J. R. *J. Am. Chem. Soc.* **1991**, *113*, 4888–4895.

[9] Bullock, R. M.; Song, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 8602–8612.

[10] Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405–1421.

0276-7333/95/2314-4031$09.00/0

Table 1. Rate Constants[a] for Hydride Transfer from Metal Hydrides to $Ph_3C^+BF_4^-$ (CH_2Cl_2, 25 °C)

metal hydride	k_{H^-} (M^{-1} s^{-1})	k_{MH}/k_{MD}
$HMn(CO)_5$	5.0×10^1	
$HCr(CO)_3Cp^*$	5.7×10^1	
$HW(CO)_3Cp$	7.6×10^1	
$HSiEt_3$	1.5×10^2	
cis-$HMn(CO)_4(PPh_3)$	2.3×10^2	
$HMo(CO)_3Cp$	3.8×10^2	1.8
$HW(CO)_3Cp^*$	1.9×10^3	1.7
$HRe(CO)_5$	2.0×10^3	
$HMo(CO)_3Cp^*$	6.5×10^3	1.7
cis-$HRe(CO)_4(PPh_3)$	1.2×10^4	
trans-$HMo(CO)_2(PCy_3)Cp$	4.3×10^5	1.7
trans-$HMo(CO)_2(PPh_3)Cp$	5.7×10^5	
trans-$HMo(CO)_2(PMe_3)Cp$	4.6×10^6	

[a] ±10% estimated uncertainty for all rate constants.

reactions (eq 1) using stopped-flow methods in CH_2Cl_2 solution.[11] Experiments carried out with an excess of metal hydride ($[MH]_0 \geq 10[Ph_3C^+BF_4^-]_0$) established the rate law: $-d[Ph_3C^+BF_4^-]/dt = k[Ph_3C^+BF_4^-][MH]$. Second-order rate constants are given in Table 1 and are listed in order of increasing kinetic hydricity.

Comparisons of these transition-metal hydrides with a main-group hydride donor[12,13] show that several transition-metal hydrides are much faster hydride donors than $HSiEt_3$, which is frequently used[14] as a hydride donor. Despite their higher homolytic bond dissociation energies,[15] third-row metal hydrides are faster hydride donors than their first-row analogs in these heterolytic reactions; e.g., $k_{HRe} > k_{HMn}$. Similarly, $HW(CO)_3Cp^*$ ($Cp^* = \eta^5$-C_5Me_5) is more hydridic than $HCr(CO)_3Cp^*$, but in this series of group 6 hydrides the second-row hydride $HMo(CO)_3Cp^*$ exhibits the fastest rate of hydride transfer of the three. For the Mo and W hydrides, the kinetics of hydride transfer are apparently influenced more strongly by electronic effects than by steric effects. For example, replacement of one CO in $HMo(CO)_3Cp$ by the electron-donating but sterically demanding PPh_3 ligand results in a rate enhancement of about 10^3.

An interpretation of the kinetics of hydride transfer from the phosphine-substituted hydrides $HMo(CO)_2(PR_3)Cp$ is complicated by the existence of cis and trans isomers.[16,17] The Mo hydride $HMo(CO)_2(PCy_3)Cp$ was found to exist as an 89:11 mixture of cis and trans isomers[18] in CD_2Cl_2. Activation parameters for the *cis*-$HMo(CO)_2(PCy_3)Cp$ → *trans*-$HMo(CO)_2(PCy_3)Cp$ isomerization evaluated from NMR line-broadening experiments at seven temperatures between −45 and +11 °C in CD_2Cl_2 were $\Delta H^\ddagger = 11.3 \pm 0.3$ kcal mol^{-1}, $\Delta S^\ddagger = -7.0 \pm 1.2$ cal K^{-1} mol^{-1}, and $\Delta G^\ddagger(298\ K) = 13.4$ kcal mol^{-1}. As described above, second-order kinetics were deduced from experiments using excess $[HMo(CO)_2(PCy_3)Cp]$. In contrast, the kinetics of hydride transfer from $HMo(CO)_2(PCy_3)Cp$ at −55 °C using excess $[Ph_3C^+BF_4^-]$ (4.5−13 mM) showed an observed first-order rate constant (0.82 s^{-1}) that was *independent* of $[Ph_3C^+BF_4^-]$. This rate constant agrees with the rate constant of 0.67 s^{-1} for cis → trans isomerization of $HMo(CO)_2(PCy_3)Cp$ measured by NMR line broadening (and extrapolated to −55 °C). Following consumption of the first 11% of the hydride (the equilibrium amount of trans isomer), the rate-limiting step under these conditions is cis → trans hydride isomerization. From the observed rate constant at the highest $[Ph_3C^+BF_4^-]$, an upper limit of $k < 63$ M^{-1} s^{-1} (at −55 °C) can be determined for the rate constant for hydride transfer from *cis*-$HMo(CO)_2(PCy_3)Cp$.

These kinetics results in CH_2Cl_2 corroborate the conclusions reached by Tilset and co-workers from their studies of related reactions in MeCN.[19−21] They found that oxidation of $HMo(CO)_2(PPh_3)Cp$[20] in MeCN in the presence of a base led to *cis*-$[(MeCN)Mo(CO)_2(PPh_3)Cp]^+$. In contrast, hydride transfer to (p-$MeOC_6H_4$)Ph_2C^+ from $HMo(CO)_2(PPh_3)Cp$[20] in MeCN led to initial formation of *trans*-$[(MeCN)Mo(CO)_2(PPh_3)Cp]^+$, followed by a slow isomerization to the thermodynamically favored cis isomer. They concluded that *trans*-$HMo(CO)_2(PPh_3)Cp$ was more reactive than *cis*-$HMo(CO)_2(PPh_3)Cp$ as a hydride donor. We assume that the trans isomers are similarly much more reactive than cis isomers for $HMo(CO)_2(PMe_3)Cp$ and $HMo(CO)_2(PPh_3)Cp$ in our experiments as well. Accordingly, the second-order rate constants reported in Table 1 are the specific rate constants for hydride transfer from *trans*-$HMo(CO)_2(PR_3)Cp$. The activation parameters for hydride transfer from *trans*-$HMo(CO)_2(PCy_3)Cp$ to $Ph_3C^+BF_4^-$ determined from the temperature dependence of the rate constants at five temperatures between −20 and +25 °C are $\Delta H^\ddagger = 4.47 \pm 0.09$ kcal mol^{-1}, $\Delta S^\ddagger = -17.8 \pm 0.3$ cal K^{-1} mol^{-1}, and $\Delta G^\ddagger(298\ K) = 9.78$ kcal mol^{-1}. Extrapolation to −55 °C gives $k = 1.9 \times 10^4$ M^{-1} s^{-1} for hydride transfer from *trans*-$HMo(CO)_2(PCy_3)Cp$; comparison of this rate constant with the upper limit estimated above for *cis*-$HMo(CO)_2(PCy_3)Cp$ indicates that the trans isomer of $HMo(CO)_2(PCy_3)Cp$ is >300 times faster as a hydride donor than the cis isomer. The rate constant reported in Table 1 for *trans*-$HMo(CO)_2(PMe_3)Cp$ at 25 °C was extrapolated from an Eyring plot of the temperature dependence of the rate constants

---

[11] See the supporting information for experimental details.

[12] For thorough studies of the kinetics of hydride transfer from a series of hydrosilanes to carbenium ions, see: Mayr, H.; Basso, N.; Hagen, G. *J. Am. Chem. Soc.* **1992**, *114*, 3060−3066. Our value of $k(HSiEt_3) = 1.5 \times 10^2$ M^{-1} s^{-1} may be compared with a previously reported[13] value of 1.1×10^2 M^{-1} s^{-1} under the same conditions.

[13] Chojnowski, J.; Fortuniak, W.; Stańczyk, W. *J. Am. Chem. Soc.* **1987**, *109*, 7776−7781.

[14] Kursanov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633−651.

[15] Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711−6717 (as modified in: *J. Am. Chem. Soc.* **1990**, *112*, 2843).

[16] Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852−5860.

[17] Kalck, P.; Pince, R.; Poilblanc, R.; Roussel, J. *J. Organomet. Chem.* **1970**, *24*, 445−452.

[18] A cis:trans ratio of 89:11 was measured by NMR for $HMo(CO)_2(PCy_3)Cp$ over the temperature range of −86 to −45 °C. There appears to be a very small temperature dependence of K_{eq}, since a ratio of 91:9 was estimated at 22 °C based on the observed J_{PH} coupling constant.[16] The temperature dependence of the equilibrium constant (K_{eq} = [cis]/[trans]) was measured for $HMo(CO)_2(PMe_3)Cp$ over the range −86 to −1 °C; $\Delta H^\circ = 0.34 \pm 0.02$ kcal mol^{-1}, $\Delta S^\circ = 1.4 \pm 0.1$ cal K^{-1} mol^{-1}, and $K_{eq}(298\ K) = 1.15$ (46% trans). Similar measurements for $HMo(CO)_2(PPh_3)Cp$ between −86 and −24 °C gave $\Delta H^\circ = 0.29 \pm 0.04$ kcal mol^{-1}, $\Delta S^\circ = 1.9 \pm 0.2$ cal K^{-1} mol^{-1}, and $K_{eq}(298\ K) = 1.62$ (38% trans).

[19] Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618−2626.

[20] Smith, K.-T.; Tilset, M. *J. Organomet. Chem.* **1992**, *431*, 55−64.

[21] In contrast to these similarities for the hydride transfer step, significant differences may exist in the kinetics of capture of the organometallic intermediates, leading to $Cp(CO)_2(PPh_3)MoFBF_3$ in CH_2Cl_2, compared to formation of $[(MeCN)Mo(CO)_2(PPh_3)Cp]^+BF_4^-$ in MeCN. NMR experiments indicated that *trans*-$Cp(CO)_2(PPh_3)MoFBF_3$ was the kinetic product resulting from hydride abstraction from $HMo(CO)_2(PPh_3)Cp$ at −78 °C; isomerization to *cis*-$Cp(CO)_2(PPh_3)MoFBF_3$ is ~95% complete within 1 h at −7 °C. Additional data and further discussion will be given in a full account of this work.

determined at four temperatures between −55 and −25 °C ($\Delta H^{\ddagger} = 2.95 \pm 0.01$ kcal mol^{-1}, $\Delta S^{\ddagger} = -18.1 \pm 0.1$ cal K^{-1} mol^{-1}, and $\Delta G^{\ddagger}$(298 K) = 8.36 kcal mol^{-1}).

While these reactions clearly involve overall hydride (H^-) transfer, the detailed mechanism might involve initial oxidation of the hydride by Ph_3C^+, followed by hydrogen atom transfer from the resultant radical cation of the metal hydride, as opposed to a single-step hydride transfer mechanism. Analogous questions have received intensive scrutiny in the context of hydride transfers related to NAD$^+$ models.[22] On the basis of electrochemical data, however, oxidation of $HMo(CO)_3Cp$ by Ph_3C^+ appears unlikely, since it is thermodynamically unfavorable by about 0.9 V ($\Delta G^{\circ} \approx 21$ kcal mol^{-1}).[19,23,24] Kinetic isotope effects ($k_{MH}/k_{MD} = 1.7-1.8$) found for some hydride/deuteride pairs are large enough to argue against rate-determining electron transfer. We interpret the data to indicate single-step hydride transfer.

A comprehensive understanding of the factors governing the kinetic hydricity of metal hydrides will require further study, but the data reported here provide some preliminary insights on the steric and electronic factors influencing the propensity of metal hydrides to function as hydride donors. Even in the absence of precise structural data on the octahedral $HMn(CO)_4(PPh_3)$ vs the four-legged piano stool geometry of the $HMo(CO)_2(PR_3)Cp$ compounds, some useful comparisons can be made. For the *trans*-$HMo(CO)_2(PR_3)Cp$ compounds, which probably have trans P−M−H angles >100°, the added steric bulk due to the phosphine has a relatively small effect on the hydride transfer kinetics. The threshold P−M−H angle below which steric effects have a substantial effect on the kinetics (steric hindrance from the PR_3 ligand offsetting the enhanced hydricity due to the electronic effect of the phosphine) is apparently reached by the time the P−M−H angles decrease to ~90° in the *cis*-$HM(CO)_4(PPh_3)$ complexes. This interpretation is congruent with the low reactivity of the *cis*-$HMo(CO)_2(PR_3)Cp$ complexes, since the expected P−M−H angles of ~80° or less in these cis isomers would entail substantial steric interference upon approach of Ph_3C^+.

Since data on the kinetics of proton transfer[3,6] and hydrogen atom transfer[4,7,8] reactions of several of the hydrides in Table 1 are already available for comparison, this series of metal carbonyl hydrides emerges as a group for which kinetic data are now available for all three modes of formal M−H bond cleavage (hydride, proton, and hydrogen atom).

Acknowledgment. This research was carried out at Brookhaven National Laboratory under Contract No. DE-AC02-76CH00016 with the U.S. Department of Energy and was supported by its Divison of Chemical Sciences, Office of Basic Energy Sciences. We thank Drs. Bruce Brunschwig, Mark Andrews, Carol Creutz, and Jerry Cook for helpful discussions.

Supporting Information Available: Text and figures giving details of the kinetics data and spectroscopic characterization of $M^+BF_4^-$ products (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

OM950513S

---

(22) For a review, see: Bunting, J. W. *Bioorg. Chem.* **1991**, *19*, 456−491. For recent results on hydride transfer from a ruthenium hydride to NAD$^+$ model compounds, see: Hembre, R. T.; McQueen, S. *J. Am. Chem. Soc.* **1994**, *116*, 2141−2142.

(23) The $E_{1/2}$ value for reduction of $Ph_3C^+ClO_4^-$ in MeCN was found from polarography[24] to be +0.27 V vs. SCE. Conversion of this value to a Cp_2Fe/Cp_2Fe^+ reference gives $E_{1/2} \approx -0.08$ V. The peak potential for oxidation of $HMo(CO)_3Cp$[19] is +0.800 V vs Cp_2Fe/Cp_2Fe^+, leading to an estimate of $\Delta E_0 \approx -0.88$ V for oxidation of $HMo(CO)_3Cp$ by Ph_3C^+ in MeCN.

(24) Volz, H.; Lotsch, W. *Tetrahedron Lett.* **1969**, *27*, 2275−2278.