Hydride Transfer Reactions of Transition Metal Hydrides: Kinetic Hydricity of Metal Carbonyl Hydrides

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Abstract: Hydride transfer from neutral transition metal hydrides (MH) to $Ph_3C^+BF_4^-$ gives M-FBF$_3$ and Ph_3CH. The rate law $-d[Ph_3C^+BF_4^-]/dt = k[Ph_3C^+BF_4^-][MH]$ was established from kinetic measurements using stopped-flow methods. Second-order rate constants determined in CH_2Cl_2 solution at 25 °C range from $k_{H^-} = 7.2 \times 10^{-1}$ M^{-1} s^{-1} to $k_{H^-} = 4.6 \times 10^{6}$ M^{-1} s^{-1}. The order of increasing kinetic hydricity is $(C_5H_4CO_2Me)(CO)_3WH$ < $(CO)_5MnH$ < $Cp^*(CO)_3CrH$ < $Cp(CO)_3WH$ < $HSiEt_3$ < *cis*-$(CO)_4(PCy_3)MnH$ < *cis*-$(CO)_4(PPh_3)MnH$ < $(C_5H_4Me)(CO)_3WH$ < $Cp(CO)_3MoH$ < $Cp^*(CO)_3WH$ < (indenyl)$(CO)_3WH$ < $(CO)_5ReH$ < $Cp^*(CO)_3MoH$ < *cis*-$(CO)_4(PPh_3)ReH$ < $Cp(NO)_2WH$ < *trans*-$Cp(CO)_2(PCy_3)MoH$ < *trans*-$Cp(CO)_2(PPh_3)MoH$ < *trans*-$Cp(CO)_2(PMe_3)MoH$ (Cp = η^5-C_5H_5, Cp* = η^5-C_5Me_5, Cy = cyclohexyl). Ranges of activation parameters for hydride transfer from *trans*-$Cp(CO)_2(PMe_3)MoH$, *trans*-$Cp(CO)_2(PCy_3)MoH$, *cis*-$(CO)_4(PPh_3)ReH$, and $Cp^*(CO)_3MoH$ are $\Delta H^\ddagger = 3.0-5.9$ kcal mol^{-1} and $\Delta S^\ddagger = -18$ to -24 cal K^{-1} mol^{-1}. The rate constant for hydride transfer (k_{H^-}) from *cis*-$Cp(CO)_2(PCy_3)MoH$ at −55 °C is 3 orders of magnitude lower than that for *trans*-$Cp(CO)_2(PCy_3)MoH$. Phosphine substitution for CO generally enhances the kinetic hydricity, with *trans*-$Cp(CO)_2(PMe_3)MoH$ being 10^4 times as reactive as $Cp(CO)_3MoH$. The electronic effect of phosphine substitution is attenuated by steric factors when the phosphine is cis to the metal hydride. The hydride transfer kinetics reported here are interpreted to be single-step hydride transfers, rather than a multiple-step mechanism involving an initial electron transfer followed by hydrogen atom transfer. A distinction is made between hydricity and nucleophilicity of metal hydrides.

Introduction

Many homogeneous catalytic processes[1] rely on transition metal hydrides. Large-scale industrial reactions such as olefin hydroformlyation, hydrocyanation, and hydrogenation all involve metal hydrides, often in more than one step of the catalytic cycle. In most cases the metal hydrides are regenerated in catalytic reactions by reaction with H_2. Transition metal hydrides are also valuable stoichiometric reagents for organic synthetic reactions. Development of a better understanding of the details of how the hydride ligand is delivered to an organic substrate is a fundamentally important goal pertinent to a wide range of catalytic reactions. The results of kinetic and mechanistic studies interrogating processes of M−H bond cleavage can provide guidance in the rational design of new catalytic reactions.

The relevance of hydride transfers from metal hydrides to bio-inorganic chemistry has also been documented. Hembre and McQueen have recently demonstrated Ru-catalyzed hydride transfers to NAD$^+$ model compounds that are relevant to hydrogenase enzymes.[2] In bio-organic chemistry related to nicotinamide coenzymes, many kinetics studies have examined hydride transfers from substituted dihydropyridines to pyridinium (and related heteroaromatic cations).[3]

Main-group metal hydrides such as $LiAlH_4$ and $NaBH_4$ are immensely useful for reduction of several types of organic functional groups. Some transition metal hydrides exhibit hydridic reactivity akin to that of main-group hydrides. Labinger and Komadina reported[4] qualitative rates of reduction of ketones by a series of metallocene hydrides; presumably, the ketone coordinates with the metal prior to hydride transfer in some or all of these cases. From studies of the relative reactivity of these metal hydrides with acetone and with $(CF_3)(CH_3)C{=}O$, Labinger and Komadina determined that the relative order of hydridic character was $[Cp_2ZrH_2]_n > Cp_2NbH_3 > Cp_2MoH_2 > Cp_2ReH$ (Cp = η^5-C_5H_5). An important conclusion drawn from their work is that the hydridic character is highest for metals to the left of the transition metal series, and falls off substantially on moving to the right of the periodic table.

Anionic metal carbonyl hydrides exhibit pronounced hydridic reactivity.[5] Darensbourg and co-workers have carried out detailed investigations on the reactions of $(CO)_5WH^-$ and a series of related anionic metal hydrides, and have demonstrated the utility of these metal hydrides in the reduction of alkyl halides,[6] acyl chlorides,[7] aldehydes[8] and ketones.[8]

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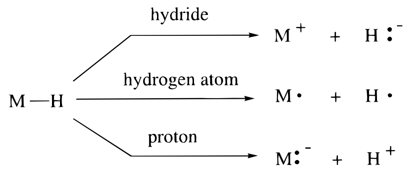
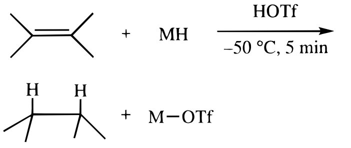
10.1021/ja9820036 CCC: $15.00

Scheme 1



Neutral metal carbonyl hydrides exhibit diverse modes of reactivity. As shown in Scheme 1, formal cleavage of the M−H bond can generate a hydride, a hydrogen atom, or a proton. Some neutral metal carbonyl hydrides (e.g., $CpW(CO)_3H$) can undergo each of these three formal modes of M−H bond rupture, in reactions with different substrates.[9] Detailed information is available on the kinetic and thermodynamic acidity of these neutral metal hydrides.[10] Relative rates of hydrogen atom transfer from metal hydrides are known for their exothermic reaction with carbon-centered radicals[11,12] and for their endothermic reaction with a substituted styrene.[11] There is thus far more quantitative kinetic information available on proton transfer and hydrogen atom transfer reactions of neutral metal carbonyl hydrides than on their hydride transfer reactions.

In this laboratory, we have shown that hydride transfer reactions of neutral metal hydrides constitute the product-forming step of ionic hydrogenations.[13] For example, ionic hydrogenation of tetramethylethylene by CF_3SO_3H and $CpW(CO)_3H$ is shown in eq 1; the mechanism involves hydride transfer from the metal to the carbenium ion formed through protonation of the olefin. Although several metal hydrides [$Cp(CO)_3WH$, $Cp^*(CO)_3WH$, $Cp(CO)_3MoH$, $(CO)_5MnH$, $(CO)_5ReH$, and $Cp^*(CO)_2OsH$; $Cp^* = \eta^5\text{-}C_5Me_5$] can be used as hydride donors in these ionic hydrogenations of olefins, this system was not suitable for a detailed evaluation of kinetic hydricity, in part because of complications from competing protonation of the metal hydride by acid.[14] Although the importance of hydride transfers from metal hydrides is clear, "the factors controlling the hydricity are far from being well-understood."[15] This paper reports a study of the kinetics of hydride transfer from a series of metal hydrides to Ph_3C^+, in an effort to evaluate the factors influencing kinetic hydricity.[16]



(1)

Results

Formation of $M{-}FBF_3$ by Hydride Transfer from MH to $Ph_3C^+BF_4^-$. Hydride transfer from metal hydrides to $Ph_3C^+BF_4^-$ proceeds as shown in eq 2, producing Ph_3CH as the organic product. Formal removal of H^- from an 18-electron metal hydride would produce a 16-electron metal cation M^+; the actual isolated product contains coordinated BF_4^-. Several of the $M\text{-}FBF_3$ complexes produced in our kinetics studies have been previously synthesized and characterized. Particularly notable is the pioneering work by Beck in synthesis and characterization of a series of $M\text{-}FBF_3$ and related complexes.[17] Each of the $M\text{-}FBF_3$ complexes produced in the kinetic studies in this paper were prepared and characterized to verify the identity of the products and to establish that the reactions were suitable for kinetic studies.

$$Ph_3C^+\,BF_4^- + MH \xrightarrow{k_{H^-}} Ph_3C{-}H + M{-}F{-}BF_3 \qquad (2)$$

Products other than $M\text{-}FBF_3$ were observed for only three hydride donors reported here: $Cp^*Cr(CO)_3H$, $Cp(NO)_2WH$, and $HSiEt_3$. Hydride transfer from $Cp^*Cr(CO)_3H$ to $Ph_3C^+BF_4^-$ gave one equivalent of Ph_3CH, as shown by NMR, but the organometallic product was not identified. The presumed initial organometallic product, $Cp^*(CO)_3CrFBF_3$, was not observed. Apparently the hydride transfer reaction occurs cleanly, but the initial product, $Cp^*(CO)_3CrFBF_3$, is thermally unstable. This is corroborated by earlier work,[18] which had shown that a thermally stable derivative, $[Cp^*Cr(CO)_3P(OMe)_3]^+BF_4^-$, could be prepared by reaction of $Cp^*Cr(CO)_3H$ with $Ph_3C^+BF_4^-$ at low temperature, followed by addition of $P(OMe)_3$. The Cr complex $CpCr(CO)_3(NCMe)^+BF_4^-$ was also found to be unstable in CH_2Cl_2 solution,[19] so the lower thermal stability of Cr complexes of this type, compared with that of analogous Mo and W compounds, appears to have some generality. Hydride transfer from $Cp(NO)_2WH$ to $Ph_3C^+BF_4^-$ produced $\{[CpW(NO)_2]_2(\mu\text{-}H)\}^+BF_4^-$. This bimetallic hydride complex was previously prepared[20] by reaction of $Ph_3C^+BF_4^-$ with two equivalents of $Cp(NO)_2WH$. Similar hydride-bridged bimetallic complexes, $[M(\mu\text{-}H)M]^+$, are formed from other combinations of MH + $M\text{-}FBF_3$. For example, Beck and Schloter prepared $\{[CpW(CO)_3]_2(\mu\text{-}H)\}^+BF_4^-$ from reaction of $CpW(CO)_3H$ with $CpW(CO)_3FBF_3$,[21] but under the conditions of our kinetics experiments, the product was $CpW(CO)_3FBF_3$. Reaction of the main group hydride donor $HSiEt_3$ with $Ph_3C^+BF_4^-$ produced $FSiEt_3$, which is in agreement with an earlier report.[22]

Kinetic Measurements of Hydride Transfer. The kinetics of hydride transfer (eq 2) were determined in CH_2Cl_2 solution by measuring the rate of disappearance of absorbance of $Ph_3C^+BF_4^-$ at 450 nm ($\epsilon = 2.5 \times 10^4$ M^{-1} cm^{-1}). The absorbance at 450 nm is at the shoulder of an absorption band for $Ph_3C^+BF_4^-$, $\lambda_{max} = 410$ and 430 nm, $\epsilon = 3.2 \times 10^4$ M^{-1} cm^{-1}. Most of the kinetics were carried out by stopped-flow techniques, but conventional UV-vis spectrophotometry was used for monitoring the slowest reactions. These experiments were carried out by using an excess of metal hydride, with $[MH]_0$ typically 10−100 times greater than $[Ph_3C^+BF_4^-]_0$. Since Ph_3C^+ reacts rapidly with water, we initially questioned whether the solvent could be dried sufficiently to permit handling of low concentrations of Ph_3C^+. Fortunately, by using CH_2Cl_2 distilled from P_2O_5 and handled in a drybox, initial concentra-

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

metal hydride	k_{H^-} (M^{-1} s^{-1})[a]
$(C_5H_4CO_2Me)(CO)_3WH$	7.2×10^{-1}
$(CO)_5MnH$	5.0×10^1
$Cp^*(CO)_3CrH$	5.7×10^1
$Cp(CO)_3WH$	7.6×10^1
$HSiEt_3$	1.5×10^2
cis-$(CO)_4(PCy_3)MnH$	1.7×10^2
cis-$(CO)_4(PPh_3)MnH$	2.3×10^2
$(C_5H_4Me)(CO)_3WH$	2.5×10^2
$Cp(CO)_3MoH$	3.8×10^2
$Cp^*(CO)_3WH$	1.9×10^3
$(Indenyl)(CO)_3WH$	2.0×10^3
$(CO)_5ReH$	2.0×10^3
$Cp^*(CO)_3MoH$	6.5×10^3
cis-$(CO)_4(PPh_3)ReH$	1.2×10^4
$Cp(NO)_2WH$	1.9×10^4
trans-$Cp(CO)_2(PCy_3)MoH$	4.3×10^5
trans-$Cp(CO)_2(PPh_3)MoH$	5.7×10^5
trans-$Cp(CO)_2(PMe_3)MoH$	4.6×10^6

[a] $<\pm 10\%$ estimated uncertainty for rate constants.

tions of $[Ph_3C^+BF_4^-]_0$ in the range of 0.05 mM could be used. Attempts to use CH_3CN solvent were thwarted by our inability to dry it sufficiently to permit handling of CH_3CN solutions of $[Ph_3C^+BF_4^-]$ at low concentrations. NMR experiments in CD_3CN were feasible, however, since higher concentrations of $Ph_3C^+BF_4^-$ were used.

A typical plot of the absorbance vs time for a stopped-flow experiment is provided in the supporting information (Figure S1). Plots of $\ln(A_t - A_\infty)$ vs time are linear, in some cases for >8 half-lives, indicating remarkably clean pseudo-first-order reactions (see Figure S2 in the supporting information). The observed rate constants (k_{obs}) were obtained from nonlinear least squares fitting of A_t to $\Delta A \exp(-k_{obs}t) + A_\infty$, where $\Delta A = A_0 - A_\infty$. Plots of k_{obs} vs [MH] are also linear (see Figures S3−S8 in the supporting information). These data establish the second-order rate law: $-d[Ph_3C^+BF_4^-]/dt = k[Ph_3C^+BF_4^-][MH]$. Table 1 gives the second-order rate constants determined for a series of metal hydrides; the hydrides are listed in order of increasing hydricity. A kinetic isotope effect ($k_{MoH}/k_{MoD} = 1.8$; Figure S7 in the supporting information) was determined by comparing the rate constant for reaction of the metal hydride $Cp(CO)_3MoH$ with that for the metal deuteride $Cp(CO)_3MoD$.[23]

In contrast to the large number of metal carbonyl hydrides with cyclopentadienyl ligands, the examples of metal carbonyl hydrides with arene ligands are far fewer. The manganese hydride $(\eta^6\text{-}C_6Me_6)(CO)_2MnH$ was prepared by Eyman and coworkers.[24] Unfortunately, we found that $(\eta^6\text{-}C_6Me_6)(CO)_2MnH$ decomposed slowly (~10% in 1 h) in CH_2Cl_2 to give free C_6Me_6 and unidentified organometallic decomposition products. Hydride transfer from $(\eta^6\text{-}C_6Me_6)(CO)_2MnH$ to $Ph_3C^+BF_4^-$ does occur cleanly in CD_3CN solution, giving $[(\eta^6\text{-}C_6Me_6)(CO)_2Mn(CH_3CN)]^+BF_4^-$. A competition experiment was carried out in which $(\eta^6\text{-}C_6Me_6)(CO)_2MnH$ and $Cp^*(CO)_3WH$ competed as hydride donors to $Ph_3C^+BF_4^-$ in CD_3CN at room temperature. From the ratio of the resulting $[(\eta^6\text{-}C_6Me_6)(CO)_2Mn(CH_3CN)]^+BF_4^-$ and $[Cp^*(CO)_3W(CH_3CN)]^+BF_4^-$ observed by NMR, the relative kinetics of hydride transfer were ~4 times as fast for $(\eta^6\text{-}C_6Me_6)(CO)_2MnH$ as for $Cp^*(CO)_3WH$.

The temperature dependence of the second-order rate constants was determined for *trans*-$Cp(CO)_2(PMe_3)MoH$, *trans*-$Cp(CO)_2(PCy_3)MoH$ (Cy = cyclohexyl, C_6H_{11}), *cis*-$(CO)_4(PPh_3)ReH$, and $Cp^*(CO)_3MoH$; activation parameters are listed in Table 2. Figure 1 shows plots of k_{obs} vs $[Cp^*(CO)_3MoH]$ for data at −20, −10, 0, 10, and 25 °C. Eyring plots of $\ln(k/T)$ vs $1/T$ are shown for *trans*-$Cp(CO)_2(PCy_3)MoH$ and *cis*-$(CO)_4(PPh_3)ReH$ in Figure 2. All of these reactions have low $\Delta H^\ddagger$ values, ranging from 3 to 6 kcal mol^{-1}. The corresponding entropies of activation (−18 to −24 cal K^{-1} mol^{-1}) are in the range expected for bimolecular reactions.

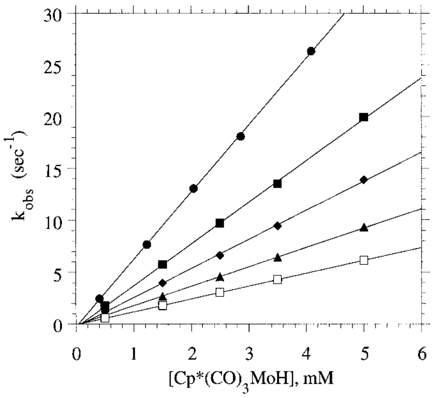

Figure 1. Plots of k_{obs} vs $[Cp^*(CO)_3MoH]$ for data at −20 °C (□), −10 °C (▲), 0 °C (◆), 10 °C (■), and 25 °C (●).

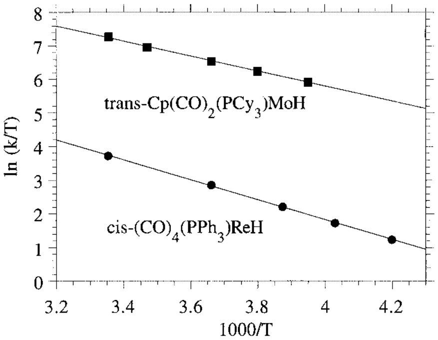

Figure 2. Eyring plots for hydride transfer from *trans*-$Cp(CO)_2(PCy_3)MoH$ (−20 to 25 °C) and *cis*-$(CO)_4(PPh_3)ReH$ (−35 to 25 °C).

Cis−Trans Interconversion of $Cp(CO)_2(PR_3)MoH$, and Kinetic Hydricity of the Cis vs Trans Isomers. The phosphine-substituted molybdenum compounds $Cp(CO)_2(PR_3)MoH$ have a "four-legged piano stool" structure and are known to exist as an interconverting mixture of cis and trans isomers;[25] $K_{eq} = k_{TC}/k_{CT}$ (eq 3). Measurements on the kinetics and thermodynamics of cis ⇌ trans interconversion of the phosphine-substituted complexes $Cp(CO)_2(PR_3)MoH$ (R = Me, Ph, Cy) were required to interpret our kinetics data completely. The hydride and Cp resonances of the cis and trans isomers of $Cp(CO)_2(PCy_3)MoH$ are readily distinguished by ^1H NMR at low temperatures. In CD_2Cl_2 at −86 °C, the hydride resonance for the cis isomer appears at δ −6.25 and has a much larger J_{PH} (60 Hz) than that found for the trans isomer (20 Hz) at δ −6.96.

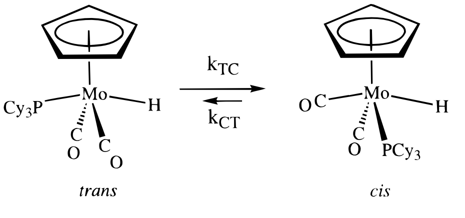

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Table 2. Activation Parameters for Hydride Transfer from Metal Hydrides to $Ph_3C^+BF_4^-$ in CH_2Cl_2

metal hydride	$\Delta H^‡$ (kcal mol^{-1})	$\Delta S^‡$ (cal K^{-1} mol^{-1})	$\Delta G^‡$ (298 K) (kcal mol^{-1})	temp range (°C)
trans-$Cp(CO)_2(PMe_3)MoH$	3.0 ± 0.1	-18 ± 1	8.4	-55 to -25
trans-$Cp(CO)_2(PCy_3)MoH$	4.5 ± 0.1	-18 ± 1	9.8	-20 to $+25$
cis-$(CO)_4(PPh_3)ReH$	5.9 ± 0.1	-20 ± 1	11.9	-35 to $+25$
$Cp^*(CO)_3MoH$	5.0 ± 0.1	-24 ± 1	12.2	-20 to $+25$

The equilibrium constant (K_{eq} = [cis]/[trans]; eq 3) for $Cp(CO)_2(PCy_3)MoH$ exhibits a very small temperature dependence. A value of $K_{eq} = 8.1$ (89% cis, 11% trans) was measured directly by NMR at −86 °C. An almost identical value (91% cis, 9% trans) was determined[25] from the averaged J_{PH} at 22 °C; the cis and trans isomers are in the fast-exchange regime at this temperature. For the PMe_3 complex $Cp(CO)_2(PMe_3)MoH$, the measured values ranged from $K_{eq} = 0.81$ at −86 °C to $K_{eq} = 1.1$ at −1 °C. A van't Hoff plot of ln K_{eq} vs $1/T$ for data collected at eight temperatures over this range provided the thermodynamic parameters $\Delta H° = 0.34 \pm 0.02$ kcal mol^{-1} and $\Delta S° = 1.4 \pm 0.1$ cal K^{-1} mol^{-1}; extrapolation to 25 °C gave $K_{eq} = 1.15$ (54% cis; 46% trans). Similar values ($\Delta H° = 0.435 \pm 0.005$ kcal mol^{-1} and $\Delta S° = 1.84 \pm 0.02$ cal K^{-1} mol^{-1}) were previously reported[26] for $Cp(CO)_2(PMe_3)MoH$ in toluene solvent. For the PPh_3 complex $Cp(CO)_2(PPh_3)MoH$ in CD_2Cl_2, we determined thermodynamic parameters of $\Delta H° = 0.34 \pm 0.01$ kcal mol^{-1} and $\Delta S° = 2.1 \pm 0.1$ cal K^{-1} mol^{-1} from measurements of K_{eq} at five temperatures between −86 and −24 °C. The extrapolated $K_{eq} = 1.7$ at 25 °C for our measurements in CD_2Cl_2 is the same as the $K_{eq} = 1.7$ reported by Faller and Anderson[25] for $Cp(CO)_2(PPh_3)MoH$ in $CDCl_3$.

Although separate resonances for the cis and trans isomers are well-resolved at low temperatures, line-broadening occurs at higher temperatures because of interconversion of the cis and trans isomers. Experimentally measured ^1H NMR line-broadening data for $Cp(CO)_2(PCy_3)MoH$ at eight temperatures over the range of −45 to 27 °C were analyzed by using a simulation program to determine the rate constants ($k_{obs} = k_{TC} + k_{CT}$) for cis $\rightleftharpoons$ trans interconversion. An Eyring plot is shown in the supporting information (Figure S9); the activation parameters for k_{CT} derived from these data are $\Delta H^‡ = 11.6 \pm 0.3$ kcal mol^{-1} and $\Delta S^‡ = -5.6 \pm 1.2$ cal K^{-1} mol^{-1}.

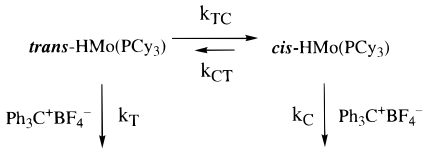
Since the hydride transfer reaction involves conversion of ionic $Ph_3C^+BF_4^-$ and neutral MH to neutral Ph_3CH and neutral $M\text{-}FBF_3$, the ionic strength of the medium changes during the hydride transfer reaction. To assess the effect of ionic strength, we also determined the kinetics of cis $\rightleftharpoons$ trans interconversion of $Cp(CO)_2(PCy_3)MoH$ in CD_2Cl_2 in the presence of added $NBu_4^+BF_4^-$ (0.11 M). Activation parameters determined for k_{CT} from measurements at six temperatures between −35 and 27 °C were $\Delta H^‡ = 13.8 \pm 0.2$ kcal mol^{-1} and $\Delta S^‡ = 1.9 \pm 0.7$ cal K^{-1} mol^{-1}. The ionic strength (0.11 M) used in this isomerization experiment is much higher than that used in any of the hydride transfer kinetics experiments, which were carried out at 13.5 mM for experiments with excess [Ph_3C^+].

The metal hydride $Cp(CO)_2(PCy_3)MoH$ is a new complex prepared in this work, but several closely related Mo and W compounds were reported previously. Faller and Anderson reported a thorough study of the kinetics of cis $\rightleftharpoons$ trans isomerizations of a series of $Cp(CO)_2(PR_3)MoX$ complexes, where X = H, halide, or alkyl.[25] For cis → trans isomerization of $Cp(CO)_2(P^nBu_3)MoH$ in $CDCl_3$, they reported $\Delta H^‡ = 11.7 \pm 0.1$ kcal mol^{-1} and $\Delta S^‡ = -7.3 \pm 0.4$ cal K^{-1} mol^{-1}. Similar values were found by Poilblanc and co-workers[26] for the cis → trans isomerization of $Cp(CO)_2(PMe_3)MoH$ in toluene-d_8: $\Delta H^‡ = 12.19 \pm 0.07$ kcal mol^{-1} and $\Delta S^‡ = -6.60 \pm 0.25$ cal K^{-1} mol^{-1}.

Since both cis and trans isomers are present in solution as an interconverting mixture, a question arises about the relative rates of hydride transfer from the two isomers. Tilset and co-workers previously reported[19] that hydride transfer from $Cp(CO)_2(PMe_3)WH$ to $Ph_2(p\text{-}MeOC_6H_4)C^+BF_4^-$ in CH_3CN gave $[Cp(CO)_2(PMe_3)W(NCCH_3)]^+BF_4^-$ as a 90:10 mixture of trans:cis isomers. Isomerization of this mixture to the thermodynamic isomer ratio of 5:95 trans:cis was very slow ($t_{1/2} \approx 40$ h).[19] These authors suggested that the predominance of the trans isomer as the kinetic product resulted from a selective reaction of the trans hydride isomer with the substituted trityl cation. Closely related experiments[27] with the Mo hydride $Cp(CO)_2(PPh_3)MoH$ similarly gave a predominance of the trans isomer of $[Cp(CO)_2(PPh_3)Mo(NCCH_3)]^+$. Since these results suggested a higher reactivity of the trans isomers of phosphine-substituted metal hydrides of this type, we decided to study the kinetics of the reaction of $Cp(CO)_2(PCy_3)MoH$ with $Ph_3C^+BF_4^-$. This hydride was selected for detailed examination since its cis isomer predominates, providing a method of separately determining the rate constants for hydride transfer from both its cis and trans isomers.

We first consider the determination of the rate constant for hydride transfer from the trans isomer, k_T, as shown in the mechanism in Scheme 2. Experiments with a sufficient excess of metal hydride ([MH] ≫ [Ph_3C^+]) were carried out with enough of the trans isomer present to completely consume the Ph_3C^+. Under these conditions, with $k_{TC} \gg k_T [Ph_3C^+]$ (i.e., the cis/trans equilibration is much faster than hydride transfer), the observed rate constant is given by eq 4. (A more detailed explanation is provided in the *Appendix*.) Thus k_T is readily determined from experiments with excess [MH] since [*trans*-MH] is known. As indicated in Table 1, rate constants k_T were determined in this manner for all three of the phosphine-substituted metal hydrides $Cp(CO)_2(PR_3)MoH$ (R = Me, Ph, Cy).

Scheme 2



$$k_{obs} = k_T[\textit{trans}\text{-MH}] \tag{4}$$

The hydride transfer reactions have low values of $\Delta H^‡$ (Table 2) so the rate constants for hydride transfer are only weakly temperature-dependent. In contrast, the rate constants for cis $\rightleftharpoons$ trans isomerization of $Cp(CO)_2(PCy_3)MoH$ exhibit a much larger temperature dependence, so the isomerization rate slows down more with decreasing temperature than does the hydride transfer rate. Thus experiments using an excess of [Ph_3C^+] were

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

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

carried out to determine the kinetic hydricity of *cis*-$Cp(CO)_2(PCy_3)MoH$. The kinetics were followed by measuring the rate of appearance of the absorbance from $Cp(CO)_2(PCy_3)MoFBF_3$ at $\lambda_{max} = 516$ nm ($\epsilon = 6.6 \times 10^2$ M^{-1} cm^{-1}). The effect of ionic strength on the rate of hydride transfer was investigated by measuring the kinetics of reaction of excess $[Ph_3C^+BF_4^-]$ (4.5 mM) with $Cp(CO)_2(PCy_3)MoH$ (0.6 mM). At 15 °C, $k_{obs} = 65$ s^{-1}. This observed rate constant decreased with increasing ionic strength (added $[NBu_4^+BF_4^-] = 5$, 10, and 16 mM), but the changes were small, being only 12% lower (58 s^{-1}) with 16 mM $[NBu_4^+BF_4^-]$.

Stopped-flow measurements at various temperatures were carried out in CH_2Cl_2 solution for reaction of $Cp(CO)_2(PCy_3)MoH$ (0.2 mM) with excess $[Ph_3C^+BF_4^-]$ (2−13 mM). The ionic strength was held constant at 13.5 mM $[BF_4^-]$ by addition of appropriate amounts of $[NBu_4^+BF_4^-]$. Only a small amount (11%) of the trans isomer is initially present. A steady-state approximation for *trans*-$Cp(CO)_2(PCy_3)MoH$ in the mechanism shown in Scheme 2 leads to the rate expressions shown in eqs 5 and 6 for these experiments that use excess $[Ph_3C^+]$. (See the *Appendix* for further details).

$$\frac{d[\text{product}]}{dt} = k_{obs}\,[\textit{cis}\text{-MH}] \qquad (5)$$

$$\text{where } k_{obs} = \left(\frac{k_{CT}k_T}{k_{TC} + k_T[Ph_3C^+]} + k_C\right)[Ph_3C^+] \qquad (6)$$

The isomerization rate constants k_{TC} and k_{CT} were independently determined by NMR as indicated earlier. By using these values, along with the values of k_T obtained as described above, the kinetics data for experiments reacting excess $Ph_3C^+BF_4^-$ with $Cp(CO)_2(PCy_3)MoH$ at constant ionic strength can be fit to eq 6 to estimate a value for k_C.[28] Figure 3 shows a fitting of the data determined at −55 °C; from this line-fitting, we determined $k_C = 19$ M^{-1} s^{-1}. For comparison, $k_T = 1.9 \times 10^4$ M^{-1} s^{-1} at −55 °C (at −55 °C, $k_{TC} = 5.4$ s^{-1}, $k_{CT} = 0.60$ s^{-1}). Thus the rate constant for hydride transfer from *cis*-$Cp(CO)_2(PCy_3)MoH$ is about a thousand times less than that for hydride transfer from *trans*-$Cp(CO)_2(PCy_3)MoH$. At the higher temperatures, where $k_C \ll (k_{CT}\ k_T)/(k_{TC} + k_T[Ph_3C^+])$, then eq 6 simplifies to eq 7

$$k_{obs} = \left(\frac{k_{CT}k_T}{k_{TC} + k_T[Ph_3C^+]}\right)[Ph_3C^+] \qquad (7)$$

for these experiments with $[Ph_3C^+] \gg [MH]$.

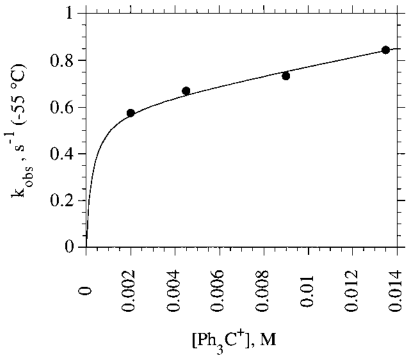

Figure 3. Plot of k_{obs} vs excess $[Ph_3C^+BF_4^-]$ for hydride transfer from $Cp(CO)_2(PCy_3)MoH$ at −55 °C with 13.5 mM $[BF_4^-]$. The curve shows the fitting of the data to eq 6.

Rearrangement of eq 7 gives eq 8.

$$\frac{1}{k_{obs}} = \frac{k_{TC}}{k_{CT}k_T[Ph_3C^+]} + \frac{1}{k_{CT}} \qquad (8)$$

Figure 4 shows a plot of $1/k_{obs}$ vs $1/[Ph_3C^+]$ at temperatures of −35, −15, and 15 °C. According to eq 8, the slope of this plot is $k_{TC}/(k_{CT}k_T)$ and the intercept is $1/k_{CT}$. At −35 °C the value of k_{CT} determined from this plot is 8.5 s^{-1}, compared with $k_{CT} = 6.2$ s^{-1} determined by NMR. As can be seen in Figure 4, the *y*-intercept is very small at 15 °C, so the value of k_{CT} is not accurately determined at this temperature. The slopes of the lines provide $k_{TC}/(k_{CT}k_T)$ values about twice as large as those determined more directly from NMR and from the stopped-flow experiments using excess $[Cp(CO)_2(PCy_3)MoH]$. One reason for the discrepancy in rate constants may be the differences in ionic strength used for determination of the isomerization rate constants vs that used in determining the hydride transfer rate constants. However, although the agreement of the values determined from Figure 4 and the independent NMR and stopped-flow measurements is not exact, it is close enough to validate the proposed mechanism shown in Scheme 2. These kinetic results therefore provide direct quantitative confirmation of the much higher reactivity of the trans isomer than the cis isomer.

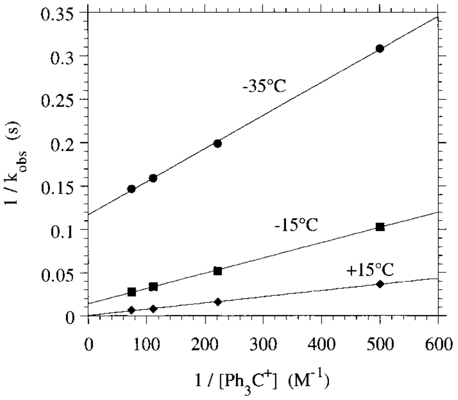

Figure 4. Plot of $1/k_{obs}$ vs $1/[Ph_3C^+BF_4^-]$ for hydride transfer from $Cp(CO)_2(PCy_3)MoH$ at −35°, −15°, and 15 °C (13.5 mM $[BF_4^-]$).

NMR Experiments on the Reaction of $Cp(CO)_2(PR_3)MoH$ with Ph_3C^+. The reactions of the phosphine-substituted molybdenum hydrides with $Ph_3C^+BF_4^-$ were also studied by low-temperature NMR. These NMR experiments are complementary to the detailed kinetic data obtained by stopped-flow studies. Prior studies[25,29] of $Cp(CO)_2(PR_3)MoX$ complexes with "four-legged piano stool" structures established ^1H NMR criteria for distinguishing cis and trans isomers. The ^1H NMR shift of the Cp protons of the trans isomer appears as a doublet ($J \approx 1.9$ Hz), typically 0.2−0.3 ppm upfield of the singlet Cp resonance of isomeric cis complexes. The reaction of $Cp(CO)_2(PPh_3)MoH$ with $Ph_3C^+BF_4^-$ was carried out at −78 °C in CD_2Cl_2, and the NMR tube was immediately inserted into an NMR probe at −80 °C. The predominant product (90%) was *trans*-$Cp(CO)_2(PPh_3)MoFBF_3$, which exhibited a doublet ($J_{PF} = 19.9$ Hz) at δ 66.6 in the ^{31}P NMR, in agreement with an earlier report by Beck

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[28] The value of k_C is most accurately determined at relatively high $[Ph_3C^+]$. In the limit of $k_T[Ph_3C^+] \gg k_{TC}$, eq 6 would simplify to $k_{obs} = k_{CT} + k_C[Ph_3C^+]$; a plot of k_{obs} vs $[Ph_3C^+]$ would give a straight line with a slope of k_C, as can be seen from Figure 3. Alternatively, at low $[Ph_3C^+]$, $k_{TC} \gg k_T[Ph_3C^+]$, and eq 6 would become $k_{obs} = \{(k_{CT}k_T/k_{TC}) + k_C\}[Ph_3C^+]$. Note that since $k_{CT}k_T/k_{TC} \gg k_C$, k_C would be poorly determined.

[29] Kalck, P.; Poilblanc, R. *J. Organomet. Chem.* **1969**, *19*, 115−121.

and co-workers.[30] The minor product (10%) exhibited a singlet in the ^{31}P NMR spectrum and is assigned as [*trans*-Cp(CO)$_2$(PPh$_3$)Mo(ClCD$_2$Cl)]$^+$BF$_4^-$, a complex with a weakly coordinating dichloromethane ligand.[21,31] The sample was slowly warmed in the NMR probe; at −30 °C, 2% of *cis*-Cp(CO)$_2$(PPh$_3$)MoFBF$_3$ had formed by isomerization of the trans isomer. Further warming to −8 °C caused more significant changes: The amount of *cis*-Cp(CO)$_2$(PPh$_3$)MoFBF$_3$ increased to 52% and the *trans*-Cp(CO)$_2$(PPh$_3$)MoFBF$_3$ dropped to 45%. The ^{31}P NMR resonance of each of these isomers was a quintet at −8 °C, indicating "spinning" of the BF$_4^-$ ligand.[30,32] After 1 h at −8 °C, only 5% of *trans*-Cp(CO)$_2$(PPh$_3$)MoFBF$_3$ remained, and the thermodynamically favored product *cis*-Cp(CO)$_2$(PPh$_3$)MoFBF$_3$ had increased to 95%. When the same reaction was carried out at room temperature and the NMR was recorded at either room temperature or at low temperature, *cis*-Cp(CO)$_2$(PPh$_3$)MoFBF$_3$ was the predominant product observed (∼99:1 cis:trans).

The reaction of Cp(CO)$_2$(PPh$_3$)MoH with Ph$_3$C$^+$OTf$^-$ (OTf = OSO$_2$CF$_3$) at 22 °C gave a 90:10 ratio of *trans*-Cp(CO)$_2$(PPh$_3$)MoOTf:*cis*-Cp(CO)$_2$(PPh$_3$)MoOTf. In contrast to the facile isomerization of *trans*-Cp(CO)$_2$(PPh$_3$)MoFBF$_3$ at low temperatures, isomerization of the metal triflate *trans*-Cp(CO)$_2$(PPh$_3$)MoOTf was very slow, requiring days at room temperature. A similar predominance of the trans product was found from the reaction of Cp(CO)$_2$(PPh$_3$)MoH with either Ph$_3$C$^+$BF$_4^-$ or Ph$_3$C$^+$OTf$^-$ at room temperature in CD$_3$CN solvent—the ratio of [*trans*-Cp(CO)$_2$(PPh$_3$)Mo(NCCD$_3$)]$^+$:[*cis*-Cp(CO)$_2$(PPh$_3$)Mo(NCCD$_3$)]$^+$ was 96:4 in both cases. Smith and Tilset[27] studied the kinetics of isomerization of [*trans*-Cp(CO)$_2$(PPh$_3$)Mo(NCCH$_3$)]$^+$ to [*cis*-Cp(CO)$_2$(PPh$_3$)Mo(NCCH$_3$)]$^+$ and found it to be very slow ($\Delta H^\ddagger = 24.2 \pm 0.4$ kcal mol^{-1}; $\Delta S^\ddagger = -3.4 \pm 1.4$ cal K^{-1} mol^{-1}; $t_{1/2} = 44$ h at 30 °C).

When the reaction of the PMe$_3$ complex Cp(CO)$_2$(PMe$_3$)MoH with Ph$_3$C$^+$BF$_4^-$ was observed by NMR at −80 °C, the dichloromethane complex [*trans*-Cp(CO)$_2$(PMe$_3$)Mo(ClCD$_2$Cl)]$^+$BF$_4^-$ made up 26% of the product mixture. About 9% of the mixture was *cis*-Cp(CO)$_2$(PMe$_3$)MoFBF$_3$, with *trans*-Cp(CO)$_2$(PMe$_3$)MoFBF$_3$ being the predominant product, as in the PPh$_3$ case. Incremental warming of the sample showed that conversion of the kinetic products, [*trans*-Cp(CO)$_2$(PMe$_3$)Mo(ClCD$_2$Cl)]$^+$BF$_4^-$ and *trans*-Cp(CO)$_2$(PMe$_3$)MoFBF$_3$, to the thermodynamic product, *cis*-Cp(CO)$_2$(PMe$_3$)MoFBF$_3$, was slower for these PMe$_3$ complexes than for the PPh$_3$ analogues. After 45 min at −10 °C followed by 20 min at 10 °C, the yield of *trans*-Cp(CO)$_2$(PMe$_3$)MoFBF$_3$ had decreased to 31%, the [*trans*-Cp(CO)$_2$(PMe$_3$)Mo(ClCD$_2$Cl)]$^+$BF$_4^-$ had decreased to 5%, and the thermodynamic product *cis*-Cp(CO)$_2$(PMe$_3$)MoFBF$_3$ had increased to 64%. The thermodynamic product mixture is ∼99:1 *cis*-Cp(CO)$_2$(PMe$_3$)MoFBF$_3$:*trans*-Cp(CO)$_2$(PMe$_3$)MoFBF$_3$. The direct NMR observation of transient [*trans*-Cp(CO)$_2$(PR$_3$)Mo(ClCD$_2$Cl)]$^+$BF$_4^-$ (R = Me, Ph) shows that the solvent CD$_2$Cl$_2$ can capture the 16-electron cation [Cp(CO)$_2$(PR$_3$)Mo]$^+$ and temporarily occupy a coordination site until a stronger ligand displaces it.

A strikingly different result was obtained for the reaction of the PCy$_3$ complex Cp(CO)$_2$(PCy$_3$)MoH with Ph$_3$C$^+$BF$_4^-$ at −78 °C in CD$_2$Cl$_2$. When this reaction was monitored by NMR at −80 °C, 95% conversion to *cis*-Cp(CO)$_2$(PCy$_3$)MoFBF$_3$ was observed; minor peaks presumed to be from *trans*-Cp(CO)$_2$(PCy$_3$)MoFBF$_3$ (4%) and [Cp(CO)$_2$(PCy$_3$)Mo(ClCD$_2$Cl)]$^+$BF$_4^-$ (1%) were observed at −80 °C but were no longer seen after the temperature was raised to −40 °C. The structure of *cis*-Cp(CO)$_2$(PCy$_3$)MoFBF$_3$ has been determined by single-crystal X-ray diffraction and will be reported separately.[33]

Hydride transfer from Cp(CO)$_2$(PCy$_3$)MoH to Ph$_3$C$^+$OTf$^-$ at 22 °C in CH$_2$Cl$_2$ similarly produced *cis*-Cp(CO)$_2$(PCy$_3$)MoOTf. In contrast to the results obtained with the PPh$_3$ complex Cp(CO)$_2$(PPh$_3$)MoH, where the trans product predominated from hydride transfers in CD$_3$CN, hydride transfer in CD$_3$CN from Cp(CO)$_2$(PCy$_3$)MoH to Ph$_3$C$^+$BF$_4^-$, Ph$_2$(MeOC$_6$H$_4$)C$^+$BF$_4^-$, or Ph$_3$C$^+$OTf$^-$ consistently gave the ratio of 85 (±1):15 (±1) for [*cis*-Cp(CO)$_2$(PCy$_3$)Mo(NCCD$_3$)]$^+$:[*trans*-Cp(CO)$_2$(PCy$_3$)Mo(NCCD$_3$)]$^+$.

Effect of Counterion on Kinetic Hydricity. The effect of counterion on the kinetic hydricity was briefly examined for two metal hydrides. For hydride transfer from Cp(CO)$_3$MoH, the rate constant found for Ph$_3$C$^+$BF$_4^-$ in CH$_2$Cl$_2$ at 25 °C ($k = 3.8 \times 10^2$ M^{-1} s^{-1}) was quite similar to that found when using Ph$_3$C$^+$PF$_6^-$ ($k = 3.5 \times 10^2$ M^{-1} s^{-1}). A second comparison was made between hydride transfer from Cp(CO)$_3$WH to Ph$_3$C$^+$BF$_4^-$ compared with Ph$_3$C$^+$BAr′$_4^-$ [Ar′ = 3,5-bis(trifluoromethyl)phenyl]. The rate constant found with Ph$_3$C$^+$BF$_4^-$ ($k = 76$ M^{-1} s^{-1}) was somewhat larger than that found for Ph$_3$C$^+$BAr′$_4^-$ ($k = 53$ M^{-1} s^{-1}). The product from the reaction of Cp(CO)$_3$WH with Ph$_3$C$^+$BAr′$_4^-$ was observed by ^{1}H NMR but was unstable in solution; it is tentatively assigned as [Cp(CO)$_3$W(ClCD$_2$Cl)]$^+$BAr′$_4^-$.

Kinetic Hydricity of Cp*(CO)$_3$MoH to Substituted (Stabilized) Trityl Cations. Addition of a methoxy group to the para position of the phenyl in trityl cation stabilizes the carbenium ion, making it a weaker hydride acceptor. The effect of sequential addition of *p*-MeO groups on Ph$_3$C$^+$ was studied by determining the kinetics of hydride transfer from Cp*(CO)$_3$MoH to trityl cations containing 0, 1, 2, or 3 *p*-MeO groups; the results are shown in Table 3. Stabilization of Ph$_3$C$^+$ by 3 *p*-MeO groups causes the rate constant to decrease by a factor of >4000 from that for unsubstituted Ph$_3$C$^+$. The effect is largest for addition of the first *p*-MeO group, which diminishes the rate constant by more than the subsequent additions.

Table 3. Rate Constants for Hydride Transfer from Cp*(CO)$_3$MoH to Ph$_n$(*p*-MeOC$_6$H$_4$)$_{3-n}$C$^+$BF$_4^-$ (n = 3, 2, 1, 0) (CH$_2$Cl$_2$, 25 °C)

trityl cation	k_{H^-} (M^{-1} s^{-1})	trityl cation	k_{H^-} (M^{-1} s^{-1})
Ph$_3$C$^+$	6.5×10^3	Ph(*p*-MeOC$_6$H$_4$)$_2$C$^+$	1.1×10^1
Ph$_2$(*p*-MeOC$_6$H$_4$)C$^+$	1.4×10^2	(*p*-MeOC$_6$H$_4$)$_3$C$^+$	1.4×10^0

A plot of log k_{H^-} vs pK_{R^+} is linear (Figure S10 in the supporting information) with a slope of −0.5. K_{R^+} values are a traditional measurement of stability of carbenium ions[34] and are based on measurements in aqueous sulfuric acid; the K_{R^+} values are defined according to eq 9. The excellent linearity of the

$$\mathrm{R^+ + H_2O \overset{K_{R^+}}{\rightleftharpoons} ROH + H^+} \tag{9}$$

plot of of log k_{H^-} vs pK_{R^+} is surprising in view of the very different solvents used in obtaining the kinetic data (CH$_2$Cl$_2$),

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(30) Sünkel, K.; Urban, G.; Beck, W. *J. Organomet. Chem.* **1983**, *252*, 187−194.

(31) Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89−115.

(32) (a) Honeychuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6056−6070. (b) Honeychuck, R. V.; Hersh, W. H. *Inorg. Chem.* **1989**, *28*, 2869−2886.

(33) Cheng, T.-Y.; Szalda, D. J.; Bullock, R. M., manuscript in preparation.

(34) *Carbonium Ions*; Olah, G. A.; Schleyer, P. v. R., Eds.; Wiley and Sons: New York, 1968; Vol. I.

compared with the thermodynamic determinations of carbenium ion stability in aqueous acidic solution.

Dimethylamino groups stabilize carbenium ions even more effectively than methoxy groups. The pK_{R^+} value for $(p\text{-}Me_2NC_6H_4)_3C^+$ is 9.36,[34] compared with 0.82 for $(p\text{-}MeOC_6H_4)_3C^+$ and −6.63 for Ph_3C^+. The reaction of $Cp(CO)_2(PMe_3)MoH$ with $Ph(p\text{-}Me_2NC_6H_4)_2C^+BF_4^-$ at room temperature was very slow, giving ~67% $Ph(p\text{-}Me_2NC_6H_4)_2CH$ after 1 h. Several unidentified organometallic products were formed, but no significant amount of $Cp(CO)_2(PMe_3)MoFBF_3$ was observed by NMR. The reaction of $(p\text{-}Me_2NC_6H_4)_3C^+BF_4^-$ with $Cp(CO)_2(PMe_3)MoH$ was even slower, leading to only ~6% $(p\text{-}Me_2NC_6H_4)_3CH$ after 2 days.

Discussion

Effect of the Metal on Kinetic Hydricity. The kinetic data reported here allow the direct comparison of kinetic hydricity of different metals with identical ligands. In all cases examined here, third-row metal hydrides exhibit faster rates of hydride transfer than their first-row analogues. For example, the third-row tungsten hydride $Cp^*(CO)_3WH$ is 33 times faster at hydride transfer than its first-row analogue $Cp^*(CO)_3CrH$. A similar ratio is found for Re vs Mn, with $(CO)_5ReH$ being 40 times faster than $(CO)_5MnH$. The relative reactivities are similar for the PPh_3-substituted examples, with *cis*-$(CO)_4(PPh_3)ReH$ being 52 times faster than *cis*-$(CO)_4(PPh_3)MnH$.

In both cases where our data allow direct comparisons, the second-row metal hydrides are even faster at hydride transfer than third-row analogues, though the differences in rate constants are less than the differences between the first and third rows. Thus $Cp^*(CO)_3MoH$ is ~3 times faster than the tungsten compound $Cp^*(CO)_3WH$; a similar reactivity ratio was found for the analogous Cp compounds, with $Cp(CO)_3MoH$ being 5 times faster than $Cp(CO)_3WH$.

These comparisons of the effect of the metal on our *neutral* metal carbonyl hydrides can be compared with earlier observations made by Darensbourg and Ash on hydride transfer reactions of *anionic* metal carbonyl hydrides.[5] Reduction of *n*-butyl bromide with anionic metal hydrides gives the hydrocarbon product and converts the organometallic product to an anionic metal bromide (eq 10).[6] The kinetics of these reactions

$$MH^- + n\text{-}BuBr \rightarrow MBr^- + n\text{-}BuH \qquad (10)$$

were found to be second-order, with $k \approx 10^{-2}-10^{-3}\ M^{-1}\ s^{-1}$ at 26 °C in tetrahydrofuran (THF). The rate constant for $(CO)_5WH^-$ was 1.8 times larger than that for $(CO)_5CrH^-$. The $P(OMe)_3$-substituted W and Cr hydrides had a similar relative ratio, with $(CO)_4[P(OMe)_3]WH^-$ being ~1.7 times faster than $(CO)_4[P(OMe)_3]CrH^-$.

The main-group hydride $HSiEt_3$ is frequently used as a hydride donor in ionic hydrogenations of organic substrates.[35] Our measurement of $k_{H^-} = 1.5 \times 10^2\ M^{-1}\ s^{-1}$ for $HSiEt_3$ places this silane hydride donor as slower than most of the transition metal hydride donors (Table 1). Mayr and co-workers reported detailed kinetic studies of hydride transfers to diarylcarbenium ions from a series of silyl hydrides and evaluated the effect of substituent effects on the hydridic reactivity of several silyl hydrides.[36]

Effect of the Ligands on Kinetic Hydricity. Systematic changes in the ligands allowed the evaluation of the effect of steric and electronic properties of different ligands on the same metal. A series of tungsten compounds containing Cp and substituted Cp ligands showed a dramatic change in hydricity as the electronic properties of the ligands were changed. The range of kinetic hydricity spans over 3 orders of magnitude for these compounds, with the rate constants decreasing in the order $(indenyl)(CO)_3WH \approx Cp^*(CO)_3WH > (C_5H_4Me)(CO)_3WH > Cp(CO)_3WH > (C_5H_4CO_2Me)(CO)_3WH$. There is clearly a substantial electronic effect caused by changing the electron density at the substituted Cp, which in turn affects the hydricity of the complex. Compared with the Cp ligand, the Cp* ligand is much larger sterically and is a better electron donor. The larger rate constants for $Cp^*M(CO)_3H$ than for $CpM(CO)_3H$ ($k_{Cp^*}/k_{Cp} = 25$ for W; $k_{Cp^*}/k_{Cp} = 17$ for Mo) indicate that electronic effects clearly predominate over steric effects. Even addition of one methyl group to the Cp ligand increases the hydricity, as seen by the hydricity of $(C_5H_4Me)(CO)_3WH$ being 3 times more than that of $Cp(CO)_3WH$. An even larger effect from the substitution of a single substituent on the Cp ligand was found for the compound containing an electron-withdrawing group on the Cp ligand, $(C_5H_4CO_2Me)(CO)_3WH$ being ~100 times slower at hydride transfer than $Cp(CO)_3WH$.

Comparisons of reactivity of indenyl (η^5-C_9H_7) complexes with related Cp or Cp* complexes have been of much interest, owing in large part to the propensity of indenyl complexes to undergo $\eta^5 \rightarrow \eta^3$ “ring slippage” reactions[37] that dramatically enhance ligand substitution rates. On the basis of electrochemical comparisons of substituted ruthenocenes containing Cp/Cp*/indenyl ligands, Gassman and co-workers concluded that indenyl was similar to Cp* in electron donation to the metal.[38] The electron-donating ability of the indenyl ligand has been ranked as greater than Cp and less than Cp* on the basis of gas-phase measurements using ion cyclotron resonance[39] and photoelectron spectra.[40] Our kinetic data indicate comparable hydridic reactivity of $(indenyl)(CO)_3WH$ and $Cp^*(CO)_3WH$, both of these being much faster hydride donors than the unsubstituted Cp complex $Cp(CO)_3WH$.

Substitution of one CO ligand by a phosphine can dramatically affect the kinetic hydricity of the metal hydride. The PPh_3-substituted Mo hydride *trans*-$Cp(CO)_2(PPh_3)MoH$ is ~1500 times faster at hydride transfer than $Cp(CO)_3MoH$. The electronic effect of the phosphine is to make the metal center more electron-rich, and this effect is manifested in the greatly enhanced kinetic hydricity of the phosphine-substituted metal hydride. The electronic effect clearly predominates over the steric effect of the phosphine. An even larger enhancement is found by substituting 1 CO for PMe_3, *trans*-$Cp(CO)_2(PMe_3)MoH$ being 10 000 times as reactive as $Cp(CO)_3MoH$. The electronic effect of the PMe_3 makes its hydride complex even more hydridic than the PPh_3-substituted analogue but with less steric interference than the PPh_3-substituted compound. In metal hydrides with very bulky phosphines, steric effects can have some influence on the kinetic hydricity. PCy_3 (cone angle[41] $\theta = 170°$) is much more sterically demanding than PMe_3 ($\theta = 118°$), and *trans*-$Cp(CO)_2(PCy_3)MoH$ is ~10 times slower than *trans*-$Cp(CO)_2(PMe_3)MoH$ at hydride transfer.

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For the PCy_3-substituted Mo complex $Cp(CO)_2(PCy_3)MoH$, we established that the kinetic hydricity of the trans isomer is much higher than that of the cis isomer. Our measurements at −55 °C (the only temperature at which we were able to determine the kinetic hydricity of the cis isomer) showed that *trans*-$Cp(CO)_2(PCy_3)MoH$ is ~1000 times faster at hydride transfer than is *cis*-$Cp(CO)_2(PCy_3)MoH$. The electronic effect of the PCy_3 phosphine in activating *trans*-$Cp(CO)_2(PCy_3)MoH$ toward hydride transfer is essentially canceled out by the steric effect in the cis isomer of the same compound, such that the rate constant of *cis*-$Cp(CO)_2(PCy_3)MoH$ for hydride transfer is similar to that of the unsubstituted complex $Cp(CO)_3MoH$. We have not accounted for different intrinsic electronic effects that the phosphine may have on the kinetic hydricity of cis vs trans isomers in these "piano stool" structures, so this factor might influence the relative reactivities as well.

Our results also provide an evaluation of the effect of phosphine substitution in six-coordinate Mn and Re complexes. The PPh_3-substituted Mn complex *cis*-$(CO)_4(PPh_3)MnH$ is more hydridic than $(CO)_5MnH$ by ~5-fold; a similar effect is observed for the Re analogues. The effect of phosphine substitution on the hydricity of these Mn and Re complexes may be compared to the effect of phosphite substitution on anionic metal hydrides $(CO)_4[P(OMe)_3]MH^-$ studied by Darensbourg (eq 10), since both of classes of metal hydrides have approximately octahedral geometry, the phosphorus ligand positioned cis to the hydride. The phosphite-substituted Cr hydride $(CO)_4[P(OMe)_3]CrH^-$ is ~17 times faster at reduction of *n*-BuBr (eq 10) than $(CO)_5CrH^-$.[6]

Reactivity of Free vs Ion-Paired [Ph_3C^+]. Several studies have measured dissociation constants (K_D) for formation of free ions from ion pairs of trityl cation.[42] The dissociation constant reported for [$Ph_3C^+SbCl_6^-$] in CH_2Cl_2 at 25 °C is $K_D = 1.6 \times 10^{-4}$ M (eq 11).[42a] Typical initial concentrations of [$Ph_3C^+BF_4^-$] used in our kinetics experiments were 0.05 mM. If we assume that K_D is similar for $Ph_3C^+SbCl_6^-$ and $Ph_3C^+BF_4^-$, our conditions would initially involve ~80% free ions and 20% ion pairs. The relative amount of free ions increases as the reaction proceeds, because of consumption of the $Ph_3C^+BF_4^-$. Since our kinetics exhibit very clean first-order rates for disappearance of [$Ph_3C^+BF_4^-$], there is no evidence for any difference in reactivity of free and ion-paired forms of $Ph_3C^+BF_4^-$. A negligible dependence on counterion (BF_4^-, PF_6^-, AsF_6^-, SbF_6^-, $SbCl_6^-$) or extent of ion pairing was previously observed in hydride transfers to Ph_3C^+ from $HSiEt_3$.[22] Mayr and co-workers noted the absence of ion-pairing effects in the kinetics of addition of alkenes to diarylcarbenium ions,[43] so comparable reactivity of free and ion-paired carbenium ions appears to have some generality in CH_2Cl_2 solution.

$$[Ph_3C^+SbCl_6^-] \overset{K_D}{\rightleftharpoons} [Ph_3C^+] + [SbCl_6^-] \qquad (11)$$

Capture of the 16-Electron "M^+" after Hydride Transfer. As discussed earlier, Tilset and co-workers found highly selective formation of the kinetic product *trans*-$[Cp(CO)_2(PR_3)M(NCCH_3)]^+$ after hydride transfer to substituted trityl cations from either $Cp(CO)_2(PMe_3)WH$[19] or $Cp(CO)_2(PPh_3)MoH$.[27] Isomerization to the thermodynamically favored product *cis*-$[Cp(CO)_2(PR_3)M(NCCH_3)]^+$ required many hours. We found a similar predominance of *trans*-$Cp(CO)_2(PPh_3)MoOTf$ from the reaction of $Cp(CO)_2(PPh_3)MoH$ with $Ph_3C^+OTf^-$. In these cases, the 16-electron $[Cp(CO)_2(PR_3)M]^+$ produced by hydride transfer is captured by a strongly binding ligand, CH_3CN or OTf^-, and subsequent trans → cis isomerization is slow. In contrast to these cases where trans products were observed as kinetic products, hydride abstractions from $Cp(CO)_2(PCy_3)MoH$ consistently gave a predominance of cis products. This was the case not only in trapping of the 16-electron cation $[Cp(CO)_2(PCy_3)Mo]^+$ by the strongly binding ligands CH_3CN and OTf^- but also in hydride transfer from $Cp(CO)_2(PCy_3)MoH$ to $Ph_3C^+BF_4^-$, which gave predominantly *cis*-$Cp(CO)_2(PCy_3)MoFBF_3$. These results clearly indicate that use of stereochemistry of the initially observed product is *not* an infallible indicator of the site from which the hydride was donated, since we observe cis products from hydride transfer from $Cp(CO)_2(PCy_3)MoH$, despite having shown by the kinetics that *trans*-$Cp(CO)_2(PCy_3)MoH$ is far more reactive than *cis*-$Cp(CO)_2(PCy_3)MoH$.

The observation of cis products from $Cp(CO)_2(PCy_3)MoH$ could be due to fast trans → cis isomerization of "$[Cp(CO)_2(PCy_3)Mo]^+$" prior to capture by either CH_3CN, OTf^-, or BF_4^-. Alternatively, these results are also consistent with initial capture of "$[Cp(CO)_2(PCy_3)Mo]^+$" to give a trans product. Dissociation of CH_3CN, OTf^-, or BF_4^- from the trans kinetic product could be followed by trans → cis isomerization and reassociation of the ligand. A higher rate of trans → cis isomerization of the PCy_3-substituted complex is corroborated by our observation of a higher rate of conversion of kinetic products [*trans*-$Cp(CO)_2LMo(ClCD_2Cl)]^+BF_4^-$ and *trans*-$Cp(CO)_2LMoFBF_3$ to the thermodynamic product *cis*-$Cp(CO)_2LMoFBF_3$ for L = PPh_3 than for L = PMe_3. The implication is that larger steric demands of phosphines accelerate the isomerization.

Comparison of Acidity vs Hydricity of Metal Carbonyl Hydrides. An understanding of the factors influencing the kinetic and thermodynamic acidity of metal hydrides is available, notably from the work of Norton's group.[10] Our results on the kinetic hydricity of many of the same metal hydrides allow certain comparisons to be made. The notion that relative propensities of proton transfer and hydride transfer modes of M−H bond cleavage might be roughly the opposite of each other is tempered by several factors.[44] Deprotonation of a metal hydride gives a metal anion that is generally a stable 18-electron species. In contrast, hydride transfer from MH gives a formally 16-electron "M^+" that differs in electron count from the metal hydride and that almost invariably requires coordination with another ligand to form a stable species. The kinetics of proton transfer from a series of metal hydrides to aniline in CH_3CN at 25 °C have been reported.[45] Figure 5 shows a plot comparing rate constants for proton-transfer reactions with those for our

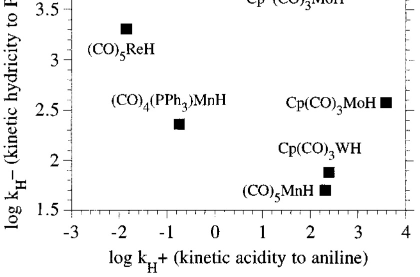

Figure 5. Plot of log k_{H^-} vs log k_{H^+} comparing kinetic hydricity with kinetic acidity.

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hydride transfer reactions. Some ligand effects on acidity vs hydricity support the idea that more electron-donating ligands enhance hydricity and diminish kinetic acidity, as seen by Cp*-$(CO)_3MoH$ being more hydridic and less acidic than Cp-$(CO)_3MoH$. A similar argument holds for $(CO)_4(PPh_3)MnH$ and $(CO)_5MnH$. The lack of a more general correlation among the different metals and ligand sets shown in Figure 5 suggests, however, that too many factors influence the acidity and the hydricity for any simple relationship to be established confidently, at least on the basis of presently available data.

Comparison of Kinetic Hydricity with Bond Strengths. The M−H bond dissociation energies (BDE's) of many of the metal hydrides studied in this work have been reported, mostly through the use of thermochemical cycles utilizing electrochemical data and pK_a data of the metal hydrides.[19,46] Figure 6 shows a plot of ln k_{H^-} vs the homolytic bond dissociation energy.[47,48] For example, the reported bond dissociation energies of $(CO)_5MnH$, $(CO)_4(PPh_3)MnH$, $Cp(CO)_3MoH$, and Cp*-$(CO)_3MoH$ differ by only ~1 kcal mol^{-1}, yet their kinetic hydricity range spans a factor of >100. The kinetic hydricity of $Cp^*(CO)_3CrH$, $(CO)_5MnH$, and $Cp(CO)_3WH$ span a range of only 1.5, whereas their reported BDEs differ by 10 kcal mol^{-1}. Clearly, there is no overall correlation of the kinetic hydricity, which involves a *heterolytic* M−H bond cleavage, with the thermodynamics of the *homolytic* BDEs.

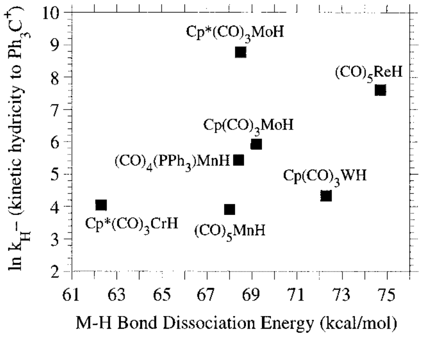
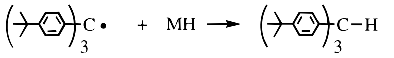


Figure 6. Plot of ln k_{H^-} vs homolytic bond dissociation energies of M−H.

Although the value of thermochemical data in interpreting kinetic trends is immense, most of the data are confined to homolytic bond dissociation energies. Berke and co-workers have reported deuterium quadrupole coupling constants for a series of metal deuterides, from which they calculated the "ionicity" of the M−D bonds.[49] Some data are available for hydride affinities of carbenium ions in solution: $\Delta G_{hydride} = -96$ kcal/mol for Ph_3C^+ in dimethyl sulfoxide.[50] Thermodynamic data on heterolytic bond energies of metal hydrides would be very useful. Bruno and co-workers recently measured equilibrium constants for hydride transfers from metal hydrides to a series of substituted trityl cations in MeCN solution.[51]

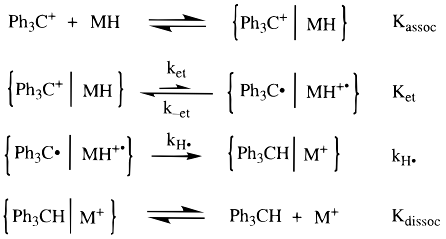
Comparison of Hydride Transfer with Hydrogen Atom Transfer. Norton and co-workers reported a detailed study of the kinetics of hydrogen atom transfer from a series of metal hydrides to the stable radical tris(*p-tert*-butylphenyl)methyl (eq 12).[12] Steric considerations are expected to be roughly similar for their substituted trityl radical, compared with the Ph_3C^+ used in our hydride transfers. Their reactions were carried out in toluene, whereas our rate constants were determined in CH_2Cl_2. Despite these differences, some comparisons of relative rate constants for these reactions may be useful for the four metal hydrides examined in both studies. Second-order rate constants (k) reported at 25 °C for eq 12 were 741 M^{-1} s^{-1} for $(CO)_5MnH$, 514 M^{-1} s^{-1} for $Cp(CO)_3MoH$, 91 M^{-1} s^{-1} for $Cp(CO)_3WH$, and 13.9 M^{-1} s^{-1} for $Cp^*(CO)_3MoH$. Of these four metal hydrides, $(CO)_5MnH$ has the highest rate constant for hydrogen atom transfer, but it is the slowest at hydride transfer. The Cp complex $Cp(CO)_3MoH$ is 37 times faster at hydrogen atom transfer than is its Cp* analogue $Cp^*(CO)_3MoH$, but the Cp* complex has a higher rate constant for hydride transfer. Apparently the enhanced hydricity is due to the electronic effect of the Cp* ligand, compared with that of the Cp ligand. For both hydrogen atom and hydride transfer reactions, the Mo hydride, $Cp(CO)_3MoH$, reacts faster than the W analogue, Cp-$(CO)_3WH$.



(12)

Mechanism of Hydride Transfer: Single-Step Hydride Transfer vs Initial Electron Transfer. Darensbourg and Ash noted that hydricity "is difficult to define experimentally because of the multiple pathways available for an overall H^- transfer."[5] We have been referring to hydricity in this paper with the implication that these reactions proceed by hydride transfer from the metal to carbon in a single step. An alternative mechanistic pathway would be an initial electron transfer, followed by hydrogen atom transfer. We now consider the viability of such a mechanism as shown in Scheme 3. The first step is simply diffusion of the metal hydride and the trityl cation together. We do not expect a particularly strong affinity of the two reagents, so $K_{assoc} < 10$ M^{-1} is estimated. The electron transfer and hydrogen atom transfer steps are the key steps and will be considered in detail below. The final steps are dissociation of Ph_3CH from M^+ and the product-forming capture of M^+ by BF_4^- to produce M-FBF$_3$. A steady-state approximation for $\{Ph_3C^{\bullet}|MH^{+\bullet}\}$ gives eq 13 as the rate constant for hydride transfer.

Scheme 3



$$Ph_3C^+ + MH \rightleftharpoons \{Ph_3C^+ | MH\} \qquad K_{assoc}$$

$$\{Ph_3C^+ | MH\} \underset{k_{-et}}{\overset{k_{et}}{\rightleftharpoons}} \{Ph_3C^{\bullet} | MH^{+\bullet}\} \qquad K_{et}$$

$$\{Ph_3C^{\bullet} | MH^{+\bullet}\} \xrightarrow{k_{H^{\bullet}}} \{Ph_3CH | M^+\} \qquad k_{H^{\bullet}}$$

$$\{Ph_3CH | M^+\} \rightleftharpoons Ph_3CH + M^+ \qquad K_{dissoc}$$

We now consider two limits based on relative magnitudes of k_{-et} and $k_{H^{\bullet}}$. If $k_{-et} \gg k_{H^{\bullet}}$, then $k_{obs} = (K_{assoc})(K_{et})(k_{H^{\bullet}})$, with

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$$k_{\mathrm{obs}} = K_{\mathrm{assoc}}\left(\frac{k_{\mathrm{et}}}{k_{-\mathrm{et}} + k_{\mathrm{H}\cdot}}\right)k_{\mathrm{H}\cdot} \tag{13}$$

the hydrogen atom transfer step being rate-limiting. The equilibrium constant for electron transfer from the metal hydride to Ph_3C^+ can be estimated from electrochemical measurements. Reduction of $Ph_3C^+PF_6^-$ in CH_3CN was studied by cyclic voltammetry and was found to be partially reversible. An estimate of $E° \approx +0.27$ V (vs a saturated calomel electrode) was given;[52] conversion to a Cp_2Fe/Cp_2Fe^+ reference gives $E° \approx -0.08$ V. Oxidation of $Cp(CO)_3MoH$ was reported by Tilset and co-workers to be quasi-reversible, with $E = 0.800$ V (vs Cp_2Fe/Cp_2Fe^+) reported for the peak potential for oxidation of this hydride.[19] From these electrochemical data, the oxidation of $Cp(CO)_3MoH$ by Ph_3C^+ is estimated to be thermodynamically unfavorable by ~0.9 V ($\Delta G° \approx 21$ kcal mol^{-1}), leading to an estimate of $K_{\mathrm{et}} \approx 10^{-16}$ (see discussion below). This very unfavorable electron transfer could be followed by hydrogen atom transfer from the oxidized metal hydride to the trityl radical. While oxidation of metal hydrides often results in proton transfers from the very acidic 17-electron $MH^{+\bullet}$ species, a substantial activation of M−H bonds toward homolytic cleavage can also result from one-electron oxidation.[19,48,53] A very fast hydrogen atom transfer could conceivably occur on the time scale of a molecular vibration, so we set an upper limit of $k_{\mathrm{H}\cdot} < 10^{13}$ s^{-1} (note that $k_{\mathrm{H}\cdot} \ll k_{-\mathrm{et}}$ also). Based on these estimates, an upper limit estimated for the rate constant of this mechanism is given in eq 14:

$$(K_{\mathrm{assoc}})\,(K_{\mathrm{et}})\,(k_{\mathrm{H}\cdot}) = (10\ \mathrm{M}^{-1})\,(10^{-16})\,(10^{13}\ \mathrm{s}^{-1}) = 10^{-2}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1} \tag{14}$$

The resulting estimated maximum rate constant is 10^{-2} M^{-1} s^{-1}, which is 4 orders of magnitude lower than the experimentally measured rate constant of 3.8×10^2 M^{-1} s^{-1} for $Cp(CO)_3MoH$. The possibility of preequilibrium electron transfer, followed by rate-limiting hydrogen atom transfer, is therefore deemed unlikely.

We now consider the other limiting case of eq 13, rate-limiting electron transfer. If $k_{-\mathrm{et}} \ll k_{\mathrm{H}\cdot}$, then eq 13 simplifies to $k_{\mathrm{obs}} = (K_{\mathrm{assoc}})(k_{\mathrm{et}})$. Using $k_{-\mathrm{et}} \leq 10^{13}$ s^{-1} and $K_{\mathrm{et}} \approx 10^{-16}$, the estimated upper limit for the rate constant for electron transfer is $k_{\mathrm{et}} < 10^{-3}$ s^{-1}. The estimated maximum overall rate constant is then $k_{\mathrm{obs}} \leq (K_{\mathrm{assoc}})(k_{\mathrm{et}}) = 10^{-2}$ M^{-1} s^{-1}, the same upper limit that was estimated for rate-limiting hydrogen atom transfer. We conclude that hydride transfer from $Cp(CO)_3MoH$ to Ph_3C^+ proceeds by a single-step hydride transfer, rather than the mechanism shown in Scheme 3. A further argument against the possibility of rate-determining electron transfer is that isotope effects as large as found for these systems [$k_{\mathrm{MoH}}/k_{\mathrm{MoD}}$ of 1.8 for $Cp(CO)_3MoH$][23] are quite unlikely in electron transfer reactions, where the M−H (M−D) bond is not cleaved.

There are potential limitations to the use of these electrochemical measurements, since the oxidations of the metal hydrides are usually irreversible. In addition, the use of electrochemical data to obtain thermodynamic quantities neglects the work terms, since the thermodynamic quantities derived from them are for separated freely diffusing species, not caged intermediates. We contend that such corrections are relatively minor and would not change our conclusions. Note that in our reaction, the work terms are expected to be negligible, since the reaction involves one neutral and one cationic species.[54]

While the electron transfer mechanism is disfavored for our system involving hydride transfer from metal to carbon, we note that it is quite viable for many other related reactions. Carbon-to-carbon hydride transfers from dihydronicotinamides are a very actively studied class of hydride transfer reactions for which mechanistic questions of electron transfer vs single-step hydride transfer have been considered in detail.[3] Kochi and co-workers recently reported kinetics of hydrogen atom transfers from methylbenzenes to photoactivated quinones. They concluded that substantial deuterium kinetic isotope effects are consistent with a mechanism initiated by electron transfer and followed by proton transfer as the product-forming step.[55]

Rigorous exclusion of the electron transfer mechanism is less secure for the phosphine-substituted metal hydrides. Phosphine-substitution makes the metal hydride more easily oxidized: oxidation of $Cp(CO)_2(PPh_3)MoH$ was reported at $E \approx +0.26$ V (vs Cp_2Fe/Cp_2Fe^+ reference).[27] Thus oxidation of this metal hydride by Ph_3C^+ would be unfavorable by only ~0.3 V ($\Delta G° \approx 7$ kcal mol^{-1}, $K_{\mathrm{et}} \approx 10^{-6}$). However, the observed rate constants for hydride transfer are larger for the phosphine-substituted hydrides. The kinetic isotope effect for hydride transfer from $Cp(CO)_2(PCy_3)MoH$ is $k_{\mathrm{MoH}}/k_{\mathrm{MoD}} = 1.7$ (see Figure S8 in the supporting information),[23] which is essentially the same as that found for $Cp(CO)_3MoH$. For the phosphine-substituted metal hydride to undergo hydride transfer by an electron transfer pathway would therefore require that the mechanism would change but the isotope effect would remain the same, and this seems untenable. Although the electron transfer mechanism is not rigorously excluded on the basis of the kinetic and electrochemical/thermodynamic data for the phosphine-substituted metal hydrides, we suggest that all of the hydride transfer reactions in this paper proceed by a single-step hydride transfer and not by a mechanism initiated by electron transfer. In recent related studies, Smith, Norton, and Tilset[56] concluded that hydride transfer from $Cp(CO)_2(PPh_3)MoH$ to protonated acetone also occurs by a single-step rather than an electron transfer mechanism.

Hembre and co-workers reported several interesting observations on Cp*(dppf)RuH [dppf = 1,1′-(bis(diphenylphosphino)-ferrocene], an unusual metal hydride that exhibits two electrochemically reversible oxidations.[57] Hydride transfer from Cp*(dppf)RuH to *N*-methylacridinium was found to occur by a single-step hydride transfer,[2] but hydride transfer to Ph_3C^+ was by an initial electron transfer followed by hydrogen atom transfer. Oxidation of metal hydrides becomes easier as the metal becomes more electron-rich. Whereas we argued above that our mono-phosphine-substituted hydrides such as $Cp(CO)_2(PPh_3)MoH$ undergo single-step hydride transfer, apparently metal hydrides with two phosphines will more generally undergo single-electron transfer when reacted with Ph_3C^+. In further support of this trend, we recently obtained evidence that reaction of Ph_3C^+ with Cp(CO)(dppe)MoH (dppe = $Ph_2PCH_2CH_2PPh_2$)

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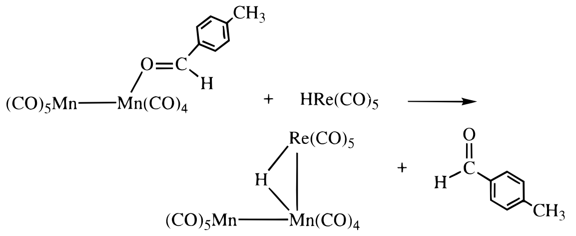
in CH_3CN proceeds by an initial electron transfer mechanism, rather than single-step hydride transfer.[58] The reaction of Ph_3C^+ with certain metal hydrides containing >2 phosphorus ligands is known to result in oxidation to give stable $MH^{+\bullet}$ species, rather than hydride transfer, as shown for $HCo[P(OPh)_3]_4$[59] and $HFeCl(dppe)_2$.[60] Hydride transfer from some metal alkyl complexes [e.g., Cp(CO)(NO)ReR[61] and $Cp_2W(CH_3)_2$[62]] to Ph_3C^+ also can occur by initial electron transfer.

We consider one additional mechanistic issue of the hydride transfer. Because most of our kinetics were carried out with $Ph_3C^+BF_4^-$, there may be a possible additional role of the counterion. Dissociation of BF_4^- would give F^- and BF_3, and the BF_3 could potentially interact with the metal hydride to increase its hydricity. However, the kinetic competence of this possible catalysis of hydride transfer by BF_3 is ruled out by the modest effect observed in kinetics experiments where BF_4^- was added to hydride transfers of $Cp(CO)_2(PCy_3)MoH$; in these experiments, the rate constants decreased slightly with higher amounts of BF_4^-.

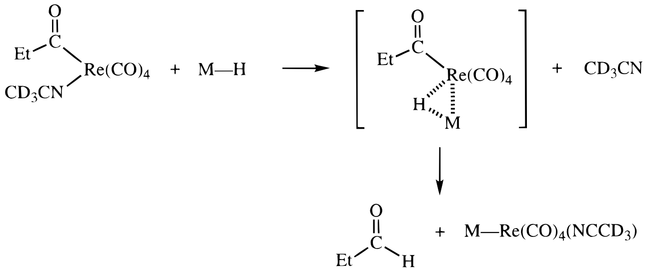
Comparison of Hydricity of $Cp(NO)_2WH$ with $Cp(CO)_3WH$. The kinetic hydricity of the tungsten nitrosyl hydride $Cp(NO)_2WH$ was determined to provide a quantitative comparison with that of the isoelectronic carbonyl hydride $Cp(CO)_3WH$. Legzdins and Martin first prepared $Cp(NO)_2WH$ and noted its hydridic reactivity.[63] The reactivity of metal nitrosyl hydrides was reviewed by Berke and Burger,[64] who attributed enhanced hydricity to metal nitrosyl hydrides compared to similar metal carbonyl hydrides. Bursten and Gatter explained the hydridic vs acidic differences in reactivity on the basis of results of molecular orbital studies of the Cr analogues, $Cp(NO)_2CrH$ and $Cp(CO)_3CrH$.[65] Our results show that the kinetic hydricity of $Cp(NO)_2WH$ exceeds that of $Cp(CO)_3WH$ by ~250-fold. We believe that a substantial reason for the difference in hydricity is the difference in formal oxidation state of the metal. Counting the nitrosyl ligands as NO^+ results in a formal oxidation state of W(0) for $Cp(NO)_2WH$, compared with a formal oxidation state of W(II) for $Cp(CO)_3WH$.

Hydricity vs Nucleophilicity of Metal Hydrides. The reactions reported in this paper clearly involve hydride transfer, since the M−H bond is cleaved as a hydride. Many discussions of reactivity patterns of metal hydrides refer to nucleophilicity of the metal hydride, with the terms "hydricity" and "nucleophilicity" apparently being used interchangeably. We consider the kinetics reported in this paper to be a true measure of hydricity, since there is no nucleophilic displacement of any "leaving group" (except for the BF_4^- counterion that is ion-paired to the Ph_3C^+). For comparison, we consider the reactions of anionic metal hydrides with alkyl halides (eq 10)[6,66] as being properly described by both terms. They are nucleophilic displacements, since H^- displaces Br^- at the carbon center, but they are also hydride transfers from the viewpoint of the metal hydride. In other reactions of metal hydrides, the pair of electrons in the M−H bond functions as a nucleophile, but without a complete hydride transfer taking place. An example is shown in eq 15, in which the nucleophilic displacement of an η^1-aldehyde ligand occurs, leading to a bridging hydride complex.[67] Nucleophilic displacement of a weakly bound ligand by a metal hydride is a synthetic procedure that has been successfully used in many cases for preparing M(μ-H)M′ complexes.[68] A quantitative assessment of the nucleophilicity of several metal hydrides was carried out by Norton and coworkers, who reacted an acyl complex of Re (solvated by CD_3CN) with a series of metal hydrides.[69] The proposed intermediate (or transition state) has a three-center two-electron bond like that found in other M(μ-H)M′ complexes mentioned above; the final products are the aldehyde and a bimetallic complex (Scheme 4). Kinetic and mechanistic data indicated that the mechanism involved dissociation of the CD_3CN ligand prior to reaction of the metal hydride; accordingly, the relative rate constants measured in their study reflected nucleophilicity of the metal hydrides toward the coordinatively unsaturated Re acyl complex. The relative rate constants exhibited interesting trends, and the authors noted that the order of relative nucleophilicity was "largely the *reverse* of the order of increasing reactivity of proton transfer onto aniline."[69] The range of rate constants measured in Scheme 4 is only ~2 orders of magnitude, but the trends in nucleophilic reactivity are strikingly different from the trends in kinetic hydricity toward Ph_3C^+. The rhenium hydride $(CO)_5ReH$ is only 1.4 times as nucleophilic (Scheme 4) as $(CO)_5MnH$ but shows a 40-fold greater rate constant of kinetic hydricity toward Ph_3C^+. An even more dramatic difference is found when comparing the effect of phosphine substitution: The phosphine-substituted tungsten hydride $Cp(CO)_2(PMe_3)WH$ is less nucleophilic than $Cp(CO)_3WH$ (by a factor of ~2) in Scheme 4, compared with an acceleration of 10^4 in hydride transfer rate constant for the molybdenum hydride *trans*-$Cp(CO)_2(PMe_3)MoH$ vs $Cp(CO)_3MoH$.



(15)

Scheme 4



Conclusions

The kinetics of hydride transfer to Ph_3C^+ from a series of neutral metal hydrides have been determined. For the complexes reported here, the rate constants for kinetic hydricity span a

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range of $>10^6$. Most of these transition-metal hydrides are more hydridic than the main group hydride $HSiEt_3$. Third-row metal hydrides are more hydridic than their first row analogues. The effect of changing metals (for a given set of ligands) is much smaller than the effect of changing ligands on a given metal. Complexes with Cp* ligands are more hydridic than those with Cp ligands, indicating that electronic effects are more influential than steric effects in determining the kinetic hydricity. Substitution of an electron-withdrawing CO ligand by an electron-donating phosphine can result in a dramatic acceleration of hydricity—the rate constant for hydride transfer from *trans*-Cp(CO)$_2$(PMe$_3$)MoH exceeds that of Cp(CO)$_3$MoH by a factor of 10^4. Steric effects partly counteract electronic effects on kinetic hydricity in metal hydrides having a cis geometry of phosphine and hydride ligands. The hydride transfers reported here are thought to occur as single-step hydride transfers, rather than electron transfer followed by hydrogen atom transfers. This development of a scale of kinetic hydricity permits comparisons with hydrogen atom transfer and proton-transfer reactions of the same metal hydrides.

Experimental Section

General. All manipulations were carried out under an atmosphere of argon by using Schlenk or vacuum-line techniques, or in a Vacuum Atmospheres drybox. ^{1}H NMR chemical shifts were referenced to the residual proton peak of CD_2Cl_2 at δ 5.32. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory (Woodside, NY). NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz for ^{1}H). IR spectra were recorded on a Mattson Polaris FT-IR spectrometer. Cp(CO)$_3$WH,[70] Cp(CO)$_3$MoH,[70] Cp*(CO)$_3$WH,[71] Cp*(CO)$_3$MoH,[72] Cp(CO)$_2$(PMe$_3$)MoH,[26] Cp(CO)$_2$(PPh$_3$)MoH,[73] Cp*(CO)$_3$CrH,[18] *cis*-(CO)$_4$(PPh$_3$)ReH,[74] the indenyl complex (η^5-C$_9$H$_7$)(CO)$_3$WH[75] Cp(NO)$_2$WH,[63] (CO)$_5$MnH,[76] (CO)$_5$ReH,[77] (CO)$_4$(PPh$_3$)MnH,[78] Ph$_3$COTf,[79] and $Ph_3C^+BAr'_4{}^-$[80] were prepared by literature methods. Cp(CO)$_3$MoD and Cp*(CO)$_3$MoD were synthesized from their corresponding metal hydrides, by exchange with CH_3OD (99.5% D, Aldrich) at room temperature, as described previously[81] for Cp(CO)$_3$MoD. $Ph_3C^+BF_4^-$ and $Ph_3C^+PF_6^-$ were purchased from Aldrich and purified by recrystallization from CH_2Cl_2/ether. Ph$_2$(*p*-MeOC$_6$H$_4$)$C^+BF_4^-$, Ph(*p*-MeOC$_6$H$_4$)$_2C^+BF_4^-$, and (*p*-MeOC$_6$H$_4$)$_3C^+BF_4^-$ were synthesized by a previously reported route,[82] from the reactions of Ar$_3$CCl with $HBF_4 \cdot OEt_2$. Ph(Me$_2$NC$_6$H$_4$)$_2$COH·HCl was purchased from Aldrich and (Me$_2$NC$_6$H$_4$)$_3$CCl (crystal violet) was purchased from Fisher. PCy$_3$ was purchased from Strem Chemicals and used as received. $HSiEt_3$ was distilled from LiAlH$_4$. THF, 1,2-dimethoxyethane (DME), Et$_2$O, and hexane were distilled from Na/benzopheneone, and CH_2Cl_2 was distilled from P_2O_5.

Kinetic Experiments. Most of the kinetic measurements were performed on a Hi-Tech Scientific SF-40 Canterbury stopped-flow apparatus with an SU-40 spectrophotometer unit. Some slow kinetics were performed on a Hewlett-Packard 8452A diode array spectrophotometer. The data were collected and analyzed on a Macintosh computer with LabVIEW and MATLAB software. For each kinetics run, 300 data points were collected and analyzed.

Sample Preparation. The CH_2Cl_2 solutions were prepared in a glovebox under an argon atmosphere. For most experiments, the solution of $Ph_3C^+BF_4^-$ was prepared as 0.1 mM and the metal hydride (0.25 mmol) was used to make a 25-mL stock solution (10 mM), which was then diluted to make 4 or 5 solutions. The metal hydride concentrations were typically 10- to 100-fold in excess of the Ph_3C^+ concentration. In the case of experiments with Cp(CO)$_3$WH, the concentration of excess [Cp(CO)$_3$WH] was varied 50-fold.

Stopped-Flow Experiments. The flow circuit was flushed with dry, oxygen-free CH_2Cl_2 before the reagent solutions were used. One reservoir syringe was then was filled with the $Ph_3C^+BF_4^-$ solution and the other with the metal hydride solution. The two drive syringes were flushed with the solutions twice before initiating the kinetic experiments and collecting data. The rate of disappearance of the absorbance was recorded at 450 nm ($\epsilon = 2.5 \times 10^4$ M^{-1} cm^{-1}, which was at the shoulder of the absorption peak for $Ph_3C^+BF_4^-$; at $\lambda_{max} = 410$ and 430 nm, $\epsilon = 3.2 \times 10^4$ M^{-1} cm^{-1}). The average first-order rate constant was obtained from at least 5 runs at each metal hydride concentration. Variation of reproducibility from run to run, with use of the same solutions, was typically <2%. This does not account for uncertainties in the concentration of [MH], due to weighing and dilution errors. As indicated in Table 1, we estimated an overall uncertainty of ≈10% for the rate constants, based on reproducibility of rate data from duplicate runs with independently prepared solutions. When the temperature of the constant-temperature bath was changed, the solutions were allowed to equilibrate, and the temperature of the bath was independently checked by using a digital thermocouple.

UV Data for Substituted Trityl Cations in CH$_2$Cl$_2$. (a) Ph$_2$(*p*-MeOC$_6$H$_4$)$C^+BF_4^-$: $\lambda_{max} = 398$ nm ($\epsilon = 1.4 \times 10^4$ M^{-1} cm^{-1}) and 478 nm ($\epsilon = 5.3 \times 10^4$ M^{-1} cm^{-1}). (b) Ph(*p*-MeOC$_6$H$_4$)$_2C^+BF_4^-$: $\lambda_{max} = 416$ nm ($\epsilon = 3.6 \times 10^4$ M^{-1} cm^{-1}) and 504 nm ($\epsilon = 8.2 \times 10^4$ M^{-1} cm^{-1}). (c) (*p*-MeOC$_6$H$_4$)$_3C^+BF_4^-$: $\lambda_{max} = 486$ nm ($\epsilon = 8.9 \times 10^4$ M^{-1} cm^{-1}).

Preparation of Cp(CO)$_2$(PCy$_3$)MoH. A solution of Cp(CO)$_3$MoH (1.00 g, 4.06 mmol) and PCy$_3$ (1.12 g, 3.98 mmol) in toluene (30 mL) was heated to 90−100 °C for 8 h. The solvent volume was reduced to ∼5 mL, and hexane (30 mL) was added. The precipitate was collected by filtration and washed with hexane (20 mL × 3) to give Cp(CO)$_2$(PCy$_3$)MoH (1.34 g, 2.69 mmol, 67%) as a pale yellow product. ^{1}H NMR (CD$_2$Cl$_2$, 22 °C): δ 5.26 (s, 5 H, *Cp*), 1.00−1.95 [br, m, 33 H, P(C$_6$*H*$_{11}$)$_3$], −6.13 (br, d, $J_{PH} = 56.7$ Hz, 1 H, Mo*H*). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 22 °C): δ 76.2 (br, s). ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 22 °C): δ 242.1 (s, *C*O), 88.8 (s, *C*$_5$H$_5$), 39.1 (d, *C*H, $^1J_{PC} = 21$ Hz), 30.0 (s, *C*H$_2$), 27.7 (d, *C*H$_2$, $^3J_{PC} = 10$ Hz), 26.5 (s, *C*H$_2$). IR (CH$_2$Cl$_2$): ν(CO) 1922 (vs), 1841 (s) cm^{-1}. Anal. Calcd for C$_{25}$H$_{39}$O$_2$PMo: C, 60.24; H, 7.89. Found: C, 59.80; H, 8.18.

Isomerization Rates of Cp(CO)$_2$(PCy$_3$)MoH Measured by NMR Line Broadening, (a) without Added [BF$_4^-$]. In the glovebox, Cp(CO)$_2$(PCy$_3$)MoH (12 mg, 0.024 mmol) in CD$_2$Cl$_2$ (∼0.5 mL) was prepared in an NMR tube with 1,2-dichloroethane as an internal line-width standard. The ^{1}H NMR data were measured on a Bruker AM-300 NMR instrument equipped with an Aspect 3000 computer and a VT-1000 variable-temperature unit. The probe temperature was calibrated[83] with MeOH (0.1% HCl) over the temperature range −86 to 27 °C. Line widths were determined by measuring the full width at half-height of the hydride resonances (average line width of the doublet) at seven different temperatures. The line widths in the absence of exchange were 2.5 Hz. A Macintosh computer program was used to simulate the line shape. This program was written by Dr. Soley S. Kristjánsdóttir; further details are provided in her Ph.D. thesis (Colorado State University, 1991). The rate constants were determined by matching computed line widths with experimental by determined ones. At −86 °C, both Cp and hydride resonances were sharp, showing no exchange of cis and trans isomers. ^{1}H NMR (−86 °C): cis isomer, δ 5.24 (s,

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Cp), −6.25 (d, J_{PH} = 60.5 Hz, Mo*H*); trans isomer, δ 5.10 (s, *Cp*), −6.96 (d, J_{PH} = 20.0 Hz, Mo*H*). The two hydride resonances started to broaden at −45 °C and coalesced at −1 °C. The two Cp resonances started to broaden at −68 °C and coalesced at −24 °C. The following data are the line widths of the hydride resonances and the rate constants for cis→trans isomerization (k_{CT}) at various temperatures: −45 °C, 3.0 Hz, 2.0 s^{-1}; −35 °C, 4.6 Hz, 6.5 s^{-1}; −24 °C, 9.3 Hz, 23 s^{-1}; −12 °C, 20.6 Hz, 65 s^{-1}; −1 °C, 31.8 Hz, 150 s^{-1}; 5 °C, 26.6 Hz, 200 s^{-1}; 11 °C, 19.7 Hz, 350 s^{-1}; 27 °C, 6.7 Hz, 1500 s^{-1}. The activation parameters for the *cis*-Cp(CO)$_2$(PCy$_3$)MoH → *trans*-Cp(CO)$_2$(PCy$_3$)MoH isomerization were $\Delta H^\ddagger = 11.6 \pm 0.3$ kcal mol^{-1}, $\Delta S^\ddagger = -5.6 \pm 1.2$ cal K^{-1} mol^{-1}, and $\Delta G^\ddagger$ (25 °C) = 13.3 kcal mol^{-1} (see Figure S9 in the supporting information for an Eyring plot of these data). Using the measured K_{eq}, we determined the activation parameters for the *trans*-Cp(CO)$_2$(PCy$_3$)MoH → *cis*-Cp(CO)$_2$(PCy$_3$)MoH isomerization: $\Delta H^\ddagger = 11.6 \pm 0.3$ kcal mol^{-1}, $\Delta S^\ddagger = -1.2 \pm 1.2$ cal K^{-1} mol^{-1} and $\Delta G^\ddagger$ (25 °C) = 12.0 kcal mol^{-1}.

(b) With Added [BF$_4^-$]. An analogous procedure with the same amount of Cp(CO)$_2$(PCy$_3$)MoH (12 mg, 0.024 mmol) as described above was used, except that 0.11 M NBu$_4$BF$_4$ (19 mg, 0.057 mmol, 2.4 equiv) was added to this NMR solution. The activation parameters for the *cis*-Cp(CO)$_2$(PCy$_3$)MoH → *trans*-Cp(CO)$_2$(PCy$_3$)MoH isomerization with 100 mM NBu$_4$BF$_4$ were $\Delta H^\ddagger = 13.8 \pm 0.2$ kcal mol^{-1}, $\Delta S^\ddagger = 1.9 \pm 0.7$ cal K^{-1} mol^{-1}, and $\Delta G^\ddagger$ (25 °C) = 13.2 kcal mol^{-1}.

Thermodynamics for Cp(CO)$_2$(PR$_3$)MoH. The cis and trans isomers were measured in CD$_2$Cl$_2$ at several temperatures. The equilibrium constant *K* was defined as [cis]/[trans]. The values of ΔH and ΔS were obtained from plots of ln *K* vs T^{-1}. The percentages of cis and trans isomers at 25 °C were obtained from the extrapolated equilibrium constants.

(a) Cp(CO)$_2$(PMe$_3$)MoH. ^{1}H NMR spectra were recorded in the range −86 to −1 °C. ^{1}H NMR (−86 °C): cis (45%), δ 5.23 (s, *Cp*), 1.41 (d, J_{PH} = 9.5 Hz, P*Me$_3$*), −6.63 (d, J_{PH} = 65.7 Hz, Mo*H*); trans (55%), δ 5.06 (s, *Cp*), 1.46 (d, J_{PH} = 9.2 Hz, P*Me$_3$*), −6.46 (d, J_{PH} = 23.1 Hz, Mo*H*). The equilibrium constants were determined by integration of the cyclopentadienyl resonances. The following equilibrium constants K_{eq} at different temperatures were found: −86 °C, 0.81; −68 °C, 0.89; −56 °C, 0.93; −45 °C, 0.95; −35 °C, 0.99; −24 °C, 1.02; −12 °C, 1.07; −1 °C, 1.08. The thermodynamic data were $\Delta H = 0.34 \pm 0.02$ kcal mol^{-1}, $\Delta S = 1.4 \pm 0.1$ cal K^{-1} mol^{-1}, and ΔG (25 °C) = −0.083 kcal mol^{-1}. At 25 °C, K_{eq} was calculated as 1.15 (54% cis, 46% trans).

(b) Cp(CO)$_2$(PPh$_3$)MoH. ^{1}H NMR spectra were recorded over the range of −86 to −24 °C. ^{1}H NMR (−86 °C): cis (55%), δ 5.13 (s, *Cp*), −5.44 (d, J_{PH} = 62.9 Hz, Mo*H*); ^{31}P NMR (−86 °C) for cis: δ 72.6. NMR data for trans (45%), ^{1}H NMR (−86 °C): δ 4.91 (s, *Cp*), −6.27 (d, J_{PH} = 21.2 Hz, Mo*H*); ^{31}P NMR (−86 °C) for trans: δ 70.6. The equilibrium constants were determined by integration of the hydride resonances. The following equilibrium constants K_{eq} were found: −86 °C, 1.20; −68 °C, 1.27; −56 °C, 1.35; −45 °C, 1.40; −35 °C, 1.44; −24 °C, 1.49. The thermodynamic data were $\Delta H = 0.34 \pm 0.01$ kcal mol^{-1}, $\Delta S = 2.1 \pm 0.1$ cal K^{-1} mol^{-1}, and ΔG (25 °C) = −0.30 kcal mol^{-1}. At 25 °C, K_{eq} = 1.66, (62% cis, 38% trans).

(c) Cp(CO)$_2$(PCy$_3$)MoH. The cis and trans isomers were measured at low temperatures (−86 to −45 °C) before the cyclopentadienyl (or hydride) resonances became too flat to be integrated accurately. ^{1}H NMR (−86 °C): cis (89%), δ 5.24 (s, *Cp*), −6.25 (d, J_{PH} = 60.5 Hz, Mo*H*); trans (11%), δ 5.10 (s, *Cp*), −6.96 (d, J_{PH} = 20.0 Hz, Mo*H*). The percentages of two isomers were almost unchanged (changed <1%) from −86 to −45 °C. At 22 °C, the ratio of cis:trans was 91:9, which was calculated from the observed average phosphorus−hydride coupling constant (J_{PH} = 56.7 Hz).

Effect of Ionic Strength on the Kinetics of Cp(CO)$_2$(PCy$_3$)MoH with Excess Ph$_3$C$^+$BF$_4^-$. Four solutions of Ph$_3$C$^+$BF$_4^-$ (9 mM) with added NBu$_4$BF$_4$ (0, 11, 21, and 32 mM) in CH$_2$Cl$_2$ were prepared in CH$_2$Cl$_2$; a solution of Cp(CO)$_2$(PCy$_3$)MoH (1.2 mM in CH$_2$Cl$_2$) was also prepared. The kinetics studies were performed at 15 °C; the concentrations of reagents were half the initial ones because the volume was doubled during mixing. The rate constants decrease with increasing concentration of [BF$_4^-$]$_0$ (total [BF$_4^-$] = [Ph$_3$C$^+$BF$_4^-$] + [NBu$_4$BF$_4$]), but the effect is small (12% change over the range studied), as tabulated below:

total [BF$_4^-$]$_0$, mM	k_{obs} (s^{-1})
4.5	65
10	61
15	59
21	58

Kinetics of Cp(CO)$_2$(PCy$_3$)MoH with Excess Ph$_3$C$^+$BF$_4^-$. Cp(CO)$_2$(PCy$_3$)MoH (5.0 mg, 0.010 mmol) was weighed in a 25-mL volumetric flask and diluted to the mark with CH$_2$Cl$_2$ to give a 0.40 mM solution. Ph$_3$C$^+$BF$_4^-$ (13.2 mg, 0.040 mmol) and NBu$_4$BF$_4$ (90.2 mg, 0.274 mmol) were weighed in a 10-mL volumetric flask and diluted to the mark with CH$_2$Cl$_2$ to give a solution of [Ph$_3$C$^+$] = 4.0 mM with total [BF$_4^-$] = 31 mM. Another three concentrations of [Ph$_3$C$^+$] (9, 18, and 27 mM) with constant total ionic strength of 31 mM [BF$_4^-$] were prepared. The concentrations of reagents for the reported results below are half of those stated here since the volume is doubled during mixing.

(a) At −55 °C. The observed rate constants for the reactions of Cp(CO)$_2$(PCy$_3$)MoH (0.2 mM) with four [Ph$_3$C$^+$BF$_4^-$] concentrations (2, 4.5, 9, and 13.5 mM) were 0.58, 0.67, 0.73, and 0.84 s^{-1}, respectively. By fitting the equation, $k_{obs} = \{k_{CT}k_T/(k_{TC} + k_T[\mathrm{Ph_3C^+}]) + k_C\}[\mathrm{Ph_3C^+}]$ (where $k_T = 1.9 \times 10^4$ M^{-1} s^{-1}, $k_{CT} = 0.60$ s^{-1}, $k_{TC} = 5.4$ s^{-1}), k_C was determined as 19 M^{-1} s^{-1} (see Figure 3).

(b) At −35, −15, and 15 °C. The k_{obs}, intercept, and slope (from the line fit of 1/k_{obs} vs 1/[Ph$_3$C$^+$BF$_4^-$]) are tabulated below.

temp (°C)	[Ph$_3$C$^+$BF$_4^-$] (mM)	k_{obs} (s^{-1})	intercept (s)	slope (s·M)
−35	2.0	3.2	1.2×10^{-1}	3.8×10^{-4}
	4.5	5.0		
	9.0	6.3		
	13	6.8		
−15	2.0	9.7	1.4×10^{-2}	1.8×10^{-4}
	4.5	19		
	9.0	30		
	13	36		
15	2.0	27	4.2×10^{-4}	7.2×10^{-5}
	4.5	64		
	9.0	120		
	13	157		

Low-Temperature NMR Experiment of Cp(CO)$_2$(PPh$_3$)MoH with Ph$_3$C$^+$BF$_4^-$ in CD$_2$Cl$_2$. Cp(CO)$_2$(PPh$_3$)MoH (12.0 mg, 0.025 mmol) and Ph$_3$C$^+$BF$_4^-$ (8.2 mg, 0.025 mmol) were added to a 5-mm NMR tube equipped with a Teflon J. Young valve. CD$_2$Cl$_2$ (~0.5 mL) was added by vacuum transfer, and the solution was thawed at −78 °C. The tube was gently shaken, giving a color change from yellow to red, and then quickly removed from the cold bath and inserted into a precooled NMR probe (−80 °C). ^{1}H NMR spectra showed the initial formation of *trans*-Cp(CO)$_2$(PPh$_3$)MoFBF$_3$ (90%) and [*trans*-Cp(CO)$_2$(PPh$_3$)Mo(ClCD$_2$Cl)]$^+$[BF$_4^-$] (10%). The temperature of the NMR probe was gradually increased. ^{1}H and ^{31}P{^{1}H} NMR data and relative yields are tabulated below.

temp (°C)	*trans*-MoFBF$_3$ (%); ^{1}H: δ Cp ^{31}P{^{1}H}: δ PPh$_3$	*cis*-MoFBF$_3$ (%); δ Cp δ PPh$_3$	*trans*-Mo(ClCD$_2$Cl)$^+$ (%); δ Cp δ PPh$_3$
−80	90; 5.30 (br) 66.6 (d, J_{PF} = 19.9)		10; 5.39 (br) 59.3 (s)
−30	88; 5.34 (d, J_{PH} = 1.9) 66.5 (s)	2; 5.64 (s) 50.3 (br)	10; 5.44 (d, J_{PH} = 1.9) 59.0 (s)
−8	45; 5.36 (d, J_{PH} = 2.1) 66.5 (quintet, J_{PF} = 4.9)	52; 5.64 (s) 50.2 (quintet, J_{PF} = 8.4)	3; 5.47 (d, J_{PH} = 1.9) 58.8 (s)

The sample in this NMR tube was then monitored at −8 °C. After 30 min, *trans*-Cp(CO)$_2$(PPh$_3$)MoFBF$_3$ decreased to 16%, *cis*-Cp(CO)$_2$(PPh$_3$)MoFBF$_3$ increased to 84%, and [*trans*-Cp(CO)$_2$(PPh$_3$)Mo(ClCD$_2$Cl)]$^+$ was no longer observed. After 1 h at −8 °C, only 5% of *trans*-

$Cp(CO)_2(PPh_3)Mo(FBF_3)$ remained and *cis*-$Cp(CO)_2(PPh_3)MoFBF_3$ increased to 95%.

An analogous reaction was carried out at 25 °C, after which the NMR tube was cooled to at −80 °C. *cis*-$Cp(CO)_2(PPh_3)MoFBF_3$ was observed, with <1% *trans*-$CpMo(CO)_2(PPh_3)FBF_3$. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C) of *cis*-$Cp(CO)_2(PPh_3)MoFBF_3$: δ 50.6 (d, $J_{PF} = 29.4$ Hz).

NMR Tube Reaction of $Cp(CO)_2(PPh_3)MoH$ with Ph_3COTf in CD_2Cl_2. A solution of $Cp(CO)_2(PPh_3)MoH$ (7.3 mg, 0.015 mmol) in CD_2Cl_2 (0.3 mL) was added to a solution of Ph_3COTf (6.0 mg, 0.015 mmol) in CD_2Cl_2 (~0.3 mL), giving a red solution. After 20 min, *trans*-$Cp(CO)_2(PPh_3)MoOTf$ and *cis*-$Cp(CO)_2(PPh_3)MoOTf$ were observed by ^1H NMR, in a ratio of 90:10. ^1H NMR of *trans*-$Cp(CO)_2(PPh_3)MoOTf$: δ 5.29 (d, 5 H, *Cp*, $J_{PH} = 2.2$ Hz); *cis*-$Cp(CO)_2(PPh_3)MoOTf$: 5.62 (s, 5 H, *Cp*). $^{31}P\{^1H\}$ NMR of *trans*-$Cp(CO)_2(PPh_3)MoOTf$: δ 66.0 (s); *cis*-$Cp(CO)_2(PPh_3)MoOTf$: 50.2 (s). The trans complex slowly isomerized to cis complex. The following ratios were recorded at various times: 6 h, trans:cis = 55:45; 21 h, trans:cis = 42:58; 46 h, trans:cis = 8:92. The equilibrium constant was not precisely determined.

NMR Tube Reaction of $Cp(CO)_2(PPh_3)MoH$ with $Ph_3C^+BF_4^-$ in CD_3CN. $Cp(CO)_2(PPh_3)MoH$ (7.3 mg, 0.015 mmol) in CD_3CN (0.3 mL) was added to a CD_3CN solution of $Ph_3C^+BF_4^-$ (5.0 mg, 0.015 mmol). After 10 min, the NMR spectrum showed a 96:4 ratio of *trans*- to *cis*-$[CpMo(CO)_2(PPh_3)(CD_3CN)]^+[BF_4]^-$. ^1H NMR: trans, δ 5.35 (d, *Cp*, $J_{PH} = 1.8$ Hz); cis, 5.65 (s, Cp). $^{31}P\{^1H\}$ NMR: trans, δ 59.6 (s); cis, 52.4 (s).

NMR Tube Reaction of $Cp(CO)_2(PPh_3)MoH$ with Ph_3COTf in CD_3CN. A solution of $Cp(CO)_2(PPh_3)MoH$ (7.3 mg, 0.015 mmol) in CD_3CN (0.3 mL) was added to a solution of Ph_3COTf (6.0 mg, 0.015 mmol) in CD_3CN (0.3 mL) to give a yellow solution. The NMR spectrum indicated a trans:cis ratio of 96:4 for $[CpMo(CO)_2(PPh_3)(CD_3CN)]^+[OTf]^-$. ^1H NMR: trans, δ 5.36 (d, *Cp*, $J_{PH} = 1.8$ Hz); cis, 5.66 (s, *Cp*). $^{31}P\{^1H\}$ NMR: trans, δ 59.7 (s); cis, 52.7 (s).

NMR Tube Reaction of $Cp(CO)_2(PCy_3)MoH$ with $Ph_3C^+BF_4^-$, (a) in CD_2Cl_2. A solution of $Cp(CO)_2(PCy_3)MoH$ (9.5 mg, 0.019 mmol) in CD_2Cl_2 (0.3 mL) was added to a CD_2Cl_2 solution of $Ph_3C^+BF_4^-$ (6.3 mg, 0.019 mmol). An NMR spectrum recorded after 10 min showed only *cis*-$Cp(CO)_2(PCy_3)MoFBF_3$. ^1H NMR: δ 5.75 (s). $^{31}P\{^1H\}$ NMR: δ 51.5 (s).

(b) in CD_3CN. The analogous procedure was performed except that CD_3CN was used. The NMR spectra indicated a trans:cis ratio of 16:84 for $[CpMo(CO)_2(PCy_3)(CD_3CN)]^+[BF_4]^-$. ^1H NMR: trans, δ 5.57 (d, *Cp*, $J_{PH} = 1.2$ Hz); cis, 5.71 (s, *Cp*). $^{31}P\{^1H\}$ NMR: trans, δ 58.6 (s); cis, 49.9 (s).

Low-Temperature NMR Experiment of $Cp(CO)_2(PMe_3)MoH$ with $Ph_3C^+BF_4^-$ in CD_2Cl_2. The NMR reaction was performed at −78 °C as described above, with $Cp(CO)_2(PMe_3)MoH$ (7.5 mg, 0.025 mmol) and $Ph_3C^+BF_4^-$ (8.4 mg, 0.025 mmol). The tube was then quickly removed from the cold bath and inserted into a precooled NMR probe (−80 °C). The ^1H and $^{31}P\{^1H\}$ NMR data and relative yields are tabulated below.

temp (°C)	*trans*-$MoFBF_3$ (%); ^1H: δ Cp δ CH_3 $^{31}P\{^1H\}$: δ PMe_3	*cis*-$MoFBF_3$ (%); δ Cp δ CH_3 δ PMe_3	*trans*-$Mo(ClCD_2Cl)^+$ (%); δ Cp δ CH_3 δ PMe_3
−80	65; 5.42 (br)	9; 5.65 (s)	26; 5.52 (br)
	1.49 (d, $J_{PH} = 9.6$ Hz)	1.53 (d, $J_{PH} = 10.5$ Hz)	1.64 (d, $J_{PH} = 10.0$ Hz)
	26.2 (d, $J_{PF} = 20.5$)	15.09 (m br)	23.41 (s)
−60	61; 5.43 (br)	8; 5.63 (s)	31; 5.53 (br)
	1.50 (d, $J_{PH} = 9.9$ Hz)	1.54 (d, $J_{PH} = 10.5$ Hz)	1.65 (d, $J_{PH} = 10.3$ Hz)
	25.8 (d, $J_{PF} = 20.7$)	14.5 (quintet, $J_{PF} = 9.5$)	23.0 (s)
−40	57; 5.44 (br)	5; 5.64 (s)	38; 5.55 (br)
	1.51 (d, $J_{PH} = 9.9$ Hz)	1.56 (d, $J_{PH} = 10.4$ Hz)	1.67 (d, $J_{PH} = 10.3$ Hz)
	25.3 (m br)	14.0 (quintet, $J_{PF} = 9.5$)	22.6 (s)
−10	72; 5.45 (d, $J_{PH} = 2.3$)	8; 5.65 (s)	20; 5.57 (d, $J_{PH} = 2.1$)
	1.53 (d, $J_{PH} = 9.9$ Hz)	1.58 (d, $J_{PH} = 10.4$ Hz)	1.69 (d, $J_{PH} = 10.3$ Hz)
	24.9 (quintet, $J_{PF} = 5.2$)	13.2 (quintet, $J_{PF} = 9.5$)	22.0 (s)

The NMR spectrum was then monitored at −10 °C for 45 min. The percentages of the three complexes changed only slightly: *trans*-$CpMo(CO)_2(PMe_3)(FBF_3)$, 69%; *cis*-$CpMo(CO)_2(PMe_3)(FBF_3)$, 12%; CD_2Cl_2 complex, 19%. The temperature was increased to 10 °C; after 20 min, the relative amounts were 31% for *trans*-$CpMo(CO)_2(PMe_3)(FBF_3)$, 64% for *cis*-$CpMo(CO)_2(PMe_3)(FBF_3)$, and 5% for [*trans*-$Cp(CO)_2(PMe_3)Mo(ClCD_2Cl)]^+$. After 30 min, only 10% of *trans*-$CpMo(CO)_2(PMe_3)(FBF_3)$ remained, *cis*-$CpMo(CO)_2(PMe_3)(FBF_3)$ had increased to 90%, and [*trans*-$Cp(CO)_2(PMe_3)Mo(ClCD_2Cl)]^+$ was no longer observed.

An analogous reaction was done at 25 °C, after which the solution was cooled to −80 °C. The products ratio was ~99:1 *cis*-$Cp(CO)_2(PMe_3)MoFBF_3$:*trans*-$CpMo(CO)_2(PMe_3)MoFBF_3$.

Low-Temperature NMR Experiment of $Cp(CO)_2(PCy_3)MoH$ with $Ph_3C^+BF_4^-$. The NMR reaction was performed at −78 °C, as described above, by using $Cp(CO)_2(PCy_3)MoH$ (15.0 mg, 0.030 mmol) and $Ph_3C^+BF_4^-$ (9.9 mg, 0.030 mmol). The tube was quickly removed from the cold bath and inserted into a precooled NMR probe (−80 °C). A $^{31}P\{^1H\}$ NMR (CD_2Cl_2, −80 °C) spectrum showed the major peak at δ 51.2 (br), which was assigned to *cis*-$Cp(CO)_2(PCy_3)MoFBF_3$ (95%), and two small peaks at δ 62.0 (br) and δ 58.9 (s), which were assigned to *trans*-$Cp(CO)_2(PCy_3)MoFBF_3$ (4%) and $[Cp(CO)_2(PCy_3)Mo(ClCD_2Cl)]^+$ (1%). When temperature was increased to −40 °C, only *cis*-$Cp(CO)_2(PCy_3)MoFBF_3$ [δ 51.3 (d, $J_{PF} = 19.2$ Hz)] was observed.

NMR Tube Reaction of $Cp(CO)_2(PPh_3)MoH$ with $Ph_3C^+BF_4^-$ in CD_2Cl_2. A solution of $Cp(CO)_2(PPh_3)MoH$ (7.3 mg, 0.015 mmol) in CD_2Cl_2 (0.3 mL) was added to a CD_2Cl_2 solution of $Ph_3C^+BF_4^-$ (5.0 mg, 0.015 mmol) to give a red-purple solution of *cis*-$Cp(CO)_2(PPh_3)MoFBF_3$.[84] ^1H NMR (CD_2Cl_2): δ 7.60−7.30 (m, 15 H, P*Ph*$_3$), 5.65 (s, 5 H, *Cp*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 50.0 (br, s). IR (CH_2Cl_2): ν(CO) 1989 (vs), 1905 (s) cm^{-1}.

NMR Tube Reaction of $Cp(CO)_2(PMe_3)MoH$ with $Ph_3C^+BF_4^-$ in CD_2Cl_2. A procedure analogous to that described above gave *cis*-$Cp(CO)_2(PMe_3)MoFBF_3$.[85] ^1H NMR (CD_2Cl_2): δ 5.66 (s, 5 H, *Cp*), 1.60 (d, P*Me*$_3$, $J_{PH} = 10.3$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 12.4 (br). IR (CH_2Cl_2): ν(CO) 1989 (s), 1898 (s) cm^{-1}.

Kinetics for *trans*-$Cp(CO)_2(PR_3)MoH$. The k_{H^-} rate constants were obtained from plots of k_{obs} vs [*trans*-$Cp(CO)_2(PR_3)MoH$]. The concentrations of trans isomers were corrected for the small temperature dependence of the equilibrium constant K_{eq}.

Kinetic Measurements by Conventional Methods for Slow Reactions. Some reactions that were relatively slow for the stopped-flow experiment were measured by conventional methods on a UV−vis spectrophotometer. The reagent solutions were prepared in the glovebox. In an H-shaped apparatus containing one 1.00-cm UV−vis spectrophotometer cell and one tube (and both sides equipped with Teflon valves), 2.0 mL (volumetric pipet) of the Ph_3C^+ solution was placed in one side and 2.0 mL (volumetric pipet) of the metal hydride solution was placed in the other side. The H-shaped apparatus was removed from the glovebox and immersed into a constant-temperature bath (25 °C) for 5 min. After the temperature was equilibrated, the two solutions were mixed by shaking vigorously, and the UV−vis cell containing the mixture was quickly placed in a cell holder in a Hewlett-Packard 8452A diode-array spectrophotometer. The cell holder of the spectrometer was thermostated at 25 °C by using a recirculating constant-temperature bath. Spectra were recorded for ~10 half-lives.

Preparation of $CpW(CO)_3FBF_3$. $CpW(CO)_3FBF_3$ was synthesized and isolated by a published method[21,86] from the reaction of $Cp(CO)_3WH$ with $Ph_3C^+BF_4^-$ in CH_2Cl_2 at −40 °C. ^1H NMR (CD_2Cl_2, 22 °C): δ 6.10 (s, 5 H, *Cp*). IR (CH_2Cl_2): ν(CO) 2067 (s), 1975 (vs) cm^{-1}. Visible region in CH_2Cl_2: $\lambda_{max} = 500$ nm, $\epsilon = 5.9 \times 10^2$ M^{-1} cm^{-1}.

Preparation of $Cp(CO)_3MoFBF_3$. $Cp(CO)_3MoFBF_3$ was synthesized and isolated by a published method[21,86] from the reaction of $Cp(CO)_3MoH$ with $Ph_3C^+BF_4^-$ in CH_2Cl_2 at −40 °C. ^1H NMR (CD_2Cl_2, 22 °C): δ 5.96 (s, 5 H, *Cp*). IR (CH_2Cl_2): ν(CO) 2076 (s), 1995 (vs) cm^{-1}.

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Preparation of $Cp^*(CO)_3WFBF_3$. A solution of $Cp^*(CO)_3WH$ (270 mg, 0.666 mmol) in CH_2Cl_2 (8 mL) was transferred by cannula to a solution of $Ph_3C^+BF_4^-$ (200 mg, 0.606 mmol) in CH_2Cl_2 (10 mL) that had been cooled to −40 °C. The solution immediately turned red and then violet. After stirring the solution at −40 °C for 20 min, the solvent was reduced to ~5 mL and hexane (~20 mL) was added by vacuum transfer to precipitate the product; the product was collected by filtration, washed with hexane (5 mL × 3), and dried under vacuum to give $Cp^*(CO)_3WFBF_3$ (250 mg, 0.51 mmol, 84%) as a purple solid. ^1H NMR (CD_2Cl_2, 22 °C): δ 2.10 (s, 15 H, *Cp**). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 232.8 (s, 1 *C*O, $^1J_{CW} = 134$ Hz), 229.6 (s, 2 *C*O $^1J_{CW} = 164$ Hz), 109.6 (s, C_5Me_5), 10.6 (s, C_5Me_5). IR (CH_2Cl_2): ν(CO) 2050 (s), 1959 (vs) cm^{-1}. Visible region in CH_2Cl_2: $\lambda_{max} = 502$ nm, $\epsilon = 6.0 \times 10^2$ M^{-1} cm^{-1}. Anal. Calcd for $C_{13}H_{15}BF_4O_3W$: C, 31.87; H, 3.09. Found: C, 31.76; H, 3.25.

Preparation of *cis*-$Cp(CO)_2(PCy_3)MoFBF_3$. A solution of $Cp(CO)_2(PCy_3)MoH$ (503 mg, 1.01 mmol) in CH_2Cl_2 (15 mL) was added to a solution of $Ph_3C^+BF_4^-$ (315 mg, 0.96 mmol) in CH_2Cl_2 (10 mL) that had been cooled to −40 °C. The solution turned dark brown immediately and then violet when the addition was completed. The solution was stirred at −40 °C for 40 min, after which the solvent was reduced to ~5 mL and hexane (25 mL) was added. The mixture was kept at −78 °C for 3 h and then filtered while cold. The precipitate was collected by filtration, washed with hexane (5 mL × 2), and dried under vacuum to give $Cp(CO)_2(PCy_3)MoFBF_3$ (477 mg, 0.82 mmol, 85%) as a violet solid. ^1H NMR (CD_2Cl_2, 22 °C): δ 5.75 (s, 5 H, *Cp*), 1.25−2.70 [br, m, 33 H, $P(C_6H_{11})_3$]. $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 51.5 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 256.1 (d, *C*O, $^2J_{CP} = 24$ Hz), 251.4 (s, *C*O), 95.5 (s, C_5H_5), 34.7 (d, *C*H, $^1J_{CP} = 17$ Hz), 29.7 (d, CH_2, $^2J_{CP} = 55$ Hz), 27.7 (d, CH_2, $^3J_{CP} = 10$ Hz), 26.5 (s, CH_2). IR (CH_2Cl_2): ν(CO) 1976 (vs), 1893 (s) cm^{-1}. Visible region in CH_2Cl_2: $\lambda_{max} = 516$ nm, $\epsilon = 6.6 \times 10^2$ M^{-1} cm^{-1}. Anal. Calcd for $C_{25}H_{38}BF_4O_2PMo$: C, 51.39; H, 6.56. Found: C, 51.40; H, 6.94.

NMR Tube Reaction of $Cp^*(CO)_3MoH$ with $Ph_3C^+BF_4^-$ in CD_2Cl_2. A procedure analogous to that described above gave $Cp^*(CO)_3MoFBF_3$.[87] ^1H NMR (CD_2Cl_2): δ 1.98 (s, 15 H, *Cp**). IR (CD_2Cl_2): ν(CO) 2056 (s), 1974 (vs) cm^{-1}.

NMR Tube Reaction of $(CO)_4(PPh_3)MnH$ with $Ph_3C^+BF_4^-$ in CD_2Cl_2. A procedure analogous to that described above gave *cis*-$(CO)_4(PPh_3)Mn(FBF_3)$.[88] ^1H NMR (CD_2Cl_2): δ 7.65−7.36 (m, 15 H, PPh_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 42.1 (br, s). IR (CD_2Cl_2): ν(CO) 2114 (m), 2044 (sh), 2028 (s), 1977 (s) cm^{-1}.

NMR Tube Reaction of $(CO)_4(PPh_3)ReH$ with $Ph_3C^+BF_4^-$ in CD_2Cl_2. A procedure analogous to that described above gave *cis*-$(CO)_4(PPh_3)Re(FBF_3)$.[88] ^1H NMR (CD_2Cl_2): δ 7.63−7.42 (m, 15 H, PPh_3). $^{31}P\{^1H\}$ NMR (22 °C): δ 16.0 (quintet, $J_{PF} = 7.3$ Hz). IR (CH_2Cl_2): ν(CO) 2121 (m), 2021 (vs), 1964 (s) cm^{-1}.

NMR Tube Reaction of $(\eta^5\text{-}C_9H_7)(CO)_3WH$ with $Ph_3C^+BF_4^-$ in CD_2Cl_2. A procedure analogous to that described above gave $(\eta^5\text{-}C_9H_7)(CO)_3W(FBF_3)$.[21] ^1H NMR (CD_2Cl_2): δ 7.77−7.74 (m, 2 H), 7.66−7.61 (m, 2H), 6.15 (d, $J = 3$ Hz, 2 H), 6.10 (m, 1H). IR (CH_2Cl_2): ν(CO) 2062 (s), 1977 (vs) cm^{-1}.

Reaction of $(CO)_5MnH$ with $Ph_3C^+BF_4^-$ in CH_2Cl_2. $(CO)_5MnH$ (3.0 mg, 0.015 mmol) was weighed in a microsyringe and then dissolved in CH_2Cl_2 (0.5 mL). This solution was mixed with a solution of $Ph_3C^+BF_4^-$ (5.0 mg, 0.015 mmol) in CH_2Cl_2 (0.5 mL). Clean formation of $(CO)_5MnFBF_3$ was observed by IR. This product has been previously prepared[89] by reacting $CH_3Mn(CO)_5$ with $Ph_3C^+BF_4^-$. IR (CH_2Cl_2): ν(CO) 2073 (vs), 2016 (m) cm^{-1}.

Reaction of $(CO)_5ReH$ with $Ph_3C^+BF_4^-$ in CH_2Cl_2. A procedure analogous to that used for the Mn analogue was performed, giving $Re(CO)_5FBF_3$.[90] IR (CH_2Cl_2): ν(CO) 2057 (vs), 2002 (m) cm^{-1}.

NMR Tube Reaction of $Cp^*(CO)_3CrH$ with $Ph_3C^+BF_4^-$. A solution of $Cp^*(CO)_3CrH$ (8.5 mg, 0.031 mmol) in CD_2Cl_2 (0.3 mL) was added to a CD_2Cl_2 solution of $Ph_3C^+BF_4^-$ (10.3 mg, 0.031 mmol) in CD_2Cl_2. The reaction mixture turned deep green immediately and then black. ^1H NMR indicated that one equivalent of Ph_3CH was formed, but the initially formed metal complex decomposed to unidentified products.

NMR Tube Reaction of $Cp(NO)_2WH$ with $Ph_3C^+BF_4^-$. $Cp(NO)_2WH$ (5.3 mg, 0.017 mmol) was dissolved in CD_2Cl_2 (~0.3 mL) to give a bright green solution, which was added to a yellow CD_2Cl_2 solution of $Ph_3C^+BF_4^-$ (5.6 mg, 0.017 mmol). The reaction mixture turned darker green immediately. The ^1H NMR spectrum of the resulting solution showed that $Cp(NO)_2WH$ was completely consumed and two metal complexes were formed, with Cp resonances at δ 6.37 and δ 6.28 (relative integration ~1:1.2), which we assigned to $\{[CpW(NO)_2]_2(\mu\text{-}H)\}^+BF_4^-$ [δ 6.37 (s, 10 H, *Cp*), −8.60 (s, 1 H, W_2H, $J_{WWH} = 113$ Hz)][20] and $CpW(NO)_2(FBF_3)$ (δ 6.28, s, 5 H, *Cp*),[91] respectively.

Reaction of $(\eta^6\text{-}C_6Me_6)(CO)_2MnH$ with $Ph_3C^+BF_4^-$ in CH_3CN. $(\eta^6\text{-}C_6Me_6)(CO)_2MnH$ (2.7 mg, 0.010 mmol) was dissolved in CH_3CN (~0.5 mL). $Ph_3C^+BF_4^-$ (3.3 mg, 0.010 mmol) was dissolved in CH_3CN (0.5 mL), and the two solutions were mixed. The solvent was evaporated and the residue was redissolved in CD_2Cl_2. The ^1H NMR showed only $[(\eta^6\text{-}C_6Me_6)(CO)_2Mn(CH_3CN)]^+[BF_4]^-$ and Ph_3CH. ^1H NMR (CD_2Cl_2) of $[(\eta^6\text{-}C_6Me_6)(CO)_2Mn(NCCH_3)]^+[BF_4]^-$: δ 2.38 (s, 3 H, CH_3CN), 2.28 (s, 18 H, C_6Me_6). IR (CD_2Cl_2): ν(CO) 2002 (vs), 1954 (vs) cm^{-1}.

Competition Reaction of $(\eta^6\text{-}C_6Me_6)(CO)_2MnH$ and $Cp^*(CO)_3WH$ with $Ph_3C^+BF_4^-$. $(\eta^6\text{-}C_6Me_6)(CO)_2MnH$ (5.5 mg, 0.020 mmol, 2 equiv) and $Cp^*(CO)_3WH$ (8.1 mg, 0.020 mmol, 2 equiv) were dissolved in CD_3CN (~0.4 mL) in an NMR tube. After the initial spectrum was taken, this solution was added to a solution of $Ph_3C^+BF_4^-$ (3.3 mg, 0.010 mmol, 1 equiv) in CD_3CN (~0.1 mL). The reaction mixture displayed a ^1H NMR spectrum that showed the formation of $[(\eta^6\text{-}C_6Me_6)(CO)_2Mn(CD_3CN)^+]$ (δ 2.23, C_6Me_6) and $[Cp^*W(CO)_3(CD_3CN)^+]$ (δ 2.13, C_5Me_5) in a ratio of 4:1, with the remaining amounts of $(\eta^6\text{-}C_6Me_6)(CO)_2MnH$ and $Cp^*(CO)_3WH$ agreeing with the product formation.

Preparation of $Na(C_5H_4CO_2Me)W(CO)_3\cdot DME$.[92] A solution of $W(CO)_6$ (7.17 g, 20.38 mmol) and $Na(C_5H_4CO_2Me)$[93] (3.32 g, 22.7 mmol) was refluxed in DME (60 mL) for 2 days. The mixture was cooled and filtered to remove some green-gray insoluble material and unreacted $W(CO)_6$. The solvent was evaporated, and the sticky orange residue was washed with ether (100 mL) to give $Na(C_5H_4CO_2Me)(CO)_3W\cdot DME$ (5.24 g, 10.39 mmol, 51% yield) as a yellow solid. After drying under vacuum for 2 days, the product still contained 1 equiv of DME. IR (CH_2Cl_2): ν(CO) 1904 (s), 1805 (s), 1761 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 5.64 (t, 2 H, $H_{2,5}$, $J_{HH} = 2.4$ Hz), 5.10 (t, 2 H, $H_{3,4}$, $J_{HH} = 2.4$ Hz), 3.62 (s, 3 H, CH_3), 3.45 (s, 4 H, CH_2 of DME), 3.28 (s, 6 H, CH_3 of DME).

Preparation of $(C_5H_4CO_2Me)(CO)_3WH$.[92] CF_3COOH (0.37 mL, 4.80 mmol) was added to a solution of $Na(C_5H_4CO_2Me)(CO)_3W\cdot DME$ (1.90 g, 3.97 mmol) in THF (60 mL) at −78 °C. The reaction mixture immediately turned yellow. The solvent was evaporated, and the resulting grayish-yellow residue was extracted with hexane (70 mL). The light-yellow solution was concentrated to 5 mL and cooled to −78 °C for 10 min. The precipitate was collected by filtration and dried under vacuum to give $(C_5H_4CO_2Me)(CO)_3WH$ (885 mg, 2.38 mmol, 60% yield) as a pale yellow solid. (More product can be isolated by extracting the residue with diethyl ether, followed by adding hexane, and concentrating the solution mixture; however, the darker yellow solids obtained need to be purified by sublimation at 60 °C). ^1H NMR (CD_2Cl_2, 22 °C): δ 6.02 (t, 2 H, $H_{2,5}$, $J_{HH} = 2.3$ Hz), 5.57 (t, 2 H, $H_{3,4}$, $J_{HH} = 2.3$ Hz), 3.78 (s, 3 H, CH_3), −7.07 (s, 1 H, *WH*, $J_{WH} = 36.5$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 22 °C): δ 215.2 (br s, *C*O), 165.0 (s, *C*OO), 95.4 (s, *C*COO), 92.2 (s, $C_{2,5}$H), 90.4 (s, $C_{3,4}$H), 52.5 (s, CH_3).

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IR (CH_2Cl_2): ν(CO) 2028 (s), 1935 (vs), 1730 (m) cm^{-1}. Anal. Calcd for $C_{10}H_8O_5W$: C, 30.64; H, 2.06. Found: C, 30.79; H, 2.03.

Preparation of ($C_5H_4CO_2Me$)(CO)$_3$WFBF$_3$. A solution of ($C_5H_4CO_2Me$)(CO)$_3$WH (374 mg, 0.95 mmol) in CH_2Cl_2 (15 mL) was added to a solution of $Ph_3C^+BF_4^-$ (300 mg, 0.91 mmol) in CH_2Cl_2 (10 mL) at −30 °C. The resulting red solution was warmed to room temperature and stirred for 70 min. The solvent was reduced to 5 mL, hexane (25 mL) was added, and the precipitates were collected by filtration, washed with hexane (5 mL × 2), and dried under vacuum to give ($C_5H_4CO_2Me$)(CO)$_3$WFBF$_3$ (370 mg, 0.77 mmol, 85% yield) as maroon solid. ^{1}H NMR (CD_2Cl_2, 22 °C): δ 6.39 (t, 2 H, $H_{2,5}$, J_{HH} = 2.4 Hz), 6.30 (t, 2 H, $H_{3,4}$, J_{HH} = 2.4 Hz), 3.84 (s, 3 H, CH_3). ^{13}C{^{1}H} NMR (CD_2Cl_2, 22 °C): δ 225.9 (s, 1 *C*O), 221.4 (s, 2 *C*O), 164.0 (s, *C*OO), 101.3 (s, $C_{2,5}$H), 96.9 (s, *C*COO), 95.1 (s, $C_{3,4}$H), 53.4 (s, *C*H$_3$). IR (CH_2Cl_2): ν(CO) 2074 (s), 1990 (vs), 1736 (m) cm^{-1}. Anal. Calcd for $C_{10}H_7BF_4O_5W$: C, 25.14; H, 1.48. Found: C, 25.72; H, 2.00.

Preparation of Ph($Me_2NC_6H_4$)$_2C^+BF_4^-$. An aqueous solution (100 mL) of Ph($Me_2NC_6H_4$)$_2$COH·HCl (500 mg, 1.31 mmol) was mixed with an aqueous solution (5 mL) of NH_4BF_4 (151 mg, 1.44 mmol). The product precipitated as fine blue-green solids and was collected by filtration and recrystallized from CH_2Cl_2/Et_2O. ^{1}H NMR (CD_2Cl_2, 22 °C): δ 7.73 (apparent t, 1 H, J_{HH} = 7.4 Hz), 7.57 (apparent t, 2 H, J_{HH} = 7.4 Hz), 7.43−7.34 (m, 6H), 6.91 (d, 4 H, J_{HH} = 9.3 Hz), 3.32 (s, 12 H, CH_3).

Preparation of ($Me_2NC_6H_4$)$_3C^+BF_4^-$. An aqueous solution (20 mL) of ($Me_2NC_6H_4$)$_3$CCl (crystal violet; 600 mg, 1.47 mmol) was mixed with an aqueous solution (5 mL) of NH_4BF_4 (154 mg, 1.47 mmol). The product precipitated as a fine purple solid and was collected by filtration and recrystallized from CH_2Cl_2/Et_2O. ^{1}H NMR (CD_2Cl_2): δ 7.35 (d, 6 H, $C_6H_4NMe_2$, J_{HH} = 9.2 Hz), 6.85 (d, 6 H, $C_6H_4NMe_2$, J_{HH} = 9.2 Hz), 3.23 (s, 18 H, CH_3).

Reaction of Cp(CO)$_2$(PMe$_3$)MoH with Ph($Me_2NC_6H_4$)$_2C^+BF_4^-$. A solution of Cp(CO)$_2$(PMe$_3$)MoH (7.5 mg, 0.025 mmol) in CD_2Cl_2 (0.3 mL) was added to a solution of Ph($Me_2NC_6H_4$)$_2C^+BF_4^-$ (10.6 mg, 0.025 mmol) in CD_2Cl_2 (0.3 mL). After 1 h, ^{1}H NMR indicated that ∼67% of Ph($Me_2NC_6H_4$)$_2$CBF$_4$ was converted to Ph($Me_2NC_6H_4$)$_2$CH. Several unidentified metal products were formed, but CpMo(CO)$_2$(PMe$_3$)(FBF$_3$) was not observed.

Reaction of Cp(CO)$_2$(PMe$_3$)MoH with ($Me_2NC_6H_4$)$_3C^+BF_4^-$. An procedure analogous to that described above was used. After 2 days, only 6% of ($Me_2NC_6H_4$)$_3$CH was formed, and no Cp(CO)$_2$(PMe$_3$)MoFBF$_3$ was observed.

Preparation of (C_5H_4Me)(CO)$_3$WH. (C_5H_4Me)(CO)$_3$WH was synthesized analogously to Cp(CO)$_3$WH[70] but with use of C_5H_4Me instead of C_5H_6. The product was isolated as an orange oil. ^{1}H NMR (CD_2Cl_2): δ 5.50 (t, 2 H, C*H*, J_{HH} = 2.2 Hz), 5.34 (t, 2 H, C*H*, J_{HH} = 2.2 Hz), 2.20 (s, 3 H, CH_3), −7.17 (s, 1 H, W*H*, J_{WH} = 37.5 Hz). IR (hexane): ν(CO) 2023 (s), 1935 (vs) cm^{-1}.

NMR Tube Reaction of (C_5H_4Me)(CO)$_3$WH with $Ph_3C^+BF_4^-$ in CD_2Cl_2. ^{1}H NMR (CD_2Cl_2) for (C_5H_4Me)W(CO)$_3$(FBF$_3$): δ 6.17 (t, 2 H, C*H*, J_{HH} = 2.0 Hz), 5.52 (t, 2 H, C*H*, J_{HH} = 2.0 Hz), 1.91 (s, 3 H, CH_3). IR (CD_2Cl_2): ν(CO): 2063 (s), 1973 (vs) cm^{-1}.

Preparation of (CO)$_4$(PCy$_3$)MnH. (CO)$_4$(PCy$_3$)MnH was first reported by Hieber and co-workers.[94] We prepared it from reaction of (CO)$_5$MnH with PCy$_3$, using a procedure analogous to that for preparation of (CO)$_4$(PPh$_3$)MnH.[78] ^{1}H NMR (CD_2Cl_2, 22 °C): δ 2.04−1.18 [br m, 33 H, P(C_6H_{11})$_3$], −7.91 (d, 1 H, Mn*H*, J_{PH} = 34.5 Hz). ^{31}P{^{1}H} NMR (CD_2Cl_2, 22 °C): δ 70.9 (s).

NMR Tube Reaction of (CO)$_4$(PCy$_3$)MnH with $Ph_3C^+BF_4^-$ in CD_2Cl_2. ^{1}H NMR (22 °C) for (CO)$_4$(PCy$_3$)MnFBF$_3$: δ 2.40−1.14 [br m, 33 H, P(C_6H_{11})$_3$] ^{31}P{^{1}H} NMR (CD_2Cl_2, 22 °C): δ 54.5 (s).

NMR Tube Reaction of Cp(CO)$_2$(PCy$_3$)MoH with Ph$_3$COTf in CD_2Cl_2. The analogous procedure described above was used. The NMR spectra were recorded immediately and only *cis*-Cp(CO)$_2$(PCy$_3$)MoOTf was observed. ^{1}H NMR: δ 5.68 (s, 5 H, *Cp*). ^{31}P{^{1}H} NMR (22 °C): δ 51.0 (s).

NMR Tube Reaction of Cp(CO)$_3$WH with $Ph_3C^+BAr'_4{}^-$ in CD_2Cl_2. Cp(CO)$_3$WH (5.0 mg, 0.015 mmol) was dissolved in CD_2Cl_2 (∼0.3 mL) and was added to a CD_2Cl_2 solution of $Ph_3C^+BAr'_4{}^-$ (16.6 mg, 0.015 mmol). The ^{1}H NMR spectrum recorded in 5 min showed a major Cp resonance at δ 6.12, tentatively assigned to [Cp(CO)$_3$W(ClCD$_2$Cl)]$^+$BAr$'_4{}^-$. After 1 day, the peak at δ 6.12 was converted to a new (unidentified) resonance at δ 5.88.

Appendix

Analysis of the Kinetics Shown in Scheme 2, Involving Cis−Trans Equilibration of MH and Hydride Transfer from Both Isomers to Ph_3C^+

When the cis/trans equilibrium of MH favors the cis isomer, we can apply the steady-state approximation to [*trans*-MH]:

$$\frac{d[trans\text{-MH}]}{dt} = k_{CT}\,[cis\text{-MH}] - k_{TC}\,[trans\text{-MT}] - k_T\,[trans\text{-MH}]\,[Ph_3C^+] = 0 \quad (A1)$$

$$[trans\text{-MH}] = \frac{k_{CT}[cis\text{-MH}]}{k_{TC} + k_T[Ph_3C^+]} \quad (A2)$$

$$\frac{-\,d[cis\text{-MH}]}{dt} = k_{CT}[cis\text{-MH}] - k_{TC}[trans\text{-MH}] + k_C[cis\text{-MH}][Ph_3C^+] \quad (A3)$$

Substitution of [*trans*-MH] into this expression for − d[*cis*-MH]/d*t*, followed by algebraic manipulation, gives

$$\frac{-\,d[cis\text{-MH}]}{dt} = \left(\frac{k_{CT}k_T}{k_{TC} + k_T[Ph_3C^+]} + k_C\right)[Ph_3C^+][cis\text{-MH}] \quad (A4)$$

Note that the rate of disappearance of *cis*-MH is equal to the rate of disappearance of [Ph_3C^+] and the rate of appearance of product:

$$\frac{-\,d[cis\text{-MH}]}{dt} = \frac{-\,d[Ph_3C^+]}{dt} = \frac{d[\text{product}]}{dt} \quad (A5)$$

Three cases encountered in this work are described below:

1. For experiments using Cp(CO)$_2$(PCy$_3$)MoH with [Ph_3C^+] ≫ [MH], the minor isomer, *trans*-MH (11%), reacts much faster than *cis*-MH. The initial part of the reaction is too fast to be observed in our stopped-flow experiments. After this initial reaction, [*trans*-MH] reaches a steady-state concentration that does not significantly change during the rest of the reaction. The steady-state approximation is then valid, and we observe this part of the reaction. The rate is pseudo-first-order, with

$$\frac{-\,d[cis\text{-MH}]}{dt} = \frac{d[\text{product}]}{dt} = k_{obs}\,[cis\text{-MH}] \quad (A6)$$

where

$$k_{obs} = \left(\frac{k_{CT}k_T}{k_{TC} + k_T[Ph_3C^+]} + k_C\right)[Ph_3C^+] \quad (A7)$$

2. For experiments using Cp(CO)$_2$(PR$_3$)MoH with [MH] ≫ [Ph_3C^+], if the cis/trans equilibration is fast and k_{TC} ≫ k_T[Ph_3C^+], then a pseudo-first-order decay is again observed, and the steady-state approximation is valid. These conditions are applicable for our experiments with excess Cp(CO)$_2$(PCy$_3$)MoH (at all conditions investigated, from −20 to 25 °C) and for the determination of k_T of *trans*-Cp(CO)$_2$(PPh$_3$)MoH at 25 °C, the only temperature at which that was studied. From eq

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[94] Hieber, W.; Faulhaber, G.; Theubert, F. *Z. Anorg. Allg. Chem.* **1962**, *314*, 125−143.

A4 we obtain

$$\frac{\mathrm{d[product]}}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{Ph_3C^+}] \tag{A8}$$

where

$$k_{\mathrm{obs}} = \left(\frac{k_{\mathrm{CT}}k_{\mathrm{T}}}{k_{\mathrm{TC}}} + k_{\mathrm{C}}\right)[cis\text{-MH}] = \left(\frac{k_{\mathrm{T}}}{K_{\mathrm{eq}}} + k_{\mathrm{C}}\right)[cis\text{-MH}] \tag{A9}$$

In our experiments, since $k_{\mathrm{T}}/K_{\mathrm{eq}} \gg k_{\mathrm{C}}$, then

$$k_{\mathrm{obs}} = \frac{k_{\mathrm{T}}}{K_{\mathrm{eq}}}[cis\text{-MH}] = k_{\mathrm{T}}[trans\text{-MH}] \tag{A10}$$

In the more general case, $k_{\mathrm{obs}} = k_{\mathrm{T}}[trans\text{-MH}] + k_{\mathrm{C}}[cis\text{-MH}]$, and whether k_{T} or k_{C} dominates depends on the relative reactivities and concentrations of the two isomers.

The reaction mechanism in Scheme 2 was also modeled by numerically integrating the rate equations (i.e., the steady-state assumption was not used). This modeling showed that when $k_{\mathrm{T}}[\mathrm{Ph_3C^+}]_0 = k_{\mathrm{TC}}$, where $[\mathrm{Ph_3C^+}]_0$ is the initial $\mathrm{Ph_3C^+}$ concentration, and $[\mathrm{MH}] \gg [\mathrm{Ph_3C^+}]$, the observed first-order rate constant is only 16% greater than the one predicted by the steady-state approximation $\{k_{\mathrm{CT}}k_{\mathrm{T}}/(k_{\mathrm{TC}} + k_{\mathrm{T}}[\mathrm{Ph_3C^+}]_0)\}[\mathrm{MH}]$. Under these conditions the growth of product appears first-order, even though the change in the trans concentration is significant, $|\mathrm{d}[trans\text{-MH}]/\mathrm{d}t| \approx k_{\mathrm{CT}}[cis\text{-MH}] \approx k_{\mathrm{TC}}[trans\text{-MH}]$.

3. For experiments using $\mathrm{Cp(CO)_2(PMe_3)MoH}$, with $[trans\text{-MH}] \gg [\mathrm{Ph_3C^+}]$, the steady-state approximation is not needed.

$$\frac{\mathrm{d[product]}}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{Ph_3C^+}], \text{ where } k_{\mathrm{obs}} = k_{\mathrm{T}}[trans\text{-MH}]$$

This is the same equation that was obtained above (eq A10). These conditions are applicable for our experiments used to determine k_{T} for $\mathrm{Cp(CO)_2(PMe_3)MoH}$ at all temperatures investigated, from −55 to −25 °C. For these experimental conditions with $\mathrm{Cp(CO)_2(PMe_3)MoH}$, $k_{\mathrm{TC}} < k_{\mathrm{T}}[\mathrm{Ph_3C^+}]$; note, however, that this treatment is independent of k_{CT} and k_{TC}.

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Supporting Information Available: Plots of kinetics data: plot of absorbance vs time for the reaction of $\mathrm{(CO)_5ReH}$ with $\mathrm{Ph_3C^+BF_4^-}$ (Figure S1); plot of $\ln(A_t - A_\infty)$ vs time for the reaction of $\mathrm{(CO)_5ReH}$ with $\mathrm{Ph_3C^+BF_4^-}$ (Figure S2); plot of k_{obs} vs [MH] for $\mathrm{(CO)_5ReH}$ (Figure S3), $\mathrm{Cp^*(CO)_3WH}$ (Figure S4), $\mathrm{Cp(CO)_3WH}$ (Figure S5), *cis*-$\mathrm{(CO)_4(PPh_3)MnH}$ (Figure S6), $\mathrm{Cp(CO)_3MoH}$ and $\mathrm{Cp(CO)_3MoD}$ (Figure S7), and *trans*-$\mathrm{Cp(CO)_2(PCy_3)MoH}$ and *trans*-$\mathrm{Cp(CO)_2(PCy_3)MoD}$ (Figure S8); Eyring plot for *cis*-$\mathrm{Cp(CO)_2(PCy_3)MoH}$ → *trans*-$\mathrm{Cp(CO)_2(PCy_3)MoH}$ isomerization (Figure S9); and plot of log $k_{\mathrm{H^-}}$ vs $\mathrm{p}K_{\mathrm{R^+}}$ for $\mathrm{Ph}_n(p\text{-}\mathrm{MeOC_6H_4})_{3-n}\mathrm{C^+BF_4^-}$, for $n = 0, 1, 2, 3$ (Figure S10) (6 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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