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Hydride Transfer from (η^5-C_5Me_5)$(CO)_2$MH (M = Fe, Ru, Os) to Trityl Cation: Different Products from Different Metals and the Kinetics of Hydride Transfer

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Reactions of the metal hydride complexes $Cp^*(CO)_2MH$ (M = Fe, Ru, Os) with $Ph_3C^+BF_4^-$ in CH_2Cl_2 were studied. Hydride transfer from $Cp^*(CO)_2FeH$ to $Ph_3C^+BF_4^-$ gives $Cp^*(CO)_2FeFBF_3$. Hydride transfer from the ruthenium hydride $Cp^*(CO)_2RuH$ to $Ph_3C^+BF_4^-$ produces the bridging hydride complex $\{[Cp^*(CO)_2Ru]_2(\mu\text{-H})\}^+BF_4^-$, indicating that $Cp^*(CO)_2RuH$ exhibits significant nucleophilicity in addition to hydridic reactivity of the Ru−H bond. The osmium hydride $Cp^*(CO)_2OsH$ reacts with $Ph_3C^+BF_4^-$ in CH_2Cl_2 to give a mixture of $Cp^*(CO)_2OsFBF_3$ and $[Cp^*(CO)_2Os(ClCH_2Cl)]^+BF_4^-$. The kinetics of these hydride transfer reactions were monitored by stopped-flow methods, leading to the second-order rate law $-d[Ph_3C^+BF_4^-]/dt = k[Ph_3C^+BF_4^-][MH]$. The temperature dependence of the rate constants was determined for the iron hydride, the osmium hydride, and the osmium deuteride $Cp^*(CO)_2OsD$. Activation parameters for hydride transfer from $Cp^*(CO)_2FeH$ are $\Delta H^\ddagger = 2.6 \pm 0.1$ kcal mol^{-1} and $\Delta S^\ddagger = -22.1 \pm 0.4$ cal K^{-1} mol^{-1}; for $Cp^*(CO)_2OsH$ the activation parameters are $\Delta H^\ddagger = 4.9 \pm 0.1$ kcal mol^{-1} and $\Delta S^\ddagger = -16.8 \pm 0.5$ cal K^{-1} mol^{-1}. A kinetic isotope effect ($k_H/k_D = 1.6$ at 0 °C) was found for the reaction of $Cp^*(CO)_2OsD$. The order of kinetic hydricity is HRu > HFe > HOs. Second-order rate constants (extrapolated to 25 °C from data collected at lower temperatures) are $k = 3.2 \times 10^5$ M^{-1} s^{-1} for $Cp^*(CO)_2OsH$ and $k = 1.1 \times 10^6$ M^{-1} s^{-1} for $Cp^*(CO)_2FeH$; for $Cp^*(CO)_2RuH$, $k > 5 \times 10^6$ M^{-1} s^{-1} is estimated at 25 °C. Rate constants were also determined for hydride transfer to $Ph_2(p\text{-}MeOC_6H_4)C^+$ at 25 °C: $k = 1.5 \times 10^5$ M^{-1} s^{-1} for $Cp^*(CO)_2RuH$, $k = 4.1 \times 10^4$ M^{-1} s^{-1} for $Cp^*(CO)_2FeH$, and $k = 3.2 \times 10^3$ M^{-1} s^{-1} for $Cp^*(CO)_2OsH$.

Transition-metal hydrides are critically important in homogeneous catalysis and are involved in more than one step of many catalytic cycles. The delivery of hydrogen to an organic substrate in hydrogenations, hydroformylations, and other catalytic reactions is accomplished by reactions with metal−hydride bonds (M−H). An understanding of the factors influencing the rates of cleavage of M−H bonds will be useful in the rational design of new catalysts and the improvement of known catalysts. Some metal hydrides exhibit diverse modes of M−H bond cleavage in reactions with different substrates. Neutral metal carbonyl hydrides can undergo cleavage of their M−H bonds by proton transfer,[1] by homolytic cleavage resulting in hydrogen atom transfer,[2] and by hydride transfer.[3]

We have been studying ionic hydrogenations, in which organic substrates are hydrogenated by sequential delivery of a proton and a hydride. These reactions require hydride transfer from a metal to carbon, as has been found for stoichiometric ionic hydrogenations of alkenes,[4] alkynes,[5] and ketones.[6] Similar hydride transfer reactions are involved in the formation of ether complexes of tungsten from the reaction of acetals with acid and metal hydrides[7] and in the preparation of ketone complexes of tungsten from the ionic hydrogenation of α,β-unsaturated ketones.[8] We recently developed a series of homogeneous catalysts based on molybdenum and tungsten that catalyze the ionic hydrogenation of ketones.[9] Hydride transfer from a metal hydride is the product-forming step in these catalytic reactions as well. Several studies have reported the thermodynamics of hydride transfer from metal hydrides.[10] In view of the prevalence of hydride transfer reactivity of metal hydrides, it is worthwhile to know how the rates of hydride transfers are influenced by the metal and ligands. We reported a detailed study of the kinetics[11] and isotope

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[1] For a review of proton-transfer reactions of metal hydrides, see: Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; Chapter 9, pp 309−359.

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

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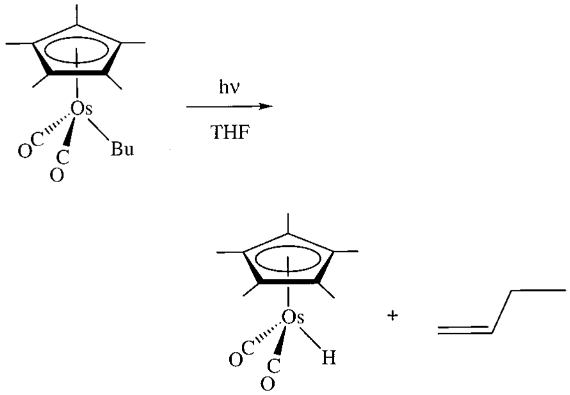
effects[12] of hydride transfer from a series of metal hydrides to Ph_3C^+ (eq 1). Hydride transfer from metal

$$Ph_3C^+BF_4^- + MH \xrightarrow{k_{H^-}} Ph_3C{-}H + M{-}F{-}BF_3 \quad (1)$$

hydrides to $Ph_3C^+BF_4^-$ produces complexes with a weakly bound BF_4^- ligand.[13] This prior work focused on the kinetic hydricity of group 6 and 7 hydrides such as $Cp(CO)_3MoH$, $Cp(CO)_3WH$, and $(CO)_5MnH$, along with phosphine-substituted derivatives of these complexes. Here we report a study of hydride transfer reactions of the group 8 metal hydrides $Cp^*(CO)_2MH$ (M = Fe, Ru, Os; $Cp^* = \eta^5\text{-}C_5Me_5$).

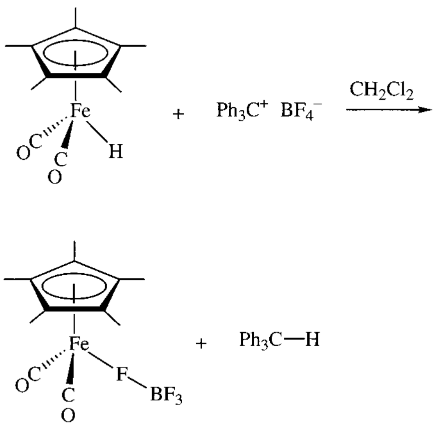
Results and Discussion

Synthesis of the Metal Hydrides $Cp^*(CO)_2MH$ (M = Fe, Ru, Os). The iron hydride $Cp^*(CO)_2FeH$ was prepared by Lapinte and co-workers from the reaction of $[Cp^*(CO)_3Fe]^+$ with $NaBH_4$.[14] We prepared $Cp^*(CO)_2FeH$ by protonation of the iron anion $[Cp^*(CO)_2Fe]^-$, which is synthesized by reduction of the dimer $[Cp^*(CO)_2Fe]_2$. A similar protonation reaction may be used for the preparation of the ruthenium hydride $Cp^*(CO)_2RuH$. An entirely different route was used for synthesis of the osmium hydride $Cp^*(CO)_2OsH$. This Os hydride was reported in 1982 by Graham and co-workers, who isolated it in 65% yield from the reaction of $Os_3(CO)_{12}$ and C_5Me_5H in an autoclave at 200 °C.[15] Geoffroy and co-workers reported that photolysis of $Cp^*(CO)_2Os(n\text{-}Bu)$ in the presence of PMe_3 gives $Cp^*(CO)(PMe_3)OsH$, while photolysis in the absence of phosphine releases 1-butene through a β-elimination reaction, and generates $Cp^*(CO)_2OsH$.[16] We developed this photochemical reaction into a viable preparative procedure (eq 2), leading to the isolation of $Cp^*(CO)_2OsH$ in high yield.



(2)

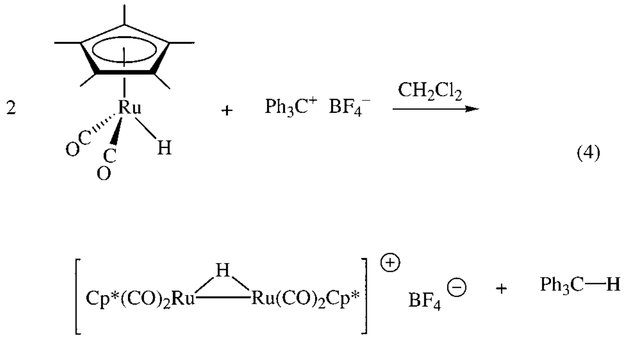
Characterization of Products Resulting from Hydride Transfer from $Cp^*(CO)_2MH$ (M = Fe, Ru, Os). Reaction of the iron hydride $Cp^*(CO)_2FeH$ with $Ph_3C^+BF_4^-$ in CH_2Cl_2 results in hydride transfer from iron to carbon (eq 3). The organometallic product was



(3)

$Cp^*(CO)_2FeFBF_3$, which was isolated and fully characterized. This complex, with a weakly bound FBF_3^- ligand, is the same type of product found in hydride transfer reactions of $Cp(CO)_3MoH$ and related Mo, W, Mn, and Re hydrides that we examined previously.[11] Our reactions use Cp*, but an iron complex with an unsubstituted Cp ligand was prepared by Mattson and Graham.[17] They reported the reaction of $Cp(CO)_2FeI$ with $AgBF_4$ and formulated the product as $Cp(CO)_2FeBF_4$, but they found that it readily decomposed.

Hydride transfer from $Cp^*(CO)_2RuH$ to $Ph_3C^+BF_4^-$ in CH_2Cl_2 (eq 4) generates a different type of product, a bimetallic complex with a bridging hydride, $\{[Cp^*(CO)_2Ru]_2(\mu\text{-}H)\}^+BF_4^-$. The initial (unobserved) product



(4)

that could result from hydride abstraction from $Cp^*(CO)_2RuH$ is the 16-electron cationic complex "$[Cp^*(CO)_2Ru]^+$", which could be weakly solvated by CH_2Cl_2, giving $[Cp^*(CO)_2Ru(ClCH_2Cl)]^+$, or might have a weakly coordinated FBF_3^- as in the analogous iron example. Regardless of the extent of stabilization of the initial complex generated from hydride abstraction, subsequent reaction of another 1 equiv of $Cp^*(CO)_2RuH$ produces the bridging hydride product. Stasunik and

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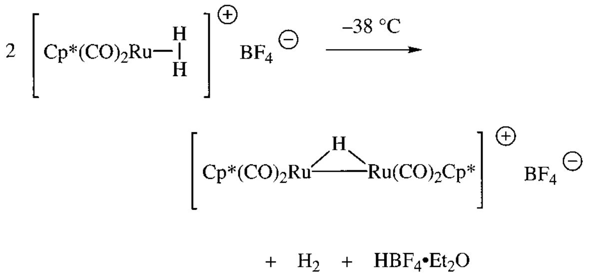
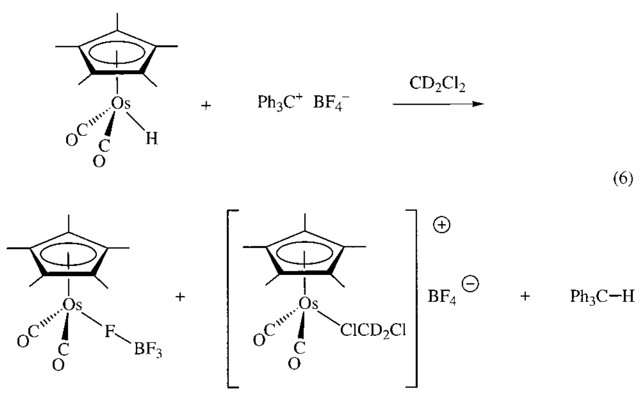
Malisch synthesized $\{[Cp^*(CO)_2Ru]_2(\mu\text{-}H)\}^+$ by protonation of the neutral dimer $[Cp^*(CO)_2Ru]_2$.[18] Heinekey and co-workers found that the same hydride-bridged complex is produced from decomposition of the dihydrogen complex $[Cp^*(CO)_2Ru(\eta^2\text{-}H_2)]^+$, as shown in eq 5.[19] Their reaction bears some similarity to the reaction in eq 4, since both form the same bimetallic product starting from a mononuclear precursor.



(5)

When $Cp^*(CO)_2OsH$ is reacted with $Ph_3C^+BF_4^-$ in CD_2Cl_2, clean hydride transfer occurred, as indicated by the detection of Ph_3CH in the NMR spectrum. An attempt to isolate the product when this reaction was carried out on a preparative scale resulted in an oily product, with no pure material being isolated. In the NMR tube reaction, one Cp* resonance was observed at room temperature, and no splitting of this singlet was observed when the solution was cooled to −100 °C. The IR spectrum, however, clearly indicated that two products were formed, since two pairs of bands were observed. One pair (2040 and 1982 cm^{-1}) is assigned as $Cp^*(CO)_2OsFBF_3$, analogous to the product from the Fe reaction. A slightly more intense pair of bands appearing at 2052 (s) and 2000 (s) cm^{-1} is assigned to a complex with a weakly coordinated CD_2Cl_2 ligand (eq 6). Addition of $Cp^*(CO)_2OsH$ resulted in the clean conversion of this mixture of Os complexes to a single species, $\{[Cp^*(CO)_2Os]_2(\mu\text{-}H)\}^+BF_4^-$, which is analogous to the hydride-bridged bimetallic Ru complex described above (eq 4). Complexes with CH_2Cl_2 or other halocarbon ligands[20] are often labile and highly reactive and are, thus, often characterized only in solution by spectroscopy.[21,22] There are, however, several examples of organometallic complexes with CH_2Cl_2 ligands that have proven stable enough for crystallographic studies.[23]

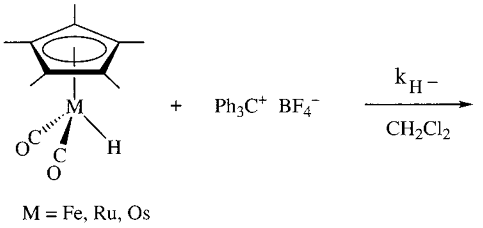


(6)

Similar results were obtained when using PF_6^- as the counterion, with IR and NMR data supporting the formation of $Cp^*(CO)_2OsFPF_5$ and $[Cp^*(CO)_2Os(ClCD_2Cl)]^+[PF_6]^-$ from the reaction of $Cp^*(CO)_2OsH$ with $Ph_3C^+PF_6^-$. Addition of CH_3CN to this mixture converts it to a single complex with an acetonitrile ligand, $[Cp^*(CO)_2Os(NCCH_3)]^+[PF_6]^-$. The THF complex $[Cp^*(CO)_2Os(THF)]^+[PF_6]^-$ was prepared similarly; its IR and NMR data agree with those reported by Graham.[15] Although FBF_3^- and FPF_5^- are weakly coordinating ligands, they bind more strongly than $BAr'_4{}^-$ (Ar′ = 3,5-bis(trifluoromethyl)phenyl). Hydride transfer from $Cp^*(CO)_2OsH$ to $Ph_3C^+BAr'_4{}^-$ yields a single product that exhibits IR bands at 2054 and 2002 cm^{-1} and is assigned as $[Cp^*(CO)_2Os(CH_2Cl_2)]^+[BAr'_4]^-$.

Beck and co-workers prepared related Mo and W complexes such as $Cp(CO)_3MoFBF_3$, $Cp(CO)_3MoFPF_5$, and $[Cp(CO)_3Mo(ClCH_2Cl)]^+[PF_6]^-$.[13,21] We found that when hydride transfers from the phosphine-substituted molybdenum hydrides $Cp(CO)_2(PR_3)MoH$ (R = Ph, Me) to $Ph_3C^+BF_4^-$ were monitored by low-temperature NMR in CD_2Cl_2, $[Cp(CO)_2(PR_3)Mo(CH_2Cl_2)]^+[BF_4]^-$ complexes were observed as kinetic products, with $Cp(CO)_2(PR_3)MoFBF_3$ being thermodynamically favored products.[11] Our studies on the $[Cp^*(CO)_2Os]^+$ system used [Os] concentrations around 0.02 M in CH_2Cl_2 solvent (15.6 M). The observation of both $Cp^*(CO)_2OsFBF_3$ and $[Cp^*(CO)_2Os(ClCD_2Cl)]^+[BF_4]^-$ under these conditions indicates that the binding of FBF_3^- to $[Cp^*(CO)_2Os]^+$ is roughly 1000 times stronger than that of CH_2Cl_2.

Kinetics of Hydride Transfer from $Cp^*(CO)_2MH$ (M = Fe, Ru, Os) to $Ph_3C^+BF_4^-$. The kinetics of hydride transfer from the Fe, Ru, and Os hydrides to $Ph_3C^+BF_4^-$ were determined in CH_2Cl_2 solution using stopped-flow techniques (eq 7), by monitoring the rate of disappearance of $Ph_3C^+BF_4^-$ at 450 nm ($\epsilon = 2.5 \times 10^4$ M^{-1} cm^{-1}). These experiments were carried out as described previously,[11] with initial concentrations of metal hydride typically 10−100 times larger than $[Ph_3C^+BF_4^-]$. Figure 1 shows a plot of the absorbance



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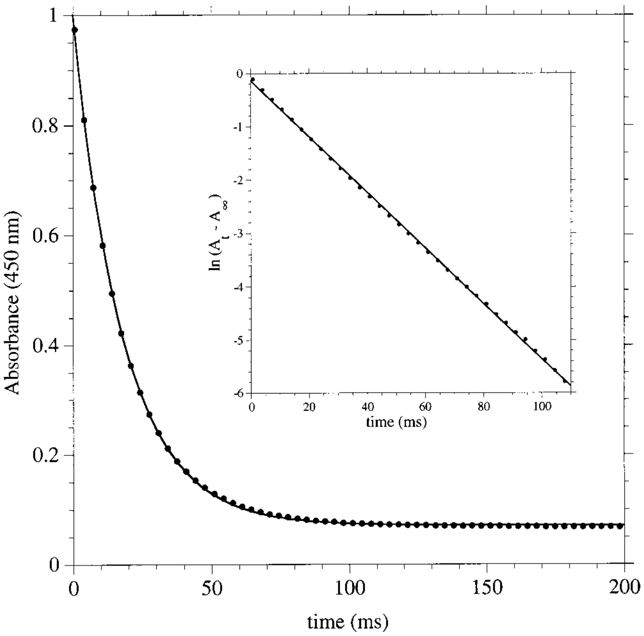

Figure 1. Plot of absorbance vs time for the reaction of $Cp^*(CO)_2OsH$ (1.5 mM) with $Ph_3C^+BF_4^-$ (0.05 mM) in CH_2Cl_2 at −30 °C. The main plot shows the stopped-flow data and the first-order fit. The inset shows a plot of $\ln(A_t - A_\infty)$ vs time for the same data, showing the linearity of this plot to more than 8 half-lives. For this and all other stopped-flow kinetics experiments, 300 data points were collected and analyzed; this plot is edited to show only every 5th point.

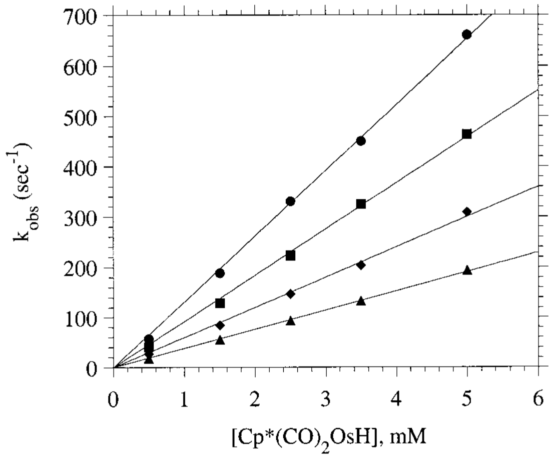

Figure 2. Plot of k_{obs} vs $[Cp^*(CO)_2OsH]$ for the reaction with $Ph_3C^+BF_4^-$ in CH_2Cl_2 at −30 °C (▲), −20 °C (◆), −10 °C (■), and 0 °C (●).

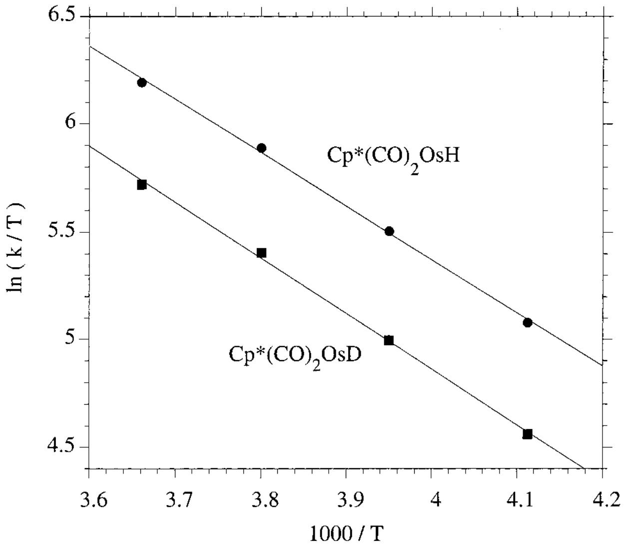

Figure 3. Plot of $\ln(k/T)$ vs $1000/T$ for the hydride transfer reactions of $Cp^*(CO)_2OsH$ (●) and $Cp^*(CO)_2OsD$ (■) with $Ph_3C^+BF_4^-$ in CH_2Cl_2.

vs time for hydride transfer from $Cp^*(CO)_2OsH$. The kinetics are very well-behaved, with plots of $\ln(A_t - A_\infty)$ vs time being linear for as much as 8 half-lives in some cases (see inset to Figure 1). The pseudo-first-order rate constants (k_{obs}) obtained from such data are plotted against the excess metal hydride concentrations, as shown in Figure 2 for hydride transfer reactions of $Cp^*(CO)_2OsH$ at variable temperatures. The slopes of these lines give the second-order rate constants for hydride transfer (k_{H^-} in eq 7). These data establish that the hydride transfer reactions follow the second-order rate law $-d[Ph_3C^+BF_4^-]/dt = k[Ph_3C^+BF_4^-][MH]$. The temperature dependence of the second-order rate constants was determined for $Cp^*(CO)_2FeH$ and $Cp^*(CO)_2OsH$ and the osmium deuteride $Cp^*(CO)_2OsD$. An Eyring plot is shown in Figure 3 for $Cp^*(CO)_2OsH$ and $Cp^*(CO)_2OsD$. The activation parameters derived from these data are given in Table 1, along with rate constants extrapolated to 25 °C. The low enthalpies of activation are similar to those reported previously for hydride transfers to $Ph_3C^+BF_4^-$ from *trans*-$Cp(CO)_2(PMe_3)MoH$, *trans*-$Cp(CO)_2(PCy_3)MoH$, *cis*-$(CO)_4(PPh_3)ReH$, and $Cp^*(CO)_3MoH$, which gave a $\Delta H^\ddagger$ range of 3.0−5.9 kcal/mol.[11]

The deuterium kinetic isotope effect[24] observed here (comparison of $Cp^*(CO)_2OsH$ vs $Cp^*(CO)_2OsD$) is $k_H/k_D = 1.6$ at 0 °C and is not significantly larger at lower temperatures (e.g., $k_H/k_D = 1.7$ at −30 °C). The maximum semiclassical isotope effect for rupture of the Os−H/Os−D bond may be calculated[24,25] using eq 8.

$$\frac{k_H}{k_D} = \exp\left\{\frac{hc}{2k_BT}(\bar{\nu}_{OsH} - \bar{\nu}_{OsD})\right\} \quad (8)$$

This equation incorporates several assumptions and is based on the zero-point energy contributions from the stretching frequencies of the Os−H and Os−D bonds. For the case of $Cp^*(CO)_2OsH$, substitution of only the Os−H (2054 cm^{-1}) and Os−D stretching frequencies gives $k_H/k_D = 4.0$ at 25 °C. The magnitudes of our observed kinetic isotope effects are significantly lower than 4.0, consistent with an early transition state for an irreversible single-step hydride transfer. A nonlinear Os−H−C geometry in the transition state could contribute to the small magnitude of the isotope effect observed here. More thorough discussions of the factors influencing kinetic isotope effects of hydride transfers from metal hydrides, and nuances of the detailed interpretation of their magnitude, have been given earlier.[12,24] Carbon-to-carbon hydride transfers have been studied in detail for NAD^+ systems, and such reactions generally exhibit much larger isotope effects,

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Table 1. Activation Parameters and Rate Constants for Hydride Transfer from Metal Hydrides to $Ph_3C^+BF_4^-$ (CH_2Cl_2)

metal hydride	$\Delta H^\ddagger$ (kcal mol^{-1})	$\Delta S^\ddagger$ (cal K^{-1} mol^{-1})	$\Delta G^\ddagger$(25 °C) (kcal mol^{-1})	k_{H^-}(25 °C) (M^{-1} s^{-1})	temp range (°C)
Cp*(CO)$_2$FeH	2.6 ± 0.1	−22.1 ± 0.4	9.2	1.1×10^6	−50 to −20
Cp*(CO)$_2$OsH	4.9 ± 0.1	−16.8 ± 0.5	10.0	3.2×10^5	−30 to 0
Cp*(CO)$_2$OsD	5.1 ± 0.1	−17.0 ± 0.6	10.2	2.0×10^5	−30 to 0

Table 2. Rate Constants for Hydride Transfer from Metal Hydrides to $Ph_2(p\text{-}MeOC_6H_4)C^+BF_4^-$ (CH_2Cl_2, 25 °C)

metal hydride	k_{H^-} (M^{-1} s^{-1})
Cp*(CO)$_2$FeH	4.1×10^4
Cp*(CO)$_2$RuH	1.5×10^5
Cp*(CO)$_2$OsH	3.2×10^3

as well as strong evidence for tunneling.[26,27] In contrast, our small isotope effects provide no evidence for tunneling in the hydride transfers from Cp*(CO)$_2$OsH, as much larger values of k_H/k_D would be expected if tunneling were involved. In addition, the temperature-dependent data provide an additional useful criterion for an assessment of the possible role of tunneling. On the basis of the differences in stretching frequencies for Os−H vs Os−D, the difference in zero-point energies for these bonds is about 0.8 kcal/mol. From the Arrhenius activation energies, $E_a^D - E_a^H = 0.2$ kcal/mol, which is much less than the differences in zero-point energies. Experimentally determined values of $E_a^D - E_a^H$ that significantly exceed the zero-point energy differences are generally taken as evidence of tunneling.[27]

The rate of hydride transfer from the ruthenium hydride is much higher than that found for either the Fe or Os analogues, and a complete study of the kinetics of hydride transfer from Cp*(CO)$_2$RuH to $Ph_3C^+BF_4^-$ could not be carried out. The reaction was studied at two concentrations of [Cp*(CO)$_2$RuH] at −55 °C, but at higher concentrations or higher temperatures, the rate of the reaction was too fast to be reliably determined using our stopped-flow equipment. On the basis of the limited data obtained, an estimate of $k_{H^-}(-55\ °C) \approx 8.6 \times 10^5$ M^{-1} s^{-1} is made for Cp*(CO)$_2$RuH. Extrapolation of the temperature-dependent data (Table 1) for Cp*(CO)$_2$FeH and Cp*(CO)$_2$OsH to −55 °C gives $k_{H^-}(-55\ °C) \approx 1.7 \times 10^5$ M^{-1} s^{-1} for Cp*(CO)$_2$FeH and $k_{H^-}(-55\ °C) \approx 1.1 \times 10^4$ M^{-1} s^{-1} for Cp*(CO)$_2$OsH. The rate constant for hydride transfer from Cp*(CO)$_2$RuH is about 5 times greater than that for Cp*(CO)$_2$FeH and roughly 80 times greater than that for Cp*(CO)$_2$OsH.

The kinetics of hydride transfer from all three Cp*(CO)$_2$MH hydrides to a substituted trityl cation was also examined. Addition of a methoxy group in the para position of one of the phenyl rings leads to a significant stabilization of the trityl cation, making it a weaker hydride acceptor. The rate constants were measured by stopped-flow methods, using the same procedure as for the unsubstituted $Ph_3C^+BF_4^-$ reactions, and the results are listed in Table 2. Comparison of the rate constants in Table 2 with those for $Ph_3C^+BF_4^-$ (Table 1) shows that hydride abstraction by the stabilized cation is more than 1 order of magnitude slower. A similar trend was found in our earlier study, with Cp*(CO)$_3$MoH being about 46 times slower (at 25 °C) at hydride transfer to $Ph_2(p\text{-}MeOC_6H_4)C^+$ than to Ph_3C^+.[11] The rate constant for hydride transfer from Cp*(CO)$_2$RuH to $Ph_2(p\text{-}MeOC_6H_4)C^+$ is about 4 times faster than that for Cp*(CO)$_2$FeH and about 47 times faster than that for Cp*(CO)$_2$OsH.

Comparison of Hydride Transfer from Cp*(CO)$_2$MH (M = Fe, Ru, Os) to Other Metal Hydrides. The data reported here for the group 8 hydrides may be compared with the results of our earlier study of hydricity of metal hydrides, which examined group 6 and 7 hydrides.[11] For Cp*(CO)$_3$CrH vs Cp*(CO)$_3$WH, and similarly for (CO)$_5$MnH vs (CO)$_5$ReH, the third-row metal hydrides exhibited a greater kinetic hydricity than their first-row analogues, by a factor of about 30−40 at 25 °C. That trend is reversed in the group 8 metal hydrides studied here, since Cp*(CO)$_2$FeH is a faster hydride donor than Cp*(CO)$_2$OsH. In all cases that we examined where the data can be directly compared, the rate constants for hydride transfer from second-row metal hydrides are greater than for the third-row analogues. The rate constant for hydride transfer from Cp*(CO)$_3$MoH exceeds that for Cp*(CO)$_3$WH, but only by a factor of about 3 at 25 °C. A larger increase in reactivity is apparent in going from Cp*(CO)$_2$RuH to Cp*(CO)$_2$OsH.

Comparison of the second-order rate constants shows that the group 8 hydrides Cp*(CO)$_2$MH are much faster hydride donors than the group 6 hydrides. Even the slowest group 8 hydride studied here, Cp*(CO)$_2$OsH, has a rate constant for hydride transfer ($k_{H^-} = 3.2 \times 10^5$ M^{-1} s^{-1}) which exceeds that of Cp*(CO)$_3$MoH ($k_{H^-} = 6.5 \times 10^3$ M^{-1} s^{-1}), by more than 1 order of magnitude at 25 °C. Since Cp*(CO)$_2$OsH has one less CO ligand than Cp*(CO)$_3$MoH, hydride transfer from Cp*(CO)$_3$MoH may have a more crowded transition state, but we do not think this is a major factor, since hydride transfers were found to be much less sensitive to steric issues compared to electronic effects.[11] The high hydricity of the Cp*(CO)$_2$MH systems may be partly due to the electronic effect of these complexes having only two CO ligands to withdraw electron density from the metal. In contrast, the three electron-withdrawing CO ligands in the Cr, Mo, and W hydrides Cp*(CO)$_3$MH could remove more electron density from the metal center, making those complexes less hydridic. Our studies on the Fe, Ru, and Os hydrides have been confined to the Cp*(CO)$_2$MH system, and we have not examined phosphine-substituted derivatives. It was shown earlier that substitution of one CO by a phosphine can substantially increase the kinetic hydricity. For example, $k_{H^-} = 5.7 \times 10^5$ M^{-1} s^{-1} for *trans*-Cp(CO)$_2$(PPh$_3$)MoH at 25 °C, which is some 3 orders of magnitude higher than that found for Cp(CO)$_3$MoH ($k_{H^-} = 3.8 \times 10^2$ M^{-1} s^{-1}). Thus the Fe, Ru, and Os hydrides, with no phosphine ligands, are of comparable kinetic hydricity to the Mo hydrides that have a phosphine ligand that dramatically en-

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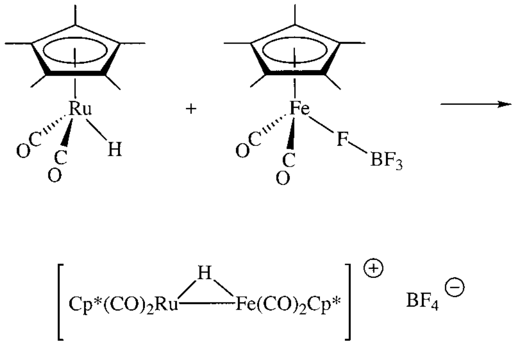
[26] (a) Kim, Y.; Truhlar, D. G.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1991**, *113*, 7837−7847. (b) Lee, I.-S. H.; Jeoung, E. H.; Kreevoy, M. M. *J. Am. Chem. Soc.* **2001**, *123*, 7492−7496.

[27] Kim, Y.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1992**, *114*, 7116−7123.

hances their hydricity. The rate constant k_{H^-} for Cp*(CO)$_2$RuH at 25 °C was not measured directly. Using the value from measurements at low temperature and the assumption that its temperature dependence is similar to that found for Cp*(CO)$_2$FeH leads to a rough estimate of $k_{H^-} \approx 5 \times 10^6$ M^{-1} s^{-1} for Cp*(CO)$_2$RuH at 25 °C. (Note that if Cp*(CO)$_2$RuH had the same activation parameters as those of Cp*(CO)$_2$OsH, then the estimated rate constant for Cp*(CO)$_2$RuH would be even higher, exceeding 10^7 M^{-1} s^{-1}.)

These hydride transfer reactions could proceed by a single-step direct hydride transfer or by a multistep mechanism initiated by electron transfer. If oxidation of the metal hydride by Ph$_3$C$^+$ occurred, then the initial product from this one-electron-transfer reaction would be the radical cation of the metal hydride (MH$^{\bullet+}$) and the carbon-centered radical, Ph$_3$C$^\bullet$; these two species would likely be present in a caged radical pair. Hydrogen atom transfer from MH$^{\bullet+}$ to Ph$_3$C$^\bullet$ would complete the overall hydride transfer. In our earlier study of hydride transfers, we were able to evaluate the viability of this alternative mechanism, relying on published data on the electrochemical oxidation of Cp(CO)$_3$MoH and reduction of Ph$_3$C$^+$.[11] We concluded that the electron transfer mechanism was much less likely than the direct hydride transfer, due largely to the barriers imposed by the oxidation of Cp(CO)$_3$MoH by Ph$_3$C$^+$ being thermodynamically unfavorable by about 0.9 V (about 21 kcal/mol). We suggest that the Fe, Ru, and Os hydrides undergo single-step hydride transfer to Ph$_3$C$^+$, though in the absence of electrochemical data for oxidation of the hydrides studied here, we cannot conclusively rule out the possible electron-transfer mechanism. The similarity of the kinetic isotope effect observed here ($k_{HOs}/k_{DOs} = 1.6$) to those found for hydride transfers from Cp*(CO)$_3$MoH, Cp(CO)$_3$MoH, Cp*(CO)$_3$WH, and *trans*-Cp(CO)$_2$(PCy$_3$)MoH ($k_H/k_D = 1.7-1.8$) also argues in favor of a common, single-step hydride transfer mechanism for all of these reactions.

The formation of Cp*(CO)$_2$FeFBF$_3$ from the hydride transfer reaction of Cp*(CO)$_2$FeH (eq 2) is expected, since analogous M−FBF$_3$ organometallic products were observed from the Mo, W, Mn, and Re hydrides studied previously. In contrast, hydride transfer from Cp*(CO)$_2$RuH produces the product with a bridging hydride (eq 4). We interpret this product to indicate that Cp*(CO)$_2$RuH exhibits significant nucleophilicity, in addition to its high hydricity. As discussed previously,[11] hydricity and nucleophilicity often parallel one another, but they are distinct properties. Hydricity refers to cleavage of an M−H bond as a hydride, while nucleophilicity is a measure of the ability of the electron pair in an M−H bond to function as a nucleophile. It is possible that Cp*(CO)$_2$RuFBF$_3$ forms initially following hydride transfer from Cp*(CO)$_2$RuH, but if this does occur, then nucleophilic displacement of the weakly bound FBF$_3^-$ by Cp*(CO)$_2$RuH must occur promptly, leading to the observed product. Nucleophilic displacement of the FBF$_3^-$ of Cp*(CO)$_2$FeFBF$_3$ was observed when Cp*(CO)$_2$FeFBF$_3$ was reacted with either Cp*(CO)$_2$RuH or Cp*(CO)$_2$OsH, as shown in eq 9 for the Ru example.



(9)

Experimental Section

General Considerations. All manipulations were carried out under an atmosphere of argon 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 CHDCl$_2$ 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)$_2$Ru]$_2$,[28] Cp*(CO)$_2$Os(*n*-Bu),[16] and Ph$_2$(*p*-MeOC$_6$H$_4$)C$^+$BF$_4^-$ [29] were prepared as previously reported. Cp*(CO)$_2$OsD was also prepared by a literature route[30] and was found by ^{1}H NMR to have 91% D. Ph$_3$C$^+$BF$_4^-$ was purchased from Aldrich, purified by recrystallization from CH$_2$Cl$_2$/Et$_2$O, and stored under argon in the dark at −30 °C.

Cp*(CO)$_2$FeH was prepared as reported previously.[31] ^{1}H NMR (CD$_2$Cl$_2$): δ 1.91 (s, 15 H, *Cp**), −11.95 (s, 1 H, Fe*H*). IR (THF): ν(CO) 1994, 1933 cm^{-1}.

Preparation of Cp*(CO)$_2$RuH. This preparation is a slight modification of that reported by Malisch.[32] Potassium (0.47 g, 12 mmol, 5 equiv) was cut into small pieces and added to a solution of [Cp*(CO)$_2$Ru]$_2$ (1.4 g, 2.4 mmol, 1 equiv) in THF (25 mL). The mixture was refluxed for 40 h and turned dark orange-brown. It was filtered through Celite, and CH$_3$COOH (1.4 mL, 24 mmol) was added. The solution turned lighter and was stirred for 30 min. The solvent was evaporated, and the residue was extracted with hexane (70 mL) and filtered. The solvent was evaporated, and the residue was sublimed at 50 °C to give pale yellow crystals (1.0 g, 3.4 mmol, 71% yield). ^{1}H NMR (CD$_2$Cl$_2$): δ 2.05 (s, 15 H, *Cp**), −10.71 (s, 1 H, Ru*H*). IR (CH$_2$Cl$_2$): ν(CO) 2005, 1939 cm^{-1}.

Preparation of Cp*(CO)$_2$OsH. A solution of Cp*(CO)$_2$Os(*n*-Bu) (400 mg, 0.912 mmol) in THF (30 mL) in a Pyrex bulb was photolyzed using an Ace-Hanovia 450 W high-pressure mercury vapor lamp. The lamp was jacketed by water, and the reaction bulb was placed ~5 cm away from the lamp. The colorless solution was irradiated and gradually turned yellow. The reaction was monitored by IR spectroscopy and was complete after 22 h. The solvent was evaporated, and the residue was sublimed at 50 °C to give white crystals of Cp*(CO)$_2$OsH (328 mg, 0.858 mmol, 94%). ^{1}H NMR (CD$_2$Cl$_2$): δ 2.20 (s, 15 H, *Cp**), −14.08 (s, 1 H, Os*H*). IR (THF): ν(CO) 1990 (s), 1928 (s); ν(OsH) 2054 (w) cm^{-1}. IR (hexane): ν(CO) 2001 (s), 1941 (s); ν(OsH) 2060 (w) cm^{-1}.

Preparation of Cp*(CO)$_2$FeFBF$_3$. A solution of Cp*(CO)$_2$FeH (250 mg, 1.01 mmol) in CH$_2$Cl$_2$ (15 mL) was added to a solution of Ph$_3$C$^+$BF$_4^-$ (317 mg, 0.96 mmol) in CH$_2$Cl$_2$ (10 mL) that was cooled to −30 °C. The solution turned red

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immediately and was stirred at −30 °C for 30 min. The solvent was reduced to 5 mL, and hexane (20 mL) was added, resulting in a precipitate. The mixture was kept at −78 °C for 30 min and then filtered while cold. The maroon solids were washed with hexane (5 mL × 2) and dried under vacuum to give Cp*(CO)$_2$FeFBF$_3$ (240 mg, 0.719 mmol, 75%). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.71 (s, 15 H, *Cp**). IR (CH$_2$Cl$_2$): ν(CO) 2054 (s), 2004 (s) cm^{-1}. Anal. Calcd for $C_{12}H_{15}BF_4O_2Fe$: C, 43.56; H, 4.57. Found: C, 43.61; H, 4.76.

NMR Tube Reaction of Cp*(CO)$_2$RuH with Ph$_3$C$^+$BF$_4^-$ in CD$_2$Cl$_2$. A solution of Cp*(CO)$_2$RuH (5.8 mg, 0.020 mmol) in CD$_2$Cl$_2$ (0.3 mL) was added to a CD$_2$Cl$_2$ solution (0.3 mL) of Ph$_3$C$^+$BF$_4^-$ (3.3 mg, 0.010 mmol) to give a yellow solution. The ^{1}H NMR spectrum showed the clean formation of {[Cp*(CO)$_2$Ru]$_2$(μ-H)}$^+$[BF$_4$]$^-$: δ 2.06 (s, 30 H, C$_5$*Me*$_5$), −17.75 (s, 1 H, Ru*H*). IR (CD$_2$Cl$_2$): ν(CO) 2046 (w), 2020 (vs), 1989 (vs) cm^{-1}. These data are in agreement with the NMR and IR data previously reported by Malisch.[18] Although this reaction as reported uses a 1:2 ratio of [Ph$_3$C$^+$] and [Cp*(CO)$_2$RuH], the same bridging hydride product was observed when a 1:1 ratio of reagents was used.

NMR Tube Reaction of Cp*(CO)$_2$OsH with Ph$_3$C$^+$BF$_4^-$ in CD$_2$Cl$_2$. A solution of Cp*(CO)$_2$OsH (4.5 mg, 0.012 mmol) in CD$_2$Cl$_2$ (0.3 mL) was added to a CD$_2$Cl$_2$ solution (0.3 mL) of Ph$_3$C$^+$BF$_4^-$ (3.9 mg, 0.012 mmol), resulting in a yellow solution. The ^{1}H NMR spectrum showed a single new Cp* resonance for the reaction at δ 2.13. A single resonance was still observed down to −100 °C; a small temperature dependence of the chemical shift was observed as the temperature was lowered incrementally, with the resonance appearing at δ 2.03 at −100 °C. However, two pairs of CO bands were observed in the IR spectrum (CD$_2$Cl$_2$). One pair was at 2040 (m) and 1982 (m) cm^{-1} and is assigned as Cp*(CO)$_2$OsFBF$_3$. The other pair of bands was observed at 2052 (s) and 2000 (s) cm^{-1} and is assigned as [Cp*(CO)$_2$Os(CD$_2$Cl$_2$)]$^+$[BF$_4$]$^-$. Another 1 equiv of Cp*(CO)$_2$OsH was added to this reaction mixture, and the ^{1}H NMR indicated the formation of {[Cp*(CO)$_2$Os]$_2$(μ-H)}$^+$[BF$_4$]$^-$. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.22 (s, 30 H, C$_5$*Me*$_5$), −19.59 (s, 1 H, Os*H*Os). IR (CD$_2$Cl$_2$): ν(CO) 2031 (m), 2011 (vs), 1976 (vs).

NMR Tube Reaction of Cp*(CO)$_2$OsH with Ph$_3$C$^+$PF$_6^-$. A solution of Cp*(CO)$_2$OsH (3.9 mg, 0.010 mmol) in CD$_2$Cl$_2$ (0.3 mL) was added to a solution of Ph$_3$C$^+$PF$_6^-$ (3.9 mg, 0.010 mmol) in CD$_2$Cl$_2$ (0.3 mL), resulting in a yellow solution. The ^{1}H NMR spectrum showed one new Cp* resonance for the reaction at δ 2.12. However, two pairs of CO bands were observed in the IR spectrum (CD$_2$Cl$_2$). One pair was at 2036 (m, sh) and 1982 (m) cm^{-1} and is assigned as Cp*(CO)$_2$OsFPF$_5$. The other pair of bands was observed at 2051 (s) and 2000 (s) cm^{-1} and is assigned as [Cp*(CO)$_2$Os(CD$_2$Cl$_2$)]$^+$[PF$_6$]$^-$. CH$_3$CN (~5 μL, 0.096 mmol) was added to this solution, and the ^{1}H NMR spectrum showed the formation of [Cp*(CO)$_2$Os(NCCH$_3$)]$^+$[PF$_6$]$^-$. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.12 (s, 15 H, C$_5$*Me*$_5$), 2.70 (s, 3 H, C*H*$_3$). IR (CD$_2$Cl$_2$): ν(CO) 2049 (s), 1993 (s).

Reaction of Cp*(CO)$_2$OsH with Ph$_3$C$^+$BAr′$_4^-$. A solution of Cp*(CO)$_2$OsH (1.9 mg, 0.005 mmol) in CH$_2$Cl$_2$ (0.3 mL) was added to a CH$_2$Cl$_2$ solution (0.3 mL) of Ph$_3$C$^+$BAr′$_4^-$ (5.5 mg, 0.005 mmol). An IR spectrum showed one pair of CO bands (2054 (s), 2002 (s) cm^{-1}) for the product, which was assigned as [Cp*(CO)$_2$Os(CH$_2$Cl$_2$)]$^+$[BAr′$_4$]$^-$.

Preparation of [Cp*(CO)$_2$Os(THF)]$^+$[PF$_6$]$^-$. A solution of Cp*(CO)$_2$OsH (4.5 mg, 0.012 mmol) in CD$_2$Cl$_2$ (0.3 mL) was added to a solution of Ph$_3$C$^+$PF$_6^-$ (4.6 mg, 0.012 mmol) in CD$_2$Cl$_2$ (0.3 mL), giving a yellow solution. THF (5 μL, 0.062 mmol) was added, and the solution turned pale yellow. The NMR spectrum showed the formation of [Cp*(CO)$_2$Os(THF)]$^+$[PF$_6$]$^-$. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.07 (s, 15 H, C$_5$*Me*$_5$), 3.95 (m, 4 H, C*H$_2$* of THF), 2.04 (m, 4 H, C*H$_2$* of THF). IR (CD$_2$Cl$_2$): ν(CO) 2036 (s), 1981 (s) cm^{-1}, in agreement with the NMR and IR data reported by Graham for this complex.[15]

Stopped-Flow Kinetics Experiments. The kinetics were determined as described in our previous study of hydride transfer reactions,[11] using a Hi-Tech Scientific SF-40 Canterbury stopped-flow instrument. All experiments were carried out using an excess of the metal hydride over the Ph$_3$C$^+$BF$_4^-$ concentration. For the kinetics of hydride transfer from Cp*(CO)$_2$RuH to Ph$_3$C$^+$BF$_4^-$, two pseudo-first-order rate constants (k_{obs}) were obtained: for [Cp*(CO)$_2$RuH] = 0.5 mM and [Ph$_3$C$^+$BF$_4^-$] = 0.05 mM, $k_{obs} = 440\ s^{-1}$; for [Cp*(CO)$_2$RuH] = 1 mM and [Ph$_3$C$^+$BF$_4^-$] = 0.05 mM, $k_{obs} = 840\ s^{-1}$. The average second-order rate constant derived from these data is $k_{H^-}(-55\ °C) \approx 8.6 \times 10^5\ M^{-1}\ s^{-1}$. When higher concentrations of [Cp*(CO)$_2$RuH] were used, the rate constants became too fast to be reliably determined using our stopped-flow instrument.

Activation parameters (Table 1) were determined from the temperature dependence of the rate constants using KINPAR, a Macintosh program provided by Prof. Jack Norton.

NMR Tube Reaction of Cp*(CO)$_2$OsH with Cp*(CO)$_2$FeFBF$_3$. A solution of Cp*(CO)$_2$OsH (5.0 mg, 0.013 mmol) in CD$_2$Cl$_2$ (0.6 mL) was added to Cp*(CO)$_2$FeFBF$_3$ (4.4 mg, 0.013 mmol), giving an orange solution. The NMR spectrum indicated the formation of [Cp*(CO)$_2$Os(μ-H)Fe(CO)$_2$Cp*]$^+$[BF$_4$]$^-$. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.18 (s, 15 H, C$_5$*Me*$_5$), 1.97 (s, 15 H, C$_5$*Me*$_5$), −22.96 (s, 1 H, Os*H*Fe). IR (CD$_2$Cl$_2$): ν(CO) 2040 (m), 2011 (vs), 1979 (vs) cm^{-1}.

NMR Tube Reaction of Cp*(CO)$_2$RuH with Cp*(CO)$_2$FeFBF$_3$. A solution of Cp*(CO)$_2$RuH (5.9 mg, 0.020 mmol) in CD$_2$Cl$_2$ (0.6 mL) was added to Cp*(CO)$_2$FeFBF$_3$ (6.7 mg, 0.020 mmol), giving an orange solution. The NMR spectrum indicated the formation of [Cp*(CO)$_2$Ru(μ-H)Fe(CO)$_2$Cp*]$^+$[BF$_4$]$^-$. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.03 (s, 15 H, C$_5$*Me*$_5$), 1.92 (s, 15 H, C$_5$*Me*$_5$), −21.63 (s, 1 H, Ru*H*Fe). IR (CD$_2$Cl$_2$): ν(CO) 2045 (m), 2012 (vs), 1987 (vs) cm^{-1}.

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