J. Am. Chem. Soc. **1994**, *116*, 8602-8612

Ionic Hydrogenations of Hindered Olefins at Low Temperature. Hydride Transfer Reactions of Transition Metal Hydrides

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Received March 3, 1994[⊛]

Abstract: Sterically hindered olefins can be hydrogenated at −50 °C in dichloromethane using triflic acid (CF_3SO_3H) and a hydride donor. Mechanistic studies indicate that these reactions proceed by hydride transfer to the carbenium ion that is formed by protonation of the olefin. Olefins that form tertiary carbenium ions upon protonation are hydrogenated in high yields (90–100%). Styrenes generally produce lower yields of hydrogenated products (50–60%). Suitable hydride donors include $HSiEt_3$ and several transition metal carbonyl hydrides ($HW(CO)_3Cp$, $HW(CO)_3Cp^*$, $HMo(CO)_3Cp$, $HMn(CO)_5$, $HRe(CO)_5$, and $HOs(CO)_2Cp^*$; $Cp = \eta^5\text{-}C_5H_5$, $Cp^* = \eta^5\text{-}C_5Me_5$). A characteristic that is required for transition metal hydrides to be effective is that the cationic dihydrides (or dihydrogen complexes) that result from their protonation must have sufficient acidity to transfer a proton to the olefin, as well as sufficient thermal stability to avoid significant decomposition on the time scale of the hydrogenation reaction. Metal hydrides that fail due to insufficient stability of their protonated forms include $HMo(CO)_2(PPh_3)Cp$, $HMo(CO)_3Cp^*$, and $HFe(CO)_2Cp^*$. Other hydrides that fail are those that are protonated to give dihydrides or dihydrogen complexes that are not sufficiently acidic to protonate olefins, as found for $HW(CO)_2(PMe_3)Cp$ and $HRu(CO)(PMe_3)Cp$.

Although all complexes with a bond from a metal to hydrogen are called metal hydrides, not all metal hydrides exhibit hydridic reactivity.[1] The hydridic reactivity associated with main group hydrides such as $LiAlH_4$ (e.g., reduction of ketones and prompt formation of H_2 upon reaction with water) is also exhibited by many early metal hydrides such as $[Cp_2ZrHCl]_n$. Anionic metal carbonyl hydrides[2] such as $HV(CO)_3Cp^-$ and $HW(CO)_5^-$ also exhibit hydridic reactivity and have been employed in the reduction of ketones,[3] alkyl halides,[4,5] and acyl chlorides.[6] Recent studies relevant to hydrogenase enzymes have involved transition metal hydrides—the metalloporphyrin hydride[7] $[HRu(OEP)(THF)]^-$ and the ruthenium hydride[8] $HRu(dppm)Cp^*$ have been found to transfer H^- to NAD^+ model compounds.

In contrast to this evidence for hydridic reactivity, *neutral* metal carbonyl hydrides such as $HW(CO)_3Cp$ often exhibit acidic behavior,[9] as found in studies of the kinetics of protonation of a variety of nitrogen-,[10] metal-,[10,11] and carbon-centered[12] bases by these hydrides. Neutral metal hydrides also exhibit hydrogen atom transfer reactions.[13] Substituted styrenes[14,15] and conjugated dienes[16] are hydrogenated by pathways involving sequential hydrogen atom transfers from metal hydrides. The diversity of metal–hydrogen bond cleavage pathways[17] available to neutral metal hydrides is demonstrated by the fact that some of these same neutral metal hydrides that undergo loss of hydrogen as a proton or as a hydrogen atom can also serve as a hydride donor to electrophilic substrates. Hydride donation from these metal hydrides has been studied in less detail than proton transfer and hydrogen atom transfer reactions, but the utility of hydride abstraction from neutral metal hydrides in organometallic synthetic procedures has been demonstrated.[18] For example, Beck and co-workers have prepared several complexes containing BF_4^- or other weakly coordinating anions by hydride abstraction, such as $Cp(CO)_3W\text{-}FBF_3$ which was isolated[19] from the reaction of $Cp(CO)_3WH$ with $Ph_3C^+BF_4^-$.

In this paper, we show how the hydridic reactivity of neutral metal hydrides can be utilized in the rapid hydrogenation of sterically hindered olefins at low temperature.[20] Mechanistic studies indicate that the key step in these reactions is hydride transfer from a neutral metal hydride to a carbenium ion formed by protonation of an olefin by a strong acid.

Results

Scope of Olefins Hydrogenated by Triflic Acid and Hydrides. Addition of triflic acid (CF_3SO_3H, abbreviated as HOTf) to a solution of $Me_2C{=}CMe_2$ and $HW(CO)_3Cp$ results in rapid

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[⊛] Abstract published in *Advance ACS Abstracts*, September 1, 1994.

[1] For a review of hydride transfer reactions of metal hydrides, see: Labinger, J. A. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1991; Chapter 10.

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[4] Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902–7915.

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[8] Hembre, R. T.; McQueen, S. *J. Am. Chem. Soc.* **1994**, *116*, 2141–2142.

[9] 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, 1991; Chapter 9.

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[13] 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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[15] Bullock, R. M.; Samsel, E. G. *J. Am. Chem. Soc.* **1990**, *112*, 6886–6898.

[16] (a) Wassink, B.; Thomas, M. J.; Wright, S. C.; Gillis, D. J.; Baird, M. C. *J. Am. Chem. Soc.* **1987**, *109*, 1995–2002. (b) Shackleton, T. A.; Baird, M. C. *Organometallics* **1989**, *8*, 2225–2232.

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

[19] (a) Beck, W.; Schloter, K. *Z. Naturforsch.* **1978**, *33b*, 1214–1222. (b) Beck, W.; Schloter, K.; Sünkel, K.; Urban, G. *Inorg. Synth.* **1989**, *26*, 96–101.

[20] For preliminary accounts of this work, see: (a) Bullock, R. M.; Rappoli, B. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1447–1448. (b) U.S. Patent 4,967,031, issued Oct. 30, 1990.

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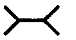
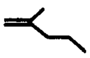
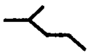
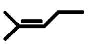
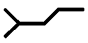
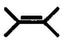
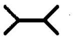
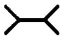
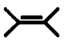
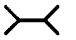
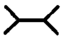
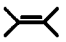
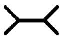
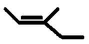
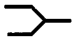
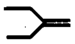
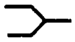
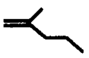
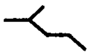
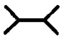
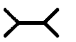
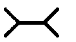
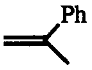
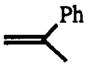
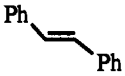
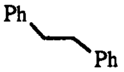
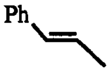
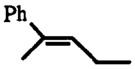
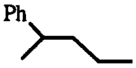
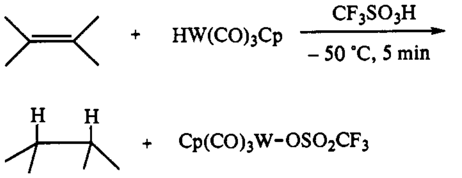
Table 1. Ionic Hydrogenations of Olefins Using Transition Metal Hydrides and HOTf

Olefin	Olefin Conc. (M)	HOTf (equiv.)	Metal Hydride (equiv.)	Product	% Yield	Conditions
	0.04	1.8	HW(CO)3Cp (2.0)		95	-50 °C, 5 min
	0.04	1.9	HW(CO)3Cp (2.0)		94	-50 °C, 5 min
	0.04	1.8	HW(CO)3Cp (2.0)		92	-50 °C, 5 min
	0.09	1.9	HMo(CO)3Cp (2.0)		99	22 °C, 5 min
	0.07	1.3	HW(CO)3Cp* (1.3)		98	22 °C, 5 min
	0.04	2.1	HOs(CO)2Cp* (2.0)		100	22 °C, 5 min
	0.05	2.0	HRe(CO)5 (3.1)		100	22 °C, 5 min
	0.05	2.3	HMn(CO)5 (3.7)		100	22 °C, 5 min
	0.13	1.1	HMo(CO)3Cp (1.0)		100	22 °C, 5 min
	0.07	1.7	HMo(CO)3Cp (1.0)		99	22 °C, 5 min
	0.13	1.2	HMo(CO)3Cp (1.0)		96	22 °C, 5 min
	0.08	2.8	HW(CO)3Cp (2.2)		89	22 °C, 5 min
	0.13	1.1	HMo(CO)3Cp (1.2)		100	22 °C, 5 min
	0.09	1.7	HW(CO)3Cp (1.3)		96	22 °C, 5 min
	0.07	1.4	HW(CO)3Cp (1.3)	$PhCH_2CH_3$	57	22 °C, 10 min
	0.11	1.2	HW(CO)3Cp (1.2)	$PhCH(CH_3)_2$	53	22 °C, 5 min
	0.14	2.1	HMn(CO)5 (3.0)	$PhCH(CH_3)_2$	66	22 °C, 5 min
	0.08	1.1	HW(CO)3Cp (1.1)		46	22°C, 5 min
	0.05	1.7	HW(CO)3Cp (2.1)	$Ph(CH_2)_2CH_3$	49	22 °C, 5 min
	0.10	1.2	HMo(CO)3Cp (1.4)		97	22 °C, 5 min

hydrogenation of the olefin (eq 1). The pale-yellow solution



(1)

containing the metal hydride and olefin immediately changes color to the deep wine-red color of the metal triflate $Cp(CO)_3WOTf$ (Tf = CF_3SO_2) upon addition of HOTf at room temperature. As shown in Table 1, excellent yields (90–100%) of hydrogenation products were obtained from olefins that were geminally disubstituted on one or both carbons (i.e., tetrasubstituted olefins, trisubstituted olefins, and 1,1-disubstituted olefins), which form tertiary carbenium ions upon protonation by acid. Several transition metal hydrides are effective in these reactions, as shown in Table 1 and discussed in a later section. The metal triflates, which were the sole organometallic products observed following hydride transfer, were also formed in high yield. Most of these olefin hydrogenations were carried out at room temperature, but high yields are also obtained from experiments conducted at temperatures as low as -50 °C.[21] In contrast to the high yields obtained from hydrogenation of olefins with simple alkyl groups, yields for hydrogenation of styrene and substituted styrenes (α-methylstyrene, β-methylstyrene, and *trans*-stilbene) are lower (46–66%). A good yield (97%) was obtained, however, for the more sterically hindered substituted styrene, (*E*)-2-phenyl-2-pentene.

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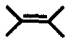
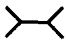
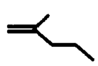
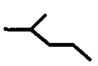
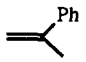
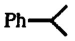
(21) It was previously claimed[20] that these hydrogenations occur at -80 °C. More recent experiments indicate the reactions are only partially complete at -80 °C, and we now believe that the -80 °C solutions warmed up when the NMR tubes were shaken. Further details and discussion of this point are provided in the Experimental Section.

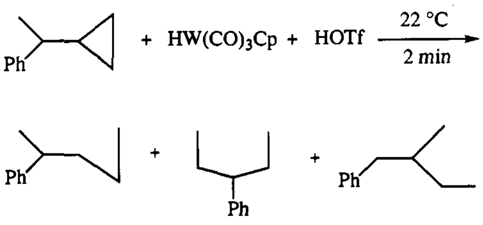
Table 2. Ionic Hydrogenations of Olefins Using $HSiEt_3$ and HOTf

Olefin	Olefin Conc. (M)	HOTf (equiv.)	$HSiEt_3$ (equiv.)	Product	% Yield	Conditions
	0.04	1.8	1.7		96	-50 °C, 5 min
	0.04	1.8	1.8		95	-50 °C, 5 min
	0.04	1.9	1.8		100	-50 °C, 5 min
	0.13	1.5	1.5		64	22 °C, 5 min

Triethylsilane is also a suitable hydride donor (Table 2) for these hydrogenations. It exhibits reactivity similar to the transition metal hydrides shown in Table 1.

Attempted Hydrogenation of Mono-Substituted and 1,2-Disubstituted Olefins. In contrast to the excellent yields of hydrogenation products found in the ionic hydrogenations listed in Table 1, the attempted hydrogenation of monosubstituted and 1,2-disubstituted olefins generally failed to produce significant yields of hydrogenation products. When HOTf was added to a solution of $HW(CO)_3Cp$ and 1-heptene, the olefin was rapidly consumed, but little or no heptane was produced, and only a trace (<1%) of $Cp(CO)_3WOTf$ was formed. The NMR spectrum observed from this reaction was identical to that recorded when 1-heptene was treated with HOTf in the absence of any metal hydride. These observations (as well as similar results from the attempted hydrogenation of cyclohexene using HOTf and $HW(CO)_3Cp$) indicate that in the absence of metal hydrides, the predominant reaction of olefins with HOTf is polymerization[22] rather than hydrogenation. Three exceptional cases (*tert*-butylethylene, allylbenzene, and 1-methyl-1,4-cyclohexadiene) were found in which the hydrogenation of a monosubstituted or a 1,2-disubstituted olefin was achieved in good yield. These examples provide mechanistic information pertinent to the accessibility of stabilized carbenium ions; details are provided in the discussion section.

Ring Cleavage Reactions of Cyclopropyl Groups. Three organic products result from the reaction of $Ph(CH_3)(c\text{-}C_3H_5)CH$ with HOTf and $HW(CO)_3Cp$ in CH_2Cl_2, as shown in eq 2. This



(2)

1 2 3

41 % 20 % 39 %

reaction was carried out at 4 different concentrations of $[HW(CO)_3Cp]_0$ ranging from 0.1 to 1.0 M. The concentration of $[Ph(CH_3)(c\text{-}C_3H_5)CH]$ was 0.02 M for all of these experiments. HOTf (2 equiv relative to $[Ph(CH_3)(c\text{-}C_3H_5)CH]$) was added to the solution, and after 2 min at 22 °C, excess NEt_3 was added to quench the reaction by consuming the remaining acid. Within experimental uncertainty, the product ratio was invariant from all four runs, giving 41% **1**, 20% **2**, and 39% **3**.

Formation of Metal Triflates from Metal Hydrides by Reaction with HOTf. The rate at which the different metal hydrides form H_2 by reaction with HOTf (eq 3) is a critical factor that influences

$$M\text{-}H + HOTf \longrightarrow M\text{-}OTf + H_2 \qquad (3)$$

their utility in these hydrogenations. A key feature making $HW(CO)_3Cp$, $HW(CO)_3Cp^*$, and $HOs(CO)_2Cp^*$ attractive as hydride donors in these hydrogenations is their relatively slow rate of formation of hydrogen upon reaction with HOTf. For example, only 8% of the triflate complex $Cp(CO)_3WOTf$ formed after 1 day at room temperature when a CD_2Cl_2 solution of $HW(CO)_3Cp$ (0.1 M) was reacted with HOTf (1.3 equiv), and 37% of the initial $HW(CO)_3Cp$ remained after 2 weeks. $HW(CO)_3Cp^*$ and $HOs(CO)_2Cp^*$ also undergo reaction 3 over a period of days or weeks at room temperature.

In contrast, the analogous reaction for the molybdenum hydride $HMo(CO)_3Cp$ was much faster. When a CD_2Cl_2 solution of $HMo(CO)_3Cp$ (0.1 M) was treated with HOTf (1.5 equiv) at room temperature, a rapid color change from pale yellow to the wine-red color of $Cp(CO)_3MoOTf$ was observed immediately. After 15 min, an 80% yield of $Cp(CO)_3MoOTf$ was observed by NMR, along with a singlet at δ 4.60 due to H_2. The yield of $Cp(CO)_3MoOTf$ increased to 93% after 3 h.

Olefin hydrogenations using either $HMn(CO)_5$ or $HRe(CO)_5$ actually *require* more than 1.0 equiv of the metal hydride and HOTf, due to competitive consumption of the hydride by reaction with HOTf (eq 3). For example, addition of HOTf (1.3 equiv) to a solution of $Me_2C{=}CMe_2$ (0.05 M) and $HMn(CO)_5$ (3.7 equiv) gave a 76% yield of the hydrogenation product, but 20% of the $Me_2C{=}CMe_2$ remained. A quantitative yield of the hydrogenation product was formed following addition of more HOTf. Similar results were obtained in the hydrogenation of $Me_2C{=}CMe_2$ with $HRe(CO)_5$. Bubbles of H_2 were observed immediately upon addition of HOTf to CD_2Cl_2 solutions of either $HMn(CO)_5$ or $HRe(CO)_5$, in the presence or absence of olefins. Trogler previously reported[23] the reaction of $HMn(CO)_5$ with neat HOTf to give H_2 and $(CO)_5MnOTf$.

Protonation of Metal Hydrides To Give Cationic Metal Dihydrides. Equation 3 does not represent an elementary reaction, since dihydrides and/or dihydrogen complexes are presumably intermediates in all of these reactions. The products resulting from protonation of $HW(CO)_3Cp$, $HW(CO)_3Cp^*$, and $HOs(CO)_2Cp^*$ were characterized by NMR at -80 °C. T_1 experiments suggest that $[(H)_2W(CO)_3Cp]^+OTf^-$, $[(H)_2W(CO)_3Cp^*]^+OTf^-$, and $[(H)_2Os(CO)_2Cp^*]^+OTf^-$ are predominantly dihydrides rather than dihydrogen complexes. However, the initial product of protonation of the metal in all of these cases could be a dihydrogen complex[24] that converts to a dihydride (or is in equilibrium with it) prior to the eventual decomposition to

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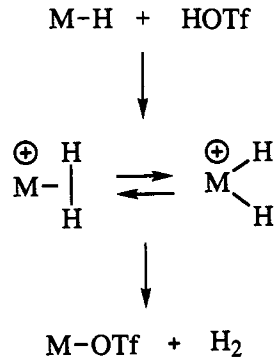
[22] For a review of carbocationic polymerization of olefins, see: Nuyken, O.; Pask, S. D. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, 1989; Vol. 3, Chapter 40.

[23] Trogler, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 6459–6460.

[24] For reviews of dihydrogen complexes, see: (a) Heinekey, D. M.; Oldham, W. J., Jr. *Chem. Rev.* **1993**, *93*, 913–926. (b) Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155–284. (c) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95–101. (d) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120–128. (e) Kubas, G. J. *Comments Inorg. Chem.* **1988**, *7*, 17–40.

Scheme 1



the metal triflate and H_2 (Scheme 1). Details of the characterization of these complexes will be published separately.[25]

Comparison of Different Metal Hydrides in Ionic Hydrogenations. As shown in Table 1, several metal hydrides ($HW(CO)_3Cp$, $HW(CO)_3Cp^*$, $HMo(CO)_3Cp$, $HMn(CO)_5$, $HRe(CO)_5$ and $HOs(CO)_2Cp^*$) serve as effective hydride donors in the ionic hydrogenation of olefins. Attempted use of other metal hydrides has revealed some of the limitations, as described below.

Hydrogenation of $Me_2C{=}CMe_2$ by HOTf and the ruthenium hydride $HRu(CO)_2Cp$ proceeds in 80% yield in C_6D_6. Several Cp resonances for unidentified ruthenium products were observed by NMR, and a thorough study of this reaction was not carried out.

Addition of HOTf to a CD_2Cl_2 solution of $Me_2C{=}CMe_2$ and $HMo(CO)_2(PPh_3)Cp$ caused an immediate color change of the solution to red, but no 2,3-dimethylbutane was observed. The metal triflate complex $Cp(CO)_2(PPh_3)MoOTf$ was formed in 99% yield. Attempted ionic hydrogenations of olefins with $HFe(CO)_2Cp^*$ as a hydride donor led to rapid formation of H_2, with the metal triflate $Cp^*(CO)_2FeOTf$ being produced in high yield. The Mo hydride $HMo(CO)_3Cp^*$ also failed in attempted ionic hydrogenations, quickly giving $Cp^*(CO)_3MoOTf$ and H_2 upon addition of acid.

Only a trace of 2,3-dimethylbutane was produced from the attempted hydrogenation of $Me_2C{=}CMe_2$ at 22 °C using HOTf and the phosphine-substituted tungsten hydride $HW(CO)_2(PMe_3)Cp$. In this case, the organometallic product was not the triflate complex, but instead the cationic dihydride $[(H)_2W(CO)_2(PMe_3)Cp]^+OTf^-$.[25-27] When the solution containing $Me_2C{=}CMe_2$ and $[(H)_2W(CO)_2(PMe_3)Cp]^+OTf^-$ was heated at 50 °C, the dihydride decomposed to give the metal triflate complex $Cp(CO)_2(PMe_3)WOTf$, but only 10% hydrogenation of the olefin was observed.

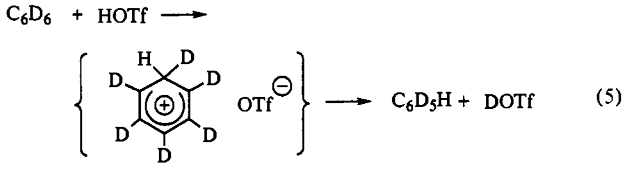
Addition of HOTf to a solution of $Me_2C{=}CMe_2$ and the phosphine-substituted ruthenium hydride $HRu(CO)(PMe_3)Cp$ resulted in protonation of $HRu(CO)(PMe_3)Cp$ to give the cationic dihydrogen complex $[(\eta^2\text{-}H_2)Ru(CO)(PMe_3)Cp]^+OTf^-$. The BF_4^- analog of this complex (along with a series of related dihydrogen complexes and dihydrides) was characterized and studied in detail by Chinn and Heinekey.[28] After 1.5 h at 22 °C, 90% of the $[(\eta^2\text{-}H_2)Ru(CO)(PMe_3)Cp]^+OTf^-$ had decomposed, but less than 5% of the $Me_2C{=}CMe_2$ had been hydrogenated.

Relative Rates of Hydride Transfer from $HW(CO)_3Cp$, $HMo(CO)_3Cp$, $HRe(CO)_5$, and $HMn(CO)_5$ to Carbenium Ions. Competition experiments were carried out in an attempt to determine the relative rates of hydride transfer to the same carbenium ion from different metal hydrides. The *apparent* relative kinetic hydricity of $HSiEt_3$ compared to $HW(CO)_3Cp$ was $k_{HSi}/k_{HW} = 3.7$ at −50 °C and 2.4 at 22 °C. Experiments comparing $HW(CO)_3Cp$ to either $HMo(CO)_3Cp$ or $HRe(CO)_5$ did not yield good reproducibility, based on two experiments for each pair of hydrides. The *apparent* relative kinetic hydricity determined from two experiments on $HW(CO)_3Cp$ vs $HMo(CO)_3Cp$ gave $k_{HW}/k_{HMo} = 1.1$ and 1.6; similar experiments on $HW(CO)_3Cp$ vs $HRe(CO)_5$ gave apparent values of $k_{HRe}/k_{HW} = 15$ and 7.

These measurements are referred to as *apparent* relative kinetic hydricity because of a caveat regarding the interpretation of these results as an accurate measure of the relative kinetic hydricity. The data appear to indicate that $HSiEt_3$ is a faster hydride donor than $HW(CO)_3Cp$, but this interpretation is uncertain if sufficiently rapid hydride transfer occurs from the silane to the tungsten cation (eq 4). Although no reaction was observed (22 °C, 1.5 h) between $HSiEt_3$ (49 mM) and the tungsten triflate complex $Cp(CO)_3WOTf$ (27 mM), this does not rule out the possibility that hydride transfer from $HSiEt_3$ to the tungsten cation (eq 4) could occur at a rate rapid enough to compete with capture of the tungsten cation by OTf^-. Coordinatively unsaturated species, such as the 16-electron cation $Cp(CO)_3W^+$, generally bind a weak donor such as CH_2Cl_2 or a weakly coordinating counterion such as BF_4^-. We found that $Cp(CO)_3W\text{-}FBF_3$[19] reacts with $HSiEt_3$ to produce $HW(CO)_3Cp$ (70% yield after 45 min at 22 °C), and we conclude that intermolecular hydride transfer from $HSiEt_3$ to $Cp(CO)_3W^+$ is feasible.

$$Cp(CO)_3W^+ + H\text{-}SiEt_3 \longrightarrow Cp(CO)_3W\text{-}H + Et_3Si^+ \qquad (4)$$

Complications Encountered with Ionic Hydrogenations in C_6D_6. These ionic hydrogenations can be carried out in aromatic solvents, but complications due to H/D exchange were encountered when these hydrogenations were carried out in C_6D_6. NMR and GC/MS analysis of the 2,3-dimethylbutane resulting from hydrogenation of the $Me_2C{=}CMe_2$ indicated some deuterium incorporation into this hydrogenation product. These observations are readily accounted for by the reversible protonation of the C_6D_6[29] solvent by HOTf, resulting in H/D exchange through the intermediacy of an arenium ion (eq 5). The DOTf can then convert the metal hydride to a metal deuteride. Use of CD_2Cl_2 solvent for most of the ionic hydrogenations reported in this paper obviated these complications.



(5)

Use of Acids Weaker than HOTf. Triflic acid was utilized in most of these experiments, but the utility of weaker acids was briefly examined. Hydrogenation of α-methylstyrene to cumene was successfully carried out using $HMn(CO)_5$ and CF_3CO_2H, but the yield (~50%) was not significantly different than that obtained using HOTf. In contrast to the successful use of CF_3CO_2H in the hydrogenation of α-methylstyrene, the attempted use of CF_3CO_2H for the hydrogenation of $Me_2C{=}CMe_2$ (with either $HMn(CO)_5$ or $HMo(CO)_3Cp$ as the hydride) at 22 °C did not yield significant amounts of hydrogenation products. In these reactions, the $Me_2C{=}CMe_2$ was slowly converted to the trifluoroacetate ester (eq 6). Tetramethylethylene was hydrogenated by methanesulfonic acid (CH_3SO_3H) and $HW(CO)_3Cp$, but the

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[25] Song, J.-S.; Szalda, D. J.; Bullock, R. M., manuscript in preparation.

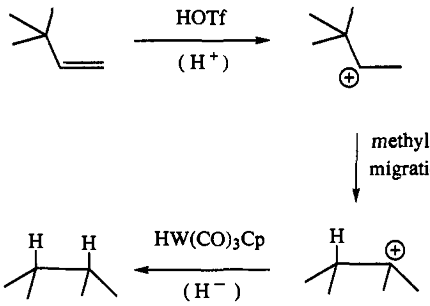
[26] Tilset and co-workers previously reported[27] the preparation of $[(H)_2W(CO)_2(PMe_3)Cp]^+$ as the BF_4^- salt. We have isolated the triflate salt $[(H)_2W(CO)_2(PMe_3)Cp]^+OTf^-$ and have characterized it by spectroscopic and crystallographic data. These results will be reported separately.[25]

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

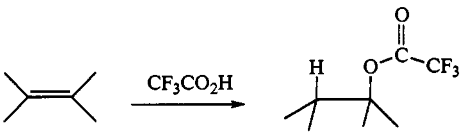
[28] Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166–5175.

[29] Bakoss, H. J.; Ranson, R. J.; Roberts, R. M. G.; Sadri, A. R. *Tetrahedron* **1982**, *38*, 623–630.

Scheme 2



reaction was very slow, requiring many hours under conditions where the analogous reaction using HOTf was complete within a few seconds. Tetramethylethylene was quickly hydrogenated by $HW(CO)_3Cp$ and $HBF_4{\cdot}OEt_2$, but detailed studies of the use of $HBF_4{\cdot}OEt_2$ have not been carried out.



(6)

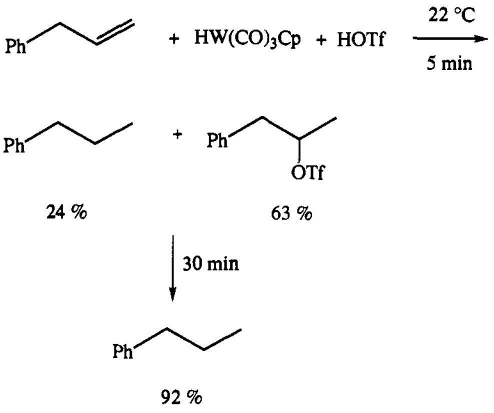
Discussion

Carbenium Ion Intermediates in the Ionic Hydrogenation of Olefins. The mechanism for all of these hydrogenations involves protonation of the olefin to generate a carbenium ion, followed by hydride transfer from the metal hydride to produce the hydrogenated product. Most of the olefins that are readily hydrogenated in high yield are either tetrasubstituted, trisubstituted, or 1,1-disubstituted. All of these types of olefins form tertiary carbenium ions upon protonation. Although simple monosubstituted olefins such as 1-heptene are polymerized rather than hydrogenated under these conditions, there are a few cases where clean hydrogenation was observed. Specific evidence for the intermediacy of carbenium ions comes from the formation of 2,3-dimethylbutane in high yield from hydrogenation of *tert*-butylethylene. As shown in Scheme 2, the secondary carbenium ion formed by protonation of *tert*-butylethylene undergoes a rapid methyl migration to generate a more stable tertiary carbenium ion. Hydride transfer from the metal hydride to this rearranged carbenium ion produces the observed product.

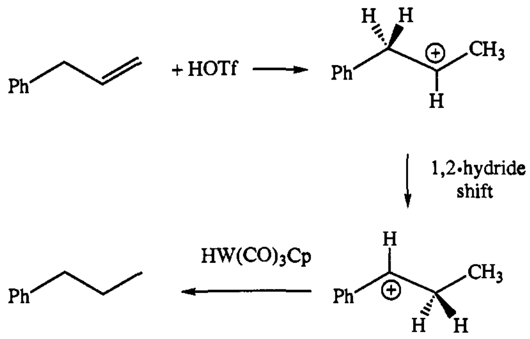
Another example of the successful ionic hydrogenation of a monosubstituted olefin is provided by the formation of propylbenzene from ionic hydrogenation of allylbenzene (Scheme 3). When HOTf was added to a solution of allylbenzene and $HW(CO)_3Cp$, a 24% yield of propylbenzene was observed after 5 min, with the major product (63% yield) being the secondary alkyl triflate $PhCH_2CH(OTf)CH_3$. After 30 min, the alkyl triflate was consumed, and the yield of propylbenzene had increased to 92%. As shown in Scheme 4, the initial intermediate formed upon protonation of allylbenzene is a secondary carbenium ion. The fact that hydrogenation (rather than polymerization) of allylbenzene does occur is probably due to the creation of a benzylic carbenium ion by a 1,2-hydride shift. This proposal is supported by the observation that other substrates that give secondary carbenium ions upon protonation (e.g., 1-heptene and cyclohexene) fail to yield hydrogenated products, whereas benzylic carbenium ions (such as the one formed by protonation of styrene) do abstract H^- from the metal hydride to give hydrogenated products.

The alkyl triflate formed as an intermediate in the hydrogenation of allylbenzene to propylbenzene was independently synthesized from the alcohol and triflic anhydride (Scheme 5). No reaction was observed between this alkyl triflate and $HW(CO)_3Cp$ in the absence of acid, indicating that spontaneous heterolysis of the alkyl triflate is not a significant contributor to the reaction pathway. When HOTf was added to a solution containing $PhCH_2CH(OTf)CH_3$ and $HW(CO)_3Cp$, formation of propylbenzene was observed. These observations suggest that formation of the hydrogenated product from the alkyl triflate requires protonation of the alkyl triflate and loss of triflic acid to generate the carbenium ion, which then abstracts H^- from the metal hydride to give the observed product. Thus the initially formed carbenium ion either abstracts a hydride to form propylbenzene directly or is trapped by triflate, giving propylbenzene indirectly through the alkyl triflate by the route shown in Scheme 5.

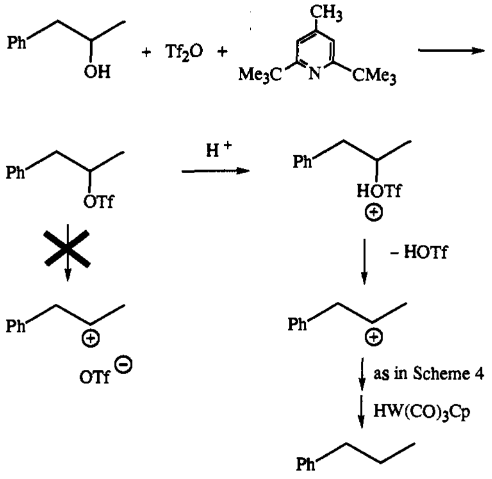
Scheme 3



Scheme 4

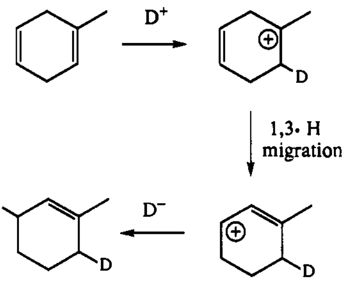


Scheme 5

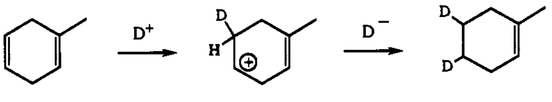


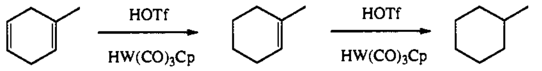
Attempted ionic hydrogenation of a 1,2-disubstituted olefin failed with cyclohexene and also with 1,3-cyclohexadiene. In contrast, addition of HOTf (1 equiv) to a CD_2Cl_2 solution of $HW(CO)_3Cp$ and 1-methyl-1,4-cyclohexadiene did result in overall hydrogenation of the 1,2-disubstituted olefin moiety, giving 1-methylcyclohexene (84% yield, eq 7). Addition of more HOTf

Scheme 6



Scheme 7

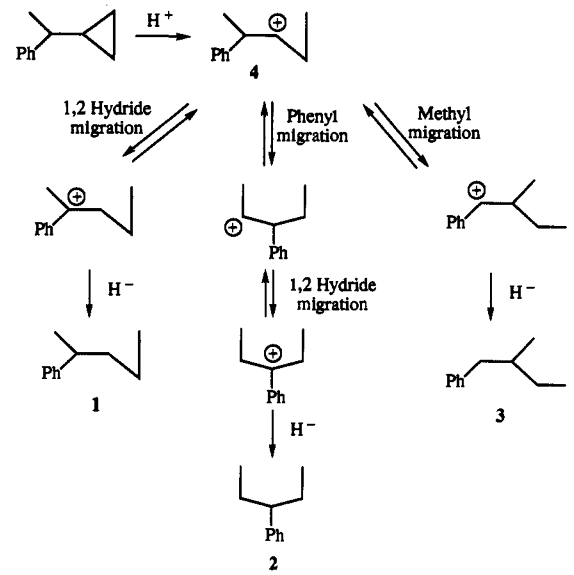




(7)

(1.3 equiv) completed the hydrogenation, producing methylcyclohexane. The success of this hydrogenation reaction suggests that the mechanism involves access to a carbenium ion that is stabilized compared to a normal secondary carbenium ion. Two condensed mechanistic possibilities are presented in Schemes 6 and 7, using deuterium labels on the acid and hydride. In Scheme 6, addition of D$^+$ produces a tertiary carbenium ion. Hydride transfer to this carbenium ion apparently does not occur, since it would lead to a different isomer than the one that is actually observed. A 1,3-H migration[30] of this tertiary carbenium ion would produce an allylic cation, which could react with the metal deuteride to give the dideuterated product shown, which has D in the allylic positions. Another possible mechanism involves delivery of D$^+$ to the less substituted double bond, generating a homoallylic cation. As shown in Scheme 7, transfer of D$^-$ to this cation would produce 1-methylcyclohexene with deuterium labels in the aliphatic positions. The ^{2}H NMR spectrum recorded after addition of 1 equiv of DOTf to a solution containing 1-methyl-1,4-cyclohexadiene (0.07 M) and DW(CO)$_3$Cp (0.16 M) at room temperature indicated that significant deuterium incorporation had taken place. Not only was deuterium present in the allylic and aliphatic positions shown in Schemes 6 and 7, but D incorporation was also observed in the vinyl position of the 1-methylcyclohexene. The extensive H/D scrambling suggests a mechanism involving reversible protonation of the starting material but does not conclusively distinguish between the two possibilities presented in Schemes 6 and 7. Other plausible intermediates may also be present, and the simplified mechanisms shown here do not show all of them. For example, the 1-methyl-1,4-cyclohexadiene could be converted to the conjugated 1-methyl-1,3-cyclohexadiene isomer by a protonation/deprotonation sequence, and subsequent protonation of this conjugated diene would lead to an allylic cation.

Scheme 8

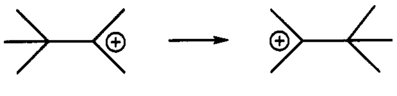


Carbenium ion rearrangements are also implicated by the products observed in the ring-opening reactions of the cyclopropyl compound Ph(CH$_3$)(c-C$_3$H$_5$)CH (eq 2). The proposed mechanism that accounts for the formation of these products is shown in Scheme 8. The first step involves electrophilic ring-opening of the cyclopropyl group[31] of Ph(CH$_3$)(c-C$_3$H$_5$)CH by reaction with HOTf, giving **4**. A 1,2-methyl migration of this initially formed secondary carbenium ion would produce a more stable benzylic carbenium ion which could then abstract hydride to form the observed methyl-migrated product **3**. Phenyl migration of **4** would produce a secondary carbenium ion of comparable stability to **4**, but a 1,2-hydride shift following the phenyl migration would lead to a more stable tertiary benzylic carbenium ion that would give **2** after hydride abstraction from HW(CO)$_3$Cp. A 1,2-hydride migration of **4** would also convert it to a more stable tertiary benzylic carbenium ion, giving rise to **1**. Direct hydride transfer to **4** could produce the observed product **1**, with no requirement for the hydride shift rearrangement.

The competition in Scheme 8 between carbenium ion rearrangements and trapping by hydride transfer can be considered according to Curtin–Hammett kinetics.[32] The observed invariance of the product ratio as the metal hydride concentration was changed indicates that the rate of equilibration among the carbenium ions is very different from the rate of hydride transfer to them. If the two rates had been similar, then the product ratio would have changed as [HW(CO)$_3$Cp] was varied. The data do not definitively prove that the carbenium ion rearrangements are faster than hydride transfer. As discussed below, however, we suggest that this is the case, since other carbenium ion rearrangements are known to be extremely fast.

Saunders and Kates determined[33] a rate constant of $k = 3.1 \times 10^7$ s^{-1} at −138 °C ($\Delta G^\ddagger = 3.1 \pm 0.1$ kcal/mol at −138 °C) for the degenerate 1,2-hydride shift in the carbenium ion shown in eq 8. Methyl migrations examined in their study were also very rapid: the rate constant for the Wagner–Meerwein rearrangement shown in eq 9 was found to be $k = 8.5 \times 10^6$ s^{-1} at −136 °C. An extrapolation to 25 °C of the rates measured at low temperature for these reactions would involve considerable uncertainty, but reasonable assumptions about the temperature dependence would suggest a lower limit of 10^9 s^{-1} at 25 °C. The rearrangements shown in Scheme 8 have a thermodynamic driving

(8)



(9)

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[30] Most examples of 1,3-H migrations are actually the result of sequential 1,2-H migrations. For a discussion of this point, see: March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; 4th ed.; John Wiley and Sons: New York, 1992; p 1062.

[31] For a review of electrophilic ring-cleavage of cyclopropanes, see: DePuy, C. H. *Top. Curr. Chem.* **1973**, *40*, 73–101.

[32] Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83–134.

[33] Saunders, M.; Kates, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 7082–7083.

force due to the formation of more stabilized rearranged carbenium ions and may have rates even higher than those of the degenerate rearrangements in eqs 8 and 9. It is therefore quite unlikely that the rates of the intermolecular hydride transfers in Scheme 8 could compete with the rates of the intramolecular rearrangements, lending support to our assertion that the rates of rearrangement in Scheme 8 are much higher than the hydride transfer rates.

Potential Utility of Ionic Hydrogenations Using HOTf, and Comparisons with Other Methods. The use of triflic acid with either metal hydrides or $HSiEt_3$ provides an exceptionally fast, high yield method for stoichiometric hydrogenation of hindered olefins at low temperature. Trisubstituted and tetrasubstituted olefins are readily hydrogenated by this method. These olefins are difficult to hydrogenate by many traditional heterogeneous or homogeneous catalytic methods, since the steric hindrance usually inhibits binding. These same alkyl groups on the olefins that impede the hydrogenation by other methods are a crucial factor in the successful hydrogenation by this method, since they provide the essential electronic stabilization of the carbenium ion intermediates in ionic hydrogenation. Hydrogenation of $Me_2C{=}CMe_2$ using Wilkinson's catalyst, $RhCl(PPh_3)_3$, is very slow, occurring at least two orders of magnitude slower than hydrogenation of 1-hexene.[34] However, Crabtree has developed a series of cationic iridium complexes that are remarkably active in the catalytic hydrogenation of $Me_2C{=}CMe_2$.[35]

More pertinent than a comparison of catalytic methods to the stoichiometric hydrogenation method developed in this work is a comparison of the efficacy of the use of our method with the stoichiometric ionic hydrogenation method developed by Kursanov and co-workers,[36] which utilizes the much weaker acid CF_3CO_2H in conjunction with $HSiEt_3$ as the hydride donor. The scope of olefins that can be hydrogenated by either of these methods is comparable, since with HOTf/transition metal hydride, HOTf/$HSiEt_3$, or $CF_3CO_2H/HSiEt_3$, the requirement is that the olefin be able to form either a tertiary or a benzylic carbenium ion upon protonation. Kursanov's method of $CF_3CO_2H/HSiEt_3$ usually employs CF_3CO_2H as both the solvent and proton source, compared to the hydrogenations shown in Tables 1 and 2 that were carried out in dichloromethane solution using a small excess of acid. Typical hydrogenation conditions for $CF_3CO_2H/HSiEt_3$ are a few hours at 50 °C, compared to 5 min at −50 °C with HOTf/$HSiEt_3$. Thus the use of the strong acid HOTf instead of CF_3CO_2H enables the same hydrogenations to be carried out much faster, at a hundred degrees lower temperature! While the insights on the hydride transfer reactions of transition metal hydrides are of significance to mechanistic organometallic chemistry, the convenience of using commercially available $HSiEt_3$ will generally make it a preferable hydride donor for most olefin hydrogenations that would be suitable to carry out using ionic hydrogenation.

The successful use of HOTf in place of CF_3CO_2H, while apparently straightforward, was surprising since it had been claimed in a review of the use of $CF_3CO_2H/HSiEt_3$ that "stronger acids cannot be used in conjunction with silanes because they react with the latter."[36c] We confirmed that $HSiEt_3$ does react rapidly with HOTf at room temperature in CD_2Cl_2 solution. Indeed, *all* of the transition metal hydrides used in this study also react with HOTf, with the stability of the resultant dihydrides being a major factor determining which metal hydrides are suitable to use. Their reaction does *not* preclude them from being used successfully together, but it does require an appropriate order of addition of reagents in some cases. In most of the experiments reported in this paper, HOTf was added to a solution containing the olefin and the hydride. When $HW(CO)_3Cp$, $HW(CO)_3Cp^*$, or $HOs(CO)_2Cp^*$ is used as the hydride donor, high yields of hydrogenation products can also be obtained when the olefin is added to the solution containing the partially protonated hydride/dihydride mixture.

Another significant difference in the use of HOTf vs CF_3CO_2H for ionic hydrogenations concerns the fate of the tertiary carbenium ion intermediate. In the hydrogenations using CF_3CO_2H and $HSiEt_3$, capture of the carbenium ion by trifluoroacetate anion is faster than hydride transfer to it from $HSiEt_3$. In the presence of acid, these trifluoroacetate ester intermediates revert to the carbenium ion and are converted to the final product by hydride transfer from $HSiEt_3$. In hydrogenations with $CF_3CO_2H/HSiEt_3$, the rate of formation of methylcyclohexane was found to be the same whether the starting material was the olefin (methylcyclohexene) or the trifluoroacetate ester.[37] This provides evidence that most of the olefin was converted to the trifluoroacetate ester prior to being converted to the hydrogenation product. In contrast, with the olefin hydrogenations using HOTf, hydride transfer occurs much faster than capture of the carbenium ion by the triflate anion to give an alkyl triflate. With the exception of the hydrogenation of allylbenzene to propylbenzene (Scheme 3), alkyl triflates were not detected as intermediates in our C=C hydrogenation experiments.

A critical factor influencing the success or failure of these ionic hydrogenation reactions is the relative rate of hydride transfer to the carbenium ion (which leads to the desired hydrogenation product) compared to the rate of addition of the olefin to the carbenium ion (which leads to polymerization). On the basis of both electronic and steric properties, secondary carbenium ions would be expected to be faster than tertiary carbenium ions at hydride abstraction from metal hydrides. At the same time, however, these less stable carbenium ions will also be more reactive toward a given olefin, as was demonstrated in a series of papers published by Mayr and co-workers[38] on the kinetics of the addition of olefins to diarylcarbenium ions. In experiments where the same olefin was reacted with a series of diarylcarbenium ions containing different substituents in the para position, they found that the less stable carbenium ions reacted much faster. For example, the rate constant at −70 °C for the reaction of 2-methyl-1-pentene with $(p\text{-}MeC_6H_4)_2CH^+$ was about 10^5 times as large as that found for reaction of the same olefin with $(p\text{-}MeOC_6H_4)_2CH^+$.[38a] Our attempts to hydrogenate olefins that form secondary carbenium ions resulted in polymerization rather than hydrogenation. The explanation for this must be an enhanced rate of polymerization of these olefins,[39] rather than a decreased rate of hydride transfer to the carbenium ions. It is clear that in the ionic hydrogenations that are successful, the rate of the hydride transfer must substantially exceed the rate of reaction of olefin with the carbenium ion, since otherwise polymerization rather than hydrogenation would occur.

Hydride Transfer from Transition Metal Hydrides. Homolytic cleavage of the M–H bond of neutral metal carbonyl hydrides,

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[37] See p 64 of ref 36b.

[38] (a) Mayr, H.; Schneider, R.; Schade, C.; Bartl, J.; Bederke, R. *J. Am. Chem. Soc.* **1990**, *112*, 4446–4454. (b) Mayr, H.; Schneider, R.; Irrgang, B.; Schade, C. *J. Am. Chem. Soc.* **1990**, *112*, 4454–4459. (c) Mayr, H.; Schneider, R.; Grabis, U. *J. Am. Chem. Soc.* **1990**, *112*, 4460–4467.

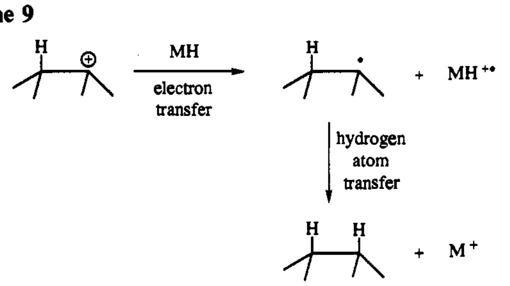
[39] The comparison of the relative rates of these processes is further complicated by the fact that the rate of polymerization is dependent on the structure of the olefin being added to a carbenium ion, as well being dependent on the carbenium ion. Mayr found[38] that when a series of different olefins was reacted with the same diarylcarbenium ion, the monosubstituted and 1,2-disubstituted olefins (which fail in our hydrogenations) reacted more slowly than the trisubstituted olefins (which are successful in our hydrogenations). Our hydrogenations (e.g., the successful hydrogenation of tetramethylethylene vs polymerization of cyclohexene under the same conditions) necessarily involve comparisons between attempted hydrogenation of different olefins, so both the olefin and the carbenium ion resulting from its protonation have changed. Despite these competing factors, the relevant conclusion that is demonstrated by our data is that hydride transfer must be significantly faster than polymerization in our olefin hydrogenations that proceed in high yield.

resulting in *hydrogen atom* transfer reactions,[13] and heterolytic cleavage of the M–H bond in *proton* transfer reactions[9] have been previously examined in detail for most of the transition metal hydrides that are found in this study to be the most effective *hydride* donors in the ionic hydrogenation of olefins. It may seem at first to be paradoxical that some of the metal hydrides that are the most effective at hydride transfer reactions are also moderately acidic. The pK_a values[9] in CH_3CN for $HMo(CO)_3Cp$ (13.9), $HMn(CO)_5$ (14.1), $HW(CO)_3Cp$ (16.1), and $HRe(CO)_5$ (21.1) indicate that all of these hydrides are more acidic than CH_3CO_2H (pK_a = 22.3)[40] but less acidic than CH_3SO_3H (pK_a = 10.0).[41] The fact that these metal hydrides are capable of donating either a proton or a hydride to a suitable substrate does not imply that the same factors favor both types of heterolytic bond cleavage. When a Cp ligand on a metal hydride is changed to Cp*, or when a CO is substituted by a phosphine, an increased electron density at the metal results. The higher electron density at the metal decreases the stability of the metal anions, which results in a lowered acidity of the metal hydrides. These same ligand changes that lower the acidity of metal hydrides would almost undoubtedly lead to a greater propensity for hydride transfer to a carbenium ion (although the increased steric demands would work in the opposite direction). Yet the results presented in this paper indicate that the metal hydrides that work well for these hydride transfer reactions are generally the ones which are relatively acidic. For example, $HMo(CO)_3Cp$ can be successfully utilized as a hydride transfer reagent. The related compounds $HMo(CO)_2(PPh_3)Cp$ and $HMo(CO)_3Cp^*$ are less acidic (and presumably more hydridic) than $HMo(CO)_3Cp$, but they are not suitable for these ionic hydrogenations. The failure of these less acidic hydrides is not due to their inability to transfer hydride to a carbenium ion. The fast rate of formation of metal triflates and hydrogen from $HMo(CO)_2(PPh_3)Cp$, $HMo(CO)_3Cp^*$, and $HFe(CO)_2Cp^*$ precludes their utility in these ionic hydrogenation reactions. Because of the rapid decomposition of the cationic dihydrides (or dihydrogen complexes) resulting from protonation of these hydrides, the neutral metal hydrides never get a chance to react with a carbenium ion. The hydrides that form observable dihydrides upon protonation ($HW(CO)_3Cp$, $HW(CO)_3Cp^*$, and $HOs(CO)_2Cp^*$) are the most versatile, since their rates of formation of metal triflates are sufficiently slow compared to their rate of hydride transfer to the carbenium ions to enable the productive hydride transfer to the carbenium ion to overcome the competing decomposition of the hydride (eq 3).

The formation of the carbenium ion intermediate may proceed by protonation of the olefin directly by triflic acid, or indirectly by initial protonation of the metal hydride to form a dihydride or dihydrogen complex, which then protonates the olefin. It is clear that protonation at the metal is not required for these reactions to be successful, since all of the proton transfer could occur directly from the acid to the olefin. The two critical requirements are that *if* the metal is protonated, then (1) the cationic dihydride must be relatively stable on the time scale of the hydrogenation reaction and (2) the cationic dihydride must be sufficiently acidic to transfer the proton to the olefin. The molybdenum hydride $HMo(CO)_2(PPh_3)Cp$ fails to meet the first requirement, while the tungsten hydride $HW(CO)_2(PMe_3)Cp$ fails to meet the second.

Mechanism of the Hydride Transfer Step. The overall reaction involves delivery of H^- from the metal to the carbenium ion. Our results do not provide an unambiguous mechanistic distinction between a single-step hydride transfer and an alternative mechanism in which the carbenium ion oxidizes the metal hydride to a radical cation, followed by hydrogen atom transfer to generate the product (Scheme 9). Hayes and Cooper reported[42] evidence for this type of two-step mechanism for the reactions of $Cp_2W(CH_3)_2$ and related complexes with Ph_3C^+. Gladysz, Parker, and co-workers found[43] a similar mechanism to be operative in hydride abstractions from a series of rhenium alkyl complexes $Cp(NO)(PPh_3)Re(R)$. On the other hand, Tilset and co-workers have concluded on the basis of chemical and electrochemical evidence that hydride transfers from $HW(CO)_2(PMe_3)Cp$,[27] $HRu(CO)(PMe_3)Cp$,[44] or $HMo(CO)_2(PPh_3)Cp$[45] to the substituted trityl cation (p-$MeOC_6H_4)Ph_2C^+BF_4^-$ occur by direct hydride transfer and not by an electron transfer mechanism. Unfortunately, certain experiments that might provide more definitive data on this question are not feasible. Rapid H/D exchange between HOTf and metal deuterides precludes the utility of an examination of the isotope effects[46] for the hydride transfer, and none of the phosphine-substituted metal hydrides examined thus far were effective, thus preventing attempts to use kinetic vs thermodynamic mixtures of cis and trans isomers to provide mechanistic information.[27,44,45]

Scheme 9



The possibility (Scheme 9) that the actual M–H cleavage step involves a hydrogen atom transfer rather than a direct hydride transfer is reminiscent of similar questions that were addressed in thorough studies of the reduction of alkyl bromides by anionic metal carbonyl hydrides such as $HW(CO)_5^-$. By using complementary (sterically hindered and unhindered) radical probes, Darensbourg, Newcomb, and co-workers[47] were able to quantitatively measure the contributions from two competing pathways. Direct displacement of bromide by hydride transfer competes with a radical chain pathway, in which the anionic metal hydride donates a hydrogen atom to an organic radical.

Comparisons with Other Reactions That Form C–H Bonds by Hydride Transfer. Notwithstanding the uncertainties mentioned above regarding the detailed mechanism of the hydride transfer step, it is clear that these hydrogenations involve stoichiometric H^- transfer to a carbenium ion, and this step bears resemblance to other reactions in which a C–H bond is formed from metal hydrides. Detailed kinetic and mechanistic studies by Doherty and Bercaw[48] on the formation of niobium alkyl complexes from $Cp^*_2Nb(CH_2{=}CHR)(H)$ led to the conclusion that the transition state involved concerted bond making and bond breaking. Although this transition state was thought to be "relatively nonpolar",[48] it was suggested that the β-carbon developed a partial positive charge, and that the hydride moved "more nearly as H^- than as H^+".[48] The reaction of acrylonitrile with $HCr(CO)_5^-$ was found by Darensbourg and co-workers[49] to produce $[(CO)_5Cr{-}CH(CN)(CH_3)]^-$. It was suggested on the basis of substituent effects on relative reactivity rates that intermolecular hydride transfer to carbon preceded Cr–C bond formation.

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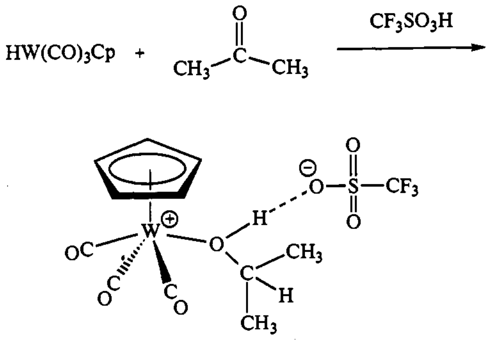
Generality of Ionic Hydrogenations Using Transition Metal Hydrides. Ongoing work is addressing questions concerning the potential utility of transition metal hydrides in the ionic hydrogenation of other organic substrates. It was recently shown[50] that aldehydes and ketones can be hydrogenated to alcohols using various acids in conjunction with transition metal hydrides as the hydride donor. The product of ionic hydrogenation of acetone



(10)

by HOTf/HW(CO)$_3$Cp is an alcohol complex for which crystallographic and spectroscopic data indicate a hydrogen bond between the alcohol OH and an oxygen on the OTf$^-$ counterion.[50] Further studies on the scope and selectivity of these ionic hydrogenations are also underway.

Conclusion

Sterically hindered olefins are hydrogenated within 5 min at -50 °C using HOTf as a proton donor and either a transition metal hydride or triethylsilane as the hydride donor. Olefins that can form a tertiary carbenium ion upon protonation are hydrogenated in high yields (90–100%) by this method. The requirement for formation of a tertiary carbenium ion generally means that this method is applicable to tetrasubstituted, trisubstituted, and 1,1-disubstituted olefins.

Transition metal hydrides exhibit high selectivity in the presence of two electrophilic substrates, carbenium ions and protons. The origin of this high selectivity is related to the fact that hydride transfer to carbenium ions is facile, whereas hydride transfer to the proton does not occur directly. Instead, the transition metal hydrides are protonated to form cationic dihydride complexes. The acidity and the thermal stability of these dihydride complexes are key factors determining which metal hydrides are suitable hydride donors for these reactions. It is remarkable that these ionic hydrogenations can be carried out in such high yield, in view of the alternative facile reaction pathways of the extremely strong acid (HOTf) with either reagent. In the absence of metal hydrides to rapidly convert the intermediate carbenium ion to hydrogenated product, olefins are polymerized by HOTf, while the hydrides react with HOTf to form H_2 and metal triflates.

Experimental Section

General. All manipulations were carried out under an atmosphere of argon using Schlenk or vacuum-line techniques, or in a Vacuum Atmospheres drybox. ^1H (300 MHz) and ^2H (46.1 MHz) spectra were recorded on a Bruker AM-300 spectrometer. The ^1H chemical shifts were referenced to the residual proton peak of the solvent, δ 5.32 for CD_2Cl_2 and δ 7.15 for C_6D_6. IR spectra were recorded on a Mattson Polaris FT-IR spectrometer.

Materials. $HW(CO)_3Cp$,[15] $HMo(CO)_3Cp$,[15] $HMo(CO)_3Cp^*$,[51] $HRu(CO)(PMe_3)Cp$,[28] $HW(CO)_2(PMe_3)Cp$,[52] $HMo(CO)_2(PPh_3)Cp$,[53] $HFe(CO)_2Cp^*$,[15] and $HW(CO)_3Cp^*$[54] were prepared as previously described and were stored under argon at -20 °C in the dark. $HMn(CO)_5$[55] and $HRe(CO)_5$[56] were prepared as previously described, stored under vacuum at -20 °C in the dark, and vacuum transferred immediately prior to each use. $HOs(CO)_2Cp^*$ was prepared by a modification of the preparation reported by Graham,[57] by reacting $LiHBEt_3$ (instead of $NaBH_4$) with $IOs(CO)_2Cp^*$.[58] The $HOs(CO)_2Cp^*$ was purified by column chromatography and sublimation. A C_6D_6 solution of $HRu(CO)_2Cp$ was prepared as previously described.[15] CH_2Cl_2 and CD_2Cl_2 were distilled from P_2O_5. Et_2O was stored over $[Cp_2TiCl]_2ZnCl_2$[59] and vacuum transferred immediately prior to use. C_6D_6 was dried over NaK and stored over $[Cp_2TiCl]_2ZnCl_2$. Organic chemicals were purchased from either Aldrich or Wiley, except for $Ph(CH_3)(c\text{-}C_3H_5)CH$,[15] which was prepared by hydrogenation of $H_2C{=}C(c\text{-}C_3H_5)Ph$[60] using $RhCl(PPh_3)_3$ catalyst and H_2 (950 psi) at 22 °C. This compound was purified by column chromatography and vacuum distillation.

Procedure for Ionic Hydrogenation Reactions. The following experiment (first entry on Table 1) is a representative example for a low-temperature ionic hydrogenation. $HW(CO)_3Cp$ (17 mg, 0.051 mmol) was added to a 5 mm screw-capped NMR tube, and CD_2Cl_2 was added to give a volume of 0.60 mL. $Me_2C{=}CMe_2$ (3 μL, 0.025 mmol) and 1,2-dichloroethane (3 μL, internal standard) were added. After recording an initial NMR spectrum, the solution was taken back into the drybox and was transferred into a 3.0 mL Pierce Reacti-Vial equipped with a Mininert valve and a magnetic stirrer. The vial was removed from the drybox, the solution was cooled to -50 °C in a constant temperature bath, and HOTf (4 μL, 0.045 mmol, 1.8 equiv) was added to the solution. The reaction mixture was stirred at -50 °C for 5 min, and excess pyridine (5 μL, 0.062 mmol) was added to consume the remaining acid. The resulting reaction mixture was warmed to room temperature, taken back into the drybox, and transferred into another NMR tube to determine the yield (95% in the specific example described here) of hydrogenated product.

Ionic hydrogenations of olefins carried out in NMR tubes were performed using the same general procedure described above, except that the transfer of the solution from the NMR tube to vial was not needed. The volume of the solution was calculated from the height of the solution in the NMR tube using a reported formula.[61] In all cases, the organic products were identified by comparison of their NMR spectra with those of authentic samples. Quantitative determination of the amounts of metal hydride starting material and metal triflate products was readily accomplished by ^1H NMR integration of the Cp resonances of the hydride and triflate complexes against an internal standard. For ionic hydrogenations using $HMn(CO)_5$ and $HRe(CO)_5$, the absence of any protons in $(CO)_5MnOTf$ and $(CO)_5ReOTf$ precluded the determination of the yield of these organometallic products by ^1H NMR, but the identity of these Mn and Re triflate complexes was readily confirmed by comparison of their IR spectra with independently prepared authentic samples.[62]

We previously claimed[20] that these hydrogenations occur at -80 °C. These earlier experiments were carried out in NMR tubes at -80 °C using the following procedure. Screw-cap NMR tubes containing CD_2Cl_2 solutions of the olefin, metal hydride, and internal standard were placed in a constant temperature bath at -80 °C, with the top 0.5 in. of the tube (including the septum through which the acid was added) left at room temperature. After addition of HOTf at -80 °C, the tubes were removed from the bath, shaken for about 1 s, and immediately re-inserted into the cold bath. Our recent experiments described above, which were carried out in small vials with constant stirring (as opposed to NMR tubes with intermittent shaking), indicate that reactions at -80 °C are only partially complete, and we conclude that the solutions in the NMR tubes in the -80 °C experiments must have warmed up during the brief contact with the cap of the NMR tubes at room temperature, leading us to the incorrect conclusion that these reactions were complete at -80 °C.

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Ionic Hydrogenation of Allylbenzene by $HW(CO)_3Cp$ and HOTf. $HW(CO)_3Cp$ (24 mg, 0.072 mmol) was added to a screw-capped NMR tube, and CD_2Cl_2 was added to give a volume of 0.60 mL. Allylbenzene (5 μL, 0.038 mmol) and 1,2-dichloroethane (4 μL, internal standard) were added. After an initial NMR spectrum was recorded, HOTf (5 μL, 0.056 mmol) was added, and the tube was shaken for 5 min at 22 °C. The ^1H NMR spectrum of the resulting wine-red solution showed the formation of $Cp(CO)_3WOTf$ (30%), propylbenzene (24%), and 2-(triflyloxy)propylbenzene (63%). After 30 min at 22 °C, $Cp(CO)_3WOTf$ (96%) and propylbenzene (92%) were observed by NMR, and the 2-(triflyloxy)propylbenzene had been completely consumed. When HOTf was added to a solution of allylbenzene in the absence of $Cp(CO)_3WH$, the solution immediately turned brown, apparently due to acid-induced polymerization. ^1H NMR (CD_2Cl_2) of propylbenzene: δ 7.29–7.09 (m, 5H, Ph), 2.58 (t, J = 7.4 Hz, 2H, $PhCH_2CH_2CH_3$), 1.63 (sextet, J = 7.4 Hz, 2H, $PhCH_2CH_2CH_3$), 0.94 (t, J = 7.4 Hz, 3H, $PhCH_2CH_2CH_3$). ^1H NMR (CD_2Cl_2) of 2-(triflyloxy)propylbenzene: δ 7.37–7.21 (m, 5H, Ph), 5.23 (sextet, J = 6.3 Hz, 1H, $PhCH_2CH(OTf)CH_3$), 3.08 (dd, J = 13.9 Hz, 6.3 Hz, 1H, $PhCH_2CH(OTf)CH_3$), 3.06 (dd, J = 13.9 Hz, 6.3 Hz, 1H, $PhCH_2CH(OTf)CH_3$), 1.51 (d, J = 6.3 Hz, 3H, $PhCH_2CH(OTf)CH_3$).

Reaction of $HW(CO)_3Cp$ with 2-(Triflyloxy)propylbenzene. $(CF_3SO_2)_2O$ (150 μL, 0.89 mmol) was added by vacuum-transfer to a solution of 1-phenyl-2-propanol (100 μL, 0.71 mmol) and 2,6-di-*tert*-butyl-4-methylpyridine (150 mg, 0.73 mmol) in CH_2Cl_2 (10 mL). The solution was stirred for 1 h at 22 °C, and the solvent was removed under vacuum. The residue was extracted with Et_2O (10 mL), and evaporation of Et_2O gave colorless 2-(triflyloxy)propylbenzene. Neat 2-(triflyloxy)propylbenzene was unstable at room temperature and decomposed within 5 min to yield an unidentified brown material. $HW(CO)_3Cp$ (32 mg, 0.098 mmol) was added to a solution of 2-(triflyloxy)propylbenzene (13 mg, 0.048 mmol) in CD_2Cl_2 (0.60 mL). After 1.5 h at 22 °C the ^1H NMR spectrum indicated no reaction. HOTf (5 μL, 0.056 mmol) was added, and the solution was shaken for 5 min at 22 °C. The ^1H NMR spectrum of the resulting wine-red solution showed the formation of $Cp(CO)_3WOTf$ and propylbenzene.

Ionic Hydrogenation of 1-Methyl-1,4-cyclohexadiene by $HW(CO)_3Cp$ and HOTf. $HW(CO)_3Cp$ (41.0 mg, 0.123 mmol) was placed in an NMR tube, and CD_2Cl_2 was added to give a volume of 0.56 mL. 1-methyl-1,4-cyclohexadiene (5 μL, 0.044 mmol) and 1,2-dichloroethane (3 μL, internal standard) were added. An NMR spectrum was recorded, and HOTf (4 μL, 0.034 mmol) was added. The color changed from pale yellow to dark orange, and an NMR spectrum taken after 5 min at 22 °C indicated the formation of 1-methylcyclohexene (84%). Additional HOTf (5 μL, 0.056 mmol) was added, and the color of the solution turned to dark wine-red. After 5 min at 22 °C, the NMR spectrum revealed the formation of methylcyclohexane (94%). The 1-methylcyclohexene and methylcyclohexane were characterized by comparison of their NMR spectra with those of authentic samples.

Cyclopropyl Ring-Opening Reactions. A CH_2Cl_2 solution of $Ph(CH_3)(c\text{-}C_3H_5)CH$ (1.0 mL of a 20 mM solution) was added to a 3.0 mL Pierce Reacti-Vial equipped with a Mininert valve and a magnetic stirrer. $HW(CO)_3Cp$ (33.4 mg, 0.1 M) and nonane (36 μL, internal standard) were added, and the solution was analyzed by gas chromatography on a Hewlett-Packard 5890A gas chromatograph using He carrier gas and a flame ionization detector. The column used was a 25 m × 0.32 mm i.d. 5% phenyl methyl silicone column. HOTf (3.5 μL, 0.04 mmol, 2 equiv based on $Ph(CH_3)(c\text{-}C_3H_5)CH$) was added. The solution was stirred at 22 °C for 2 min and was then quenched with NEt_3 (10 μL, 0.072 mmol). The products were analyzed by GC. This experiment was repeated using $[HW(CO)_3Cp]$ concentrations of 0.2, 0.5, and 1.0 M. Within experimental uncertainty (±2%), the product ratios were independent of the initial concentration of $HW(CO)_3Cp$, giving $PhCH(CH_3)^nPr$ (41%), $PhCHEt_2$ (20%), and $PhCH_2CH(CH_3)Et$ (39%). The identity of each of these organic products was confirmed by NMR and by comparison of their GC retention times with those of authentic samples obtained from Wiley.

Reaction of $DW(CO)_3Cp$ with HOTf. $DW(CO)_3Cp$ (30 mg, 0.090 mmol) was added to a screw-capped NMR tube, and CD_2Cl_2 was added to give a volume of 0.55 mL. 1,2-Dichloroethane (3 μL, internal standard) was added, and the solution was cooled to −78 °C. HOTf (4 μL, 0.045 mmol) was added and the tube was shaken three times. An NMR spectrum recorded at −85 °C indicated that H/D exchange had already occurred, since the hydride resonance of $HW(CO)_3Cp$ was observed. The Cp resonance for the dihydride/dideuteride was observed at δ 5.92. The dihydride resonance for $[(H)_2W(CO)_3Cp]^+OTf^-$ was observed at δ −2.07, and a resonance at δ −2.12 is assigned as $[HDW(CO)_3Cp]^+OTf^-$.

Reaction of $HW(CO)_3Cp$ with HOTf at 22 °C. $HW(CO)_3Cp$ (19.5 mg, 0.058 mmol) was added to a 5 mm screw-capped NMR tube, and CD_2Cl_2 was added to give a volume of 0.59 mL. 1,2-Dichloroethane (3 μL, internal standard) was added, and an NMR spectrum was recorded. HOTf (7 μL, 0.079 mmol) was added to the pale yellow solution, and the tube was shaken at 22 °C. After 24 h at room temperature, the solution was pale orange, the yield of $Cp(CO)_3WOTf$ (δ 6.00) was 8%, and a small peak at δ 4.60 was observed for H_2. The dihydride $[(H)_2W(CO)_3Cp]^+OTf^-$ is not directly observable at room temperature, but the coalesced Cp peak for the rapidly exchanging mixture of hydride and dihydride appears at δ 5.61, compared to δ 5.52 for $HW(CO)_3Cp$ in the absence of HOTf. The hydride resonance of $HW(CO)_3Cp$ is not observed (broadened into the baseline) under these conditions.

Reaction of $HMo(CO)_3Cp$ with HOTf. Using a procedure analogous to that described above for $HW(CO)_3Cp$, a CD_2Cl_2 solution of $HMo(CO)_3Cp$ (0.1 M) was treated with HOTf (1.5 equiv) at room temperature. The solution turned to wine-red immediately upon mixing, and an NMR spectrum recorded at t = 15 min indicated an 80% yield of $Cp(CO)_3MoOTf$. A broad ($w_{1/2} \approx 100$ Hz) resonance at δ 11.6 was observed for the acid; a similarly broad resonance was observed at δ −5.57 for the hydride. The yield of $Cp(CO)_3MoOTf$ increased to 93% after 3 h.

Reaction of $DMo(CO)_3Cp$ with HOTf. $DMo(CO)_3Cp$ (17 mg, 0.069 mmol) was added to a 5 mm screw-capped NMR tube, and CD_2Cl_2 was added to give a volume of 0.63 mL. 1,2-Dichloroethane (3 μL, internal standard) was added, and an NMR spectrum was recorded at −33 °C. The solution was cooled to −78 °C, HOTf (10 μL, 0.11 mmol) was added, and the tube was shaken twice. The ^1H NMR spectrum of the resulting wine-red solution at −33 °C showed the formation of $Cp(CO)_3MoH$ (51%) and $Cp(CO)_3MoOTf$ (16%) along a small peak at δ 4.57 due to H_2. After 3 h at 22 °C, 95% of $Cp(CO)_3MoOTf$ had formed.

Ionic Hydrogenation of $Me_2C{=}CMe_2$ by $HW(CO)_2(PMe_3)Cp$ and HOTf. $HW(CO)_2(PMe_3)Cp$ (20 mg, 0.052 mmol) was added to a screw-capped NMR tube, and CD_2Cl_2 was added to give a volume of 0.76 mL. Tetramethylethylene (4 μL, 0.034 mmol) and 1,2-dichloroethane (3 μL, internal standard) were added. An NMR spectrum was recorded, and HOTf (4 μL, 0.045 mmol) was added. An NMR spectrum of the pale yellow solution taken 5 min after addition of the HOTf indicated that $[(H)_2W(CO)_2(PMe_3)Cp]^+OTf^-$[26] had formed. After 2 h at 22 °C, only 3% of 2,3-dimethylbutane was observed in the ^1H NMR spectrum. After the solution was heated for 20 h at 50 °C, the yield of 2,3-dimethylbutane had increased to 10%, but most of the dihydride had decomposed to give $Cp(CO)_2(PMe_3)WOTf$ (75%).

Reaction of $Me_2C{=}CMe_2$ with $[(H)_2W(CO)_2(PMe_3)Cp]^+OTf^-$. $[(H)_2W(CO)_2(PMe_3)Cp]^+OTf^-$ (28 mg, 0.053 mmol) was added to a screw-capped NMR tube, and CD_2Cl_2 was added to give a volume of 0.62 mL. Tetramethylethylene (6 μL, 0.050 mmol) and 1,2-dichloroethane (2 μL, internal standard) were added, and the tube was heated for 7 h at 22 °C. The ^1H NMR spectrum of the resulting solution showed the formation of 2,3-dimethylbutane in 3% yield.

Attempted Ionic Hydrogenation of $Me_2C{=}CMe_2$ by $HRu(CO)(PMe_3)Cp$ and HOTf. $HRu(CO)(PMe_3)Cp$ (16 mg, 0.059 mmol) was added to a 5 mm screw-capped NMR tube, and CD_2Cl_2 was added to give a volume of 0.75 mL. Tetramethylethylene (4 μL, 0.034 mmol) and 1,2-dichloroethane (4 μL, internal standard) were added, and an NMR spectrum was recorded. HOTf (5.5 μL, 0.062 mmol) was added to the solution, and the tube was shaken for 5 min at 22 °C. The ^1H NMR spectrum of the resulting yellow solution showed the formation of $[Cp(CO)(PMe_3)Ru(\eta^2\text{-}H_2)]^+OTf^-$ (69%). After 1.5 h at 22 °C, 90% of the $[(\eta^2\text{-}H_2)Ru(CO)(PMe_3)Cp]^+OTf^-$ had decomposed, but less than 5% of the $Me_2C{=}CMe_2$ had been hydrogenated.

Competition Experiments between $HW(CO)_3Cp$ and $HSiEt_3$ as Hydride Donors. Using the general procedure for low-temperature reactions described above, a CD_2Cl_2 solution (0.65 mL) of $Me_2C{=}CMe_2$ (0.02 M), $HW(CO)_3Cp$ (0.098 M), and $HSiEt_3$ (0.12 M) containing 1,2-dichloroethane as the internal standard was treated with HOTf (6 μL, 0.097 M, 5 equiv based on $Me_2C{=}CMe_2$) at −50 °C for 5 min. Pyridine (7 μL, 0.12 M) was added to quench the reaction, and the solution was analyzed by NMR. 2,3-Dimethylbutane was formed in 97% yield. On the basis of this amount of hydrogenation product, 0.17 equiv of $HW(CO)_3Cp$ were consumed and 0.77 equiv of $HSiEt_3$ were consumed. The *apparent* relative kinetic hydricity of $HSiEt_3$ compared to $HW(CO)_3Cp$ determined by these data is $k_{HSi}/k_{HW} = 3.7$.

A related experiment was carried out at 22 °C in an NMR tube, in which a CD_2Cl_2 solution of $Me_2C{=}CMe_2$ (0.14 M), $HW(CO)_3Cp$ (0.17 M), and $HSiEt_3$ (0.17 M) containing 1,2-dichloroethane as the internal standard was treated with HOTf (6 μL, 0.056 M, 0.4 equiv based on $Me_2C{=}CMe_2$) at 22 °C for 5 min. On the basis of the amount of hydrogenation product formed, 0.26 equiv of $HW(CO)_3Cp$ were consumed and 0.63 equiv of $HSiEt_3$ were consumed. The *apparent* relative kinetic hydricity determined by this experiment is $k_{HSi}/k_{HW} = 2.4$.

Competition Experiments between Transition Metal Hydride Donors. NMR tubes containing CD_2Cl_2 solutions of $Me_2C{=}CMe_2$ (~0.02 M) and 5–10 equiv each of two different transition metal hydrides were treated with HOTf (~1 equiv based on $Me_2C{=}CMe_2$) at room temperature. In the case of competition between $HW(CO)_3Cp$ and $HMo(CO)_3Cp$, the amounts of both of the starting hydrides and both of the metal triflates resulting after hydride transfer could be determined, since each of these species had a Cp resonance that could be integrated by ^1H NMR. The *apparent* relative kinetic hydricity determined from two separate experiments is $k_{HW}/k_{HMo} = 1.1$ and 1.6. In the competition between $HW(CO)_3Cp$ and $HRe(CO)_5$, the amount of $(CO)_5ReOTf$ had to be determined indirectly from the amount of organic hydrogenation product and the amount of $Cp(CO)_3WOTf$ formed in the reaction, since the amount of $(CO)_5ReOTf$ cannot be determined by ^1H NMR. The assumption that $[(CO)_5ReOTf] = [(CH_3)_2CHCH(CH_3)_2] - [Cp(CO)_3WOTf]$ is justified on the basis of the excellent mass balances verified by NMR in cases of $HW(CO)_3Cp$ and $HMo(CO)_3Cp$, where the metal triflate yields could be directly measured and compared to the yield of hydrogenation product. The *apparent* relative kinetic hydricity determined from two separate experiments is $k_{HRe}/k_{HW} = 15$ and 7.

Reaction of $Cp(CO)_3W{-}FBF_3$ with $HSiEt_3$ To Produce $HW(CO)_3Cp$. $Ph_3C^+BF_4^-$ (115 mg, 0.348 mmol) was added to a solution of $HW(CO)_3Cp$ (105 mg, 0.314 mmol) in CH_2Cl_2 (5 mL) at –40 °C. After the solution was stirred for 5 min at –40 °C, an IR spectrum recorded at room temperature exhibited ν_{CO} bands at 2065 and 1973 cm^{-1}, indicating clean and complete conversion to $Cp(CO)_3W{-}FBF_3$.[19] $HSiEt_3$ (100 μL, 0.626 mmol) was added, and the red solution turned to violet within a few seconds. The solution was warmed from –40 °C to room temperature and was stirred at room temperature for 45 min. An IR spectrum of the red-orange solution indicated the formation of $HW(CO)_3Cp$ (70% yield by quantitative IR measurement).

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