Single-Step Hydride Transfer from $CpMo(CO)_2(PPh_3)H$ to Protonated Ketones

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The only alcohol complex formed during the ionic hydrogenation of acetone by $CpMo(CO)_2(PPh_3)H$ (**1b**) and CF_3SO_3H in acetonitrile is *trans*-$CpMo(CO)_2(PPh_3)(i\text{-}PrOH)^+$ (**4**); on standing the coordinated isopropyl alcohol of **4** is replaced by solvent, forming *trans*-$CpMo(CO)_2(PPh_3)(CH_3CN)^+$ (**2b**). Treatment of **1b** in the same solvent with CF_3SO_3H alone yields the more stable cis acetonitrile complex **3b**. The final products from treating an acetonitrile solution of acetone and **1b** with CF_3SO_3H thus include both **2b** and **3b**. The trans stereochemistry of **4** implies that the ionic hydrogenation of acetone by **1b** involves a single-step hydride transfer rather than separate e^- and $H^\bullet$ transfers. The equilibrium constant for the protonation of acetone by CF_3SO_3H in CH_3CN at 25 °C is 2.4×10^{-2}, and the rate constant for hydride transfer from **1b** to Me_2COH^+ is 12 300 M^{-1} s^{-1} under the same conditions. Other ketones undergo ionic hydrogenation more slowly.

Introduction

Transfer of hydrogen from transition metals, as a proton (H^+), a hydrogen atom ($H^\bullet$), or a hydride (H^-), is an important step in numerous catalytic and stoichiometric processes.[1] Apparent "hydride" transfer to protonated ketones, aldehydes, alkynes, and olefins is a step in the "ionic hydrogenation" of these substrates;[2] such transfers also appear to be a key step in the catalytic reduction of nicotinamide cofactors[3] and may be involved in the hydrogenase-catalyzed transfer of reducing equivalents from H_2 to such species.[4] However, it has been unclear whether these reactions occur by single-step hydride transfer (Scheme 1) or by stepwise transfer of an electron and a hydrogen atom (Scheme 2). The same alternatives (removal of H^- in a single step or removal of $H^\bullet$ after initial one-electron oxidation) exist for the removal of "hydride" from organic ligands.

There have been several efforts at distinguishing between these alternatives in the "hydride" abstraction

Scheme 1

$$M{-}H + E^+ \rightarrow M^+ + E{-}H$$

Scheme 2

$$M{-}H + E^+ \rightarrow M{-}H^{\bullet+} + E^\bullet$$

$$M{-}H^{\bullet+} + E^\bullet \rightarrow M^+ + E{-}H$$

reactions that occur when organometallic complexes are treated with trityl reagents. In 1982 Hayes and Cooper isolated a radical cation from the reaction of $Cp_2W(CH_3)_2$ with Ph_3C^+.[5a] In 1985 Gladysz, Cooper, and co-workers found that electron transfer from $CpRe(NO)(PPh_3)R$ to Ph_3C^+ was uphill;[5b] in 1987 Gladysz, Parker, and co-workers trapped with O_2 the trityl radicals resulting from electron transfer from $CpRe(NO)(PPh_3)R$ to Ph_3C^+ and established a stepwise (Scheme 2) mechanism for these "hydride" transfer reactions.[5c] More recently, Cheng and Bullock have examined the reactions of various hydride complexes with Ph_3C^+ and have argued for a single-step (Scheme 1) mechanism from the unfavorable equilibrium constants for electron transfer and from the values (1.7−1.8) of k_H/k_D.[5d]

In 1994 Hembre and McQueen showed that "hydride" transfer from Cp*(dppm)RuH to *N*-methylacridinium occurred without reduction of methyl viologen dication ($[MV]^{2+}$), despite the less negative potential of the latter; they concluded that the transfer did not involve an initial one-electron reduction and that its mechanism was thus that given in Scheme 1.[4b] Recently Hembre, McQueen, and Day have found that Cp*(dppf)RuH undergoes facile one-electron oxidation—the first step of Scheme 2.[4c]

Some of us have previously reported that "hydride" transfer from $CpM(CO)_2(L)H$ (M = W, L = PMe_3, **1a**;

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(1) (a) *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1991. (b) Eisenberg, D. C.; Norton, J. R. *Isr. J. Chem.* **1991**, *31*, 55−66. (c) Bullock, R. M. *Comments Inorg. Chem.* **1991**, *12*, 1. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 80−95, 381−389, and Chapters 10 and 13. (e) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992; Chapters 2, 3, 4, and 8.

(2) (a) Song, J.-S.; Szalda, D. J.; Bullock, R. M.; Lawrie, C. J. C.; Rodkin, M. A.; Norton, J. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1233. (b) Bullock, R. M.; Song, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 8602. (c) Bullock, R. M.; Luan, L.; Song, J.-S. *J. Org. Chem.* **1995**, *60*, 7170.

(3) (a) Steckhan, E.; Herrmann, S.; Ruppert, R.; Dietz, E.; Frede, M.; Spilka, E. *Organometallics* **1991**, *10*, 1568. (b) Ryabov, A. D.; Menglet, D. L.; Levi, M. D. *J. Organomet. Chem.* **1991**, *421*, C16. (c) Westerhausen, D.; Herrmann, S.; Hummel, W.; Steckhan, E. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1529.

(4) (a) Collman, J. P.; Wagenknecht, P. S.; Hembre, R. T.; Lewis, N. S. *J. Am. Chem. Soc.* **1990**, *112*, 1294. (b) Hembre, R. T.; McQueen, S. *J. Am. Chem. Soc.* **1994**, *116*, 2141. "dppm" = $Ph_2PCH_2PPh_2$. (c) Hembre, R. T.; McQueen, J. S.; Day, V. W. *J. Am. Chem. Soc.* **1996**, *118*, 798. "dppf" = 1,1′-bis(diphenylphosphino)ferrocene.

(5) (a) Hayes, J. C.; Cooper, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 5570. (b) Asaro, M. F.; Bodner, G. S.; Gladysz, J. A.; Cooper, S. R.; Cooper, N. J. *Organometallics* **1985**, *4*, 1020. (c) Bodner, G. S.; Gladysz, J. A.; Nielsen, M. F.; Parker, V. D. *J. Am. Chem. Soc.* **1987**, *109*, 1757. (d) Cheng, T.-Y.; Bullock, R. M. *Organometallics* **1995**, *14*, 4031.

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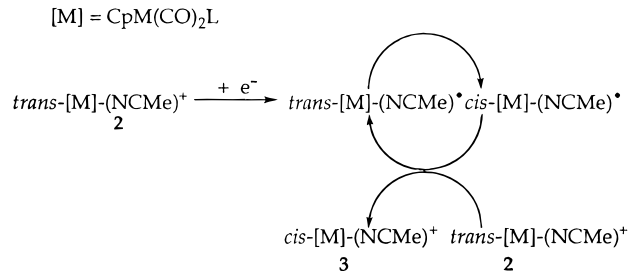
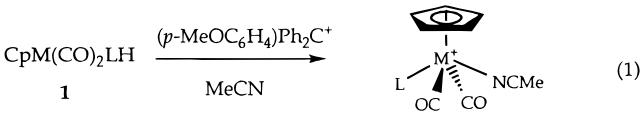
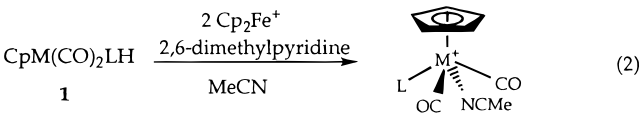
Scheme 3



M = Mo, L = PPh_3, **1b**) to Ph_2ArC^+ (Ar = *p*-$MeOC_6H_4$) in MeCN gives mainly *trans*-$CpM(CO)_2L(NCMe)^+$ (**2**) (reaction 1), while the oxidation of these hydrides by single-electron reagents (e.g., Cp_2Fe^+) in the presence of base gives mainly *cis*-$CpM(CO)_2L(NCMe)^+$ (**3**) (reaction 2).[6]

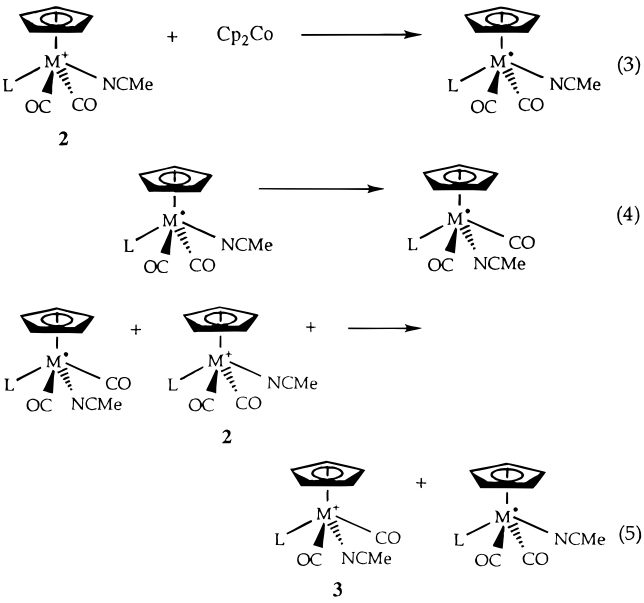


(1)



(2)

The cis cation **3** is more stable than the trans cation **2**. The latter is converted to **3** by *catalytic* amounts of a reducing agent (Cp_2Co),[6] implying the mechanism shown in Scheme 3: the radical formed by reduction (eq 3) undergoes facile isomerization to the cis stereoisomer (eq 4), which can reduce another 1 equiv of **2** (eq 5).

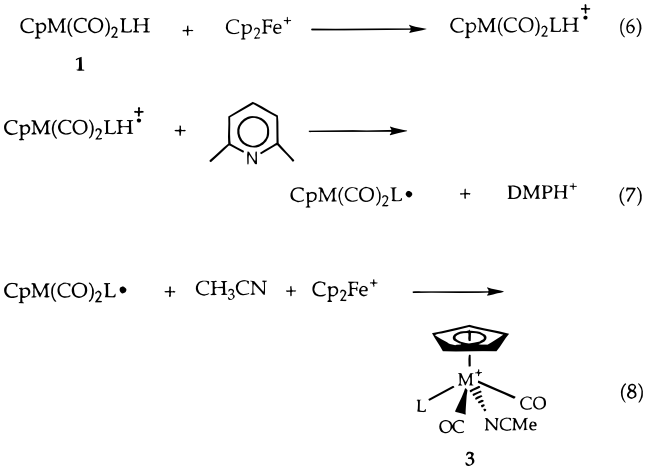


(3)

(4)

(5)

As reaction 2 gives the thermodynamic product **3** while reaction 1 gives the kinetic product **2**, we have suggested[6] that reaction 2 involves an intermediate permitting equilibration of stereochemistry, while reaction 1 is a true hydride transfer (Scheme 1). It is reasonable to suggest that the intermediate in reaction **2** is the 17-electron $CpM(CO)_2L^\bullet$, leading to the mechanism in eqs 6−8.



(6)

(7)

(8)

We now suggest that this difference in stereochemical outcome (**2** vs **3**) can be used to distinguish between Scheme 1 and Scheme 2 mechanisms for other hydride transfer reactions. The mechanism in Scheme 1 should give **2**, whereas the electron transfer mechanism (Scheme 2) should give **3**.

Results and Discussion

Reaction of $CpMo(CO)_2(PPh_3)H$ (1b) and Acetone in the Presence of Acid. When the hydride **1b** and acetone were dissolved in acetonitrile-d_3 and excess acid (either CF_3SO_3H or HBF_4) was added, ^1H NMR showed the formation of isopropyl alcohol as well as *trans*-$CpMo(CO)_2(PPh_3)(NCMe)^+$ (**2b**), *cis*-$CpMo(CO)_2(PPh_3)(NCMe)^+$ (**3b**), and another organometallic product **4**. When the solution was stored at ambient temperature, the resonances of **4** disappeared at the same rate that the resonances for isopropyl alcohol and **2b** grew in—with a half-life of approximately 45 min.

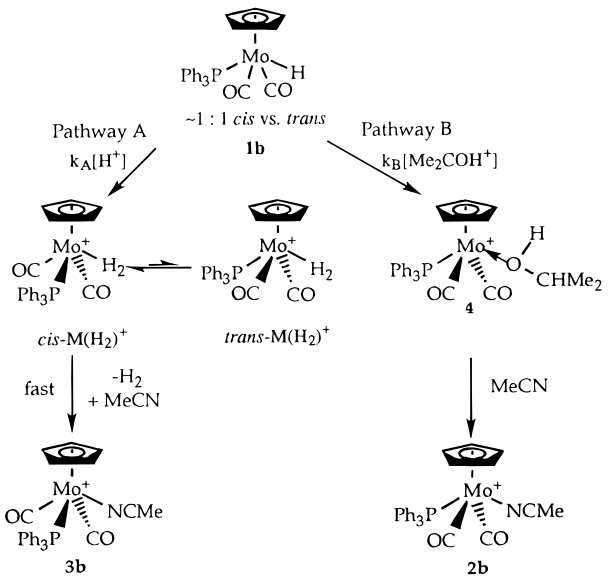
Its ^1H NMR spectrum showed that **4** contained coordinated isopropyl alcohol; the formation of **4** is parallel to the previously reported formation of $CpW(CO)_3(i\text{-PrOH})^+$ from $CpW(CO)_3H$ and protonated acetone.[2a] The ^{31}P splitting (2.3 Hz) of the Cp ^1H resonance of **4** was characteristic of the trans isomer of the four-legged piano-stool complex $CpM(CO)_2(PR_3)X$;[7] the single methyl ^1H doublet of the coordinated *i*-PrOH showed that a plane of symmetry passed through it. Compound **4** was thus *trans*-$CpMo(CO)_2(PPh_3)(i\text{-PrOH})^+$. The subsequent conversion of **4** to **2b** is merely the displacement of isopropyl alcohol by acetonitrile, a better donor ligand (Scheme 4); **2b** and *i*-PrOH are formed in a 1:1 ratio.

When **1b** was dissolved in acetonitrile-d_3 and treated with excess acid, only **3b** and H_2 were observed. This observation suggested that some of the **3b** formed in the **1b**/acetone/acid reaction arose from direct reaction of the acid with **1b**. Two competing reaction pathways have thus been drawn in Scheme 4: pathway A, forming **3b** from **1b** and acid, and pathway B, forming **4** (and eventually **2b**) from **1b**, acetone, and acid.

(6) (a) Ryan, O. B.; Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2618. (b) Smith, K.-T.; Tilset, M. *J. Organomet. Chem.* **1992**, *431*, 55.

(7) Manning, A. R. *J. Chem. Soc. A* **1967**, 1984.

Scheme 4



Dependence of Product Ratio on Me_2COH^+ Concentration. The [Me_2COH^+] involved in pathway B should (because of the speed with which such protonation equilibria become established) reflect the equilibrium extent of protonation of acetone. If Scheme 4 is correct, and if the cis and trans isomers present[8] in a solution of **1b** equilibrate rapidly, the product ratio (**4** + **2b**)/**3b** should depend on the ratio of pathway B to pathway A, i.e., on [H^+] vs [Me_2COH^+]. At constant acidity and excess acetone, the initial product ratio (**4** + **2b**)/**3b** should be linear in [Me_2COH^+].

Equilibrium for the Protonation of Acetone by Triflic Acid. The absorption maximum that acetone shows at 274 nm disappears when it is protonated. This fact was used to estimate the equilibrium constant K_{eq} for eq 9, the protonation of acetone by CF_3SO_3H in CH_3CN. (A pK_a value of 2.6 has been reported[9] for CF_3SO_3H in that solvent.) If eqs 11−13 are substituted into eq 10, the latter becomes eq 14. (A_1 is the absorbance when only acetone is present, and A_2 is the absorbance of the same solution after acid is added.)

The absorbances A_1 and A_2 were measured at 274, 290, and 300 nm for four different ratios of $[Me_2CO]_0$ to $[CF_3SO_3H]_0$. A plot of the left vs right functions in eq 14 (Figure 1) gave a straight line as predicted. The slope implied $K_{eq} = [2.4(4)] \times 10^{-2}$, in reasonable agreement with an early report from conductivity data that the pK_a of Me_2COH^+ in CH_3CN is ~ -0.1.[10] The concentrations of acetone calculated from that value of K_{eq} implied an extinction coefficient of 16.0(3) M^{-1} cm^{-1} for acetone at 274 nm, a value close to that reported for the $n \rightarrow \pi^*$ transition of acetone in other solvents.[11]

Effect of [Me_2COH^+] on the Product Ratio from Acetone/1b/Acid. We were therefore able to calculate [Me_2COH^+] from the amounts of acetone and CF_3SO_3H present in any reaction with **1b**. At low [Me_2COH^+], the ^{1}H NMR measured ratios of **4** + **2b** to **3b** showed (Figure 2) the expected linear dependence on [Me_2COH^+]; however, at sufficient high [Me_2COH^+] the ratio of **4** + **2b** to **3b** leveled off to a constant value, 17(2). The fact that the line for low Me_2COH^+ concentrations went through the origin implied that, as assumed in Scheme 4, path A gave only the cis **3b** and none of the trans **2b**.

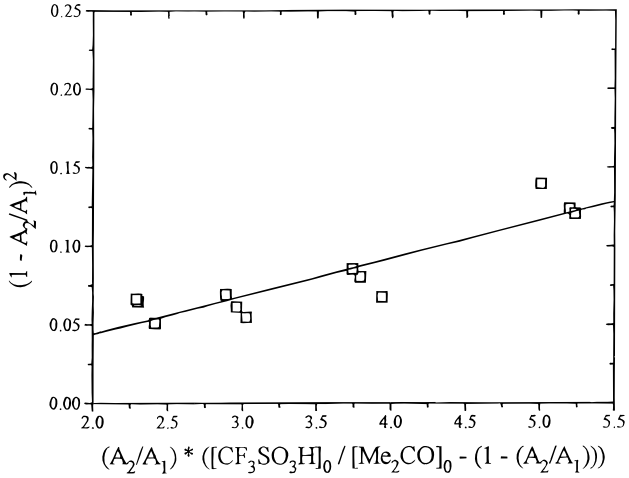


Figure 1. Determination of K_{eq}, the equilibrium constant for protonation of acetone by triflic acid in CH_3CN (see eq 14).

$$Me_2CO + CF_3SO_3H \overset{K_{eq}}{\rightleftharpoons} Me_2COH^+ + CF_3SO_3^- \quad (9)$$

$$K_{eq} = \frac{[Me_2COH^+][CF_3SO_3^-]}{[Me_2CO][CF_3SO_3H]} \quad (10)$$

$$[Me_2COH^+] \approx [CF_3SO_3^-] = \left(1 - \frac{A_2}{A_1}\right)[Me_2CO]_0 \quad (11)$$

$$[Me_2CO] = \frac{A_2}{A_1}[Me_2CO]_0 \quad (12)$$

$$[CF_3SO_3H] = [CF_3SO_3H]_0 - \left(1 - \frac{A_2}{A_1}\right)[Me_2CO]_0 \quad (13)$$

$$\left(1 - \frac{A_2}{A_1}\right)^2 = K_{eq}\left\{\frac{A_2}{A_1}\left(\frac{[CF_3SO_3H]_0}{[Me_2CO]_0} - \left(1 - \frac{A_2}{A_1}\right)\right)\right\} \quad (14)$$

Thermodynamic Stability of 4 vs Its Cis Analog 5. Scheme 4 also assumes that only the trans alcohol complex **4** is formed by hydride transfer from **1** to protonated acetone. An alternative pathway B would begin with the formation of **5**, the cis analog of **4**, followed by rapid isomerization of **5** to **4**. To check out this possibility, **5** was prepared independently (eq 15) by dissolving **1b** in a 1:1 mixture of CH_2Cl_2 and isopropyl alcohol and adding HBF_4. The ^{1}H NMR of the product in CD_2Cl_2 showed that only cis **5** (and no trans **4**) was formed. (Two signals were observed for the coordinated *i*-PrOH methyl groups and a singlet for the Cp resonance, both indicating the unsymmetric cis structure.) However, when **5** was dissolved in CD_3CN (eq 16), the color immediately changed from red to brown, and ^{1}H NMR showed that **3b** was the only complex present.

(8) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852.
(9) Fujinaga, T.; Sakamoto, I. *J. Electroanal. Chem. Interfacial Electrochem.* **1977**, *85*, 185. As quoted by: Izutsu, K. *Acid-Base Dissocation Constants in Dipolar Aprotic Solvents*; Blackwell: Oxford, 1990; p 28.
(10) Kolthoff, I. M.; Chantooni, M. K., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 8539.
(11) For example, in heptane the extinction coefficient is 15 M^{-1} cm^{-1} for the acetone absorption at 279 nm. Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 5th ed.; Wiley: New York, 1991; p 296.

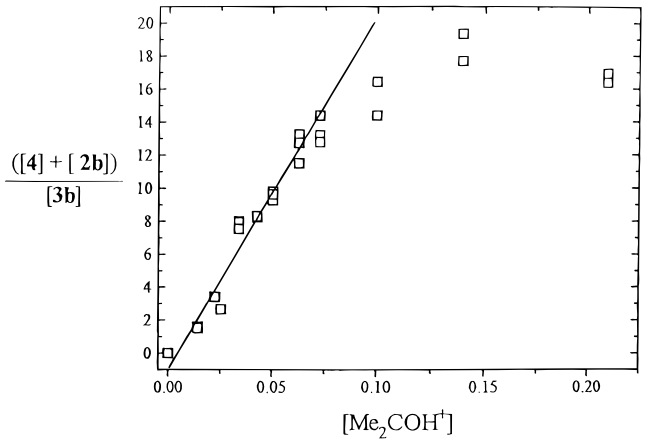
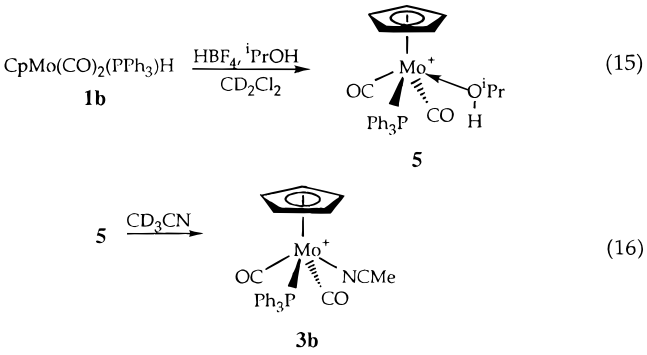


Figure 2. Dependence of (**4** + **2b**)/**3b** on [Me_2COH^+] when **1b** was treated with excess acetone in the presence of CF_3SO_3H (CD_3CN, 25 °C).



Thus, ligand exchange (replacement of isopropyl alcohol by acetonitrile) is much faster (seconds instead of hours) for **5** than for its trans analog **4**. It is thus unlikely that any **5** is formed during the reaction of **1b** with Me_2COH^+ (pathway B), because free isopropyl alcohol is formed only in conjunction with **2b** (1:1 ratio observed); the formation of **5** would have led to additional alcohol.

Why is ligand exchange for **5** so much faster than for **4**? The likely explanation is steric. The alcohol ligand in **5** is cis to the sterically demanding PPh_3 ligand and thus dissociates faster than the alcohol ligand in **4**.

Kinetic Considerations for the Formation of 4. We have assumed that the interconversion of the cis and trans isomers of **1b** is fast relative to their reaction with H^+ (pathway A) or with Me_2COH^+ (pathway B). The first-order rate constants for *cis*-**1b** ⇌ *trans*-**1b** are known in $CDCl_3$,[8] and they should not change appreciably with solvent.

Comparison requires knowing the absolute rate of pathway A or B. We have therefore used stopped-flow methods to examine the reaction of **1b** with Me_2COH^+. The UV−vis spectrum of the product **4** showed an absorbance maximum at 486 nm that was easily monitored. When 0.807 mM **1b** was treated with 170 mM acetone and 28.5 mM CF_3SO_3H in CH_3CN at 25 °C, the absorbance grew from zero to 0.21; the reaction showed only a single exponential, with an observed first-order rate constant of 108 s^{-1}.[12] When the reaction was assumed to be first-order in Me_2COH^+,[13] a *second-order* rate constant of 12 300 M^{-1} s^{-1} was deduced from the calculated [Me_2COH^+] of 8.76 mM.

In the *linear* portion of Figure 2, [Me_2COH^+] < 0.10 M, this *second-order* rate constant would have produced *pseudo-first-order* rate constants less than the first-order rate constant for cis → trans isomerization of **1b**. For example, when [Me_2COH^+] = 0.05 M, the first-order rate constant for the disappearance of **1b** by pathway B would be 615 s^{-1} at 25 °C in CH_3CN. The rate constant for the isomerization of *cis*-**1b** to *trans*-**1b** is 1560 s^{-1} at the same temperature in $CDCl_3$.[8]

Of course, the first-order rate constants for *cis*-**1b** ⇌ *trans*-**1b** no longer exceed those for hydride transfer to Me_2COH^+ at higher concentrations of that electrophile. It seems likely that the trans isomer of **1b** is more reactive toward Me_2COH^+. In earlier papers[6] we have suggested on steric grounds (suppression of the reactivity of a cis hydride ligand by the large PR_3) that only the trans stereoisomer of a substituted hydride such as **1b** can transfer hydride to Ph_2ArC^+. Cheng and Bullock have shown that the trans isomer of $CpMo(CO)_2(PCy_3)H$ reacts with Ph_3C^+ at least 300 times more rapidly than the cis isomer.[5d] The exclusive formation of the trans alcohol complex **4** in pathway B is consistent with our proposal that only the trans isomer of **1b** reacts with Me_2COH^+.

The fact that the plot in Figure 2 becomes level at [Me_2COH^+] ≥ 0.10 M confirms that cis → trans isomerization of **1b** can become rate-limiting (eq 17). Cheng and Bullock have also identified this situation in the reaction of $CpMo(CO)_2(PCy_3)H$ with Ph_3C^+.[5d]

$$\textit{cis}\text{-}\mathbf{1b} \xrightarrow{\text{slow}} \textit{trans}\text{-}\mathbf{1b} \xrightarrow[\text{fast}]{[Me_2COH^+]} \mathbf{4} \qquad (17)$$

Why Are the Cis Cations 3b and 5 the Only Products from the Reaction of 1b with Acid? Much evidence suggests that hydride complexes are protonated more readily on the hydride ligand than on the metal.[14] The kinetic products of such protonations are frequently dihydrogen complexes. There is, however, no obvious reason why *cis*-**1** should be protonated more readily than *trans*-**1**. It is possible that *trans*-$CpMo(CO)_2(PPh_3)(H_2)^+$ isomerizes to *cis*-$CpMo(CO)_2(PPh_3)(H_2)^+$ faster than H_2 is replaced by MeCN (Scheme 4) or *i*-PrOH (eq 15). There is reason to believe the cis dihydrogen complex would be more stable: an analogous tungsten dihydride complex has the structure shown in Figure 3.[6a,15]

Ionic Hydrogenation of Other C=O Bonds. Experiments similar to those described for acetone were also performed for other ketones and aldehydes. An immediate reaction was observed in all cases when the hydride **1b** and a ketone or aldehyde **6** was dissolved in CD_3CN and triflic acid added (eq 18). ^1H NMR spectra showed that both **2b** and **3b** were formed, along

(12) The observation of a single rate constant implies that "Boundary Condition II" (conformational interconversion faster than conversion of either stereoisomer to product) holds and that the situation can be described by the Winstein−Holness equation k_B(obs) = (mole fraction of **1** that is cis)[k_B(cis)] + (mole fraction of **1** that is trans)[k_B(trans)]. See section D1 in: Seeman, J. I. *Chem. Rev.* **1983**, *83*, 83.

(13) The reaction of *i*-PrCHO with $CpMo(CO)_3H$ in CD_2Cl_2 in the presence of excess CF_3CO_2H has been shown to be first-order in *i*-PrCHO and first-order in $CpMo(CO)_3H$.[2a]

(14) (a) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865. (b) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166. (c) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875. (d) Kristjánsdóttir, S. S.; Norton, J. R. In ref 1a, Chapter 9. (e) Parkin, G.; Bercaw, J. E. *J. Chem. Soc., Chem. Commun.* **1989**, 255. (f) Hamon, P.; Toupet, L.; Hamon, J.-R.; Lapinte, C. *Organometallics* **1992**, *11*, 1429.

(15) Bullock, R. M.; Song, J.-S.; Szalda, D. J. *Organometallics* **1996**, *15*, 2504−2516.

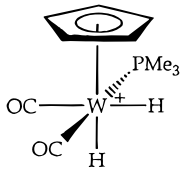
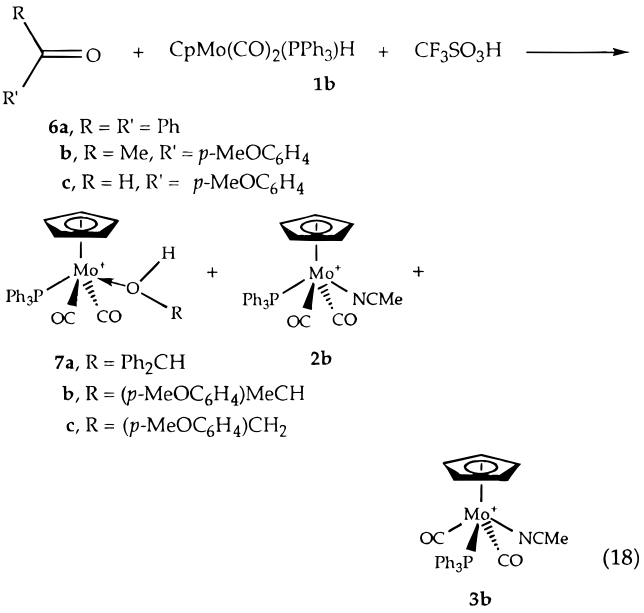


Figure 3. Structure (from ref 15) of the dihydride $CpW(CO)_2(PMe_3)H_2^+$.



(18)

with trans alcohol complexes **7** analogous to **4**. However, the cis CD_3CN complex **3b** was the main product, formed in yields between 55 and 65% in all cases. The coordinated alcohols in **7a** and **7b** were replaced by acetonitrile more rapidly (at ambient temperature $t_{1/2}$ = 6 and 17 min, respectively) than the isopropyl alcohol in **4**, while the coordinated alcohol in **7c** was replaced more slowly (at ambient temperature $t_{1/2}$ = 68 min) than the isopropyl alcohol of **4**. The exchange rates probably reflect the steric bulk of the alcohol ligands and its effect on the ease with which they dissociate.

The formation of more **3b** than with acetone implies that for these ketones pathway A is substantially faster than pathway B. Presumably hydride transfer from **1b** is slower to the cations from **6** than to protonated acetone.

Conclusion

The fact that only *trans* alcohol complexes are formed by pathway B in Scheme 4 implies that these reactions are true hydride transfers (Scheme 1), rather than electron transfers followed by hydrogen atom transfers (Scheme 2).

Experimental Section

General Procedures. All manipulations involving inorganic and organometallic compounds were carried out by vacuum line, Schlenk, syringe, or inert atmosphere box techniques. Acetonitrile was distilled from P_4O_{10}; CD_3CN and CD_2Cl_2 were vacuum-transferred from P_4O_{10}; ether was distilled from sodium benzophenone ketyl; acetone was stored over $MgSO_4$.

Residual ^1H shifts in the deuterated solvents were used as internal standards in the ^1H NMR spectra. $CpMo(CO)_2(PPh_3)H$ (**1b**) was prepared according to published procedures.[16]

Reaction of 1b with Protonated Acetone. In a typical experiment **1b** (6.0 mg, 0.0125 mmol) was dissolved in CD_3CN (0.5 mL) in an NMR tube. The tube was sealed by a septum, and acetone (8 μL, 0.1088 mmol) and triflic acid (30 μL, 0.341 mmol) were added by syringe. The solution immediately turned red. The ^1H NMR spectrum was recorded immediately (within 10 min) and showed **3b** (9%), **2b** (13%), and **4** (78%) as products. ^1H NMR (CD_3CN): **3b**-d_3, δ 5.65 (s, 5H);[6b] **2b**-d_3, δ 5.35 (d, J_{PH} = 1.8 Hz, 5H);[6b] **4**, δ 5.37 (d, J_{PH} = 2.3 Hz, 5H), 4.25 (d, J_{HH} = 7.8 Hz, 1H), 3.56 (doublet of septet, J_{HH} = 7.8 Hz, J_{HH} = 6.4 Hz, 1H), 1.16 (d, J_{HH} = 6.4 Hz, 6H). Free isopropyl alcohol was also observed at δ 4.62 (septet, J_{HH} = 6.1 Hz, 1H) and 1.39 (d, J_{HH} = 6.1 Hz, 6H).

Protonation of 1b. The hydride **1b** (5.8 mg, 0.012 mmol) was dissolved in CD_3CN (0.5 mL) in an NMR tube, and triflic acid (1.2 μL, 0.014 mmol) was added. Gas evolution (H_2) was observed. ^1H NMR (CD_3CN) showed **3b**-d_3 as the only product: δ 7.2−7.7 (m, 15 H), 5.65 (s, 5 H).[6b] A signal for dissolved H_2 was also observed at δ 4.56 (s).

Equilibrium Constant Determination for the Equilibrium between Acetone and Triflic Acid. Four different solutions of acetone (3, 3, 4, and 5 μL, respectively) in 3 mL of acetonitrile were prepared, and the UV spectra were recorded for each solution. Triflic acid (20, 30, 20, and 20 μL, respectively) was added, and the UV spectra were recorded again. The absorbances A_1 (without acid) and A_2 (with acid) were measured at three different wavelengths (274, 290, and 300 nm, respectively) for each of the four solutions; the decrease in absorbance was typically between 25 and 35%. The results from this experiment are shown in Figure 1 and give the equilibrium constant as 2.4(4) × 10^{-2}; the intercept is zero within experimental error.

Dependence of Product Ratio from Acetone/1b/Acid on [Acetone]. Samples of **1b** (6.0 mg, 0.0125 mmol each) were dissolved in CD_3CN (0.5 mL each) in NMR tubes. Acetone (varying from 1 to 150 μL) was added to the tubes; then triflic acid (30 μL, 0.341 mmol) was added. The tubes were stored in liquid nitrogen until their NMR spectra were recorded. The ratios (**4** + **2b**)/**3b** were determined by integration of the peaks. The results are given in Figure 2. When [Me_2COH^+] was <0.075 M, the ratio (**4** + **2b**)/**3b** showed a linear dependence on [Me_2COH^+]; linear regression gave a slope of 213(13) and an intercept of −0.9(0.6).

Synthesis of *cis*-5. The hydride **1b** (50.0 mg, 0.104 mmol) was dissolved in a mixture of dichloromethane (3 mL) and isopropyl alcohol (3 mL). HBF_4·Et_2O (250 μL, 1.83 mmol) was added, and the solution was stirred for 20 min. Some of the solvent was removed under vacuum, and diethyl ether was added until the red product precipitated (34.2 mg, 0.055 mmol, 53%). ^1H NMR (CD_2Cl_2): δ 5.70 (s, 5 H), 3.00 (m, 1 H), 2.68 (d, J_{HH} = 3.2 Hz, 1 H), 1.06 (d, J_{HH} = 6.3 Hz, 3H), 0.36 (d, J_{HH} = 6.2 Hz, 3H). When this compound was dissolved in CD_3CN, it reacted rapidly with that solvent to form **3b**.

Stopped-Flow Observation of the Reaction of 1b with Protonated Acetone. One solution contained **1b** (15.5 mg, 0.0323 mmol) and acetone (500 μL, 6.80 mmol) in acetonitrile (20.0 mL); the other contained triflic acid (100 μL, 1.14 mmol) in acetonitrile (20.0 mL). These solutions were placed in two reservoirs in a High-Tech SF-41 Canterbury stopped-flow apparatus (equipped with an RSM-1000 scanning system from OnLine Instruments). An increase in absorbance of up to 0.21 was observed when these solutions were mixed. The *pseudo-first-order* rate constant ($k_{obs} = k_B$[Me_2COH^+]) was determined for eight different "shots" of 500 μL (250 μL from each solution); the average was 108 s^{-1}. The calculated [Me_2COH^+] of 8.7 mM gave a *second-order* rate constant (k_B) of 12 300 M^{-1} s^{-1}.

Reaction between 1b and Ph_2COH^+. An NMR tube was charged with **1b** (6.2 mg, 0.013 mmol) and benzophenone (**6a**;

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4.3 mg, 0.024 mmol) and dissolved in CD_3CN (0.5 mL). Triflic acid was added (2.0 μL, 0.023 mmol), and the color immediately changed from light yellow to dark red. The ^1H NMR spectrum (after 10 min) showed that **3b** (63%) was the main product. Also observed were **2b** (29%) and **7a** (8%). ^1H NMR for **7a** (CD_3CN): δ 5.39 (d, J_{HP} = 2.3 Hz, 5 H). The signals for coordinated diphenylmethanol were hidden under the phenyl signals between 7.2 and 7.9 ppm. Free diphenylmethanol was observed with one signal at δ 6.30 (d, J_{HH} = 7.8 Hz, 1 H). The coordinated diphenylmethanol in **7a** exchanged with CD_3CN ($t_{1/2}$ = 6 min) to form **2b**.

Reaction between 1b and (*p*-MeO-C_6H_4)(Me)COH$^+$. An NMR tube was charged with **1** (7.2 mg, 0.015 mmol) and (*p*-MeO-C_6H_4)(Me)CO (**6b**; 3.5 mg, 0.023 mmol) and dissolved in CD_3CN (0.5 mL). Triflic acid was added (2.0 μL, 0.023 mmol), and the color immediately changed from light yellow to dark red. After 10 min the ^1H NMR spectrum showed that **3b** (66%) was the main product. Also observed were **2b** (14%) and **7b** (20%). ^1H NMR for **7b** (CD_3CN): δ 5.30 (d, J_{HP} = 2.0 Hz, 5 H), 4.8 (d, 1 H), 3.82 (s, 3 H). The signal for the methoxy group for free alcohol was observed at δ 3.74 (s, 3 H). The other signals for coordinated and free alcohol were hidden under the phenyl signals between δ 7.0 and 7.6. Exchange of the coordinated alcohol in **7b** with CD_3CN formed **2b**-d_3 with $t_{1/2}$ = 17 min.

Reaction between 1b and (*p*-MeO-C_6H_4)(H)COH$^+$. An NMR tube was charged with **1b** (6.6 mg, 0.014 mmol) and (*p*-MeO-C_6H_4)(H)CO (**6c**; 5.5 μL, 0.045 mmol) dissolved in CD_3CN (0.5 mL). Triflic acid was added (4.0 μL, 0.046 mmol), and the color immediately changed from light yellow to dark red. The ^1H NMR spectrum (after 10 min) showed that **3b** (56%) was the main product. Also observed were **2b** (14%) and **7c** (30%). ^1H NMR for **7c** (CD_3CN): δ 5.34 (d, J_{HP} = 2.4 Hz, 5 H), 4.52 (d, J_{HP} = 5.9 Hz, 1 H), 3.79 (s, 3 H). The signal for the methoxy group of free alcohol was observed at δ 3.73 (s, 3 H). The other signals for coordinated and free alcohol were hidden under the phenyl signals between δ 7.0 and 7.6. Exchange of the coordinated alcohol in **7c** with CD_3CN formed **2b**-d_3 with $t_{1/2}$ = 68 min.

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