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Catalytic ionic hydrogenations of ketones using molybdenum and tungsten complexes †

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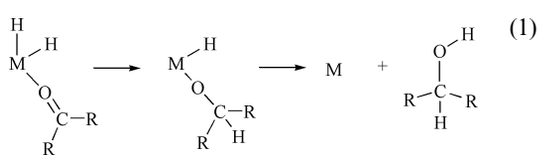
Ketone complexes $[CpM(CO)_2(PR_3)(\eta^1\text{-}Et_2C{=}O)]^+BAr'_4{}^-$ (R = Ph or Me; M = Mo or W) were prepared from hydride transfer from $Cp(CO)_2(PR_3)MH$ to $Ph_3C^+BAr'_4{}^-$ [Ar′ = 3,5-bis(trifluoromethyl)phenyl] in the presence of 3-pentanone. These ketone complexes are catalyst precursors for hydrogenation of $Et_2C{=}O$ under mild conditions (23 °C, <4 atm H_2). Analogous catalytic hydrogenations are obtained from reaction of the PCy_3 complexes $Cp(CO)_2(PCy_3)MH$ with $Ph_3C^+BAr'_4{}^-$. The proposed mechanism involves displacement of the ketone by H_2, producing a cationic metal dihydride $[CpM(CO)_2(PR_3)(H)_2]^+$. Proton transfer from the dihydride gives a protonated ketone, followed by hydride transfer from the neutral metal hydride $CpM(CO)_2(PR_3)H$ to produce the alcohol complex $[CpM(CO)_2(PR_3)(Et_2CHOH)]^+$. The free alcohol product is released from the metal through displacement by H_2 or ketone, completing the catalytic cycle. In most cases, conversion of the ketone or alcohol complexes to the dihydride is the turnover-limiting step of the catalytic cycle, with ketone and alcohol complexes being observed during the reaction. For reactions using the W–PCy_3 system, the dihydride $[CpW(CO)_2(PCy_3)(H)_2]^+$ is observed as the resting state of the catalytic process. Proton transfer is slow and becomes turnover-limiting in this case. The Mo catalysts are more active than W, and the dependence on phosphine is $PCy_3 > PPh_3 > PMe_3$. The turnover rates are slow, with the fastest initial rate of about 2 turnovers per hour found for the Mo–PCy_3 system. This ionic hydrogenation mechanism does not require coordination of the ketone to the metal for the hydrogenation, thus differing from traditional mechanisms where coordination of a ketone to a metal precedes insertion of the ketone into a M–H bond.

Introduction

Hydrogenation of ketones to alcohols is a reaction of fundamental importance and practical utility, being used in the synthesis of fine chemicals as well as compounds used in the pharmaceutical and agricultural industries. Main group hydride reagents such as $NaBH_4$ and $LiAlH_4$ are often used for the reduction of C=O bonds; these reactions are well-developed and immensely useful, but they consume stoichiometric amounts of the hydride reagent and produce waste by-products.

Many transition metal homogeneous hydrogenation catalysts have been developed. Rhodium dihydride catalysts for ketone hydrogenation were reported by Shrock and Osborn over 30 years ago,[1] and highly enantioselective hydrogenations using Rh catalysts have been reported more recently.[2] Ruthenium phosphine complexes have also been shown to be effective catalysts for ketone hydrogenations.[3] The traditional mechanism for these hydrogenations involves coordination of the ketone to the metal, followed by insertion of the ketone into a metal–hydrogen bond (eqn. (1)).[4] The alcohol product is released from



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the metal through a reductive elimination reaction involving the second metal hydride bond. This type of mechanism relies on the ability of the metal hydride bond to insert ketones. If such a step were not required, then new types of catalysts could potentially be developed based on different mechanisms for delivery of H_2 to the C=O bond. In addition to attempting to develop catalytic pathways that rely on different reactivity patterns for the M–H bonds, this offers the possibility of using less costly metals such as molybdenum or tungsten as alternatives to the use of more expensive rhodium or ruthenium in the well-established pathways cited above.

An example of the potential that alternative hydrogenation methods offer is provided by the fantastically reactive Ru catalysts developed by Noyori and co-workers.[5,6] Some of these catalyze the highly enantioselective hydrogenation of ketones using H_2, while others operate by transfer hydrogenation, using isopropanol as the source of the hydrogen. These and related catalysts that now appear to proceed through mechanisms that do not require coordination of the ketone to the metal will be discussed in a later section.

An alternative method for delivery of H_2 is through ionic hydrogenation, in which a proton and a hydride are sequentially transferred to a ketone or other substrate. Kursanov and co-workers pioneered the use of CF_3CO_2H as the H^+ source and $HSiEt_3$ as the H^- donor for use in the stoichiometric ionic hydrogenations of ketones and numerous other unsaturated organic compounds.[7] The versatile reactivity patterns of metal hydrides suggest the possibility of using a metal hydride bond as a source of protons, and a second metal hydride bond as a hydride donor in ionic hydrogenations. These two types of heterolytic cleavage have been demonstrated. Metal hydrides can serve as acids; the kinetic and thermodynamic aspects of proton transfer from metal hydrides have been established.[8] Metal hydrides can function as hydride donors,[9] and the kinetics of hydride transfer reactions from a series of metal hydrides toward Ph_3C^+ have been reported.[10,11]

In view of our intention of having both proton and hydride donors for the metal-catalyzed ionic hydrogenation of ketones, the next goal was to incorporate both of these reactions in a

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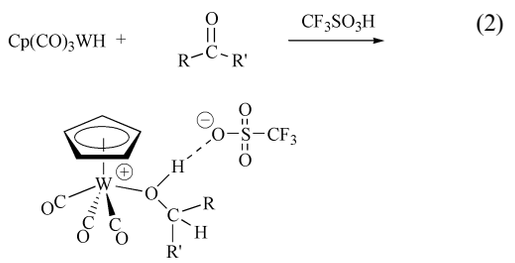
single metal center. Meeting this challenge requires proper balancing of both steps, since an acidic dihydride as the proton donor would be coupled to a conjugate base (the metal hydride) that must be adequately hydridic to carry out the hydride transfer. Each step of the mechanism may be sensitive to the steric and electronic properties of the ligands, and these effects could be opposite for the proton and hydride transfers. For example, a more electron-donating phosphine (*e.g.*, PMe_3 > PPh_3) will make a cationic MH_2^+ less acidic,[8] but will also make the neutral MH more hydridic.[10,11]

We established the use of transition metal hydrides as the hydride donor in stoichiometric ionic hydrogenations. The C=C bonds of some hindered alkenes are hydrogenated at −50 °C through reaction with HOTf (OTf = OSO_2CF_3) and metal carbonyl hydrides.[12] The C≡C bonds of certain alkynes are also hydrogenated by HOTf and $Cp(CO)_3WH$,[13] and related reactions can be used for the conversion of acetals to ether complexes.[14] Ionic hydrogenations of aldehydes or ketones by HOTf and $Cp(CO)_3WH$ lead to the formation of kinetically stabilized alcohol complexes (eqn. (2)).[15,16] The viability of



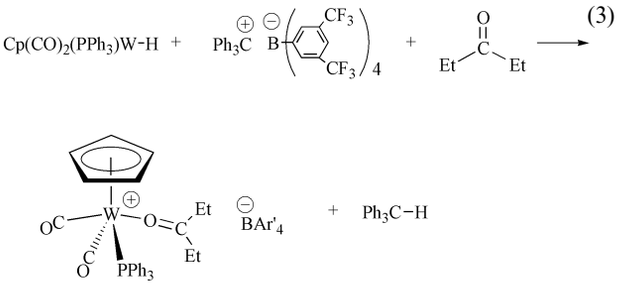
(2)

using metal hydrides as the hydride donor is thus demonstrated, albeit in reactions that require stoichiometric amounts of both the acid and the hydride donor. The goal of making such reactions catalytic in the metal would be more interesting, using hydrogen as the ultimate source of both H^+ and H^-. Obtaining this goal requires two key reactions of the catalyst in addition to the hydride transfer reactions already demonstrated—it must be capable of protonating the ketone and capable of reacting with H_2 to regenerate two M–H bonds. Our initial success in this endeavor was reported in a preliminary communication.[17] We report here the preparation of ketone complexes of molybdenum and tungsten, and a study of their use in catalytic hydrogenation of ketones by an ionic mechanism.

Results and discussion

Synthesis of ketone complexes $[Cp(CO)_2(PR_3)M(\eta^1\text{-}Et_2C{=}O)]^+$

Ketone complexes are often prepared by addition of a ketone to a metal complex containing a weakly coordinating ligand. Beck and co-workers extensively developed the chemistry of metal complexes with weakly bound BF_4^- and PF_6^- ligands.[18] They prepared Mo and W complexes such as $Cp(CO)_3MoFBF_3$ by reaction of $Cp(CO)_3MoH$ with $Ph_3C^+BF_4^-$.[19,20] Reaction of these M–FBF_3 complexes with ketones produced cationic ketone complexes.[19,21] The ketone complexes used in our studies were synthesized by a closely related method, using BAr'_4^- [Ar′ = 3,5-bis(trifluoromethyl)phenyl] as the counter ion. Hydride transfer from $Cp(CO)_2(PPh_3)WH$ to $Ph_3C^+BAr'_4^-$ in the presence of 3-pentanone, produces the ketone complex *cis*-$[CpW(CO)_2(PPh_3)(\eta^1\text{-}Et_2C{=}O)]^+BAr'_4^-$ (eqn. (3)). This complex was isolated as an orange solid in 88% yield and was characterized by ^1H, ^{13}C and ^{31}P NMR, IR, and elemental analysis. The ^{13}C resonance of the bound ketone carbonyl appears at δ 236.2, which is downfield of the carbonyl resonance of free $Et_2C{=}O$ at δ 212.5. The CO ligand *trans* to PPh_3 appears as a doublet ($^2J_{PC}$ = 6 Hz) at 240.1; the CO ligand *cis* to PPh_3 has a larger coupling constant ($^2J_{PC}$ = 21 Hz).[22] A weak band in the IR spectrum at 1632 cm^{-1} is assigned to the ν(C=O) of the bound ketone, at an energy lower than that of



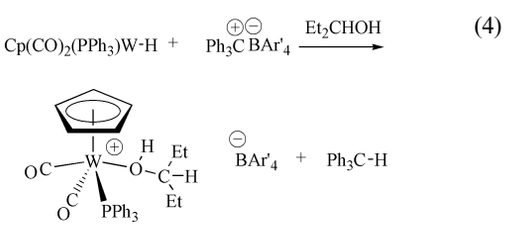
(3)

the corresponding band of free $Et_2C{=}O$ at 1712 cm^{-1}. These spectroscopic characteristics indicate that the ketone in $[CpW(CO)_2(PPh_3)(\eta^1\text{-}Et_2C{=}O)]^+$ is bound to tungsten through donation from a lone pair on oxygen, in an η^1, or σ, bonding mode, based on diagnostic NMR and IR criteria established to distinguish between $\eta^1(\sigma)$ and η^2 (π) bonding modes.[23]

Similar reactions of the molybdenum and tungsten hydrides $Cp(CO)_2(PPh_3)MoH$, $Cp(CO)_2(PMe_3)MoH$, and $Cp(CO)_2(PMe_3)WH$ led to the isolation of the corresponding ketone complexes. These ketone complexes decompose slowly when left in CD_2Cl_2 solution for a few days, but this decomposition is inhibited by the presence of excess free ketone, *i.e.*, conditions under which the catalytic reactions are carried out. Whereas the isolated sample of $[CpW(CO)_2(PPh_3)(\eta^1\text{-}Et_2C{=}O)]^+$ was the *cis* isomer, the ketone complexes $[CpMo(CO)_2(PPh_3)(Et_2C{=}O)]^+$, $[CpMo(CO)_2(PMe_3)(Et_2C{=}O)]^+$, and $[CpW(CO)_2(PMe_3)(Et_2C{=}O)]^+$ were initially observed as mixtures of *cis* and *trans* isomers. Prior studies of neutral and cationic Mo and W complexes with "four-legged piano stool" geometries established ^1H NMR criteria to readily distinguish *cis* from *trans* isomers.[10,24] The Cp resonance of the *trans* isomer is a doublet (J_{PH} ≈ 2 Hz) appearing about 0.2–0.3 ppm upfield of the singlet resonance due to the Cp of the *cis* isomer. Isomerization of the isolated *cis*/*trans* mixture occurs readily under mild conditions. For example, the *trans* isomer of $[CpMo(CO)_2(PPh_3)(Et_2C{=}O)]^+$ dominated in the isolated product, but an NMR spectrum taken after 16 hours showed nearly complete isomerization to the *cis* isomer, with only 2% *trans* isomer remaining. The isomerization appears to occur only in solution and not in the solid state.

Synthesis of alcohol complexes $[Cp(CO)_2(PR_3)M(Et_2CHOH)]^+$

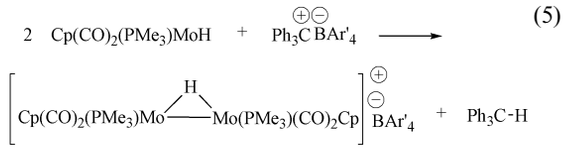
The alcohol complexes *cis*-$[CpM(CO)_2(PPh_3)(Et_2CHOH)]^+$ were prepared (eqn. (4)) for both M = Mo and W, from reac-



(4)

tions similar to those used in the preparation of the ketone complex (eqn. (3)). These alcohol complexes were isolated and fully characterized. The *trans* isomers of these same alcohol complexes were prepared through hydrogenation of the ketone complexes, as will be discussed in a later section.

Reaction of $CpMo(CO)_2(PMe_3)H$ with $Ph_3C^+BAr'_4^-$ in CH_2Cl_2, followed by addition of Et_2CHOH, did not produce $[CpMo(CO)_2(PMe_3)(Et_2CHOH)]^+$, but instead led to the isolation of $\{[CpMo(CO)_2(PMe_3)]_2(\mu\text{-}H)\}^+BAr'_4^-$, a bimetallic complex with a bridging hydride (eqn. (5)). Hydride transfer from $CpMo(CO)_2(PMe_3)H$ to Ph_3C^+ would produce $[CpMo(CO)_2(PMe_3)(CH_2Cl_2)]^+$, in which the 16-electron cation "$CpMo(CO)_2(PMe_3)^+$" is weakly solvated by CH_2Cl_2. Evidence for this complex was obtained from low-temperature NMR experiments in hydride abstractions from $CpMo(CO)_2(PMe_3)H$

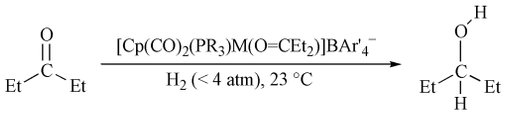


(5)

with $Ph_3C^+PF_6^-$.[10] Reaction of a second equivalent of $CpMo(CO)_2(PMe_3)H$ with $[CpMo(CO)_2(PMe_3)(CH_2Cl_2)]^+$ would displace the weakly bound solvent ligand, producing the bridging hydride complex. This reaction pathway may be favored due to the higher nucleophilicity of $CpMo(CO)_2(PMe_3)H$ compared to $CpMo(CO)_2(PPh_3)H$. The Mo–H bond of $CpMo(CO)_2(PMe_3)H$, with a trialkylphosphine PMe_3, is expected to be less acidic than $CpMo(CO)_2(PPh_3)H$, which has a PPh_3 ligand.[8] Norton and co-workers found examples where the nucleophilicity of metal hydrides was largely the *opposite* of the order of kinetic acidity.[25] Thus our reaction is consistent with their observations, since $CpMo(CO)_2(PMe_3)H$ would appear to be more nucleophilic than $CpMo(CO)_2(PPh_3)H$. Reactions in which a neutral metal hydride reacts with an unsaturated (or weakly coordinated) metal complex have led to many other examples of bridging hydrides, as reviewed by Venanzi.[26] Another synthetic route to bridging hydride complexes is through protonation of metal–metal bonded dimers. Nataro and Angelici previously reported that $\{[CpMo(CO)_2(PMe_3)]_2(\mu\text{-}H)\}^+OTf^-$ is formed by protonation of the neutral dimer with HOTf.[27] As expected, our complex with the BAr'_4^- counter ion has IR and NMR spectra very similar to those reported[27] for Angelici's complex with the OTf^- counter ion.

Catalytic hydrogenations with ketone complexes $[Cp(CO)_2(PPh_3)M(\eta^1\text{-}Et_2C{=}O)]^+$ (M = Mo, W)

When solutions of the isolated ketone complexes in CD_2Cl_2 were reacted under H_2 with $Et_2C{=}O$, hydrogenation of the C=O bond occurs, leading to the alcohol product Et_2CHOH (eqn. (6)). These experiments were carried out in NMR tubes sealed



(6)

under 1 atm H_2 at liquid nitrogen temperatures. When warmed to room temperature, this leads to an actual pressure in the tube of almost 4 atmospheres. Under these conditions the concentration of H_2 dissolved in the CD_2Cl_2 is about 15 mM, as determined by integration of the resonance for dissolved H_2 at δ 4.60. The amount of H_2 in solution determined by ^1H NMR integration is less than the actual amount because of the presence of 25% *para*-H_2 present in H_2, so a correction factor has to be applied to account for this, multiplying the integrated amount by 1.33 to determine the actual concentration. The total amount of H_2 in the tube is sufficient to hydrogenate all of the ketone, but most of it is in the gas phase above the solution. A variety of concentrations and conditions were used to test the various ketone complexes as catalysts. A standard set of conditions was chosen for comparison of the catalysts: 25–30 mM $[CpM(CO)_2(PR_3)(Et_2C{=}O)]^+BAr'_4^-$ and 300 mM $Et_2C{=}O$ (10–12 equivalents) in CD_2Cl_2 at 23 °C under <4 atmospheres H_2. An internal standard for integration of the ^1H spectra was used. Carrying out these experiments with only about 10 equivalents of ketone provided a sufficiently low ratio of ketone to metal such that the organometallic complexes as well as the organic starting material and products could all be integrated accurately by ^1H NMR. In addition, ^{31}P spectra were recorded, providing an independent measure on the relative amounts of the organometallic species.

Fig. 1 shows the time profile of the concentrations from the catalytic hydrogenation of $Et_2C{=}O$ by $[CpW(CO)_2(PPh_3)(Et_2C{=}O)]^+BAr'_4^-$. Slow hydrogenation occurs, producing the alcohol Et_2CHOH, giving 1 turnover in 4 days and 4 turnovers after 24 days. Fig. 2 shows a comparison of the activity of

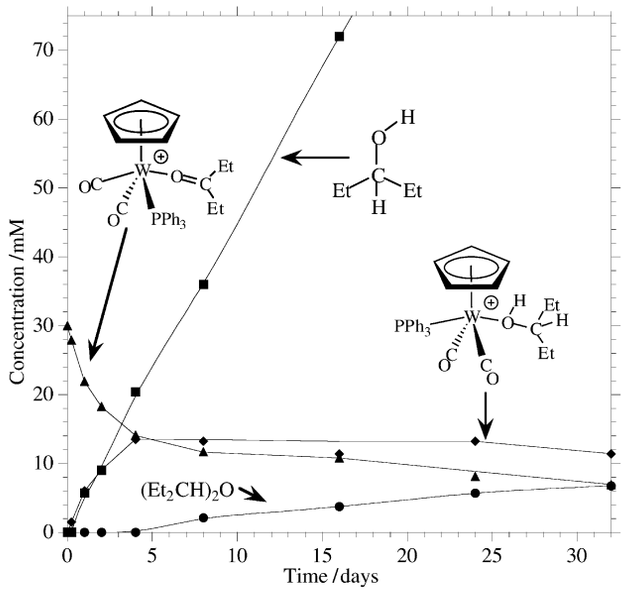


Fig. 1 Time profile of the catalytic hydrogenation of $Et_2C{=}O$ (300 mM) by $[CpW(CO)_2(PPh_3)(Et_2C{=}O)]^+$ (30 mM) under H_2 (<4 atm) in CD_2Cl_2 at 23 °C.

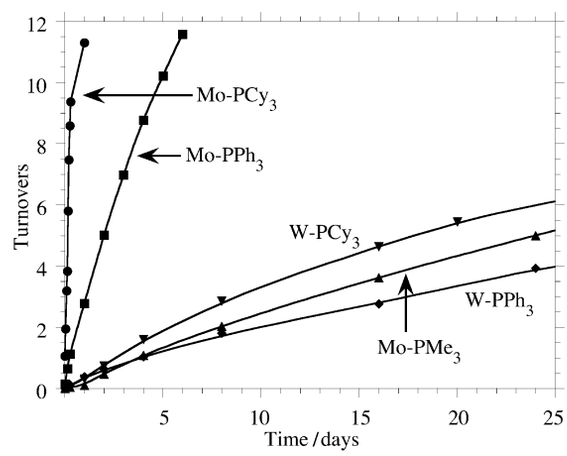
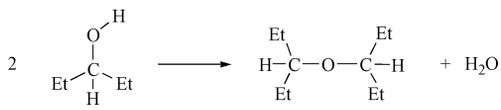


Fig. 2 Comparison of catalytic hydrogenation of $Et_2C{=}O$ (300 mM) by $[CpM(CO)_2(PR_3)(Et_2C{=}O)]^+$ (25–30 mM) under H_2 (<4 atm) in CD_2Cl_2 at 23 °C.

this and other catalysts. The formation of the hydrogenation product alcohol is accompanied by smaller amounts of the ether $(Et_2CH)_2O$ arising from condensation of two alcohols (eqn. (7)) After 24 days, the concentration of the alcohol Et_2CHOH was 102 mM and that of the ether $(Et_2CH)_2O$ was 6 mM.

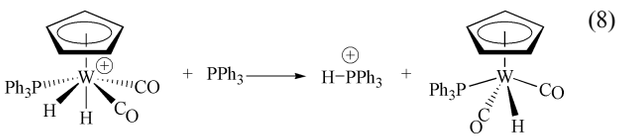


(7)

As the reaction proceeds, the concentration of the initial ketone complex $[CpW(CO)_2(PPh_3)(Et_2C{=}O)]^+$ decreases, with the concomitant appearance of new NMR resonances due to the alcohol complex *trans*-$[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+$. We previously found that alcohol complexes were formed in stoichiometric ionic hydrogenations of ketones (eqn. (2)), and these new observations show they are involved in catalytic hydrogenations as well. The concentration of this alcohol complex surpasses that of the ketone complex as the reaction proceeds.

As indicated in Fig. 1, ketone and alcohol complexes were the predominant tungsten products throughout the catalytic

reaction. Information about a catalyst deactivation pathway was provided by observation of about 8% of the phosphonium cation $HPPh_3^+$, identified by ^{31}P NMR and confirmed by comparison with an independently prepared sample. The protonated phosphine presumably forms by protonation of free PPh_3 by the cationic dihydride $[CpW(CO)_2(PPh_3)(H)_2]^+$, as shown in eqn. (8). Small amounts of the neutral tungsten hydride $CpW(CO)_2(PPh_3)H$ are also observed at the end of the catalytic reaction, as implied by the stoichiometry of eqn. (8). While the



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formation of $HPPh_3^+$ according to eqn. (8) appears entirely plausible, the more pertinent question concerns the origin of the free PPh_3. Our observations do not identify which intermediate(s) undergo loss of phosphine. The formation of the free phosphine indicates that decomposition of one tungsten species has occurred, but the problem is compounded by the subsequent reactivity. Since the protonation of the phosphine consumes a proton, it removes a second tungsten species from the functioning catalytic cycle.

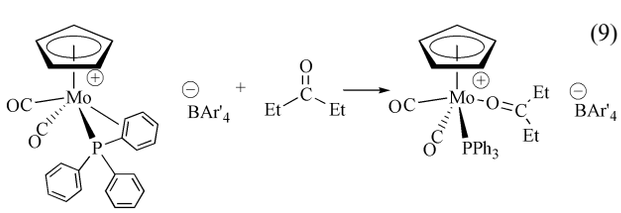
As noted above, the decline in the concentration of the ketone complex during the catalysis is accompanied by the appearance of *trans*-$[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+$. This alcohol complex is produced as the predominant product (94%) when a CD_2Cl_2 solution of $[CpW(CO)_2(PPh_3)(Et_2C{=}O)]^+$ (29 mM) is reacted with 65 atm (950 psi) hydrogen at 22 °C in the presence of Et_2CO (5 equivalents) for 17 hours. This reaction gives 1.3 turnovers, indicating that the higher pressure of hydrogen accelerates the catalysis, but only by about a factor of three. We found earlier that the rate of hydride transfer from *trans*-$Cp(CO)_2(PCy_3)MoH$ to $Ph_3C^+BF_4^-$ was much faster than that from the isomeric *cis*-$Cp(CO)_2(PCy_3)MoH$.[10] The observation of the *trans* alcohol complex under catalytic conditions indicates that the alcohol binds to the metal at the site from which the hydride was transferred, without loss of stereochemistry at the metal center. In our earlier studies of stoichiometric hydrogenation of ketones using HOTf and $Cp(CO)_3WH$, it was recognized that there must be some W–O bond formation in the transition state, prior to complete W–H bond rupture.[15,16]

The availability of both *cis* and *trans* isomers of the alcohol complex $[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+$ invites a comparison of their spectroscopic characteristics. The two isomers are readily distinguished by ^1H, ^{13}C or ^{31}P NMR. The methyl resonances of the Et_2CHOH ligand of *cis*-$[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+$ are non-equivalent in the both the ^1H and ^{13}C NMR spectra, while they are equivalent in the *trans* isomer. The chemical shifts of the OH resonances are of particular interest. The OH resonance of *trans*-$[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+$ is a doublet (J_{HH} = 8.4 Hz) at δ 5.59. In contrast, the chemical shift of the OH of *cis*-$[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+$ $BAr'_4{}^-$ appears at δ 0.10, with couplings to both CH (J_{HH} = 8.2 Hz) and P (J_{PH} = 2.9 Hz). Similar coupling constants but an even more upfield chemical shift (δ −0.62) were found for the OH resonance of the molybdenum alcohol complex *cis*-$[CpMo(CO)_2(PPh_3)(Et_2CHOH)]^+$ $BAr'_4{}^-$. The chemical shifts of alcohol complexes can be strongly influenced by hydrogen bonding of the OH. In our studies of alcohol complexes synthesized by stoichiometric ionic hydrogenations of ketones, we found that the OH resonance of $[CpW(CO)_3(Me_2CHOH)]^+BAr'_4{}^-$ appears at δ 2.41, while $[CpW(CO)_3(Me_2CHOH)]^+OTf^-$ exhibits a resonance for its OH at δ 7.34.[16] The triflate complex was shown by X-ray crystallography to have strong hydrogen bonding of the OH with an oxygen of the triflate anion, and the downfield shift of the OH in the triflate complex suggests hydrogen bonding is maintained in solution. But addition of acetone to a solution of $[CpW(CO)_3(Me_2CHOH)]^+BAr'_4{}^-$ caused its OH resonance to shift downfield to δ 6.74, suggesting that acetone was serving as a hydrogen bond acceptor in an O–H ··· O hydrogen bond.[16] A plausible explanation for the different chemical shifts of the OH protons of the *cis* and *trans* alcohol complexes is that hydrogen bonding to free ketone is occurring in *trans*-$[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+$ and other *trans* alcohol complexes, which are observed during the hydrogenations, with excess ketone present. In contrast, the spectra for the *cis* alcohol complexes are recorded on isolated samples with no ketone present to serve as a hydrogen bond acceptor.

When isolated *cis*-$[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+$ was used as a catalyst precursor for the hydrogenation of Et_2CO, the alcohol complex was promptly converted to the ketone complex *cis*-$[CpW(CO)_2(PPh_3)(Et_2C{=}O)]^+$, with <3% of the alcohol complex remaining after 15 minutes. As the hydrogenation proceeds, the *trans* alcohol complex *trans*-$[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+$ forms. This *trans* alcohol complex exists in the presence of ketone, and has a much higher kinetic stability towards displacement by ketone, compared to the *cis* alcohol complex.

Catalysis of ketone hydrogenation using the analogous Mo–PPh_3 complex enabled a comparison of W and Mo complexes under the same conditions. Catalysis by the Mo complex $[CpMo(CO)_2(PPh_3)(Et_2C{=}O)]^+BAr'_4{}^-$ produces 3 turnovers in the first day (Fig. 2), which is significantly faster than that observed with the W analog. The time progression of the metal complexes observed during catalysis is similar in this Mo case to the W example discussed above, with *trans*-$[CpMo(CO)_2(PPh_3)(Et_2CHOH)]^+BAr'_4{}^-$ becoming the major Mo species as the catalysis proceeds.

An alternative catalyst precursor was shown to produce catalysis comparable to that described above from the isolated ketone complex $[CpMo(CO)_2(PPh_3)(Et_2C{=}O)]^+BAr'_4{}^-$. We reported that hydride transfer from $CpMo(CO)_2(PPh_3)H$ to $Ph_3C^+BAr'_4{}^-$ produces a complex with an η^3-PPh_3 ligand, in which one C=C bond of the arene ring is coordinated to the molybdenum.[28] Use of this complex as a catalyst precursor for ketone hydrogenations was successful, and NMR spectra indicated that the ketone readily displaced the C=C bond, producing *cis*-$[CpMo(CO)_2(PPh_3)(Et_2C{=}O)]^+BAr'_4{}^-$ (eqn. (9)).



(9)

Along with modifying the phosphine ligand bonded to the metal, we briefly examined the effect of changing from an unsubstituted Cp ligand to the more bulky and more electron-donating C_5Me_5 (Cp*) ligand. Hydride transfer from Cp*-$Mo(CO)_2(PPh_3)H$ to $Ph_3C^+BAr'_4{}^-$ in the presence of Et_2CO produced evidence for the formation of a ketone complex analogous to that found in the Cp example. Surprisingly, however, negligible hydrogenation of $Et_2C{=}O$ was observed at <4 atm H_2 at 23 °C.

Catalytic hydrogenations with Mo and W complexes with PCy_3 and PMe_3 ligands

Hydride transfer from $Cp(CO)_2(PCy_3)MoH$ to $Ph_3C^+BAr'_4{}^-$ in CD_2Cl_2 in the presence of $Et_2C{=}O$ gave a single Mo product, as evidenced by ^1H and ^{31}P NMR spectra. Resonances for $Et_2C{=}O$ were broadened in the ^1H NMR, suggesting exchange of free and bound ketone, and the ketone complex $[CpMo(CO)_2(PCy_3)(Et_2C{=}O)]^+$ was not isolated. Hydride abstraction from $Cp(CO)_2(PCy_3)MoH$ (10 mM) in the presence of a large excess (100 equiv.) of $Et_2C{=}O$ was carried out, and H_2 (<4 atm) was

added. Hydrogenation of the ketone occurred at 23 °C, giving 18 turnovers after 5 hours, and increasing to 28 turnovers in 20 hours. Although this Mo complex produces the most active hydrogenation catalyst of the series we have examined here, it decomposes as the reaction proceeds. The formation of $HPCy_3^+$ as a decomposition product was verified by ^{31}P NMR. This product accounted for about 65% of the total integrated ^{31}P NMR intensities after 20 hours. The rate of hydrogenation decreases as the reaction proceeds, offering evidence that decomposition products play little or no role in the catalysis.

When hydrogenation of $Et_2C{=}O$ was carried out under our standard conditions (30 mM Mo, 300 mM ketone) enabling comparisons to other catalysts (Fig. 2), $Cp(CO)_2(PCy_3)MoH/Ph_3C^+BAr'_4{}^-$ produced about 6 turnovers in the first 4 hours. Monitoring the progress of the reaction by NMR provided evidence for the formation of the alcohol complex $[CpMo(CO)_2(PCy_3)(Et_2CHOH)]^+$ but this complex was not isolated for definitive characterization.

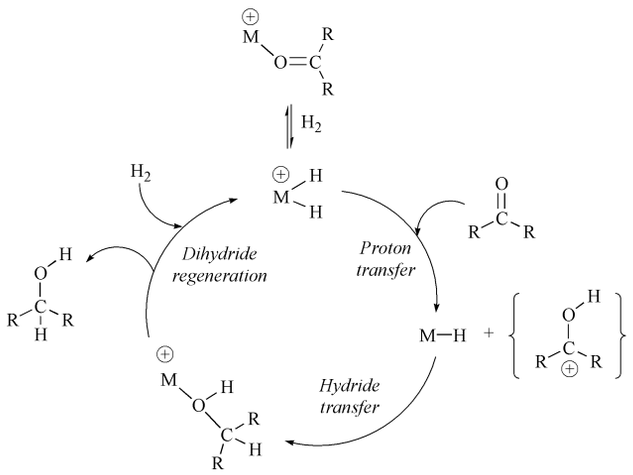
The use of other counter ions was studied qualitatively for catalysis with the Mo–PCy_3 system. We previously prepared *cis*-$Cp(CO)_2(PCy_3)MoFBF_3$ in our study of the kinetics of hydride transfer.[10] When excess $Et_2C{=}O$ is added to this complex, displacement of the weakly bound BF_4^- ligand occurs, and hydrogenation of the ketone occurs at room temperature under H_2 (<4 atm). The formation of $HPCy_3^+$ was observed as a decomposition product in this example as well, and this catalytic reaction was not studied in detail. Hydride transfer to $Ph_3C^+PF_6^-$ from $Cp(CO)_2(PCy_3)MoH$ in the presence of excess $Et_2C{=}O$ also gave evidence for a ketone complex, and hydrogenation of $Et_2C{=}O$ occurred at room temperature. Along with the formation of $HPCy_3^+$ as a decomposition product, other unidentified ^{31}P NMR resonances were observed that may be due to decomposition of the PF_6^- counter ion. Very slow catalysis of ketone hydrogenation was observed using $Cp(CO)_2(PCy_3)MoOTf$ at <4 atm H_2. Apparently the triflate anion is coordinated too strongly to Mo to provide significant catalytic activity under the mild conditions used for the reactions with $BAr'_4{}^-$, BF_4^- and PF_6^- anions.

The reactivity of the W complex with a PCy_3 ligand provided an informative contrast to the Mo analog. Following hydride transfer from $Cp(CO)_2(PCy_3)WH$ to $Ph_3C^+BAr'_4{}^-$, no definitive evidence was obtained for the bound ketone complex $[CpW(CO)_2(PCy_3)(Et_2C{=}O)]^+$. The NMR data do not distinguish between several possible products, such as a fluxional ketone complex, or a complex of constitution $[CpW(CO)_2(PCy_3)]^+$, possibly with an agostic interaction with a CH bond of the phosphine ligand. An agostic interaction involving a CH of one PCy_3 ligand was shown by X-ray crystallography for $W(CO)_3(PCy_3)_2$,[29] and kinetics studies by Hoff and co-workers provide evidence for a role of this agostic interaction in ligand substitution reactions.[30] Further study would be required to identify the initial product found in our studies, but the focus of our current efforts is on the reactivity under catalytic conditions. When hydrogen is added to the solution under our standard conditions (Fig. 2), hydrogenation of the ketone occurs, with 3 turnovers occurring after 8 days. This W–PCy_3 complex produces a slower catalyst than the Mo–PCy_3 complex, similar to the trend found in the comparison of W *vs.* Mo for the PPh_3 ligands. Also the increase in reactivity observed upon changing from PPh_3 to PCy_3 is less pronounced for the W case than for the Mo example. The most conspicuous difference is found in the metal-containing complexes observed during the progress of the catalytic reaction. The dihydride[31] $[CpW(CO)_2(PCy_3)(H)_2]^+BAr'_4{}^-$ is observed as the predominant tungsten complex during the reaction, differing from the other examples discussed above where ketone and alcohol complexes persisted during the catalysis.

Hydrogenation of $Et_2C{=}O$ is catalyzed by $[CpMo(CO)_2(PMe_3)(Et_2C{=}O)]^+BAr'_4{}^-$ (Fig. 2) but the reaction is much slower (2 turnovers in 8 days) than that observed for the Mo catalysts with PPh_3 or PCy_3 ligands. *cis* and *trans* isomers of the ketone complex were the dominant species observed during the catalysis, though other ^{31}P resonances appeared later in the reaction that may be due to the alcohol complex. Use of the tungsten analog, $[CpW(CO)_2(PMe_3)(Et_2C{=}O)]^+BAr'_4{}^-$, gave even slower reactivity, with only 2.3 turnovers being found after 16 days. The phosphonium compound $HPMe_3^+$ was observed as a decomposition product in both the Mo and W cases, but in much smaller amounts compared to the catalytic runs with PPh_3 and PCy_3.

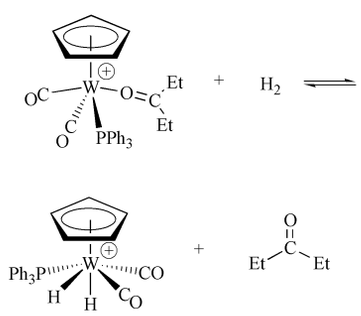
Mechanistic considerations

Scheme 1 shows the proposed mechanism for the catalytic ionic



Scheme 1

hydrogenation of ketones catalyzed by molybdenum and tungsten complexes $[CpM(CO)_2(PR_3)(Et_2C{=}O)]^+BAr'_4{}^-$. Starting from the catalyst precursor ketone complexes, displacement of the coordinated ketone by hydrogen is required to produce the cationic metal dihydride (eqn. (10)). For most of the systems



(10)

studied here the ketone complexes $[CpM(CO)_2(PR_3)(Et_2C{=}O)]^+$ are observed during the catalytic reaction as monitored by NMR (and later in the reaction the alcohol complexes). Thus conversion of the ketone or alcohol complex to the dihydride is the turnover-limiting step of the catalytic cycle in most cases.

A complete determination of the dependence of the catalytic rate on hydrogen pressure has not been made, but as noted above a comparison of the amount of hydrogenation of $Et_2C{=}O$ by $[CpW(CO)_2(PPh_3)(Et_2C{=}O)]^+$ under <4 atm H_2 compared to 65 atm H_2 shows that the higher pressure makes it only about three times faster. This suggests that the rate of catalysis is not strongly dependent on $[H_2]$ under these conditions, and that the mechanism for displacement of the ketone by H_2 is largely dissociative. Factors that promote dissociation of the ketone or alcohol from the metal are expected to enhance the rate of conversion to the dihydride, and this is proposed as the primary explanation for complexes with PCy_3 ligands producing faster catalysts than those with the smaller phosphines PPh_3 and

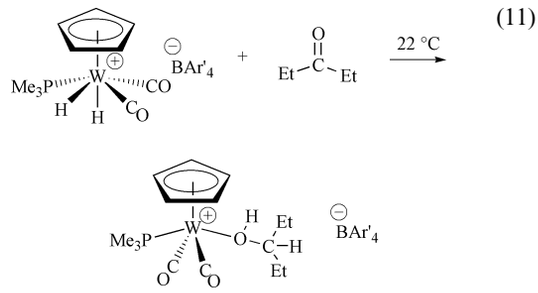
PMe_3. The rate of these catalytic reactions increases with increasing size of the phosphines, based on the steric measure of cone angles[32] (θ), with PCy_3 ($\theta = 170°$) > PPh_3 ($\theta = 145°$) > PMe_3 ($\theta = 118°$). An important mechanistic distinction between the traditional catalysts (eqn. (1)) and our ionic hydrogenation catalysts concerns coordination of the ketone. In the conventional mechanism, ketone coordination is required, and insertion of the ketone into the M–H bond forms the C–H bond. Ketone binding is observed in most of our cases, but is not required for the hydrogenation to proceed. Dissociation of the ketone is the slow step, since displacement of the ketone by H_2 is necessary to form the dihydride complex that carries out the hydrogenation. The proton and hydride transfer from the M–H bonds occurs to free rather than bound ketone in our catalytic reactions.

The catalytic experiments were carried out using $[CpW(CO)_2(PPh_3)(Et_2C{=}O)]^+$ under H_2 with excess ketone added, but the existence of the equilibrium shown in eqn. (10) was verified from a reaction of $[CpW(CO)_2(PPh_3)(Et_2C{=}O)]^+$ with hydrogen (<4 atm H_2) in the absence of added ketone. After 2 hours, 40% of the ketone complex had been converted to the dihydride $[CpW(CO)_2(PPh_3)(H)_2]^+$. At t = 18 hours, about 85% conversion to the dihydride was found, giving an *apparent* $K_{eq} \approx 2$ for eqn. (10). By the time this spectrum was recorded, however, some hydrogenation of the ketone had occurred, as expected. The equilibrium is established very slowly, contributing to the slow rate of catalysis, which requires the formation of the dihydride complex. Although a reliable value of K_{eq} was not determined from these experiments, the observation of the formation of the dihydride documents the viability of this step as a part of the catalytic cycle. Since alcohol complexes are formed as the catalysis proceeds, displacement of the alcohol ligands by H_2 is also required to maintain the catalysis. A solution of *cis*-$[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+$ placed under H_2 at 22 °C was also shown to release the free alcohol and produce the dihydride $[CpW(CO)_2(PPh_3)(H)_2]^+$.

The tungsten dihydrides $[CpW(CO)_2(PR_3)(H)_2]^+$ were all previously synthesized (R = Me, Ph, Cy) by protonation of the neutral hydrides $CpW(CO)_2(PR_3)H$.[31] The dihydrides can be isolated, and were fully characterized, including a crystal structure for $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$. Even though they are dihydrides in their stable form, this does not preclude η^2-H_2 dihydrogen complexes[33] as intermediates in the formation of the dihydrides. Norton and co-workers recently studied the kinetics of protonation of $CpW(CO)_2(PMe_3)H$, and found that protonation of the W–H bond to produce $[CpW(CO)_2(PMe_3)(\eta^2\text{-}H_2)]^+$ is faster than protonation of the metal to give the dihydride directly.[34] Analogous dihydrogen complexes could be unobserved intermediates in the formation of the dihydrides from the reactions of the ketone (and alcohol) complexes with H_2.

While the steric properties of the phosphines are a major factor influencing the rates, the thermodynamics are also important. Third row metals tend to form stronger bonds to hydrogen (and other ligands) than second row metals; for $Cp(CO)_3MH$ the M–H bond is about 3 kcal mol^{-1} stronger for M = W than for M = Mo,[35] so the increased stability of the tungsten dihydrides is not surprising. The dihydrides are known for the tungsten complexes but have not been observed for molybdenum. It is possible that the molybdenum complexes form dihydrogen complexes rather than dihydrides that are active (but unobserved) in the catalytic cycle. Whether a dihydride or a dihydrogen complex is formed is not critically important, as long as the form that exists under catalytic conditions has sufficient acidity to enable the required proton transfer to the ketone.

Once the dihydride complex is formed, the next step in the hydrogenation mechanism is proton transfer to the ketone. Evidence for the viability of this proton transfer step comes from eqn. (11), where $Et_2C{=}O$ is stoichiometrically hydrogen-



(11)

ated by $[CpW(CO)_2(PMe_3)(H)_2]^+BAr'_4{}^-$, through proton transfer from the dihydride and hydride transfer from the neutral metal hydride. This reaction is 90% complete in 1 hour, and produces the *trans* alcohol complex. Ketone protonation presumably occurs by a direct tungsten-to-oxygen proton transfer. This may also be true in hydrogenations of aldehydes and ketones that we previously reported using $[CpW(CO)_2(PMe_3)(H)_2]^+OTf^-$.[16] In the case of the hydrogenations by dihydrides with the OTf^- counter ion, however, there exists the alternative possibility that the proton transfer is mediated by OTf^- as a kinetically competent proton carrier. Darensbourg and co-workers found that chloride and other anions can mediate proton transfers from cationic dihydrides and thereby influence the rates of proton transfer.[36]

In contrast to the resting state of the catalyst being the ketone and alcohol complexes for most cases, the reactions carried out starting with $Cp(CO)_2(PCy_3)WH$ show the dihydride $[CpW(CO)_2(PCy_3)(H)_2]^+$ as the predominant metal complex. In this case, the proton transfer step is slow and becomes turnover-limiting. The slower rate here, compared to the W–PPh_3 complex, may be due to steric hindrance in the transition state for proton transfer from $[CpW(CO)_2(PCy_3)(H)_2]^+$ to the ketone, with the bulky PCy_3 ligand impeding approach of the ketone. The PMe_3 dihydride $[CpW(CO)_2(PMe_3)(H)_2]^+BAr'_4{}^-$, with a PMe_3 ligand that is similar to PCy_3 electronically but very different sterically, is faster at proton transfer. A related thermodynamic issue affecting the relative stability of the ketone complex *vs.* the dihydride in the PCy_3 case may be the destabilization of bonding of the ketone to the metal, again owing to the size of the PCy_3 ligand. The small size of two hydride ligands allows them to bond to tungsten with less hindrance from the bulky PCy_3 ligand.

The kinetics and thermodynamics of proton transfer from metal hydrides are well documented.[8] Cationic metal dihydrides and dihydrogen complexes can be especially acidic;[33] a dicationic dihydrogen complex studied by Morris and co-workers was shown to be more acidic than HOTf.[37] Norton and co-workers reported a pK_a of 5.6 for $[CpW(CO)_2(PMe_3)(H)_2]^+$ in CH_3CN. Protonated acetone in CH_3CN is reported to have p$K_a \approx -0.1$.[38,39] These values lead to the conclusion that the proton transfer from metal to oxygen of the ketone in our reactions is thermodynamically uphill. This analysis assumes that the relative pK_a values are not greatly different in our solvent CD_2Cl_2, compared to the CH_3CN in which these pK_a measurements were made. Stoichiometric hydrogenations of ketones by $[CpW(CO)_2(PMe_3)(H)_2]^+$ proceed smoothly when carried out in CD_3CN, supporting the contention that the change in solvent will not invalidate any of these conclusions. Proton transfers from the dihydride $[CpW(CO)_2(PMe_3)(H)_2]^+$ as the proton source are likely less favorable thermodynamically compared to those from the PPh_3 analog. The dihydride $[CpW(CO)_2(PPh_3)(H)_2]^+$ is presumably more acidic, based on trends in pK_a values of neutral metal hydrides when electronic properties of ligands are changed.[8] Similarly, we assume that the unobserved Mo dihydride $[CpMo(CO)_2(PMe_3)(H)_2]^+$ is more acidic than the W analog. This is also in accord with observed trends in acidities as metals are varied; $Cp(CO)_3MoH$ is a stronger acid than $Cp(CO)_3WH$ thermodynamically (pK_a = 13.9 in CH_3CN for $Cp(CO)_3MoH$; pK_a = 16.1 in CH_3CN for $Cp(CO)_3WH$).[40] The

rates follow the same order as the thermodynamics, with the kinetics of proton transfer to aniline from $Cp(CO)_3MoH$ being faster than from $Cp(CO)_3WH$.[41]

The unfavorable equilibrium for proton transfer from the dihydride to the ketone does not prevent the reaction from proceeding since the hydride transfer from the neutral metal hydride to the protonated ketone is fast. Metal hydrides have long been known to be capable of undergoing cleavage of the M–H bond as a hydride.[9] We reported the kinetics of hydride transfer from a series of metal carbonyl hydrides to $Ph_3C^+BF_4^-$ in CH_2Cl_2,[10,11] and found that the rate constants for the kinetic hydricity span a range of over 10^6 (eqn. (12)). The second-order

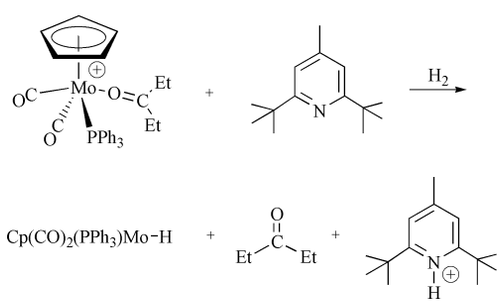
$$M\text{–}H + Ph_3C^+BF_4^- \xrightarrow{k_{H^-}} M\text{–}FBF_3 + Ph_3C\text{–}H \qquad (12)$$

rate constant at 25 °C for hydride transfer to $Ph_3C^+BF_4^-$ from $Cp(CO)_3MoH$ was $k_{H^-} = 3.8 \times 10^2$ M^{-1} s^{-1}, compared to $k_{H^-} = 7.6 \times 10^1$ M^{-1} s^{-1} for $Cp(CO)_3WH$. It is thus reasonable to expect the Mo complexes postulated in Scheme 1 to be both faster proton donors as well as faster hydride donors in comparison to the corresponding W complexes. These steps may not have a direct influence on the turnover rate of the catalytic cycle, however, since the turnover-limiting step in most cases is displacement of the ketone/alcohol ligand by H_2.

Substitution of one CO ligand by a phosphine dramatically increases the kinetic hydricity (eqn. (12)): $k_{H^-} = 4.3 \times 10^5$ M^{-1} s^{-1} for *trans*-$Cp(CO)_2(PCy_3)MoH$, $k_{H^-} = 5.7 \times 10^5$ M^{-1} s^{-1} for *trans*-$Cp(CO)_2(PPh_3)MoH$, and $k_{H^-} = 4.6 \times 10^6$ M^{-1} s^{-1} for *trans*-$Cp(CO)_2(PMe_3)MoH$.[10] The electronic effect is as expected, with the electron-donating phosphine ligands making the metal hydride more hydridic. The observation that electronic effects predominate over steric influences certainly favors using these metal hydrides as hydride donors. Even the metal hydride with the most bulky phosphine, $Cp(CO)_2(PCy_3)MoH$ has a rate constant for hydride transfer that is about three orders of magnitude faster than that for $Cp(CO)_3MoH$. Our measurements for hydride transfer used Ph_3C^+ as the hydride acceptor, whereas the hydrogenations in the catalytic reactions involve a protonated ketone as the hydride acceptor. The rate constant for hydride transfer from $Cp(CO)_2(PPh_3)MoH$ to protonated acetone was reported to be 1.2×10^4 M^{-1} s^{-1} in CH_3CN.[39] It was concluded that hydride transfer from $Cp(CO)_2(PPh_3)MoH$ to protonated acetone proceeds by a single-step hydride transfer[39] rather than the alternative mechanism involving an electron transfer followed by hydrogen atom transfer. Evidence for a single-step hydride transfer was also presented[10] for hydride transfers to $Ph_3C^+BF_4^-$, providing another similarity between these two types of hydride transfer reactions. Consideration of all of these hydride transfer kinetics indicates that the hydride transfer reactions producing alcohol in our reactions (Scheme 1) are sufficiently fast to overcome the unfavorable thermodynamics of the proton transfer step.

Although no molybdenum dihydrides have been directly observed, the involvement of molybdenum ketone complexes in the heterolytic cleavage of H_2 has been demonstrated. Addition of H_2 (<4 atm) to a CD_2Cl_2 solution containing the ketone complex $[CpMo(CO)_2(PPh_3)(Et_2C{=}O)]^+BAr'_4^-$ and the hindered amine base 2,6-di-*tert*-butyl-4-methylpyridine gave the neutral molybdenum hydride in 81% yield in 5 minutes (eqn. (13)). This could proceed through formation of the

(13)



unobserved molybdenum dihydride $[CpMo(CO)_2(PPh_3)(H)_2]^+$ (or dihydrogen complex $[CpMo(CO)_2(PPh_3)(\eta^2\text{-}H_2)]^+$), followed by intermolecular deprotonation by the amine base. An alternative mechanism to consider for this reaction would involve an intermediate or transition state having a Mo ··· H ··· H ··· N interaction. Numerous examples of M–H ··· H–N interactions have been discovered since 1994, with examples involving iridium being particularly prevalent.[42] Interactions of this type can be involved in the base-promoted heterolytic cleavage of hydrogen.[43] This unconventional bonding to hydrogen involving protic and hydridic hydrogens has been called a dihydrogen bond, and recent reviews of this topic have been published.[44]

Comparison with other hydrogenation catalysts

Most of the ketone hydrogenation catalysts previously reported use expensive metals such as Rh and Ru. In contrast, our method uses molybdenum and tungsten, which are much less expensive. Costs of metal starting materials fluctuate, but precious metals like Rh can be orders of magnitude more expensive than Mo or W. The cost of the metal is one of many issues that can affect the overall economics of conducting hydrogenation on an industrial scale; specialized ligands can also add substantially to the cost of the catalyst.

The advantage of inexpensive metals must be balanced against the activity obtained. At this early stage of development, the catalysts described here are orders of magnitude less reactive than the ruthenium catalysts reported by Noyori and co-workers.[5,6] Our efforts thus far have focused on the rational design of catalytic systems that could be demonstrated to hydrogenate ketones under mild conditions of temperature and pressure. The results described here provide evidence for the viability of unconventional mechanisms for catalytic hydrogenations. It is expected that further studies may ultimately lead to the design of more efficient catalysts, based on the mechanistic understanding gained thus far.

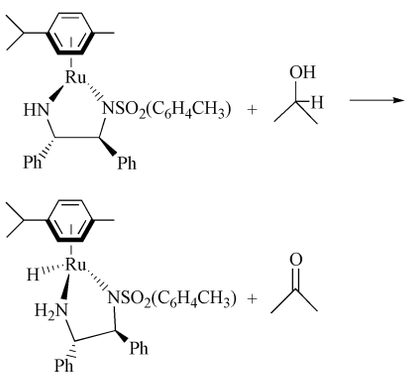
While homogeneous catalysis of ketone hydrogenation is dominated by the use of ruthenium and rhodium complexes, there is some precedent for the use of chromium, molybdenum and tungsten. Darensbourg and co-workers extensively developed the chemistry of anionic metal carbonyl hydrides such as $HCr(CO)_5^-$, with an emphasis on hydride transfer reactivity of these complexes.[45] Stoichiometric hydrogenations of aldehydes and ketones were accomplished[46] using acids together with metal hydrides such as $HM(CO)_5^-$ (M = Cr, W) and phosphite-substituted derivatives like $HW(CO)_4[P(OMe)_3]^-$. In the case of reactive aldehydes like benzaldehyde, insertion of the aldehyde into the M–H bond to give a metal alkoxide was observed, and the alcohol was released by addition of acetic acid. In contrast, they found that hydrogenation of ketones required acid addition first to activate the carbonyl towards nucleophilic attack by the metal hydride. Catalytic hydrogenation of cyclohexanone was accomplished using $(CO)_5W(OAc)^-$ at 125 °C and 600 psi H_2.[47] The mechanism proposed for these hydrogenations involved conversion of $(CO)_5W(OAc)^-$ to the hydride $(CO)_5WH^-$. Then insertion of the aldehyde or ketone into the M–H bond would produce an anionic alkoxide that could be cleaved by HOAc to produce the alcohol product and regenerate the $(CO)_5W(OAc)^-$. A related catalyst for hydrogenation of acetophenone was produced by reaction of $M(CO)_6$ (M = Cr, Mo, W) with NaOMe in methanol.[48] Reaction conditions of 70 °C and 1450 psi H_2 pressure were used for the Mo case, with higher temperatures (100–120 °C) being required for catalysts starting from $Cr(CO)_6$ or $W(CO)_6$. In this case also the intermediacy of $HM(CO)_5^-$ and anionic metal alkoxide intermediates were proposed.

Brunet and co-workers reported recent developments in the use of the anionic metal carbonyl hydride $HCr(CO)_5^-$ as a *transfer* hydrogenation catalyst.[49] In their experiments, 20%

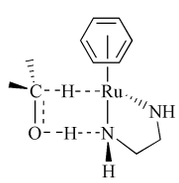
$KHCr(CO)_5$ was used with HCO_2H–NEt_3 to catalyze the hydrogenation of ketones at room temperature. The metal hydride $HCr(CO)_5^-$ is regenerated in this reaction through decarboxylation of $[HCO_2Cr(CO)_5]^-$.

Noyori and co-workers developed a family of remarkably reactive ruthenium catalysts for the asymmetric transfer hydrogenation of ketones under mild conditions.[5] These transfer hydrogenations use isopropanol or formic acid as the hydrogen source, and provide very high turnover numbers of the catalyst and enantiomeric purity of the alcohol products. The mechanism of these metal–ligand bifunctional catalysts has been studied experimentally and by theoretical studies.[50] Eqn. (14) shows

(14)



the preparation of a ruthenium hydride complex through reaction with isopropanol; Scheme 2 shows the computed transition



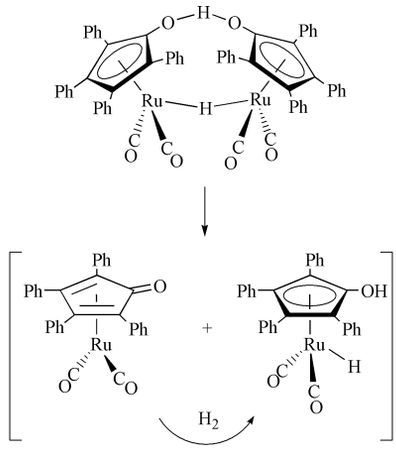
Scheme 2

state for the hydrogenation of an aldehyde. A key issue in the hydrogenation was found to be hydrogen bonding of the oxygen of the substrate to the amine NH bond; this activation of the carbonyl substrate, in conjunction with the hydricity of the Ru–H bond, results in the smooth hydrogenation of the C=O bond. A key mechanistic issue relevant to our studies on Mo and W complexes is that the ruthenium complex is an 18-electron complex that has no vacant coordination site. This case, like our ionic hydrogenations, does *not* require binding of the ketone to the metal but requires a metal complex capable of delivering hydrogen to the unsaturated substrate. Andersson and co-workers reported highly enantioselective transfer hydrogenation catalysts based on ruthenium(arene)(amino alcohol) complexes,[51] and a computational study supported a six-membered transition state, with concerted transfer of H^- from the metal and H^+ from the NH bond.[52]

Asymmetric catalytic hydrogenations have also been accomplished starting from chiral $RuCl_2$(diphosphine)(1,2-diamine) complexes as catalyst precursors, with activation being achieved by addition of a strong base like KO^{t}Bu.[6] These catalysts also appear to involve a mechanism similar to that described above for the (arene)ruthenium complexes. Morris and co-workers also discovered ruthenium(diphosphine)(1,2-diamine) complexes that exhibit exceptionally high reactivity for ketone hydrogenations using H_2.[53]

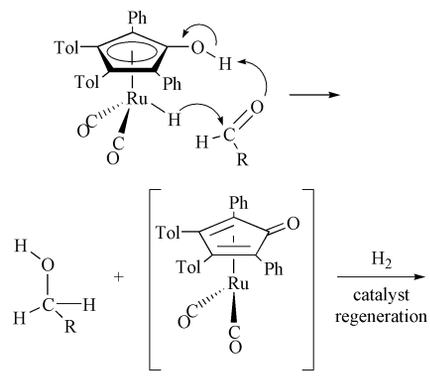
Shvo and co-workers reported a novel type of ruthenium complex that was shown to catalyze hydrogenation of ketones, aldehydes, alkenes and alkynes.[54] The hydrogenation of ketones was carried out at 145 °C at 500 psi H_2. The bimetallic catalyst precursor is bridged both by a bridging hydride as well as through the phenyl-substituted cyclopentadienone ligands. Under hydrogen pressure, a mononuclear ruthenium active species is formed (eqn. (15)). Recent mechanistic experiments

(15)



by Casey and co-workers provide evidence for the *concerted* delivery of H^+ from the OH site from the hydroxycyclopentadienyl ligand, and H^- from the RuH.[55] Eqn. (16) depicts the mechanism for this polar hydrogenation of an aldehyde.

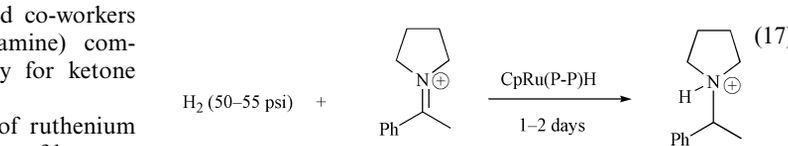
(16)



The hydrogenations from the different ruthenium systems above are all thought to proceed through concerted delivery of a proton (from an NH or OH site) and a hydride (from a metal hydride). This *concerted* mechanism contrasts with our ionic hydrogenation system, where *sequential* proton transfer and hydride transfer steps are proposed. All of these cases are distinct from traditional mechanisms where coordination of the ketone or other substrate is required. These new types of catalysts are generally coordinatively saturated, 18-electron complexes that have no readily accessible vacant site for binding of a ketone.

The mechanism of stepwise proton and hydride transfers operative in our catalytic ketone hydrogenations is similar to the mechanism proposed by Magee and Norton for hydrogenation of C=N double bonds using a ruthenium catalyst (eqn. (17)).[56] They found that enantioface selective catalytic hydrogenation of the C=N bonds of iminium cations could be accomplished using a ruthenium hydride with chiral diphosphine ligands. In our catalysts, displacement of the ketone by H_2 was usually the slow step of the catalytic cycle. In contrast, hydride transfer was the turnover-limiting and enantioselectivity-determining step in eqn. (17).

(17)



We also discovered a ruthenium catalyst that carries out the ionic hydrogenation of ketones.[57] The bimetallic ruthenium complex with a bridging hydride, $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$, catalyzes the selective deoxygenation of 1,2-propanediol to *n*-propanol in the presence of added acid. The mechanism of the deoxygenation of diols involves generation of an aldehyde as an

observable intermediate, and this aldehyde is hydrogenated under the reaction conditions. Ketones were hydrogenated by $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ in the absence of added acid. These hydrogenations were proposed to proceed through the highly acidic dihydrogen complex $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+$ generated from $\{[CpRu(CO)_2]_2(\mu\text{-}H)\}^+OTf^-$ under the reaction conditions.

Experimental

General

All manipulations were carried out under an atmosphere of argon using Schlenk or vacuum-line techniques, or in a Vacuum Atmospheres drybox. ^{1}H NMR chemical shifts were referenced to the residual proton peak of CD_2Cl_2 at δ 5.32. Elemental Analyses were carried out by Schwarzkopf Microanalytical Laboratory (Woodside, NY). NMR spectra were recorded on a Bruker AM-300 spectrometer (300 MHz for ^{1}H). IR spectra were recorded on a Mattson Polaris FT-IR. Et_2O and hexane were distilled from Na–benzophenone, and CH_2Cl_2 was distilled from P_2O_5. $Cp(CO)_2(PPh_3)WH$,[58,59] $Cp(CO)_2(PPh_3)MoH$,[58] $Cp(CO)_2(PCy_3)WH$,[31] $Cp(CO)_2(PCy_3)MoH$,[10] $Cp(CO)_2(PMe_3)WH$,[59] $Cp(CO)_2(PMe_3)MoH$,[59] $[CpW(CO)_2(PMe_3)(H)_2]^+BAr'_4{}^-$,[31] $Ph_3C^+BAr'_4{}^-$,[60] [Ar′ = 3,5-bis(trifluoromethyl)phenyl] and $[H(Et_2O)_2]^+BAr'_4{}^-$ [61] were prepared by previously reported routes.

Syntheses

Synthesis of *cis*-$[CpW(CO)_2(PPh_3)(Et_2C{=}O)]^+BAr'_4{}^-$. $Ph_3C^+BAr'_4{}^-$ (288.5 mg, 0.26 mmol) and Et_2CO (100 μL, 0.95 mmol) were combined in a flask. CH_2Cl_2 (8 mL) was added, giving a yellow solution. Addition of $CpW(CO)_2(PPh_3)H$ (148.5 mg, 0.26 mmol) caused the solution to become red-orange. After 5 minutes of stirring, hexane (30 mL) was slowly added until the solution became cloudy and a reddish-orange oil precipitated. Upon standing at room temperature, the oil solidified into small microcrystals within a few minutes. This orange solid was collected by filtration, and washed with hexane (3 × 5 mL). Yield 354 mg (0.23 mmol, 88%). ^{1}H NMR (CD_2Cl_2: δ 7.73 (br, 8H, *o*-H), 7.57 (br, 4H, *p*-H), 7.25–7.31, 7.50–7.54 (m, 15H, PPh_3), 5.76 (s, 5H, Cp), 2.20 (dq, J_{HH} = 18.2 Hz, 7.3 Hz, 2H, CH_2), 1.59 (dq, J_{HH} = 18.2 Hz, 7.3 Hz, 2H, CH_2), 0.73 (t, J_{HH} = 7.3 Hz, 6H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 37.1 (s, $^1J_{PW}$ = 277 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 240.1 (d, $^2J_{PC}$ = 6 Hz, CO *trans* to P); 239.7 (d, $^2J_{PC}$ = 21 Hz, CO *cis* to P), 236.2 (s, $Et_2C{=}O$), 162.2 (1 : 1 : 1 : 1 quartet, J_{CB} = 50 Hz, *ipso*-C of $BAr'_4{}^-$), 135.2 (s, *ortho*-C of $BAr'_4{}^-$), 134.1 (d, $^2J_{PC}$ = 11 Hz, *ortho*-C of PPh_3), 132.6 (d, $^4J_{PC}$ = 2 Hz, *para*-C of PPh_3), 130.0 (d, $^3J_{PC}$ = 10 Hz, *meta*-C of PPh_3), 129.6 (d, $^1J_{PC}$ = 49 Hz, *ipso*-C of PPh_3), 129.3 (q, $^2J_{CF}$ = 29 Hz, *meta*-C of $BAr'_4{}^-$′), 125.0 (q, $^1J_{CF}$ = 272 Hz, *C*F_3), 117.9 (br s, *para*-C of $BAr'_4{}^-$), 95.9 (s, Cp), 37.0 (s, CH_2), 8.9 (s, CH_3). IR (CH_2Cl_2): ν(CO) 1974 (vs), 1895 (s); ν(C=O) 1632(w) cm^{-1}. Found: C, 48.95; H, 2.98. $C_{62}H_{42}BF_{24}O_3PW$ requires C, 49.10; H, 2.79%.

Synthesis of *cis*-$[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+BAr'_4{}^-$. $Ph_3C^+BAr'_4{}^-$ (249.0 mg, 0.225 mmol) and $CpW(CO)_2(PPh_3)H$ (128.2 mg, 0.226 mmol) were combined in a 50 mL flask. CH_2Cl_2 (8 mL) was added, generating a dark red-orange solution. Et_2CHOH (49 μL, 0.46 mmol) was added, and after 5 minutes of vigorous stirring, Et_2O (20 mL) was slowly added, followed by cyclohexane (20 mL), but no precipitate formed. Upon addition of heptane (5 mL), the reaction mixture became cloudy, and a red-orange precipitate began to appear. Additional heptane (5 mL) was added, and a red-orange solid was collected by filtration. Yield 304.4 mg (0.20 mmol, 89%). ^{1}H NMR (CD_2Cl_2): δ 7.74 (br, 8H, *o*-H), 7.56 (br, 4H, *p*-H), 7.27–7.34, 7.56–7.64 (m, PPh_3, 15H), 5.74 (s, 5H, Cp), 3.37 (m, CH, 1H), 0.83–1.20 (m, 4H, CH_2), 0.58 (t, J_{HH} = 7.4 Hz, 3H, CH_3), 0.40 (t, J_{HH} = 7.4 Hz, 3H, CH_3), 0.10 (dd, J = 8.2 Hz, 2.9 Hz, 1H, OH). ^{31}P NMR (CD_2Cl_2): δ 41.0 (s, $^1J_{PW}$ = 276 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 241.6 (d, $^2J_{PC}$ = 4 Hz, CO *trans* to P); 239.8 (d, $^2J_{PC}$ = 21 Hz, CO *cis* to P), 162.2 (1 : 1 : 1 : 1 quartet, J_{CB} = 50 Hz *ipso*-C of $BAr'_4{}^-$), 135.2 (s, *ortho*-C of $BAr'_4{}^-$), 133.9 (d, $^2J_{PC}$ = 11 Hz, *ortho*-C of PPh_3), 133.4 (d, $^4J_{PC}$ = 2 Hz, *para*-C of PPh_3), 131.0 (d, $^3J_{PC}$ = 10 Hz, *meta*-C of PPh_3), 129.3 (qm, $^2J_{CF}$ = 31 Hz, *meta*-C of $BAr'_4{}^-$), 127.8 (d, $^1J_{PC}$ = 49 Hz, *ipso*-C of PPh_3), 125.0 (q, $^1J_{CF}$ = 272 Hz, *C*F_3), 117.9 (septet, $^3J_{CF}$ = 272 Hz, *para*-C of $BAr'_4{}^-$), 94.8 (s, Cp), 93.6 (d, $^3J_{CP}$ = 2 Hz, *C*HOH), 26.6 (s, CH_2), 26.6 (s, CH_2), 8.5 (s, CH_3), 8.1 (s, CH_3). IR (CH_2Cl_2): ν(OH) 3433 (w, br); ν(CO) 1974 (s), 1894 (s) cm^{-1}. Found: C, 49.04; H, 2.99. $C_{62}H_{44}BF_{24}O_3PW$ requires C, 49.04; H, 2.92%.

***trans*-$[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+BAr'_4{}^-$.** *cis*-$[CpW(CO)_2(PPh_3)(Et_2C{=}O)]^+BAr'_4{}^-$ (48.4 mg, 0.031 mmol) was dissolved in CD_2Cl_2 (1.1 mL) in a glass vial, and Et_2CO (16 μL, 0.15 mmol) was added. The solution was placed in a Parr high pressure reactor vessel and H_2 (65 atm) was added. After 17 hours at 22 °C, the pressure was released, and an NMR spectrum showed 92% conversion to *trans*-$[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+BAr'_4{}^-$, along with 8% of $[CpW(CO)_2(PPh_3)(Et_2C{=}O)]^+$ remaining. ^{1}H (CD_2Cl_2): δ 7.73 (br, 8H, *o*-H), 7.57 (br, 4H, *p*-H), 7.1–7.2, 7.43–7.56 (m, 15 H, PPh_3), 5.59 (d, J = 8.4 Hz, 1H, OH), 5.39 (d, J_{PH} = 2.4 Hz, 5H, Cp), 3.37 (m, CH, 1H), 1.35–1.55 (m, CH_2, 4H), 0.93 (t, J_{HH} = 7.5 Hz, 6H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 30.6 (s, $^1J_{PW}$ = 197 Hz).

Synthesis of $[CpMo(CO)_2(PPh_3)(Et_2C{=}O)]^+BAr'_4{}^-$. $Ph_3C^+BAr'_4{}^-$ (224.0 mg, 0.202 mmol) and $CpMo(CO)_2(PPh_3)H$ (99.2 mg, 0.206 mmol) were combined in a 50 mL flask. Et_2CO (100 μL, 0.95 mmol) was added, then CH_2Cl_2 (5 mL) was added, generating a dark red-orange solution. After 5 minutes of vigorous stirring, Et_2O (20 mL) was slowly added, but no precipitation ensued. Addition of hexane (20 mL) caused a dark red solid precipitate to form. The product was collected by filtration and washed with hexane. Yield 177.8 mg (0.124 mmol, 61%) of a *cis*–*trans* mixture. ^{1}H NMR (CD_2Cl_2) of *trans* isomer: δ 7.73 (br, 8H, *o*-H), 7.56 (br, 4H, *p*-H), 7.25–7.32, 7.50–7.55 (m, 15H, PPh_3), 5.40 (d, J_{PH} = 2.5 Hz, 5H, Cp), 2.50 (q, J_{HH} = 7.3 Hz, 4H, CH_2), 1.07 (t, J_{HH} = 7.3 Hz, 6H, CH_3). ^{1}H NMR (CD_2Cl_2) of *cis* isomer: δ 7.73 (br, 8H, *o*-H), 7.56 (br, 4H, *p*-H), 7.25–7.32, 7.50–7.55 (m, 15H, PPh_3), 5.61 (s, 5H, Cp), 2.09 (dq, J_{HH} = 18.2 Hz, 7.3 Hz, 2H, CH_2), 1.62 (dq, J_{HH} = 18.2 Hz, 7.3 Hz, 2H, CH_2), 0.73 (t, J_{HH} = 7.3 Hz, 6H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 59.6 (s, *trans* isomer); 53.9 (s, *cis* isomer). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) of *cis* isomer: δ 248.5 (d, $^2J_{PC}$ = 29 Hz, CO *cis* to P); 247.1 (d, $^2J_{PC}$ = 3 Hz, CO *trans* to P), 236.2 (s, $Et_2C{=}O$), 162.2 (1 : 1 : 1 : 1 quartet, J_{CB} = 50 Hz, *ipso*-C of $BAr'_4{}^-$), 135.2 (s, *ortho*-C of $BAr'_4{}^-$), 133.8 (d, $^2J_{PC}$ = 11 Hz, *ortho*-C of PPh_3), 132.4 (d, $^4J_{PC}$ = 2 Hz, *para*-C of PPh_3), 130.0 (d, $^1J_{PC}$ = 48 Hz, *ipso*-C of PPh_3), 130.0 (d, $^3J_{PC}$ = 10 Hz, *meta*-C of PPh_3), 129.3 (qm, $^2J_{CF}$ = 31 Hz, *meta*-C of $BAr'_4{}^-$), 125.0 (q, J_{CF} = 272 Hz, *C*F_3), 117.9 (septet, $^3J_{CF}$ = 4 Hz, *para*-C of $BAr'_4{}^-$), 97.5 (s, Cp), 36.8 (s, CH_2), 8.9 (s, CH_3). IR (CH_2Cl_2): ν(CO) 1992 (s), 1910 (vs); ν(C=O) 1643 (w); 1610 (vw) cm^{-1}. Found: C, 51.83; H, 2.95. $C_{62}H_{42}BF_{24}MoO_3P$ requires C, 52.12; H, 2.96%.

Synthesis of *cis*-$[CpMo(CO)_2(PPh_3)(Et_2CHOH)]^+BAr'_4{}^-$. $Ph_3C^+BAr'_4{}^-$ (208.1 mg, 0.188 mmol) and $CpMo(CO)_2(PPh_3)H$ (96.2 mg, 0.200 mmol) were combined in a 50 mL flask. CH_2Cl_2 (5 mL) was added, producing a dark red-orange solution. Immediately afterwards, Et_2CHOH (100 μL, 0.93 mmol) was added. After 5 minutes of vigorous stirring, Et_2O (5 mL) was added, followed by hexane (10 mL). Addition of more hexane (20 mL) resulted in precipitation of a dark red-orange solid. The product was collected by filtration and washed with hexane. Yield: 211.7 mg (0.148 mmol, 79%). ^{1}H (CD_2Cl_2): δ 7.73 (br, 8H, *o*-H), 7.56 (br, 4H, *p*-H), 7.26–7.33, 7.59–7.67 (m, 15H,

PPh_3), 5.58 (s, 5H, Cp), 3.17 (m, CH, 1H), 0.88–1.20 (m, 4H, CH_2), 0.57 (t, J_{HH} = 7.4 Hz, 3H, CH_3), 0.40 (t, J_{HH} = 7.4 Hz, 3H, CH_3), −0.62 (dd, J = 8.2 Hz, 3.3 Hz, 1H, OH). ^{31}P NMR (CD_2Cl_2): δ 58.3 (s). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 248.6 (d, $^2J_{PC}$ = 30 Hz, CO *cis* to P); 248.2 (s, CO *trans* to P), 162.2 (1 : 1 : 1 : 1 quartet, J_{CB} = 50 Hz, *ipso*-C of BAr'_4^-), 135.2 (s, *ortho*-C of BAr'_4^-), 133.7 (d, $^2J_{PC}$ = 11 Hz, *ortho*-C of PPh_3), 133.2 (d, $^4J_{PC}$ = 2 Hz, *para*-C of PPh_3), 130.4 (d, $^3J_{PC}$ = 10 Hz, *meta*-C of PPh_3), 130.2 (d, $^1J_{PC}$ = 42 Hz, *ipso*-C of PPh_3), 129.3 (qm, $^2J_{CF}$ = 34 Hz, *meta*-C of BAr'_4^-), 125.0 (q, $^1J_{CF}$ = 272 Hz, CF_3), 117.9 (septet, $^3J_{CF}$ = 4 Hz *para*-C of BAr'_4^-), 96.6 (s, Cp), 90.9 (s, *C*HOH), 26.8 (s, CH_2), 8.6 (s, CH_3), 8.2 (s, CH_3). IR (CH_2Cl_2): ν(OH) 3459 (w, br); ν(CO) 1986 (vs), 1912 (s) cm^{-1}. Found: C, 52.18; H, 3.06. $C_{62}H_{44}BF_{24}MoO_3P$ requires C, 52.05; H, 3.10%.

***trans*-[CpMo(CO)$_2$(PPh$_3$)(Et$_2$CHOH)]$^+$BAr′$_4^-$.** The *trans* isomer of this alcohol complex was observed during hydrogenations catalyzed by $[CpMo(CO)_2(PPh_3)(Et_2C{=}O)]^+$. ^{1}H ($CD_2Cl_2$): δ 7.74 (br, 8H, *o*-H), 7.56 (br, 4H, *p*-H), 7.18–7.28, 7.45–7.55 (m, 15 H, PPh_3), 5.31 (d, J_{PH} = 2.4 Hz, 5H, Cp), 4.96 (d, J = 8.6 Hz, 1H, OH), 3.18 (m, CH, 1H), 1.40–1.55 (m, CH_2, 4H), 0.88 (t, J_{HH} = 7.5 Hz, 6H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 61.1 (s).

Synthesis of *trans*-[CpW(CO)$_2$(PMe$_3$)(Et$_2$CHOH)]$^+$BAr′$_4^-$. Et_2CO (11 μL, 0.10 mmol) was added to a solution of $[CpW(CO)_2(PMe_3)(H)_2]^+BAr'_4^-$ (35.3 mg, 0.0283 mmol) in CD_2Cl_2 (0.72 mL). The solution turned light orange, and conversion to *trans*-$[CpW(CO)_2(PMe_3)(Et_2CHOH)]^+$ was about 90% complete in 1 hour. ^{1}H (CD_2Cl_2): δ 7.73 (br, 8H, *o*-H), 7.57 (br, 4H, *p*-H), 5.46 (d, J_{PH} = 2.6 Hz, 5H, Cp), 5.36 (d, J = 8.4 Hz, 1H, OH), 3.28 (m, CH, 1H), 1.67 (d, J_{PH} = 9.9 Hz, 9 H, $P(CH_3)_3$), 1.35–1.51 (m, CH_2, 4H), 0.87 (t, J_{HH} = 7.5 Hz, 6H, CH_3). ^{31}P NMR (CD_2Cl_2): δ −15.1 (s, $^1J_{PW}$ = 179 Hz).

Synthesis of [CpMo(CO)$_2$(PMe$_3$)(Et$_2$C=O)]$^+$BAr′$_4^-$. $Ph_3C^+BAr'_4^-$ (360.5 mg, 0.326 mmol) and $CpMo(CO)_2(PMe_3)H$ (97.4 mg, 0.331 mmol) were combined in a 50 mL flask. Et_2CO (100 μL, 0.95 mmol) was added, then CH_2Cl_2 (5 mL) was added, generating a dark red-orange solution. After brief stirring, hexane (20 mL) was slowly added. The product precipitated out of solution as an oil. Decanting the supernatant and triturating with pentane (30 mL) resulted in the conversion of the oil to a solid. The product was collected by filtration and washed with pentane. Yield 337.4 mg (0.272 mmol, 83%). The *cis* : *trans* ratio was 0.7 : 1. ^{1}H NMR (CD_2Cl_2) of *trans* isomer: δ 7.72 (br, 8H, *o*-H), 7.57 (br, 4H, *p*-H), 5.47 (d, J_{PH} = 2.5 Hz, 5H, Cp), 2.46 (q, J_{HH} = 7.4 Hz, 4H, CH_2), 1.61 (d, J_{PH} = 9.9 Hz, 9 H, $P(CH_3)_3$), 1.07 (t, J_{HH} = 7.4 Hz, 6H, CH_3). ^{1}H NMR (CD_2Cl_2) of *cis* isomer: δ 7.72 (br, 8H, *o*-H), 7.57 (br, 4H, *p*-H), 5.62 (s, 5H, Cp), 2.46 (q, J_{HH} = 7.4 Hz, 4H, CH_2, overlapped with same resonance for the *trans* isomer), 1.54 (d, J_{PH} = 9.9 Hz, 9 H, $P(CH_3)_3$), 1.09 (t, J_{HH} = 7.4 Hz, 6H, CH_3). ^{31}P NMR (CD_2Cl_2): δ 20.8 (s, *trans* isomer); 9.7 (s, *cis* isomer). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) of *cis*–*trans* mixture, in the presence of ≈ 2 equiv. free $Et_2C{=}O$: δ 248.3 (d, J_{PC} = 32 Hz, CO *cis* to P; *cis* isomer); 247.1 (d, J_{PC} = 4 Hz, CO *trans* to P; *cis* isomer), 241.0 (d, J_{PC} = 27 Hz, CO; *trans* isomer), 238.0 (d, J_{PC} = 2 Hz, $Et_2C{=}O$, *cis* isomer), 235.7 (d, J_{PC} = 2 Hz, $Et_2C{=}O$, *trans* isomer), 161.7 (1 : 1 : 1 : 1 quartet, *ipso*-C, J_{CB} = 50 Hz), 135.3 (s, *ortho*-C), 129.3 (q, *meta*-C, $^2J_{CF}$ = 28 Hz), 125.1 (q, J_{CF} = 272 Hz, CF_3), 118.0 (s, *para*-C), 96.4 (Cp), 95.8 (Cp), 37.4 (CH_2), 37.1 (CH_2), 20.1 (d, J_{PC} = 36 Hz, $P(CH_3)_3$), 17.4 (d, J_{PC} = 30 Hz, $P(CH_3)_3$), 9.2 (CH_3), 8.9 (CH_3). IR (CH_2Cl_2): ν(CO) 1986 (vs), 1900 (vs); ν(C=O) 1646 (w); 1611 (vw) cm^{-1}. Found: C, 45.49; H, 2.80. $C_{47}H_{36}BF_{24}MoO_3P$ requires C, 45.43; H, 2.92%. When an CD_2Cl_2 solution of this *cis*–*trans* mixture was allowed to stand at room temperature for 2 days, the *cis* : *trans* ratio increased to 1.1 : 1, but some decomposition of the alcohol complex was also observed.

Synthesis of [CpW(CO)$_2$(PMe$_3$)(Et$_2$C=O)]$^+$BAr′$_4^-$. $Ph_3C^+BAr'_4^-$ (152.8 mg, 0.138 mmol) and $CpW(CO)_2(PMe_3)H$ (57.2 mg, 0.150 mmol) were combined in a 50 mL flask. Et_2CO (100 μL, 0.95 mmol) was syringed onto the solids, followed by addition of CH_2Cl_2 (5 mL), which generated a dark orange solution. Hexane (15 mL) was added, and an oil precipitated out of solution. After standing for two hours, no solids were observed, so more hexane (5 mL) was added, and the reaction mixture was stirred vigorously. After two additional hours, some solid had formed. The supernatant was decanted, and the precipitate was triturated with pentane (20 mL), collected by filtration, and washed with pentane, giving an orange microcrystalline solid (123 mg, 0.0924 mmol, 67%). The *cis* : *trans* ratio was about 1.6 : 1. ^{1}H NMR (CD_2Cl_2) of *trans* isomer: δ 7.73 (br, 8H, *o*-H), 7.58 (br, 4H, *p*-H), 5.56 (d, J_{PH} = 2.4 Hz, 5H, Cp), 2.55 (q, J_{HH} = 7.4 Hz, 4H, CH_2), 1.60 (d, J_{PH} = 9.7 Hz, 9 H, $P(CH_3)_3$), 1.07 (t, J_{HH} = 7.4 Hz, 6H, CH_3). ^{1}H NMR (CD_2Cl_2) of *cis* isomer: δ 7.73 (br, 8H, *o*-H), 7.58 (br, 4H, *p*-H), 5.82 (s, 5H, Cp), 2.55 (q, J_{HH} = 7.4 Hz, 4H, CH_2, overlapped with same resonance for the *trans* isomer), 1.71 (d, J_{PH} = 10.0 Hz, 9 H, $P(CH_3)_3$), 1.10 (t, J_{HH} = 7.4 Hz, 6H, CH_3). ^{31}P NMR (CD_2Cl_2): δ −15.6 (s, $^1J_{PW}$ = 192 Hz, *trans* isomer); −17.2 (s, $^1J_{PW}$ = 262 Hz, *cis* isomer). IR (CH_2Cl_2): ν(CO) 1971 (s), 1884 (s); ν(C=O) 1632 (w); 1611 (w) cm^{-1}. Found: C, 42.12; H, 2.87. $C_{47}H_{36}BF_{24}WO_3P$ requires C, 42.43; H, 2.73%.

Synthesis of [{CpMo(CO)$_2$(PMe$_3$)}$_2$(μ-H)]$^+$BAr′$_4^-$. $Ph_3C^+BAr'_4^-$ (332.0 mg, 0.300 mmol) and $CpMo(CO)_2(PMe_3)H$ (91.5 mg, 0.311 mmol) were combined in a 50 mL flask, and CH_2Cl_2 (5 mL) was added. Immediately afterwards, Et_2CHOH (100 μL, 0.93 mmol) was added. It appeared that much of the $Ph_3C^+BAr'_4^-$ remained unreacted, so additional $CpMo(CO)_2(PMe_3)H$ (25 mg, 0.085 mmol) was added, which caused the color of the solution to darken. The dark maroon precipitate that formed upon the addition of hexane was collected by filtration. Yield: 142.0 mg (0.098 mmol, 33%). ^{1}H (CD_2Cl_2): δ 7.72 (br, 8H, *o*-H), 7.56 (br, 4H, *p*-H), 5.22 (d, J_{PH} = 1.8 Hz, 10H, Cp), 1.68 (d, J_{PH} = 9.9 Hz, 18 H, $P(CH_3)_3$), −19.92 (t, $^2J_{PH}$ = 11 Hz, 1 H, hydride). IR (CH_2Cl_2): ν(CO) 1981 (m), 1955 (m), 1896 (s) cm^{-1}. Found: C, 42.84; H, 2.88. $C_{52}H_{41}BF_{24}Mo_2O_4P_2$ requires C, 43.06; H, 2.85%.

NMR tube kinetics experiments

A standard solution of Et_2CO in CD_2Cl_2 was prepared by dissolving bibenzyl (136.7 mg, 0.750 mmol; internal standard for ^{1}H NMR integration) and Et_2CO (792 μL, 7.50 mmol) in a 25 mL volumetric flask. The flask was filled to the mark with CD_2Cl_2, giving a 300 mM solution of Et_2CO. For $[CpW(CO)_2(PPh_3)(Et_2C{=}O)]^+BAr'_4^-$, $[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+BAr'_4^-$, $[CpMo(CO)_2(PPh_3)(Et_2C{=}O)]^+BAr'_4^-$, $[CpW(CO)_2(PMe_3)(Et_2C{=}O)]^+BAr'_4^-$, and $[CpMo(CO)_2(PMe_3)(Et_2C{=}O)]^+BAr'_4^-$ the following procedure was used: 0.021 mmol of the metal complex was weighed and transferred into a 5 mm NMR tube equipped with a Young valve. Then 0.7 mL of the standard 300 mM solution of Et_2CO in CD_2Cl_2 was added, giving a catalyst concentration of 30 mM. (If 0.8 mL is added, then the concentration of the metal will drop to 26 mM, such that 11.4 equivalents of ketone will be present, rather than the intended 10 equivalents.) In all cases the solid dissolved and the solution turned red-orange. The tube was then frozen in liquid nitrogen, evacuated on a high vacuum line, then filled with 1 atm H_2. The valve was closed, and the tube was warmed to room temperature. Using this procedure, the pressure of H_2 after the solution was warmed to room temperature should be <4 atm (298/77 = 3.9). The pressure was maintained by periodically refilling with H_2 as needed. All reactions were carried out at room temperature (23 °C). In an attempt to promote better diffusion of the H_2 gas into the solvent, the tubes were spun slowly end-over-end using a mechanical stirring motor

mounted sideways. The catalytic reactions of the PCy_3 complexes were prepared by *in situ* reactions of $Ph_3C^+BAr'_4{}^-$ with $CpW(CO)_2(PCy_3)H$ or $CpMo(CO)_2(PCy_3)H$ (see below); otherwise they were treated in the same manner as those described above.

Results shown in Fig. 2 include formation of the alcohol Et_2CHOH and its subsequent conversion to the ether $(Et_2CH)_2O$. Amounts of these two products are given here. For catalysis with $[CpW(CO)_2(PPh_3)(Et_2C{=}O)]^+BAr'_4{}^-$, $[Et_2CHOH]$ = 93 mM and $[(Et_2CH)_2O]$ = 6 mM, at t = 24 days, for a total of 3.9 turnovers. For catalysis with $[CpW(CO)_2(PPh_3)(Et_2CHOH)]^+BAr'_4{}^-$, the concentration of alcohol formed in the reaction (*i.e.*, after subtracting the alcohol ligand present at the start of the reaction) $[Et_2CHOH]$ = 95 mM and $[(Et_2CH)_2O]$ = 86 mM, at t = 25 days, for a total of 4.1 turnovers. For catalysis with $[CpMo(CO)_2(PPh_3)(Et_2C{=}O)]^+BAr'_4{}^-$, $[Et_2CHOH]$ = 255 mM and $[(Et_2CH)_2O]$ = 46 mM, at t = 6 days, for a total of 11.6 turnovers. For catalysis with $[CpW(CO)_2(PMe_3)(Et_2C{=}O)]^+BAr'_4{}^-$, $[Et_2CHOH]$ = 124 mM and $[(Et_2CH)_2O]$ = 3 mM, at t = 24 days, for a total of 4.3 turnovers. For catalysis with $[CpMo(CO)_2(PMe_3)(Et_2C{=}O)]^+BAr'_4{}^-$, $[Et_2CHOH]$ = 101 mM and $[(Et_2CH)_2O]$ = 25 mM, at t = 24 days, for a total of 5.0 turnovers.

Reaction of $CpMo(CO)_2(PCy_3)H$ with $Ph_3C^+BAr'_4{}^-$. 0.8 mL of the standard 300 mM solution of Et_2CO in CD_2Cl_2 was added to an NMR tube containing $Cp(CO)_2(PCy_3)MoH$ (10.6 mg, 0.021 mmol) and $Ph_3C^+BAr'_4{}^-$ (23.2 mg, 0.021 mmol), and H_2 (<4 atm) was added as described above. The hydride transfer proceeded cleanly, as evidenced by the formation of Ph_3CH (δ 5.56, s, C*H*). A singlet Cp resonance at δ 5.63 as observed in the ^{1}H NMR and a singlet at δ 49.1 in the ^{31}P NMR are assigned to the ketone complex $[CpMo(CO)_2(PCy_3)(Et_2C{=}O)]^+$. Resonances for $Et_2C{=}O$ were significantly broadened in the ^{1}H NMR, suggesting exchange of free and bound ketone. These resonances overlap with ^{1}H NMR resonances due to the PCy_3 ligand and were not definitely assigned. Also observed during the catalytic reaction was a singlet Cp resonance at δ 5.73 in the ^{1}H NMR and a singlet at δ 48.4 in the ^{31}P NMR, which are assigned to the alcohol complex $[CpMo(CO)_2(PCy_3)(Et_2CHOH)]^+$. At t = 24 hours, $[Et_2CHOH]$ = 272 mM and $[(Et_2CH)_2O]$ = 34 mM, for a total of 11.3 turnovers.

Reaction of $CpW(CO)_2(PCy_3)H$ with $Ph_3C^+BAr'_4{}^-$. 0.7 mL of the standard 300 mM solution of Et_2CO in CD_2Cl_2 was added to an NMR tube containing $Cp(CO)_2(PCy_3)WH$ (12.4 mg, 0.021 mmol) and $Ph_3C^+BAr'_4{}^-$ (23.2 mg, 0.021 mmol), and H_2 (<4 atm) was added as described above. As in the Mo analog above, the observation of Ph_3CH indicated a clean hydride transfer. The dihydride $[CpW(CO)_2(PCy_3)(H)_2]^+BAr'_4{}^-$[31] was the predominant metal complex observed throughout the hydrogenation. After 24 days, $[Et_2CHOH]$ = 130 mM and $[(Et_2CH)_2O]$ = 17 mM, for a total of 5.4 turnovers. Only about 2% $HPCy_3^+$ was observed at t = 8 days, indicating less decomposition compared to the Mo example.

Independent synthesis and identification of $HPR_3^+BAr'_4{}^-$

The phosphonium cations observed as decomposition products in the catalytic reactions were independently synthesized and characterized. $[H(Et_2O)_2]^+BAr'_4{}^-$ (5.3 mg, 0.0052 mmol, 0.5 equiv.) was added to PCy_3 (3.1 mg, 0.011 mmol) in CD_2Cl_2 (0.6 mL). The ^{31}P NMR resonance due to free PCy_3 (δ 11.1) broadened, and a broadened new resonance appeared at δ 33.6. This is apparently due to proton transfer exchange between PCy_3 and $HPCy_3^+$. Addition of 1 equiv. $[H^+(Et_2O)_2]^+BAr'_4{}^-$ resulted in the disappearance of the resonance for PCy_3, and the resonance for $HPCy_3^+$ (δ 34.6, $^1J_{PH}$ = 440 Hz) was no longer broadened. Analogous experiments showed line broadening upon partial protonation of PPh_3 (^{31}P at δ −5.0) to give $HPPh_3^+$ (^{31}P at δ 8.1), and for protonation of PMe_3 (^{31}P at δ −61) to give $HPMe_3^+$ (^{31}P at δ −4.2, $^1J_{PH}$ = 487 Hz, $^2J_{PH}$ = 15 Hz)

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