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Homogeneous Catalysis with Inexpensive Metals: Ionic Hydrogenation of Ketones with Molybdenum and Tungsten Catalysts

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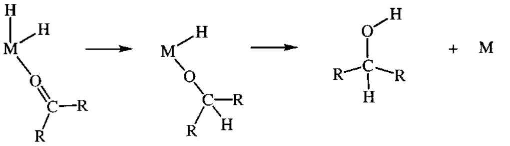
Hydrogenation of the C═O double bond of ketones and aldehydes is a reaction of substantial industrial importance and is utilized in the production of numerous chemicals in the agricultural, pharmaceutical, and other fine chemical industries. Detailed mechanistic studies of hydrogenation reactions played an instrumental role in the development of our modern understanding of the role of transition metal complexes in activating hydrogen and delivering it to an unsaturated organic molecule. The accepted mechanism[1] involves coordination of the ketone to the metal, followed by insertion into a metal−hydrogen bond (eq 1). The hydrogenated product is released from the metal through formal reductive elimination from a second metal−hydrogen bond. These reactions traditionally use precious metals (notably Rh and Ru)[2−4] as catalysts, so alternative methods utilizing less expensive metals could offer substantial benefits.

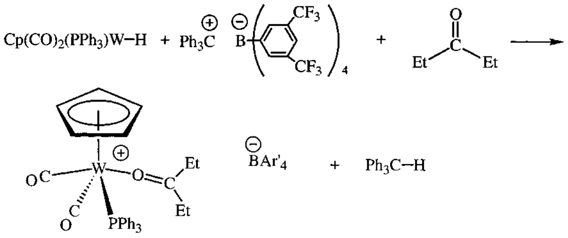


(1)

We report here a new class of homogeneous hydrogenation catalysts based on molybdenum or tungsten, unusual metals for hydrogenation catalysis. These catalysts were specifically designed to operate by an ionic mechanism, which requires that the metal complex be capable of reacting with H_2, then sequentially delivering H^+ followed by H^- to a ketone. *Stoichiometric* ionic hydrogenations are used in organic synthetic procedures, with CF_3CO_2H commonly used as the proton source and $HSiEt_3$ as the hydride donor.[5] We previously reported stoichiometric metal-mediated ionic hydrogenations of ketones,[6] alkenes,[7] and alkynes.[8] Kinetic and mechanistic studies[6,9] on stoichiometric ionic hydrogenations of C═O bonds indicate preequilibrium protonation of the substrate followed by rate-determining hydride transfer from the metal.

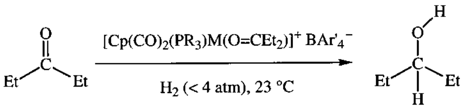
Metal hydrides are known to function as proton donors, and kinetic and thermodynamic studies of the acidity of neutral metal carbonyl hydrides are well-documented.[10] Cationic metal hydrides and dihydrogen complexes can be especially acidic.[11] Metal hydrides are also capable of undergoing cleavage of the M−H bond as a hydride.[12] We reported[13] the kinetics of hydride transfer from a series of neutral metal hydrides to Ph_3C^+ where the kinetic hydricity of metal hydrides was found to span a range of rate constants of over 10^6. Successful implementation of a catalytic hydrogenation cycle requires proper balancing of proton transfer and hydride transfer abilities, together with the critical closure of the catalytic cycle by the reaction of a metal complex with H_2.

The reaction of $Cp(CO)_2(PPh_3)WH$ ($Cp = \eta^5\text{-}C_5H_5$) with $Ph_3C^+\text{-}BAr_4'^-$ [Ar′ = 3,5-bis(trifluoromethyl)phenyl] in CH_2Cl_2 solution in the presence of 3-pentanone resulted in hydride transfer from tungsten to carbon, followed by binding of the ketone ligand to tungsten. The resulting product, $[Cp(CO)_2(PPh_3)W(\eta^1\text{-}O{=}CEt_2)]^+$ $BAr_4'^-$, was isolated as an orange solid in 88% yield (eq 2).[14]



(2)

When a solution of $[Cp(CO)_2(PPh_3)W(\eta^1\text{-}O{=}CEt_2)]^+$ $BAr_4'^-$ is treated with 3-pentanone under H_2 (<4 atm) at room temperature, catalytic hydrogenation of the C═O bond of the ketone occurs, producing 3-pentanol (eq 3). Monitoring the progress of the reaction by ^1H NMR spectroscopy indicates that the ketone complex decreases in concentration, and the analogous alcohol complex, $[Cp(CO)_2(PPh_3)W(Et_2CHOH)]^+$ $BAr_4'^-$, forms. In catalytic hydrogenations carried out in NMR tubes, the concentration of the alcohol complex increased to a maximum of ∼60% of the total tungsten-containing species. This alcohol complex has been independently synthesized and characterized.[14] Its use as a catalyst precursor results in activity comparable to that observed with the ketone complex. At later stages of the reaction, some of the 3-pentanol is converted to the ether $(Et_2CH)_2O$ (typically <10%).



(3)

A series of hydrogenation experiments were carried out with < 4 atm H_2 at 23 °C (Figure 1). These reactions carried out in NMR tubes are not optimized for obtaining the highest catalytic activity, but they provide a comparison of the catalytic activity under controlled conditions. For Mo and W complexes containing PCy_3 ligands the ketone complexes were not isolated; the catalytically active complex was prepared in situ by hydride transfer from $Cp(CO)_2(PCy_3)MH$ (M = Mo or W) to $Ph_3C^+BAr_4'^-$

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[14] Spectral and analytical data for ketone and alcohol complexes are in the Supporting Information.

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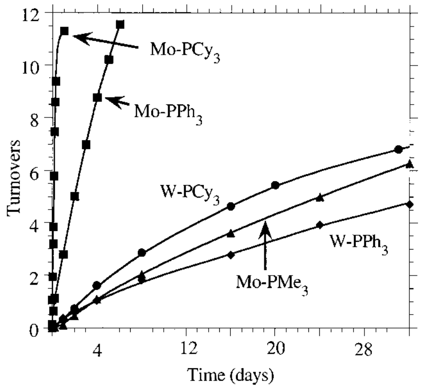


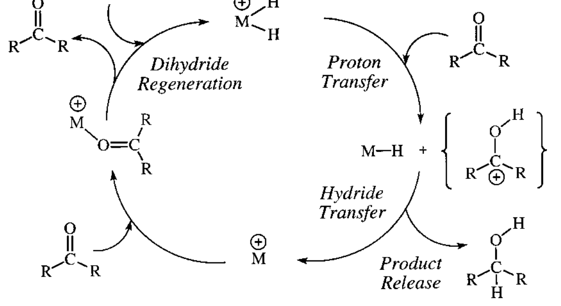
Figure 1. Catalytic activity for hydrogenation of O=CEt$_2$ (10−12 equiv) by $[Cp(CO)_2(PR_3)M(\eta^1\text{-}O{=}CEt_2)]^+$ $BAr_4'^-$ (30 mM) at 23 °C and <4 atm H_2 in CD_2Cl_2.

in the presence of O=CEt$_2$. Approximate initial rates (1−2 turnovers) for the Mo catalysts are 2 turnovers/h for Mo−PCy$_3$, 0.2 turnovers/h for Mo−PPh$_3$, and 0.01 turnovers/h for Mo−PMe$_3$. Steric effects of the phosphines apparently predominate over electronic effects, presumably by promoting dissociation of the ketone from the metal. The effect of counterions was briefly investigated with catalysts generated from $Cp(CO)_2(PCy_3)MoH + Ph_3C^+X^-$. Catalysis was observed for X = BF_4^-, PF_6^-, and OTf $^-$ (OTf = OSO_2CF_3) but the activity was generally highest with $BAr_4'^-$.

The proposed mechanism for this new homogeneous hydrogenation catalytic cycle is shown in Scheme 1. The ketone bound to the metal is displaced by hydrogen to produce a cationic dihydride complex, containing two M−H bonds. These dihydride complexes have not been directly observed for Mo but have been isolated in some cases for W, including an X-ray diffraction study of $[Cp(CO)_2(PMe_3)W(H)_2]^+OTf^-$.[15] Proton transfer from the acidic cationic dihydride to the ketone gives a neutral metal hydride and protonated ketone. The metal hydride then transfers hydride to the protonated ketone, forming the C−H bond and generating the alcohol. The 16-electron organometallic cation ("M$^+$" in Scheme 1) is captured by ketone, completing the catalytic cycle.

Mechanistic experiments provide support for the proposed pathway. Stoichiometric hydrogenations of acetone by $[Cp(CO)_2(PMe_3)W(H)_2]^+OTf^-$ in either CD_3CN or CD_2Cl_2 are essentially complete in 15 min at room temperature, giving observable 2-propanol complexes[6,9] as the initial products. Protonation of a ketone by the dihydride $[Cp(CO)_2(PMe_3)W(H)_2]^+$ is thermodynamically unfavorable (pK_a = 5.6[16] in CH_3CN for $[Cp(CO)_2(PMe_3)W(H)_2]^+$; p$K_a$ ≈ −0.1[9,17] for Me_2COH^+ in CH_3CN), but the hydride transfer to protonated ketone is fast[9] so hydrogenation proceeds smoothly. The proton-transfer step could proceed through direct metal to oxygen proton transfer, or may be mediated by OTf$^-$ as a kinetically active proton carrier.[18] Further evidence for heterolytic cleavage of H_2 comes from the reaction of $[Cp(CO)_2(PPh_3)Mo(\eta^1\text{-}O{=}CEt_2)]^+BAr_4'^-$ with H_2 (<4 atm) in the presence of the hindered base 2,6-di-*tert*-butyl-4-methylpyridine. This reaction produced ~80% of neutral hydride $Cp(CO)_2(PPh_3)MoH$ after 5 min, presumably through the intermediacy of the unobserved dihydride (or dihydrogen) complex of Mo, which is then deprotonated by the base.

Scheme 1



As the catalytic reaction proceeds, the formation of $[CpW(CO)_2(PR_3)(Et_2CHOH)]^+$ (which re-enters the catalytic cycle) is accompanied by other organometallic products, such as $CpW(CO)_2(PR_3)H$ and $CpW(CO)_2(PR_3)H_2^+$. Most revealing is the formation of protonated phosphine, HPR_3^+. The formation of this product suggests that phosphine dissociates from the metal and is protonated by MH_2^+. Identification of this as a catalyst decomposition pathway provides valuable mechanistic information that is guiding the development of the next generation of these catalysts.

Some precedent does exist for hydrogenation by Mo complexes. Ketones can be catalytically hydrogenated by $(CO)_5Mo(OAc)^-$, but higher temperatures (125 °C) and pressures (600 psi) were used.[19] A related catalyst for hydrogenation of acetophenone was produced from reaction of $Mo(CO)_6$ with MeOH/NaOMe (70 °C, 1450 psi H_2 pressure).[20] In both of these cases the catalysis is thought to proceed through the anionic metal hydride $HMo(CO)_5^-$, with the mechanism apparently involving metal alkoxide intermediates (cf. eq 1) rather than the proton transfer and hydride transfer processes proposed in Scheme 1.

The Mo and W systems reported here use cheap metals, whereas traditional ketone hydrogenation catalysts use more expensive metals such as Rh and Ru. The advantage of inexpensive metals must be balanced against the catalytic activity obtained, since some Ru catalysts[3] are orders of magnitude more reactive than our Mo complexes. The new hydrogenation catalysts developed here exploit the versatile reactivity patterns accessible from transition metal hydrides, through the reactivity of acidic and hydridic M−H bonds. Other hydrogenation catalysts based on Ru[21] or Rh[22] apparently proceed through heterolytic pathways where an M−H bond and an O−H (or N−H) bond are formed from reaction with H_2. Hidai and co-workers recently reported heterolytic cleavage of H_2 with Ru catalysts for hydrogenolysis of silyl enol ethers,[23] and for conversion of coordinated N_2 to NH_3. Catalysts that rely on mechanisms involving heterolytic cleavage of H_2 offer promising opportunities for further development, and our results provide an initial step in the development of a new series of Mo and W catalysts based on this concept.

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Supporting Information Available: Preparative procedures and spectroscopic characterization of ketone and alcohol complexes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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