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Solvent-free ketone hydrogenations catalyzed by molybdenum complexes†

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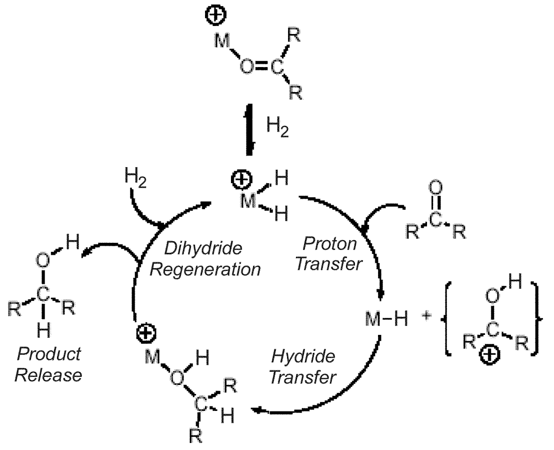
Et_2C=O is hydrogenated under solvent-free conditions using a catalyst prepared by hydride abstraction from $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PCy_2]$; the catalyst functions at low catalyst loadings (< 0.4 mol%).

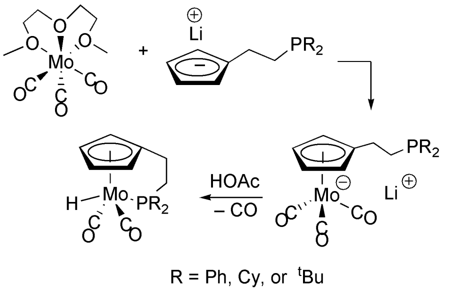
Environmental concerns provide a compelling incentive to develop chemical reactions that minimize waste production. The development of solvent-free (or 'solventless') reactions[1,2] is an especially attractive goal in the context of Green Chemistry,[3] since solvents are used on a large scale (over 15 billion kilograms of organic solvents produced worldwide annually!).[1] Catalytic hydrogenations of ketones and other organic substrates are traditionally carried out using platinum-group metals like rhodium and ruthenium,[4] though there are a few examples of catalysts not requiring precious metals. Darensbourg and co-workers reported the catalytic hydrogenation of ketones at 125 °C using 5 mol% $[W(CO)_5(OAc)]^-$ as the catalyst precursor.[5] Our research on the reactivity of metal hydrides has led to a class of homogeneous hydrogenation catalysts using the base metals molybdenum and tungsten.[6] Research on these 'Cheap Metals for Noble Tasks' offers the potential for development of new types of catalysts that may provide cost savings and potentially other advantages over conventional homogeneous catalysts. One goal of our research is to develop catalysts based on inexpensive metals that may be useful in industrial processes to replace stoichiometric reagents like $LiAlH_4$ or $NaBH_4$. Our efforts thus far have concentrated on using the mechanistic understanding gained from studies of proton transfer and hydride transfer reactions of metal hydrides to guide the rational design of catalysts. A series of ketone complexes, $[CpM(CO)_2(PR_3)(\eta^1\text{-}Et_2C{=}O)]^+BAr'^-_4$ [R = Ph or Me; M = Mo or W; Ar′ = 3,5-bis(trifluoromethyl)phenyl], were shown to function as catalyst precursors for the hydrogenation of ketones under mild conditions (room temperature, 4 atm H_2).[6] The proposed mechanism for these ionic hydrogenations is shown in Scheme 1.



Scheme 1

The turnover rates are relatively slow, however, and the catalysts suffer decomposition. We report here a new generation of Mo catalysts that exhibits substantially improved lifetimes, and which are shown to be effective for the hydrogenation of ketones under solvent-free conditions and low catalyst loadings.

The appearance of phosphonium cations, HPR_3^+, in catalytic reactions using $[CpM(CO)_2(PR_3)(\eta^1\text{-}Et_2C{=}O)]^+$ suggested that the decomposition pathway involved dissociation of a phosphine, which is protonated under the reaction conditions. We sought to prepare catalysts with improved lifetimes by suppression of phosphine dissociation through chelation of the phosphine to the cyclopentadienyl ring by a two-carbon bridge. Reaction of $(CO)_3Mo(diglyme)$[7] with $Li^+[C_5H_4(CH_2)_2PR_2]^-$ [8] produced $Li^+\{Mo(CO)_3[\eta^5\text{-}C_5H_4(CH_2)_2PR_2]\}^-$. IR spectra of the ν(CO) bands were similar to those previously analyzed in detail for $Li^+Mo(CO)_3Cp^-$,[9] and ^{31}P NMR peaks at δ −13.2 (R = Ph), −1.8 (R = Cy) and 31.8 (R = ^{t}Bu) were indicative of uncoordinated phosphines. Protonation of the anionic complexes with HOAc led to formation of the molybdenum hydrides $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PR_2]$‡ and expulsion of one CO as the phosphine coordinates to the metal. The metal hydrides exhibit broad ^{31}P NMR resonances at δ 74.4 (R = Ph), −80.6 (R = Cy) and 103.8 (R = ^{t}Bu), consistent with coordination of the phosphine to the metal. The ^{31}P NMR resonance of $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PCy_2]$ at −89 °C de-coalesces into two shaper resonances ($\omega_{1/2} \approx 7$ Hz) at δ 78.7 (98%) and 89.3 (2%). The ^1H NMR spectrum of $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PCy_2]$ recorded at −89 °C also indicates 98% *trans* isomer. These spectra indicate that the hydrides exist as an interconverting mixture of *cis* and *trans* isomers. Isomerization between the *trans* and *cis* isomers was reported previously for closely related complexes with unsubstituted Cp ligands such as $CpMo(CO)_2(PPh_3)H$,[10] $CpMo(CO)_2(PMe_3)H$,[11] and $CpMo(CO)_2(PCy_3)H$.[12] Whereas such isomerizations are well-known, it is notable that the *trans* isomer strongly predominates in $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PCy_2]$, in contrast to $HMo(CO)_2(PCy_3)$ where the *cis* isomer is favored by a ratio of 9:1.[12] The structure of $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PCy_2]$ was determined by single crystal X-ray diffraction and indicates the *trans* isomer in the solid state; details of the structure will be given in a full paper.



The metal hydrides, $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PR_2]$, react cleanly with HOTf (OTf = OSO_2CF_3) at room temperature to form *cis*- and *trans*-$Mo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PR_2](OTf)$, presumably through unobserved dihydride or dihydrogen complexes that

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† Electronic supplementary information (ESI) available: additional spectroscopic data and description of the synthetic procedures. See http://www.rsc.org/suppdata/cc/b4/b401760a/

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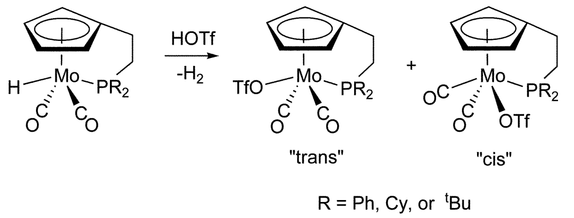
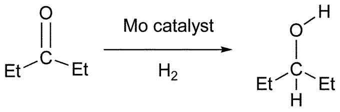


eliminate H_2. Clean hydride transfer reactivity from $HMo(CO)_2[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2PR_2]$ to $Ph_3C^+BF_4^-$ in CD_3CN is observed, producing complexes with acetonitrile ligands, *trans*- and *cis*-$Mo(CO)_2[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2PR_2(NCCD_3)]^+BF_4^-$. The *cis* and *trans* isomers of these complexes are readily distinguished by their ^1H NMR spectra. The *trans* isomers have a plane of symmetry and exhibit two sets of resonances for the C_5H_4 protons. In contrast, the *cis* isomer has no plane of symmetry, so its cyclopentadienyl protons appear as four separate multiplets.

In our earlier studies, the ketone complexes $[CpM(CO)_2PR_3(Et_2C{=}O)]^+BAr'_4{}^-$ (M = Mo, W; R = Ph, Me) were isolated and used as the catalyst precursors. Catalysis from $CpM(CO)_2(PCy_3)H$ was initated by carrying out the hydride transfer *in situ*, without isolation of the ketone complex. Similar reactions of $HMo(CO)_2[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2PPh_2]$ with $Ph_3C^+BAr'_4{}^-$ with 1–2 equivalents of $Et_2C{=}O$ gave spectral evidence for the formation of the ketone complexes, but pure ketone complexes were not isolated. Thus the catalytic reactions were carried out by hydride transfer from the metal hydride to $Ph_3C^+BAr'_4{}^-$ *in situ*, as was done for the PCy_3 complexes previously.

Initial conditions for the catalytic hydrogenations were identical to those used earlier in the non-bridged systems (30 mM metal hydride + 30 mM $Ph_3C^+BAr'_4{}^-$ in CD_2Cl_2 under 4 atm H_2 at 23 °C, 10 equivalents of $Et_2C{=}O$ (initially 300 mM). Under these conditions, the C_2-PCy_2 catalyst produced 2.8 turnovers in 6 h, indicating that it is less reactive than the catalyst formed from $CpMo(CO)_2(PCy_3)H$, which produced about 8.6 turnovers in 6 h. Although the new C_2-bridged catalyst is initially less active than the related complex without the C_2 bridge, an advantage of the C_2-bridged complex is its much longer lifetime compared with the unbridged catalyst precursor. While these conditions provided a direct comparison of the bridged *vs.* unbridged catalysts and afforded the convenience of direct NMR tube monitoring of the reaction, they were not ideal since it was necessary to periodically replenish the reaction tube with more ketone and H_2. Solvent-free hydrogenations were carried out neat $Et_2C{=}O$, and the results are summarized in Table 1.



The PCy_2-bridged systems give higher turnovers than analogs with either a PPh_2 or P^tBu_2 bridge. The C_2-bridge that chelates the cyclopentadienyl to the phosphine clearly confers substantial additional stability to the complex, as shown by the experiments at 50 and 75 °C. In contrast, the unchelated systems reported earlier showed some decomposition even at room temperature. The $BAr'_4{}^-$ anion gives superior performance compared with the BF_4^- anion, presumably due to more facile decmposition pathways available to the BF_4^- complexes. Another improvement over the unchelated earlier systems is that complexes with a bound triflate ligand give catalysis, though as shown in the table for reactions with $HMo(CO)_2[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2PCy_2]$, the $BAr'_4{}^-$ counterion provides a better performance than the complex with a bound triflate. Although most experiments were carried out at 4 atm H_2, a higher pressure can be beneficial. Of particular note is the complete hydrogenation of neat $Et_2C{=}O$ catalyzed by 0.35 mol% Mo complex in 8 days at 50 °C at 55 atm H_2.

Table 1 Hydrogenation of $Et_2C{=}O$ by $HMo(CO)_2[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2PR_2]$ + $Ph_3C^+BAr'_4{}^-$ or $Mo(CO)_2[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2PR_2](OTf)$. 4 atm H_2, except where noted

R	A^-	T/°C	Mo/mol%	TON(total) t = 10 days[a]
Ph	$BAr'_4{}^-$	50	0.35	62 [1]
Cy	$BAr'_4{}^-$	23	0.35	23 [< 1]
Cy	$BAr'_4{}^-$	50	0.35	132 [10]
Cy	$BAr'_4{}^-$	50	0.35	283 [34][b]
Cy	BF_4^-	50	0.35	99 [6]
Cy	OTf	50	0.35	120 [4]
Cy	OTf	75	0.086	462 [16]
^{t}Bu	$BAr'_4{}^-$	50	0.35	82 [6]

[a] TON (turnover number) after 10 days. The number in brackets indicates the TON for the ether condensation product, $(Et_2CH)_2O$. [b] H_2 pressure of 55 atm; hydrogenation complete at t = 8 days.

This new generation of Mo catalysts was rationally designed from mechanistic principles to disfavor a decomposition pathway identified for previously studied complexes. Several advantages were found with these new complexes, including low catalyst loadings (< 0.4 mol%), higher thermal stability, substantially longer lifetimes (hundreds of turnovers), and utility under solvent-free conditions. Further improvements are being sought to produce catalysts that might provide attractive replacements for stoichiometric hydrogenation reagents like $LiAlH_4$.

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Notes and references

‡ Spectral data for $HMo(CO)_2[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2PCy_2]$: ^1H NMR (400 MHz, CD_2Cl_2): δ −5.81 (d, $^2J_{PH}$ = 26.8, 1H, MoH), 1.24–2.00 (m, 22H, Cy), 2.38 (m, 2H, PCH_2), 2.47 (m, 2H, $C_5H_4CH_2$), 4.96 (br, 2H, α-C_5H_4), 5.09 (m, 2H, β-C_5H_4); $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2): δ 80.6 (br, $\omega_{1/2}$ = 200 Hz); $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ 25.8 (br, PCH_2), 26.7 (s, *m*- or *p*-Cy), 27.6 (d, $^2J_{CP}$ = 13 Hz, *o*-Cy), 29.0 (s, *m*- or *p*-Cy), 37.0 (d, $^2J_{CP}$ = 23 Hz, *ipso*-Cy), 37.3 (v br, $C_5H_4CH_2$), 81.8 (s, *o*-C_5H_4), 87.4 (s, *m*-C_5H_4), 125.1 (d, $^3J_{CP}$ = 6 Hz, *ipso*-C_5H_4), 234 (v br, CO); IR (THF): ν(CO) = 1927 (s), 1848 (vs) cm^{-1}; Anal. calc. for $C_{21}H_{31}O_2PMo$ (442.4): C, 57.02; H, 7.06. Found: C, 56.92, H, 6.99%. Additional spectroscopic data and a description of the synthetic procedures are provided in the ESI.†

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