Molybdenum Carbonyl Complexes in the Solvent-Free Catalytic Hydrogenation of Ketones

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The heterodifunctional ligand Li[η^5-$C_5H_4(CH_2)_2PR_2$] (R = Ph, Cy, and ^{t}Bu) reacts with $Mo(CO)_3$(diglyme) to give the molybdenum anion complex Li{$Mo(CO)_3$[η^5-$C_5H_4(CH_2)_2PR_2$]}. Protonation with HOAc gives the metal hydride complexes $HMo(CO)_2$[η^5:η^1-$C_5H_4(CH_2)_2PR_2$], in which the phosphine and cyclopentadienyl ligands are linked by a two-carbon bridge. Crystal structures of $HMo(CO)_2$[η^5:η^1-$C_5H_4(CH_2)_2PR_2$] with all three R groups (R = Ph, Cy, and ^{t}Bu) are reported. Syntheses of the C_3-bridged complex, $HMo(CO)_2$[η^5:η^1-$C_4H_5(CH_2)_3PPh_2$], and a W analogue, $HW(CO)_3$[η^5-$C_5H_4(CH_2)_2P^tBu_2$], were carried out by analogous routes. Hydride transfer to $Ph_3C^+BAr'_4{}^-$ [Ar′ = 3,5-bis(trifluoromethyl)phenyl] from the catalyst precursors $HMo(CO)_2$[η^5:η^1-$C_5H_4(CH_2)_2PR_2$] leads to homogeneous catalysts for hydrogenation of ketones, with the best performance being found for R = Cy. Protonation of $HMo(CO)_2$[η^5:η^1-$C_5H_4(CH_2)_2PR_2$] by HOTf leads to metal triflate complexes (TfO)$Mo(CO)_2$-[η^5:η^1-$C_5H_4(CH_2)_2PR_2$], which are used in ketone hydrogenation. Compared to the previously prepared complexes that did not have the phosphine and Cp linked together, these new complexes provide catalysts that have much longer lifetimes (up to about 500 turnovers) and higher thermal stability. Solvent-free ketone hydrogenation can be carried out with these complexes at catalyst loadings as low as 0.1 mol %.

Homogeneous catalysts for hydrogenation of ketones traditionally use ruthenium or rhodium complexes that operate by a mechanism where binding of the ketone to the metal and subsequent insertion of the ketone into a M−H bond are key steps.[1] An alternative mechanism for ketone hydrogenation that does not require an insertion into an M−H bond is ionic hydrogenation, in which H_2 is delivered to the ketone in the form of a proton (H^+) and a hydride (H^-).[2] Ionic hydrogenations offer the possibility of removing the need for precious metals, since inexpensive metals such as Mo and W hydride complexes are well-established to function as proton donors[3] and as hydride donors.[4−6]

One of our goals is to develop catalysts based on inexpensive metals that could eventually become competitive with stoichiometric reagents such as $LiAlH_4$ or $NaBH_4$. While these main group reagents are immensely useful for many reductions, their use produces stoichiometric amounts of waste. One of the principles of green chemistry[7,8] is that catalysts are preferred over stoichiometric reagents.

Several studies have reported the use of Cr, Mo, or W complexes as homogeneous catalysts for hydrogenation of C=O bonds. Darensbourg and co-workers reported extensive studies on the reactivity of anionic metal carbonyl hydrides[9] and found that anionic catalysts such as $[(CO)_5M(OAc)]^-$ (M = Cr, Mo, W) or the bimetallic complexes $[(\mu\text{-H})M_2(CO)_{10}]^-$ served as catalyst precursors for ketone hydrogenations.[10] Typical conditions were 5 mol % catalyst at 125 °C for 24 h, leading to a maximum of about 18 turnovers. Related anionic catalysts were reported by Markó[11] and by Fuchikami.[12] Transfer hydrogenation of ketones was reported by Brunet and co-workers, who used 20 mol % $K^+[(CO)_5CrH]^-$ as the catalyst precursor.[13] Tyler and co-workers have

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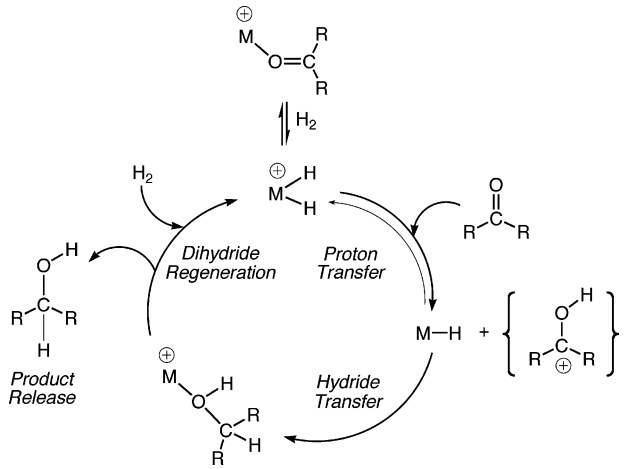
developed the aqueous chemistry of molybdenocene complexes and have reported transfer hydrogenation of ketones using isopropyl alcohol as the source of hydrogen.[14] Kuo and co-workers carried out studies on ketone hydrogenations using $Cp_2MoH(OTf)$ (OTf = OSO_2CF_3) in water.[15] These examples show that Mo and other inexpensive metals can function as homogeneous catalysts for hydrogenation of aldehydes or ketones, but this area is still not well-developed compared to catalysis by precious metals, so further mechanistic information and new classes of catalysts are being sought.

Recent progress has been made in the use of inexpensive, nontoxic metals as homogeneous catalysts for hydrogenation of C=C bonds. Chirik and co-workers recently discovered a series of Fe complexes that serve as very efficient catalyst precursors for the hydrogenation of alkenes under 1 atm H_2 at room temperature.[16] Daida and Peters reported a series of Fe precatalysts with tris(phosphino)borate ligands that hydrogenate alkenes under mild conditions.[17]

We have shown that metal hydrides are capable of functioning as hydride donors in the presence of acids and have reported the use of $HW(CO)_3Cp$ and other metal hydrides in the stoichiometric ionic hydrogenation of alkenes,[18] alkynes,[19] ketones,[20] and acyl chlorides.[21] Related reactions involving hydride transfer showed that ether complexes resulted from reactions of acetals with metal hydrides and acids.[22] These stoichiometric reactivity studies led to the development of a series of Mo and W catalysts for homogeneous hydrogenation of ketones.[23,24] Hydride abstraction from $HM(CO)_2Cp(PR_3)$ (M = Mo, W; R = Me, Ph, Cy; Cy = cyclohexyl) in the presence of $Et_2C=O$ gave ketone complexes $[M(CO)_2Cp(PR_3)(\eta^1\text{-}Et_2C=O)]^+BAr'_4^-$ [Ar′ = 3,5-bis(trifluoromethyl)phenyl], which are catalyst precursors for the homogeneous hydrogenation of ketones.[23,24] The Mo catalysts were faster than the analogous W complexes, and the dependence of turnover rate as a function of phosphine was found to be $PCy_3 > PPh_3 > PMe_3$. Mechanistic experiments supported the proposed ionic mechanism shown in Scheme 1, involving proton transfer from a cationic dihydride and hydride transfer from a neutral metal hydride. While these catalysts functioned under mild conditions (23 °C, 4 atm H_2) the turnover rates were slow. The formation of phosphonium cations (HPR_3^+) in the catalytic reactions suggested that a phosphine ligand was dissociating and was being protonated under the reaction conditions. Recognition of this decomposition pathway suggested that catalysts designed to suppress phosphine dissociation might provide longer lifetimes. Here we report the synthesis, structures, and catalytic reactivity of complexes in which the Cp and phosphine ligands are linked by a hydrocarbon bridge.[25] These complexes have several advantages over the first-generation nonbridged complexes reported previously. These improved catalyst precursors exhibit enhanced thermal stability and can be used at low catalyst loading (0.1−0.4 mol %). Furthermore, these catalysts can be used under solvent-free[26] conditions, with a ketone as both substrate and solvent. Recent progress in solvent-free ketone hydrogenation was reported by Özkar and Finke, who found that Ir(0) nanocluster catalysts hydrogenate acetone.[27]

Scheme 1



Results and Discussion

Synthesis and Characterization of $HMo(CO)_2[\eta^5\text{-}C_5H_4(CH_2)_2PR_2]$. Heterodifunctional ligands that have a hydrocarbon chain linking phosphine and cyclopentadienide ligands have been used in many organometallic complexes and catalysts.[28] The reaction of $Mo(CO)_3$(diglyme)[29] with $Li[C_5H_4(CH_2)_2PR_2]$[30,31] (R = Ph, Cy, and ^{t}Bu) at room temperature formed the anionic intermediates $Li\{Mo(CO)_3[\eta^5\text{-}C_5H_4(CH_2)_2PR_2]\}$ (**1**, Scheme 2) in high yield. The five metal carbonyl bands observed in the IR spectrum between 1902 and 1715 cm^{-1} are very similar to those previously observed in the spectrum of the unsubstituted Cp complex Li-

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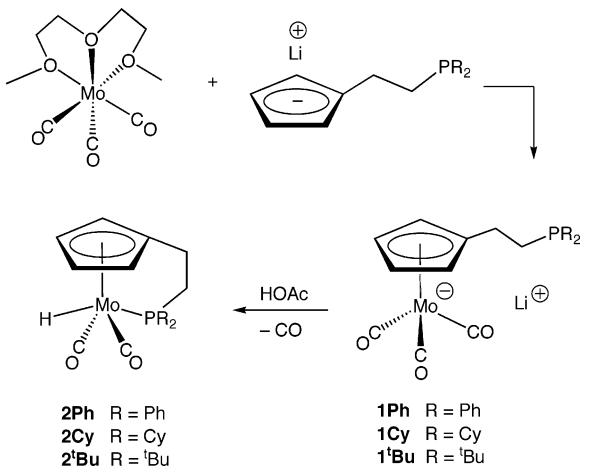
Scheme 2



$[Mo(CO)_3Cp]$.[32] The appearance of five bands for three CO ligands is due to the presence in THF solution of ion pairs, such as a Mo−CO···Li^+ interaction.[33] The ^{31}P NMR resonances of $Li\{Mo(CO)_3[\eta^5\text{-}C_5H_4(CH_2)_2PR_2]\}$ at δ −13.2 (**1Ph**, R = Ph), −1.8 (**1Cy**, R = Cy) and 31.8 (**1^{t}Bu**, R = ^{t}Bu) are shifted only slightly downfield (<3 ppm) from the starting ligands, supporting the assignment of "dangling phosphine" complexes.

Addition of acetic acid to complexes **1** led to the formation of the hydride complexes *trans*-$HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PR_2]$ (**2Ph**, R = Ph; **2Cy**, R = Cy; **2^{t}Bu**, R = ^{t}Bu). Use of $Mo(CO)_3$(diglyme) was significantly cleaner and gave higher yields than reactions using $Mo(CO)_3(NCMe)_3$ as the starting Mo complex. The *trans*-hydrides are pale yellow air-sensitive crystalline solids. The hydrides appear to be stable in solution, showing only minor signs (<5%) of decomposition after many days in CD_2Cl_2 at room temperature.

Coordination of the phosphine to the metal is accompanied by a substantial (72−87 ppm) downfield shift from the resonance of the "dangling phosphine" intermediates **1**. The ^{31}P NMR spectra of hydrides had resonances at δ 74.4 (**2Ph**) 80.6 (**2Cy**), and 103.8 (**2^{t}Bu**). At room temperature, the ^{31}P NMR resonances are broad, with $\omega_{1/2} \approx 30$ Hz for complexes **2Ph** and **2^{t}Bu**, and $\omega_{1/2} \approx 200$ Hz for **2Cy**. At −89 °C the ^{31}P NMR resonance of **2Cy** has decoalesced to give two sharper peaks ($\omega_{1/2} \approx 7$ Hz) at δ 78.7 (98%) and 89.3 (2%). This provides evidence that the hydride complex **2Cy** undergoes *cis*−*trans* isomerization.

Isomerization between *trans* and *cis* isomers was studied previously for closely related complexes with unsubstituted Cp ligands such as $HMo(CO)_2Cp(PPh_3)$,[34] $HMo(CO)_2Cp(PMe_3)$,[35] and $HMo(CO)_2Cp(PCy_3)$.[5] For $HMo(CO)_2Cp(PCy_3)$,[5] $^2J_{HP} = 20$ Hz for the *trans* isomer and $^2J_{HP} = 60$ Hz for the *cis* isomer. The magnitude of the J_{HP} ($^2J_{HP} = 26.8$ Hz) observed at δ −5.81 at 25 °C for **2Cy** suggests a predominance of the *trans* isomer, and low-temperature spectra provide further support for this assignment. The ^1H NMR of **2Cy** recorded at −89 °C exhibits a hydride resonance at −6.13 (d, $^2J_{HP} = 21.9$ Hz, 98%) for the *trans* isomer, while the resonance for the *cis*-hydride is observed at −6.17 (d, $^2J_{HP} \approx 53$ Hz, 2%; partially overlapped with *trans* isomer). In contrast, the unbridged complex $HMo(CO)_2Cp(PCy_3)$ favors the *cis* isomer by a 9:1 ratio.[5] All resonances in the ^{13}C NMR spectrum of the C_2-PCy_2 hydride, **2Cy**, were assigned using a combination of ^1H NMR, ^{13}C NMR, and 2D HMQC experiments (see Figure S1 in the Supporting Information).

The W analogues of these Mo complexes were investigated. The reaction of $W(CO)_3(NCEt)_3$[36] with $Li[C_5H_4(CH_2)_2P^tBu_2]$ at room temperature formed the anionic intermediate $Li\{W(CO)_3[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2P^tBu_2]\}$. Protonation by acetic acid led to the formation and isolation of the tungsten hydride complex *trans*-$HW(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2P^tBu_2]$, which was fully characterized by spectroscopy and elemental analysis. Synthetic details and spectroscopic characterization are provided in the Supporting Information.

Structural Characterization of $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_4H_5(CH_2)_2PR_2]$ Complexes (2Ph, 2Cy, and 2^{t}Bu). The X-ray crystal structures of **2Ph**, **2Cy**, and **2^{t}Bu** were determined, and ORTEP diagrams are shown in Figures 1−3. Table 1 provides information on the data collection and structure refinement; additional crystallographic information is provided in the Supporting Information. Selected bond lengths and bond angles are given in Table 2.

The Mo−P bond lengths of **2** range from 2.4343(5) to 2.5256(5) Å going from R = Ph to Cy to ^{t}Bu. This variation and changes in the P(1)−C(3)−C(4) bond angles reflect an increase in the steric bulk of the phosphine ligands. The Mo−H distances are listed here but are subject to the normal uncertainties of metal hydride positions determined by X-ray crystallography, which often provides M−H distances that are 0.1−0.2 Å shorter than their true distances.[37]

Synthesis and Characterization of $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_3PPh_2]$. The related ligand with a C_3-

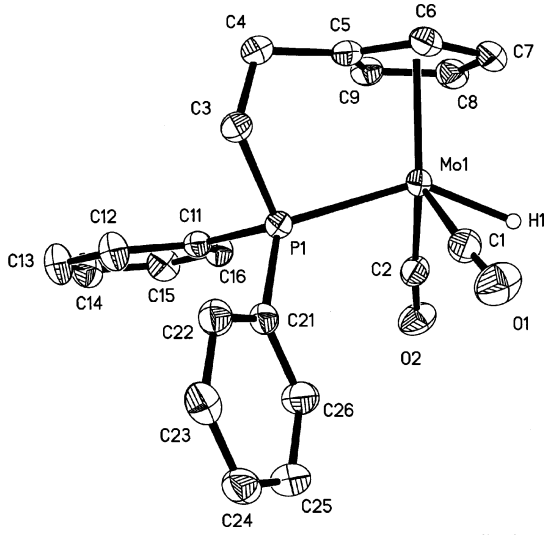


Figure 1. Molecular structure of $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PPh_2]$·toluene, **2Ph**. Thermal ellipsoids were drawn at the 50% probability level. The toluene molecule and all hydrogens except H(1) were removed for clarity.

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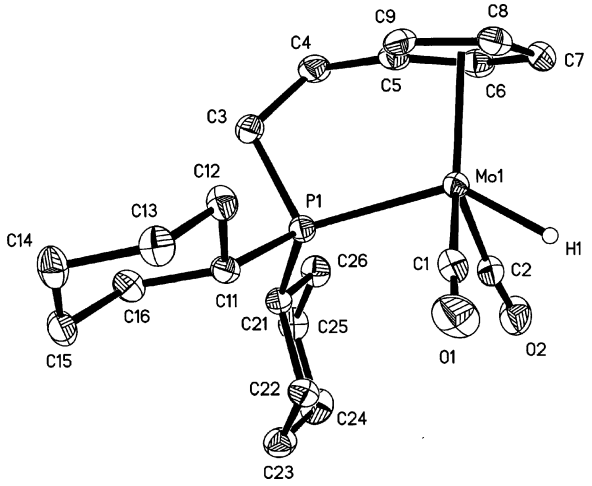

Figure 2. Molecular structure of $HMo(CO)_2[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2PCy_2]$, **2Cy**. Thermal ellipsoids were drawn at the 50% probability level. All hydrogens except H(1) were removed for clarity.

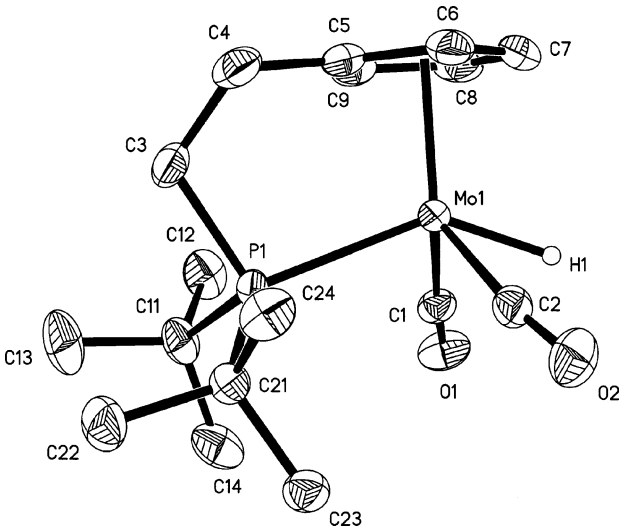

Figure 3. Molecular structure of $HMo(CO)_2[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2P^tBu_2]$, **2^{t}Bu**. Thermal ellipsoids were drawn at the 50% probability level. All hydrogens except H(1) were removed for clarity.

bridge linking the phosphine and cyclopentadienyl, $Li[C_5H_4(CH_2)_3PPh_2]$, was prepared from $Cl(CH_2)_3Br$, by sequential replacement of the two halogens through reaction with $LiPPh_2$ and NaCp, followed by deprotonation with *n*-BuLi to give the Li^+ salt of the substituted cyclopentadienide.[31] The heterodifunctional ligand, $Li[C_5H_4(CH_2)_3PPh_2]$, reacts with $Mo(CO)_3$(diglyme) to give the molybdenum anion complex $Li\{Mo(CO)_3[\eta^5\text{-}C_5H_4(CH_2)_3PPh_2]\}$, which subsequently reacts with HOAc to produce the hydride *trans*-$HMo(CO)_2[\eta^5:\eta^1\text{-}C_4H_5(CH_2)_3PPh_2]$ (**3**; Scheme 3). Additional details of the NMR data, including complete assignments of ^{13}C NMR resonances based on HMQC data, are found in the Supporting Information (Figure S2).

Formation of Cationic Acetonitrile Complexes. Hydride transfer from metal hydrides to Ph_3C^+ is well-known.[38] We previously reported the kinetics of hydride transfer of a series of metal hydrides to $Ph_3C^+BF_4^-$.[5,6] When carried out in CH_2Cl_2, these reactions produce

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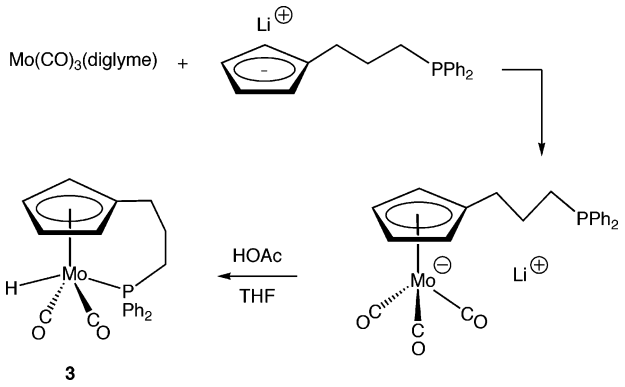
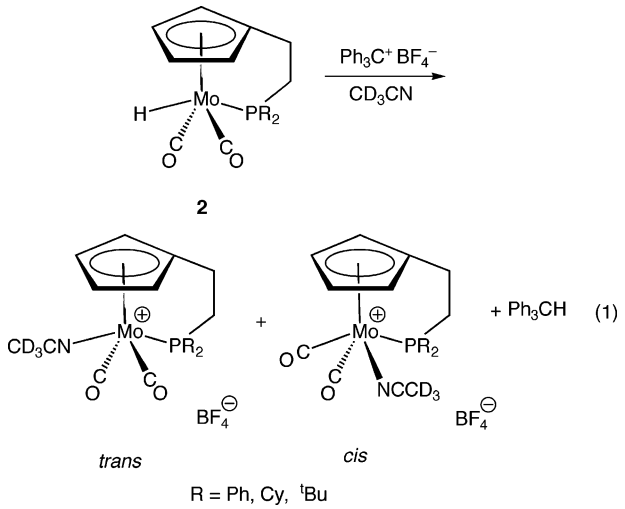
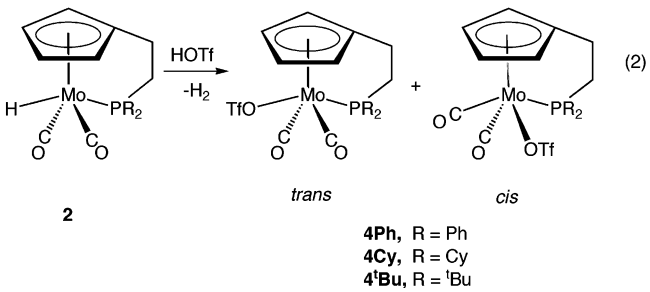
Scheme 3



M-FBF_3 complexes, but in CH_3CN, the acetonitrile coordinates to the metal, giving $M(NCCH_3)^+BF_4^-$ complexes. The C_2-bridged molybdenum hydrides **2** cleanly transfer hydride upon reaction with $Ph_3C^+BF_4^-$ in CD_3CN to give complexes with acetonitrile ligands, *trans*- and *cis*-$[Mo(CO)_2[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2PR_2](NCCD_3)]^+BF_4^-$ (eq 1). Further details and characterization of these complexes are in the Supporting Information.



Formation of Isolable Mo-OTf Complexes. The C_2-hydrides, **2**, react cleanly with HOTf (OTf = OSO_2CF_3) at room temperature to form *cis*- and *trans*-$(TfO)Mo(CO)_2[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2PR_2]$ (**4**, eq 2) presumably through the unobserved dihydride or dihydrogen complexes that eliminate H_2. Tungsten phosphine com-



plexes such as $HW(CO)_2Cp(PMe_3)$ are protonated by HOTf to give dihydrides; the structure of $[(H)_2W(CO)_2Cp(PMe_3)]^+OTf^-$ was determined by X-ray crystal-

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Table 1. Crystallographic Data and Details of Refinement $HMo(CO)_2[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2PR_2]$, where R = Ph, Cy, ^{t}Bu (2Ph, 2Cy, and 2^{t}Bu)

	$HMo(CO)_2[C_5H_4(CH_2)_2PPh_2]$, **2Ph**	$HMo(CO)_2[C_5H_4(CH_2)_2PCy_2]$, **2Cy**	$HMo(CO)_2[C_5H_4(CH_2)_2P^tBu_2]$, **2^{t}Bu**
formula	$C_{21}H_{19}MoPO_2 \cdot C_7H_8$	$C_{21}H_{31}MoPO_2$	$C_{17}H_{27}MoPO_2$
fw	522.44	442.39	390.32
temp (°C)	−100	−100	−100
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	9.076(1)	8.182(1)	9.185(1)
b (Å)	9.946(1)	15.618(1)	14.562(1)
c (Å)	14.473(1)	15.861(1)	13.358(1)
α (deg)	97.07(1)		
β (deg)	94.46(1)	100.90(1)	98.94(1)
γ (deg)	111.60(1)		
V, Å^3	1194.8	1990.2	1764.9
Z	2	4	4
μ(Mo), cm^{-1}	6.22	7.33	8.16
ρ calc (g cm^{-1})	1.452	1.476	1.469
cryst size (mm)	0.23 × 0.25 × 0.41	0.17 × 0.37 × 0.42	0.27 × 0.35 × 0.42
cryst character	yellow prism	light gold wedge	irregular gold block
2θ range (deg)	2.9−56.5	2.6−56.6	4.2−56.6
total no. of reflns	7505	12880	10796
no. of unique reflns, $I \geq 3.0\sigma(I)$	4727	3015	3322
no. of params	293	350	194
R_1	0.024	0.026	0.022
R_w	0.030	0.025	0.026
goodness of fit	1.43	0.76	1.04

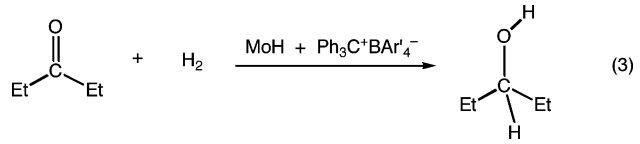
Table 2. Selected Bond Lengths (Å) and Angles (deg) $HMo(CO)_2[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2PR_2]$ (R = Ph (2Ph) Cy (2Cy), and ^{t}Bu (2^{t}Bu)

	R		
	Ph (**2Ph**)	Cy (**2Cy**)	^{t}Bu (**2^{t}Bu**)
Mo(1)−H(1)	1.680(23)	1.595(31)	1.660(26)
Mo(1)−P(1)	2.4343(5)	2.4664(7)	2.5256(5)
Mo(1)−C(1)	1.959(2)	1.960(3)	1.959(2)
Mo(1)−C(2)	1.953(2)	1.955(3)	1.959(2)
Mo(1)−P(1)−C(3)	103.14(5)	105.0(1)	103.31(7)
P(1)−C(3)−C(4)	108.2(1)	111.7(2)	113.1(1)
C(3)−C(4)−C(5)	112.3(1)	111.3(2)	112.1(2)

lography.[39] In contrast, Poli and co-workers found that H_2 was produced rapidly when the Mo hydride complex $HMo(CO)_2Cp(PMe_3)$ was protonated, and they suggested that the initial product of protonation was an unobserved dihydrogen complex rather than a dihydride.[40] The Mo dihydrides or dihydrogen complexes are not directly observed, so it is possible that the Mo example forms a dihydrogen complex even though the W analogue forms an isolable dihydride.

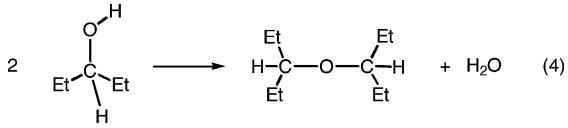
These triflate complexes with C_2-PR_2 bridges were isolated as intensely colored red or purple solids. In contrast to the C_2-hydrides **2** and the cationic C_2-acetonitrile complexes, the triflates **4Cy** and **4^{t}Bu** preferentially form the *cis* isomer. The bright red solid $(TfO)Mo(CO)_2[\eta^5:\eta^1\text{-}C_5H_4(CH_2)_2PCy_2]$ (**4Cy**) was found to have a *cis:trans* product ratio of 6:1 in CD_2Cl_2. The ratio does not significantly change after 2 days in solution. The triflate complex **4Cy** was also formed in an NMR tube reaction by hydride abstraction from **2Cy** using Ph_3COTf.

Hydrogenations of Et_2C=O in CD_2Cl_2 under 4 atm H_2. We previously showed that molybdenum and tungsten complexes with monodentate phosphines hydrogenate ketones such as Et_2C=O at room temperature under 4 atm H_2.[23,24] The ketone complexes, $[M(CO)_2Cp(PR_3)(Et_2C{=}O)]^+BAr'_4{}^-$ (M = Mo, W; R = Ph, Me), were isolated and used as catalyst precursors. Catalysis with the PCy_3 complexes was carried out by hydride transfer to $Ph_3C^+BAr'_4{}^-$ from $HM(CO)_2Cp(PCy_3)$ in the presence of Et_2C=O. Ketone complexes were not isolated for these PCy_3 complexes, and NMR data suggested exchange of free and bound ketone. Catalytic reactions (eq 3) were initiated by reacting the hydride complexes with Ph_3C^+ in the presence of Et_2C=O, followed by addition of hydrogen. Our initial studies using the bridged C_2-PR_2



(3)

complexes were designed to directly compare their catalytic activity to those of the previously reported unbridged PR_3 catalyst systems under the same reaction conditions. The reactions were conducted in CD_2Cl_2 with initial concentrations of 30 mM catalyst precursor and 300 mM Et_2C=O, under 4 atm H_2 at room temperature (23 °C). ^{1}H NMR indicated the appearance of the product alcohol, Et_2CHOH, as well as smaller amounts of its ether, $(Et_2CH)_2O$, arising from condensation of two alcohols (eq 4). Figure S3 in the Supporting Information shows the time profile of product formation for a typical catalytic reaction.



(4)

We thought that avoiding an alkyl chloride such as CD_2Cl_2 might produce a more stable catalyst, because

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

(40) (a) Quadrelli, E. A.; Kraatz, H.-B.; Poli, R. *Inorg. Chem.* **1996**, *35*, 5154−5162 (b) Galassi, R.; Poli, R.; Quadrelli, E. A.; Fettinger, J. C. *Inorg. Chem.* **1997**, *36*, 3001−3007.

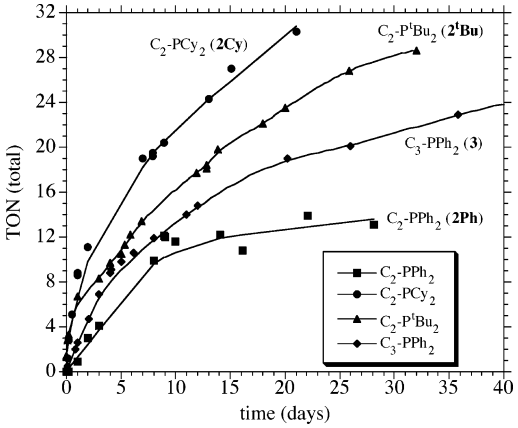


Figure 4. Hydrogenation of $Et_2C{=}O$ by a series of C_2- and C_3-bridged catalysts, generated in situ by reaction of **2** or **3** with $Ph_3C^+BAr'_4{}^-$ in the presence of $Et_2C{=}O$. Initial reaction conditions: 30 mM MoH, 300 mM $Et_2C{=}O$, 4 atm H_2 in CD_2Cl_2 at 23 °C. Additional $Et_2C{=}O$ was added in 10 equiv increments. Hydrogen was replenished as needed.

of the possibility of decomposition of the catalyst through reactivity with CD_2Cl_2. But a reaction conducted in C_6D_5Cl instead of CD_2Cl_2 gave a significant decrease in the catalysis rate, compared to reactions in CD_2Cl_2. When the hydrogenation was carried out at 70 °C instead of 23 °C in CD_2Cl_2, the reaction was worse, apparently due to limited thermal stability of the catalyst at elevated temperatures in CD_2Cl_2.

Figure 4 summarizes the results for the ionic hydrogenation of $Et_2C{=}O$ for the series of C_2-bridged (**2**) and C_3-bridged (**3**) phosphine catalyst precursors. Of the C_2-bridged catalysts **2Cy** forms the most active catalyst, followed by the **2^{t}Bu** and **2Ph** systems. This reactivity trend is similar to those of the unbridged system, where the Mo-PCy_3 catalyst was superior to Mo-PPh_3.[23,24] The C_3-bridged-PPh_2 system is more reactive than its C_2-bridged-PPh_2 analogue under these reaction conditions.

The unbridged Mo-PCy_3 catalyst precursor $HMo(CO)_2Cp(PCy_3)$ gave a more active catalyst than the bridged **2Cy** catalyst. While **2Cy** produced 2.8 turnovers in 6 h, $HMo(CO)_2Cp(PCy_3)$ led to about 8.6 turnovers in 6 h.[23,24] This comparison is based on related catalysts with cyclohexyl groups on the phosphine, but note that the steric bulk of the untethered catalyst is larger, since it has a PCy_3 ligand, while the tethered complex **2Cy** has a C_2H_4 bridge linking the PCy_2 moiety to the cyclopentadienyl. Decomposition of the unbridged Mo-PCy_3 catalyst occurs much more quickly than for the new bridged catalysts. Thus, even though the bridged catalysts give slower initial rates, they are longer lived, and thus give higher TON numbers.

In all cases, complex ^1H NMR spectra of the C_2-bridged and C_3-bridged catalytic solutions were observed. Generally one or two major species were observed, along with minor species. We were unable to characterize all the species in solution or to make a definitive assignment of the resting state. It appears that both ketone and alcohol complexes are present, especially in the C_2-PPh_2 and C_3-PPh_2 systems, but attempted isolation of pure ketone complexes was not successful. For the previously studied unbridged systems, *cis* and *trans* isomers of the ketone complexes, $[M(CO)^2Cp(PR_3)(Et_2C{=}O)]\ ^+BAr'_4{}^-$, were the major species observed during catalysis. In addition, the alcohol complexes were observed during the catalytic reaction and were isolated in some cases.[24] The mechanism of catalysis with the bridged complexes is presumed to be the same as that established for the nonbridged systems, but the evidence is less definitive for the C_2-bridged complexes studied here.

Ionic hydrogenations were also studied in a solution of 90% $Et_2C{=}O$/10% benzene-d_6 (as a lock solvent for the NMR); i.e., 8.5 M $Et_2C{=}O$. This avoided the use of chlorinated solvents but still enabled the reactions to be monitored by NMR. These hydrogenations gave catalytic activity in the order C_2-PCy_2 > C_3-PPh_2 > C_2-PPh_2; see Figure S4 in the Supporting Information.

Solvent-Free Hydrogenations. The ideal solvent for hydrogenation of ketones is the neat ketone.[7] Much lower catalyst loadings were used in these solvent-free reactions, with some experiments employing about 0.1 mol % catalyst. As in the NMR tube experiments, the catalysts using $BAr'_4{}^-$, BF_4^-, or PF_6^- counterions were generated in situ by reaction of $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_nPR_2]$ (**2** or **3**) or $HMo(CO)_2Cp(PR_3)$ with $Ph_3C^+A^-$ ($A^- = BAr'_4{}^-$, BF_4^-, or PF_6^-). The corresponding triflate complexes, $(TfO)Mo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PR_2]$ (**4Cy** and **4^{t}Bu**) or $(TfO)Mo(CO)_2Cp(PR_3)$ (R = Ph, Cy), were added as isolated solids to the ketone.

Results for the hydrogenations of neat $Et_2C{=}O$ are summarized in Table 3. An arbitrary sampling time of t = 10 days was chosen, and most reactions were sampled again at t = 30 days. Separate variation of ligands, temperature, pressure, counterion, and catalyst loading allowed a comparison of the results of independently varying each of these parameters.

For the bridged complexes, **2Cy** is a better catalyst precursor than the related **2Ph** at all temperatures studied. The C_2-$PtBu_2$ complex **2^{t}Bu** gives an improved performance compared to **2Cy** at 23 °C, but the trend is reversed at 50 and 75 °C, suggesting thermal instability of **2^{t}Bu** at elevated temperatures. Comparison of C_2 vs C_3 bridge lengths for **2Ph** vs **3** shows that their performance is similar.

Increasing the reaction temperature from 23 °C to 50 °C results in about 6 times as many turnovers for **2Cy** at t = 10 days and an even larger increase for **2Ph**. While an increase from 23 °C to 50 °C improved the turnover frequency for all catalysts, a further increase to 75 °C was not always beneficial. The increase in TON on going from 50 °C to 75 °C was modest in some cases. Furthermore, in some of the examples conducted at 75 °C, little or no additional turnovers were detected at t = 30 days compared to t = 10 days, suggesting that the catalyst was deactivated after 10 days.

As was found from the experiments in CD_2Cl_2, the counterion can have a large effect on the rate of catalysis. The $BAr'_4{}^-$ anion provides more turnovers than those obtained by using BF_4^- or PF_6^-. The effect of H_2 pressure was examined for reactions using the Mo-C_2-PCy_2 system. An increase in turnover frequency was found for reactions carried out under 56 atm (820 psi initial H_2 pressure at 23 °C, before heating) compared to reactions conducted at 4 atm. Of particular interest are the results shown in entry 10, where use of 0.35 mol % **2Cy** (50 °C; 56 atm H_2) produced 94% hydrogenation of $Et_2C{=}O$ after 3 days, corresponding

Table 3. Hydrogenation of Neat 3-Pentanone by Mo Catalysts at 23, 50, or 75 °C

line	catalyst precursor	ligand	anion	T, °C	mol % cat.	$P(H_2)$ at RT (atm)	TON_{total} at ca. 10 days[a,b]	TON_{total} at ca. 30 days[b]
1	**2Ph**	C_2-PPh_2	$BAr'_4{}^-$	23	0.35	4	6	20
2	**2Ph**	C_2-PPh_2	$BAr'_4{}^-$	50	0.35	4	62	
3	**2Ph**	C_2-PPh_2	$BAr'_4{}^-$	75	0.17	4	87	87
4	**3**	C_3-PPh_2	$BAr'_4{}^-$	23	0.35	4		15
5	**3**	C_3-PPh_2	$BAr'_4{}^-$	50	0.35	4		105
6	**3**	C_3-PPh_2	$BAr'_4{}^-$	75	0.17	4	88	89
7	**2Cy**	C_2-PCy_2	$BAr'_4{}^-$	23	0.35	4	23	59
8	**2Cy**	C_2-PCy_2	$BAr'_4{}^-$	50	0.35	4	120	
9	**2Cy**	C_2-PCy_2	$BAr'_4{}^-$	50	0.12	4	122	177
10	**2Cy**	C_2-PCy_2	$BAr'_4{}^-$	50	0.35	56	283 (5 days)	
11	**2Cy**	C_2-PCy_2	BF_4^-	50	0.35	4	99	137
12	**2Cy**	C_2-PCy_2	PF_6^-	50	0.35	4	78	124
13	**4Cy**	C_2-PCy_2	OTf	50	0.35	4	120	212
14	**2Cy**	C_2-PCy_2	$BAr'_4{}^-$	75	0.17	4	141	206
15	**2Cy**	C_2-PCy_2	BF_4^-	75	0.17	4	74	102
16	**4Cy**	C_2-PCy_2	OTf	75	0.17	4	388	482
17	**4Cy**	C_2-PCy_2	OTf	75	0.086	4	462	621
18	**4Cy**	C_2-PCy_2	OTf	75	0.086	54	481	482
19	**2^{t}Bu**	C_2-P^tBu_2	$BAr'_4{}^-$	23	0.35	4	46	49
20	**2^{t}Bu**	C_2-P^tBu_2	$BAr'_4{}^-$	50	0.35	4	82	112
21	**2^{t}Bu**	C_2-P^tBu_2	$BAr'_4{}^-$	75	0.17	4	65	81
22	**4^{t}Bu**	C_2-P^tBu_2	OTf	75	0.17	4	45	58
23	$HMo(CO)_2Cp(PCy_3)$	PCy_3	$BAr'_4{}^-$	23	0.35	4	37	
24	$HMo(CO)_2Cp(PCy_3)$	PCy_3	$BAr'_4{}^-$	50	0.35	4	72	111
25	$HMo(CO)_2Cp(PCy_3)$	PCy_3	PF_6^-	50	0.35	4	13	19
26	$HMo(CO)_2Cp(PCy_3)$	PCy_3	BF_4^-	50	0.35	4	19	22
27	$TfOMo(CO)_2Cp(PCy_3)$	PCy_3	OTf	50	0.17	4	8	13
28	$HMo(CO)_2Cp(PCy_3)$	PCy_3	$BAr'_4{}^-$	75	0.17	4	55	57
29	$TfOMo(CO)_2Cp(PCy_3)$	PCy_3	OTf	75	0.17	4	18	22
30	$TfOMo(CO)_2Cp(PPh_3)$	PPh_3	OTf	75	0.17	4	6	13

[a] TON_{total} includes the formation of the $(Et_2CH)_2O$, which typically comprises 5−10% of the concentration of the predominant product alcohol. See Table S1 in the Supporting Information for further details. [b] Actual time of sampling for 10 days ranged from 9.6 to 10.7 days; actual time of sampling for the 30 day time ranged from 28.9 to 32 days. See Table S1 in the Supporting Information for further details.

to about 90 turnovers/day. At $t = 5$ days, essentially complete (99.5%) hydrogenation of neat ketone to the alcohol had occurred. In contrast to the marginal performance obtained with counterions such as BF_4^- or PF_6^- in most cases, the activity of the Mo-OTf complex with the Mo-C_2-PCy_2 system is comparable to that using $BAr'_4{}^-$. When the triflate complex **4Cy** is dissolved in CD_3CN, the nitrile binds to the metal, giving $\{Mo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PCy_2(NCCD_3)]\}^+OTf^-$; this reactivity is encouraging since ionization of the bound triflate to form a triflate counterion is needed for these catalyst precursors to operate by an ionic mechanism. Comparison of lines 8 and 13 shows comparable performance for $BAr'_4{}^-$ vs OTf, and the experiments at 75 °C for the Mo-C_2-PCy_2 system give better results for OTf (cf. line 14 vs line 16). An appealing aspect of using complexes with triflate counterions (or triflate ligands) is their cost-effectiveness, since triflates are less expensive than borate anions such as $BAr'_4{}^-$. Comparison of lines 17 and 18 surprisingly shows no significant increase in activity when the Mo-OTf system is carried out under higher pressures of H_2, in contrast to the results using the $BAr'_4{}^-$ counterion for the Mo-C_2-PCy_2 system. Use of the Mo-C_2-PCy_2 system with OTf is sufficiently reactive and long-lived to result in total TONs in the range of 500, which is a marked improvement in lifetime over the previously reported unbridged systems.

In addition to the higher turnover numbers obtained with the new bridged catalysts reported here, a further improvement is that lower catalyst loadings can be successfully employed. All of the experiments in Table 3 use less than 0.4 mol % catalyst loading, and some experiments demonstrated that catalysts loadings as low as 0.1 mol % can be used successfully.

The last nine entries in Table 3 provide a comparison of the unbridged vs bridged catalysts. Since our previous investigations used these complexes in CD_2Cl_2,[23,24] it was worthwhile to assess how these catalysts might perform under the solvent-free conditions examined here for the bridged catalysts. The improved lifetime found in neat $Et_2C{=}O$ does suggest that some of the decomposition previously found for these catalysts was likely due to decomposition caused by reactions with the CD_2Cl_2 solvent. Despite this observation, however, the unbridged catalysts still give lower turnovers compared to the bridged catalyst precursors reported here.

Conclusions. A series of new molybdenum carbonyl hydride complexes with a C_2 bridge linking the Cp and phosphine ligands was prepared and fully characterized. Abstraction of hydride from these catalyst precursors with $Ph_3C^+BAr'_4{}^-$ in the presence of $Et_2C{=}O$ leads to ketone hydrogenation. These catalysts slowly hydrogenate $Et_2C{=}O$ at 23 °C and 4 atm H_2 pressure, but are more active at higher temperatures (50 or 75 °C) and higher pressures. The maximum turnover frequency obtained for **2Cy** is about 90 turnovers/day (over a 3 day period) at 50 °C at 56 atm H_2 pressure. The new catalysts are used in the solvent-free hydrogenation of ketones, and they can be used at low loading of catalyst (0.1−0.4 mol %). The $BAr'_4{}^-$ provided much longer lifetimes and turnover frequencies compared to catalysts with either BF_4^- or PF_6^- anions. A molybdenum triflate complex, $(TfO)Mo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PCy_2]$, was found to provide catalytic activity similar to that found using

the $BAr'_4{}^-$ anion, providing an advantage in the use of less expensive triflate counterions compared to $BAr'_4{}^-$. The Mo catalysts represent a substantial improvement over previously prepared catalysts, which had no bridge between the cyclopentadienyl and phosphine ligands. We seek further improvements in an attempt to move this type of complex toward practical utility.

Experimental Section

General Methods. All manipulations were carried out under an argon atmosphere using standard Schlenk or vacuum line techniques or in a drybox. THF, Et_2O, toluene, hexane, and pentane were distilled from Na/benzopheneone, and CH_2Cl_2 was distilled from P_2O_5. Deuterated NMR solvents were similarly dried and vacuum transferred. HOTf and HOAc were purified by distillation. 3-Pentanone was dried over molecular sieves and vacuum transferred. Reaction solutions were stored in the absence of light for all long-term reactions. $Mo(CO)_3$(diglyme),[29] $Mo(CO)_3(NCMe)_3$,[41] $Ph_3C^+BAr'_4{}^-$,[42] Ph_3COTf,[43] spiro[2.4]hepta-4,6-diene,[44] and $LiC_5H_4(CH_2)_nPR_2$ (n = 2, R = Ph and ^{t}Bu; n = 3, R = Ph)[31] were prepared following literature methods. The related ligand with R = Cy, $LiC_5H_4(CH_2)_2PCy_2$, was prepared by an analogous procedure; details are in the Supporting Information. $Ph_3C^+BF_4^-$ and $Ph_3C^+PF_6^-$ were purchased from Aldrich and purified by recrystallization from CH_2Cl_2/Et_2O. Most NMR tube experiments were carried out in NMR tubes equipped with a Teflon J. Young valve. Reactions carried out under hydrogen gas were filled with 1.0−1.1 atm H_2 at 77 K (liquid N_2), and the valve was closed. This corresponds to a pressure of about 4 atm at room temperature (298/77 = 3.9). NMR measurements were recorded on Bruker AM-300 NMR or Bruker Avance 400 instruments. ^{1}H NMR spectra were referenced to the residual proton peaks of the deuterated solvents, and ^{31}P NMR spectra were referenced to 85% H_3PO_4. NMR probe temperatures were determined using the standard MeOH test.[45] IR measurements were recorded on a Mattson Polaris FT-IR spectrometer. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory (Woodside, NY).

Preparation of $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PPh_2]$ (2Ph). $Mo(CO)_3$(diglyme) (557 mg, 1.77 mmol) and $LiC_5H_4(CH_2)_2PPh_2$ (504 mg, 1.77 mmol, 1.00 equiv) were placed in a Schlenk flask, and THF (20 mL) was added. The solution was stirred for 2 h at room temperature, at which time the reaction was ∼80% complete. The solution was refluxed for an additional 2 h. IR spectra [ν(CO) in THF: 1903 (s), 1906 (sh), 1804 (s), 1784 (m), 1715 (s) cm^{-1}] and ^{31}P{^{1}H} NMR spectra [(THF) δ −13.2] were consistent with the formation of $Li\{Mo(CO)_3[\eta^5\text{-}C_5H_4(CH_2)_2\text{-}PPh_2]\}$. HOAc (100 μL, 1.92 mmol, 1.08 equiv) was added to the yellow solution, which lightened, and salt formation was observed. The solution was stirred for 3 h at room temperature, and the solvent was evaporated. The residue was extracted with toluene (25 mL) and filtered. The resulting pale red air-sensitive solution was diluted with pentane (30 mL) and stored in a −30 °C freezer. $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PPh_2]$ crystallized as a yellow solid (230 mg, 0.530 mmol, 30% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ −5.25 (d, $^2J_{PH}$ = 27.6, 1H, MoH), 2.34 (dt, $^2J_{PH}$ = 28.1 Hz, $^3J_{HH}$ = 6.8 Hz, 2H, PCH_2), 3.00 ("q", $^3J_{PH} = {}^3J_{HH}$ = 7.4 Hz, 2H, $C_5H_4CH_2$), 5.10 (br, 2H, C_5H_4), 5.30 (br, 2H, C_5H_4), 7.42−7.55 (m, 10H, Ph). ^{31}P{^{1}H} NMR (121.9 MHz, CD_2Cl_2): δ 74.4 (br, $w_{1/2}$ = 32 Hz). IR (THF): ν(CO) = 1939 (s), 1864 (vs) cm^{-1}. Depending on crystallization conditions, the crystals contain up to 1 equiv of toluene. The sample sent for elemental analysis was shown by ^{1}H NMR to contain 0.2 molar equiv of toluene. Anal. Calcd for $C_{21}H_{19}O_2PMo\cdot$0.2toluene: C, 59.80; H, 4.57. Found: C, 59.93; H, 4.56.

General Methods for Crystal Structure Determinations. X-ray diffraction data were collected using Mo Kα radiation on a Bruker SMART 1K CCD diffractometer using a standard focus tube. The structures were solved by direct methods using teXsan(SIR-92) and were refined using Z program suite (Calabrese). Refinement was by full-matrix least squares on F. All non-hydrogen atoms were refined anisotropically. Scattering factors, including anomalous terms for Mo and P, were from International Table for X-ray Crystallography, Vol. IV. Further details on the crystallography are provided in the Supporting Information.

Preparation of $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PCy_2]$ (2Cy). A solution of $LiC_5H_4(CH_2)_2PCy_2$ (733.8 mg, 2.48 mmol) in THF (10 mL) was added to a solution of $Mo(CO)_3$(diglyme) (777.6 mg, 2.48 mmol, 1.00 equiv) in THF (15 mL). The yellow solution was stirred for 30 min at room temperature. IR spectra [ν(CO) in THF: 1902 (s), 1890 (sh), 1805(s), 1779 (m), 1714 (s) cm^{-1}] and ^{31}P{^{1}H} NMR spectra [(THF) δ −1.8] were consistent with the formation of $Li\{Mo(CO)_3[\eta^5\text{-}C_5H_4(CH_2)_2\text{-}PCy_2\}$. HOAc (180 μL, 3.14 mmol, 1.27 equiv) was added, the color of the solution lightened to a pale yellow, and salt formation was observed. The solvent was evaporated, and the residue was extracted with toluene (25 mL). The reaction mixture was filtered, and the toluene was evaporated. Recrystallization from a mixture of toluene, THF, and pentane at −30 °C produced $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2PCy_2]$ as a pale yellow solid (557.0 mg, 1.26 mmol, 51% yield). The NMR assignments below were determined with the help of ^{1}H, ^{1}H{^{31}P}, ^{31}P{^{1}H}, ^{13}C{^{1}H}, ^{1}H−^{13}C HMQC, and ^{1}H−^{1}H COSY. ^{1}H 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{^{1}H} NMR (162.0 MHz, CD_2Cl_2): δ 80.6 (br, $w_{1/2}$ = 200 Hz). ^{13}C{^{1}H} 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. Calcd for $C_{21}H_{31}O_2PMo$: C, 57.02; H, 7.06. Found: C, 56.92; H, 6.99.

Preparation of $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2P^tBu_2]$ (2^{t}Bu). A solution of $Mo(CO)_3$(diglyme) (793.2 mg, 2.52 mmol) in THF (10 mL) was added to a solution of $LiC_5H_4(CH_2)_2P^tBu_2$ (616.8 mg, 2.52 mmol, 1.00 equiv) in THF (10 mL). The solution was stirred for 1.5 h at room temperature. IR spectra [ν(CO) in THF: 1902 (s), 1890 (sh), 1807 (s), 1780 (m), 1715 (s) cm^{-1}] and ^{31}P{^{1}H} NMR spectra [(THF) δ 31.8] were consistent with the formation of $Li\{Mo(CO)_3[\eta^5\text{-}C_5H_4(CH_2)_2P^tBu_2\}$. HOAc (170 μL, 2.97 mmol, 1.18 equiv) was added. The yellow solution darkened to orange, and salt formation was observed. After 30 min at room temperature, solvent was evaporated. The residue was extracted with toluene (25 mL) and filtered, and the solvent was evaporated. Recrystallization from toluene/hexane at −30 °C produced $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2P^tBu_2]$ as a yellow solid (710 mg, 1.82 mmol, 72% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ −5.74 (d, $^2J_{PH}$ = 24.6, 1H, MoH), 1.34 (d, $^3J_{PH}$ = 12.9 Hz, 18 H, ^{t}Bu), 2.34−2.51 (m, 4H, CH_2's), 4.96 (br, 2H, C_5H_4), 5.07 (br, 2H, C_5H_4). ^{31}P{^{1}H} NMR (121.9 MHz, CD_2Cl_2): δ 103.8 (br, $w_{1/2}$ = 34 Hz). IR (THF): ν(CO) = 1922 (s), 1845 (vs) cm^{-1}. Anal. Calcd for $C_{17}H_{27}O_2PMo$: C, 52.31; H, 6.97. Found: C, 52.36; H, 7.17.

Preparation of $HMo(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_3PPh_2]$ (3). $LiC_5H_4(CH_2)_3PPh_2$ (1.543 g, 5.17 mmol) was dissolved in THF (30 mL), giving an orange solution. This solution was added to a solution of $Mo(CO)_3$(diglyme) (1.625 g, 5.17 mmol, 1.00 equiv) in THF (30 mL). The resulting intense yellow-brown solution was stirred for 1 h at room temperature. IR spectra

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[ν(CO) in THF: 1902(s), 1892 (sh), 1804(s), 1779 (m), 1717 (s) cm^{-1}] and $^{31}P\{^1H\}$ NMR spectra [(THF) δ −14.4] were consistent with the formation of $Li[Mo(CO)_3[\eta^5\text{-}C_5H_4(CH_2)_3PPh_2]$ as the predominant product. HOAc (100 μL, 1.92 mmol, 1.08 equiv) was added, and salt formation was observed. After stirring at room temperature for 1.5 h, the solvent was evaporated and the residue was extracted with toluene (25 mL). The reaction mixture was filtered, the solvent volume was reduced to 15 mL, and pentane (15 mL) was added. A yellow solid formed at −30 °C, along with an orange oil. While the actual yield of the reaction was approximately 80% by NMR, only a small amount of solid could be isolated in analytically pure form (190 mg, 0.43 mmol, 8% yield). The NMR assignments below were determined with the help of ^1H, $^1H\{^{31}P\}$, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, $^1H-^{13}C$ HMQC, and $^1H-^1H$ COSY. ^1H NMR (400 MHz, CD_2Cl_2): δ −5.95 (br d, $^2J_{PH}$ = 33.9 Hz, 1H, Mo*H*), 1.60 (t m, $^2J_{PH}$ = 24.5 Hz, 2H, PCH_2), 2.20 (m, CH_2), 2.49 (m, CH_2), 5.04 (br, 2H, *m*-C_5H_4), 5.27 (br, 2H, *o*-C_5H_4), 7.37−7.40 (m, 6H, *m*- and *p*-Ph), 7.57 (m, 4H, *o*-Ph). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2): δ 54.9 (br, $w_{1/2}$ = 200 Hz). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2): δ 22.0 (br s, PCH_2), 27.7 (s, PCH_2CH_2), 28.2 (v br, $C_5H_4CH_2$), 86.9 (br, *o*-C_5H_4), 88.4 (s, *m*-C_5H_4), 104.2 (vbr, *ipso*-C_5H_4), 130.2 (s, *p*-Ph), 128.8 (s, *m*-Ph), 132.6 (d, $^2J_{PC}$ = 10 Hz, *o*-Ph), 139.1 (br d, $^1J_{PC}$ = 43.2 Hz, *ipso*-Ph), 234 (v br, CO). IR (THF): ν(CO) = 1936 (s), 1858 (vs) cm^{-1}. The sample sent for elemental analysis had 0.5 equiv of toluene, as determined by ^1H NMR. Anal. Calcd $C_{22}H_{21}O_2PMo\cdot 0.50$toluene: C, 62.46; H, 5.14. Found: C, 62.14; H, 5.26.

Preparation of (TfO)Mo(CO)$_2$[η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$PPh$_2$] (4Ph). $HMo(CO)_2[\eta^5\text{:}\eta^1\text{-}C_5H_4(CH_2)_2PPh_2]$ (29.9 mg, 6.95×10^{-5} mol) was dissolved in toluene (2 mL). HOTf (7.0 μL, 7.9×10^{-5} mol, 1.1 equiv) was added to the solution. The pale yellow solution rapidly darkened to deep purple. The solution was stirred for 30 min at room temperature. Hexane (2 mL) was added to the toluene solution, and $(TfO)Mo(CO)_2[\eta^5\text{:}\eta^1\text{-}C_5H_4(CH_2)_2PCy_2]$ **(4Ph)** crystallized at −30 °C as a purple-red solid (165.0 mg, 0.28 mmol, 62% yield; 1.5:1 mixture of *trans:cis* isomers). The *trans:cis* ratio did not significantly change in CD_2Cl_2 after 18 h at room temperature. ^1H NMR (400 MHz, CD_2Cl_2): δ 2.09 (dt, 2H, $^2J_{HP}$ = 27.6 Hz, $^3J_{HH}$ = 7.0 Hz, *trans*-PCH_2), 2.50−2.56 (m, 1H, *cis*-CH_2), 2.72 (m, 2H, *trans*-$C_5H_4CH_2$), 2.91−3.03 (m, 1H, *cis*-CH_2), 3.36−3.45 (m, 2H, *cis*-CH_2), 4.71 (m, 1H, *cis*-C_5H_4), 4.85 (m, 1H, *cis*-C_5H_4), 5.78 (m, 2H, *trans*-C_5H_4), 5.95 (m, 2H, *trans*-C_5H_4), 6.28 (m, 1H, *cis*-C_5H_4), 6.31 (m, 1H, *cis*-C_5H_4). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 63.3 (*cis*, 39%), 74.9 (*trans*, 61%).

Preparation of (TfO)Mo(CO)$_2$[η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$PCy$_2$] (4Cy). $HMo(CO)_2[\eta^5\text{:}\eta^1\text{-}C_5H_4(CH_2)_2PCy_2]$ (201.0 mg, 0.454 mmol) was dissolved in CH_2Cl_2 (6 mL). HOTf (40 μL, 67 mg, 0.45 mmol) was added to the solution. The pale yellow solution rapidly darkened to deep red. The solution was stirred for 30 min at room temperature. The solvent was evaporated, and the product was recrystallized from toluene at −30 °C. **4Cy** crystallized as a red solid (165.0 mg, 0.28 mmol, 62% yield). The isolated product is a 6:1 mixture of *cis:trans* isomers. The product ratio did not significantly change in CD_2Cl_2 after 2 days at room temperature. ^1H NMR (300 MHz, CD_2Cl_2): δ 1.20−2.52 (m, *cis*- and *trans*-CH_2 and Cy), 2.69−2.85 (m, *cis*- and *trans*-CH_2), 4.58 (m, 1H, *cis*-C_5H_4), 4.63 (m, 1H, *cis*-C_5H_4), 5.65 (m, 2H, *trans*-C_5H_4), 5.70 (m, 2H, *trans*-C_5H_4), 6.13 (m, 1H, *cis*-C_5H_4), 6.20 (m, 1H, *cis*-C_5H_4). ^{31}P NMR (121.9 MHz, CD_2Cl_2): δ 66.5 (*cis*), 79.1 (*trans*). IR (THF): ν(CO) = 1980 (s), 1869 (s) cm^{-1}. Anal. Calcd for $C_{22}H_{30}O_5F_3PSMo$: C, 44.75, H, 5.12. Found: C, 44.59; H, 5.04.

Preparation of (TfO)Mo(CO)$_2$[η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$P^{t}Bu$_2$] (4^{t}Bu). $HMo(CO)_2[\eta^5\text{:}\eta^1\text{-}C_5H_4(CH_2)_2P^tBu_2]$ (163.4 mg, 0.419 mmol) was dissolved in toluene (4 mL). HOTf (36 μL, 61 mg, 0.41 mmol) was added to the solution. The pale yellow solution initially turned dark purple, then blood red. The solution was stirred for 30 min at room temperature. The product began to precipitate from the solution. The mixture was stored at −30 °C overnight to complete the crystallization. $(TfO)Mo(CO)_2[\eta^5\text{:}\eta^1\text{-}C_5H_4(CH_2)_2P^tBu_2]$ **(4^{t}Bu)** was isolated as an orange-red solid (177.5 mg, 0.33 mmol, 81% yield, >95% pure). The isolated product is a 9:1 mixture of *cis:trans* isomers. ^1H NMR (400 MHz, CD_2Cl_2) of *cis* isomer: δ 1.29 (d, $^2J_{HP}$ = 13.2 Hz, CH_3 of ^{t}Bu), 1.43 (d, $^2J_{HP}$ = 13.0 Hz, CH_3 of ^{t}Bu), 2.56−2.88 (m, CH_2's), 4.53 (m, 1H, C_5H_4), 4.66 (m, 1H, C_5H_4), 5.97 (m, 1H, C_5H_4), 6.11 (m, 1H, C_5H_4). ^1H NMR (400 MHz, CD_2Cl_2) of *trans* isomer: δ 1.45 (overlapping with cis, CH_3 of ^{t}Bu), 1.95 ("q", $^3J_{PH} = {}^3J_{HH}$ = 7.6 Hz, 2H, $C_5H_4CH_2$), 2.26 (dt, $^2J_{PH}$ = 23.8 Hz, $^3J_{HH}$ = 7.2 Hz, 2H, PCH_2) 5.71 (m, 4H, C_5H_4). ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ 114.1 (*trans*), 94.4 (*cis*). IR (THF): ν(CO) = 1992 (s), 1904 (w), 1862 (s) cm^{-1}.

Hydrogenations of 3-Pentanone in CD_2Cl_2. A series of hydrogenations of 3-pentanone were performed in CD_2Cl_2 in 5 mm NMR tubes equipped with a J. Young valve, following a procedure described previously.[24] Experiments were prepared by placing $HMo(CO)_2[\eta^5\text{:}\eta^1\text{-}C_5H_4(CH_2)_nPR_2]$ (2.1×10^{-5} mol, n = 2, R = Ph, Cy, ^{t}Bu and n = 3, R = Ph) and 1 equiv (2.1×10^{-5} mol) of $Ph_3C^+A^-$ (A^- = $BAr'_4{}^-$, $BF_4{}^-$, or $PF_6{}^-$) in an NMR tube, followed by 700 μL of a CD_2Cl_2 solution that was 300 mM in 3-pentanone. Typical concentrations were 300 mM in 3-pentanone, 30 mM in catalyst, and 30 mM in bibenzyl, an internal standard for ^1H NMR integrations. The resulting solutions ranged from dark orange to purple in color; the tubes were wrapped in foil to avoid possible photochemical reactions. The NMR tubes were filled with H_2 (~1.1 atm) while frozen in liquid nitrogen, giving about 4 atm H_2 when warmed to room temperature. The available headspace of the NMR tube allowed for about 1.5 mL of H_2 to be added. Even at 4 atm, this meant that at most 11 molar equiv of H_2 were present during the reaction. Additional H_2 was therefore added during the reactions as needed. In many cases, additional 3-pentanone (21.2 μL, 10.0 equiv) was added to the NMR tubes after most of the substrate had been hydrogenated. The additional substrate was added in the drybox under argon, then H_2 was added again.

The hydrogenations were monitored by ^1H and ^{31}P NMR. The TON (turnover number) was determined on the basis of the methine CH integrations of the pentanol and its ether in the ^1H NMR. In cases where the CH_2 peak (δ 2.93) of the internal standard (bibenzyl) overlapped with other resonances, the *ortho*-phenyl resonance of the $BAr'_4{}^-$ anion (δ 7.74, broad) was used as an integration standard.

Hydrogenations of Neat 3-Pentanone (30 mM catalyst, >100 mL of H$_2$ at 4 atm). A series of hydrogenations of neat 3-pentanone were performed in glass tubes under H_2 at 23, 50, and 75 °C. The reactions were not stirred, since stirring appeared to have little, if any, effect on the rate of hydrogenation. The catalysts were formed in situ by placing **2** or **3** (2.1×10^{-5} mol, 1 equiv) and $Ph_3C^+A^-$ (A = $BAr'_4{}^-$, $BF_4{}^-$, or $PF_6{}^-$; 2.1×10^{-5} mol; 1 equiv) in a small vial and adding 3-pentanone (630 μL, 537 mg, 6.24 mmol, 283 equiv). After all the solids had dissolved, the reaction solution was transferred to a 125 mL glass bulb with a Teflon valve. The solution was removed from the drybox, connected to a vacuum line, and freeze−pump−thawed two times. The sample was frozen a third time, and the entire tube was submersed in liquid N_2. The tube was then filled with 1.1 atm H_2, sealed, and warmed to room temperature. The resulting tube contained about 4.1 atm H_2 (125 mL at 4.1 atm, 20.1 mmol, 1000 equiv) at room temperature. The tube was warmed to the appropriate temperature. Samples were removed for analysis at 10, 20, and 30 days. Reactions using isolated catalyst precursors such as **4**, $(TfO)Mo(CO)_2Cp(PCy_3)$, or $(TfO)Mo(CO)_2Cp(PPh_3)$ were prepared by dissolving the isolated complexes in 3-pentanone; all other conditions were identical.

The samples were removed by cooling the solution to 77 K (liquid N_2) and flowing H_2 over the solution. The tube was then warmed to room temperature, and a 60 μL aliquot was

removed. All manipulations took place under 1 atm hydrogen. After sampling, the tube was once again cooled with liquid nitrogen and evacuated. The tube was then filled with 1.1 atm H_2 at 77 K, sealed, and placed back in the constant-temperature bath. The aliquot (60 μL) was dissolved in 500 μL of CD_2Cl_2 (in the air) for NMR analysis.

High-pressure reactions were performed in a clean stainless steel Parr microreactor (100 mL). A typical reaction involved placing **2Cy** (27.9 mg, 6.30×10^{-5} mol) and $Ph_3C^+BAr'_4{}^-$ (69.6 mg, 6.30×10^{-5} mol, 1.00 equiv) in the reactor, in the glovebox. 3-Pentanone (1.9 mL, 1.62 g, 17.9 mmol, 285 equiv) was added by syringe to give a red solution. The reactor was sealed under argon and removed from the glovebox. The reactor was then placed under 820 psi H_2. The reactor was warmed to 50 °C, and the reaction was run for about 10 days (the pressure increased to 860 psi at 50 °C). The reactor was then cooled to room temperature, and the reactor was *slowly* depressurized. The reactor was then opened, and a small aliquot of the solution was removed. The sample was dissolved in CD_2Cl_2, and the ^{1}H NMR was taken and analyzed as before. The TON values were most accurately determined by comparing the CH_2 resonances of the ketone with the product alcohol and ether resonances. Integration of the CH_3 resonances usually agreed within 5% (and often within 1%), but this tends to be less accurate, as the CH_3 resonances are barely baseline separated in the ^{1}H NMR spectrum.

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Supporting Information Available: Spectral data on $\{M(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_nPR_2](NCCD_3)\}^+$ complexes, additional NMR characterization and assignments for **2Cy** and **3**, characterization of $HW(CO)_2[\eta^5{:}\eta^1\text{-}C_5H_4(CH_2)_2P^tBu_2]$, an expanded version of Table 3, details on the preparation of $LiC_5H_4(CH_2)_2PCy_2$, further crystallographic details, and additional information and plots of catalytic experiments in CD_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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