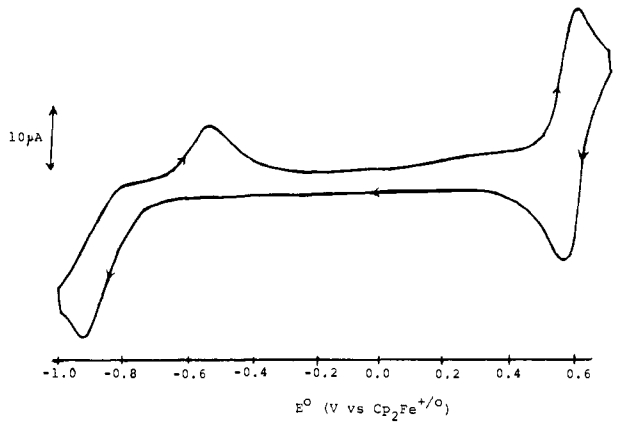

Figure 12. Cyclic voltammogram of $[Ru^{IV}(OEP)O(EtOH)]$ in CH_2Cl_2/py [0.1 M $[Et_4N]BF_4$] at a glassy carbon electrode. Scan rate, 100 mV s^{-1}. $Cp_2Fe^{+/0}$ occurred at 0.1 V vs $Ag/AgNO_3$.

to the Ru(IV)/(III) couple since the reduction of porphyrinato ring occurs at a more negative potential.[22] From the electrochemical results, we find that the Ru(IV) state is greatly stabilized by the π-donating oxo ligand.

Aerobic Epoxidation of Olefin by $[Ru^{VI}(OEP)(O)_2]$. Unlike the case of $[Ru^{VI}(TMP)(O)_2]$,[3b,e] no catalytic aerobic epoxidation has been observed with **1** in dichloromethane even under an oxygen pressure of 10 atm. Under such conditions, the ruthenium product was found to be $[Ru^{IV}(OEP)(OH)]_2O$. Thus the result indicates that rapid reoxidation of Ru(IV) to Ru(VI) by O_2 in dichloromethane is unlikely and thus the $[Ru^{IV}(OEP)O]$ intermediate once generated undergoes rapid dimerization (see earlier section). In alcohol, **1** can catalyze aerobic epoxidation of olefins. Nevertheless, the yield is very low: only 3 equiv per day of norbornene oxide was detected when $[Ru^{VI}(OEP)(O)_2]$ was allowed to react with norbornene under 1 atm oxygen at room temperature. This indicates that the intermediate $[Ru^{IV}(OEP)O]$ can take up oxygen to give **1** but at a very slow rate. The competition of ethanol with oxygen for the binding to Ru(IV) possibly explains why **1** is ineffective in the aerobic epoxidation.

Concluding Remarks

The study of metal-oxo complexes of synthetic octaethylporphyrin is of importance because their structural and spectral properties are likely to resemble closely those of the analogous complexes of protoporphyrin IX, which is the prosthetic group found in many heme enzymes. However, the studies in this area are rather sparse. In this work we have demonstrated that the oxoruthenium(IV) and -(VI) complexes of octaethylporphyrin can be easily prepared. These compounds should be good biomimetic model systems for the oxo-iron intermediates in the catalytic oxidative reactions of the monooxygenase enzymes. The success in the synthesis of this class of compounds lies in the use of weakly coordinating solvent, which suppresses the μ-oxo dimerization process. We believe that this synthetic methodology may be also applicable to the isolation of other high-valent metal-oxo complexes of octaethylporphyrin. $[Ru^{VI}(TMP)(O)_2]$ can catalyze aerobic epoxidation of olefins because the intermediate $[Ru^{IV}(TMP)O]$ does not dimerize in noncoordinating solvents. The fact that **2** is unreactive toward olefins in ethanol suggests that the catalytic cycle in the aerobic epoxidation by $[Ru^{VI}(TMP)(O)_2]$ involves the interconversion of the Ru(IV) and Ru(VI) species.

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Registry No. 1, 123051-65-0; **2**, 123073-89-2; **3**, 123051-66-1; $[Ru^{IV}(OEP)(^{18}O)(EtOH)]$, 123051-67-2; $[Ru^{IV}(OEP)(OH)]_2O$, 77089-60-2; $[Ru^{II}(OEP)(CO)(MeOH)]$, 89530-39-2; $[Ru^{VI}(OEP)(O_2)]^+$, 123051-68-3; $[Ru^{III}(OEP)O(EtOH)]^-$, 123051-69-4; $[Ru^{II}(TPP)(CO)(MeOH)]$, 89555-37-3; norbornene, 498-66-8; styrene, 100-42-5; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; *exo*-epoxynorbornane, 3146-39-2; styrene oxide, 96-09-3; benzaldehyde, 100-52-7; *cis*-stilbene oxide, 1689-71-0; *trans*-stilbene oxide, 1439-07-2.

Hydride-Mediated Homogeneous Catalysis. Catalytic Reduction of α,β-Unsaturated Ketones Using $[(Ph_3P)CuH]_6$ and H_2

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Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405. *Received March 29, 1989*

Abstract: Hydride-mediated reduction of α,β-unsaturated ketones *catalytic* in the hydride reagent is reported using $[(Ph_3P)CuH]_6$ and molecular hydrogen. The reaction proceeds at room temperature and is highly regioselective, affording either the product of conjugate reduction or complete 1,4- and 1,2-reduction to the saturated alcohol, depending on reaction conditions. In the presence of excess phosphine, the process is homogeneous and chemoselective: isolated double bonds are not hydrogenated, even under forcing conditions. This novel catalytic reduction appears to proceed via the heterolytic activation of molecular hydrogen by highly reactive copper(I) enolate and alkoxide intermediates.

Catalytic hydrogenation is essential methodology for the reduction of unsaturated organic substrates. The use of molecular hydrogen together with a catalytic quantity of a metal or metal complex provides reliable, safe, and relatively inexpensive reduction procedures, amenable both to laboratory synthesis and large-scale processes. In contrast, hydride reduction methodology is stoichiometric in hydride, less attractive both practically and economically for selective reductions beyond laboratory scale. Hydride methodology, however, offers chemoselectivity complementary to common catalytic hydrogenation systems and constitutes an important and formidable objective for new catalysis.

In its simplest conceivable form, the development of catalytic methodology for hydride-mediated reduction of organic carbonyl functionality requires a chemical system that simultaneously meets two principal requirements. First, and obviously, the initial metal

(1) Du Pont Young Faculty Awardee, 1988-1989. Union Carbide Innovation Recognition Program Awardee, 1989.

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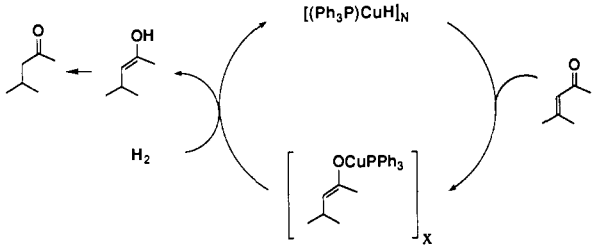
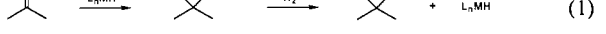
Scheme I



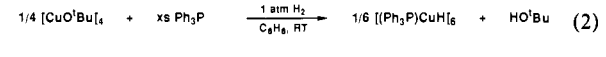
hydride complex must be sufficiently reactive to transfer the hydride ligand to the organic substrate. Second, this transfer must result in an intermediate metal complex capable of activating hydrogen heterolytically (eq 1, illustrated for ketone reduction).[2]



(1)

This process effectively provides both the "protic" quench, releasing the product alcohol, and concomitant regeneration of an active metal hydride complex. In this way, the active hydride is generated catalytically from hydrogen. Heterolytic hydrogen activation by transition-metal complexes has been well-established in a variety of contexts,[3] and one example of such a process applied to the catalytic reduction of cyclohexanone and benzaldehyde has been recently reported.[4]

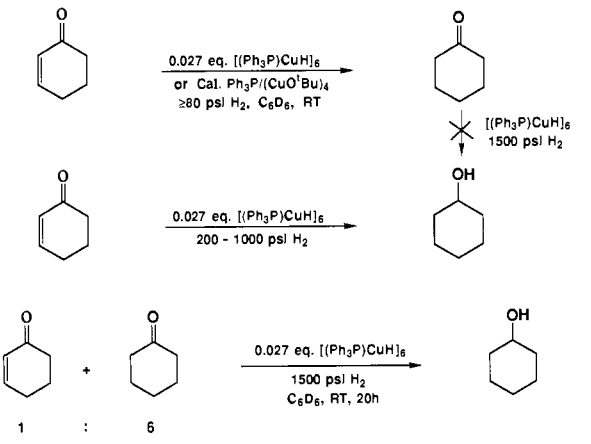
Our interest in developing catalytic hydride reductions was stimulated by the report of Caulton and Goeden that the reaction of $(CuO^tBu)_4$ and excess Ph_3P under hydrogen yielded *tert*-butyl alcohol and the known copper(I) hydride hexamer, $[(Ph_3P)CuH]_6$ (eq 2).[5,6] This apparent heterolytic hydrogenolysis of the cop-



(2)

per–oxygen bond[7] proceeds readily at ambient temperature and 1 atm of hydrogen. We have previously established that complex **1** is sufficiently hydridic to initiate the conjugate reduction of α,β-unsaturated ketones and esters.[8] Based on the assumption that this conjugate reduction occurs via an intermediate copper(I) enolate,[9] a catalytic cycle for hydride reduction was envisioned (Scheme I, $N = 6$). Unstabilized copper(I) enolates are unknown,

Scheme II



although such species have been previously postulated as reactive intermediates[10,11] and stable enolate complexes of β-dicarbonyl compounds have been previously prepared.[12] With the exception of copper(I) *tert*-butoxide[13] and the more stabilized copper(I) phenoxides,[14] copper(I) alkoxides themselves are reported to be unstable, decomposing at room temperature by a combination of free-radical and β-elimination pathways.[15] Interestingly, corresponding gold(I) enolates bearing phosphine ligands have been prepared and are definitively metal–carbon bonded.[16]

Results and Discussion

Initial Observations. Reaction of 2-cyclohexen-1-one with a catalytic amount of $[(Ph_3P)CuH]_6$ (**1**) under hydrogen (as low as 80 psi) in benzene at room temperature gives slow turnover (<0.5/h) to cyclohexanone as the exclusive organic product (Scheme II). Catalytic reduction is also observed using $(CuO^tBu)_4$ and triphenylphosphine, which presumably procedes via in situ generation of an active hydride reagent.[17] No reaction beyond stoichiometric is observed under 1 atm of hydrogen. Faster conversions are obtained under greater hydrogen pressure (≥200 psi), but surprisingly, complete reduction to cyclohexanol is observed at longer reaction times. The chemical yield of reduced substrate is high, and the regioselectivity parallels that observed in stoichiometric reductions:[8] no 2-cyclohexen-1-ol, the product of direct 1,2-reduction, is detected.

In contrast, no reduction of cyclohexanone to cyclohexanol by $[(Ph_3P)CuH]_6$ is observed, even under high pressure (>1500 psi H_2) and prolonged reaction time. To resolve this apparent inconsistency, the reaction of cyclohexanone containing a small

(2) In this context, the term "heterolytic" is used to describe the overall hydrogen activation process and is not intended to connote more mechanistic detail than our investigations warrant.

(3) Reviews: Brothers, P. J. *Prog. Inorg. Chem.* **1981**, *28*, 1. James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319. James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973, and references therein.

(4) Tooley, P. A.; Ovalles, C.; Kao, S. C.; Darensbourg, D. J.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1986**, *108*, 5465.

(5) Goeden, G. V.; Caulton, K. G. *J. Am. Chem. Soc.* **1981**, *103*, 7354.

(6) Original synthesis of complex **1**: Churchill, M. R.; Bezman, S. A.; Osborn, J. A.; Wormald, J. *Inorg. Chem.* **1972**, *11*, 1818. Bezman, S. A.; Churchill, M. R.; Osborn, J. A.; Wormald, J. *J. Am. Chem. Soc.* **1971**, *93*, 2063.

(7) Net heterolytic activation of hydrogen by other Cu(I) salts has been extensively documented: Calvin, M. *Trans. Faraday Soc.* **1938**, *34*, 1181. Calvin, M. *J. Am. Chem. Soc.* **1939**, *61*, 2230. Weller, S.; Mills, G. A. *J. Am. Chem. Soc.* **1953**, *75*, 769. Wright, L. W.; Weller, S. *J. Am. Chem. Soc.* **1954**, *76*, 3345. Wright, L.; Weller, S.; Mills, G. A. *J. Phys. Chem.* **1955**, *59*, 1060. Calvin, M.; Wilmarth, W. K. *J. Am. Chem. Soc.* **1956**, *78*, 1301. Wilmarth, W. K.; Barsh, M. K. *J. Am. Chem. Soc.* **1956**, *78*, 1305. Chalk, A. J.; Halpern, J. *J. Am. Chem. Soc.* **1959**, *81*, 5846. Chalk, A. J.; Halpern, J. *J. Am. Chem. Soc.* **1959**, *81*, 5852 and references therein.

(8) Mahoney, W. S.; Brestensky, D. M.; Stryker, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 291.

(9) While definitive proof of the intermediacy of unstable oxygen-bonded copper enolates in this reduction remains elusive, circumstantial evidence is strong (ref 8), including direct spectroscopic evidence. Stoichiometric reduction of cyclohexenone (0.16 equiv of $[(Ph_3P)CuH]_6$) in rigorously dry, deoxygenated benzene-d_6 at room temperature in the presence of excess triphenylphosphine (3 equiv per Cu) gives a gold homogeneous solution that contains, in addition to small amounts of cyclohexenone and cyclohexanone, an intermediate consistent with the copper–oxygen-bonded enolate formulation. ^1H NMR (300 MHz, C_6D_6): δ 4.58 (br s, 1 H), 2.15 (br s, 2 H), 1.92 (br s, 2 H), 1.56 (br m, 4 H). All attempts to isolate this material, or independently prepare a nonstabilized copper(I) enolate, have as yet resulted in decomposition.

(10) Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 431.

(11) There is considerable evidence that simple copper(I) enolates are not involved in organocuprate and copper-catalyzed Grignard conjugate addition chemistry; however, some involvement of the copper in reactions of the enolate produced during conjugate addition is highly probable. See: Posner, G. H.; Lentz, C. M. *J. Am. Chem. Soc.* **1979**, *101*, 934 and references therein.

(12) Nast, R.; Mohr, R.; Schultze, C. *Chem. Ber.* **1963**, *96*, 2127. Yamamoto, T.; Kubota, M.; Miyashita, A.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1835 and references therein. See also: Tsuda, T.; Chujo, Y.; Saegusa, T. *J. Am. Chem. Soc.* **1978**, *100*, 630.

(13) Tsuda, T.; Hashimoto, T.; Saegusa, T. *J. Am. Chem. Soc.* **1972**, *94*, 658. See also: Tsuda, T.; Habu, H.; Horiguchi, S.; Saegusa, T. *J. Am. Chem. Soc.* **1974**, *96*, 5930.

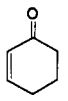
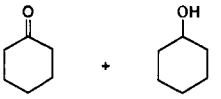
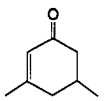
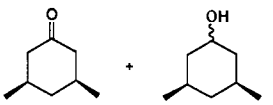
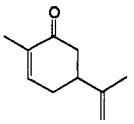
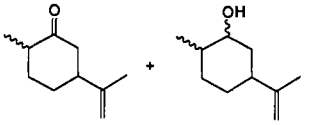
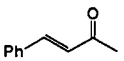
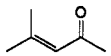
(14) Reichle, W. T. *Inorg. Chim. Acta.* **1971**, *5*, 325. Kawaki, T.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 1499. Eller, P. G.; Kubas, G. J. *J. Am. Chem. Soc.* **1977**, *99*, 4346. Kubota, M.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2909 and references therein. Berry, M.; Clegg, W.; Garner, C. D.; Hillier, I. H. *Inorg. Chem.* **1982**, *21*, 1342. Fiaschi, P.; Floriani, C.; Pasquali, M.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1986**, *25*, 462 and references therein.

(15) Whitesides, G. M.; Sadowski, J. S.; Lilburn, J. *J. Am. Chem. Soc.* **1974**, *96*, 2829. Bochmann, M.; Wilkinson, G.; Young, G. B.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1863. Yamamoto, T.; Kubota, M.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 680 and references therein.

(16) See: Murakami, M.; Inouye, M.; Suginome, M.; Ito, Y. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 3649 and references therein.

(17) Because $[(Ph_3P)CuH]_6$ is substantially more stable and easier to handle than $(CuO^tBu)_4$ itself, the hydride complex was used throughout this study.

Table I. Catalytic Hydride-Mediated Reduction of α,β-Unsaturated Ketones Using $[(Ph_3P)CuH]_6$ and H_2

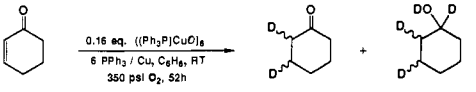
entry/substrate	reduction conditions[a]	product(s)[b,c]	yield, %
			
1	1000 psi H_2, 5 h	34:66	
2	1700 psi H_2, 13 h	0:100	
3	1000 psi H_2, 5 h, 6 equiv of Ph_3P/Cu	70:30	
4	1000 psi H_2, 5 h, 6 equiv of Ph_3P/Cu, excess Hg^0	74:26	
5	500 psi H_2, 1 h, 6 equiv of Ph_3P/Cu	79:21	90[d]
6	200 psi H_2, 1 h, 6 equiv of Ph_3P/Cu	91:9	
			
7	1000 psi H_2, 20 h	40:17[e]	
8	500 psi H_2, 48 h, 6 equiv of Ph_3P/Cu	0:100 (38:62 Eq:Ax[f])	95[d]
			
9	1000 psi H_2, 25 h	stoichiometric conversion only	
10	1000 psi H_2, 25 h, 6 equiv of Ph_3P/Cu	78:22	
11	1000 psi H_2, 25 h, 6 equiv of Ph_3P/Cu, THF solvent	100:0 (~3:1 Eq:Ax)	
12[g]	1000 psi H_2, 75 h, 6 equiv of Ph_3P/Cu	0:100[h]	83[i]
			
13	1000 psi H_2, 10 h	91:9	
14	1000 psi H_2, 10 h, 12 equiv of Ph_3P/Cu	20:71 (9 allylic alcohol)	
15	1000 psi H_2, 10 h, 12 equiv of Ph_3P/Cu, excess Hg^0	23:68 (9 allylic alcohol)	
16	1000 psi H_2, 48 h, 12 equiv of Ph_3P/Cu	0:92 (8 allylic alcohol)	95[j]
			
17	1000 psi H_2, 20 h	97:3	
18	1000 psi H_2, 20 h, 6 equiv of Ph_3P/Cu	89:7 (2 allylic alcohol)[e]	88[d]

[a] All reactions: 2.7 mol % $[(Ph_3P)CuH]_6$, C_6D_6, room temperature, 0.5 M in substrate, except entry 12. [b] Product ratios determined by relative NMR integration; zeros denote no material detected. [c] All products were identified by comparison with authentic materials. [d] Yield determined by NMR integration against internal standard at long pulse delay. [e] Remainder starting material. [f] Stereochemical ratios determined by ^1H NMR. [g] 0.8 mol% $[(Ph_3P)CuH]_6$ catalyst used. [h] See experimental for stereochemical assignments. [i] Yield of isolated, purified material. [j] Total yield of isolated alcohols.

amount of cyclohexenone was investigated, and resulted in complete conversion of both materials to cyclohexanol as the exclusive product (Scheme II). The most straightforward interpretation of these results is to consider that, although the hydride hexamer is used to initiate the reduction, the relevant catalytically active intermediate is the copper enolate, of unknown degree of aggregation. Heterolytic hydrogenolysis by this alkoxide species may kinetically produce hydridic copper complexes other than the hexamer (Scheme I, $N \neq 6$), which are more reactive than the thermodynamically stable hexameric complex. Reaggregation of these hydridic fragments to the hexamer is apparently slow relative to reduction of substrate or decomposition; under these reaction conditions, no $[(Ph_3P)CuH]_6$ is observed on depletion of the organic substrate. Additionally, the crude reaction mixture is dark and heterogeneous, with the bulk of the copper-containing residues recovered as a black precipitate.

Under these reaction conditions, the catalytic reduction of unsaturated ketones could not be generalized (Table I). While simple acyclic substrates were reduced effectively (entries 13 and 17), reaction of cyclic compounds bearing additional substituents at either the α- or β-position proceeded minimally beyond stoichiometric reduction, if at all (entries 7 and 9). These results may be attributed to competitive decomposition of the postulated copper(I) enolate intermediate relative to productive hydrogenolysis, even under high hydrogen pressure. Such instability parallels that observed in stoichiometric conjugate reductions using $[(Ph_3P)CuH]_6$.[8]

Catalysis with Added Phosphine. In an attempt to stabilize the catalytically active intermediate, excess triphenylphosphine was added to the reduction conditions. While it is unclear whether the added phosphine functions to saturate the coordination sphere of the intermediate or simply to inhibit destructive dissociation of the previously coordinated phosphine, several significant effects were observed (Table I). Catalytic reaction mixtures now maintained apparent homogeneity (vide infra), and the copper was recovered as $[(Ph_3P)CuH]_6$ (≥80% isolated).[18] In the case of cyclohexenone itself, the rate of conversion was attenuated, allowing isolation of the ketone product with good selectivity at lower hydrogen pressures (entry 6). Reduction of cyclohexenone using $[(Ph_3P)CuD]_6$ under deuterium atmosphere (350 psi, 52 h) gave both 2,3-dideuteriocyclohexanone and 1,2,3-trideuteriocyclohexanol-*O*-*d*, as anticipated (eq 3).



(3)

The most dramatic consequence of phosphine addition, however, is on the generality of the catalytic process (Table I). The homogeneous catalytic reduction may be successfully applied to

(18) Reduction of cyclohexenone using 0.04 equiv of $(CuO^tBu)_4$ and 4 equiv of PPh_3/Cu gave conversions comparable to that obtained using $[(Ph_3P)CuH]_6$ and 3 equiv of PPh_3/Cu. In both experiments, the copper was recovered as $[(Ph_3P)CuH]_6$.

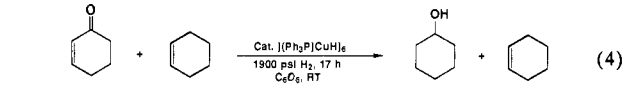
substrates with substituents on either carbon of the double bond, although catalyst turnover is qualitatively slower. The examples selected for the table highlight conditions under which selective conjugate reduction or complete 1,4- and 1,2-reduction was obtained. For both cyclic and acyclic substrates, the chemical yields of reduced product are uniformly high (entries 5, 8, 12, 16, and 18). Several additional comments are warranted. Only for 3,5-dimethylcyclohexenone (entries 7 and 8) is the rate of the second reduction competitive with initial conjugate reduction, preventing selective reduction to the ketone stage, although the regioselectivity for conjugate reduction is nonetheless maintained. In this system, the initial conjugate reduction is highly stereoselective (>100:1)[8], but the carbonyl reduction is not, variably producing alcohols ranging in ratio from approximately 1:1 to 2:1, favoring the axial hydroxyl group, depending on reaction conditions. For carvone, the initial reduction gives an approximately 3:1 ratio of ketone products, favoring the thermodynamically preferred diequatorial substituents. No reduction of the isolated double bond of carvone is observed, even after prolonged reaction time. A dramatic solvent effect is also noted: in the coordinating solvent THF,[19] turnover is further attenuated, allowing the isolation of the conjugate reduction product exclusively (entries 10 and 11).

Acyclic substrates proved somewhat more resistant to carbonyl reduction, consistent with rate differences previously observed in hydride reductions of cyclic and acyclic ketones.[20] For 4-phenyl-3-buten-2-one, a larger excess of Ph_3P is required to maintain reaction homogeneity (entries 14–16). With added phosphine, direct 1,2-reduction of this substrate was observed as a minor reaction pathway, producing the allylic alcohol product in <10% yield.[21] No allylic alcohol was produced in the absence of Ph_3P (entry 13). A small amount of allylic alcohol was also detected in the reduction of mesityl oxide, again only in the presence of excess phosphine (entry 18).

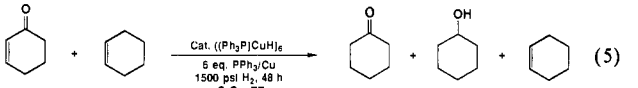
Calculation of turnover numbers and rates for this catalytic reduction is complicated by the unknown nuclearity of the catalytically active hydride complex and by the possibility of multiple reactive hydride, alkoxide, and mixed hydrido–alkoxide species. Assuming the maximum possible six hydride equivalents per hexamer in the initiation of the catalytic reduction, "lower limit" turnover numbers (two catalyst turnovers per reduction to alcohol) in the range 40–50 have been obtained (e.g., entry 12), although no attempt to establish a maximum turnover number has been made. Turnover rates for this catalytic reduction vary markedly depending on reaction conditions and substrate. On the basis of reaction times and the amount of catalyst (Table I) and assuming the limiting case of mononuclear catalyst units, turnover ranges from as fast as approximately 8/h (entry 5) to as slow as 0.25/h (entry 11).

Although reaction homogeneity is difficult to determine unambiguously, under conditions of excess phosphine, the presence of excess elemental mercury[22] had no significant impact on the course of the catalytic reduction of either 2-cyclohexen-1-one or 4-phenyl-3-buten-1-one (entries 4 and 15). In the absence of excess phosphine, the presence of mercury resulted in suppression of catalytic activity.

Catalytic Hydride Reduction or Catalytic Hydrogenation? To establish the distinction between the copper(I)-mediated catalytic reduction described in this report and standard catalytic hydrogenation processes, control experiments were conducted by adding reducible alkene substrates to active catalytic reductions under vigorous conditions. This procedure subjects the added alkene to all catalytically active copper species present during the reduction.[23] Catalytic reduction of cyclohexenone in the presence of an excess of cyclohexene gave no detectable hydrogenation of the isolated double bond, with or without added triphenylphosphine (eq 4 and 5). With added 1-hexene, reduction of cyclohexenone

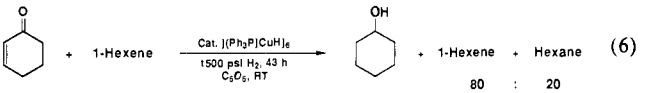


(4)

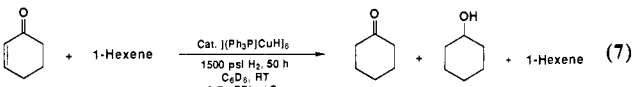


(5)

in the absence of excess triphenylphosphine resulted in partial hydrogenation to *n*-hexane and accompanying decomposition of copper species to insoluble materials (eq 6). Under homogeneous conditions, however, no hydrogenation of 1-hexene was detected, and the hydride hexamer re-formed cleanly (eq 7). Interestingly, in the presence of added alkene, overall conversion to reduced substrate is also inhibited, suggesting that competitive coordination, but not reduction, of the unactivated alkene may be mechanistically relevant.

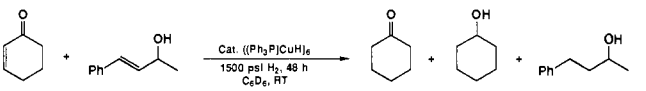


(6)

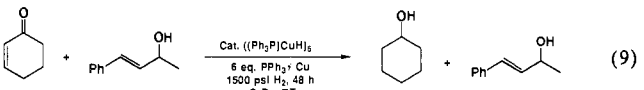


(7)

As a final control, 4-phenyl-3-buten-2-ol was added to the catalytic reduction of cyclohexenone (eq 8 and 9). These experiments serve two purposes: first, as a probe for competitive catalytic hydrogenation of an alkene substrate activated toward



(8)



(9)

hydrogenation,[24] and second, to provide some insight into the formation of this material during the reduction of 4-phenyl-3-buten-2-one in the presence of excess phosphine. In the absence of added triphenylphosphine, addition of this allylic alcohol to an active catalytic reduction of cyclohexenone under forcing conditions resulted in complete hydrogenation of the double bond (eq 8). No hydrogenolysis of the alcohol moiety was observed. Under homogeneous conditions, in the presence of excess phosphine, no olefin isomerization or further reduction could be detected. Thus, it is unlikely that the allylic alcohol produced during catalysis with excess phosphine reacts further under these conditions. Although these results leave open the possiblity that under nonhomogeneous conditions allylic alcohol is formed and subsequently reduced to saturated alcohol, no allylic alcohol is observed in catalytic reductions run to partial conversion.

Taken together, these competition experiments reveal the occurrence of accompanying, presumably heterogeneous, processes in reactions run in the absence of added phosphine, but confirm that the homogeneous reaction is unusually resistant to reduction of nonpolar unsaturated functionality.

Conclusions. In summary, hydride reduction methodology *catalytic* in the hydride source has been demonstrated using stable,

(19) Tetrahydrofuran appears to be a generally acceptable solvent for reductions using $[(Ph_3P)CuH]_6$, despite the reported instability of the hexamer in this medium (ref 6).

(20) See, e.g.: Brown, H. C.; Muzzio, J. *J. Am. Chem. Soc.* **1966**, *88*, 2811. Davis, R. E.; Carter, J. *Tetrahedron* **1966**, *22*, 495.

(21) Under conditions of added phosphine insufficient to maintain reaction homogeneity, the amount of allylic alcohol produced becomes highly variable. This phenomenon is under investigation.

(22) See discussion in: Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855 and references therein.

(23) $[(Ph_3P)CuH]_6$ itself is inert to common alkenes, including 1,1-diphenylethylene: Geerts, R. L.; Caulton, K. G. Unpublished results.

(24) This conjugated alkene is substantially polarized and has the potential for chelation activation through the allylic alcohol functionality.

readily available, copper(I) complexes and molecular hydrogen. In its present form, this methodology has been applied to regioselective conjugate reduction and subsequent carbonyl reduction of α,β-unsaturated ketones. The reaction is homogeneous in the presence of excess triphenylphosphine and proceeds at room temperature under conveniently accessible hydrogen pressures. Aside from the inconvenience of the slow turnover rate, one limitation as yet restricts both general application and mechanistic investigations of this novel catalytic process. As is evident from the proposed catalytic scheme and our experimental results, the catalytically active intermediate and consequently all relevant reaction parameters, are substrate dependent. Removal of this substrate dependence provides the focus of our continuing investigations.

Experimental Section

General Experimental. All manipulations were carried out under an inert atmosphere with standard glovebox and Schlenk techniques. Benzene and THF were distilled from sodium/potassium benzophenone ketyl and stored under nitrogen. Organic substrates were dried over magnesium sulfate and purified by distillation under nitrogen. Hydrogen (Air Products, ultrahigh purity grade) and deuterium (Linde, C.P. grade) were used without further purification. All high-pressure reactions were performed in a glass-lined stainless steel reactor of local construction. Preparation of $[(Ph_3P)CuH]_6$ was according to literature methods.[5,25] ^1H NMR spectra were recorded on a Varian XL-300 or Bruker AM-500 spectrometer and referenced against the protium residual in the deuterated solvent (benzene-d_6 $\delta = 7.15$, THF-d_8 $\delta = 3.58$). ^2H NMR spectra were recorded at 55.4 MHz on a Nicolet NT-360 spectrometer. Identification of organic products was made by high-field ^1H NMR comparison to authentic samples obtained commercially or prepared independently by unambiguous methods.[26] NMR yields were determined at long pulse delay by integration against an internal standard.

General High-Pressure Reactions. A. No Added Phosphine. In the glovebox, $[(Ph_3P)CuH]_6$ (20 mg, 0.010 mmol), benzene-d_6 (0.80 mL), and a magnetic stirbar were combined in a glass vial that was subsequently placed in a stainless steel reactor. Organic substrate (0.37 mmol) was added; the reactor was quickly sealed, removed from the glovebox, and charged with H_2 gas. Stirring was initiated after pressurization. Upon completion, the pressure was reduced, and the reactor was taken back into the glovebox and opened; the contents were transferred to an NMR tube. Centrifugation of the NMR tube was performed when necessary.

B. Added Phosphine. The same procedure as described above was used. Triphenylphosphine (0.37 mmol unless otherwise stated) was added before solvent.

Reduction of 2-Cyclohexen-1-one (Entry 5). Procedure B was used with a reaction pressure of 500 psi for 1 h. Upon completion, the reactor was opened in the glovebox to reveal a dark red solution with no visible precipitate or copper mirror plating. Toluene (10.0 μL, 0.0940 mmol) was added an as internal standard and ^1H NMR analysis showed cyclohexanone and cyclohexanol (79:21 respectively) in 90% yield.

Reduction of 3,5-Dimethylcyclohexenone (Entry 8). Procedure B was used with a reaction pressure of 500 psi for 48 h and 0.5 mL solvent. Upon completion, the reactor was opened in the glovebox to reveal a bright red solution. For yield determination, toluene (10.0 μL, 0.0940 mmol) was added to this solution as an internal standard, and the entire contents were transferred to a Y-tube, rinsing the reaction vial once with 0.1 mL of benzene-d_6. The Y-tube was removed from the glovebox, frozen, and evacuated to 1×10^{-5} mmHg. The volatiles were distilled under vacuum; a heat gun was used to ensure complete transfer of all volatile material. ^1H NMR spectroscopy revealed a mixture of 3(β),5-(β)-dimethylcyclohexan-1(α)-ol and 3(α),5(α)-dimethylcyclohexan-1-(α)-ol (62:38) by comparison with an authentic sample (see supplementary material). Integration of either the methyl resonances or the hydrogen α to the hydroxy functionality against the toluene standard gave a combined chemical yield of 95%.

Reduction of (*R*)-(−)-Carvone (Entry 12). Procedure B was used with 1.28 mmol (0.192 g, 200 μL) of carvone (0.8 mol % $[(Ph_3P)CuH]_6$) and a reaction pressure of 1000 psi for 75 h. Upon completion, the reactor was opened in the air, the vial was capped, and the reaction mixture was stirred for 3 h, during which time the original red homogeneous solution darkened and copper-containing decomposition products precipitated. Filtration through Celite and evaporation of the solvent in vacuo gave crude product. Purification by flash chromatography[27] gave 0.163 g (83% yield) of a mixture of four isomers of dihydrocarveol. The two major isomers (ca. 90% of the isolated alcohols) were identified as 2-(*R*)-methyl-5(*R*)-(2-propenyl)cyclohexan-1(*S*)-ol and 2(*S*)-methyl-5-(*R*)-(2-propenyl)cyclohexan-1(*R*)-ol (2:1 ratio, respectively) by comparison with a commercial sample (see supplementary material).

Reduction of 4-Phenyl-3-buten-2-one (Entry 16). Procedure B was used with a reaction pressure of 1000 psi for 48 h, and Ph_3P (192 mg, 0.73 mmol) was added. Upon completion, the reactor was opened in the air, the vial was capped, and the reactor was stirred for 3 h, during which time the original red homogeneous solution darkened and copper-containing decomposition products precipitated. Filtration through Celite and evaporation of the solvent in vacuo gave crude product. Purification by flash chromatography[27] gave 4-phenylbutan-2-ol and 4-phenyl-3-buten-2-ol (92:8) in a combined yield of 95%.

Reduction of 4-Methyl-3-penten-2-one (Entry 18). Procedure B was used with a reaction pressure of 1000 psi for 20 h. Upon completion, the reactor was opened in the glovebox to reveal a bright red solution into which toluene (10.0 μL, 0.0940 mmol) was added. ^1H NMR of this solution showed $[(Ph_3P)CuH]_6$ and the organic products 4-methyl-2-pentanone, 4-methyl-2-pentanol, 4-methyl-3-penten-2-ol, and 4-methyl-3-penten-2-one in a ratio of 89:7:2:2, respectively. Integration against the toluene internal standard gave a combined yield of 88% for reduced products.

Isotopic Labeling. In the glovebox, $[(Ph_3P)CuH]_6$ (20 mg, 0.010 mmol), Ph_3P (96 mg, 0.37 mmol), benzene (0.80 mL), and a magnetic stirbar were combined in a glass vial that was subsequently placed in a stainless steel reactor. 2-Cyclohexen-1-one (35 μL, 0.36 mmol) was added using a syringe; the reactor was quickly capped, removed from the glovebox, and charged with D_2 (350 psi). After stirring 52 h, the pressure was reduced, and the reactor taken back into the glovebox and opened to reveal a dark red solution and a small amount of copper mirror plating the walls of the vial. Analysis by ^2H NMR spectroscopy showed $[(Ph_3P)CuD]_6$ ($\delta = 3.55$), cyclohexanone-*2,3*-d_2 ($\delta = 1.93, 1.30$), and cyclohexanol-*O-1,2,3*-d_4 (mixture of isomers, $\delta = 3.39, 1.70, 1.55, 1.16, 1.07$).

Reduction of 2-Cyclohexen-1-one in the Presence of Hg Metal (Entry 4). Procedure B was used with a reaction pressure of 1000 psi for 5 h. Mercury metal (0.5 mL) was added before the solvent. ^1H NMR analysis of the resulting bright red solution showed $[(Ph_3P)CuH]_6$ and both cyclohexanone and cyclohexanol (76:24).

Reduction of 4-Phenyl-3-buten-2-one in the Presence of Hg Metal (Entry 15). Procedure B was used with a reaction pressure of 1000 psi for 10 h. Mercury metal (0.5 mL) was added before the solvent. ^1H NMR analysis of the resulting bright red solution showed $[(Ph_3P)CuH]_6$, 4-phenyl-2-butanone, 4-phenyl-2-butanol, and 4-phenyl-3-buten-2-ol; the ratio of the organic products was 23:68:9, respectively.

Reduction of 2-Cyclohexen-1-one in the Presence of Cyclohexene. A. No Added Phosphine. General procedure A was used with a reaction pressure of 1000 psi for 10 h. Cyclohexene (62 μL, 0.61 mmol) was added prior to the addition of 2-cyclohexen-1-one. The crude reaction mixture was a dark red solution with very faint copper mirror plating the walls of the vial. ^1H NMR analysis showed cyclohexene and both 2-cyclohexen-1-one and cyclohexanone (75:25).

B. With Added Phosphine. General procedure B was used with a reaction pressure of 1500 psi for 48 h. Cyclohexene (62 μL, 0.61 mmol) was added prior to the addition of 2-cyclohexen-1-one. The crude reaction mixture was a dark red solution with a very faint copper mirror plating the walls of the vial. ^1H NMR analysis showed cyclohexene, $[(Ph_3P)CuH]_6$, and both cyclohexanone and cyclohexanol (58:42).

Reduction of 2-Cyclohexen-1-one in the Presence of 1-Hexene. A. No Added Phosphine. General procedure A was used with a reaction pressure of 1500 psi for 43 h. 1-Hexene (46 μL, 0.37 mmol) was added prior to the addition of 2-cyclohexen-1-one. The crude reaction mixture was very dark red with a black precipitate coating the walls of the vial. ^1H NMR analysis showed cyclohexanol and both 1-hexene and hexane (80:20).

B. With Added Phosphine. General procedure B was used with a reaction pressure of 1500 psi for 50 h. 1-Hexene (46 μL, 0.37 mmol) was added prior to the addition of 2-cyclohexen-1-one. ^1H NMR analysis of the resulting very dark red solution showed 1-hexene and both cyclohexanone and cyclohexanol (89:11).

Reduction of 2-Cyclohexen-1-one in the Presence of 4-Phenyl-3-buten-2-ol. A. No Added Phosphine. General procedure A was used with a reaction pressure of 1500 psi for 48 h. 4-Phenyl-3-buten-2-ol (55 mg, 0.37 mmol) was added prior to the solvent. The crude reaction mixture

(25) Simplified, one-pot procedure for the preparation of $[(Ph_3P)CuH]_6$: Brestensky, D. M.; Huseland, D. E.; McGettigan, C.; Stryker, J. M. *Tetrahedron Lett.* **1988**, *29*, 3749.

(26) Hudlicky, M. *Reductions In Organic Chemistry*; Wiley: New York, 1984, and references therein.

(27) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

was orange with some copper plating the walls of the vial. ^{1}H NMR analysis showed $[(Ph_3P)CuH]_6$, 4-phenyl-2-butanol, and both cyclohexanol and cyclohexanone (86:14).

B. With Added Phosphine. General procedure B was used with a reaction pressure of 1500 psi for 48 h. 4-Phenyl-3-buten-2-ol (42 mg, 0.28 mmol) was added prior to solvent. ^{1}H NMR analysis of the resulting bright red homogeneous solution showed $[(Ph_3P)CuH]_6$, 4-phenyl-3-buten-2-ol, and cyclohexanol.

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Supplementary Material Available: High-field (500-MHz) ^{1}H NMR spectral data for the reduced products (2 pages). Ordering information is given on any current masthead page.

Single-Crystal X-ray and Neutron Diffraction Studies of an η^2-Dihydrogen Transition-Metal Complex: *trans*-$[Fe(\eta^2\text{-}H_2)(H)(PPh_2CH_2CH_2PPh_2)_2]BPh_4$

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Contribution from the Chemistry Departments, University of Southern Maine, Portland, Maine 04103, Brookhaven National Laboratory, Upton, New York 11973, and University of Toronto, St. George and Scarborough Campuses, Toronto, Ontario M5S 1A1, Canada. *Received March 14, 1989*

Abstract: The H–H distance in the η^2-H_2 ligand in $[Fe(\eta^2\text{-}H_2)H(dppe)_2]BPh_4$, **1**-$BPh_4$, dppe = $PPh_2CH_2CH_2PPh_2$, is 0.816 (16) Å as determined by neutron diffraction on a crystal of volume 2.62 mm^3 at 20 K: 1-BPh_4 is monoclinic, space group $C2/c$, a = 16.999 (7) Å, b = 16.171 (2) Å, c = 22.114 (5) Å, β = 102.52 (2)°, U = 5934.4 (2) Å^3, and D_c = 1.315 g cm^{-3} for Z = 4; $R(F)$ = 0.071, $R(F^2)$ = 0.110, $R_w(F^2)$ = 0.113 for 4116 reflections with $I \geq 3\sigma(I)$. The H–H separation is 0.87 (3) Å as determined by X-ray diffraction at 298 K: monoclinic, $C2/c$, a = 17.327 (3) Å, b = 16.407 (4) Å, c = 22.224 (3) Å, β = 102.87 (1)°, U = 6159.2 (1) Å^3, and D_c = 1.267 g cm^{-3} for Z = 4; $R(F)$ = 0.038, $R_w(F)$ = 0.034, for 3673 reflections ($I \geq 3\sigma(I)$). These η^2-H_2 distances agree with the X-ray value of 0.89 (11) Å reported for the tetrafluoroborate salt, **1**-BF_4. As was found for **1**-BF_4, **1**-BPh_4 contains an η^2-H_2 ligand that is symmetrically side-on bonded to the iron and trans to the terminal hydride such that the Fe has a distorted octahedral configuration. These diffraction studies serve to calibrate H–H distances obtained by the T_1 NMR method for dihydrogen complexes in solution where the H_2 ligand is suggested to be rapidly spinning. The H–H distance is the same as that in $W(\eta^2\text{-}H_2)(CO)_3(P(i\text{-}Pr)_3)_2$ despite the fact that the tungsten complex has a more labile H_2 ligand. The terminal hydride–iron distance of 1.535 (12) Å as determined by neutron diffraction is shorter than the distances to the dihydrogen ligand (H–Fe = 1.616 (10) Å). This is the first experimental demonstration of this expected difference in metal bonding to hydride and H_2. There is no disorder of ligands apparent in the structure at 20 K.

Neutron diffraction studies have played a crucial role in the characterization of polyhydride complexes in the solid state.[2] Of some 30 structures examined, none had revealed a short H–H distance attributable to H–H bonding until the η^2-dihydrogen complexes $M(\eta^2\text{-}H_2)(CO)_3(P(i\text{-}Pr)_3)_2$, M = Mo, W, were reported in 1984.[3] The H–H bond length in the tungsten complex is 0.82 (1) Å. In 1985, the Morris group reported the preparation and characterization of the complexes *trans*-$[M(\eta^2\text{-}H_2)(H)(dppe)_2]$-$BF_4$, M = Fe, Ru.[4] The Fe complex displayed properties that were somewhat different from those reported for the Mo and W complexes, including a lower lability of H_2 with respect to exchange with hydrogen gas, deprotonation of H_2 by strong bases, intramolecular exchange of H atoms between dihydrogen and hydride ligands, a slightly smaller ^1J(H,D) coupling constant in the η^2-HD complex (32[5] versus 34 Hz), and a longer minimum T_1 value for the H_2 ligand (8.5 ± 1.0 ms at 200 MHz for (H_2)Fe and ≤ 4 ms at 250 MHz for (H_2)W).[4,5] The H–H distance from X-ray diffraction of 0.89 (11) Å is not precise enough to say whether the bond is longer than that in the above W complex, as might have been expected judging by some of these properties. An NMR method for determining H–H distances in polyhydride complexes based on spin–lattice relaxation times[6] provided an ambiguous answer since the distance could be 1.09 Å if rotation of the dihydrogen group were slow compared to the tumbling of the molecule (i.e., if the dihydrogen correlation time were less than that of the terminal hydride ligand) or it could be 0.86 Å if the

(1) (a) University of Southern Maine. (b) Brookhaven National Laboratory. (c) University of Toronto.

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(5) (a) Bautista, M.; Earl, K. A.; Morris, R. H.; Sella, A. *J. Am. Chem. Soc.* **1987**, *109*, 3780. Here ^1J(H,D) was reported as 30 Hz for $[Fe(HD)(D)(dppe)_2]BF_4$ at 200 MHz. (b) A recently obtained ^{1}H NMR spectrum with better resolution at 400 MHz of $[Fe(HD)(D)(dppe)_2]BF_4$ has given a value of 32 ± 1 Hz for ^1J(H,D). Drouin, S. D.; Morris, R. H. Unpublished results.

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