Anionic Group 6 Transition-Metal Carbonyl Hydrides as Reducing Agents. Ketones, Aldehydes, and Epoxides†

Paul L. Gaus,*[1] S. C. Kao,*[2] Kay Youngdahl, and Marcetta Y. Darensbourg*

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received August 22, 1984*

Abstract: Studies of the reducing ability of anionic group 6 transition-metal hydrides $HM(CO)_5^-$ and *cis*-$HM(CO)_4P(OMe)_3^-$ (M = Cr, W) toward aldehydes and ketones are reported. Formaldehyde (as paraformaldehyde) reacts with all hydrides used, yielding spectroscopically observable addition products, presumed to be alkoxide intermediates, which are quenched by Brønsted acids, yielding alcohols. Other aldehydes are unreactive with $HM(CO)_5^-$ except in the presence of acid, in which case reduction occurs readily. With the more active *cis*-$HM(CO)_4P(OMe)_3^-$ reagents aldehydes react to yield observable intermediates which are readily hydrolyzed to alcohols. Ketones are unreactive with all hydrides studied except in the presence of Brønsted acids. A variety of ketones have been investigated, and the problem of balancing acid assistance of ketone reduction vs. acid destruction of the reactive hydrides has been addressed. A facile H/D exchange reaction using methanol-d_1 as the deuterium source to generate $DM(CO)_4L^-$ permits deuterium delivery to the carbonyl carbon of ketones and aldehydes.

A great deal of study has been given to the use of main group hydrides as reducing agents for organic chemistry. For example, the well-known hydrides of boron,[3] aluminum,[4] tin,[5] and tellurium[6] have been developed to such an extent that highly sophisticated reagents offer reductions of a range of functional groups, with impressive selectivities and stereospecificities.

Hydrides of the transition elements are less well developed as synthetic reagents, but an intriguing variety of anionic mononuclear hydrides is presently becoming available, and studies of their reducing abilities are beginning to appear in the literature. These include the dianionic group 5 hydrides, $HM(CO)_5^{2-}$ (M = V, Nb, Ta);[7] the anionic group 6 hydrides $HM(CO)_5^-$ (M = Cr, Mo, W);[8] and the anionic group 8 hydrides $HFe(CO)_4^-$,[9] $HRu(CO)_4^-$,[10] and $HFe_2(CO)_8^-$.[11] One should also include the cyclopentadienyl derivatives $CpV(CO)_3H^-$,[12] $CpRe(CO)_2H^-$,[13] $CpMo(CO)_3H$,[12a] Cp_2ZrH_2,[14] Cp_2MoH_2 and Cp_2WH_2,[15] Cp_2ReH,[15] $Cp_2Zr(H)Cl$,[14a,c,16] $Cp_2Zr(Cl)BH_4$,[17] and Cp_2NbH_3.[18] Hydrides such as $HRu(O_2CHRCHRCOR')(PPh_3)_3$[19] and $(Ph_3P)_2Ph_2\overline{PC_6H_4}Ru-H_2^-$[20] have also been used as stoichiometric and catalytic reducing agents, respectively. Even acidic hydrides such as $HCo(CO)_4$[21] and $HMn(CO)_5$[22] can serve as reducing agents, with the proper substrates. Other ligands such as phosphines can be introduced into such hydrides by substitution of a CO ligand, giving an impressive range of reducing agents with tunable reactivities. Furthermore, in some cases, such as the *cis*-$HM(CO)_4P^-$ reagents used in this study, the inclusion of a chiral phosphine ligand presents a potential source of asymmetric reduction agents.

In previous reports, the anionic group 6 hydrides $HM(CO)_5^-$ (M = Cr, W) and *cis*-$HM(CO)_4P^-$ (M = Cr, W; P = $P(OMe)_3$ or PR_3) have been shown to reduce alkyl halides[8a,c] and acid chlorides.[8d] We report here studies of the stoichiometric reduction of aldehydes, ketones, and epoxides. Although we are primarily concerned with establishing the reactivity patterns of these and other hydrides, we also hope that these reagents will become useful synthetically. At their current stage of development, these hydrides would be the reduction reagent of choice in limited instances. However, since anionic transition-metal hydrides are regenerable from inexpensive starting materials, CO and base,[23] fundamental knowledge of their reaction chemistry should encourage technical developments in hydride synthesis.

Experimental Section

Materials. The hydrides $HM(CO)_4L^-$ were prepared as the PPN^+ salts (PPN^+ = bis(triphenylphosphine)imminium) by using published procedures.[24] The purity of the hydrides was assessed by elemental analysis and IR and NMR spectra. These hydrides were stored and handled in an argon-filled glovebox. The reagents CH_3CO_2H, PhOH,

† The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

(1) Present address: The College of Wooster, Wooster, OH 44691.
(2) Present address: Union Carbide, River Road, Bound Brook, NJ 00805.
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and CH_3OH were obtained from Aldrich, Gold Label. The deuterated analogues (including D_2O) were similarly obtained from Aldrich, >99.5% enrichment. The aldehydes, ketones, and epoxides were obtained predominantly from Aldrich in the highest available state of purity. All such liquids were further purified by fractional distillation, often at reduced pressure, and stored under dry N_2 prior to use. Solids were used without further purification. THF and hexane solvents were distilled under N_2 from purple Na/benzophenone and stored under N_2, over activated 4 Å molecular sieves, until needed. Acetonitrile was dried over CaH_2, multiply distilled from P_2O_5, and stored under N_2, over activated 4 Å molecular sieves. Other solvents, solutions, and reagents were deoxygenated with an extended N_2 flush immediately prior to use.

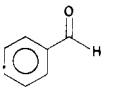
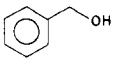
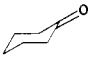
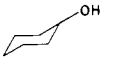
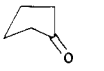
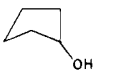
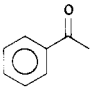
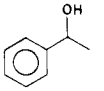
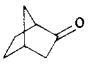
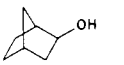
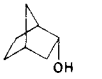
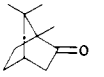
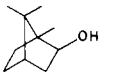
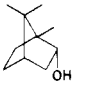
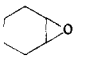
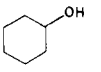
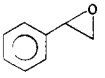
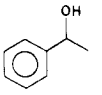
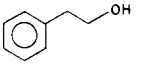
Reductions. All reductions were performed with stoichiometric amounts of substrate, hydride, and acid. The order of addition of these three reactants was only important when the most strongly hydridic hydrides were used in conjunction with the stronger acids such as CH_3CO_2H, as described in the Results Section. Reactions which were to be monitored with GC, IR, GC/MS, or GC/FTIR were performed with 5.0×10^{-5} mol of each reactant in 5.0 mL of THF solution. Reactions which were to be monitored by ^1H or ^2H NMR were performed with $1-2 \times 10^{-4}$ mol of each reactant in 1–3 mL of THF; dilutions were then made where GC or IR data were also desired. In all of the methods described below, the hydride was weighed in the glovebox directly into a flask or NMR tube and sealed with a septum. Solvents, solutions, and reagents were then added outside the glovebox with standard syringe or cannulation techniques. All reductions were allowed to proceed under N_2 in these sealed flasks, at 25 °C.

Method I: To the hydride, in a septum-sealed flask, was added 5.0 mL of a previously deoxygenated solution of organic substrate (1.0×10^{-2} M) in THF. An equivalent of acid was then added (syringe), and reaction was allowed to proceed at room temperature, with stirring. For some aldehydes, a color change was noticed after addition of the substrate and before addition of the acid. As described in the Results section, IR spectroscopy indicated formation of intermediate alkoxides which were immediately quenched upon addition of acid. **Method** II: To the hydride, in a septum-sealed flask, was added 5.0 mL of a previously deoxygenated solution of organic substrate and acid (both 1.0×10^{-2} M) in THF. The reaction was allowed to stir at room temperature in the sealed flask or (for mechanistic studies involving ketones) under a positive pressure of N_2 or CO. This method was especially used for ketones and epoxides, where, as described in the Results section, reaction between the hydride and the organic substrate did not proceed to any noticeable extent in the absence of acid. **Method** III: When pre-equilibration of the hydrides with deuterated acids was desired, or when the hydride was not especially sensitive to acid, the hydride and the acid (as a solution in THF) were mixed first. This method was especially useful for reactions which were monitored by ^2H NMR. Thus the hydride was treated with an equivalent of acid dissolved in the appropriate volume of THF solvent. The desired amount of organic substrate was then added with a syringe.

Chromatographic Techniques. Gas chromatographic analyses were performed on a Perkin-Elmer Sigma 2 instrument with Carbowax or Porapak T columns by Alltech. Products were initially identified by comparison of retention times with standards and by co-injection with pure samples. Other methods (IR, ^2H and ^1H NMR, GC/FTIR, or GC/MS) were always used to monitor the disappearance of reactants and to establish the product identities. Yields were determined by GC analysis, comparing integrated peak intensities with gravimetric standards of the known products. GC/FTIR studies were performed on the combination of a Perkin-Elmer Sigma 3B gas chromatograph interfaced with an IBM IR/85 FTIR. GC/MS data were collected at the Texas A&M Center for Trace Characterization Mass Spectrometric Analysis on a Hewlett Packard 5710A gas chromatograph in line with a Hewlett Packard 5980 mass spectrometer.

Spectroscopic Methods. Infrared spectra were recorded in 0.1-mm CaF_2 cells on a Perkin-Elmer 283 spectrophotometer (calibrated against CO and H_2O) or on an IBM IR85 FTIR. ^1H NMR spectra were obtained on a Varian EM390 and ^2H NMR on a Varian XL200, referenced against THF.

Table I. GC Yields for Reductions[a] with $PPN^+HCr(CO)_5^-/CH_3CO_2H$[b] (Functional Group Dependence)

entry	reactant	product	% yield (time, h)
I-1		CH_3OH	98 (0.5)
I-2			98 (1)
I-3			90 (1)
I-4			70 (70)
I-5			95 (4)
I-6			35 (24)
I-7			45 (72)
I-8A			2 (8)
I-8B			50 (8)
I-9			5 (24)
			0 (24)
I-10			0 (100)
I-11			0 (100)
			0 (100)

[a] Reactions were performed in dry THF, under N_2 at 25 °C. The mole ratio of the hydride, substrate, and acid (added in that order) was 1:1:1. [b] Reactions which gave low yields did so in proportion to the amount of hydride reagent lost to acid-promoted decomposition ($-H_2$) to the unreactive dimer μ-$H[Cr(CO)_5]_2^-$. The other metal carbonyl product was $Cr(CO)_5(O_2CCH_3)^-$. [c] As paraformaldehyde.

Results

Reduction of Aldehydes. Aldehydes were rapidly and efficiently reduced by the reagents $HM(CO)_4L^-$ in THF solvent, at room temperature. Complete reduction to the alcohol required 1 equiv of an acid such as acetic acid or phenol. Weak proton donors such as water or methanol did not in general promote these reductions, paraformaldehyde excepted; see Tables I, II and III. The order

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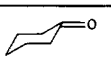
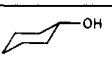
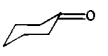
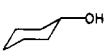
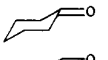
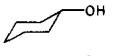
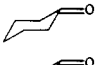
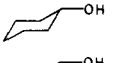
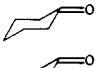
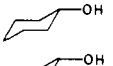
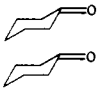
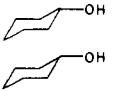
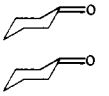
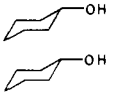
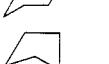
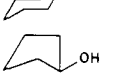
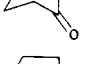
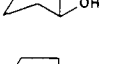
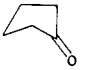
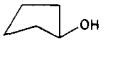
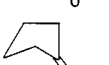
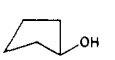
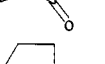
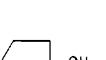
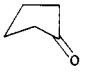
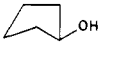
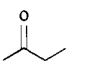
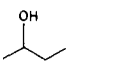
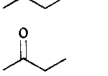
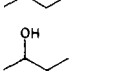
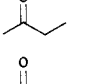
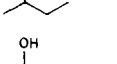
Table II. GC Yields for Reductions[a] with Various Acids with the Hydride $PPN^+HM(CO)_4L^-$ (Acid and L Dependence)

entry	acid	M	L	substrate	product	% yield[b]
II-1A	CH_3CO_2H	Cr	CO			95
II-1B	C_6H_5OH	Cr	CO			52[c]
II-1C	H_2O	Cr	CO			11[c]
II-1D	CH_3OH	Cr	CO			0
II-2A	CH_3CO_2H	Cr	$P(OMe)_3$			11[d]
II-2B	C_6H_5OH	Cr	$P(OMe)_3$			71[c]
II-2C	H_2O	Cr	$P(OMe)_3$			6[c]
II-2D	CH_3OH	Cr	$P(OMe)_3$			0
II-3A	CH_3CO_2H	Cr	CO			34[d]
II-3B	C_6H_5OH	Cr	CO			12[c]
II-4A	CH_3CO_2H	Cr	$P(OMe)_3$			1[d]
II-4B	C_6H_5OH	Cr	$P(OMe)_3$			44[c]
II-5A	CH_3CO_2H	Cr	CO			47[c]
II-5B	C_6H_5OH	Cr	CO			8[c]
II-6A	CH_3CO_2H	Cr	$P(OMe)_3$			25[d]
II-6B	C_6H_5OH	Cr	$P(OMe)_3$			56[c]

[a] Reactions performed as described in footnote *a* of Table I. [b] Yields as checked by GC (based on starting ketone concentration) after 24 h of reaction. [c] This reaction gave low yields after 24 h due to slow reaction. After only 24 h, active hydride reagent was still available for reaction. Eventually, yields were higher. (See Tables I and III for maximized yields.) The data are used here as a measure of relative rate. [d] This reaction gave a low yield due to the loss of the hydride reagent to HOAc-promoted decomposition ($-H_2$) to the unreactive dimers μ-$H[M(CO)_4L]_2^-$.

of addition of the hydride, the acid, or the aldehyde did not significantly affect the yields of these reactions, although more concentrated solutions of hydride and acetic acid did decompose (with loss of H_2) if not used immediately for reduction of an aldehyde. When deuterated acetic acid was used (Method III), rapid exchange of hydrogen for deuterium gave the corresponding deuterides $DM(CO)_4L^-$, which, in every case, delivered deuterium to the carbonyl carbon of the aldehyde to give C-deuterated alcohol products RCH(D)OH, as indicated by ^2H NMR.

Paraformaldehyde. Immediate reaction was observed upon mixing THF solutions of $HM(CO)_4L^-$ (M = Cr, W; L = CO, $P(OMe)_3$) and paraformaldehyde. The color of the reaction solution changed from orange to yellow for L = CO, M = Cr. In all cases, immediate changes in the ν_{CO} region of the infrared spectrum indicated the formation of an anionic species containing an O-donor ligand. For example, ν_{CO} IR bands for the product of the reaction between $HCr(CO)_5^-$ and paraformaldehyde were identical with those of a solution prepared by mixing carefully dried $PPN^+OCH_3^-$ with photochemically generated THF·$Cr(CO)_5$: ν_{CO} 2050 (w), 1922 (s), 1855 (m) cm^{-1}. Repeated attempts to isolate this, presumably $CH_3OCr(CO)_5^-$, and other alkoxide complexes were unsuccessful. Solid products were invariably contaminated by μ-$H[M(CO)_4L]_2^-$, indicating the regeneration of the hydride $HM(CO)_4L^-$, presumably by β-elimination from **1**. The monomeric hydrides characteristically displace any labile ligand such as OR^- from $M(CO)_4LX^-$ (X^- = labile ligand), to yield the stable bridging hydride dimeric anions. The alkoxides were also especially sensitive to weak acids such as trace water. Thus the reaction with paraformaldehyde is presumed

$$HM(CO)_4L^- + (CH_2O)_x \rightarrow \underset{\mathbf{1}}{(CO)_4LM\text{–}OCH_3^-} \quad (1)$$

$$\mathbf{1} + H^+ \rightarrow CH_3OH + [M(CO)_4L] \quad (2)$$

to proceed as in eq 1 and 2. With M = W, L = $P(OMe)_3$, product **1** is of the cis configuration (ν_{CO} 2001 (vw), 1900 (sh), 1870 (s), 1815 (m) cm^{-1}).

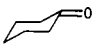
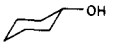
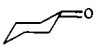
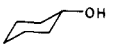
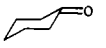
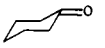
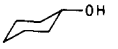
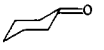
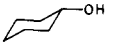
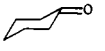
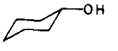
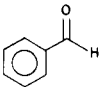
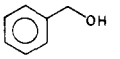
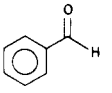
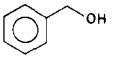
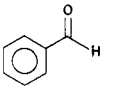
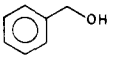
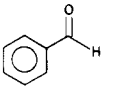
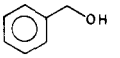
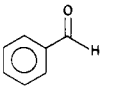
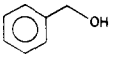
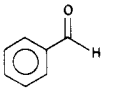
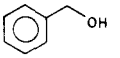
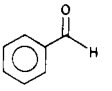
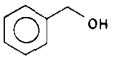
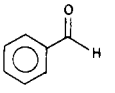
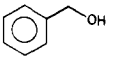
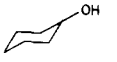
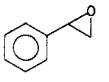
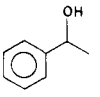
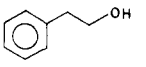
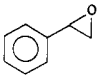
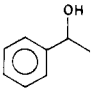
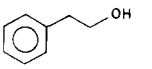
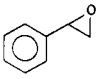
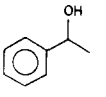
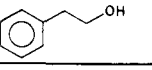
Addition of a Brønsted acid (CH_3CO_2H or H_2O) to **1** produced methanol, eq 2, identified by NMR and by GC analysis. If acetic acid was used as the quenching reagent, the pentacoordinate metal complex product of eq 2 was trapped as the acetate, $M(CO)_4L(OAc)^-$.[25] With water as the quenching reagent, transient ν_{CO} IR bands were observed in positions similar to the CH_3O^- complexes, indicating the possibility that $M(CO)_4L(OH)^-$ was formed.

The full reduction to methanol could be performed stepwise (Method I) as in eq 1 and 2, or paraformaldehyde could be added to a combined THF solution of the hydrides and acid quencher (Method III) without affecting yields. With acetic acid, however, there was a tendency to lose reducing agent through H_2 elimination, eq 3, if the paraformaldehyde was not added quickly.

$$HM(CO)_4L^- + H^+ \rightarrow H_2 + [M(CO)_4L] \quad (3)$$

(25) (a) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S.; Kudaroski, R. *Inorg. Chem.* **1982**, *21*, 1656. (b) Cotton, F. A.; Darensbourg, D. J.; *Kolthammer*, B. W. S. *J. Am. Chem. Soc.* **1981**, *103*, 398.

Table III. GC Yields for Reductions[a] with Various Acids with the Hydrides $PPN^+HM(CO)_4L^-$ with Either CH_3CO_2H (Entry A) or C_6H_5OH (Entry B), at 25 °C (Dependence on the Reducing Agent[b])

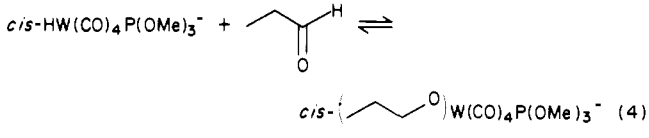
entry	acid	M	L	substrate	product	% yield (time, h)
III-1A	A	Cr	CO			95 (4)
III-1B	B	Cr	CO			65 (66)
III-2A	A	Cr	$P(OMe)_3$			11 (24)
III-2B	B	Cr	$P(OMe)_3$			71 (65)
III-3A	A	W	CO			92 (24)
III-4A	A	W	$P(OMe)_3$			45 (24)
III-5A	A	Cr	CO			90 (1 h)
III-5B	B	Cr	CO			65 (36)
III-6A	A	Cr	$P(OMe)_3$			31 (36)
III-6B	B	Cr	$P(OMe)_3$			73 (70)
III-7A	A	W	CO			100 (0.25)
III-8A	A	W	$P(OMe)_3$			90 (0.25)
III-8B	B	W	$P(OMe)_3$			95 (24)
III-9A	A	W	PPh_3			25 (24)
III-10A	A	W	$P(OMe)_3$			0 (24)
III-11B	B	W	$P(OMe)_3$			10 (72)
						1 (72)
			Other Hydrides			
III-12A	A		μ-$HW_2(CO)_{10}^-$			0 (24)[c]
						30 (24)[c]
III-12B	B		μ-$HW_2(CO)_{10}^-$			0 (24)[c]
						11 (24)[c]

[a] Reactions performed as described in footnote *a*, Table I, except where noted. [b] Reactions which gave low yields did so in proportion to the amount of hydride reagent lost to acid-promoted decomposition ($-H_2$) to the unreactive dimers μ-$H[M(CO)_4L]_2^-$; entries III-12A,B excepted. [c] Yields after 24 h at 80–100 °C.

With all of the group 6 hydrides, reactions 1 and 2 were quantitative and rapid. Yields in THF at room temperature were typically 98%, entry I-1. In contrast, the group 8 anionic hydride $HFe(CO)_4^-$ did not react with paraformaldehyde in the absence of acid, and it reduced paraformaldehyde in the presence of acid only slowly.

Propionaldehyde. When $HCr(CO)_5^-$ and $HW(CO)_5^-$ were used, very slow reaction with propionaldehyde was observed when no acid was added to the reaction mixture (Method I). That is, over the course of days, very little alkoxide analogous to **1** above was observed. Upon addition of acetic acid, a 98% yield of 1-propanol was obtained within 0.5–1 h, entry I-2.

The phosphite substituted hydride *cis*-$HW(CO)_4P(OMe)_3^-$ reacted more readily with propionaldehyde in the absence of acid, giving IR spectroscopic changes indicative of an anionic O-donor ligand complex: ν_{CO} 2005 (w), 1883 (s), 1838 (m), 1814 (w) cm^{-1}. Over the course of 1 h, the maximum changes in ν_{CO} correspond to ca. 80% conversion to the alkoxide, **2**, eq 4. Addition of acetic acid immediately gave propanol in 98% yield.



(4)

2

Benzaldehyde. The results of addition of 1 equiv of benzaldehyde to group 6 hydrides were similar to that reported above for propionaldehyde. Benzaldehyde reacted only sluggishly and incompletely with either $HW(CO)_5^-$ or $HCr(CO)_5^-$ in the absence of acid. In the presence of acid, however, reaction was consumated within 20 min at room temperature, as monitored by IR, to give benzyl alcohol in high yield.

The more hydridic $HW(CO)_4P(OMe)_3^-$ reacted immediately with benzaldehyde in the absence of acid (Method I) to give **3** (ν_{CO} 2001 (vw), 1882 (s), 1812 (m) cm^{-1}), as in eq 5. As expected,

$$cis\text{-}HW(CO)_4P(OMe)_3^- + PhCHO \rightleftharpoons cis\text{-}(PhCH_2O)W(CO)_4P(OMe)_3^- \quad (5)$$

the alkoxide **3** was immediately quenched even by weak acids such as H_2O to give benzyl alcohol. Proton NMR studies corroborated the appearance of **3** according to eq 5. When freshly distilled PhCHO was added to a THF solution of PPN^+ *cis*-$HW(CO)_4P(OMe)_3^-$, the aldehydic proton resonance at 10.31 ppm disappeared, as a peak at 5.6 ppm grew in. Addition of acetic acid destroyed this resonance, and a new peak at 4.70 ppm appeared. For comparison, control reactions included the in situ preparation of a THF solution of $Na^+OCH_2Ph^-$ (from Na^0 and $PhCH_2OH$) which gave a methylene resonance at 4.77 ppm. Addition of this solution to Et_4N^+ *cis*-$ClW(CO)_4PPh_2Me^-$ resulted in diminution of the resonance at 4.77 ppm and appearance of a new resonance at 5.45 ppm, assumed to be *cis*-$PhCH_2OW(CO)_4PPh_2Me^-$. Addition of a deficiency of acetic acid resulted in complete removal of the 4.77-ppm resonance with no loss of intensity of the 5.45-ppm peak. Further addition of acid was required to destroy the 5.45-ppm resonance. The new resonance which appeared was at 4.60 ppm (reference solution of $PhCH_2OH$ = 4.58 ppm in THF). Similar results were obtained in CD_3CN solvent. It must be stressed that the presence of adventitious proton sources, such as water or benzoic acid (impurity in PhCHO), can interfere with the observation of the metal-bound benzyloxide intermediate, **3**.

The facile reversibility of rection 5 was suggested by the following experiment. Benzaldehyde, $HW(CO)_4P(OMe)_3^-$, and CH_3OD were reacted in THF. The hydride (1 equiv) and methanol-d_1 (10 equiv) were added first to give $DW(CO)_4P(OMe)_3^-$, followed by benzaldehyde (10 equiv). Under these conditions, the benzyloxide product was somewhat hydrolyzed by the excess methanol to give the carbon-deuterated alcohol, PhCH(D)OD. (The level of enrichment here was not determined.) More importantly, the excess unreacted benzaldehyde was found to be significantly enriched with deuterium at the carbonyl carbon, based on the observation of a substantial ^2H NMR resonance (δ = 9.95) assigned to PhCDO. Thus it is demonstrated that $HW(CO)_4P(OMe)_3^-$ catalyzes reaction 6, an H/D exchange which, as established by control experiments, does not occur in the absence of the tungsten hydride.

$$PhCHO + CH_3OD \rightleftharpoons PhCDO + CH_3OH \quad (6)$$

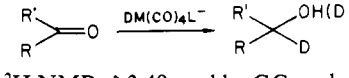
Yields in excess of 90% benzyl alcohol were obtainable with all of the hydrides discussed here, using the proper combination of acid and anionic metal hydride. Entries III-5A,5B and III-6A,6B in Table III demonstrate this point. Within 1 h the yield of $PhCH_2OH$ from the reaction of $HCr(CO)_5^-/PhCHO/CH_3COOH$ was 90%. Using the less acidic phenol gave a much slower reduction; after 36 h the yield was only 65%. The rate was enhanced on going to the combination $HCr(CO)_4P(OMe)_3^-/PhOH$ (entry III-6B), but attempts to use the phosphite-substituted $HCr(CO)_4P(OMe)_3^-$ with the stronger acid HOAc gave extensive loss of hydride ($-H_2$) and lower yields, entry III-6A. Reaction of benzaldehyde with $HW(CO)_5^-$ (entry III-7A) and $HW(CO)_4P(OMe)_3^-$ (entry III-8A) was so fast that these hydrides successfully tolerated the strong acid HOAc. Reasonable yields were also obtained with PhOH, entry III-8B. The anion $HW(CO)_4PPh_3^-$ was not effective as a reducing agent for benzaldehyde with HOAc, due to extensive decomposition of this hydride ($-H_2$), entry III-9A.

Reduction of Ketones. Compared with aldehydes, ketones were less readily reduced to alcohols by the reagents $HM(CO)_4L^-$. Nevertheless, as shown in Tables I, II, and III, a range of ketones do react at room temperature, in THF solvent, in the presence of 1 equiv of acid. The yields reported here are improved by use of lower temperatures, longer reaction times, or excess hydride reagents. Slow addition of dilute acids to solutions of the ketone and hydride in THF also gives yields which are improved over those reported here. In contrast to aldehydes, none of the ketones studied here reacted with the hydrides $HM(CO)_4L^-$ in the absence of acid. Thus no spectroscopic changes indicative of partially reduced intermediate alkoxides were observed upon reaction of any of the ketones with any of the hydrides. Reduction to alcohol proceeded only upon addition of acid.

Reactions could be monitored with ^2H NMR by pre-equilibrating the hydrides with 1 to 2 equiv of DOAc (Method III) and then adding the ketone. Under these conditions α-deuterated alcohols were produced with high (>90%) deuterium enrichment. Specific examples are mentioned below.

Cyclohexanone. Reduction of cyclohexanone was studied extensively as a model for ketones in general. Reduction with $HCr(CO)_5^-/HOAc$ (entry I-5) gave cyclohexanol in high yield within 2 h at room temperature. The yield was determined by GC analysis of the product solution as well as by monitoring the disappearance of the ketone carbonyl absorption at 1720 cm^{-1} in the infrared spectrum. The metal-containing product was $Cr(CO)_5OAc^-$, ν_{CO} 2061 (w), 1918 (s), 1850 (m) cm^{-1}.[25] The alcohol product was identified conclusively by GC/MS analysis and comparison with an authentic sample. As indicated in entries II-1A-D, the reduction was fastest when the strong acid HOAc was used. PhOH (entry II-1B) eventually gave acceptable yields (90%), but the reaction was slow (only 52% yield after 24 h). Weaker acids such as water (entry II-1C) gave slow reaction, and the weakest acid methanol (entry II-1D) did not promote reduction at all. The more hydridic $HCr(CO)_4P(OMe)_3^-$, in conjunction with the strong acid HOAc, was not useful as a reductant (entry II-2A) due to HOAc-promoted elimination of dihydrogen. This decomposition was avoided by use of the weaker acid PhOH (entry II-2B).

All of the hydrides $HM(CO)_4L^-$, when pre-equilibrated with 1 equiv of DOAc, delivered deuterium to the carbonyl carbon of cyclohexanone, as in eq 7. The C-1 deuterated cyclohexanol was



(7)

identified by ^2H NMR, δ 3.49, and by GC analysis. Comparison of the integrated intensities of the pre-equilibrated deuteride ($DM(CO)_4L^-$ before addition of cyclohexanone) and of the deuterated cyclohexanol product indicated very efficient (>90%) transfer of deuterium to the carbonyl carbon. Some label was also surely lost to exchange between the first formed protio-alcohol product and the as yet unreacted $DM(CO)_4L^-/HOAc$, to give cyclohexanol-d_1. It was not possible to determine the extent of this due to the coincidence of the resonances for THF–solvent

(natural abundance ^2H), DOAc, and the expected small percentage of alcohol-d_1 product. Other ketones which were studied were also deuterated at the carbonyl carbon by the reagents $HM(CO)_4L^-$/DOAc.

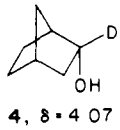
In efforts to probe the mechanism of the reductions of ketones in general, rates of cyclohexanone reduction were compared in the presence and in the absence of CO (as a saturated solution in THF). The presence of excess CO did not affect the rates of cyclohexanone reduction. Also, the reagent mixture $HCr(CO)_5^-$/HOAc did not exchange coordinated CO with excess ^{13}CO within the 2 h typically needed for extensive reduction of cyclohexanone. Thus lability on the part of the CO ligands in $HM(CO)_4L^-$ is not needed for efficient reduction of ketones.

Cyclopentanone. One equivalent of the reagents $HM(CO)_4L^-$/HA was not as efficient for the reduction of cyclopentanone as was the case for cyclohexanone above. $HCr(CO)_5^-$/HOAc gave 35% conversion to cyclopentanol (entry I-6). Yields could be increased greatly by use of excess hydride reagent. The best yield under stoichiometric conditions was obtained with the strongly hydridic $HCr(CO)_4P(OMe)_3^-$ used with the weak acid PhOH (entry II-4B). For synthetic purposes, yields reported in Table II are improved with longer reaction times. The data of Tables I and II, however, indicate less facile reduction for 5-membered-ring ketones, as is the case with the borohydride reagents.

2-Butanone. Reduction of 2-butanone by the reagent $HCr(CO)_5^-$/HOAc (entry I-4) gave 2-butanol in 70% yield. The reaction was slow, giving only 47% yield of 2-butanol after 24 h (entry II-5A). The weak acid phenol promoted reduction much more sluggishly (entry II-5B). Yields were not improved by use of the more hydridic reagent $HCr(CO)_4P(OMe)_3^-$ (entry II-6A), except where it was used in conjunction with phenol (entry II-6B).

Acetophenone. The reagent $HCr(CO)_5^-$/HOAc gave a 45% yield of secondary phenethyl alcohol (entry I-7) when used in stoichiometric amounts. This ketone was also reduced more slowly than the related benzaldehyde.

Norbornanones. Some stereoselectivity was observed in the reduction of 2-norbornanone (entry I-8A,B). $HCr(CO)_5^-$/HOAc preferentially gave the *endo*-norborneol **4** (50% yield, entry I-8B) rather than the *exo*-norborneol (2% yield, entry I-8A). The reagent $HCr(CO)_5^-$/HOAc was much less reactive toward the sterically hindered camphor (entry I-9), giving, in contrast, the exo alcohol, as determined by GC analysis. ^2H NMR was especially useful in identifying the products of these reductions, as follows: The reagents $HCr(CO)_5^-$/DOAc were pre-equilibrated in THF and the norbornanone was added subsequently (Method III). Deuteration at the α-carbon was confirmed by observation of the ^2H NMR resonance as shown below



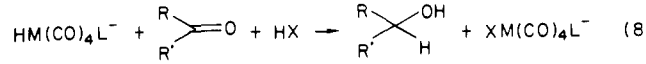
4, δ = 4.07

The chemical shift shown above is characteristic of stereochemistry.[26] Use of ^2H NMR circumvented the usual problem with norbornane systems: endo and exo protons are normally obscured by the envelope of resonances associated with the rest of the ring system.

Reduction of Epoxides. Under stoichiometric conditions, the epoxides styrene oxide and cyclohexene oxide were not reduced by any of the hydrides (Entries I-10, I-11, III-10A), except the strongly hydridic $HW(CO)_4P(OMe)_3^-$ in conjunction with the weak acid PhOH (Entry III-10B), where 10% yield of secondary phenethyl alcohol was achieved after 3 days at room temperature, along with a trace of the primary alcohol. Better yields were obtained with the hydride-bridged dimer anion μ-$HW_2(CO)_{10}^-$, which showed a preference for the formation of the primary phenethyl alcohol (entry III-12A,B).

Discussion

With these latest results, the group 6 hydrides $HM(CO)_4L^-$ and the corresponding deuterides $DM(CO)_4L^-$ are shown to be useful reductants for ketones and aldehydes. The reaction consumes an equivalent of acid, as shown in eq 8, where R, R′ = alkyl,



(8)

aryl, hydrogen; M = Cr, W; L = CO, $P(OMe)_3$, PPh_3; and HX is a Brønsted acid. Since reaction of the hydrides with alkyl halides[8a,c] and acyl chlorides[8d] does not require acid, a natural and useful selectivity is therefore available. Because the weak acid methanol does not promote reduction of aldehydes (See Table II), it can be used safely as a pre-equilibration reagent, eq 9, to give the deuterides.[8b] The deuterides which are prepared by this

$$HM(CO)_4L^- + CH_3OD \rightleftharpoons DM(CO)_4L^- + CH_3OH \quad (9)$$

in situ method are then useful (even in the presence of the methanol reagent of eq 9) for the selective reduction of acyl chlorides to aldehydes. Further reduction of aldehyde to alcohol requires a second equivalent of hydride and a stronger Brønsted acid.

When reduction of ketones or aldehydes is desired, an acid can be chosen to promote the reduction without decomposing the hydride as in eq 3. For most aldehydes, where reduction can be performed in a stepwise fashion to give presumed metal-bound alkoxides, weak acids such as phenol and H_2O are sufficiently acidic to hydrolyze the metal alkoxides to alcohol. For ketones, a stronger acid such as HOAc was required, because the acid assistance requirement was greater. Still, for reductions of ketones with the strongly hydridic, phosphite-substituted hydrides such as $HW(CO)_4P(OMe)_3^-$, it was possible to use weaker acids and obtain respectable yields. Although a determination of relative reactivity is not straightforward in these reactions, under comparable conditions the order is *cis*-$HW(CO)_4P(OMe)_3^-$ > $HW(CO)_5^-$ > $HCr(CO)_5^-$. This order is the same as that for hydride/halide displacement reactions observed for primary alkyl halides[8a] and acyl chlorides.[8d]

The mechanism for these reductions of aldehydes and ketones appears to involve nucleophilic attack by the hydride at the carbonyl carbon. For aldehydes, this leads straightforwardly to observable alkoxides in the absence of acid. No such intermediates were observed for reduction of ketones. The group 6 hydrides are, evidently, not hydridic enough for this. On the other hand, the oxophilic zirconium reagent, Cp_2ZrH_2, reduces ketones to alkoxides,[14] as do the borohydrides.[3b] The less hydridic $HFe(CO)_4^-$[8a] requires stronger acids such as CF_3CO_2H to promote reduction of ketones; no intermediate species were observed either in the absence of the presence of acid.[28] The activation of ketones by addition of perfluoroalkyl substituents has also promoted metal hydride addition reactions.[14,28] Group 8 transition-metal alkoxides have recently been isolated from the reaction of fluoroketones with the metal hydrides $HCo(N_2)L_3$, $HRhL_4$, and H_2RuL_4 (L = PPh_3).[27]

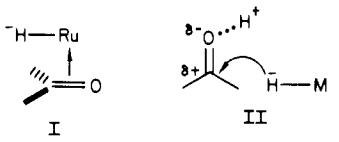
The mechanism for the reduction of ketones does not require lability by the ligands in the reductant $HM(CO)_4L^-$. If this were not true, the rates of reduction of cyclohexanone would have been sensitive to excess CO ligand. The combined reagent $HCr(CO)_5^-$/HOAc also does not exchange with free ^{13}CO. These results do not support, for these coordinately saturated group 6 anionic hydrides, the associative mechanism suggested by Gray, Pez, and Waller, where coordination to the metal center by the ketone carbonyl (I) precedes reduction.[20]

The acid dependences reported here indicate that the ketone carbonyl must be activated toward nucleophilic attack as in II. This sort of activation would be less important for ketones of great

(26) The Sadtler Index NMR spectra assigns the resonance at 4.19 ppm ($CDCl_3$ solution) to the H on the alcoholic carbon of *endo*-2-norbornanol while the analogous hydrogen in the exo isomer is at 3.72 ppm.

(27) Pettit, R.; Kao, S. C., unpublished results.

(28) Hayashi, Y.; Komiya, S.; Yamamoto, T.; Yamamoto, A. *Chem. Lett.* **1984**, 1963.



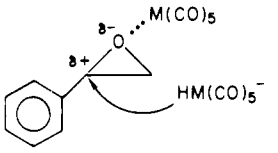
I II

polarity, i.e., the fluoroketones.

Some associative character in the reduction of ketones is suggested by the steric effects reported here. Straight-chain ketones and more substituted ketones such as acetophenone are less readily reduced. The norbornanone system is most favorably reduced from the less hindered side to give the endo alcohol (entry I-8B). The severely congested camphor is not reduced effectively (entry I-9). As for the borohydrides,[3r] cyclopentanone is less readily reduced then cyclohexanone.

The group 6 hydrides do not reduce epoxides, $HW(CO)_4P(OMe)_3^-$ excepted (entry III-11). Even this, the most hydridic of the group 6 hydrides, reacts only sluggishly with styrene oxide. Better yields were obtained with the dimeric hydride-bridged μ-$HW_2(CO)_{10}^-$, entries III-12. Here a 30% yield of primary phenethyl alcohol was obtained at 80–100 °C, after 24 h. The dimeric hydride is known to disassociate at these temperatures, as in eq 10.[23,29] The Lewis acid fragment $[M(CO)_5^0]$ might

$$\mu\text{-}HM_2(CO)_{10}^- \rightleftharpoons HM(CO)_5^- + [M(CO)_5] \qquad (10)$$



III

promote reduction of the epoxide as in structure III. This is similar to the cation-assisted epoxide ring opening by Na^+ or K^+ salts of $CpFe(CO)_2^-$.[30] It is interesting that reduction of styrene oxide by μ-$HM_2(CO)_{10}^-$ gives the primary phenylethyl alcohol, while the monomeric $HW(CO)_4P(OMe)_3^-$ favors the secondary phenethyl alcohol, entry III-IIB. This may be explained on the basis of steric effects.

The ease with which the hydrides $HM(CO)_4L^-$ add to carbon centers (in the absence of added H^+) follows the general order acyl chlorides[8d] > alkyl halides[8a,c] $\rightleftarrows$ aldehydes > ketones. This follows the trend one expects for reactions involving hydride transfer reagents, and it further establishes the hydridic character of the reagents $HM(CO)_4L^-$. We have little evidence which would further define the H^- transfer, i.e., whether by heterolytic M–H^- bond cleavage and H^- transfer in the collision complex or by a stepwise single-electron transfer to the organic carbonyl group followed by H· abstraction. Since the negative charge is hydride rather than metal based,[32] it is unlikely that α-hydroxyalkyl complexes are serious contenders as possible intermediates.[22b] Earlier a case was made for increased hydridic character (H^- transfer capability) in the P-donor ligand substituted hydrides such as $HW(CO)_4P(OMe)_3^-$.[8a] This is the most likely explanation for the enhanced reactivity of such reagents over the all-carbonyl $HW(CO)_5^-$ reagent as observed in this study of carbonyl reduction. The role of the organic substrate in governing electron transfer vs. H^- transfer is recognized, however. In this regard we mention preliminary studies which attempted to identify SET vs. hydride transfer character in anionic transition-metal hydrides. The reduction of nitrobenzene to aniline is expected to require extensive electron-transfer character on the part of reducing agents.[31] The P-substituted anion $HW(CO)_4P(OMe)_3^-$ is no better than $HW(CO)_5^-$ as a reductant for nitrobenzene.[32] Both reagents are poorer than $HFe(CO)_4^-$ in this process.[31] The implication is that the group 6 transition-metal hydrides, particularly the phosphorus-donor-ligand derivatives, are better H^--transfer reagents than electron-transfer reagents. Hydride transfer as H^- is most appealing for the acid-assisted carbonyl reductions reported above.

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Registry No. CH_3OH, 67-56-1; $CH_3(CH_2)_2OH$, 71-23-8; $PhCH_2OH$, 100-51-6; $CH_3CH_2CH(OH)CH_3$, 78-92-2; $PhCH(OH)CH_3$, 98-85-1; $Ph(CH_2)_2OH$, 60-12-8; CH_2O, 50-00-0; CH_3CH_2CHO, 123-38-6; PhCHO, 100-52-7; $CH_3CH_2COCH_3$, 78-93-3; $PPN^+Cr(CO)_4CO^-$, 95340-84-4; $PPN^+Cr(CO)_4P(OMe)_3^-$, 95217-20-2; $PPN^+HW(CO)_4CO^-$, 78709-76-9; $PPN^+HW(CO)_4P(OMe)_3^-$, 95248-67-2; $PPN^+HW(CO)_4PPh_3^-$, 82963-30-2; μ-$HW_2(CO)_{10}$, 73740-64-4; *exo*-1,7,7-trimethyl-2-norbornanol, 124-76-5; cyclohexanone, 108-94-1; 1,7,7-trimethyl-2-norbornanal, 76-22-2; cyclohexanol, 108-93-0; cyclopentanol, 96-41-3; *exo*-2-norbornanol, 497-37-0; *endo*-2-norbornanol, 497-36-9; cyclopentanone, 120-92-3; acetophenone, 98-86-2; 2-norbornanone, 497-38-1; cyclohexene epoxide, 286-20-4; phenyloxirane, 96-09-3.

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