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Anionic Group 6 Hydrides and Carboxylates as Homogeneous Catalysts for Reduction of Aldehydes and Ketones

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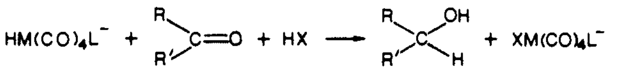
Abstract: The catalytic reduction of aldehydes and ketones to alcohols has been successfully effected through the use of $M(CO)_5B^-$ (M = Cr, W, Mo; B = Brønsted base) under hydrogen pressure in THF or MeOH. Both organic ($CH_3CO_2^-$) and inorganic [$Mn(CO)_5^-$] Brønsted bases have been utilized for these reactions. Mechanistic models of this process include the ligand-assisted heterolytic cleavage of H_2, an alkoxide-stabilized oxidative-addition dihydride, or an η^2-H_2 group 6 metal carbonyl as intermediates which are expected to produce a highly reactive group 6 anionic hydride. Subsequent steps involve hydride attack on the carbonyl carbon followed by protonation to produce the alcohol.

The use of main group metal hydrides, such as $LiAlH_4$, for the reduction of aldehydes and ketones suffers from the drawback that stoichiometric quantities of these reagents are required.[1a] Transition-metal hydrides may serve as attractive alternatives, rendering these reduction processes involving less active substrates catalytic in metal. For example, cationic $RhH_2(PMe_3)_2L_2^+$ complexes have been found to catalyze the reduction of ketones under mild conditions in the presence of small quantities of water.[1b] In addition, the anionic hydride complex, $RuH_2(PPh_3)_2(PPh_2C_6H_4)^-$, has been demonstrated to catalytically hydrogenate ketones and aldehydes.[1c] Mechanistically both these processes are thought to proceed via the intermediary of metal alkoxides. The similarity in catalytic properties of anionic ruthenium and cationic rhodium hydrides was manifested further in studies which reveal these species to behave as active catalysts or catalyst precursors for the hydrogenation of anthracene.[1d]

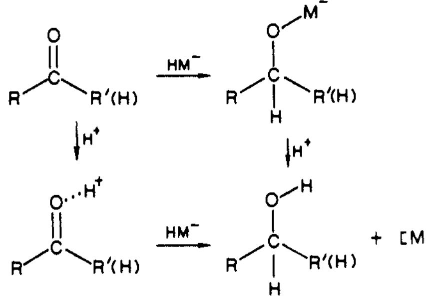
Recently we reported the stoichiometric conversion of aldehydes and ketones to alcohols using anionic group 6 carbonyl hydrides ($HM(CO)_5^-$ (M = Cr, W) and *cis*-$HW(CO)_4PR_3^-$ (R = OMe, Ph)) in the presence of a slight excess of organic acid or H_2O.[2] A variety of aldehydes and ketones were reduced, and product yields were found to be dependent upon both the hydride and acid used.



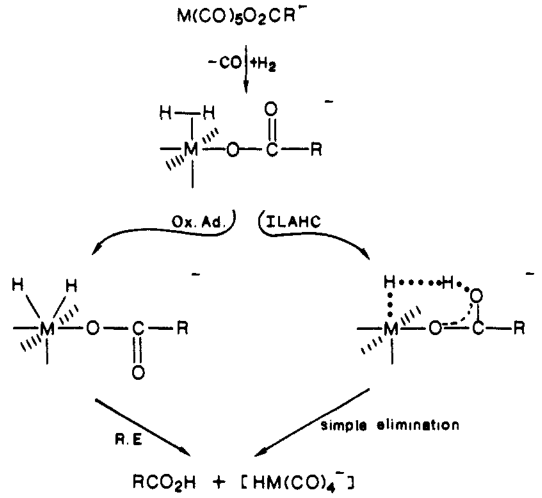
$$HM(CO)_4L^- + RR'C{=}O + HX \longrightarrow RR'C(OH)H + XM(CO)_4L^- \quad (1)$$

R, R' = alkyl, aryl, hydrogen; L = CO, P(OMe)$_3$, PPh$_3$; M = Cr, W; HX = bronsted acid

Scheme I



Scheme II



Two pathways were proposed to be operative in these reductions (Scheme I). In the first, appropriate for the reaction of formaldehyde or benzaldehyde with anionic hydride, an intermediate metal alkoxide was spectroscopically observable in the absence of added acid. Quenching with acid resulted in the formation of the alcohol. In the second pathway, less reactive aldehydes and all ketones first needed the addition of acid, presumably to activate the C–O double bond for nucleophilic attack by the hydride. In these cases, in the absence of added acids, no reaction leading to observable intermediate alkoxides occurred.

In a separate study on the catalytic hydrogenation of CO_2 to yield, in the presence of alcohol solvent, alkyl formates, similar anionic hydrides, $HM(CO)_5^-$ and μ-$HM_2(CO)_{10}^-$, as well as $RCO_2M(CO)_5^-$ (R = CH_3, H) were found to be effective catalysts.[3] Since the insertion of CO_2 into anionic metal hydrides is a well-known, low-energy process, two possibilities, as shown in Scheme II, were suggested for the main energy barrier to the catalysis. The scheme begins with CO loss from the starting acetate or formate and is followed by H_2 addition, initially as an η^2-H_2-complex.[4] Subsequent oxidative addition and reductive elimination would yield the products of acid and hydride. Alternatively and more appealing, intramolecular ligand assisted

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(1) (a) See, for example: Fieser, M.; Fieser, L. F. *Reagents for Organic Synthesis* Wiley-Interscience: New York; Vol. 2, p 243. (b) Schrock, R. R.; Osborn, J. A. *Chem. Commun.* **1970**, 567. (c) Grey, R. A.; Pez, G. P.; Wallo, A.; Corsi, J. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 235. (d) Halpern, J. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 244.

(2) (a) Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428. (b) Kao, S. C.; Gaus, P. L.; Youngdahl, K.; Darensbourg, M. Y. *Organometallics* **1984**, *3*, 1601.

(3) Darensbourg, D. J.; Ovalles, C. *J. Am. Chem. Soc.* **1984**, *106*, 3750.

(4) (a) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451. (b) Upmacis, R. K.; Gadd, G. E.; Poliakoff, M.; Simpson, M. B.; Turner, J. J.; Whyman, R.; Simpson, A. F. *J. Chem. Soc., Chem. Commun.* **1985**, 27. (c) Church, S. P.; Grevels, F.-W.; Herman, H.; Schaffner, K. *J. Chem. Soc., Chem. Commun.* **1985**, 30. (d) Sweany, R. L. *J. Am. Chem. Soc.* **1985**, *107*, 2374.

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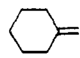
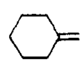
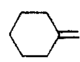
Table I. Catalytic Hydrogenation of Benzaldehyde and Cyclohexanone with $PPN^+ M(CO)_5(OAc)^-$ in THF Solution[a]

				metal carbonyl products[c]		
entry	M	substrate	turnovers[b]	$M(CO)_5OAc^-$	$M(CO)_6$	μ-$HM_2(CO)_{10}^-$
1	W		10.1	70	5	25
2	W	PhCHO	16.8	85	5	10
3	Mo		3.5	95	5	
4	Mo	PhCHO	17.5	95	5	
5	Cr		18	15	35	50
6	Cr	PhCHO	16.4	20	20	60

[a] $[PPN^+ M(CO)_5OAc^-] = 0.010$ M; [substrate] = 0.20 M; initial pressure of H_2 = 600 psig at room temperature loading, 700 psig at operating temperature, 125 °C. [b] Turnovers defined for 24 h as mmol of alcohol formed/mmol of catalyst used. Alcohols, cyclohexanol, and benzyl alcohol, identified and quantitated by GLC with a Perkin Elmer Sigma 2 gas chromatograph with FID; carbowax, 2M column. [c] Product distribution estimated from ν(CO) IR (IBM FTIR 85). Organometallic product recovery ≥95%.

heterolytic cleavage (ILAHC) provides a simple path to the products without invoking drastic electronic rearrangements.[3,5]

Since the products formed in this process, carboxylic acid and metal hydride, are those needed to effect aldehyde/ketone reduction, the two experiments were combined to produce a group 6 based system for catalytic reduction of those functional groups. Herein, we report the results of these studies.

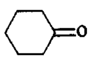
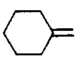
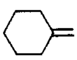
Experimental Section

All syntheses and sample transfers were performed under O_2-free conditions by standard techniques (drybox, Schlenk-line (N_2)). Reactions were performed in 10-mL stainless steel microreactors under an atmosphere of the appropriate gas (H_2, N_2, D_2, or CO). Initial gas-loading pressures were 600 psig at 23 ± 2 °C. Reactions were run at 125 °C with stirring for a 24-h period.

(A) Materials. The solvents tetrahydrofuran (THF) and methanol (MeOH) were distilled from the appropriate drying and oxygen-scavenging agents immediately prior to use. Common reagents were obtained from standard vendors (Aldrich and Strem Chemical Co.). Benzaldehyde and cyclohexanone were fractionally distilled under nitrogen before use. Other reagents were degassed and otherwise used as received. Preparations of the following were as reported in the literature: $PPN^+M(CO)_5(OAc)^-$ (M = Cr, Mo, W; PPN^+ = bis(triphenylphosphine)iminium; $OAc^- = O_2CCH_3^-$);[3] $PPN^+\mu$-$HM_2(CO)_{10}^-$ (M = Cr, W);[6a] $Et_4N^+(\mu$-$H)Mo_2(CO)_{10}^-$;[6b] $PPN^+MnCr(CO)_{10}^-$;[7] $PPN^+HM(CO)_5^-$ (M = Cr, W);[8] $PPN^+W(CO)_4(PMe_3)(OAc)^-$.[9] The Et_4N^+ salt of $W(CO)_5OPh^-$ was prepared by reaction of $W(CO)_5 \cdot THF$ with $Et_4N^+OPh^-$ under CO.[10c] Research grade hydrogen and carbon monoxide were purchased from Air Products. Deuterium was purchased from Airco. Gases were passed through Gas Purifier cartridges (Matheson) before use.

(B) Instrumentation. Infrared spectra were obtained on a Perkin-Elmer 283B spectrophotometer or an IBM FTIR/85 spectrometer with 0.1 mm CaF_2 solution cells. ^2H NMR spectra were measured on a Varian XL200 spectrometer. Alcoholic product analysis was monitored by GLC on a Perkin-Elmer Sigma 2 gas chromatograph with flame ionization detector. A 10% Carbowax on Chromosorb W H.P. column with 80/100 mesh, 2M × $^1/_8$ in stainless steel tubing was used in the analysis. GC/MS data were collected at the Texas A&M Center for Trace Characterization on a Hewlett Packard 5710A gas chromatograph in line with a Hewlett Packard 5980 mass spectrometer. Other mass spectral data were collected on a KRATOS MS 50 TA. GC/FTIR studies were performed on the combination of a Perkin-Elmer Sigma 3B gas chromatograph interfaced with an IBM FTIR/85.

Table II. Catalytic Hydrogenation of Benzaldehyde and Cyclohexanone with μ-$HM_2(CO)_{10}^-$ in THF Solution[a]

entry	M	substrate	turnovers[b]	catalyst recovery, %
7	W		11.6	95
8	W	PhCHO	16	85
9	Mo		18	90
10	Mo	PhCHO	8.6	50
11	Cr		4.1	95
12	Cr	PhCHO	14.4	60

[a] Catalyst:substrate = 1:20; 125 °C, 24 h. [b] Cr and W as PPN^+ salts. Mo as Et_4N^+ salt.

(C) Reactions. (1) Reductions with $PPN^+M(CO)_5OAc^-$ Catalysts: Cyclohexanone or Benzaldehyde. In a typical experiment, the acetate catalyst (0.05 mmol) was weighed into a vial and covered with a serum cap, and the system was evacuated. In a separate and evacuated vessel were mixed 5 mL of THF, the substrate (1 mmol, 20-fold excess), and a weighed out amount of internal standard (hexane). The two vessels and the minireactor were placed inside the drybox where the catalyst and substrate solution were subsequently mixed and sealed inside the reactor. Upon removal from the glovebox, the reactor was pressurized to 600 psig of hydrogen at room temperature and left to stir for 24 h at 125 °C. Product analyses were by GLC, GC/MS, or GC/IR for organics. Organometallic products were identified by IR. Yields of organometallic products were determined spectrophotometrically. Results are listed in Table I.

(2) Control Experiments. (a) Reductions were carried out with μ-$HM_2(CO)_{10}^-$ in an identical manner to those described above except the bridging carbonyl hydrides of Cr, Mo, or W were used as catalyst precursor either as their PPN^+ or Et_4N^+ salts. Results are listed in Table II. (b) In other control experiments, metal carbonyl catalyst precursor, solvent, or pressurizing gas were changed. These were run in an analogous manner to 1. Results are listed in Table III. (c) Periodic blank experiments were carried out in the microreactors. Benzaldehyde, solvent, and internal standard were pressurized in the bomb with hydrogen and left to stir for 24 h. No reduced product was ever observed at the end of these runs.

(3) Deuterium Labeling Studies. A catalyst solution comprised of $PPN^+W(CO)_5OAc^-$/cyclohexanone/THF/internal standard was loaded in the minireactor and pressurized with deuterium (600 psig at room temperature). After 24 h at 125 °C, the products were analyzed. GC/MS revealed *d*-label incorporation in the alcoholic product and in the remaining substrate. PPN^+ μ-$DW_2(CO)_{10}^-$ was formed in 40% yield as determined by IR and was identified as the deuteride by its charac-

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(5) (a) Halpern, J.; Milne, J. B. *Second International Congress on Catalysis*; Technip: Paris, 1961; p 445. (b) Halpern, J. *J. Organomet. Chem.* **1980**, *200*, 133. (c) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1983**, *2*, 682. (d) James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319. James, B. R. *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press Ltd.: Great Britian, 1982; Vol. 8, Chapter 51, p 285.

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Table III. Control Experiments Associated with the Catalytic Hydrogenation of Cyclohexanone by Anionic Group 6 Metal Carbonyl Derivatives at 125 °C, 700 psig[a]

entry	catalyst	gas	solvent	turnovers	distribution of organometallic products
13	$W(CO)_6$	H_2	THF	0	100%, $W(CO)_6$
14	$W(CO)_5OAc^-$	N_2	THF	0	20%, $W(CO)_6$ 80%, $W(CO)_5OAc^-$
15	$W(CO)_5OAc^-$	D_2	THF	6.7	5%, $W(CO)_6$ 55%, $W(CO)_5OAc^-$ 40%, μ-$DW_2(CO)_{10}^-$
16	$W(CO)_5OAc^-$	CO/H_2[b]	THF	1.3	80%, $W(CO)_6$ 20%, $W(CO)_5OAc^-$
17	*cis*-$W(CO)_4(PMe_3)(OAc)^-$	H_2	THF	0	decomposed
18	$HW(CO)_5^-$	H_2	THF	3.9	5%, $W(CO)_6$ 95%, μ-$HW_2(CO)_{10}^-$
19	μ-$HW_2(CO)_{10}^-$	H_2	THF	11.6	5%, $W(CO)_6$ 95%, μ-$HW_2(CO)_{10}^-$
20	μ-$HW_2(CO)_{10}^-$[c]	N_2	THF	.2	5%, $W(CO)_6$ 95%, μ-$HW_2(CO)_{10}^-$
21	$W(CO)_5OAc^-$	H_2	MeOH	13.2	75%, $W(CO)_6$ 25%, μ-$HW_2(CO)_{10}^-$
22	μ-$HW_2(CO)_{10}^-$	H_2	MeOH	17	60%, $W(CO)_6$ 40%, μ-$HW_2(CO)_{10}^-$
23	$MnCr(CO)_{10}^-$	H_2	THF	2.1	>90%, $MnCr(CO)_{10}^-$

[a] See footnotes to Table I and Experimental Section. [b] Initial loading P_{CO} = 100 psig, P_{H_2} = 500 psig. [c] K^+ salt.

teristic resonance in the ^2H NMR spectra at −12.7 ppm.

(4) H_2/D_2 Activation. To a stainless-steel 10-mL microreactor was added 50 mg of $PPN^+Cr(CO)_5OAc^-$ in 5 mL of THF. A pressure mixture of 300 psi of H_2:300 psi of D_2 (1:1) was loaded at 25 °C. The reactor was brought to and maintained at 125 °C for 24 h at which time the gas layer was analyzed by mass spectrometry. MS revealed the formation of HD. IR analysis of the organometallic products showed 75% μ-$DCr_2(CO)_{10}^-$ + μ-$HCr_2(CO)_{10}^-$, 10% $Cr(CO)_6$, and 15% PPN^+-$Cr(CO)_5OAc^-$. A reactor run simultaneously containing only THF and 600 psi of the H_2/D_2 mixture showed no HD formation.

(5) High-Pressure FTIR Studies. High-pressure FTIR experiments were carried out as described by Moser et al.,[11] making use of a cylindrical internal reflectance cell with a silicon crystal in a Parr autoclave, generously supplied by Spectra Tech, Inc. (Barnes Analytical). In a typical experiment, catalyst, substrate, and solvent were loaded inside the autoclave in the drybox and sealed. Brought outside, the bomb was slowly pressurized to 660 psig of hydrogen at ambient temperature. Placed inside the optical bench of the IBM FTIR/85, the bomb was heated to 125 °C and reached a final pressure of 740 psig. Spectra were periodically taken of the solution. Control experiments were run in an analogous manner, except Ar was used as the pressurizing gas.

(6) Synthesis of [PPN][W(CO)$_4$(OAc)THF]. In a typical preparation, 0.15 g of $PPNW(CO)_5OAc^-$ was dissolved in 60 mL of THF and photolyzed (Hanovia-Hg-450W lamp) for 5–5.5 h. The resulting orange solution exhibited bands in the FTIR carbonyl region at 1998 (w), 1858 (s), 1842 (m), and 1808 (m) cm^{-1}. The adduct, $PPNW(CO)_4(OAc)$-(THF), was formed in approximately 85% yield. **(a) Reaction with CO.** The [PPN][W(CO)$_4$(OAc)(THF)] adduct was exposed to ~1 atm of CO at room temperature. A color change from orange to yellow was observed along with IR bands consistent with [PPN][W(CO)$_5$OAc$^-$] (2059 (w), 1955 (sh), 1907 (s), 1842 (m) cm^{-1}). **(b) Reaction with PMe$_3$.** To 20 mL of a 2.7 × 10^{-3} M solution of the THF adduct was added 10 μL of PMe_3 (~3 equiv). IR bands characteristic of $PPNW(CO)_4$-$(OAc)(PMe)_3$ were observed.[9]

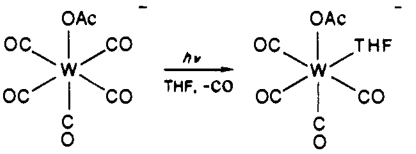
(7) Reaction of Hydrogen with $Et_4N^+W(CO)_5OPh^-$. To 100 mg of a sample of $Et_4N^+W(CO)_5OPh^-$ was added 5 mL of THF in the drybox. The solution was sealed inside the minireactor and brought outside. The reactor was pressurized to 600 psig of hydrogen at room temperature and heated to 125 °C for 24 h. Product analysis by GLC showed the formation of phenol. Infrared analysis showed the organometallic products to be comprised of $W(CO)_6$ (~10%), μ-$HW_2(CO)_{10}^-$ (~85%), and an unknown product with ν(CO) band at 1914 cm^{-1} making up ~5% of the reaction solution.

Results and Discussion

The anionic group 6 acetates, $M(CO)_5OAc^-$, as their bis(triphenylphosphine)iminium (PPN^+) salts, have been found to be catalysts for the hydrogenation of cyclohexanone and benzaldehyde to cyclohexanol and benzyl alcohol, respectively, with turnover numbers per 24 h generally >15. The conditions for the reaction were moderate pressures of hydrogen (600 psig at ambient temperature) and a reaction temperature of 125 °C. Table I summarizes the results of these reactions.

As shown in Table I, both $M(CO)_6$ and μ-$HM_2(CO)_{10}^-$ may be formed over the course of the catalytic cycle. The $M(CO)_6$ species (inactive as a catalyst, Table III) is the result of the decomposition of $M(CO)_5OAc^-$ under the reaction conditions. The dimer hydride μ-$HM_2(CO)_{10}^-$ arises from the known reaction of $HM(CO)_5^-$ and $M(CO)_5^\circ$ or $M(CO)_6$,[12] and its presence is evidence that reactive monomeric anionic hydrides are generated under reaction conditions. A separate experiment showed that μ-$HW_2(CO)_{10}^-$ is generated from $W(CO)_5OAc^-$ and H_2 in the absence of aldehyde or ketone. Table II lists results from catalytic runs made with the dimer hydrides as catalyst precursors. In all cases but that of Cr, the dimer hydrido species were found to be at least as active as the acetate complexes for hydrogenation of cyclohexanone and benzaldehyde.

In situ FTIR spectra were taken over the course of a catalytic run with $PPN^+W(CO)_5OAc^-$ as catalyst precursor and cyclohexanone as substrate. Observed over a typical 24-h reaction period were bands corresponding to the acetate, μ-$HW_2(CO)_{10}^-$, and new bands at 1861 cm^{-1} (m) and 1805 cm^{-1} (w) *existing* only at 125 °C (Figure 1). These new bands correspond to a $W(CO)_4OAc^-$ species as its THF adduct. A separate photochemical experiment showed the same infrared band pattern could be generated upon photolysis of the pentacarbonyl tungsten acetate in THF solution.



(2)

Carbon monoxide was found to inhibit the catalysis. In a reaction with initial loading pressure of 100 psig of CO and 500 psig of H_2, the product yield of reduction of cyclohexanone was markedly decreased (Table III, entry 16). Under these conditions a large amount of $W(CO)_6$ was formed, thus loss of active catalyst most likely accounts for the decrease in conversion.

Use of D_2 instead of H_2 yielded cyclohexanol-d_1 and -d_2, entry 15, Table III. In addition, the unreacted cyclohexanone was found to be substantially enriched in deuterium. The fragmentation

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[11] Moser, W. R.; Cnosser, J. E.; Wang, A. W.; Krouse, S. A. *J. Catal.* **1985**, *95*, 21.

[12] Darensbourg, M. Y.; Deaton, J. C. *Inorg. Chem.* **1981**, *20*, 1644.

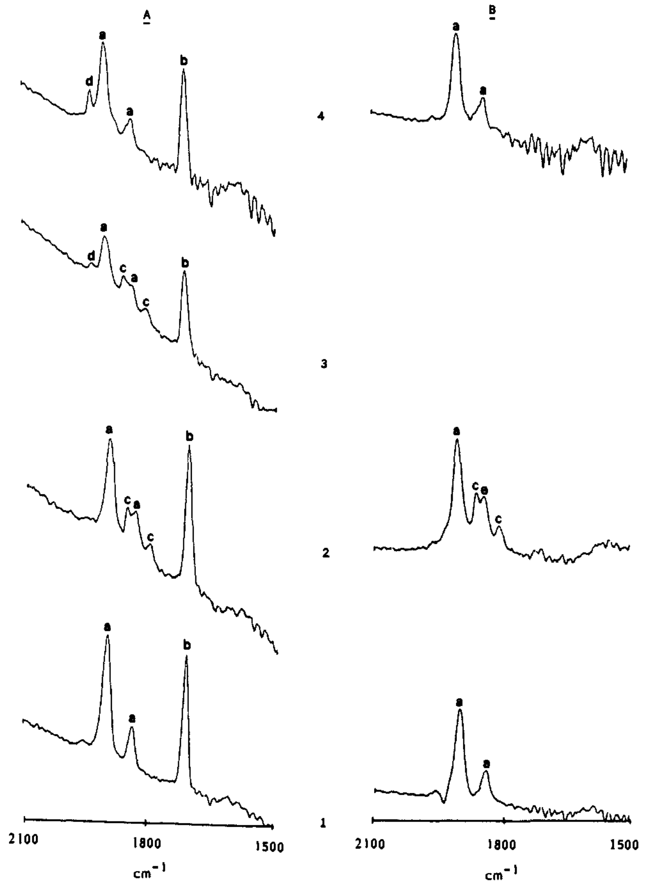
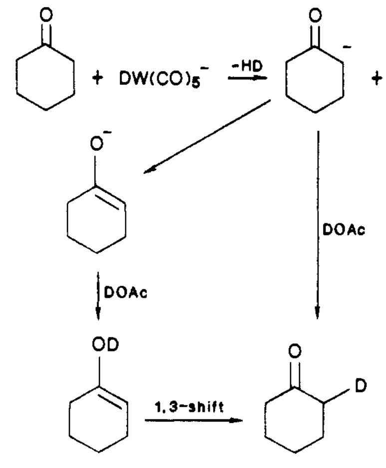
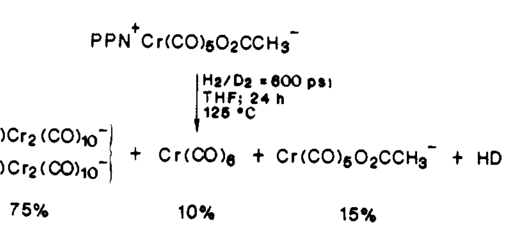


Figure 1. High-pressure infrared spectra in THF solution. (A) Catalyst solution of $PPN^+W(CO)_5OAc^-$ (a)/cyclohexanone (b) under 660 psig of H_2 initial loading. (1) Initial spectrum 0.01 M $PPN^+W(CO)_5(OAc)^-$ (a)/0.2 M cyclohexanone (b) in THF at 25 °C/660 psig of H_2. (2) Spectrum after 1 h at 125 °C. The $PPN^+W(CO)_4OAc(THF)^-$ (c) was observed at 1861 cm^{-1} (m) and 1805 cm^{-1} (w). (3) Spectrum after 5 h at 125 °C. The band at 1939 cm^{-1} is due to $PPN^+\mu\text{-}HW_2(CO)_{10}^-$ (d). (4) Final spectrum after 24 h of reaction, cooled to 25 °C. (B) Control reaction 0.01 M $PPN^+W(CO)_5(OAc)^-$ (a) in THF under 660 psig of Ar initial loading. (1) Initial spectrum at 25 °C. (2) Spectrum after 1 h at 125 °C. The PPN^+ salt of $W(CO)_4OAc(THF)^-$ was observed at 1861 cm^{-1} (m) and 1805 cm^{-1} (w). (4) Final spectrum after cooling to 25 °C.

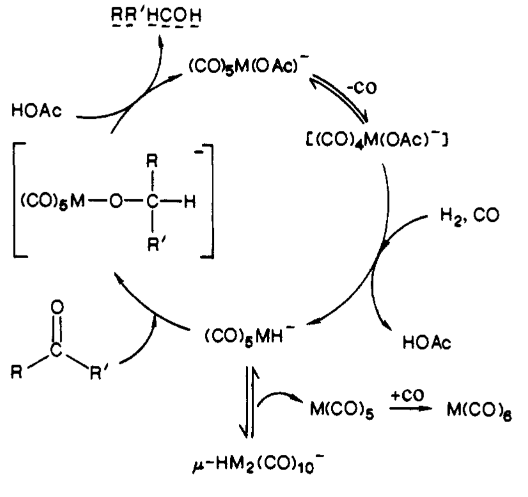
Scheme III



Scheme IV



Scheme V



pattern of the mass spectrum of cyclohexanone recovered from these reactions indicated deuterium enrichment to be at the α-C of cyclohexanone.[13] A reasonable explanation for this enrichment might be the base-catalyzed abstraction of a proton from the α-C followed by protonation with a D^+ source (Scheme III).

Organometallic product recovery after these experiments showed $W(CO)_5OAc^-$ and $\mu\text{-}DW_2(CO)_{10}^-$ to be the predominant products. Conversion of cyclohexanone was found to decrease for the 24-h period with D_2 (6.7 T.O) vs. that for H_2 (10.1 T.O.).

Separate experiments showed the $M(CO)_5OAc^-$ anions to be catalysts for formation of HD in mixtures of H_2 and D_2. In the presence of equal pressures of H_2 (300 psig) and D_2 (300 psig), a THF solution of $PPN^+Cr(CO)_5OAc^-$ over the 24 h typical of normal catalytic runs catalyzed the formation of substantial amounts of HD (Scheme IV). Mass spectroscopy indicated two peaks at mass 3, one assigned to H_3^+ and one to HD^+. Since it is unlikely for the HD^+ radical cation to be formed by an ion–molecule process, we conclude that the HD observed arises from the cross reaction between $HCr(CO)_5^-$/DOAc and $DCr(CO)_5^-$/HOAc.

Catalysis was enhanced in MeOH solutions of both $W(CO)_5OAc^-$ and $(\mu\text{-}H)W_2(CO)_{10}^-$. In the more protic solvent, turnover numbers of 13.2 and 17 were observed for the acetate and dimer hydride, respectively, as cyclohexanone was reduced (Table III, entries 21 and 22). The greater activity observed in MeOH concurs with previously observed results of CO_2 reduction with these same catalyst systems.[3]

Scheme V summarizes a reaction pathway consistent with the observed chemistry. Initially, CO is lost from the $M(CO)_5(OAc)^-$ species to produce an unsaturated, highly reactive tetracarbonyl consistent with observations made in the high-pressure FTIR studies. Subsequent H_2-addition leads to the heterolytic cleavage product (see Scheme II). This is a reasonable step based on the results of the H_2/D_2 exchange experiment. Further support is gained from the production of $\mu\text{-}HM_2(CO)_{10}^-$ (M = Cr, W) in pressure mixtures of H_2 and $M(CO)_5OAc^-$. An alkoxide intermediate is proposed (based on previous stoichiometric observations)[1] to form by reaction of the $M\text{–}H^-$ with the carbonyl group. We note that such alkoxy metal pentacarbonyls have not been observed for a range of organic carbonyls. It is possible that such species are intermediates only in the cases of aldehydes and activated ketones. Finally, protonation of the alkoxide occurs with HOAc to form the alcohol product and reform the $M(CO)_5OAc^-$.

While this paper was in preparation, a report of the homogeneous hydrogenation of ketones with a catalyst based on $M(CO)_6$/NaOMe/MeOH (M = Cr, Mo, W) appeared in the lit-

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(13) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 1981; p 25.

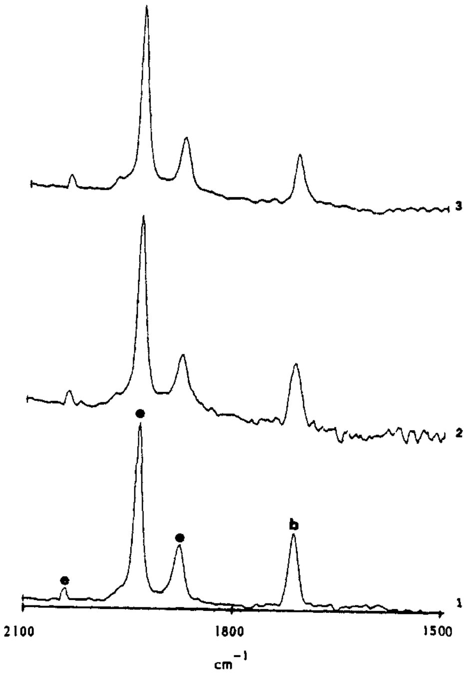


Figure 2. High-pressure infrared spectra of 0.01 M PPN$^+$$\mu$-$HW_2(CO)_{10}^-$ (e)/0.2 M cyclohexanone (b) in THF solution. (1) Initial spectrum at 25 °C under 660 psig of H_2. (2) Spectrum after 11 h at 125 °C/740 psig of H_2. (3) Final spectrum after 24 h of reaction, cooled to 25 °C.

erature.[14] The proposed catalytic cycle gave an entry into the formation of the highly reactive $HM(CO)_5^-$ monomers,[1] gained via the splitting of dihydrogen. However, their proposal that both H atoms for the carboxyl reduction came about from $HM(CO)_5^-$ was not consistent with our observations on the stoichiometric reactions.[1,2]

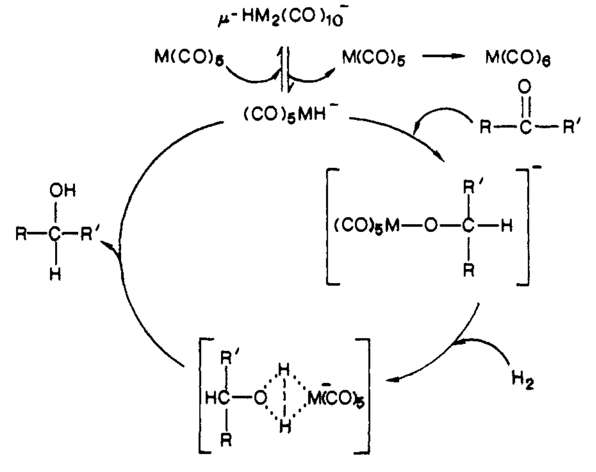
As mentioned above, Table II lists results from catalytic runs made with the isolated PPN$^+$ and Et_4N^+ salts of μ-$HM_2(CO)_{10}^-$ (M = Cr, Mo, W). Turnover numbers found for these species showed that in all cases but that of Cr, the hydride dimers were at least as active for the reduction of benzaldehyde and cyclohexanone as the acetate complexes. Moreover, the very CO labile μ-$HMo_2(CO)_{10}^-$ complex was found to be more active than the molybdenum acetate complex for the reduction of cyclohexanone. Catalyst recovery was 50% or greater in all cases. The only other IR observable product was $M(CO)_6$ (inactive as a catalyst, Table III).

In situ high-pressure FTIR spectra were taken over the course of one catalytic run employing PPN$^+$ μ-$HW_2(CO)_{10}^-$ as catalyst precursor and cyclohexanone as substrate (Figure 2). The disappearance of the ketone band was followed over the catalytic period. Observed in the IR were bands corresponding to dimeric hydride and ketone *only*! No intermediate metallo species were seen.

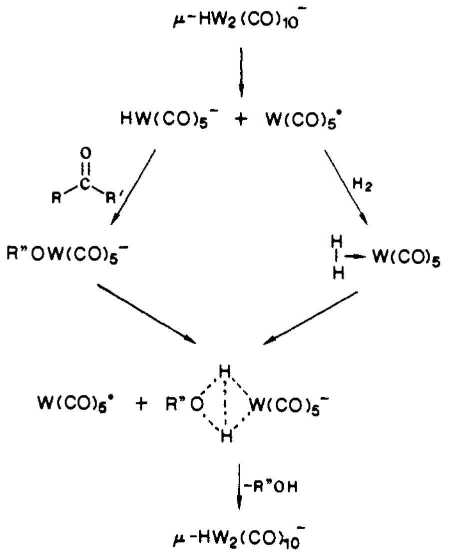
The monomeric hydride, $HW(CO)_5^-$, was also used as a cyclohexanone reduction catalyst (entry 12, Table III). At the end of the reaction period, the predominant metallo product was μ-$HW_2(CO)_{10}^-$. Upon allowing the reaction to continue for an additional 24 h, reduction proceeded with increased activity matching that of an original source of μ-$HW_2(CO)_{10}^-$.

Scheme VI is a proposed catalytic cycle with μ-$HM_2(CO)_{10}^-$ as catalyst or catalyst precursor. It begins with the active anionic hydride addition to produce the alkoxide. Although few isolated $ROM(CO)_5^-$ species are known, the established chemistry of $PhOM(CO)_5^-$ suggests ligand lability for M–OPh$^-$ as well as M–CO.[10] Hence a site for H_2 interaction would be generated. Indeed, reaction of $PhOW(CO)_5^-$ as its Et_4N^+ salt under 600 psi of dihydrogen at 125 °C produced phenol and μ-$HW_2(CO)_{10}^-$. Our proposed intermediate at the 6 o'clock position in Scheme VI is based on this and the following experiments. In the presence

Scheme VI



Scheme VII



of H_2, the neutral alkoxide Mn(OEt)(dppe)$(CO)_3$ has been shown to undergo hydrogenolysis to produce CH_3CH_2OH.[15] Furthermore, evidence for an anion-stabilized dihydride or η^2-dihydrogen complex has previously been presented in our H/D exchange studies of group 6 anionic hydrides (eq 3).[16]

$$MeOD + HW(CO)_5^- \rightarrow [(OC)_5W\overset{H}{\underset{D}{\vdots}}OMe^-] \rightarrow DW(CO)_5^- + MeOH \quad (3)$$

Although the conditions of this catalysis are rigorous and μ-$HM_2(CO)_{10}^-$ dimers are known to cleave as indicated in Scheme VI,[17] the apparent superiority of μ-$HW_2(CO)_{10}^-$ over $HW(CO)_5^-$ is intriguing. The most reasonable assumption is that μ-$HW_2(CO)_{10}^-$ acts as a convenient storage bank for the reactive $HM(CO)_5^-$ monomers, protecting them from degradation. Nevertheless, as seen above, when $HW(CO)_5^-$ is used as the original catalyst precursor and it degrades to produce μ-$HW_2(CO)_{10}^-$, activity goes up! A possible explanation is that there is a two-metal requirement as indicated in Scheme VII.

The reaction chemistry represented in Schemes V and VI overlaps significantly, the major difference being that Scheme V initiates catalysis, the active metal hydride, with the acetate function. The acetate is substantially regenerated as shown in

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(14) Marko, L.; Nagy-Magos, Z. *J. Organomet. Chem.* **1985**, *285*, 193.

(15) Dombek, B. D. *Ann. N.Y. Acad. Sci.* **1983**, *415*, 176.

(16) Gaus, P. L.; Kao, S. C.; Darensbourg, M. Y.; Arndt, L. W. *J. Am. Chem. Soc.* **1984**, *106*, 4752.

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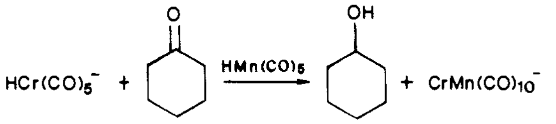
the catalyst recovery (Table I) as well as in situ studies. Nevertheless, the entry into μ-$HM_2(CO)_{10}^-$ catalysis (Scheme VI) is available from the acetate complex. Note that the major difference in reactivity of the μ-$HM_2(CO)_{10}^-$ and the $AcOM(CO)_5^-$ catalyst (or catalyst precursors) is in the case of M = Cr and substrate = cyclohexanone. This reduction has been shown to be difficult in the stoichiometric chemistry of $HCr(CO)_5^-$/acid/cyclohexanone.[1,2] In fact, the addition of ketone to $HCr(CO)_5^-$ does *not* occur in the absence of acid, and in Scheme V that event most probably occurs in reverse of the representation of Scheme V. That is the acetic acid is expected to serve as an acid promoter, activating the ketone functionality *prior* to hydride attack (as earlier represented in Scheme I).

Finally, the concept of group 6 metal pentacarbonyl complexes with Brønsted base ligands as catalyst precursors may be extended to less traditional bases. We have found the heterobimetallic anion, $MnCr(CO)_{10}^-$,[7] to be a catalyst (Table III, entry 23) for hydrogenation of cyclohexanone. A separate experiment demonstrated that the system $HCr(CO)_5^-/HMn(CO)_5$ could be used to reduce cyclohexanone to cyclohexanol (eq 5). Entry 23 shows the mixed metal dimer to be less efficient than the hydrido or acetato-metal pentacarbonyls as expected for the soft $Mn(CO)_5^-$ base having little configurational mobility for the simultaneous dissociation ($\mathrm{Mn}^{\delta-}\cdots\mathrm{Cr}$) and formation ($\mathrm{Mn}^{\delta-}\cdots\mathrm{H}^{\delta+}$) of bonds. Bases with more than one pair of unshared electrons more readily achieve transition states required in heterolytic cleavage.[5] These studies are continuing.



(4)

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Registry No. $W(CO)_5(OAc)^-\cdot PPN^+$, 36515-92-1; $Mo(CO)_5(OAc)^-\cdot PPN^+$, 76107-32-9; $Cr(CO)_5(OAc)^-\cdot PPN^+$, 99016-85-0; μ-$HW_2(CO)_{10}^-\cdot PPN^+$, 56172-01-1; μ-$HMo_2(CO)_{10}^-\cdot PPN^+$, 77214-68-7; μ-$HCr_2(CO)_{10}^-\cdot PPN^+$, 62341-83-7; PhCHO, 100-52-7; cyclohexanone, 108-94-1.

On the Mechanism of the Cyclooctatetraene Synthesis from Ethyne Employing Nickel Catalysts

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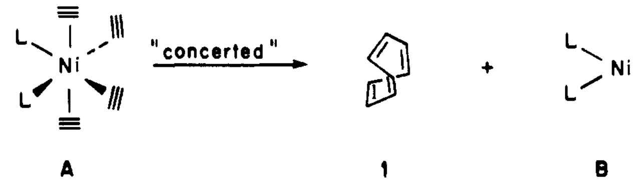
Abstract: The mechanism of the Reppe cyclization to cyclooctatetraene was investigated by employing ethyne-*1*-^{13}*C* as a substrate in the nickel-catalyzed reaction. The specific catalytic systems studied were nickel acetylacetonate–calcium carbide and nickel acetylacetonate–diethylaluminum ethoxide. In both cases, the label pattern in the cyclooctatetraene produced was consistent with either a stepwise coupling or concerted "zipper-type" mechanism of formation. These results preclude the possibility of cyclobutadiene or benzene intermediates or any carbon–carbon bond cleavage processes which do not leave the original connectivity in the alkyne intact. These conclusions were based upon analysis of the isotopic label in C_4 fragments, obtained by chemical degradation of the cyclooctatetraene produced.

The nickel-catalyzed cyclotetramerization of ethyne to cyclooctatetraene (COT) is a striking example of the capabilities of organometallic chemistry. Since its discovery by Reppe,[1] the reaction has been the subject of both synthetic and mechanistic inquiries.[3,4] While much information was garnered from these studies, there was little conclusive evidence to dismiss any of a variety of mechanisms postulated including a concerted process, stepwise growth at one or more nickel centers, or processes which contain either nickel–cyclobutadiene or nickel–benzene compounds as intermediates. It was our intent to try to distinguish among some of these possibilities using a labeling experiment. Preliminary results of this work have been published.[2]

For the purpose of discussion in this paper and in order for the reader to understand the motivation for our experiments, mechanistic alternatives have been grouped into four areas: concerted mechanisms, stepwise coupling sequences, mechanisms which feature symmetric intermediates such as cyclobutadiene or benzene, and those processes that may involve cleavage of the original alkyne triple bonds.

Concerted Mechanism. The simplest mechanism to envision is one in which the nickel atom acts as a template with all four ethyne molecules simultaneously bound to the metal prior to coupling (Scheme I). This view, espoused particularly by Schrauzer,[5] suggests that the critical intermediate, A, is an oc-

Scheme I



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