Organometallics **1985,** *4,* 83–91

of THF. The solution rapidly turned light yellow brown. After 24 h the solvent was removed in vacuo, and the residue was extracted with ether. The mixture was filtered and the ether removed in vacuo to yield a yellow powder. Recrystallization from ether/pentane (−30 °C) afforded 0.352 g (86%) of yellow plates in two crops. The compound is insoluble in pentane and benzene: ^{1}H NMR (CDCl$_3$) δ 1.30 (s, 27, OCMe$_3$); ^{13}C NMR (CD$_2$Cl$_2$) δ 31.99 (q, J_{CH} = 128 Hz, OCMe_3), 81.30 (s, OCMe$_3$), 124.3 (s, J_{CW} = 71 Hz, CCN), 215.2 (s, J_{CW} = 310 Hz, CCN); IR (Nujol) 2100 cm^{-1} (ν_{CN}). Anal. Calcd for WC$_{21}$H$_{40}$O$_3$N$_2$: C, 45.66; H, 7.30. Found: C, 47.49, 48.00; H, 7.77, 7.84. The analysis samples were superb crystals, absolutely pure by high-field ^{1}H NMR. We have no explanation.

W(CH)(OCMe$_3$)$_3$(quin). Acetylene (1.24 mmol, 27.8 mL of gas), purified by passage through a saturated sodium bisulfite trap (to remove acetone) followed by a concentrated sulfuric acid trap (to remove water), was added by syringe to a Schlenk flask containing W$_2$(OCMe$_3$)$_6$ (1.24 mmol, 1.00 g), pyridine (6.20 mmol, 500 μL), and quinuclidine (2.48 mmol, 0.276 g) in 70 mL of pentane that had been cooled to −78 °C in a dry ice/ethanol bath. The initially dark red-purple solution slowly changed color to forest green. As the solution warmed slowly to room temperature, the color changed to medium brown. After 24 h the solvent was removed in vacuo to yield a brown powder that is pure W(CH)(OCMe$_3$)$_3$(quin) by ^{1}H NMR. Pure samples can be isolated by sublimation (25 °C/0.001 μm/0 °C probe/0.34 g (26%)) but the compound appears to be thermally sensitive. Sublimation at room temperature is preferred, although it is extremely slow: ^{1}H NMR (C$_6$D$_6$) δ 1.52 (s, 27, OCMe$_3$), 5.15 (s, 1, J_{HW} = 90 Hz, W(CH)); ^{13}C NMR (C$_6$D$_6$) δ 30.35 (q, J_{CH} = 125 Hz, OCMe_3), 74.53 (s, OCMe$_3$), 247.1 (d, J_{CH} = 147 Hz, J_{CW} = 287 Hz, W(CH)). Anal. Calcd for WC$_{20}$H$_{41}$O$_3$N: C, 45.55; H, 7.84. Found: C, 45.67; H, 8.21.

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Relative Reactivity and Mechanistic Studies of the Hydride-Transfer Reagents HM(CO)$_4$L$^-$ (M = Cr, W; L = CO, PR$_3$)[†]

S. C. Kao,* Cris Tina Spillett, Carlton Ash, Richard Lusk, Y. K. Park, and Marcetta Y. Darensbourg*

Department of Chemistry, Texas A&M University, College Station, Texas 77843

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A series of anionic transition-metal hydrides have been compared according to their ability to reduce halocarbons (primarily alkyl bromides) to hydrocarbons. The 6B hydrides HM(CO)$_4$L$^-$ (M = Cr, W; L = CO, PR$_3$) are highly efficient hydride-transfer reagents, displacing X from a wide variety of C–X bonds, including tertiary centers, and tolerant of functionalities such as nitro groups, ketones, and aldehydes. A facile H/D exchange process with CH$_3$OD or D$_2$O readily converts the MH$^-$ reagents into deuterium delivery reagents. There is little difference between the reactivity of HM(CO)$_5^-$ with primary vs. secondary vs. tertiary alkyl bromides; however, the *cis*-HM(CO)$_4$PR$_3^-$ anions are far more reactive with the less hindered primary than branched alkyl halides. A comparison of the second-order rate constants for bromide displacement from *n*-BuBr established an order of reactivity for simple monomeric carbonyl hydrides *cis*-HW(CO)$_4$P$^-$ > *cis*-HCr(CO)$_4$P$^-$ > HW(CO)$_5^-$ > CpV(CO)$_3$H$^-$ > HCr(CO)$_5^-$ > HRu(CO)$_4^-$ > *trans*-HFe(CO)$_3$P$^-$ >> HFe(CO)$_4^-$ (no reaction). The relative reactivity was shown to correlate with the extent of electron density localized at the M–H bond as indicated by hydride site specific contact ion pairing with Na$^+$ in THF solution. Various mechanistic probes suggested the reagents most prone to contact ion pairing at the M–H$^-$ site to react with RX via S$_N$2 processes whereas the complexes with the anionic charge delocalized were more prone to electron-transfer mechanisms.

Introduction

The hydride transfer ability of anionic metal hydrides is of significance in formulating reasonable models for the reduction of metal-bound carbon.[1] Additional interest is in developing the chemistry of soluble anionic transition-metal hydrides since their intermediacy in the water-gas shift reaction suggests that such hydrides are catalytically regenerable from inexpensive raw materials, CO, and base. Thus Pettit convincingly showed the utility of HFe(CO)$_4^-$ as reagent and catalyst for the reduction of aromatic nitro compounds to amines[2] as well as the reduction of acid chlorides to aldehydes.[3]

Another potentially useful reduction is that of alkyl halides by active transition-metal hydrides (or deuterides). This reaction has been used as a mechanistic probe of metal hydride reactivity,[4] and it might also be used as a basis for establishing the factors that determine the relative ability of a transition-metal complex to release the H$^-$ ligand. It became obvious to us during our studies of monomeric HM(CO)$_5^-$ anions (M = Cr, Mo, W)[5-7] that no comprehensive (or, for that matter, limited) relative re-

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[†] This contribution is dedicated to our good friend Earl Muetterties, whose valued scientific insight will continue to guide.

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activity study existed for even the simple anionic metal carbonyl hydrides. Although a reactivity scale for anionic metal hydrides is expected to itself be dependent upon the substrate chosen, a study of halide displacement from RX would provide a particularly appropriate comparison of transition-metal hydrides with each other, with main-group metal hydrides, and with transition-metal carbonyl anions.[8] A preliminary report of this work presented such a reactivity scale which, when based on the reduction of straight-chain alkyl halides, is as follows:[9] *cis*-$HW(CO)_4P(OMe)_3^-$ > *cis*-$HCr(CO)_4P(OMe)_3^-$ > $HW(CO)_5^-$ > $CpV(CO)_3H^-$ > $HCr(CO)_5^-$ > $HRu(CO)_4^-$ >> $HFe(CO)_4^-$ (no reaction). The reactivity scale is however substrate dependent. For example, reactivity of the more basic but sterically hindered hydrides *cis*-$HM(CO)_4P(OMe)_3^-$ (M = Cr, W) with tertiary carbon centers is diminished to a level less than the $HM(CO)_5^-$ species. Herein we detail and expand these experiments and report control reactions of import to mechanistic considerations.

Experimental Section

A. Methods and Materials. An inert-atmosphere glovebox and Schlenk and/or high-vacuum techniques were used for all sample transfers and sample manipulations. All solvents were dried over appropriate agents (tetrahydrofuran (THF) and hexane, the purple Na^0/benzophenone scavenger; diethyl ether, lithium aluminum hydride; methanol, $CaSO_4$), distilled, and transferred under nitrogen. Acetonitrile was pretreated with CaH_2 and then distilled under N_2 from P_2O_5. Common reagents were purchased from standard vendors. All organic halides were distilled from P_2O_5, discarding the first and last 10% fractions. These reagents were stored under N_2 for a maximum of 2 weeks.

B. Instrumentation. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer. Proton nuclear magnetic resonance spectra were recorded on a 90-MHz Varian EM-390 spectrophotometer and ^2H spectra on a Varian XL200. Gas chromatographic analyses were performed on a Perkin-Elmer Sigma 2 gas chromatograph, equipped with flame ionization detector. Columns used in product analyses were (1) 6 ft × 0.25 in. picric acid on Graphpac 80/100 (C_4 hydrocarbons), (2) 6 ft × 0.125 in. 10% Apiezon L on Chromosorb W-HP, and (3) 6 ft × 0.125 in. 105 OV-17 on Chromosorb W-HP (C_6 hydrocarbons). Peak area integrations were performed by multiplying the peak widths at half-height by the peak heights or by electronic integration.

C. Preparations and Reactions. 1. Preparation of Anionic Metal Hydride Complexes. Bis(triphenylphosphine)nitrogen(1+) (PPN^+) salts of $HM(CO)_5^-$ (M = Cr, W) were synthesized by the borohydride method as reported previously.[10] The analogous deuterides were either prepared and isolated in the same manner, using borodeuteride substituted for borohydride, or generated and used in situ.[6] The in situ method of generating DM^- reagents involved mixing a THF solution of the anionic hydrides with a tenfold molar excess of CH_3OD prior to adding the alkyl halide.

The synthesis and spectral properties of the P-donor ligand-substituted complexes *cis*-$HM(CO)_4P(OMe)_3^-$ (M = Cr, W) and *cis*-$HW(CO)_4PR_3^-$ (R = Me, Ph) have been reported previously.[11] Other anions $HRu(CO)_4^-$,[12] $HFe(CO)_4^-$,[13] and $CpV(CO)_3H^-$[4] were prepared according to literature procedures and isolated as their PPN^+ salts. The *trans*-$HFe(CO)_3P(OMe)_3^-$ anion was prepared by a procedure similar to that reported by Edens[14] and Ellis[15] and isolated as its PPN^+ salt. Spectral data (THF solution) are as follows: IR (ν(CO) 1942 (m), 1841 (vs) cm^{-1}; ^1H NMR δ -9.22 (d, J_{P-H} = 13.5 Hz). The elemental analysis (Galbraith Labs) of $PPN^+HFe(CO)_3P(OMe)_3^-$ was less than satisfactory (Anal. calcd (found): C, 62.78 (60.46); H, 5.02 (5.13). However, the analogous $PPN^+HFe(CO)_3P(OEt)_3^-$, of practically identical spectral characteristics, gave the following analysis: C, 63.92 (63.92); H, 5.48 (5.12).[16]

2. Reactions of Anionic Hydrides with Organic Halides. General Method. The reactions of anionic hydrides with various organic halides, with the exception of the kinetic studies (see below), were conducted in the following manner. Solid samples of the hydrides of interest were weighed inside the glovebox and placed in septum capped flasks. Outside the drybox, solutions of the appropriate organic halides were added to these samples by syringe. Solutions were then stirred at room temperature overnight and subjected to analysis.

Product Analysis. Organometallic products were identified by their IR and NMR spectra as compared to spectra of known compounds. Volatile organic products were identified by gas chromatography on the reaction mixtures through coinjection with authentic samples on the three columns mentioned above. In most cases (both for volatiles and nonvolatiles) organic products were also identified by NMR. Unless otherwise noted, reaction products were quantified (GC yields) by means of an external standard of known concentration for the compound being analyzed and dissolved in the solvent used for the reaction. In the reaction of $DW(CO)_5^-$ with α-bromoethylbenzene, the incorporation of deuterium in the α-carbon of the resulting ethylbenzene was indicated by a diminished quartet of the methylene protons at δ 2.63 (1.2 H, J = 7.5 Hz) as well as a broadened doublet at δ 1.14 (3 H, J = 7.5 Hz) for the methyl protons. On the basis of this NMR study, it was concluded that one of the methylene protons of the final product was 80% deuterated. Other deuterium labeling experiments were followed by ^2H NMR.

3. Kinetic Measurements. Inside the drybox solid samples (0.2 mmol) of hydrides were placed in straight tubes (30-mL capacity) with a stopcock at one end and a small septum cap tightly wired to its outlet. Outside the box an appropriate solvent (10 mL) was added, and the flask was immersed in a constant temperature bath. After temperature equilibration (ca. 5 min), 10 mL of an organic halide solution preequilibrated to the same temperature was introduced and timing began. Except where noted, the RX concentration was in 20-fold excess to the hydride, ensuring pseudo-first-order reaction conditions. Similar runs to check the effect of added ligands were prepared by adding a 20-fold excess or by the saturating (in the case of CO) of such reagents to the carbonylate solution prior to addition of organic halides. Samples (0.2 mL) were periodically withdrawn, and the reaction rate was monitored by the observed decrease in intensity of an isolated ν(CO) infrared absorbance of the hydride. A minimum of ten data points was obtained for each kinetic run. Rate constants were calculated by using a linear least-squares program for the pseudo-first-order rate plots of ln ($A_t - A_\infty$) vs. time, where A_t is the absorbance at time t and A_∞ is the absorbance at time infinity. The observed rate constants (k_{obsd}), the standard deviation, and the error at the chosen confidence limit were calculated by using standard least-squares fitting programs. Second-order rate constants (k_2) were obtained by dividing k_{obsd} by [RX]. Activation parameters (ΔH and ΔS) were obtained by plotting $-\ln k_2$ vs. $1/T$, where T is the temperature (K) of each individual run. Again, a standard computer program was applied for the data processing and the error analysis at the chosen confidence level.

4. Competition Reactions. (a) Competition between Linear and Branched Alkyl Bromides for HM^- (M = $Cr(CO)_5$, $W(CO)_4L$ (L = CO, $P(OMe)_3$, PMe_3, PPh_3), $Cr(CO)_4P(OMe)_3$, $Fe(CO)_3P(OMe)_3$). A THF solution (10 mL) of *n*-butyl bromide and *tert*-butylbromide (0.15-mmol each) was added to a septum-capped flask containing 0.05 mmol of the HM^-. The reaction mixture was stirred overnight at room temperature. GC

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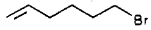
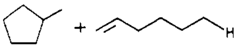
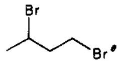
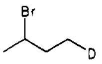
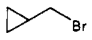
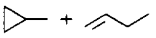
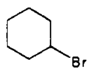
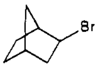
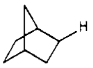
[16] A series of *trans*-$HFe(CO)_3P^-$ anions have been synthesized in our laboratories and a manuscript describing their full characterization, including one X-ray crystal structure determination, ($Et_4N^+HFe(CO)_3PPh_3^-$), is in preparation.

Table I. Products of Reaction of $PPN^+HW(CO)_5^-$ with Organic Halides

halide	product	yield,[a] %
n-C_4H_9Br	n-C_4H_{10}	83
2-C_4H_9Br	n-C_4H_{10}	85
t-C_4H_9Br	i-C_4H_{10}	81
n-C_4H_9I	n-C_4H_{10}	89
n-C_4H_9Cl	no reaction	
$C_6H_5CH_2Cl$	$C_6H_5CH_3$	85
$C_6H_5CH_2Br$	$C_6H_5CH_3$	99
C_6H_5COCl	C_6H_5CHO	80
$C_6H_5CH(CH_3)Br$[b]	$C_6H_5CH(CH_3)D$	95
α-bromocamphor[c]	camphor	70
C_6H_5Br	C_6H_6	80
1-bromoadamantane	adamantane	70
 [d]		80
 [e]		90
		80
	c-C_6H_{12}	>80
		>80

[a] GC yields. [b] Isolated $DW(CO)_5^-$ used. [c] Isolated (weighed) yield. [d] Product ratio of methylcyclopentane to 1-hexene of 1.6:1. [e] $DW(CO)_5^-$ generated in situ; see Experimental Section. [f] Product ratio of methylcyclopropane to 1-butene of ca 1:3.5.

analysis of the final reaction product revealed the hydrocarbon distributions shown in Table V.

(b) Competition between $HW(CO)_5^-$ and $CpV(CO)_3H^-$ for n-Butyl Bromide. A THF solution (2 mL) of n-butyl bromide (0.03 M) was added to a septum-capped flask containing a solution (10 mL) or $HW(CO)_5^-$ and $CpV(CO)_3H^-$ (0.006 M each) in the same solvent. The reaction mixture was stirred at room temperature for 10 h. The IR spectrum of the resulting solution indicated $BrW(CO)_5^-$ [2066 (vw), 1918 (s), 1852 (m) cm^{-1}] and $CpV(CO)_3H^-$ as the products.

(c) Competition between Ligand Scavenging Agents, Br^-, PPh_3, and $HW(CO)_5^-$ for $W(CO)_5 \cdot THF$. A 0.05 M solution (10 mL) of $W(CO)_5 \cdot THF$ (prepared by the photolysis reaction of $W(CO)_6$ in THF) was added to a solution (20 mL) of PPNBr (0.30 g, 0.5 mmol) and PPh_3 (0.30 g, 1.1 mmol) in the same solvent. An IR sample taken right after the mixing revealed the sole presence of $BrW(CO)_5^-$. Other competition reactions were carried out in the same manner.

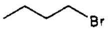
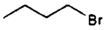
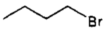
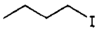
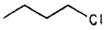
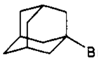
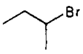
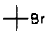
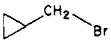
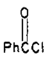
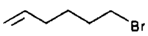
Results

Scope of Reaction. For all reactive metal hydrides the metal-containing product was that of a simple H^-/X^- exchange as illustrated by eq 1. Comparison of relative $\nu(CO)$ IR band areas of reactant vs. product indicated quantitative conversion.

$$HM^- + RX \rightarrow MX^- + RH \qquad (1)$$

Table I contains a listing of organic halides used in reaction with $PPN^+HW(CO)_5^-$ and the (minimum) yield of hydrocarbon product as determined by gas chromatography. Similar yields of hydrocarbons were obtained in almost all cases using $HW(CO)_4P(OMe)_3^-$ and $HCr(CO)_5^-$ as reducing agents. The chromatograms were carefully examined for traces of R–R coupling products and elimination products. No coupling products were found, and only in one case, that of reaction of $HW(CO)_4P(OMe)_3^-$ and t-C_4H_9Br, was an elimination product (isobutene, trace) present. Note that the product obtained upon reaction of $DW(CO)_5^-$ with $C_6H_5CH(CH_3)Br$ is the alkane-d_1, established by ^1H NMR. The significance of this result is that the metal reductant is the sole source of hydride (deuteride).

Table II. Second-Order Rate Constants[a] for the Reaction of $PPN^+HW(CO)_5^-$ with Various Alkyl Halides in Tetrahydrofuran at 26.0 °C

entry	RX	additive	10^3k_2,[b] s^{-1} M^{-1}
1			3.31 (±0.13)[c]
2		d	3.22 (±0.09)
3		CO	3.66 (±0.12)
4		PPh_3	3.70 (±0.08)
5		hydroquinone	3.42 (±0.15)
6		e	8.33 (±0.86)
7			>10
8			no reaction
9	$PhCH_2Cl$		1.68 (±0.09)
10	$PhCH_2Br$		>10
11	PhBr		0.37 (±0.045)
12			0.27 (±0.014)
13			1.79 (±0.05)
14			2.81 (±0.16)
15			3.00 (±0.22)
16			>10
17			3.86 (±0.07)

[a] Calculated by dividing the pseudo-first-order k_{obsd} by [RX] which was in all cases in 20-fold excess. [b] Errors are, except where noted, those of individual runs calculated at the 90% confidence limit. [c] This k_2 value is the average of four runs, and the error is the average of that of the individual runs. Reproducibility was within <10%. [d] The reagent was $PPN^+DW(CO)_5^-$. [e] The solvent was CH_3CN.

The convenient in situ method for H/D exchange, eq 2, permits deuterium labeling of alkanes without isolation of the transition-metal deuteride.[6] The demonstration of selective reduction of 1,3-dibromobutane to give 2-bromobutane made use of this feature.

$$HM^- + CH_3OD \rightleftharpoons DM^- + CH_3OH \qquad (2)$$

Kinetics. The reaction of monomeric 6B metal carbonyl hydrides with most alkyl halides proceeded at a rate convenient for monitoring by conventional $\nu(CO)$ IR techniques. Reactions of RX with the anionic metal carbonyl hydrides were carried out under pseudo-first-order conditions for the metal hydrides with RX generally at a 20-fold excess. Plots of the ln $(A_t - A_\infty)$ of an isolated $\nu(CO)$ band vs. time were linear over at least 3 half-lives for the 6B metal hydrides and $CpV(CO)_3H^-$. A first-order dependence on [RX] was established for two RX, $C_6H_5CH_2Cl$, and n-BuBr by varying [RX] from a 20- to a 60-fold excess in which cases a constant value for $k_2 = k_{obsd}$ [RX] was obtained (Figure 1). The second-order rate constants in the established rate law, eq 3, assumed valid for all

$$\text{rate} = k_2[HM^-][RX] \qquad (3)$$

reactions studied, are found in Tables II and III. In one case (entry 17, Table II) the starting amount of $HW(CO)_5^-$ was varied over a 3-fold concentration range. Differences in pseudo-first-order rate constants were not significant. The $HRu(CO)_4^-$ was active in the reduction of n-BuBr to

Table III. Reaction of PPN^+HM^- with RX: Dependence on HM^-

M	10^3k_2,[a,b] s^{-1} M^{-1}		
	n-C_4H_9Br	2-C_4H_9Br	t-C_4H_9Br
$Cr(CO)_5$	1.79 (±0.05)	1.65 (±0.28)	3.17 (±0.08)
$W(CO)_5$	3.31 (±0.13)	1.79 (±0.05)	2.81 (±0.16)
$Cr(CO)_4P(OCH_3)_3$	~30	1.89 (±0.06)	0.81 (±0.05)
$W(CO)_4P(OCH_3)_3$	~50	4.24 (±0.18)	0.21 (±0.01)
$CpV(CO)_3$	2.20 (±0.06)		0.33 (±0.03)
$Ru(CO)_4$	~1.0[c]		
$Fe(CO)_4$	no reaction	no reaction	no reaction
$Fe(CO)_3P(OCH_3)_3$	0.025 (±0.002)[d]		

[a] Error limits represent 90% confidence limit. [b] Reactions were carried out at 26 °C. [c] This system was not well behaved, see text; k_2 estimated from half-life. [d] Determined in the presence of a 10-fold excess of $P(OMe)_3$.

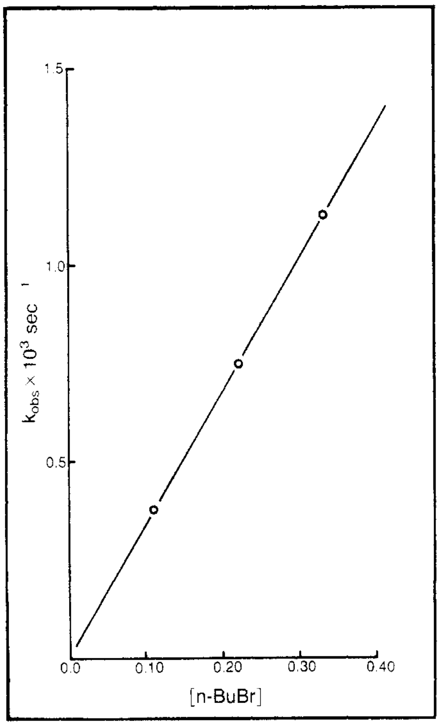


Figure 1. A plot of the dependence of k_{obsd} on alkyl halide concentration for the reaction of $PPN^+HW(CO)_5^-$ with n-BuBr in THF at 20 (±1) °C.

butane (ca. 40% yield by GC) but was kinetically ill-behaved. The rate constant listed in Table III was estimated from the observed half-life of the hydride.

Kinetic studies of *trans*-$HFe(CO)_3P(OMe)_3^-$ (hereafter expressed as $HFe(CO)_3P^-$) were problematical. The organometallic products identified in the reaction described by (4) were present in roughly equal amounts; no BrFe-

$$HFe(CO)_3P^- + RBr \rightarrow RH + HFe(CO)_4^- + trans\text{-}Fe(CO)_3P_2 \quad (4)$$

$(CO)_3P(OMe)_3^-$ was detected.[17] The half-life for disappearance of the starting hydride was ca. 2.5 hrs and low yields of RH were obtained. Addition of a 10-fold excess of $P(OMe)_3$ substantially suppressed the formation of $HFe(CO)_4^-$ and also depressed the reaction rate to a $t_{1/2}$ of over 8 h. The difficulties encountered in the $HFe(CO)_3P(OMe)_3^-$ studies are presumed to be due to ligand lability in the product $BrFe(CO)_3P(OMe)_3^-$, generating coordinatively unsaturated fragments capable of converting the reactive phosphite hydride into inactive $HFe(CO)_4^-$.

The reactions of $PPN[HW(CO)_5]$ with three organic halides n-C_4H_9Br, t-C_4H_9Br, and $C_6H_5CH_2Cl$ and of $PPN[HW(CO)_4P(OMe)_3]$ with t-C_4H_9Br, over a temperature range of 20 °C, have been examined. Example Arrhenius plots are given in Figure 2. Activation energy parameters are presented in Table IV.

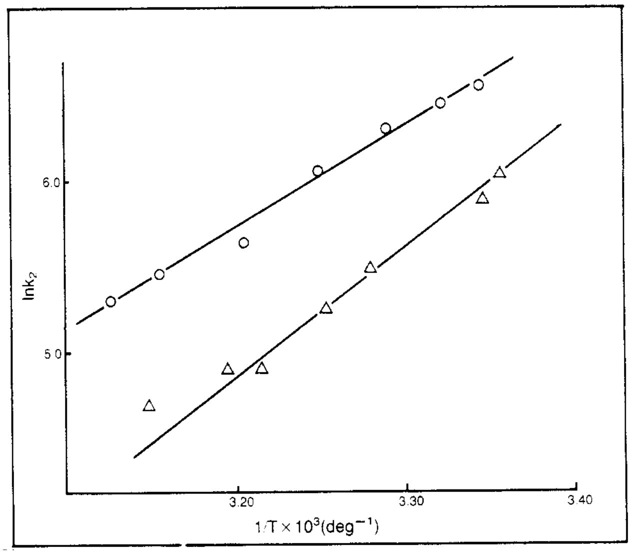


Figure 2. Arrhenius plots for the reaction of $PPN^+HW(CO)_5^-$ with n-BuBr (○) and of $PPN^+HW(CO)_4P(OMe)_3^-$ with t-BuBr (△). Derived parameters are given in Table IV.

Table IV. Activation Parameters for the Reaction of $PPN[HW(CO)_4L]$ with RX in THF

L	RX	ΔH,[a] kcal/mol	ΔS,[a] eu
CO	n-C_4H_9Br	12.6 ± 1.8	−29.5 ± 6.3
CO	t-C_4H_9Br	12.0 ± 1.8	−32.1 ± 6.2
CO	$C_6H_5CH_2Cl$	11.4 ± 1.3	−35.2 ± 4.4
$P(OMe)_3$	t-C_4H_9Br	13.3 ± 1.8	−31.4 ± 6.4

[a] Error limits for activation parameters calculated at the 90% confidence limit, including errors in individual kinetics runs.

Reactivity. Table II contains k_2 values for the reaction of $PPN^+HW(CO)_5^-$ with various organic halides in THF. Entries 1, 7, and 8, as well as 9 and 10, show a dependence of rate on X that is in accordance with the normal reactivity of RX: I > Br > Cl. Entries 11, 12, and 14 provide examples of reactivity where S_N2 pathways are usually expected to be precluded. The highly activated RX molecules of entries 10 and 16 show reaction rates too rapid for monitoring by our conventional techniques. Thus a typical reactivity dependence on the composition of R is observed: benzoyl > benzyl > alkyl > aryl > adamantyl. Within the alkyls, the reactivity observed is primary ≈ tertiary ≥secondary (entries 1, 13, and 14). The remaining entries of Table II were part of attempts to probe the mechanism of hydride transfer and will enter into a later discussion.

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[17] Abel, E. W.; Butler, I. S.; Jenkin, C. R. *J. Organomet. Chem.* **1967**, *8*, 382.

Table V. A Comparison of Selectivity in the Reductions of Linear and Branched RBr by Anionic Metal Hydrides[a]

MH^-	n-C_4H_{10}/ t-C_4H_{10} [b]	n-C_4H_{10}/ n-C_5H_{12} [b]
$HW(CO)_5^-$	75/25	65/35
cis-$HW(CO)_4P(OMe)_3^-$	100/tr[d]	100/0
cis-$HW(CO)_4PMe_3^-$	100/tr	100/0
cis-$HW(CO)_4PPh_3^-$	100/tr	100/0
$HCr(CO)_5^-$	15/85	50/50
cis-$HCr(CO)_4P(OMe)_3^-$	75/25	90/10
trans-$HFe(CO)_3P(OMe)_3^-$	90/10	

[a] A 1:1 mixture of each RBr in a 3-fold molar excess to the MH^- (0.05 mmol) was stirred in 10 mL overnight. [b] Hydrocarbon products derived from 1:1 mixture of n-C_4H_9Br/t-C_4H_9Br. [c] Hydrocarbon products derived from 1:1 mixture of n-C_4H_9Br/2-bromopentane. [d] Trace amounts.

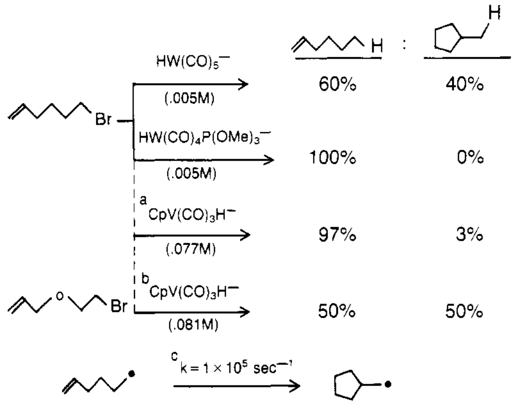
The data of Table III compare the reactivities of several metal hydrides toward n-C_4H_9Br, *sec*-C_4H_9Br, and t-C_4H_9Br. With n-BuBr reactivity differences between the simple anionic carbonyl hydrides could be established, presumably free from steric influences. The first column in Table III indicates greater reactivity for the heavier congener of an isostructural anion (W > Cr; Ru >> Fe), as well as for phosphite-substituted anions. The relative reactivity implied by these rate constants for $CpV(CO)_3H^-$ and $HW(CO)_5^-$ was substantiated by a competition study in which a deficiency of n-BuBr was added to an equimolar mixture of the two hydrides. The less reactive $CpV(CO)_3H^-$ survived the reaction; all $HW(CO)_5^-$ was converted into $BrW(CO)_5^-$.

There was no reaction of $HFe(CO)_4^-$ with C_4 aliphatic alkyl bromides, cyclohexyl bromide, or n-octyl bromide. Reaction of $HFe(CO)_4^-$ with benzyl chloride occurred extremely slowly (days). The reduction of $C_6H_5C(O)Cl$, with $Me_4N^+HFe(CO)_4^-$ (2:3 molar ratio) in CH_2Cl_2 solvent, is reported to require 1.25 h (yielding benzaldehyde, 91%).[3] For comparison we reacted $PPN^+HW(CO)_5^-$ with the same acid chloride in a 1:1 ratio in THF and attempted to monitor the reaction by ^1H NMR. The reaction was complete within minutes, i.e., by the first spectrum taken, and benzaldehyde was obtained as sole organic product;[7] $ClW(CO)_5^-$ was the organometallic product.

As discussed above for $HW(CO)_5^-$, the $HCr(CO)_5^-$ reacts with almost equal facility with the primary, secondary, and tertiary butyl bromides and there are only minor differences between the reactivity of $HCr(CO)_5^-$ and $HW(CO)_5^-$. The $P(OMe)_3$-substituted 6B hydrides are, however, ca. 2 orders of magnitude more reactive with n-BuBr than are their all PR_3) analogues. The data in the second column of Table III, reactivity with *sec*-C_4H_9Br, show less of a difference between the $P(OMe)_3$-substituted and the nonsubstituted 6B metal hydrides. For example, *cis*-$HW(CO)_4P(OMe)_3^-$ is only 1 order of magnitude more reactive than $HW(CO)_5^-$, and both chromium hydrides are of similar reactivity. This trend develops further in the last series of Table III. With the highly hindered t-C_4H_9Br the $P(OMe)_3$ derivatives are actually *less* reactive than $HW(CO)_5^-$ or $HCr(CO)_5^-$. Again the difference is most pronounced for the tungsten hydrides.

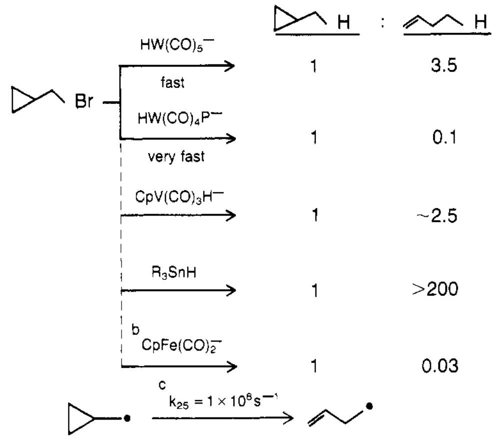
Selectivity. In order to verify the selectivity implied above for reactions of $HM(CO)_4L^-$ (M = Cr, W; L = CO, Pr_3) toward primary vs. secondary or tertiary RX, the competitive reactions shown in Table V were carried out. The slight kinetic differences noted in Table III between $HCr(CO)_5^-$ and $HW(CO)_5^-$ for primary vs. secondary or tertiary RX were corroborated, and the major difference in the reactivity of n-C_4H_9Br and t-C_4H_9Br toward *cis*-$HW(CO)_4P(OMe)_3^-$ led to 100% selectivity for reduction of the less hindered alkyl halide. All other substituted hydrides gave the same high selectivity. The reaction of *trans*-$HFe(CO)_3P(OMe)_3^-$ with a mixture of n-$C_4H_{10}Br$ and t-$C_4H_{10}Br$ was also checked for selectivity. Since the iron hydride is unstable in the absence of added phosphite (vide supra), the reaction was run in the presence of a 10-fold excess of $P(OMe)_3$. The product ratio (Table V) showed a 9:1 preference for the primary alkyl bromide.

Scheme I



[a] Reference 4. [b] The analogous oxy products are obtained.[4] [c] Reference 18.

Scheme II



[a] Concentrations of the hydrides: $[HW(CO)_5^-]$ = $[HW(CO)_4P(OMe)_3^-]$ = 0.005 M; this work; $[CpV(CO)_3H^-]$ = 0.03 M;[4] $[R_3SnH]$ = 0.037 M.[4] [b] Products isolated as the $CpFe(CO)_2R$ derivatives.[19] [c] Reference 20.

Reactions for Mechanism Probes. 1. Reactions with 6-Bromo-1-hexene. $PPN^+HW(CO)_5^-$ reacted with 6-bromo-1-hexene in THF (1:1 molar ratio, 26 °C) to produce, after 10 h in ca. 80% yield, a mixture of 1-hexene and methylcyclopropane distributed as indicated in Scheme I, as assayed by GC. The analogous reaction with $PPN^+HW(CO)_4P(OMe)_3^-$ produced only 1-hexene in 85% yield within 1 h. The k_2 value for this reaction is given in Table II.

2. Reactions with Cyclopropylcarbinyl Bromide. The reaction products of $HW(CO)_5^-$ with cyclopropylcarbinyl bromide (Scheme II) were a mixture of 1-butene and methylcyclopropane in a ratio of 3.5:1 as determined

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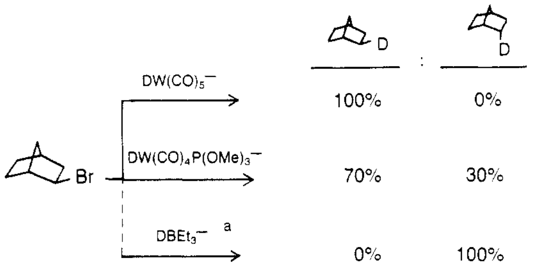
(18) Lal, D.; Griller, D.; Husband, S.; Ingold, K. U. *J. Am. Chem. Soc.* **1974**, *96*, 6355.

(19) San Filippo, J., Jr.; Silbermann, J.; Fagan, P. J. *J. Am. Chem. Soc.* **1978**, *100*, 4834.

(20) Maillard, B.; Forest, D.; Ingold, K. U. *J. Am. Chem. Soc.* **1976**, *98*, 7024.

Scheme III



[a] Reference 21.

by GC. The k_2 rate constant for this reaction is given in Table II and is typical of all alkyl bromides studied. The $HW(CO)_4P(OMe)_3^-$ reagent reacts much more rapidly (<10 min) yielding a preponderance of methylcyclopropane (Scheme II).

3. Reactions with *n*-Butyl Tosylate. The displacement of tosylate by hydride was extremely slow for $HCr(CO)_5^-$ ($t_{1/2} \approx 33$ h) and $HW(CO)_5^-$ ($t_{1/2} > 8$ h) but more facile for *cis*-$HW(CO)_4P(OMe)_3^-$ ($t_{1/2} = 22$ min). The possible organometallic products $TsOW(CO)_5^-$ or $(TsO)W(CO)_4P(OMe)_3^-$ were not observed. Instead the reactant hydride concentration was diminished by aggregation with the 16-electron, coordinative unsaturates, $[W(CO)_5{}^0]$ or $[W(CO)_4P^0]$ yielding μ-$HW_2(CO)_{10}^-$ or μ-$HW_2(CO)_8P_2^-$.[11] The dimeric hydrides were not reactive with RX.

4. Reaction with *exo*-2-Bromonorbornane. $PPN^+HW(CO)_5^-$ reacted with *exo*-2-bromonorbornane in THF to give norbornane in 80% yield. When the corresponding deuterium derivative $DW(CO)_5^-$ was used, a deuterated norbornane was produced. Deuterium NMR of the product indicated that the deuterium was selectively incorporated (>95%) into the exo position (δ 1.49) of the norbornane (Scheme III). In contrast the reaction between $DW(CO)_4P(OMe)_3^-$ and *exo*-2-bromonorbornane was found to be very slow (reaction time of days at 26 °C) and yielded a mixture of exo- and endo-deuterated products in total yield of 54%.

5. Other Control Reactions. A potential intermediate in these hydride transfer reactions, e.g., $[W(CO)_5{}^0]$ or $W(CO)_5{\cdot}THF$, was generated photochemically in THF and treated with equimolar mixtures of PPN^+Br^- and $PPN^+HW(CO)_5^-$. On time of mixing both $BrW(CO)_5^-$ and μ-$HW_2(CO)_{10}^-$ were obtained as products, in equal amounts. A similar reaction was carried out with of Br^- and PPh_3 competing for $W(CO)_5{}^0$. The sole product observed was $BrW(CO)_5^-$, indicating that Br^- is more reactive than PPh_3 toward $W(CO)_5{}^0$.

Discussion

Relative Reactivities of MH^- Anions. This discussion begins with a short review of factors that influence a reaction very similar to the one used here to establish anionic metal hydride reactivity. The well-known nucleophilicity scale of Dessy, Pohl, and King[8] was developed for the series of simple metal carbonyl anions and is aptly compared to the anionic hydride reactivity series.

relative reactivity of M^- toward R^1–X:

$$M^- + RX \rightarrow MR + X^-$$

$$CpFe(CO)_2^- > CpRu(CO)_2^- > CpNi(CO)^- > Re(CO)_5^- > CpW(CO)_3^- > Mn(CO)_5^- > CpMo(CO)_3^- > CpCr(CO)_3^- > Co(CO)_4^-$$

relative reactivity of MH^- toward R^1–X:

$$MH^- + RX \rightarrow MX^- + RH$$

$$HW(CO)_4P^- > HCr(CO)_4P^- > HW(CO)_5^- > CpV(CO)_3H^- > HCr(CO)_5^- > HRu(CO)_4^- > trans\text{-}HFe(CO)_3P^- >> HFe(CO)_4^- \text{ (no reaction)}$$

As presented by King,[22] the major factors of import to the position of a metal nucleophile in the nucleophilicity scale include the following: (1) The coordination number of the anion vs. the resulting metal alkyl derivatives. E.g., coordination numbers changes of 4 → 5 and 6 → 7 are less favored than 5 → 6. (2) In any isostructural series, nucleophilicity increases as the metal becomes heavier. A notable and unexplained exception in the Dessy, Pohl, and King series is $CpFe(CO)_2^- > CpRu(CO)_2^-$. (3) Ligands such as C_5H_5, of π-acceptor ability poorer than CO, increase the metal's nucleophilicity.

In connection with point 3, our own studies showed the enhanced reactivity of phosphorous-donor ligand-substituted $PMn(CO)_4^-$ over $Mn(CO)_5^-$ (as well as the considerable effects of counterions in low polarity solvents).[23]

A decade later Pearson and Figdore attempted to unify reports of transition-metal nucleophilicity.[24] They compiled an extensive list of reactivities of both neutral and anionic metal nucleophiles with emphasis on the interplay of simple S_N2 halide substitutions and free radical pathways. The chemistry and resulting discussions were complex and impressive of the hazards of firm conclusions made on the basis of conventional physical organic mechanistic guides.

The relative reactivities of simple anionic transition-metal hydrides toward the RX halide/hydride exchange reaction are expected to be little influenced by metal coordination number. The observation, albeit of a limited series of geometries, is in agreement with that expectation. The metal trend however is quite clear and compatible with that in the Dessy, Pohl, and King nucleophilicity scale. Within a periodic table family series, the heavier metal hydrides are more reactive as hydride donors. The dependency of hydride donor character and periodic table position of the metal is also in agreement with the work of Labinger and Komadina.[25] Those workers examined the ability of structurally similar neutral transition-metal hydrides to reduce ketones. Their series demonstrated as well greater reactivity for the less electronegative, early transition-metal hydrides: $Cp_2ZrH_2 > [CpTiH]_2C_{10}H_8 > Cp_2NbH_3 > Cp_2TaH_3 > Cp_2Nb(H)(CO) > Cp_2MoH_2$. Our series of anionic metal hydrides have also been examined for relative abilities to reduce ketones and aldehydes.[26] Relative reactivities are the same as in the halide/hydride exchange reaction.

Substituent phosphine ligands enhance hydridic character of the anionic hydrides toward reduction of primary halocarbon centers. Also, the good donor character of the Cp ligand helps place the light transition-metal hydride $CpV(CO)_3H^-$ relatively high in the reactivity scale, i.e., similar in reactivity to $HW(CO)_5^-$. A preliminary report of the dianionic hydride $HV(CO)_5^{2-}$ suggests it to be an excellent H^- transfer agent, as expected from the dinegative charge.[27]

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(21) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1973**, *95*, 1669.

(22) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417.

(23) Darensbourg, M. Y.; Darensbourg, D. J.; Drew, D.; Burns, D. *J. Am. Chem. Soc.* **1976**, *98*, 3127.

(24) Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541.

(25) Labinger, J. A.; Komadina, K. H. *J. Organomet. Chem.* **1978**, *155*, C25.

(26) Kao, S. C.; Gaus, P. L.; Darensbourg, M. Y., submitted for publication.

Hence a comparison of anionic transition-metal nucleophilicity and anionic transition-metal hydride reactivity as hydride sources indicates definite similarities. In fact kinetic data on the reactions of allyl chloride and $HCr(CO)_5^-$, $CpW(CO)_3^-$, and $CpMo(CO)_3^-$ ($t_{1/2}$ = 83, 79, and 400 min, respectively, at 26 °C and a 20-fold excess of RCl; THF solution, PPN^+ salts)[28] placed the hydride much higher in reactivity than $CpMo(CO)_3^-$ and only slightly poorer than $CpW(CO)_3^-$. The metal hydride site might be regarded as a reactive site possibly more accessible to substrates than metal-based nucleophiles.[29]

Synthetic Applications of Anionic Transition-Metal Hydrides. As indicated by Table I, the anionic transition metal hydrides reduce a variety of halocarbons yielding the corresponding hydrocarbons in high yield. The 6B hydrides appear to be the best behaved of all metal carbonyl hydrides studied in these reductions and also display certain selectivities. For example the $HM(CO)_5^-$ anions reduce acyl chlorides to aldehydes, only reducing them further (to alcohols) in the presence of acids.[26] Other functional groups such as ketones, nitro groups, and isolated olefins are tolerated during the halide displacement by hydride. The 6B hydrides are also tunable by substituent phosphorous donor ligands. Regioselectivity is found in multihalogenated substrates due to the preference of the *cis*-$HM(CO)_4P^-$ anions for primary C–X sites.

The drawbacks of these hydrides as practical synthetic reagents center around their air sensitivity and resultant difficulties in synthesis and handling. If the anionic 6B transition-metal hydrides are to be developed as practical or large scale synthetic reagents, an in situ synthesis/regeneration is required. The report of phase-transfer catalysis synthesis of $HM(CO)_5^-$ (from CO and base) is encouraging in this regard.[30] A more impressive use of these reagents might evolve from their unique ability to become selective deuterium or tritium delivery agents, of import to the synthesis of isotopically labeled sophisticated organics and bioorganics. Another, potentially very powerful, application of the 6B hydrides is based on their ability to be modified by phosphine ligands. It is highly likely that a chiral ligand adjacent to the hydride site will deliver of H^- or D^- to chiral organic substrates with retention of optical purity.[31]

The use of anionic transition-metal organometallics as tools in organic chemistry is well established. In fact, an alternate route to the reduction of alkyl halides might be based on the sequential addition of electrophiles (eq 5) in

$$[M^{2-}] \xrightarrow{RX} [M]R^- \xrightarrow{HX} RH + M^0 \qquad (5)$$

the manner opposite to what is described herein. The alkyl anions $M(CO)_5R^-$ (M = Cr, Mo) have been prepared by addition of alkyl halides to $M(CO)_5^=$,[32] and protonation yielded the alkane.[33] This reaction has not been studied in detail. The analogous iron dianion $Fe(CO)_4^{2-}$ or Collman's reagent[34] is commercially available and can also be used in reaction 5. This disadvantage of this approach is that the dianions are not mild and selective reducing agents; additional reducible groups such as aldehydes or other C–X sites would not survive the reaction. Furthermore the facility with which CO inserts into Fe–R bonds does not permit formation of alkane uncontaminated by aldehyde.[35]

Scheme IV

$$\xrightarrow{\text{Increasing Tendency for Na}^{+}\cdots\text{HM}^{-}\text{ Interaction}}$$

$$\xleftarrow{\text{Increasing Tendency for Na}^{+}\cdots\text{OC—M Interaction}}$$

$HFe(CO)_4^-$, $HV(Cp)(CO)_3^-$, $HCr(CO)_5^-$, $HW(CO)_5^-$, $HCr(CO)_4P(OMe)_3^-$, $HW(CO)_4P(OMe)_3^-$

Mechanistic Considerations. An extensive study of the mechanism of hydride transfer of one anionic transition-metal hydride $CpV(CO)_3H^-$ has been carried out by Kinney, Bergman, and Jones.[4] Despite an occasional mechanistic probe anomaly, the preponderance of evidence made a convincing case for the intermediacy of free radicals, generated in a chain process, similar to the reactions of n-Bu_3SnH.[36] The rate constant for the chain propagation step, in which a hydrogen atom is transferred from a hydridovanadium radical anion (eq 6), was estimated to be 2×10^7 M^{-1} s^1.[4] The forementioned anomalies were interpreted in terms of contributions from ionic or two-electron pathways, indicative of a dependence of mechanistic path on the substrate.

$$[CpV(CO)_3H]^-\cdot + R\cdot \xrightarrow{k_{HTS}} RH + [CpV(CO)_3]^- \qquad (6)$$

Our study of hydride transfer from a relatively broad series of anionic transition-metal hydride sources permits evaluation of the effect of metal center as well as ligands on reaction paths available to $M–H^-$ bonds. Noted above were distinct differences in reaction rates as well as in selectivity of C–X bond types as the metal was varied and the ligand was modified. We have selected several of the same mechanistic probes used by Kinney, Bergman, and Jones and executed them primarily on two hydrides $HW(CO)_5^-$ and *cis*-$HW(CO)_4P(OMe)_3^-$. These results are compared and discussed below.

Ion Pairing. The nature of contact ion pair interactions of alkali cations and anionic carbonyl hydrides provides evidence of fundamental differences in electron density distribution as affected by metal and by ligand modification of anionic hydrides.[5] Spectral data indicates an increasing tendency for Na^+ ion interaction at the $M–H^-$ bond site in the series given in Scheme IV. Sodium ion interaction at the carbonyl oxygen was maximized for $HFe(CO)_4^-$.

The conclusion of the ion-pairing study was that electron density is more delocalized toward the left of the series and more localized on the H^- or at the $M–H^-$ bond site toward the right. It is reasonable to expect that the electron distribution made manifest here should also be expressed in mechanistic studies of hydride/halide exchange reactions. In fact, there is observed a major difference in selectivity of the hydrides that have received extensive study. In the cases of $HCr(CO)_5^-$, $HW(CO)_5^-$, and $CpV(CO)_3H^-$ there is low selectivity toward primary vs. secondary vs. tertiary. In the case of $HW(CO)_4P^-$ and $HCr(CO)_4P^-$ there is selectivity, with primary >> secondary > tertiary. This selectivity difference possibly implies different mechanistic paths, both between the $M–H^-$ reagents and within the RX series. The following reactions

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(27) Ellis, J. E.; Warnock, G. F. P. *J. Am. Chem. Soc.* **1984**, *106*, 5016.

(28) Darensbourg, M. Y.; Park, Y. K., unpublished results.

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(30) Gibson, D. H.; Ahmed, F. U.; Philips, K. R. *Organometallics* **1982**, *1*, 679.

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(32) Ellis, J. E.; Hagen, G. P. *Inorg. Chem.* **1977**, *16*, 1357.

(33) Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 7565.

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(35) Cooke, M. P., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 6080.

(36) Menapace, L. W.; Kuivila, H. G. *J. Am. Chem. Soc.* **1964**, *86*, 3047.

were used in attempts to define those paths.

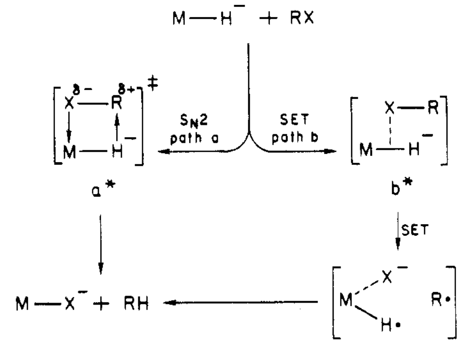
Ring-Closing Experiments: Scheme I. The observation of cyclized product in the reaction of 6-bromo-1-hexene with hydride sources is often cited as an indication of radical intermediates.[18] In that regard, the results summarized in Scheme I suggest radical character associated with reaction of $HW(CO)_5^-$. The failure to observe any methylcyclopentane in the $HW(CO)_4P(OMe)_3^-$ reaction can be considered as evidence contrary to a radical intermediate or as evidence that the $HW(CO)_4P^-$ radical might transfer hydrogen faster than the rate of ring closing. [Thus Bergman, Kinney, and Jones, unconvinced that the small percentage of cyclized product from reaction of 6-bromo-1-hexene and $CpV(CO)_3H^-$ signified ionic character in H^- transfer, used the analogous ether shown in Scheme I whose radical had a faster cyclization rate.[4] The enhancement of cyclized product supported their contention.] On the basis of comparisons of the neutral compounds $HMn(CO)_5$ vs. $HMn(CO)_4P$ (and the rapid H atom transfer from $HMn(CO)_5$ to $\cdot Mn(CO)_4P$),[37] the radical $\cdot HW(CO)_4P$ would actually be expected to have a *greater* W–H bond energy than $\cdot HW(CO)_5$. Hence the argument of more rapid H· transfer from $\cdot HW(CO)_4P$ than from $\cdot HW(CO)_5$ is not, at this time, a convincing one.

Ring-Opening Experiments: Scheme II. The most definitive mechanistic application of the ring opening of cyclopropylcarbinyl radicals as generated by reduced organometallics has been carried out by San Filippo, Silbermann, and Fagan.[19] With results supported by detection of organic radicals by electron spin resonance,[38] they were able to show that the $CpFe(CO)_2^-$ anion produces substantial amounts of ring-opened product $CpFe(CO)_2(CH_2CH_2CH{=}CH_2)$ only in the case of cyclopropylcarbinyl iodide. They concluded that an S_N2 path rather than a radical pathway was operational in the alkylation of $CpFe(CO)_2^-$ by the analogous bromide. In contrast $n\text{-}Bu_3SnH$ generates mainly cyclopropylcarbinyl radicals that undergo ring opening. The results shown in Scheme II for the anionic hydrides again suggest considerably more radical character for $HW(CO)_5^-$ than for $HW(CO)_4P(OMe)_3^-$. In this reaction $HW(CO)_5^-$ and $CpV(CO)_3H^-$ are comparable.

Reactivity with Tosylate. The emerging picture of $HW(CO)_5^-$ and $HW(CO)_4P(OMe)_3^-$ is that the former reacts with alkyl bromides with considerable radical character and the latter, with more ionic character. Consistent with this are relative reactivities toward alkyl tosylates. The phosphite-substituted anion reacts with *n*-BuOTs only slightly slower than it reacts with *n*-BuBr. Since alkyl tosylates are not prone to substitution via free radical paths,[24] such a similarity in rates could signify similar S_N2 paths for the bromide and the tosylate. In contrast, the all-carbonyl $HW(CO)_5^-$ reacts *extremely* slowly with the tosylate and the $HCr(CO)_5^-$, hardly at all.

Stereoselective Deuterium Delivery. A front side approach of $DW(CO)_5^-$ at the less hindered side of *exo*-2-bromonorbornane is assumed to explain the retention of configuration at the substitution center, as indicated in Scheme III. The observation of some endo-deuterium delivery for the $DW(CO)_4P^-$ reagent suggests partial ionic character (back-side attack) of the more active hydride. For comparison, Brown and co-workers observed that the reduction of *exo*-2-bromonorbornane with $LiBDEt_3$ resulted in the exclusive formation of the *endo*-d-isomer.[21]

Scheme V



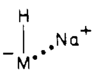
The observation was accepted as evidence for an S_N2 mechanism.

Mechanism Scheme. With most evidence pointing toward ionic character for reactions of the $HW(CO)_4P(OMe)_3^-$ reagent and electron-transfer character for reactions of the $HW(CO)_5^-$ reagent, it is appropriate to speculate on possible pathways and to pursue implications of those possibilities.

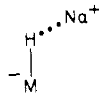
Path a of Scheme V is expected to obtain for the phosphite-substituted hydride and for the alkyl halides most apt to undergo S_N2 type substitution (R = primary and secondary; X = Cl, Br). Path b is appropriate for all-carbonyl or charge-delocalized hydride reagents, reacting with primary, secondary, or tertiary centers, as well as for the phosphite-substituted hydride in reaction with tertiary centers. The large negative entropy of activation (Table IV) is taken in support of the ordered transition state presumed important for both pathways. It must be noted, however, that neither the $\Delta S^\ddagger$ nor the $\Delta H^\ddagger$ show any trends or differences that can be claimed significant within the experimental error.

More M–H bond breaking (heterolytically) is appropriate to the transition state of path a than to that of path b. In that connection the lack of a KIE for $HW(CO)_5^-$ vs. $DW(CO)_5^-$ reaction with *n*-BuBr (Table II, entry 2) is cited. Other KIE measurements important to the mechanistic argument were difficult to obtain. The rate of $HW(CO)_4P(OMe)_3^-$ with n-BuBr was estimated to be ca. 2.0 times more rapid than that of $DW(CO)_4P(OMe)_3^-$; however the number is not precise.

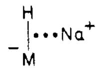
The transition state of path a is drawn essentially the same as that expected in the halide/hydride exchange reaction of LiCl and $HW(CO)_4P(OMe)_3^-$ which yields exclusively $ClW(CO)_4P(OMe)_3^-$ and presumably LiH. That is, a strictly ionic mechanism obtains.[5] However, whether oxidative addition to M (yielding M(H)R) occurs cannot be differentiated from transition state a* which transfers H^- to $R^{\delta+}$ concomitant with M–X bond formation. Both possibilities may be considered as classical S_N2 reactions with nucleophilicity based at the metal site for the former and at the hydride site for the latter. The problem of differentiating the two is analogous to that encountered in determining the sites of contact ion pairing in solutions of $Na^+\ HW(CO)_4P^-$: metal (structure A) vs. hydride (B).[5]



A



B



C

The predicament was avoided by describing the interaction as existing at the M–H bond density site (C). For the phosphite-substituted 6B anionic hydrides we feel S_N2 reactivity occurs at the H^- site (D) for the following reasons: (1) The hydride ligand has considerable anionic

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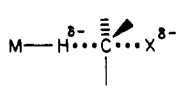
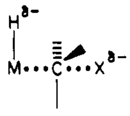
(37) Nappa, M. J.; Santi, R.; Diefenbach, S. P.; Halpern, J. *J. Am. Chem. Soc.* **1982**, *104*, 619.

(38) Krusic, P. J.; Fagan, P. J.; San Filippo, J., Jr. *J. Am. Chem. Soc.* 1977, *99*, 250.

character as evidenced by the displacement of Cl^- from LiCl.[5] (2) The expansion of coordination number (6 → 7) is unfavorable, particularly when the entering group is bulky, i.e., a trigonal carbon (structure E).



D



E

The transition state of path b (Scheme V) is analogous to those of classical inner-sphere electron-transfer reactions. Although the structure is depicted as $X^{\delta-}$ interaction at the M–H bond density site, we cannot distinguish that and interaction of $X^{\delta-}$ at the metal. A precedent for the latter was provided by Crabtree, Faller, et al. in the isolated complex $Ir(H)_2(C_6H_4I_2)(PPh_3)_2]^+$ in which the iodides of diiodobenzene are bound to the iridium hydride.[39] Note that the transition state of b* provides rationale for the order of magnitude difference in rate of $HW(CO)_4P(OMe)_3^-$ and $HW(CO)_5^-$ with t-BuBr. Greater repulsion between the $Br^{\delta-}$ and the more negative W–H⁻ site of the phosphite hydride should raise the E_{act}. We reemphasize however that the small differences in ΔH^{*} or ΔS^{*} required to account for even this highly significant rate difference cannot be discerned within experimental error.

Both pathways are drawn in a manner so as to avoid generating a coordinatively unsaturated 16-electron $M(CO)_4L^0$ species. Control experiments showed that the reactant $HM(CO)_4L^-$ is a trapping agent for $M(CO)_4L^0$, similar in efficiency to X^-, yet μ-$HM_2(CO)_8L_2^-$ species are never observed. Other controls noted the lack of effect on alkyl halide/metal hydride reaction rate or products upon addition of CO or PPh_3. *We must conclude that free $M(CO)_4L^0$ is never formed but is always in close proximity, or partially bonded to, X^-.*

Comments and Conclusions

The implication of the above mechanistic study, together with literature precedents, is that the anionic transition-metal hydrides may transfer hydride via one of (a minimum of) two pathways. Hence a "reactivity scale" is a tenuous concept, dependent as it is on the predominant path associated with a particular substrate. For example, the $HW(CO)_4P(OMe)_3^-$ reagent is good reducing agent for primary alkyl halides (the S_N2 path), but not for tertiary centers (the SET path). The $HFe(CO)_4^-$ anion is extremely poor as a hydride source for alkyl halides, is reasonably reactive toward acid chlorides (pathway undetermined), and readily reduces nitro groups to amines, even in the presence of acid chlorides.[3] Our 6B hydrides, highly reactive toward C–X bonds, have less reactivity toward nitro groups.[7] Had we selected the reduction of nitrobenzene as reference substrates in this relative reactivity comparison, the above reactivity series would most likely be opposite.

There is an interesting comparison between the contact ion pairing study[5] and mechanistic paths selected by anionic transition-metal hydrides. Ionic hydride-transfer character is in correlation with localization of negative charge on the hydride ligand is indicated by the tendency of Na^+ to interact at the M–H⁻ site. Delocalization of negative charge as evidenced by the observation of Na^+ interaction at CO oxygen sites *apparently* correlates with electron-transfer ability. The series presented in Scheme IV can thus be used in a predictive manner, permitting selection of reagents for their hydride transfer vs. their electron-transfer character:

$$\xrightarrow{\text{Increasing Tendency for H}^-\text{ Transfer}}$$

$$\xleftarrow{\text{Increasing Tendency for SET Processes}}$$

$HFe(CO)_4^-$, $HV(Cp)(CO)_3^-$, $HCr(CO)_5^-$, $HW(CO)_5^-$, $HCr(CO)_4P(OMe)_3^-$, $HW(CO)_4P(OMe)_3^-$

With use of this approach we have reexamined literature data on the dehalogenation of organic halides by $HFe(CO)_4^-$.[40] The organic halides studied by Alper were activated aromatic bromides, bromomaleic anhydride, and α-bromocamphor, all of which are precursors of fairly stable radicals. We contend that in view of the fact that $HFe(CO)_4^-$ will not reduce primary alkyl bromides, all of the reactions described by Alper are electron transfer in character rather than S_N2.

Finally, the practical aspects of this series is reemphasized. Reagent selection may be based on the relative activity of the hydrides. For example, the $HM(CO)_5^-$ reagents are excellent mild reducing agents for acid chlorides, yielding only aldehydes, whereas the $HM(CO)_4P^-$ reagents overreact and produce some alkoxide as well as aldehyde.[7] The latter phosphite hydrides are, in fact, similar in reactivity to Brown's Super-Hydride (Aldrich), Li^+ $HBEt_3^-$, reported as being the "most powerful nucleophile available to organic chemists".[41] Certainly the development of anionic transition-metal hydrides as synthetic reagents is embryonic compared to main-group metal or metalloid hydrides. However it is conceivable that certain of the anionic transition-metal hydrides (deuterides) might become in cases a hydride transfer reagent of choice.

Acknowledgment. This work was supported by the National Science Foundation (CHE 83-04162) and (in part) by the Robert A. Welch Foundation.

Registry No. [PPN][*cis*-$HCr(CO)_4P(OMe)_3$], 89676-28-8; [PPN][*cis*-$HW(CO)_4P(OMe)_3$], 82963-28-8; [PPN][*cis*-$HW(CO)_4PMe_3$], 82963-32-4; [PPN][*cis*-$HW(CO)_4PPh_3$], 82963-30-2; [PPN][$HRu(CO)_4$], 79408-52-9; [PPN][$HFe(CO)_4$], 56791-54-9; [PPN][$CpV(CO)_3H$], 68738-02-3; [PPN][*trans*-$HFe(CO)_3P(OMe)_3$], 93303-97-0; [PPN][$HCr(CO)_5$], 78362-94-4; [PPN][$HW(CO)_5$], 78709-76-9; n-C_4H_9Br, 109-65-9; n-C_4H_9I, 542-69-8; $C_6H_5CH_2Cl$, 100-44-7; $C_6H_5CH_2Br$, 100-39-0; C_6H_5Br, 108-86-1; sec-C_4H_9Br, 78-76-2; t-C_4H_9Br, 507-19-7; C_6H_5COCl, 98-88-4; 1-bromoadamantane, 768-90-1; cyclopropylmethyl bromide, 7051-34-5; 6-bromo-1-hexene, 2695-47-8.

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(39) Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, *J. J. Am. Chem. Soc.* **1982**, *1*, 1361.

(40) Alper, H. *Tetrahedron Lett.* **1975**, *27*, 2257.

(41) Brown, H. C.; Krishnamurthy, S. *Aldrichim. Acta* **1979**, *12*, 3.