Relative Reactivities of Anionic Transition-Metal Hydrides. Reduction of Alkyl Halides

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Summary: A comparison of the second-order rate constants for halide displacement from *n*-BuBr by H^- derived from anionic transition-metal hydrides established the following order of reactivity: *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 lack of dependence of reactivity on degree of branching of the alkyl halide for $HM(CO)_5^-$ (M = Cr, W) and a dramatic diminishing of reactivity for $HM(CO)_4P(OMe)_3^-$, 1° >> 2° > 3°, resulted in a different order of reactivity on the basis of *t*-BuBr: $HCr(CO)_5^-$ > $HW(CO)_5^-$ > *cis*-$HCr(CO)_4P(OMe)_3^-$ > $CpV(CO)_3H^-$ > *cis*-$HW(CO)_4P(OMe)_3^-$ >> $HFe(CO)_4^-$ (no reaction). Mechanistic probes were applied to reactions of $HW(CO)_5^-$ and *cis*-$HW(CO)_4P(OMe)_3^-$, and preliminary results suggest the former to involve some radical character (single electron transfer) and the latter to react with considerable ionic character (H^- transfer).

The monomeric group 6B transition-metal hydrides, $HM(CO)_5^-$, can be prepared by a variety of routes,[1,2] including the reaction of $M(CO)_6$ with base, i.e., the central component of the water-gas shift reaction,[3] and the reaction suggestive of an inexpensive regenerable source of reactive hydride. We have been studying the hydride-transfer ability of these and other anionic metal hydrides to metals, carbon centers, and metal-bound carbon. The group 6B hydrides and their phosphorus-donor-substituted derivatives are particularly reactive towards the reduction of organic halides (including tertiary alkyl halides) with reactivity approaching that of powerful main group metal hydride sources such as Brown's HBR_3^- reagents.[4] This paper is a preliminary report of the hydride/halide exchange reaction described by eq 1. We have also established an order of reactivity for several anionic transition-metal carbonyl hydrides based on rate constants k_2 (eq 2) for reaction with RX.

$$M{-}H^- + RX \rightarrow M{-}X^- + RH \qquad (1)$$

$$\text{rate} = k_2[MH^-][RX] \qquad (2)$$

The yields of hydrocarbon products resulting from reaction 1, where $M{-}H^- = HW(CO)_5^-$ as hydride source (bis(triphenylphosphine)nitrogen(1+) salt, PPN^+, in THF solution), were analyzed by gas chromatography for the following cases: n-C_4H_9Br (n-C_4H_{10}, 83% yield), 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%), α-bromocamphor (camphor, 70%), C_6H_5Br (C_6H_6, 80%), and 1-bromoadmantane (adamantane, 70%). No elimination products were observed. The product obtained upon reacting $DW(CO)_5^-$ with $C_6H_5CH(CH_3)Br$ was established by ^1H NMR to be $C_6H_5CH(CH_3)D$ (95%), signifying that the metal reductant is the sole source of hydride (deuteride).

Table I. Rate Constants for the Reaction of $[PPN]HW(CO)_5$ with RX in THF Solution at 26.0 °C[a]

RX	$k_2 \times 10^3$ s^{-1} M^{-1}	RX	$k_2 \times 10^3$ s^{-1} M^{-1}
n-C_4H_9I	>10	2-C_4H_9Br	1.79 (±0.05)
n-C_4H_9Br	3.31 (±0.13)	t-C_4H_9Br	2.81 (±0.16)
n-C_4H_9Cl	*b*	1-bromoadamantane	0.268 (±0.014)
$C_6H_5CH_2Cl$	1.68 (±0.09)	C_6H_5Br	0.369 (±0.045)
C_6H_5COCl	>10	$C_6H_5CH_2Br$	>10

[a] Reactions were run under pseudo-first-order conditions with RX in 20-fold excess. $[HW^-]$ = 0.005 M. Errors calculated at 90% confidence limit. [b] No reaction.

Chart I. Reactivity of Anionic Metal Carbonyl Hydrides As Established for the Reaction $[M]H^- + RX \rightarrow [M]X^- + RH$[a]

For R = 1° (n-BuBr)

cis-$HW(CO)_4P(OMe)_3^-$ > *cis*-$HCr(CO)_4P(OMe_3)^-$ >

~50 ~30

$HW(CO)_5^-$ > $CpV(CO)_3H^-$ > $HCr(CO)_5^-$ >

3.31 (±0.13) 2.20 (±0.06) 1.79 (±0.05)

$HRu(CO)_4^-$ >> $HFe(CO)_4^-$

1.0 *b*

For R = 3° (t-BuBr)

$HCr(CO)_5^-$ > $HW(CO)_5^-$ > *cis*-$HCr(CO)_4P(OMe)_3^-$ >

3.17 (±0.08) 2.81 (±0.16) 0.81 (±0.05)

$CpV(CO)_3H^-$ > *cis*-$HW(CO)_4P(OMe)_3^-$ >> $HFe(CO)_4^-$

0.33 (±0.03) 0.21 (±0.01) *b*

[a] Values cited are second-order rate constants, $k_2 \times 10^3$ s^{-1} M^{-1}, measured in THF solution at 26.0 °C for bis(triphenylphosphine)nitrogen(1+) salts of the hydrides. Errors calculated at the 90% confidence limit. [b] No reaction.

The rates of several reactions were monitored by changes in ν(CO) (IR), and the kinetic rate expression 2 was established. From the second-order rate constants found in Table I the following conclusions may be drawn. For reaction with $HW(CO)_5^-$, the order of reactivity of RX is I > Br > Cl; and of RX is 1° ≈ 3° > 2°. The latter result suggests a mechanism other than S_N2 displacement of X. Corroborating this is the reactivity seen with bromoadamantane, bromobenzene, and *t*-BuBr, substrates normally not subject to nucleophilic displacement. The typical reactivity dependence on the composition of R is benzoyl > benzyl > alkyl > aryl > adamantyl. Activation parameters were determined for three of the organic halide reductions, and a negative value of ΔS^* was obtained in all cases.[5]

The rates of reaction of n-C_4H_9Br and t-C_4H_9Br with a range of different transition-metal carbonyl hydrides were determined, and an order of reactivity was established (Chart I). In cases where the differences in rate constants were small, relative reactivities were verified by competitive reaction of an equimolar mixture of the two hydrides with

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(5) The activation parameters for the three organic halides determined over a temperature range of 20 °C (26–46 °C): ΔH^* (kcal/mol) = 12.6 ± 0.18 (n-C_4H_9Br), 12.0 ± 0.18 (t-C_4H_9Br), 11.4 ± 0.13 ($C_6H_5CH_2Cl$); ΔS^* (eu) = −29.5 ± 6.3 (n-C_4H_9Br), −32.1 ± 6.2 (t-C_4H_9Br), −35.2 ± 4.4 ($C_6H_5CH_2Cl$). Errors calculated at 90% confidence limit.

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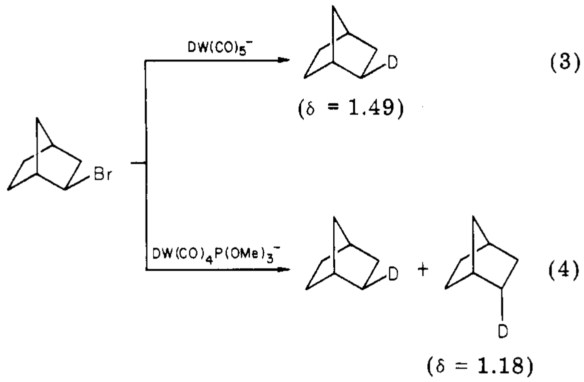
a deficiency of RX. As noted from Chart I, the group 8B hydrides, $HM(CO)_4^-$ (M = Fe, Ru), were less reactive than their group 6B analogues toward these H/X displacement reactions. (Only the most reactive halides (such as acid chlorides) have been reported to be reduced by $HFe(CO)_4^-$.[6]) The phosphite-substituted metal hydrides $HM(CO)_4P^-$ are more reactive toward primary alkyl halides than are their pentacarbonyl analogues. Such enhanced reactivity was anticipated as the substitution of CO by a P-donor ligand increases the partial negative charge on the hydride.[7] However, this enhanced reactivity is not observed for the branched alkyl halides. There is actually a 250-fold diminution of reactivity through the series n-C_4H_9Br, 2-C_4H_9Br,[8] and t-C_4H_9Br for *cis*-$HW(CO)_4P(OMe)_3^-$, resulting in a *reversal* of reactivity order for *cis*-$HW(CO)_4P(OMe)_3^-$ and $HW(CO)_5^-$ for reductions of tertiary centers. In fact the reduction of a mixture of t-BuBr and n-BuBr by $HW(CO)_4P(OMe)_3^-$ produces n-C_4H_{10} exclusively, whereas the same mixture of bromides yields a mixture of n-C_4H_{10} and i-C_4H_{10} with $HW(CO)_5^-$ as reductant. Such a pronounced ligand effect is expected to be very useful in developing selective transition-metal hydride transfer agents.

Several experiments of import to the mechanism of hydride transfer are under way and will be presented in the full report of this study. Two especially noteworthy results are as follows. The reaction of $HW(CO)_5^-$ with 6-bromo-1-hexene in THF solution yielded a mixture of 1-hexene and methylcyclopentane (1.6:1 ratio, 80% overall yield) whereas $HW(CO)_4P(OMe)_3^-$ produced only 1-hexene, 85% yield, under identical reaction conditions. The detection of cyclized products derived from bromoalkenes during hydride/halide displacement has been used as an indicator of radical species in reactions of the mechanistically well-characterized $CpV(CO)_3H^-$ as well as tin hydrides.[9] By this criterion $HW(CO)_5^-$ appears to react with at least some radical character; however this test provided no positive evidence for the involvement of radicals in the case of $HW(CO)_4P(OMe)_3^-$. These hydrides, $HW(CO)_5^-$ and $HW(CO)_4P(OMe)_3^-$, reacted with *exo*-2-bromonorborane to yield norbornane. The $HW(CO)_5^-$ reaction requires a few hours and the phosphite hydride requires days at room temperature. When the corresponding deuterides were used the ^2H NMR of the norbornane product indicated a highly selective (exo) incorporation with $DW(CO)_5^-$, eq 3, but a mixture of exo- and endo-deuterated products for $DW(CO)_4P(OMe_3)_3^-$, eq 4.



The result of eq 3 suggests a front-side displacement with a specificity that is quite surprising in view of the 6-bromo-1-hexene study described above. The result in eq 4 implies at least some inversion at the substitution center, analogous to the similarly slow reduction of *exo*-2-bromonorbornane with $LiBDEt_3$ which resulted in the exclusive formation of *endo-d* isomer.[4] In that case the inversion at the substitution center was taken as evidence for an S_N2 mechanism. At this stage in our investigation we can only conclude the obvious: (1) the all-carbonyl hydride appears to have some radical character associated with its alkyl halide reductions; (2) the phosphite-substituted hydride may have considerable ionic character and little radical character associated with its hydride-transfer reactions; and (3) an ordered transition state is appropriate to both.[5,10]

The current status of the literature involving metal hydrides, SET processes, and stereochemistry[11] (retention, inversion, or racemization of configuration) would permit various (and lengthy) interpretations of our results. Furthermore the balance in M–H bond character leading to H· transfer, SET, or H^- transfer has been noted in other systems,[12] and it is not surprising that ligand effects might also alter M–H reactivity. Regardless of mechanism, the value of the above study is in the established reactivity order and in the potential development of useful hydride-transfer reagents.

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Registry No. *cis*-$HW(CO)_4P(OMe)_3^-$, 82963-27-7; *cis*-$HCr(CO)_4P(OMe)_3^-$, 89210-44-6; $HW(CO)_5^-$, 77227-36-2; [PPN]$HW(CO)_5$, 78709-76-9; $DW(CO)_5^-$, 89210-45-7; $CpV(CO)_3H^-$, 68738-01-2; $HCr(CO)_5^-$, 18716-81-9; $HRu(CO)_4^-$, 77482-04-3; $HFe(CO)_4^-$, 18716-80-8; n-BuBr, 109-65-9; t-BuBr, 507-19-7; n-C_4H_9I, 5423-69-8; $C_6H_5CH_2Cl$, 100-44-7; C_6H_5COCl, 98-88-4; 2-C_4H_9Br, 78-76-2; C_6H_5Br, 108-86-1; $C_6H_5CH_2Br$, 100-39-0; $C_6H_5CH(CH_3)Br$, 585-71-7; 1-bromoadamantane, 768-90-1; α-bromocamphor, 76-29-9; 6-bromo-1-hexene, 2695-47-8; *exo*-2-bromonorbornane, 2534-77-2; *exo*-2-*d*-norbornane, 22642-76-8; *endo*-2-*d*-norbornane, 22642-75-7.

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(6) (a) Cole, T. E.; Pettit, R. *Tetrahedron Lett.* **1977**, 781. (b) There has been a report on the dehalogenation of organic halides in an in situ generated $HFe(CO)_4^-$ which was conducted in a highly polar medium. Alper, H. *Ibid.* **1975**, 2257.

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(8) $k_2 = 4.24\ (\pm 0.18) \times 10^{-3}\ s^{-1}\ M^{-1}$.

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(10) The activation parameters for the reaction of *cis*-$HW(CO)_4P(OMe)_3^-$ and t-BuBr at 26 °C are $\Delta H^{\ddagger}$ (kcal/mol) = 13.3 ± 1.8 and $\Delta S^{\ddagger}$ (eu) = −31.4 ± 6.4. Errors calculated at 90% confidence limit.

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Haptotropic Rearrangements. Kinetics and Mechanism of the Rearrangement of $Mn(\eta^6\text{-}C_{13}H_9)(CO)_3$ to $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$

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Summary: The rate constants and activation parameters for the following rearrangements in hexane have been