J. Am. Chem. Soc. 1987, 109, 3313-3317

Competing Nucleophilic Displacement and Radical Chain Reduction in Reactions of Transition-Metal Hydride Anions with Alkyl Bromides

Carlton E. Ash, Philip W. Hurd, Marcetta Y. Darensbourg,* and Martin Newcomb*

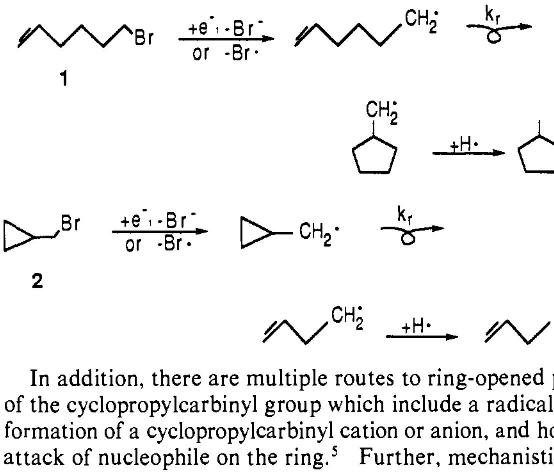
Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843.
Received October 27, 1986

Abstract: The reactions of group 6 metal hydrides, $PPN^+HM(CO)_4L^-$ (M = Cr, L = CO; M = W, L = CO, $P(OMe)_3$), with two mechanistic probes, 6-bromo-1-hexene (**1**) and 4-bromo-3,3-dimethyl-1-butene (**3**), in THF at 25 °C were studied. Neopentyl-like probe **3** was reduced (presumably) exclusively by a radical chain process, and the second-order rate constants (k_H) for hydrogen atom abstraction from $HM(CO)_4L^-$ by the intermediate radical, 2,2-dimethyl-3-butenyl, were determined. Unhindered probe **1** was reduced by both an S_N2 pathway and a radical chain process. The second-order rate constants for hydrogen atom abstraction from $HM(CO)_4L^-$ by 5-hexenyl were estimated, and the percentages of reduction of **1** by the S_N2 pathway and the radical chain process were calculated; the percentage of reduction by the S_N2 pathway increased in the order $HCr(CO)_5^- < HW(CO)_5^- < HW(CO)_4P(OMe)_3^-$. The combination of a hindered and an unhindered probe as used in this study has expanded the utility of mechanistic probes by permitting quantitation of competing pathways.

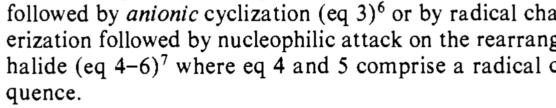
Anionic main group and transition-metal hydrides exhibit a rich reactivity toward electrophilic substrates, especially polar organic compounds. The formal result of their reactivity is hydride (H^-) transfer. The actual mechanism by which the hydride is transferred has been the object of much research and controversy. Several anionic transition-metal hydrides have been prepared and investigated as to their spectral properties, solution ion-pairing characteristics, and reactivity.[1] In a survey of reactivity the following landmark reactions have been used: competition experiments with primary/tertiary carbon centers; comparative rates of reaction for organic halides vs. tosylates, stereospecific addition of deuterium; and reduction of precursors which give radicals that are subject to rapid skeletal rearrangements. On the basis of the exhaustive study of the $CpV(CO)_3H^-$ hydride by Kinney, Bergman, and Jones[2] and extended to studies of $HM(CO)_5^-$ (M = Cr, W), $HM(CO)_4^-$ (M = Fe, Ru), *cis*-$HW(CO)_4PR_3^-$, and *trans*-$HFe(CO)_3PR_3^-$ in our laboratories[3,4] it appears that *three* pathways are discernible in *alkyl halide* reductions by these anionic transition-metal hydrides:[1] (1) radical mechanisms,[2] (2) S_N2, hydride site nucleophilicity,[3] and (3) S_N2, metal site nucleophilicity (oxidative addition).[4]

Pathway 3 is appropriate for those hydrides whose metal centers are prone to oxidative addition. For example, electrophilic addition to the Fe(O) center of d^8, TBP $HFe(CO)_3PR_3^-$ leads to a very reasonable d^6, O_h, Fe(II) intermediate, $(H)(R)Fe(CO)_3PR_3$.[3] Since oxidative addition is not favored for the d^6, O_h $HM(CO)_5^-$ hydrides and derivatives, other reaction pathways emerge. In fact several reaction probes indicated contributions from both pathways 1 and 2 for these hydrides.[3] Although no single reaction probe provided quantitative or conclusive evidence for a particular mechanism or combination of mechanisms, taken altogether we concluded that the amount of apparent hydride transfer via an S_N2 pathway varied according to the metal hydride: $CpV(CO)_3H^- \approx HCr(CO)_5^- < HW(CO)_5^- <$ *cis*-$HCr(CO)_4P(OMe)_3^- <$ *cis*-$HW(CO)_4P(OMe)_3^-$.[3] Interestingly the order of reactivity by an apparent 2-electron, hydride-transfer path correlated well with the ability of Na^+ cations to interact with the anion at the M–H⁻ bond site.[3] A delocalization of negative charge, as indicated by Na^+ interaction with carbonyl oxygen, seemed to correspond with increased radical behavior in the reductions.

Radical probe (or so-called radical "clock") reactions based on skeletal rearrangements (eq 1 and 2) have become useful tools for mechanistic studies. Despite widespread use, probes such as 6-bromo-1-hexene, **1**, and cyclopropylcarbinyl bromide, **2**, have inherent problems. Specifically, if the rate of trapping of the first-formed radical by some hydrogen source is faster than the radical rearrangement, the S_N2 process would be indistinguishable from a radical process.



(1)



(2)

In addition, there are multiple routes to ring-opened products of the cyclopropylcarbinyl group which include a radical process, formation of a cyclopropylcarbinyl cation or anion, and homo-S_N2 attack of nucleophile on the ring.[5] Further, mechanistic probes like **1** can give cyclized products by halogen metal exchange followed by *anionic* cyclization (eq 3)[6] or by radical chain isomerization followed by nucleophilic attack on the rearranged alkyl halide (eq 4–6)[7] where eq 4 and 5 comprise a radical chain sequence.

To avoid some of these problems we have adopted a two radical probe methodology to identify and to separate quantitatively concurrent reaction pathways which appeared to be operative in the anionic metal hydride reductions. The two radical probes employed were **1** and 4-bromo-3,3-dimethyl-1-butene, **3**. The latter undergoes the sequence of reactions shown in eq 7. The major advantages that the neopentyl-like bromide **3** offers over

---

[1] Darensbourg, M. Y.; Ash, C. E. *Adv. Organomet. Chem.*, in press.

[2] (a) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 635. (b) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902.

[3] (a) Kao, S. C.; Spillet, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83. (b) Kao, S. C.; Darensbourg, M. Y. *Organometallics* **1984**, *3*, 646.

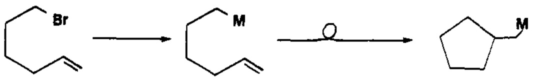
[4] (a) Ash, C. E.; Delord, T.; Simmons, D.; Darensbourg, M. Y. *Organometallics* **1986**, *5*, 17. (b) Cole, T. E.; Pettit, R. *Tetrahedron Lett.* **1977**, *9*, 781.

[5] (a) Newcomb, M.; Smith, M. G. *J. Organomet. Chem.* **1982**, *228*, 61–70. (b) Alnajjar, M. S.; Smith, G. F.; Kuivila, H. G. *J. Org. Chem* **1984**, *49*, 1271.

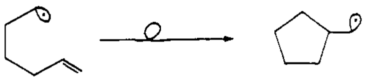
[6] Bailey, W. F.; Patricia, J. J.; DelGobbo, V. C.; Jarret, R. M.; Okarma, P. J. *J. Org. Chem.* **1985**, *50*, 1990–2000.

[7] Newcomb, M.; Sanchez, R. M.; Kaplan, J. *J. Am. Chem. Soc.* **1987**, *109*, 1195–1199.

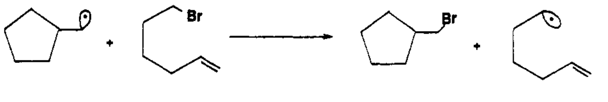
0002-7863/87/1509-3313$01.50/0



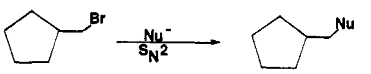
(3)



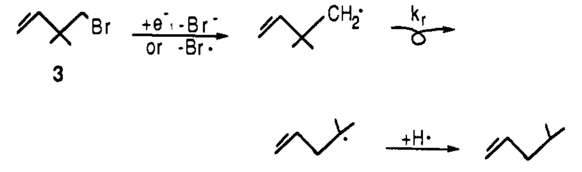
(4)



(5)



(6)



(7)

1 are a faster rearrangement rate for the radical and, more importantly, an inherent lack of reactivity toward nucleophilic halide displacement. In addition, an anionic product formed from **3** will not rearrange.[8] Since **1** is vulnerable to reduction by both radical chain or S_N2 mechanisms and **3** is more likely to undergo only radical reductions, complementary results can be obtained by reacting both with a potential reducing agent.[9]

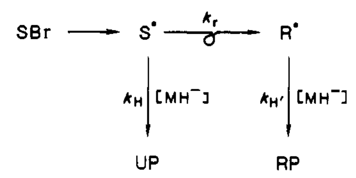
Experimental Section

Materials. The THF solvent used in all reactions was dried over potassium or sodium benzophenone ketyl under a nitrogen atmosphere. All reagents used were reagent grade and were commercially available. Unless otherwise noted, all reagents were purified before use; the purity of each reagent was determined by gas chromatography and NMR spectroscopy. Prior to use 6-bromo-1-hexene was distilled under nitrogen and then stored over activated 3A molecular sieves. It was purchased from Wiley Organics. The anionic pentacarbonyl metal hydrides, $HCr(CO)_5^-$ and $HW(CO)_5^-$, were prepared as their PPN^+ (bis(triphenylphosphine)iminium) salts according the procedure described in the literature.[10] The $P(OMe)_3$-substituted complex, $HW(CO)_4P(OMe)_3^-$, was also prepared as described previously.[11]

4-Bromo-3,3-dimethyl-1-butene (3) was prepared by a modification of the reported method[12] wherein $CBrCl_3$ was substituted for CBr_4.[13] Bromide **3** was purified by preparative GC on a glass column containing 10% OV-101 on Chromosorb 750 and was >98% pure by analytical GC.

Radical Probe Reactions. Appropriate stock THF solutions of the respective organic halide (radical probe) were prepared in volumetric flasks. Prior to addition of the stock solution to the anionic transition-metal hydride, it was thoroughly degassed by vacuum freeze–thaw method four times. All reactions were carried out in 5-mL volumetric flasks to which an appropriate weighed amount of metal hydride had been added in an argon atmosphere glovebox. Weighing of the solid metal hydride was done on a Mettler PE360 top-loading balance accurate to ±0.001 g. Prior to addition of the THF/organic halide solution, the reaction vials were sealed with two rubber septa, further covered with parafilm, and wrapped with aluminum foil to minimize light exposure. Aliquot transfer of 5 mL of the radical probe stock solution to the metal hydride was accomplished by stainless steel cannula under N_2 pressure. A small nitrogen pressure was left in the reaction vessel. The reactions were allowed to stir at ambient temperatures for 18–23 h. At the end of reaction, the volatile organics were transferred by trap-to-trap high-vacuum distillation into another 5-mL volumetric flask. After distillation, the flasks were removed from the vacuum line, and the products were analyzed by gas chromatography with use of either a Varian 2400 gas chromatograph with a Supelco 30 m × 0.75 mm wide-bore SPB-5 capillary column or a Varian 3400 gas chromatograph with a J&W Scientific 15 m × 0.52 mm megabore DB-1 capillary column. The amount of hydrocarbons produced and the amount of unreacted alkyl halide were both quantitatively measured by using nonane as an internal standard. A weighed amount of nonane was placed in each distilled product mixture prior to injection in the gas chromatograph.

Scheme I



Results and Discussion

Data Treatment. Table I lists the reaction data for reduction of 6-bromo-1-hexene (**1**) by the metal hydrides. Table II contains similar data for 4-bromo-3,3-dimethyl-1-butene (**3**). The ratio of unrearranged to rearranged products, [UP]/[RP], and the percent completion of reaction as monitored by hydrocarbon produced and consumption of alkyl halide were determined by gas chromotography. The organometallic products in reactions with both probes were the corresponding metal bromide. In reductions with $HW(CO)_4P(OMe)_3^-$ a small amount of μ-$H[W(CO)_4P(OMe)_3]_2^-$ was observed as organometallic product. With **1**, reactions were carried out *both* with probe as the limiting reagent and in excess. For reactions in which the probe was used in excess and the metal hydride concentrations were small, the concentration of hydride throughout the reaction varied enormously since in these runs all reactions went to completion. Therefore, in this class of reactions the mean hydride concentration and [UP]/RP] ratio were averaged to create one data point in a graphical analysis. Reactions where the radical probe was used in excess generally were avoided to minimize the possibility of radical chain isomerization of the probe.[7] Also by using the metal hydride in excess, the change in concentration of the hydride was minimal and the quantity of hydrocarbon products was increased. With **3**, all reactions were run with the metal hydride in excess; therefore, no averaging of the low metal concentrations was necessary. In contrast to **1**, in which all reactions went to completion, **3** gave complete reaction only with $PPN^+ HCr(CO)_5^-$. The percent completion was taken into account when determining the average metal hydride concentration throughout the reaction. A graphical approach for the determination of k_H was used in all reactions except in the reaction of $PPN^+ HW(CO)_4P(OMe)_3^-$ with **3**. In these studies, scatter in the product ratio and percent yield was observed in seven different runs, therefore, the k_H reported represents a simple average of the k_H values obtained for each run.

Approach to the Analysis. An outline of the key steps involved in a radical skeletal rearrangement probe is presented in Scheme I.

In Scheme I, SBr is the radical probe substrate, S· is the substrate radical intermediate, R· is the rearranged radical, MH^- is the group 6 anionic metal hydride, UP is the unrearranged product, and RP is the rearranged product. Since there is a competition for the substrate radical along two reaction paths, the rates of formation of the rearranged, RP, and unrearranged products, UP, can be expressed as follows:

$$d[UP]/dt = k_H[S^\bullet][MH^-] \qquad (8)$$

$$d[RP]/dt = k_r[S^\bullet] \qquad (9)$$

The latter expression holds as long as $k_{H'}[MH^-] \gg k_{-r}$ which is the case in the two radical probes considered here.[14] At any time,

---

(8) Newcomb, M.; Glenn, A. G., unpublished results.

(9) From our studies of rates of halogen atom transfer, it is known that bromine atom transfer from either probe halide to a carbon radical is too slow to be important in this study.[7]

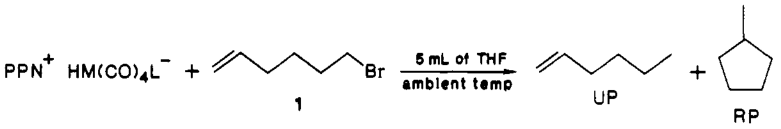
(10) Slater, S. G.; Darensbourg, M. Y. *Inorg. Synth.* **1983**, *22*, 181.

(11) Slater, S. G.; Lusk, R.; Schumann, B. F.; Darensbourg, M. Y. *Organometallics* **1982**, *1*, 1662.

(12) Newcomb, M.; Williams, W. G.; Crumpacker, E. L. *Tetrahedron Lett.* **1985**, *26*, 1183–1184.

(13) Newcomb, M.; Sanchez, R. M., unpublished results.

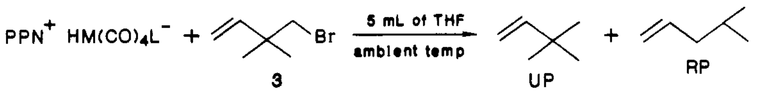
Table I. Reaction Data[a] of Metal Hydrides with 6-Bromo-1-hexene



M	L	[MH⁻]	[MH⁻av]	[1]	[UP]/[RP]	{[UP]/[RP]}/[MH⁻av]	% conversion[b]	time[c]	k_H[d]
Cr	CO	0.007	0.004	0.055	1.78	508	100	17.0	12.7
Cr	CO	0.010	0.005	0.055	3.35	670	100	18.0	16.7
Cr	CO	0.014	0.007	0.055	2.20	315	100	19.0	7.8
Cr	CO	0.007	0.004	0.063	3.50	1000	100	20.0	25.0
Cr	CO	0.010	0.005	0.063	2.43	486	100	19.0	12.2
Cr	CO	0.014	0.007	0.063	2.56	366	100	18.0	9.2
Cr	CO	0.018	0.009	0.063	3.63	403	100	17.0	10.1
Cr	CO	0.082	0.073	0.019	16.5	228	100	22.3	5.7
Cr	CO	0.123	0.114	0.019	67.7	596	100	21.6	14.9
W	CO	0.010	0.005	0.065	13.56	2712	100	17.0	67.8
W	CO	0.014	0.007	0.065	19.37	2767	100	18.0	69.2
W	CO	0.018	0.009	0.065	9.11	1012	100	18.5	25.3
W	CO	0.041	0.032	0.019	233	7397	100	21.0	184.9
W	CO	0.082	0.073	0.019	685	9448	100	20.5	236.2
W	$P(OMe)_3$	0.010	0.005	0.065	∞		100	17.0	~5000

[a] [ ] represents concentration in molarity. [b] Percentage of RH relative to RH plus RBr. [c] Reaction time in hours. [d] Hydrogen atom apparent trapping rate constant, $k_H(10^7\ M^{-1}\ s^{-1})$.

Table II. Reaction Data[a] of Metal Hydrides with 4-Bromo-3,3-dimethyl-1-butene



M	L	[MH⁻]	[MH⁻av]	[3]	[UP]/[RP]	{[UP]/[RP]}/[MH⁻avg.]	% conversion[b]	time[c]	k_H[d]
Cr	CO	0.041	0.031	0.02	0.090	2.86	100	19.5	17.2
Cr	CO	0.082	0.072	0.02	0.220	3.06	100	18.5	18.4
Cr	CO	0.123	0.113	0.02	0.350	3.10	100	17.3	18.6
Cr	CO	0.164	0.154	0.02	0.460	2.99	100	16.0	17.9
W	CO	0.041	0.037	0.02	0.037	1.00	40	23.7	6.0
W	CO	0.082	0.079	0.02	0.085	1.07	27	22.7	6.4
W	CO	0.123	0.122	0.02	0.180	1.48	13	21.7	8.9
W	CO	0.164	0.163	0.02	0.230	1.41	13	20.7	8.5
W	$P(OMe)_3$	0.020	0.020	0.012	0.129	6.52	3.5	21.5	39.1
W	$P(OMe)_3$	0.020	0.020	0.006	0.068	3.44	8	22.5	20.6
W	$P(OMe)_3$	0.040	0.040	0.023	0.142	3.59	4	20.5	21.5
W	$P(OMe)_3$	0.041	0.039	0.02	0.071	1.81	18	20.0	10.8
W	$P(OMe)_3$	0.060	0.058	0.021	0.068	1.16	17	21.0	7.0
W	$P(OMe)_3$	0.082	0.080	0.021	0.75	0.94	20	20.0	5.6
W	$P(OMe)_3$	0.082	0.079	0.02	0.061	0.77	26	21.0	4.6
W[e]	$P(OMe)_3$	0.020	0.020	0.006	0.006	0.31	14.5	23.5	1.8

[a] [ ] represents concentration in molarity. [b] Percentage of RH relative to RH plus RBr. [c] Reaction time in hours. [d] Hydrogen atom apparent trapping rate constant, $k_H(10^6\ M^{-1}\ s^{-1})$. [e] Na^+ used as counterion in this reaction instead of PPN^+.

t, the above rate laws require the ratio of [UP] to [RP] to be as in eq 10. In eq 10 we employed the average MH^- concentration.

$$[UP]/[RP] = k_H[MH^-]/k_r \qquad (10)$$

Since products arise from the competition of a first-order rearrangement vs. a second-order trapping reaction, the error introduced by using the average MH^- concentration rather than the integrated concentration is less than 1%. Given an unrearranged-to-rearranged ratio measured by GLC analysis and the appropriate rearrangement rate constant, k_r, the hydrogen atom trapping rate constant, k_H, could be determined. The rearrangements of the radicals from both probes, **1** and **3**, have been well characterized.[17] The radical rearrangement rate constants, k_r, at 25 °C are known to be 2.5×10^5 and $6.0 \times 10^6\ s^{-1}$ for the radicals from **1**, and **3**, respectively.

The analytical expressions above show MH^- as the hydrogen atom source, but initially this was not known. Expression 10 provides a means for testing a potential hydrogen atom donor

---

(14) The smallest k_H value we observed was ca. $2 \times 10^6\ M^{-1}\ s^{-1}$, and $k_{H'}$ values are expected to be similar in magnitude. Thus, the smallest $k_{H'}[MH^-]$ value in this work is ca. $4 \times 10^4\ s^{-1}$, and more typically these values are ca. $5 \times 10^5\ s^{-1}$. Ring opening of cyclopentylmethyl can occur in benzene, but apparently it does not occur in THF where THF traps this radical with a pseudo-first-order rate constant of ca. $6 \times 10^3\ s^{-1}$ at 50 °C.[15] The back rearrangement of 1,1-dimethyl-3-butenyl, a tertiary radical, is expected to be much slower than the rearrangement of the parent radical 3-butenyl, a primary radical, which is known to occur with a rate constant of ca. $5 \times 10^3\ s^{-1}$ at 25 °C.[16]

(15) Newcomb, M.; Park, S. U. *J. Am. Chem. Soc.* **1986**, *108*, 4132–4234.

(16) Effio, A.; Griller, D.; Ingold, K. U.; Beckwith, A. L. J.; Serelis, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 1734–1736.

(17) The temperature-dependent function for cyclization of 5-hexenyl is $\log k/s^{-1} = (10.37 \pm 0.32) - (6.85 \pm 0.42)/\theta$,[18] and that for rearrangement of 2,2-dimethyl-3-butenyl is $\log k/s^{-1} = (10.64 \pm 0.28) - (5.26 \pm 0.28)/\theta$[19] ($\theta = 2.3RT$ kcal/mol, errors are 2σ).

(18) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739–7742.

(19) See footnote 3 in ref 15.

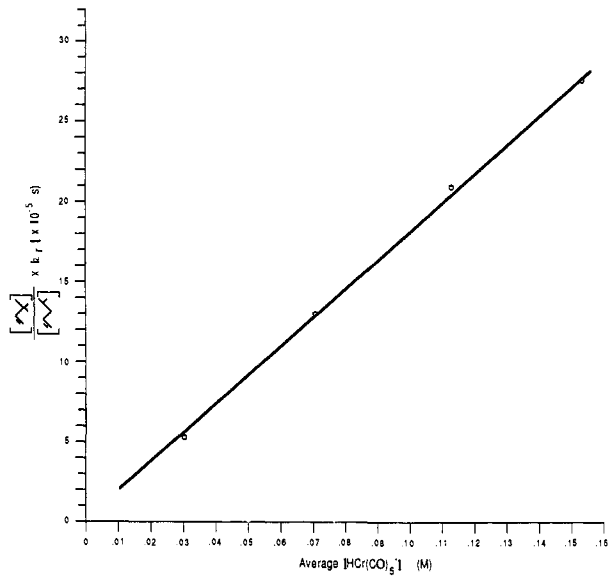


Figure 1. A plot of product ratio × k_r vs. the average metal hydride concentration throughout the reaction.

Scheme II

Initiation

$$\mathrm{RBr} + \text{init.} \longrightarrow \mathrm{R}^{\bullet} + \mathrm{Br}^-$$

or

$$\mathrm{HM(CO)_4L^-} + \text{init.} \longrightarrow \mathrm{M(CO)_4L^{\bullet -}}$$

Chain Propagation

$$\mathrm{R}^{\bullet} + \mathrm{HM(CO)_4L^-} \longrightarrow \mathrm{RH} + \mathrm{M(CO)_4L^{\bullet -}}$$

$$\mathrm{M(CO)_4L^{\bullet -}} + \mathrm{RBr} \longrightarrow \mathrm{R}^{\bullet} + \mathrm{BrM(CO)_4L^-}$$

source. According to (10) the [UP]/[RP] ratio should be directly proportional to the hydrogen atom source concentration. In this work the metal hydride was suspected as the hydrogen atom source, since THF is known to react too slowly to trap either probe radical before rearrangement.[15] Reactions with both **1** and **3** were carried out by varying the concentration of anionic metal hydride (Tables I and II). For reactions with **1**, an increasing [UP]/[RP] ratio with increasing metal hydride concentration cannot be taken as definitive proof that the anionic reductant is the hydrogen atom source, since the same relationship would hold if an S_N2, hydride transfer mechanism was concurrently operative. Therefore, neopentyl-like **3**, which should have an insignificant amount of S_N2 displacement,[20] is the more reasonable substrate for testing the hydrogen atom source. Figure 1 clearly shows that in the reaction with **3** the [UP]/[RP] ratio is directly dependent on the anionic metal hydride concentration. If the trapping agent had been some radical intermediate such as $MH^{\bullet}$ formed by electron transfer from MH^- to RBr, then the [UP]/[RP] ratio should not have been a direct function of MH^- concentration.[21] Thus, the hydrogen atom source was the anionic transition-metal hydride, and eq 10 provides a graphical approach for determining the apparent trapping rate constant, k_H. That is, the slope of the line in Figure 1 is the apparent k_H. For probe **1** the "k_H" derived from such an analysis is expected to represent contributions from composite paths. This is further discussed below.

Table III. Apparent k_H Values for Trapping Alkyl Radicals by MH^- at 25 °C in THF

MH^-	radical	k_H,[a] $M^{-1}\ s^{-1}$
$PPN^+HCr(CO)_5^-$	5-hexenyl	1.4 (±0.7) × 10^8
$PPN^+HW(CO)_5^-$		2.6 (±0.2) × 10^9
$PPN^+HW(CO)_4P(OMe)_3^-$		~5 × 10^{10}
$PPN^+HCr(CO)_5^-$	2,2-dimethyl-3-butenyl	1.81 (±0.05) × 10^7
$PPN^+HW(CO)_5^-$		0.96 (±0.09) × 10^7
$PPN^+HW(CO)_4P(OMe)_3^-$		1.6 (±1.2) × 10^7
$Na^+HW(CO)_4P(OMe)_3^-$		1.8 × 10^6

[a] Error limits are 1σ.

Analysis. As suggested by Bergman, Kinney, and Jones for $CpV(CO)_3H^-$,[2] and in analogy to established organotin hydride reaction mechanisms, a radical chain (S_H2) mechanism, Scheme II, best fits the data observed here for the 1-electron reduction process. Consistent with this chain mechanism, coupling products were not observed with any of the hydrides used. The initiating and terminating steps have not been studied.

In this study the above S_H2 mechanism is assumed to be the only mechanism available for the reduction of **3** since it is inherently sluggish toward S_N2 displacement. Now we consider the primary alkyl bromide probe, **1**. *If* the reaction of a given metal hydride with 6-bromo-1-hexene proceeded by a sequence identical with that of **3** and *if* this were the only reaction pathway then it would be reasonable to expect that the k_H value should be somewhat less than that derived for the neopentyl bromide probe. The relative rates for the hydrogen atom trapping of a neopentyl vs. a primary radical are estimated as ca. 1.5:1.[22] Instead, as shown Table III, the values obtained for "k_H" (10^8–10^{10} $M^{-1}\ s^{-1}$) with the hexenyl probe **1** were many times *larger* than those obtained with the neopentyl-like probe **3**. These data alone suggested that either an S_N2 process competed with radical reduction of **1** or some steric influence was being observed in the trapping of the neopentyl radical by $HM(CO)_4L^-$. The latter explanation is, however, not likely to explain the much larger *difference* in k_H for **1** and **3** with $HW(CO)_5^-$ than with $HCr(CO)_5^-$. The steric hindrances of these two reductants should be approximately equal and would not explain the disparity in the observed k_H values.

The yield of rearranged product was larger for the reaction of $HCr(CO)_5^-$ with **1** than that found with either of the other hydrides. This observation supported the argument that $HCr(CO)_5^-$ displayed a larger percentage of radical chain mechanism in its reduction of unhindered alkyl halides compared to the other hydrides used. As further proof, in $HCr(CO)_5^-$ reductions of **1** and **3**, **1** gave apparent k_H values of only 8 times that found for **3**, while with $HW(CO)_5^-$ and $HW(CO)_4P(OMe)_3^-$ the differences were 270 and 3200 times faster for **1**, respectively. These differences between k_H values for the three hydrides inversely paralleled the amount of rearranged product in the reaction of **1** with the respective hydride. These results clearly demonstrate that a major component in the reduction of unhindered primary alkyl bromides with these anionic group 6 metal hydrides must be nucleophilic substitution. The increasingly larger differences in k_H values indicates the order of increasing amount of S_N2 character: $HCr(CO)_5^- < HW(CO)_5^- < HW(CO)_4P(OMe)_3^-$.

The percent conversion of reaction within 20 h is notable to further substantiate the above claims. For all three hydrides 100%

---

(20) In typical nucleophilic substitution reactions, primary halides react about 4 × 10^4 times as fast as neopentyl halides; cf.: Streitwiesser, A., Jr. *Solvolytic Displacement Reactions*; McGraw-Hill: New York, 1962.

(21) In fact, $MH^{\bullet}$ formed by electron transfer from MH^- to RBr can be excluded as the hydrogen atom source by kinetic considerations. If an electron transfer reaction was followed by hydrogen atom donation within the solvent cage, then the ratio of products would not vary when the concentration of MH^- was changed. Alternatively, if free radicals were involved and $R^{\bullet}$ reacted with $MH^{\bullet}$ in a non-chain pathway, the following analysis applies. In reactions of probe **3** with $PPN^+HW(CO)_5^-$, the total consumption of RBr was less than 0.008 M in 20 h or the throughput of the reaction was ca. 1 × 10^{-7} M s^{-1}. Since the reaction trapping the radical from probe **3** was about 0.1 times as fast as rearrangement of this radical, the pseudo-first-order rate constant for trapping was about 6 × 10^5 s^{-1}. Therefore, the average concentration of $R^{\bullet}$ in these studies was only about 2 × 10^{-13} M, and in a non-chain pathway, the concentration of $R^{\bullet}$ and $MH^{\bullet}$ would be equal. If these species reacted with one another with diffusion controlled rates, then the maximum throughput from this reaction would be less than 2 × 10^{-11} M in 20 h or many orders of magnitude less than that observed.

(22) At 25 °C the ratio of rate constants for reaction of neopentyl radical with $n\text{-}Bu_3SnH$ compared to that of a primary radical is 1.3:1.[23] At 50 °C the ratio of the rate constants for reaction of 2,2-dimethyl-3-butenyl compared to 5-hexenyl is 1.6:1 for reduction by $(c\text{-}C_{16}H_{11})_2PH$ and 2.1:1 for reduction by 1,4-cyclohexadiene.[15]

(23) Johnston, L. J.; Lusztyk, J.; Wayner, D. D. M.; Abeywickreyma, A. N.; Beckwith, A. L. J.; Scaiano, J. C.; Ingold, K. U. *J. Am. Chem. Soc.* **1985**, *107*, 4594–4596.

completion of reaction was obtained in the reduction of **1** over the time allotted. For $HCr(CO)_5^-$, which displayed the largest amount of radical behavior in reaction with **1**, complete consumption of **3** was found. However, with $HW(CO)_5^-$ and $HW(CO)_4P(OMe)_3^-$, substantial amounts of unreacted **3** were observed with $HW(CO)_4P(OMe)_3^-$ consuming the least amount of **3** in the time allotted (ca. 20 h). This is consistent with the above conclusions since **3** should react mainly via a radical process.

The above qualitative conclusions can be carried a step further by quantitatively breaking down the percent reaction by either the one- or two-electron processes. Assuming that **3** provides an accurate value for k_H and that $k_{H(neopentyl)} = 1.5k_{H(hexenyl)}$, the ratio of [UP]/[RP] which should have been obtained from **1** if only a radical chain mechanism had existed may be computed. The observed [UP]/[RP] ratio from **1** was larger than this calculated value, and the amount of excess unrearranged product is assumed to derive from the competitive S_N2 pathway. Knowing the amount of product(s) which came from both pathways permits us to compute the percent of total reduction by both the radical chain, S_H2, and nucleophilic substitution, S_N2, mechanisms for the three hydrides reacting with **1**. The results are given below:

$PPN^+HCr(CO)_5^-$: 10% S_H2; 90% S_N2

$PPN^+HW(CO)_5^-$: 0.3% S_H2; 99.7% S_N2

$PPN^+HW(CO)_4P(OMe)_3^-$: 0.03% S_H2; 99.97% S_N2

Of course, the percentage of the competing reactions will depend on the concentrations of reagents in a manner which we cannot predict from this work because the radical chain initiation and termination steps are not known. However, the important point is that the use of only 6-bromo-1-hexene as a radical probe with these hydrides would have given a qualitative indication that radical intermediates had been formed but would have given poor values for the rates of hydrogen atom abstraction when applied quantitatively.

Interestingly, air stability of the respective hydrides correlates with the amount of radical character in the reduction of alkyl bromides. For example, $HCr(CO)_5^-$ which showed the largest radical component decomposed to μ-$HCr_2(CO)_{10}^-$ immediately in solution upon exposure to air while solutions of $HW(CO)_4P(OMe)_3^-$ could be exposed to air for hours without significant decomposition. While these results might suggest that the radical initiation step is related to the one-electron oxidation potentials for the respective hydrides, relative potentials obtained from cyclic voltammograms of the respective hydrides in THF showed little correlation.[24]

With identification of $HM(CO)_4L^-$ as the hydrogen atom transfer agents and calculation of accurate rate constants for this step provided by reactions with **3**, inference can be made as to the relative homolytic bond strength of the hydrides used if we ignore possible steric effects. It is generally accepted that the metal–hydrogen bond strength increases upon descent of a triad.[1] This is also the result obtained by comparing k_H for $PPN^+HCr(CO)_5^-$ and $PPN^+HW(CO)_5^-$, 1.81×10^7 and 9.64×10^6 M^{-1} s^{-1}, respectively. That is, $HCr(CO)_5^-$ undergoes hydrogen atom abstraction almost twice as fast as $HW(CO)_5^-$. Because of the large error associated with k_H for $PPN^+HW(CO)_4P(OMe)_3^-$, conclusions concerning this value are not warranted.

Conclusions and Comments

This work suggests that concurrent pathways, an ionic hydride transfer (S_N2 path) and a radical chain mechanism (S_H2), account for the reduction of unhindered alkyl bromides by group 6 anionic transition-metal hydrides. Furthermore, the two-probe approach permits a quantitative dissection of the competitive pathways. Mechanistic conclusions and estimated k_H values for a radical reaction taken from reductions of unhindered primary radical probes are suspect when an S_N2 reduction component has not been ruled out.

In this work 4-bromo-3,3-dimethyl-1-butene provided conclusions to be made concerning the radical reduction mechanism because the neopentyl-like bromide should not be susceptible to S_N2 displacement.[20] The proposed radical chain mechanism is identical with that established for Bu_3SnH reductions of RBr and favored by Bergman, Kinney, and Jones for the $CpV(CO)_3H^-$ reductions of certain RBr radical probes.[2] What our work adds to the latter is evidence that the observed unrearranged products arise both from direct trapping of unrearranged $R^\bullet$ and from hydride displacement of Br^- from the original RBr substrate. Such an explanation might also be warranted in reductions with $CpV(CO)_3H^-$. While evidence for a radical mechanism was overwhelming for reactions of this hydride with probe reagents, only small amounts of rearranged reduced product were obtained with use of the cyclopropylcarbinyl probe **2**.[2] This anomaly was accounted for by a "two-electron" reduction process.

It is interesting to note that the radical reduction velocity of 6-bromo-1-hexene by any of the hydrides used here is apparently very slow. For instance, $PPN^+HCr(CO)_5^-$ displays 90% S_N2 and 10% S_H2 in its reduction of **1**. Thus, under our conditions the relative velocity of the S_N2 pathway was 9 times that of the radical path. However, a comparison of previously measured k_2 values[3] with the k_H values reported here for 1° bromide reductions reveals that k_H is about 3 to 4 orders of magnitude larger than k_2. That is, group 6 metal hydrides donate $H^\bullet$ to an alkyl radical with greater facility than they donate H^- to an alkyl bromide. Little can be said concerning why the radical path is slow in the reduction of **1** because the initiating and terminating steps are still unknown. The starting anionic metal hydride may actually be involved in the terminating steps as suggested by decreasing percent completion of reduction of **3** with increasing $PPN^+HW(CO)_5^-$ concentration (Table II).

While $PPN^+HCr(CO)_5^-$ seems to prefer S_N2 displacement in **1**, it should not be concluded that this path will be followed with other electrophiles. Earlier competition experiments showed that $PPN^+HCr(CO)_5^-$ reduces 3° bromides faster than 1° bromides.[3] Thus, for 3° bromide reductions by $PPN^+HCr(CO)_5^-$ the radical chain reaction velocity must be many times greater than that for either reduction pathway of 1° bromides. **This is clear evidence that the substrate to be reduced can elicit substantially different reaction behavior from metal hydrides. We would suggest that more positive carbon centers (as in the carbonyl carbon of acyl halides) generate hydride transfer character whereas less electrophilic carbon centers (as in alkyl iodides and some alkyl bromides) are better matched for 1-electron or radical processes, also readily accommodated by the anionic metal hydrides.** It is therefore reasonable that intermediate situations exist wherein similar barriers provide access to contemporaneous paths, i.e., exclusive reaction paths are not mandated.

Acknowledgment. Support for this research has been provided by the National Science Foundation, Grant No. CHE-8603664 (M.Y.D.) and CHE-85087076 (M.N.). Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the Americal Chemical Society (M.N.). C. E. Ash expresses appreciation to the Gulf Corp. for a Gulf Research and Development Fellowship. We thank Anne Glenn for experimental assistance.

Registry No. 1, 2695-47-8; **3**, 97797-99-4; $PPN^+HCr(CO)_5^-$, 78362-94-4; $PPN^+HW(CO)_5^-$, 78709-76-9; $PPN^+HW(CO)_4P(OMe)_3^-$, 82963-28-8.

---

(24) Cyclic voltammograms for all three hydrides were obtained in THF with 0.2 M $Bu_4N^+PF_6^-$ as supporting electrolyte and a sweep rate of 200 mV/s. *Irreversible* oxidation peak potentials of +0.30, +0.45, and +0.10 V were observed for $PPN^+HCr(CO)_5^-$, $PPN^+HW(CO)_5^-$, and $PPN^+HW(CO)_4P(OMe)_3^-$, respectively.