

A Comparison of The Leaving Group Ability of Transition Metal Carbonyl Anions vs. Halides: Reaction of MH^- with $M'-R$ ($MH^- = HW(CO)_4^-$, $P(OMe)_3^-$, $HW(CO)_5^-$, $HCr(CO)_5^-$, $HFe(CO)_4^-$; $M'-R = CpMo(CO)_3(CH_3)$, $CpMo(CO)_3\{CH_2CH(CH_2)_2\}$)

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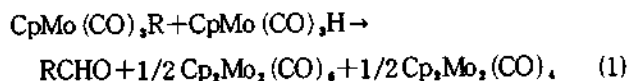
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The anionic transition metal hydrides ($HW(CO)_4P(OMe)_3^-$, $HW(CO)_5^-$, $HCr(CO)_5^-$, $HFe(CO)_4^-$) react with transition metal alkyl ($CpMo(CO)_3(CH_3)$) to yield CH_4 and CH_3CHO in addition to the inorganic products ($CpMo(CO)_3^-$, etc.). The reaction of these anionic metal hydrides with $CpMo(CO)_3\{CH_2CH(CH_2)_2\}$ may lead to an elucidation of the reaction mechanisms involved; the organic product distributions are among CH_4 , $CH_2=CHCH_2CH_3$, and $CH_3CH(CH_2)_2$, depending upon the anionic metal hydride used. These anionic metal hydrides also are reported to undergo a hydride-halide exchange reaction with organic halides; therefore, these similar reactions have been compared in terms of leaving group ability ($CpMo(CO)_3^-$ vs. Br^-) and the mechanistic pathways.

Introduction

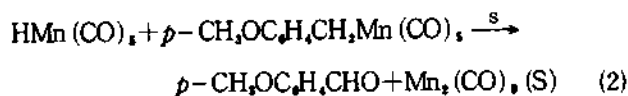
The hydride-halide exchange is observed in the reaction of anionic transition metal hydride with organic halide. This reaction implies that the metal carbonyl anion has a ligating ability similar to that of halide. Therefore, it is worth while to investigate the reaction of the anionic metal hydrides (e.g., $HCr(CO)_5^-$, $HW(CO)_5^-$, $HW(CO)_4\{P(OMe)_3\}^-$, $HFe(CO)_4^-$) with metal alkyl complexes such as $CpMo(CO)_3(CH_3)$ and $CpMo(CO)_3(\Delta)$. Here in this reaction an alkyl migratory insertion to CO is anticipated to occur at the metal moiety ($CpMo(CO)_3$), thus creating an open site for the hydride attack.¹⁻⁴

Bergman, *et al.*¹ proposed that the formation of an acyl species from $CpMo(CO)_3R$ occurs at the rate-determining step prior to the aldehyde formation as shown in eq. 1.



R=Me, Et

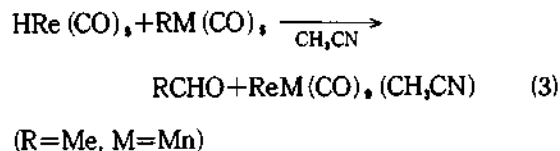
Halpern and coworkers^{2,4} proposed a similar mechanism in the reaction of $HMn(CO)_5$ with $p-CH_3OC_6H_4CH_2Mn(CO)_5$ in acetone or acetonitrile as shown in eq. 2.



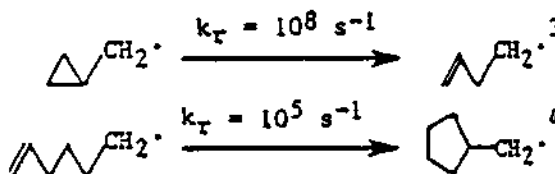
S=Solvent

Similar results consistent with the involvement of an acyl intermediate were observed by Warner and Norton³ in the reaction of the neutral transition metal hydrides, (e.g., $HRe(CO)_5$, $H_2Os(CO)_4$, $HMn(CO)_5$ and $CpW(CO)_3H$), with several alkyl metal carbonyl complexes such as $MeMn(CO)_5$, $EtRe(CO)_5$, $MeFe(CO)_2Cp$, and $Me_2Os(CO)_4$ in solvents of

different coordinating abilities as in eq. 3.

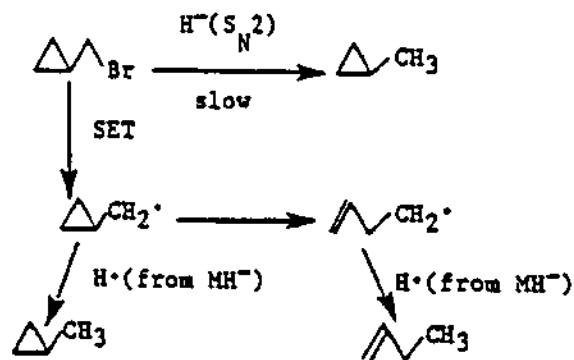


Winter and coworkers⁵ found that $LiBHET_3$ reacts with $CpMo(CO)_3(CH_3)$ in THF at ambient temperature to give the anionic acetaldehyde complex $[Mo(\eta^2-MeCHO)(CO)_3(\eta^5-C_5H_5)]^-$ as the predominant organomolybdenum product with very small quantities of the anion $CpMo(CO)_3^-$. It is one of our goals to understand the mechanistic pathway (H^- transfer vs. Single electron transfer) for the reactions of MH^- with $M'R$ (M, M' = transition metal carbonyl moiety). One of the ways to distinguish one from the other pathway is to utilize some specific R group such as $\sphericalangle CH_2$, or ∇CH_2 in our metal carbonyl system ($CpMo(CO)_3$). Such species have been well defined as to skeletal rearrangement of radical intermediates.^{6,7}



Several workers have attempted to understand the reaction pathway merely based on the organic product distribution (e.g., Δ : ∇ , \sphericalangle : ∇ , \sphericalangle : ∇) in reactions of the transition metal hydride with RX (R = Δ , ∇ , \sphericalangle ; X = halide).⁸ Ash and Newcomb⁹ found that, for example, the reaction with anionic metal hydride with $\Delta^{\wedge}Br$ can produce $\Delta^{\wedge}CH_3$ either via H^- transfer (S_N2) or single electron path or both as illustrated in Scheme 1.

Therefore, $CpMo(CO)_3(CH_3)$ can be modified to $CpMo$



Scheme 1

(CO)₃(Δ) to be more informative of the reaction pathway in the reaction of MH⁻ with M-R. Efforts will be made (1) to understand the reaction mechanism involved; (2) to compare the relative reactivity of the anionic hydrides with both the reaction pathway and the organic product distribution; and, (3) to determine the factors affecting the leaving group ability of transition metal carbonyl anion (CpMo(CO)₃⁻ vs. halide (Br⁻)) in the reaction of MH⁻ with M-R in THF at ambient temp.

Experimental

An inert-atmosphere glove box and Schlenk line and/or high-vacuum techniques were employed for most of sample transfers and sample manipulations. Infrared spectra were recorded on either an IBM FTIR/32, IBM FTIR/85, or Perkin Elmer 283B spectrophotometer. Proton nuclear magnetic resonance spectra were obtained from either a 90 MHz Varian EM-390 or Varian XL200 MHz Spectrometer. ¹³C nuclear magnetic resonance spectra were recorded on the Varian XL200 MHz spectrometer. ESR spectra were recorded on a Varian E-6S EPR spectrometer. Gas chromatographic analyses were performed on a Perkin-Elmer Sigma 2 gas chromatograph, equipped with flame ionization detector. GC-MASS data were collected on a Hewlett-Packard 2671G recorder connected with a 5790A series gas chromatograph and 5970A series mass selective detector. Reaction temperature control was achieved with either Haake A81 or Precision R20 thermostat. Most of weighings and transfers of compounds were done under an Ar atmosphere in the glove box (HE-63-P Vacuum Atmosphere Co.). Photoreactions were performed using a 450 watt Hg vapor lamp covering a rather broad range of UV-VIS wave lengths. Solvents were distilled under N₂ from appropriate drying and O₂ scavenging agents: tetrahydrofuran (THF) and toluene, Na/benzophenone; hexane, Na/benzophenone/diglyme; methylene chloride, P₂O₅; acetonitrile, CaH₂ followed by P₂O₅; ethanol, Mg/I₂.¹⁰ Common reagents were purchased from ordinary vendors and used as received without further purification. The organic halides were usually distilled from P₂O₅ and several freeze-thaw cycles were applied prior to use.

Preparation of Transition Metal Carbonyl Hydrides.

PPN⁺HM(CO)₅⁻ (M = Cr, W) were synthesized by the borohydride method as reported previously.¹¹ The synthesis and

spectral properties of the phosphorus-donor ligand substituted complexes, PPN⁺ *cis*-HM(CO)₄PR₃⁻ (M = Cr, W; R = OMe, Me, Ph)¹² have also been reported. Other hydrides such as PPN⁺HFe(CO)₄⁻¹³ and HMn(CO)₅⁻¹⁴ were prepared according to the literature. The PPN⁺ *trans*-HFe(CO)₃P(OMe)₃⁻ was prepared by a procedure similar to that reported by Edens¹⁵ and Ellis.¹⁶

Preparations of M(CO)₅THF (M = Cr, W)¹⁷. A degassed THF (100 ml) slurry of M(CO)₆ (0.05 mmol) was photolyzed under a UV lamp (450 W Hg Hanovia Lamp) for one hour. The product solution is orange colored. ν (CO)IR(THF), Cr(CO)₅THF, 1938(s), 1984(m); W(CO)₅THF, 1936(s), 1895(m).

Preparations of Other Mononuclear Transition Metal Carbonyl Compound CpMo(CO)₃CH₃.¹⁸ To the THF solution (50 ml) of Na⁺CpMo(CO)₃⁻ (2.73 g; 10.18 mmol) was added CH₃I (0.634 ml; 10.18 mmol) via syringe. This solution was stirred at ambient temp. for about 6 hr. The reaction mixture was concentrated under vacuum and then purified by a column chromatography using mixed solvent system (hexane and CH₂Cl₂ 1:1 by vol.) and silica gel to yield a bright yellow product. The yield was 1.76 g (66.5%). ν (CO)IR(THF) 2005(s), 1923(s) ¹H-NMR (C₆D₆) C₅H₅ (4.57 ppm), CH₃ (0.50).

CpMo(CO)₃(Δ). Cyclopropylcarbonyl iodide was prepared as described.¹⁹ To a THF solution (110 ml) of Na⁺CpMo(CO)₃⁻ (2.14 g; 8 mmol) was added another THF solution of cyclopropylcarbonyl iodide at room temp. and stirred for more than 20 hr. After the reaction was over, this solution was concentrated under vacuum. The crude product was then purified by column chromatography using silica gel (100-200 mesh) as a stationary phase and mixed solvent system (CH₂Cl₂ and hexane 1:1 by vol.) as a mobile phase to obtain a bright yellow solid. The yield was 1.60 g (67%). ν (CO)IR(THF) 2007(m), 1920(s). ¹H-NMR (CDCl₃) 5.32(s), 1.62(d), 1.30-0.25(m) ¹³C-NMR(CDCl₃) 92.50; 18.81, 11.00, 9.03 MASS (m/e) 301.98.

Reactions of PPN⁺HM(CO)₄L⁻ (M = Cr; L = CO, M = W; L = P(OCH₃)₃) with CpMo(CO)₃. THE (10 ml) was added to a mixture of PPN⁺HM(CO)₄L⁻ (0.2 mmol) and CpMo(CO)₃(CH₃) (0.2 mmol) at room temp. and stirred for 5 hr. This reaction was monitored by ν (CO)IR and the organic product was determined by GC.

Reactions of M⁺HM(CO)₄L⁻ (M⁺ = PPN, Na; M = Cr, W; L = CO, P(OCH₃)₃) with CpMo(CO)₃. (Δ) the reaction of the anionic transition metal hydride with CpMo(CO)₃(Δ) was performed in THF at 26°C and monitored by ν (CO)IR. Most of the reaction except the reaction of PPN⁺HFe(CO)₄⁻ with CpMo(CO)₃(Δ) were complete within one hour. The two reactants were used in equimolar ratio (0.10 mmol, each) in THF (20 ml). The determination of Δ vs. Δ /ratio was made based on the area % of the two products by the GC over the course of a 10 hr reaction period.

The Reaction of PPN⁺HCr(CO)₅⁻ with CpMo(CO)₃(Δ). The reaction of PPN⁺HCr(CO)₅⁻ with CpMo(CO)₃(Δ) is assumed to produce CpMo(CO)₅⁻ (ν (CO)IR (THF), 1896(s), 1780(s)) and PPN⁺ μ -HCr₂(CO)₁₀⁻ (2026(w), 1940(s), 1877(m)).

Reactions of PPN⁺HCr(CO)₅⁻, PPN⁺HFe(CO)₄⁻, K⁺HB(CH₂CH₃)₃⁻ with CpMo(CO)₃(Δ). These reactions were performed under the same conditions as in the previous reaction.

⁺PPN⁺ = bis(triphenylphosphine)iminium cation

Reaction of $\text{PPN}^+\text{HCr}(\text{CO})_5^-$ with cyclopropylcarbonylbromide. THF solution (1.0 ml) of cyclopropylcarbonylbromide (0.10 mmol) was added to $\text{PPN}^+\text{HCr}(\text{CO})_5^-$ (0.10 mmol) and additional degassed THF (19 ml) was added to this reaction solution. This solution was stirred at room temp. for 12 hr and monitored by $\nu(\text{CO})\text{IR}$ and GC.

Reactions of $\text{PPN}^+\text{HCr}(\text{CO})_5^-$ with $\text{CpMo}(\text{CO})_3\Delta\Delta$ in the Presence of $\text{Na}^+\text{B}(\text{C}_6\text{H}_5)_4^-$. This reaction was performed under the same condition as in the previous reaction of $\text{PPN}^+\text{HCr}(\text{CO})_5^-$ with $\text{CpMo}(\text{CO})_3\Delta\Delta$ except a two-fold excess of $\text{Na}^+\text{B}(\text{C}_6\text{H}_5)_4^-$ (0.20 mmol) was added.

Gas Chromatographic Analysis on the reaction of the Anionic Transition Metal Hydride with $\text{CpMo}(\text{CO})_3\Delta\Delta$. All GC analysis were carried out using Perkin-Elmer Sigma 2 Gas Chromatograph, equipped with a flame ionization detector. Column used in product analysis was 6 ft \times 0.25 in picric acid on Graphac 80/100 (C_4 Hydrocarbons). Peak areas were obtained by electronic integration. Usually THF (20 ml) was added to a mixture of anionic metal hydride (0.10 mmol) and $\text{CpMo}(\text{CO})_3\Delta\Delta$ (0.10 mmol) in a tightly rubber-septummed flask via syringe under N_2 atmosphere and stirred at ambient temp. for 10 hr until an injection of that solution or gas was made for gas chromatographic run.

GC-MASS Spectral Analysis on the Reaction of the Anionic Transition Metal Hydride with $\text{CpMo}(\text{CO})_3\Delta\Delta$. THE (usually 3 ml) was added to the mixture of anionic metal hydride (0.3 mmol) and $\text{CpMo}(\text{CO})_3\Delta\Delta$ (0.3 mmol) at ambient temp. and shaken vigorously to get a homogeneous solution. A few hours later, a THF solution containing organic products was obtained by using a cold trap technique under vacuum. An injection of this solution was made to either 5980A mass spectrometer with direct insertion probe or to 5710A gas chromatograph attached to 5980A mass spectrometer with 5933A data system where the same picric acid column was employed under the similar temp. conditions as in GC.

Results and Discussion

Reactions of $\text{PPN}^+\text{HCr}(\text{CO})_5^-$ with $\text{CpMo}(\text{CO})_3(\text{CH}_3)$.

The reaction of $\text{PPN}^+\text{HCr}(\text{CO})_5^-$ with $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ produced $\text{PPN}^+\text{CpMo}(\text{CO})_3^-$, $\text{PPN}^+\mu\text{-HCr}_2(\text{CO})_{10}^-$ (2025 (w), 1940 (s), 1880 (m)), and CH_4 as a major product. The ratio of CH_4 : CH_3CHO is 4:1.

A $^1\text{H-NMR}$ spectrum for this reaction was obtained in d^6 -acetone at -60°C , -20°C , $+20^\circ\text{C}$, respectively, as a monitor of the reaction. At both -60°C , and -20°C , no reaction was observed; however, at 20°C $\text{PPN}^+\mu\text{-HCr}_2(\text{CO})_{10}^-$ ($^1\text{H-NMR}$ (CD_3COCD_3), -19.52 ppm) and unknown product (δ , -17.21 ppm) appeared. At this point in the reaction (a few min), the ratio of $^1\text{H-NMR}$ peaks ($\text{HCr}(\text{CO})_5^-$: unknown: $\mu\text{-HCr}_2(\text{CO})_{10}^-$) was roughly 7:3:1. This ratio changed to 1:1:3 after about 25 min and finally, 1.5 hours later, only the peak for $\mu\text{-HCr}_2(\text{CO})_{10}^-$ remained. However, some unreacted $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ was observed in the $\nu(\text{CO})\text{IR}$ of the reaction solution. The unknown complex is most likely an intermediate as shown in Figure 1. This possible intermediate can be supported by the following informations: (1) the $\nu(\text{CO})\text{IR}(\text{THF})$ for this reaction solution shows a small broad peak around 1600 cm^{-1} , a typical position for an acyl carbonyl group. (2) $^1\text{H-NMR}$ spectrum showed a singlet at 4.95 ppm (s, η -

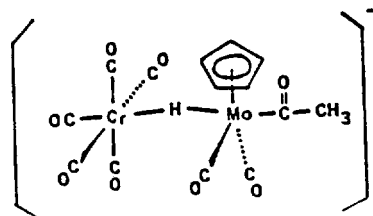


Figure 1. Possible intermediate in the reaction of $\text{PPN}^+\text{HCr}(\text{CO})_5^-$ with $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ in THF at 20°C .

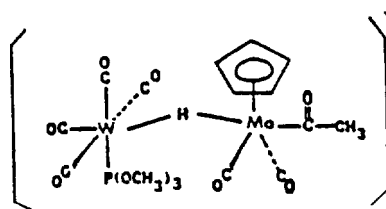


Figure 2. Possible intermediate in the reaction of $\text{PPN}^+\text{HW}(\text{CO})_4\text{P}(\text{OMe})_3^-$ with $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ in THF at 20°C .

C_5H_5), 2.12 ppm (s, $\eta\text{-(CO)CH}_3$), and -17.21 ppm (s, $\mu\text{-H}$). The high field shift is diagnostic for a $\mu\text{-H}$ attached to Cr.²⁰ Winter *et al.*²¹ proposed the same intermediate in the reaction of $\text{Li}^+\text{BHET}_3^-$ with $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ as shown in Figure 1. (3) The $^1\text{H-NMR}$ spectrum for the possible intermediate (Figure 1) showed three singlets at 4.90 ppm (s, 5H, C_5H_5), 2.25 ppm (s, 3H, CH_3), and -5.15 ppm (s, 1H, Mo-H). As this complex has a terminal hydride, $^1\text{H-NMR}$ peak for the terminal hydride is far downfield (-5.15 ppm) compared to the bridging hydride peak (-17.21 ppm) of the intermediate shown in Figure 1. (4) The gas chromatogram for the reaction of $\text{PPN}^+\text{HCr}(\text{CO})_5^-$ with $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ showed one tiny peak at 0.3 min and another big peak at 14.6 min. By using spiking techniques with authentic compound, the peaks were assigned to CH_4 and CH_3CHO , respectively. These two organic products may also suggest the possible intermediate in Figure 1.

The reaction of $\text{PPN}^+\text{HW}(\text{CO})_4\{\text{P}(\text{OMe})_3\}^-$ with $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ yielded $\text{PPN}^+\text{CpMo}(\text{CO})_3^-$ ($\nu(\text{CO})\text{IR}$ (THE) 1896 (s), 1780 (s)), but there were several unidentified $\nu(\text{CO})$ bands (1992 (w), 1885 (s), 1850 (m), 1832 (m), 1815 (m)) and $\nu(\text{CO})$ band at 1590 cm^{-1} is presumably due to acyl $\nu(\text{CO})$. About half of the unreacted $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ was observed after 12 hr reaction at ambient temperature. This reaction was also monitored by $^1\text{H-NMR}$ at -60°C , -20°C , and $+20^\circ\text{C}$, respectively. No reaction was observed below -20°C . At -20°C , a similar intermediate as shown in Fig. 1 was assumed to form during the reaction as depicted in Fig. 2.

$^1\text{H-NMR}$ spectrum for this presumed heterobimetallic bridging hydride is as follows: 7.74–7.55 ppm (m, 30H from 6(C_6H_5) of PPN^+), 5.25 ppm (s, 5H, $-\text{C}_5\text{H}_5$), 3.67–3.46 ppm (m, 9H, $\text{P}(\text{OCH}_3)_3$), 1.46 ppm (s, 3H, $-\text{C}(\text{O})\text{CH}_3$), -11.92 ppm (t, 1H, W-H-Mo; $J_{\text{W-H}} = 21.27$ Hz). $^1\text{H-NMR}$ for this reaction in THF at ambient temp. after about 10 min showed no resonances between 0 ppm and -20 ppm, indicating reaction completion. The GC for this reaction showed a peak at 0.3 min which is again assumed to be due to CH_4 . There was also a small broad peak around 14.5 min presumably due to acetaldehyde, but only in trace amounts. The reaction of PPN^+

Table 1. The Organic and Inorganic Products from the Reaction of the Anionic Metal Hydride with $\text{CpMo}(\text{CO})_3\text{CH}_3$ in THF.

Anionic Metal Hydrides	Inorganic Products	Organic Products
$\text{PPN}^+\text{HFe}(\text{CO})_4^-$	$\text{CpMo}(\text{CO})_3^-$ Fe Species	CH_4 (major)
$\text{PPN}^+\text{HCr}(\text{CO})_5^-$	$\text{CpMo}(\text{CO})_3^-$ $\mu\text{-HCr}_2(\text{CO})_{10}^-$	CH_4 (major) CH_2CHO (minor)
$\text{PPN}^+\text{HW}(\text{CO})_4\{\text{P}(\text{OMe})_3\}^-$	$\text{CpMo}(\text{CO})_3^-$ W species	CH_4 (major) CH_3CHO (minor)

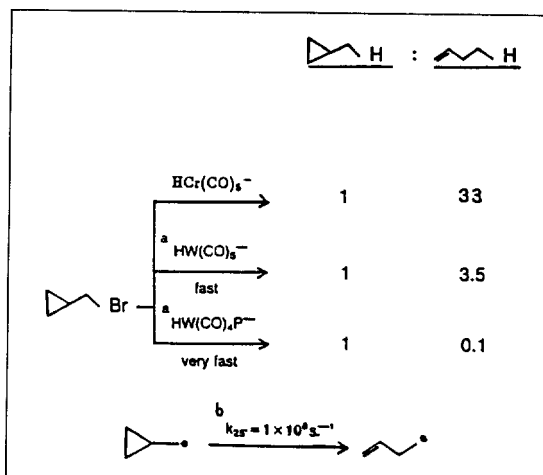
Table 2. The Organic and Inorganic Products from the Reaction of the Anionic Metal Hydride with $\text{CpMo}(\text{CO})_3(\Delta\Delta)$ in THF.

Anionic Metal Hydrides	Inorganic Products	Organic Products
$\text{PPN}^+\text{HFe}(\text{CO})_4^-$	$\text{CpMo}(\text{CO})_3^-$ Fe Species	CH_4 (major), Δ , $\Delta\Delta$ (minor)
$\text{PPN}^+\text{HCr}(\text{CO})_5^-$	$\text{CpMo}(\text{CO})_3^-$ $\mu\text{-HCr}_2(\text{CO})_{10}^-$	Δ , $\Delta\Delta$ (major), CH_4 (minor)
$\text{PPN}^+\text{HW}(\text{CO})_5^-$	$\text{CpMo}(\text{CO})_3^-$ $\mu\text{-HW}_2(\text{CO})_{10}^-$	$\Delta\Delta$ (major), CH_4 (minor)
$\text{PPN}^+\text{HW}(\text{CO})_4\{\text{P}(\text{OMe})_3\}^-$	$\text{CpMo}(\text{CO})_3^-$ W species	CH_4 (major)

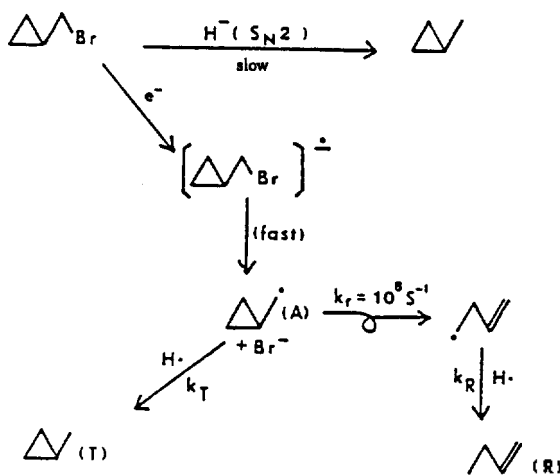
$\text{HFe}(\text{CO})_4^-$ with $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ produced $\text{PPN}^+\text{CpMo}(\text{CO})_3^-$ ($\nu(\text{CO})\text{IR}$ (THF), 1896(s), 1780(s)) in THF over the course of more than 12 hr reaction at room temp. The $^1\text{H-NMR}$ spectrum of this reaction solution in d^6 -acetone at 20°C showed $\text{PPN}^+\text{HFe}(\text{CO})_4^-$ (7.77–7.53 ppm (m, 30H's from 6(C_6H_5 of PPN^+), -8.76 ppm (s, H-Fe)) and $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ (5.50 ppm (s, 5H's, - C_5H_5), 0.33 ppm (s, 3H's - CH_3)). There was no indication of forming an intermediate. CH_4 evolution was observed by using GC. These anionic transition metal hydrides may attack the metal (Mo) site of $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ to form an intermediate such as those in Figure 1 and 2. This intermediate may then react with another anionic transition metal hydride to yield the anionic bridging hydride and $\text{CpMo}(\text{CO})_3^-$ with the evolution of CH_4 .

Reactions of the Anionic Transition Metal Hydride with $\text{CpMo}(\text{CO})_3(\Delta\Delta)$ in THF. The reaction of $\text{PPN}^+\text{HCr}(\text{CO})_5^-$ with $\text{CpMo}(\text{CO})_3(\Delta\Delta)$ produced $\text{PPN}^+\text{CpMo}(\text{CO})_3^-$ and $\text{PPN}^+\mu\text{-HCr}_2(\text{CO})_{10}^-$ with the evolution of methylcyclopropane, 1-butene, and CH_4 . This reaction was modified by adding two-fold excess of $\text{Na}^+\text{B}(\text{C}_6\text{H}_5)_4^-$ so as to see the counterion effect; however, no appreciable difference in the products and reaction time was observed. $\text{PPN}^+\text{HW}(\text{CO})_5^-$, $\text{PPN}^+\text{HFe}(\text{CO})_5^-$, and $\text{PPN}^+\text{HW}(\text{CO})_4\{\text{P}(\text{OCH}_3)_3\}^-$ were tried to react with $\text{CpMo}(\text{CO})_3(\Delta\Delta)$ yielded same $\text{CpMo}(\text{CO})_3^-$ and some difference were observed in the organic products. These results are shown in Table 1 and 2.

There was no observable change in the $^1\text{H-NMR}$ spectrum of $\text{CpMo}(\text{CO})_3(\Delta\Delta)$ in d^6 -acetone for five hours ambient temp. Therefore this complex is not likely to undergo any isomeric rearrangement such as $\text{CpMo}(\text{CO})_3(\Delta\Delta)$ at least during the reaction interval (ca. one hour) with the anionic metal hydride.



^a Concentrations of the hydrides: $[\text{HW}(\text{CO})_5^-] = [\text{HW}(\text{CO})_4\{\text{P}(\text{OMe})_3\}^-] = [\text{HCr}(\text{CO})_5^-] = 0.005\text{M}$, ref. 22. ^b Ref. 6.

Scheme 2**Scheme 3**

Reactions of the Anionic Metal Hydrides with $\Delta\Delta$ Br. The reaction of $\text{PPN}^+\text{HCr}(\text{CO})_5^-$ with $\Delta\Delta$ Br was carried out under the same conditions as in the previous reaction of the anionic hydride with $\text{CpMo}(\text{CO})_3(\Delta\Delta)$.

This reaction yielded $\text{PPN}^+\text{BrCr}(\text{CO})_5^-$ ($\nu(\text{CO})\text{IR}$ (THF) 2045(w), 1916(s), 1850(m)), however, much more slowly than the previous reactions of anionic hydride with $\text{CpMo}(\text{CO})_3(\Delta\Delta)$, under the same conditions. Organic products were identified by GC to be Δ and $\Delta\Delta$ (1:33). No bridging hydride ($\text{PPN}^+\mu\text{-HCr}_2(\text{CO})_{10}^-$) was observed. Our previous work showed that the more active hydride (e.g., $\text{HW}(\text{CO})_4\text{P}(\text{OCH}_3)_3^-$) is more likely to undergo hydride transfer (H^-) than the less hydridic hydride (e.g., $\text{HW}(\text{CO})_5^-$) in the reaction with $\Delta\Delta$ Br as shown in Scheme 2.

Evaluation of the Organic Product Distribution (Δ vs. $\Delta\Delta$). Both in the Reaction of the Anionic Metal Hydride with $\text{CpMo}(\text{CO})_3(\Delta\Delta)$ and in the Reaction of the Anionic Metal Hydride with $\Delta\Delta$ Br. Typically the anionic transition metal hydride undergoes a hydride (H^-) and halide exchange reaction with alkyl halide via either $\text{S}_{\text{N}}2(\text{H}^-$ transfer) or single electron transfer pathway.^{22,23} With cyclopropylcarbinylbromide the anionic metal hydride will react to yield products according to the mechanistic pathway and

relative rates as illustrated in Scheme 3.

In the reaction the product *T* or Δ can be produced via either an S_N2 or SET path. The S_N2 reaction is usually assumed to be much slower than a SET reaction. In our reaction of $PPN^+HCr(CO)_5^-$ with $\Delta^{\wedge}Br$, 97% of the ring-opened product (Δ) was obtained, even though this reaction is much slower (hrs) than the other reaction of the anionic metal hydride with $CpMo(CO)_3(\Delta)$ (-one hr). Supposing that all the hydride reaction with $CpMo(CO)_3(\Delta)$ are involved in SET pathway as far as this organic product ratio (Δ vs. Δ) is concerned, k_T for each reaction may be approximated using the equations.

$$\frac{d[T]}{dt} = \frac{k_r[A][H\cdot]}{k_r[A]} = \frac{[T]}{[R]} = \frac{k_r[H\cdot]}{k_r} \quad (4)$$

As anionic metal hydride is assumed to be the $[H\cdot]$ source, the average concentration of anionic metal hydride is substituted for $[H\cdot]$. Thus, equation 4 can be rewritten as follows (eq. 5).

$$\frac{k_r[MH^-]_{av}}{k_r} = \frac{[\Delta]}{[\Delta]} \quad (5)$$

Therefore, k_T for each reaction of the anionic hydride with either $CpMo(CO)_3(\Delta)$ or $\Delta^{\wedge}Br$ can be calculated using the equation 5. This k_T for a specific reaction will be utilized in understanding the possible mechanistic reaction pathway, particularly as to whether it is involved in S_N2 or SET.

Comparison of the Leaving Group Ability of Transition Metal Carbonyl Anion ($CpMo(CO)_3^-$) vs. Halide (Br^-). The Mo-C bond of $CpMo(CO)_3(\Delta)$ is quite different from the Br-C bond of cyclopropylcarbonyl bromide in several respects. It is known that M-H bond dissociation energy (estimated 50-60 kcal/mol) compared with the M-C bond dissociation energy (estimated 30-40 kcal/mol).²⁴ However, CH_3-Br bond dissociation energy is 70 kcal/mol and $H_2C=CHCH_2-Br$ (47 kcal/mol).²⁵ Therefore, Mo-C bond is more likely cleaved than C-Br bond. This may suggest that $CpMo(CO)_3^-$ is a better leaving group than Br^- . In addition to this electronic factor in comparison of leaving group ability, there seems to be a steric factor, too. As $CpMo(CO)_3^-$ group is supposed to be much bulkier than Br^- , $CpMo(CO)_3^-$ will be the better leaving group. The comparison of the bond dissociation energy, steric factor and the reaction rate showed $CpMo(CO)_3^-$ to be a better leaving group than Br^- . As is observed in Scheme 4, $CpMo(CO)_3(\Delta)$ has five possible sites for attack whereas $\Delta^{\wedge}Br$ has two possible sites for attack, including the homo S_N2 possibility.

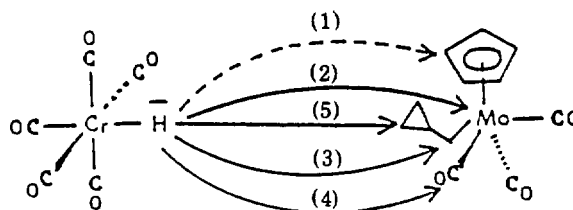
Counterion Effect. As is observed in reactions (1 and 2), no observable counterion effect was detected either on the product distribution (Δ vs. Δ) or on the reaction rate. The minor change (50 min vs. 40 min) in reaction time required is believed due to the formation of bridging hydride ($\mu-HCr_2(CO)_{10}^-$) during the counterion exchange reaction. This bridging hydride formation also led to a less amount of the organic products (Δ and Δ) of interest than the amount of the same product in the reaction without $Na^+B(C_6H_5)_4^-$.

²D-Isotope Effect. No isotope effect on the organic pro-

Table 3. The Organic Product Distribution and k_T for the Reaction of Anionic Metal Hydride with $\Delta^{\wedge}X$ ($X = \text{Bromide}, CpMo(CO)_3$)

Item #	Reactants	Δ : Δ	$k_T(S^{-1} M^{-1})$	Other Organic Products (%)
1	$PPN^+HCr(CO)_5^-$ $CpMo(CO)_3(\Delta)$	29%:71%	6.6×10^{10}	24
2	$PPN^+HCr(CO)_5^-$ $Na^+B(C_6H_5)_4^-$	29%:71%	6.6×10^{10}	46
3	$PPN^+HW(CO)_5^-$ "	100%:0%	0	18
4	$PPN^+DW(CO)_5^-$ "	100%:0%	0	19
5	$PPN^+HW(CO)_4$ { $P(OMe)_3$ } ⁻	0%:0%	0	100
6	$PPN^+HFe(CO)_4^-$ "	96%:4%	1.6×10^9	79
7	$PPN^+HCr(CO)_5^-$ $\Delta^{\wedge}Br$	97%:3%	1.2×10^9	<1

$$[MH^-]_{initial} = 5 \times 10^{-3}M, [MH^-]_{av} = ([MH^-]_{fin} + [MH^-]_{initial})/2$$



Scheme 4

duct distribution (Δ vs. Δ) as well as the reaction rate was observed in the reaction of $PPN^+HW(CO)_5^-$ with $CpMo(CO)_3(\Delta)$ in THF.

Reaction Pathway Considerations. The reaction of $PPN^+HCr(CO)_5^-$ with $\Delta^{\wedge}Br$ is believed to follow an electron transfer pathway (radical chain path) due to organic product ratio (Δ vs. $\Delta = 97:3$) and almost no side organic product (<1%). However, the apparent k_T (Scheme 3) for the reaction of $PPN^+HCr(CO)_5^-$ with $CpMo(CO)_3(\Delta)$ is almost 60 times larger than that for the reaction of the same hydride with $\Delta^{\wedge}Br$ (k_T in the Table 3). The apparent k_T for the former reaction is within the order of diffusion control limit rate ($\sim 10^{10}S^{-1}$). This enormously large number for the apparent k_T may imply that there may be other pathways possibly leading to the cyclized product (Δ) in addition to the single electron pathway. Other possible paths maybe either via S_N2 pathway, the pathway involving an attack of hydride on the metal center (Mo) of $CpMo(CO)_3(\Delta)$, or that involving an attack of hydride on carbon center of the coordinated CO of $CpMo(CO)_3(\Delta)$ as illustrated in Scheme 4.

The hydride's attack was observed in our previous reactions of the anionic transition metal hydride with $[CpMo(CO)_3]^-$. However, the other three seem to be possible.

For example, in path (2), H^- attack on Mo metal center should promote CO insertion into the Mo-alkyl (Δ) to form an acyl group so as to meet the 18-electron rule and to avoid steric bulkiness of ligand coordinated to the metal (Mo). This

Mo complex containing the acyl group should either undergo decarbonylation and/or reductive elimination.

In path (4), $M-H^-$ attack at a carbonyl carbon should create anionic formyl complex; however, the fact that no formyl species was observed in the previous reactions of the anionic metal hydride such as $HCr(CO)_5^-$, and $HW(CO)_4(OMe)_3^-$ with $CpMo(CO)_3(CH_3)$ may rule out this possibility.

As is mentioned before, pathways (3) and (5) indicate the direct hydride attack (or e^- transfer followed by H^- abstraction from some H^- source) on the α -carbon of the alkyl group ($\Delta^{\wedge}Mo$) leading to the organic product distribution (\wedge/\wedge and Δ/Δ).

The last possible path involves homo S_N2 where anionic metal hydride attacks the carbon of the cyclopropyl ring ($\rightarrow\Delta^{\wedge}$). This cyclopropyl group may then undergo ring opening to produce 1-butene and $CpMo(CO)_3^-$.

The mechanistic implications concerned in this reaction ($MH^- + CpMo(CO)_3(\wedge/\Delta)$) are much more complicated than is expected to be in the analogous reaction with $\Delta^{\wedge}X$ ($X =$ halide). In case of the reaction of the anionic metal hydride with $CpMo(CO)_3(\wedge/\Delta)$, the leaving group ($CpMo(CO)_3$) can be a site for attack by the anionic metal hydride in three different ways (metal atom, CO, and potentially Cp ring, Scheme 4). The halide leaving group cannot be a site to be attacked by anionic metal hydride in the reaction of the anionic metal hydride with $\Delta^{\wedge}X$.

In case of the reaction of $PPN^+HCr(CO)_5^-$ with $CpMo(CO)_3(\wedge/\Delta)$, there seems to be no plausible reason why k_T in Table 3 should be zero, except the reason for that this more reactive hydride is more likely to donate an electron to the Mo metal center instead of transfer of hydride (H^-) to the same site. This radical anion $[CpMo(CO)_3(\wedge/\Delta)]^-$ could yield the ring opened anion $[CpMo(CO)_3\wedge/\wedge]^-$ prior to H^- abstraction or bond homolysis. An alternative explanation is that this reaction may solely undergo the homo- S_N2 pathway to produce ring-opened product (\wedge/\wedge).

The reaction of $PPN^+HW(CO)_4P(OMe)_3^-$ with $CpMo(CO)_3(\wedge/\Delta)$ seems to follow a totally different pathway from that in the reaction of the anionic metal hydride with $\Delta^{\wedge}Br$, based on the organic product distribution in Table 3. This strong anionic hydride is most likely to attack Mo metal center to produce $CpMo(CO)_3^-$, some unidentified organometallic compound and CH_4 . However the mechanism for methane formation is not at all understood.

In the case of $PPN^+HFe(CO)_4^-$ with $CpMo(CO)_3(\wedge/\Delta)$ the pathway 3, Scheme 4 represents only a small portion of the electron transfer products (\wedge/\wedge and Δ/Δ ; 21% of the total organic product observed), based on the GC peak area %. Nevertheless, the possibility of a homo- S_N2 pathway should not be overlooked in this reaction.

Further work should be done especially on the reaction of $PPN^+HW(CO)_4\{P(OCH_3)_3\}^-$ with $CpMo(CO)_3(\wedge/\Delta)$ so as to elucidate its mechanistic reaction pathways.

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