Comparative Reactivities of Two Isoelectronic Transition-Metal Hydrides with Transition-Metal Carbonyls and Alkyls

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Abstract: The two isoelectronic hydrides $PPN^+CpV(CO)_3H^-(1)$ and $-CpMo(CO)_3H(2)$ react with a variety of metal carbonyls and alkyls. Treatment of Fe(CO)₅, Cr(CO)₆, (CH₃C₅H₄)V(CO)₄, CH₃Re(CO)₅, and (CH₃CO)Re(CO)₅ with 1 produces $HFe(CO)_4$, $HCr(CO)_5$, $(CH_3C_5H_4)V(CO)_3H^-$, $(H)(CH_3)Re(CO)_4$, and $(H)(CH_3CO)Re(CO)_4$, respectively, and $CpV(CO)_4$ (3). 1 also catalyzes ligand substitution reactions in 3 and CpFe(CO)(PPh₃)(COCH₃). In comparison 2 reacts only with $CH_{3}Mn(CO)_{5}$ and $CpMo(CO)_{3}R$ (R = CH_{3} , $C_{2}H_{5}$, $CH_{2}C_{6}H_{5}$) producing aldehydes and the dimers $[CpMo(CO)_{3}]_{2}$ (4a) and [CpMo(CO)₂]₂ (5a). Reaction of 2 with ethylene produces ethane and diethyl ketone. 1 is proposed to react by an electron-transfer mechanism, whereas 2 is proposed to react by hydrogen transfer to a vacant coordination site. The relationship of the molybdenum hydride/alkyl reaction to the final step in hydroformylation (oxo process) is discussed.

Because of their unique structural and dynamic properties, as well as their importance in catalytic processes, metal hydrides have occupied a central role in organotransition-metal chemistry for many years. Recently it has become clear that metal-metal interactions are strongly affected by the presence of hydride ligands, and many metal-bridging hydrides have been characterized and studied in both binuclear and higher nuclearity cluster systems.¹ Given the strong effect of the hydride ligand on metal-metal interactions, it seems reasonable that metal hydrides should react readily with other transition-metal complexes. Recent studies have shown that this is indeed the case. In the most interesting of these reactions it has been demonstrated that certain metal hydrides interact readily with partners such as metal carbonyl and alkyl complexes, initiating reactions which result ultimately in the formation of hydrocarbons, aldehydes, and products resulting from the reduction of complexed carbon monoxide.

In one series of studies, Gladysz has reported^{2,3} the triethylborohydride reduction of $M_2(CO)_{10}$ ($M_2 = Mn_2$, Re_2 , ReMn), $CpMn(CO)_2(NO)^+$, $Re(CO)_5(PPh_3)^+$, $Mn(CO)_4(PPh_3)_2^+$, Ir- $(\dot{CO})_3(PPh_3)_2^+$, and $CpMo(CO)_3(PPh_3)^+$. In each case the observation of a formyl species in which one of the carbon monoxide ligands had been reduced was seen by NMR. Casey has also reported⁴ the reduction of several metal carbonyls and of $CpRe(CO)_2(NO)^+$ with triisopropoxyborohydride to obtain CpRe(CO)(NO)(CHO) and with triethylborohydride to obtain $CpRe(NO)(CHO)_2^-$, in which one and two new carbon-hydrogen bonds are formed, respectively. In cases involving metal alkyls, the reduction of $Cp_2Zr(CH_3)_2$ with $CpMo(CO)_3H$ has been reported⁵ to form methane and the mixed-metal dimer, Cp₂- $(CH_3)Zr-Mo(CO)_3Cp$. Labinger has recently proposed⁶ that reduction of Fe(CO)₅ with Cp₂NbH₃ proceeds through an intermediate similar to $(CO)_4$ Fe $(CHO)^-$. Also, Caulton has found⁷ that both Cp₂ReH and Cp₂MH₂ (M = Mo, W) reduce bis(cyScheme I

$$C_{P}V(CO)_{4} \xrightarrow{1)} N_{3}/THF PPN^{+}[C_{P}V(CO)_{3}H]^{-}$$

$$3 \xrightarrow{3)} H_{2}O \qquad 1$$

$$1 + Fe(CO)_{5} \xrightarrow{} 3 + PPN^{+}HFe(CO)_{4}^{-}$$

$$1 + Cr(CO)_{6} \xrightarrow{} 3 + PPN^{+}HCr(CO)_{5}^{-}$$

$$1 + MeC_{P}V(CO)_{4} \xrightarrow{} 3 + PPN^{+}[MeC_{P}V(CO)_{3}H]^{-}$$

clopentadienyl)acetylcarbonylzirconium(IV), forming derivatives in which the acetyl functionality has been formally reduced to an alkoxy group. In the hydroformylation of olefins, $HCo(CO)_4$ has been proposed⁸ to be the species responsible for the reduction of an acylcobalt complex in the formation of aldehyde.

We report here a comparison of the products and mechanisms of reaction of two isoelectronic (but perhaps not isostructural⁹) metal hydrides, PPN⁺[$(\eta^5-C_5H_5)V(CO)_3H$]⁻ (1)^{10a} and $(\eta^5-C_5H_5)M_0(CO)_3H$ (2),^{10b} with transition-metal carbonyls, alkyls, and acyls. Several facile reactions of these complexes have been uncovered, most resulting in the formation of new M-H and/or C-H bonds. The major mechanistic difference found is that 1 can act as an electron-transfer agent due to its reducing nature whereas 2 acts as a hydride ligand, coordinating to the vacant site of an unsaturated metal species.¹¹

Results and Discussion

A. Reactions of PPN⁺CpV(CO)₃H⁻ with Metal Carbonyls. In 1958, Fischer reported¹² the reduction of $CpV(CO)_4$ (3), with sodium metal in liquid ammonia or with sodium amalgam in THF,

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⁽¹⁰⁾ PPN⁺ refers to the bulky organic counterion $[(Ph_3P)_2N]^+$.

⁽¹⁰⁾ PPN' refers to the bulky organic counterion [(Ph₃P₁₂N]*. (a) Kinney, R. J.; Jones, W. D.; Bergman, R. G. J. Am. Chem. Soc. 1978, 100, 7902.
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Scheme II



 $CpFe(CO)(PPh_3)(COCH_3) + CO \xrightarrow{1} CpFe(CO)_2(COCH_3) + PPh_3$

to give $(Na^+)_2[CpV(CO)_3]^2$. More recently, we found that this dianion may be protonated with water and the sodium ion replaced by bis(triphenylphosphiniminium) ion^{10a} (Scheme I). This yellow, microcrystalline hydride is characterized by two ¹H NMR resonances (δ 4.60 (5 H), -6.72 (1 H)) and two infrared carbonyl stretching frequencies (1887, 1775 cm⁻¹) in THF solution.

Reactions of 1 with several metal carbonyls are summarized in Scheme I. When a 0.14 M THF- d_8 solution of 1 is treated with 1 equiv of Fe(CO)₅ at room temperature, new ¹H NMR resonances are observed at δ 5.20 and -8.80, characteristic of 3 and PPN⁺HFe(CO)₄^{-,13} respectively. At this concentration, red crystals of analytically pure PPN+HFe(CO)₄- precipitate and can be isolated by decanting the solvent and washing with hexane. The reaction of 1 with $Cr(CO)_6$ (0.15 M each) at room temperature produced a solution with ¹H NMR resonances at δ 5.20 (characteristic of 3), δ -6.88 (s, 1 H, 51% based on 1), and δ -19.4 (s, 1 H, 15% based on 1), the latter two resonances being assigned¹⁴ to $HCr(CO)_5$ and $H[Cr(CO)_5]_2$, respectively. An IR spectrum of the solution showed the carbonyl stretching frequencies of $CpV(CO)_{4}$ (2008, 1915 cm⁻¹).

Complex 1 also undergoes an unusual self-exchange reaction with 3, as demonstrated by the use of a chemical label on the cyclopentadiene ring. An equimolar solution of 1 and (CH₃C₅- H_4)V(CO)₄ in THF- d_8 is observed by NMR to equilibrate with 3 and $(CH_3C_5H_4)V(CO)_3H^-$ at room temperature over a 12-h period.

B. Reaction of PPN⁺V(CO)₃H⁻ with Metal Alkyls and Acyls. No reaction is observed between 1 and $CpFe(CO)_2(CH_3)$ (0.10 M each) at room temperature in THF solution. However, $CH_3Mn(CO)_5$ reacts instantaneously with 1 (0.17 M each) under identical conditions producing small quantities of methane (5%, GC, NMR). The formation of brown precipitates characteristic of extensive decomposition of the metal species is observed.

In keeping with the premise that metal complexes are generally more stable as one moves down a column in the periodic table, we examined the reaction of 1 with $CH_3Re(CO)_5$ (0.09 M each) in THF next. Temperatures of 50 °C were now required for reaction, producing quantitative yields of 3 and a new material. Although this complex was too sensitive to allow isolation, we propose it is $(CO)_4 Re(CH_3)(H)^-$ on the basis of its ¹H NMR (δ -0.65 (d, J = 3 Hz, 3 H), -5.56 (br, 1 H)) spectrum. Continued thermolysis (50 °C) of the solution in the presence of CO produced methane and $Re(CO)_5$, providing additional support for the identity of the initially formed complex (Scheme II). Upon reaction of 1 with (CH₃CO)Re(CO)₅ (0.12 M each) in THF-d₈, ¹H NMR resonances attributable to 3 (δ 5.20) and PPN⁺- $(CO)_4 Re(COCH_3)(H)^- (\delta 2.20 (s, 3 H), -4.38 (br, 1 H))^{15} ap$ peared (90% yield) after the mixture was heated at 50 °C for 2 h. These reactions each add a new member to the relatively small groups of presently known alkyl- and acylmetal hydrides.

Surprisingly, an initial attempt to repeat the latter reaction using freshly prepared 1 and (CH₃CO)Re(CO)₅ under apparently Jones, Huggins, and Bergman

Scheme III

$$CpV(CO)_{3}H^{-} + ML_{n} \longrightarrow Cp\dot{V}(CO)_{3}H + ML_{n}^{-}$$

$$ML_{n}^{-} \longrightarrow ML_{n-1}^{+} + L$$

$$ML_{n-1}^{-} \longrightarrow ML_{n-1}^{+} + L$$

$$ML_{n-1}^{-} \longrightarrow ML_{n-1}^{+} + CpV(CO)_{3}$$

$$ML_{n-1}^{-} \longrightarrow CpV(CO)_{3}L$$

$$\downarrow cp\dot{V}(CO)_{3}H$$

$$\downarrow + ML_{n-1}L'$$

Scheme IV

.. . . .

$$X + ML_{n} \longrightarrow X' + ML_{n-1} + L$$

$$ML_{n-1}^{\dagger} + CpV(CO)_{3}H^{\dagger} \longrightarrow HML_{n-1}^{\dagger} + CpV(CO)_{3}^{\dagger}$$

$$CpV(CO)_{3}^{\dagger} + ML_{n} \longrightarrow CpV(CO)_{3} + ML_{n-1}^{\dagger} + L$$

identical conditions showed mostly unreacted starting material and only 5% product by NMR after 2 h. This problem was solved when it was discovered that small quantities of a strong reducing agent greatly accelerated the reaction. For example, addition of 1 mg of Na metal caused the reaction to go to completion after 1 h at 50 °C. Na₂CpV(CO)₃ (20 mol %) was found to be a most effective catalyst, causing an instantaneous reaction at -20 °C. Upon reexamining the reactions of $Fe(CO)_5$ and $Cr(CO)_6$ with 1, we observed hydride transfer to occur 3-4 times more rapidly when a trace of $Na_2CpV(CO)_3$ was added to the solution.

Reaction of 1 with $CpMo(CO)_3(C_2H_5)$ in THF-d₈ at room temperature produced a 30% yield of propionaldehyde (NMR: δ 9.68 (t, J = 1.7 Hz, 1 H), 2.38 (q of d, J = 7.3, 1.7 Hz, 2 H), 1.04 (t, J = 7.3 Hz, 3 H)). At longer reaction times we observed broadening of NMR resonances and the formation of precipitates, suggesting decomposition of the metal species.

C. Ligand Substitution Reactions Catalyzed by 1. No reaction between PPh₃ (0.23 M) and CpV(CO)₄ (0.25 M) was observed in THF- d_8 solution in the absence of light. However, upon introducing 40 mol % of 1, a smooth substitution reaction was evident by ¹H NMR, producing CpV(CO)₃(PPh₃)¹⁶ (δ 4.73 (d, $J_{\rm Ph} = 1.5$ Hz)) as 3 was consumed. No change in the size or shape of the Cp resonance of 1 (4.60 ppm) was found. Substitution of CO by PMe₃ is also catalyzed by 1 under similar conditions, producing a quantitative yield (NMR) of CpV(CO)₃(PMe₃)¹⁶ in 15 min (δ 4.90 (5 H, d, J_{PH} = 1.9 Hz), 1.44 (9 H, d, J_{PH} = 8.7 Hz)).

As stated above, 1 and 3 exchange hydride and CO ligands. However, we have also observed catalytic ligand substitution in a system which does not undergo such exchange. CpFe(CO)-(PPh₃)(COCH₃) reacts with neither 1 nor CO (1 atm) at 50 °C in THF solution. However, addition of 1 to a solution of CpFe(CO)(PPh₃)(COCH₃) under a CO atmosphere induces exchange of CO for PPh₃ at 50 °C, producing signals attributable to PPh₃ and CpFe(CO)₂(COCH₃)^{17a} (NMR: δ 4.93 (s, 5 H), 2.50 (s, 3 H)) as the resonances of CpFe(CO)(PPh₃)(COCH₃) diminish.17b

D. Mechanism of Reaction of PPN⁺CpV(CO)₃H⁻ with Metal Carbonyls. All of the observed reactions can be explained in terms of the electron-transfer process shown in Scheme III. We suggest the first step involves a rate-determining electron transfer from 1 to the metal substrate, inducing ligand dissociation in the latter. This 17-electron intermediate can then react by hydrogen atom transfer (path A) or ligand attack (path B). In the case of path A, hydride transfer produces directly the observed metal hydride anion and a "CpV(CO)3" fragment, which then captures a ligand

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Scheme V

$$ML_{n} + CpV(CO)_{3}H^{-} \longrightarrow Cp\dot{V}(CO)_{3}H + ML_{n-1}^{-} + L \qquad (5-1)$$

$$\mathsf{ML}_{\mathsf{n}-\mathsf{l}}^{\dagger} + \mathsf{L}' \longrightarrow \mathsf{L}'\mathsf{ML}_{\mathsf{n}-2}^{\dagger} + \mathsf{L}$$
(5-2)

$$L'ML_{n-2}^{-} + Cp\dot{V}(CO)_{3}H \longrightarrow L'ML_{n-2} + CpV(CO)_{3}H^{-}$$
 (5-3)

$$L'ML_{n-2}$$
 (5-4)

$$L^{ML}n^{-2} L^{+} L^{ML}n^{-1}$$
(5-5)

from solution. The effect of added strong reducing agent (Scheme II) supports the electron-transfer hypothesis. In this case (Scheme IV), it is our guess that reducing agent X initiates a chain in which further reduction steps are induced by $CpV(CO)_3^{-1}$.

It seems likely that catalytic substitution also involves ligand dissociation from the metal substrate after electron transfer from 1. However, the 17-electron intermediate now picks up a ligand from solution (path B in Scheme III), producing a 19-electron species that rapidly transfers an electron back to the neutral vanadium species to form 1 and a substituted metal substrate.

A variant of the ligand substitution mechanism in Scheme III invokes substitution in 17-electron species ML_{n-1} (Scheme V), as suggested by Brown for other radical-induced substitutions.¹⁸ Again, electron transfer from 1 induces loss of a ligand and forms a 17-electron intermediate (eq 5-1). Ligand substitution forms a new 17-electron compound (eq 5-2). Electron transfer from this species back to $CpV(CO)_{3}H$ regenerates 1 (eq 5-3) and forms a 16-electron compound that then captures a ligand from solution, forming the substituted product (eq 5-4 and 5-5).

However, the experimental evidence speaks against this mechanism due to the required intermediacy of the 16-electron species in eq 5-2 and 5-3. In the case of phosphine substitution in $CpV(CO)_4$, the corresponding intermediate, $CpV(CO)_2(PR_3)$, should coordinate a second ligand from solution, forming the known¹⁹ CpV(CO)₂(PR₃)₂ (eq 5-4). However, no disubstituted product is observed (as little as 5% would be detected). Also, in the vanadium-catalyzed substitution of phosphine for CO in CpFe(CO)(PPh₃)(COCH₃), the corresponding 16-electron intermediate should rapidly decarbonylate to give CpFe(CO)₂(CH₃), yet none of this latter product is observed. Insertion of CO into the iron-methyl bond in CpFe(CO)₂(CH₃) has been reported¹⁷ to occur at 125 °C and 200 psi, suggested that deinsertion of CO in the intermediate $CpFe(CO)(COCH_3)$ species is facile. However, under our catalytic conditions, $CpFe(CO)_2(COCH_3)$ is formed at 50 °C and 1 atm. Both of the above observations tend to argue against the substitution mechanism outlined in Scheme V.

E. Reactions of CpMo(CO)₃H with Transition-Metal Carbonyls and Alkyls. We have also examined the reduction capability of the neutral hydride $CpMo(CO)_{3}H(2)$ toward transition-metal alkyls and carbonyls. No reaction was observed between 2(0.2)M) and either $Fe(CO)_5 (0.3 \text{ M})$ or $Cr(CO)_6 (0.2 \text{ M})$ in THF- d_8 solution after 24 h at 70 °C. With the latter carbonyl, thermal decomposition of 2 produced the known²⁰ dimer $[CpMo(CO)_3]_2$ (4a) (and presumably hydrogen gas) as previously reported.¹⁰⁶ At no time were any formyl (δ 10–20) or new hydride (δ 0 to –20) resonances observed. With Fe(CO)5, metal was observed to form on the walls of the vessel.

Reaction of 2 with $(CH_3)Mn(CO)_5$ (0.23 M each) in THF-d₈ was complete after a few hours at room temperature. NMR analysis indicated the formation of dimers 4a (δ 5.40), CpMo- $(CO)_3$ -Mn $(CO)_5$ (δ 5.49),²¹ [CpMo $(CO)_2$]₂ (5a, δ 5.27),²² and Scheme VI

(

$$\begin{array}{c} & & & \\ & & \\ \text{CO}_{3}\text{MoH} & + & \text{CH}_{3}\text{Mn}(\text{CO})_{5} & \longrightarrow & \text{CH}_{3}\text{CHO} + [\text{CpMo}(\text{CO})_{3}]_{2} + [\text{CpMo}(\text{CO})_{2}]_{2} \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & &$$

$$\begin{array}{c} & \bigoplus_{H} + \bigoplus_{(CO)_{3}MOR} & \longrightarrow_{R-C} \bigoplus_{H} + \frac{1}{2} Cp_{2}Mo_{2}(CO)_{6} + \frac{1}{2} Cp_{2}Mo_{2}(CO)_{4} \\
 2 & 6a, R = C_{2}H_{5} \\
 6b, R = CH_{3} \\
 6c, R = CH_{2}Ph
\end{array}$$

Scheme VII

$$Cp(CO)_{3}Mo - R \xrightarrow{k_{1}} Cp(CO)_{2}Mo - C - R \qquad (7-1)$$
6
(7-1)

$$Cp(CO)_2Mo-C=R \xrightarrow{4}_{K_{-2}} Cp(CO)_2Mo+R-C=O$$
 (7-2)

$$R-\tilde{C}=O+2 \xrightarrow{M_3} RCHO + Cp(CO)_3 Mo$$
(7-3)

$$Cp(CO)_2Mo + Cp(CO)_3Mo + \frac{m_4}{2} [Cp_2Mo_2(CO)_5] \rightarrow 4a + 5a (7-4)$$

Table I. Second-Order Rate Constants for the Reaction of $CpMo(CO)_{3}H$ with $CpMo(CO)_{3}R$ in THF- d_{8}

R	T, ℃	$k, M^{-1} s^{-1}$	-
C_2H_s (6a)	50	4.0×10^{-3}	
CH ₃ (6b)	50	2.5×10^{-4}	
CH, C, H, (6c)	50	2.5×10^{-5}	
CH ₃ ^a (7b)	50	2.3×10^{-4}	
$C_2 H_5 (6a)$	25	8.5×10^{-4}	

^{*a*} Cp replaced by $CH_3C_5H_4$.

presumably $Mn_2(CO)_{10}$. Acetaldehyde was also detected by NMR $(\delta 2.07 (d, J = 3 Hz, 3 H), 9.66 (q, J = 3 Hz, 1 H))$ (Scheme VI). The yield of aldehyde was observed to increase to 70% and then slowly decrease to 50% with longer reaction times. Broadening of the ¹H NMR resonances was also seen, indicating that metal decomposition products were formed. Apparently consumption of CO in forming acetaldehyde results in a deficiency of ligands for the metal centers, so that as the reaction proceeds a small quantity of the unsaturated metal products decompose in a fashion that also destroys some acetaldehyde. In keeping with the concept that second- and third-row metal complexes are more stable than their first-row analogues and recalling the successful application of this strategy to the reactions of 1 with (CH₃)M- $(CO)_5$ (M = Mn, Re), we examined the reduction of (CH_3) Re-(CO)₅ by 2 (0.22 M each). However, no reaction was observed after several days at room temperature.

The most successful reduction employing 2 was found with the compounds $CpMo(CO)_3R$ (6a, $R = C_2H_5$; 6b, $R = CH_3$; 6c, R = $CH_2C_6H_5$) (Scheme VI). Here, the problem of CO deficiency is less serious because the consumption of CO in forming aldehyde is accommodated by the formation of material having a metalmetal triple bond (5a). A THF- d_8 solution of 2 and 6a (0.12 M in each reactant) showed a smooth conversion into propionaldehyde and the dimers $[CpMo(CO)_3]_2$ (4a) and $[CpMo(CO)_2]_2$ (5a) at temperatures between 25 and 50 °C.

With the ethyl and methyl complexes 6a and 6b, a quantitative yield of aldehyde was also observed by NMR. With the benzyl complex 6c, only a 62% yield of benzaldehyde was measured; some toluene ($\sim 25\%$) was also detected. Higher concentrations of 2 gave decreased amounts of toluene relative to benzaldehyde.

Kinetic studies of the reaction of 6a, 6b, and 6c with 2 were conducted at 25 °C in THF- d_8 solution, the quantities of each

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Figure 1. HPLC traces of mixtures of Cp- and MeCp-substituted molybdenum-carbonyl dimers $(1 \times 25 \text{ cm} \text{ columns packed with Ultra$ sphere-ODS (Altex) reversed-phase adsorbent; CH₃CN elution solvent).(a) Synthetic mixture of all six dimers (individual identities of peaks areindicated on figure). (b) Product mixture resulting from reaction ofMeCpMo(CO)₃H (2b) with CpMo(CO)₃C₂H₅ (6a) (darkened circles $(<math>\bullet$) indicate products resulting from decomposition of hydride during chromatography).

compound being determined by ${}^{1}H$ NMR integration of the appropriate resonances relative to an internal standard (ferrocene). The rate of aldehyde formation was found to be first order in each reactant (Table I).

F. Mechanisms of CpMo(CO)₃H Reactions. The drastic change in the reactivity of 2 compared with 1 and the change in the type of products (aldehydes vs. alkanes) suggest that these hydrides react by different mechanisms. The demonstrated propensity of RMn(CO)₅ and CpMo(CO)₃R to form acyl derivatives^{23,24} and the observation of aldehyde products in their reactions with 2 strongly implicates metal—acyl intermediates. The relative reactivities of **6a**, **6b**, and **6c** (Table I) also parallel their reactivities in phosphine-induced CO-insertion reactions.²³ One possible mechanism, shown in Scheme VII, involves CO insertion followed by homolysis of the molybdenum-acyl bond, the aldehyde being formed in a subsequent step involving hydrogen



Scheme IX



abstraction from 2 by the acyl radical. The formation of toluene from 6c can be accommodated by metal-benzyl bond homolysis to form a relatively stable benzyl radical followed by hydrogen transfer from 2. A similar mechanism has been proposed by Halpern and co-workers for the production of toluene from $HMn(CO)_5$ and $(CO)_5Mn(CH_2C_6H_5)$.²⁵ Alternatively, benzyl radicals could be formed by decarbonylation of the PhCH₂CO radical. Due to the lower stability of methyl and ethyl radicals, metal-alkyl bond homolysis and acyl radical decarbonylation might not be kinetically competitive with insertion, so that with alkyl substituents only acyl radicals, leading to aldehyde, would be formed.

Because (1) compounds 6 are stable in the absence of 2 and (2) the aldehyde forming reaction is first order in 2, the alkyl migration and molybdenum-acyl bond cleavage reactions (eq 7-1 and 7-2) must be rapid and reversible, with hydrogen abstraction from 2 being rate determining, if the mechanism in Scheme VII is operable. This prediction was tested by heating an equimolar mixture of 6b and $(CH_3C_5H_4)Mo(CO)_3(CD_3)$ in THF-d₈ to 50 °C. None of the expected crossover product, $(CH_3C_5H_4)Mo(C-O)_3(CH_3)$ (7b), was observed by ¹H NMR, where as little as 1% could have been detected (Scheme VIII). Addition of 2 to this solution induces the smooth formation of the expected aldehydes, with no 7b being observed at any intermediate times. Consequently, aldehyde production cannot be occurring by the mechanism shown in Scheme VII.

However, the reaction of the benzyl compound 6c with 2 is somewhat more complicated. When a mixture of 6c and $(C-H_3C_5H_4)Mo(CO)_3(CD_2C_6D_5)$ was heated at 50 °C in THF- d_8 , a small amount of $(CH_3C_5H_4)Mo(CO)_3(CH_2C_6H_5)$ (7c) was observed to grow in by ¹H NMR. This observation, and the formation of toluene upon reaction with 2, can be rationalized by assuming that the benzyl radical is stable enough²⁶ that in this case molybdenum-carbon bond cleavage is competitive with CO insertion. Consequently, some crossover is observed in the absence of 2, and some toluene is formed in addition to aldehyde in the presence of 2.

A preferred mechanism for the formation of aldehyde that fits the observed kinetics and crossover experiments involves reversible CO insertion to generate the coordinatively unsaturated acyl, **8** (Scheme IX). Evidence for the formation of this intermediate in carbonylation and phosphine-substitution reactions has been available for some time.²⁷ Unsaturated complex **8** is then trapped by **2** in a rate-determining step; subsequent reactions producing aldehyde (**4a**) and **5a** occur rapidly.

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Scheme X



Cp(CO)₂ Mo=Mo(CO)₂ Cp

Cp'(CO)2 Mo≡Mo(CO)2Cp'

5 a

5c

The means by which hydrogen is transferred from 2 (i.e., the nature of intermediate(s) 9) is of some interest.²⁸ Several possible intermediates are shown in Scheme X. Because 2 is a weak acid,²⁹ one likely path involves proton transfer, forming $CpMo(CO)_3^{-1}$ and a cationic acyl hydride (9a) that reductively eliminates aldehyde.³⁰ The cationic and anionic metal fragments can then recombine, ultimately forming 4a and 5a. In the reduction of 6a with 2 under an atmosphere of CO, an attempt to trap the $CpMo(CO)_3$ intermediate with a 10-fold excess of CH_3I was unsuccessful (no 6b was formed). In addition, if 2 is merely acting as an acid in these reactions, then other acids of comparable pK_a should also react with 6 to produce aldehydes. However, when **6b** is treated with acetic acid, no reaction occurs. With the stronger acid CF₃COOH reaction does occur, but methane is the sole organic product. The reactivity of 6a with a less acidic molybdenum hydride has also been investigated. Replacing a CO ligand in 2 with PMe₃ should produce a more basic metal center, so that a decrease in the reaction rate should be observed if proton transfer is involved in the cleavage of intermediate 9. However, CpMo-(CO)₂(PMe₃)H reacts slightly faster than 2, again producing aldehyde along with a mixture of phosphine-substituted dimers.

The possibility also exists that hydrogen *atom* transfer occurs between 2 and 8, forming metal-centered radicals 9b. Reductive elimination of aldehyde then produces $CpMo(CO)_3$ and $CpMo(CO)_2$, which recombine and ultimately form dimers 4a and 5a. To the extent that these radicals escape the initial solvent cage (a process which should be very rapid), their generation should lead to dimers formed from combination of two initial $CpMo(CO)_3$ radicals, and two $CpMo(CO)_2$ radicals, as well as dimers formed by combination of the two $CpMo(CO)_n$ fragments which were present in the initial hydride-acyl solvent cage.

To test this alternative, we ran the reaction of $CpMo(CO)_3H$ (2a) with $MeCpMo(CO)_3CH_3$ (7b), in an attempt to determine whether the dimers formed always "remember" their compounds of origin (i.e., only crossed Me/CpMe dimers observed) or whether some dimers arise from metals both originally bound to hydride or to alkyl (Cp/Cp or MeCp/MeCp dimers). The first problem to be solved in carrying out this study was an analytical one; i.e., we needed to be able to quantitatively separate and analyze for all six possible mixed and symmetrical dimers shown in Scheme XI. This problem has been dealt with earlier by using mass

spectral techniques;⁴⁰ we have found^{41a} that these materials can be resolved by using HPLC on reversed-phase columns (see Figure 1). This allowed us to carry out the 2a/7b reaction and analyze quantitatively for all the molybdenum dimer products. At the temperature required to achieve a reasonable rate for the reaction, we did observe that the crossed dimers 4b and 5b were the ones predominantly formed. However, a significant amount of 4a was observed as well, because of competing decomposition of the hydride under these conditions.^{41b} A cleaner experiment was achieved by treating MeCpMo(CO)₃H (2b) with the more reactive ethylmolybdenum complex $CpMo(CO)_3C_2H_5$ (6a) at room temperature and by employing a deficiency of hydride. As shown in Figure 1, under these conditions crossed dimers 4b and 5b were clearly the major products; only traces of symmetrical dimers were observed. The conclusion from these results is that summarized in Scheme XI; i.e., dimers are formed only from the two Mo fragments which interact in the initial Mo-H/Mo-acyl collision complex rather than from free (uncaged) molybdenum radicals derived from 9b.

A third alternative involves hydride transfer between 2 and 8. This mechanism gives $[CpMo(CO)_3]^+$ and an anionic hydridoacyl intermediate (9c in Scheme X). Reductive elimination gives aldehyde and $[CpMo(CO)_2]^-$, which recombines with [CpMo- $(CO)_3]^+$. This seems to be the least likely mechanism, due to the generally poor hydride-donating ability of $Cp(CO)_3MoH$ (i.e., it is actually a weak acid and does not react with moderate electrophiles such as organic carbonyl compounds). Although this pathway is difficult to rule out rigorously, suggestive evidence against the formation of $[Cp(CO)_3Mo]^+$ is provided by the fact that running the hydride/alkyl reaction in the presence of 1 M LiCl gives no $Cp(CO)_3MoCl.^{31}$

Finally there exists a "concerted" mechanism in which 8 and 2 form a bridging hydride (9d; Scheme X), and then this complex undergoes reductive elimination of aldehyde. It may be that a second molecule of CO is lost from 9d before reductive elimination. This would account for our observation that 5a is the principal metal-containing product observed by NMR at early reaction times. In view of the fact that several stable dimers similar to 9d are known, this seems to us to be the most likely mechanism. However, we cannot say whether oxidation addition of the M-H bond to the second metal center takes place, leading to a further intermediate 9e, or whether direct elimination of aldehyde from 9d is possible.

G. Reactions of Molybdenum Hydrides and Alkyls with Olefins. It was reported some time ago^{32} that hydride 2 adds to ethylene at 100 °C to give molybdenum-ethyl complex 6a. This seemed perplexing, in view of our finding that 6a and 2 react to give aldehyde at substantially lower temperatures. In addition, the determination that 6a was the product of this reaction was made only on the basis of observation of typical ethyl resonances in the alkyl region of the NMR spectrum of the crude reaction product;³² however, independently prepared 6a shows only a single alkyl line in the proton NMR due to accidental equivalence of the methyl and methylene chemical shifts in this complex. For these reasons, we decided to reinvestigate the reactions of hydrides 2 and alkyls 6 with ethylene.

In our hands, reaction of 2 (0.32 M) with ethylene (0.61 M) did in fact lead to a reaction mixture which exhibited typical ethyl resonances in the proton NMR spectrum, as reported earlier.³² However, distillation of the volatile materials from this solution and analysis by gas chromatography demonstrated that the compound responsible for these absorptions was not **6a** but rather was diethyl ketone, formed in 15% yield. Also observed was a 36% yield of ethane. After 24 h at 100 °C, neither **6a** nor propionaldehyde was detected. It seemed likely, however, that **6a** was an intermediate in the production of diethyl ketone. In agreement with this hypothesis, reaction of independently prepared

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Scheme XII



ethylmolybdenum complex 6a with ethylene at 100 °C gave an approximately 10% yield of diethyl ketone. In addition, the corresponding methylmolybdenum complex 6b reacted with ethylene at 100 °C to produce methyl ethyl ketone in 50% yield. We conclude from these observations that complex 6b is formed from 2 and ethylene at 100 °C, but under these conditions reaction with additional ethylene is rapid and ketone rather than 6b is the final product.

One perplexing aspect of these reactions concerns the source of the new hydrogen atom in the ketone product. It seemed most likely to us that the ultimate source of this hydrogen was another molecule of ethylene, and this was demonstrated by showing that reaction of **6b** with C_2D_4 gave completely ethyl-deuterated 2butanone. In order to complete the stoichiometry of the reaction, we propose that one molecule of methyl vinyl ketone is formed for each molecule of 2-butanone (see mechanistic discussion below). Methyl vinyl ketone is easily polymerized and might not be expected to survive our reaction conditions. In agreement with this, a small amount of a material with a retention time identical with that methyl vinyl ketone was detected by gas chromatography of the 2/6b reaction mixture. When a significant amount of the unsaturated ketone was added to the initial reaction mixture, heating to 100 °C caused its rapid disappearance.

A sequence which summarizes our conclusions about the mechanisms of reactions of molybdenum alkyls 6 with alkenes, as well about the metal alkyl/metal hydride reactions discussed earlier in this paper, is summarized in Scheme XII. We believe all these reactions begin by reversible CO insertion in 6, generating small quantities of transient, coordinatively unsaturated intermediate 8. In the absence of ethylene, the open coordination site now allows attack by a molecule of hydride, leading to a second intermediate such as 9d (cf. Scheme X and previous discussion of possible structures for this species). Reductive elimination then leads to aldehyde and, ultimately, molybdenum dimers.

In order to explain the alkene reactions discussed above, we must assume that ethylene is also capable of trapping intermediate 8. In this case, π -complex 10 is formed, and this undergoes insertion into the metal-acyl bond, followed by oxygen coordination to molybdenum, to give 11 (we have observed a similar O-coordination-driven insertion recently in a molybdenum-based alkyne cyclization reaction;³³ ethylene has also been shown to insert in metal acyls formed from alkyltetracarbonylferrates³⁴). β -Elimination in this intermediate leads to methyl vinyl ketone and molybdenum hydride 12 (perhaps containing a molecule of solvent in its coordination shell). Reaction between 11 and hydride 12, in much the same fashion that 2 interacts with 8, leads to bridging hydride 13. Once again, reductive elimination leads to the final product (in this case, ketone) and molybdenum dimers. It is

interesting that in the reaction of hydride 2 with ethylene, only ketone, and no aldehyde, is produced. This indicates that when present in sufficient concentration, ethylene competes very successfully with the hydride for intermediate 8.

Conclusion

We showed earlier that in its reactions with organic halides, vanadium hydride 1 participates as a hydrogen atom donor in a radical chain process (much like that found for trialkyltin hydrides) and provided evidence against a direct electron-transfer mechanism in this system.^{10a} With the more electron-deficient metal-carbonyl reaction partners discussed in this work, 1 does interact by electron transfer, the ultimate mode of reaction being exchange of hydride in 1 for CO in the metal substrate. When overall hydride transfer is either thermodynamically or kinetically unfavorable, catalytic ligand substitution in the substrate is observed. In contrast, the less highly reducing molybdenum is a more passive reagent and must wait for the formation of a vacant coordination site before hydride transfer can occur.

Reaction of 2 with compounds 6a-c serves as a close model for the terminal step in the oxo (hydroformylation) reaction. The classic mechanism for this process involves oxidative addition of H₂ to an unsaturated cobalt acyl, followed by reductive elimination, as the means by which free aldehyde is produced. A reasonable alternative, bimolecular reaction of the cobalt acyl with HCo(C-O)4, was considered many years ago,35 but it was not until recently that conclusive experimental evidence for the operation of this step in hydroformylation was obtained.^{8,36} The cobalt hydride/ cobalt acyl reaction involved in the oxo process and the molybdenum hydride/molybdenum acyl reactions discussed in this paper are two members of a rapidly growing, and increasingly important, class of organometallic reactions.

Experimental Section

All solvents were distilled from Na/benzophenone/tetraglyme prior to use and all manipulations performed either in a Vacuum Atmospheres Corp. inert atmosphere box or on a high vacuum line. CpV(CO)4, Na- $(diglyme)^+V(CO)_6^-$, $[CpMo(CO)_3]_2$, $[(CH_3C_5H_4)Mo(CO)_3]_2$, $Mn_2(C-1)^+V(CO)_6^-$, $[CpMo(CO)_3]_2$, $Mn_2(C-1)^+V(CO)_6^-$, $Mn_2(C-1)^+V(CO)_6^-$, $Mn_2(C-1)^+V(CO)_6^-$, $[CpMo(CO)_3]_2$, $Mn_2(C-1)^+V(CO)_6^-$, $[CpMo(CO)_3]_2$, $Mn_2(C-1)^+V(CO)_6^-$, $[CpMo(CO)_6^-$, $[CpMo(CO)_3]_2$, $Mn_2(C-1)^+V(CO)_6^-$, $[CpMo(CO)_3]_2$, $Mn_2(C-1)^+V(CO)_6^-$, $[CpMo(CO)_6^-$, $[CpMo(CO)_6^ O_{10}$, $Re_2(CO)_{10}$, $Cr(CO)_6$, $Fe(CO)_5$, and $[CpFe(CO)_2]_2$ were obtained from the Alfa Corp. or Strem Chemical Co. PPN+CpV(CO)₃H^{-,10a} CH₃Mn(CO)₅,³⁷ CH₃Re(Co)₅,³⁸ and CpFe(CO)(PPh₃)(COCH₃)³⁹ were prepared as previously described. $CpMo(CO)_3H$, $CoMo(CO)_3R$ (R = CH_3 , C_2H_5) and $CpFe(CO)_2(CH_3)$ were prepared by the method of Piper and Wilkinson.¹⁰⁶ The methyl-Cp derivatives were prepared analogously from the corresponding methyl-Cp dimer. Deuterated derivatives were prepared by using CD₃I or C₆D₅CD₂Br.

¹H NMR spectra were recorded on a 180-MHz FT-NMR instrument equipped with a Brücker superconducting magnet and a Nicolet 1180 FT-NMR computer, or on a Varian EM-390 spectrometer. IR spectra were recorded on a Perkin-Elmer 283 infrared spectrometer.

High-pressure liquid chromatography (HPLC) employed an Altex Scientific Inc. Model 110A high-pressure pump, a Rheodyne Model 905-42 variable volume injector valve, and an Altex Model 153 UV-vis detector equipped with a 2-mm pathlength 254-nm wavelength kit. Separations were achieved by using a 1×25 cm ultrasphere-ODS (Altex) reversed-phase column claiming complete coverage of the active sites. The solvent was degassed by continuously purging the solvent reservoir with argon.

Preparation of (CH₃C₅H₄)V(CO)₄. A 2.88-g (0.125-mol) sample of sodium and 10 g of methylcyclopentadiene monomer (0.125 mmol) were dissolved in 50 mL of dimethoxyethane (DME). After the mixture was stirred overnight, the solvent was removed (30 °C (10⁻² mm)) and the remaining solid recrystallized from THF/hexane at -30 °C. A 1.3-g (11.8-mmol) sample of solid $Na^+(CH_3C_5H_4)^-$ was dissolved in 30 mL of THF and 3.55 g (13.4 mmol) of HgCl₂ added. A solution of 5 g (11.8 mmol) of Na(DME)₂⁺V(CO)₆⁻ in 10 mL of THF was added slowly as the solution became red-orange. After 1 h the THF was removed (35 °C (10⁻² mm)) and the remaining material was taken up in 50 mL of H₂O plus 50 mL of petroleum ether. The H₂O layer was extracted with

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petroleum ether $(2 \times 25 \text{ mL})$, and the combined ether layers were washed with water $(2 \times 50 \text{ mL})$ and dried (MgSO₄). The petroleum ether was removed (25 °C (20 mm)) and the remaining oil chromatographed on a silica gel column $(2 \times 15 \text{ cm})$ by using petroleum ether as eluant. The yellow fraction was collected, the solvent removed (25 °C (20 mm)), and the remaining solid sublimed $(50 \text{ °C} (10^{-2} \text{ mm}))$ to yield 200 mg (15%) of $(CH_3C_5H_4)V(CO)_4$: NMR $(THF-d_8)$: $\delta 5.16 (2 \text{ H})$, 5.05 (2 H), 2.01 (3 H); mass spectrum, m/e 242, 214, 186, 158, 130, 51. Anal. Calcd for $C_{10}H_7O_4V$: C, 49.61; H, 2.91. Found: C, 49.38, H, 2.97.

Reaction of PPN⁺CpV(CO)₃H⁻ with (CH₃C₅H₄)V(CO)₄. A 31-mg (0.054-mmol) sample of (CH₃C₅H₄)V(CO)₄ and 40 mg (0.054 mmol) of PPN⁺CpV(CO)₃H⁻ were dissolved in 0.47 mL of THF- d_8 in an NMR tube. NMR spectra recorded over the next 12 h showed the disappearance of (CH₃C₅H₄)V(CO)₄ and CpV(CO)₃H⁻ (δ 4.60) and the appearance of CpV(CO)₄ (δ 5.20) and (CH₃C₅H₄)V(CO)₃H⁻ (δ 4.58 (2 H), 4.42 (2 H), 1.86 (3 H)).

Reaction of CpV(CO)₃H⁻ with Fe(CO)₅ and Cr(CO)₆. A similar reaction of 51 mg (0.069 mmol) of PPN⁺CpV(CO)₃H⁻ with 9.3 μ L (0.069 mmol) of Fe(CO)₅ in 0.5 mL of THF-d₈ produced isolable crystals¹³ of PPN⁺HFe(CO)₄⁻ (25 mg, 47%) upon standing for 12 h. Anal. Calcd for C₄₀H₃₁P₂NFeO₄: C, 67.91; H, 4.42; N, 1.98. Found: C, 67.51; H, 4.58; N, 1.94. No (CHO)Fe(CO)₄⁻ was observed at any time during the reaction. Cr(CO)₆ (47 mg, 0.21 mmol) reacted with PPN⁺CpV(CO)₃H⁻ to give a solution containing CpV(CO)₄, HCr(CO)₅⁻, and H[Cr(CO)₅]₂⁻ (see text), assigned on the basis of data supplied¹⁴ by Professor M. Y. Darensbourg.

Reaction of PPN⁺CpV(CO)₃H⁻ with CH₃Mn(CO)₅ and CH₃Re(CO)₅. A THF- d_8 solution (0.5 mL) of 61 mg (0.082 mmol) of PPN⁺CpV-(CO)₃H⁻ was added to a THF- d_8 solution (0.5 mL) of 18 mg (0.086 mmol) of CH₃Mn(CO)₅ in an NMR tube. The solution turned brown within 5 min. The ¹H NMR showed the disappearance of CpV(CO)₃H⁻ with the concurrent formation of CpV(CO)₄. Traces of CH₄ (~5%) were observed by NMR and by GC (9 ft × ¹/₁₆ in. Poropak Q, 80 °C).

A similar mixture of 14.3 mg (0.042 mmol) of CH₃Re(CO)₅ and 30.4 mg (0.041 mmol) of PPN⁺CpV(CO)₃H⁻ in 0.46 mL of THF-d₈ under 1 atm of CO showed a slow reaction at 25 °C forming methane. Heating this solution to 50 °C resulted in a faster reaction rate $(r_{1/2} \simeq 2 \text{ h})$, forming a new (unisolable) complex, assigned structure $[cis-(CH_3)(H)-\text{Re}(CO)_4^-]$, on the basis of its NMR spectrum (δ -0.65 (3 H, d, J_{H-H} = 3 Hz), δ -5.56 (1 H, br)). Eventually all the CH₃Re(CO)₅ disappeared and only 3 (plus CH₄) was observed. As the hydride disappeared, the amount of methane increased. A second complex, believed to be *trans*-3, was also observed in 10% yield (NMR: δ 0.30 (3 H, s), -4.30 (1 H, s)). This solution was treated with 5 μ L of CH₃I, and a large methyl resonance due to CH₃Re(CO)₅ (δ -0.20) was observed.

Preparation of (CH₃CO)Re(CO)₅. A 1.0-g (1.5-mmol) sample of Re₂(CO)₁₀ was reduced with 1.5 mL of 0.65% Na/Hg amalgam in 10 mL of THF. The solution was decanted from the mercury and 0.22 mL (3.1 mmol) of CH₃COCl added. After 15 min the solvent was removed (0 °C (10^{-3} mm)) and the remaining solid sublimed to a -78 °C probe, yielding 500 mg (44%) of (CH₃CO)Re(CO)₅: NMR (THF- d_8) δ 2.47; IR (THF) 2125 (w), 2060 (w), 2009 (s), 1996 (sh), 1612 (w) cm⁻¹. Anal. Calcd for C₇H₃ReO₆: C, 22.77; H, 0.82. Found: C, 22.56; H, 0.87.

Reaction of PPN⁺CpV(CO)₃H⁻ with (CH₃CO)Re(CO)₅. A 35-mg (0.047-mmol) sample of (CH₃CO)Re(CO)₅ and 18 mg (0.049 mmol) of CpV(CO)₃H⁻ were sealed under vacuum in an NMR tube along with 0.4 mL of THF- d_8 . When the solution was heated at 50 °C, new singlets were observed to grow in slowly over 24 h at δ 2.20 (3 H) and -4.38 (1 H) attributable¹⁵ to (H)(CH₃CO)Re(CO)₄⁻. A quantitative yield of CpV(CO)₄ was also produced. Due to the long reaction time, extensive decomposition of the rhenium product occurred. Attempts to isolate this material by precipitation were not successful, producing only oily materials.

Catalysis of the Reaction of PPN⁺CpV(CO)₃H⁻ with (CH₃CO)Re(C-O)₅. A. With Sodium Metal. A 35-mg (0.047-mmol) sample of PPN⁺CpV(CO)₃H⁻, 18 mg (0.049 mmol) of (CH₃CO)Re(CO)₅, and 1.0 mg of sodium metal were weighed into an NMR tube attached to a ground-glass joint, 0.4 mL of THF- d_8 was distilled in, and the tube was scaled. After the mixture was heated to 50 °C for 30 min, NMR analysis showed a 50% yield of the H(COCH₃)Re(CO)₄⁻ product.

B. With Na₂CpV(CO)₃. A 37-mg (0.050-mmol) sample of PPN⁺-CpV(CO)₃H⁻, 21 mg (0.057 mmol) of (CH₃CO)Re(CO)₅, and 5 mg (0.02 mmol) of Na₂CpV(CO)₃ were weighed into an NMR tube, and 0.54 mL of THF- d_8 was transferred in at 77 K. The tube was sealed under vacuum and thawed, and the contents were mixed. After 5 min an NMR spectrum was recorded, showing a quantitative yield of CpV-(CO)₄ (δ 5.20) and H(CH₃CO)Re(CO)₄⁻ (δ 2.20 (s, 3 H), δ -4.38 (br, 1 H)).

Catalysis of the Reaction of PPN⁺(CpV(CO)₃H)⁻ with Fe(CO)₅ and Cr(CO)₆ by Na₂CpV(CO)₃. A 49-mg (0.066-mmol) sample of PPN⁺-CpV(CO)₃H⁻, 3 mg (0.01 mmol) of Na₂CpV(CO)₃, and 0.78 mL of THF- d_8 were placed in a septum-capped NMR tube in the dry box. An NMR spectrum of the heterogeneous solution was recorded (Na₂CpV-(CO)₃ is insoluble in THF). As 8.7 μ L (0.065 mmol) of Fe(CO)₅ was introduced through the septum with a syringe, the solution became homogeneous. NMR spectra were recorded over the next 40 min, showing the appearance of CpV(CO)₄ and HFe(CO)₄⁻. Comparison of the percent completion (60%) after 10 min in this reaction to a separate reaction without added Na₂CpV(CO)₃ showed that the dianion-catalyzed reaction proceeded ca. 4 times faster.

A similar reaction of 41 mg (0.055 mmol) of PPN⁺CpV(CO)₃H⁻, 24 mg (0.11 mmol) of Cr(CO)₆, and 2 mg (0.01 mmol) of Na₂CpV(CO)₃ in 0.53 mL of THF- d_8 was examined by NMR after 10 min. Comparison of this reaction to one without added Na₂CpV(CO)₃ showed a rate increase of about 3.6.

Reaction of PPN⁺CpV(CO)₃H⁻ with CpMo(CO)₃(C₂H₅). A solution of 55 mg (0.074 mmol) of PPN⁺CpV(CO)₃H⁻ dissolved in 0.5 mL of THF- d_8 was added by syringe to 21 mg (0.077 mmol) of CpMo(CO)₃-(C₂H₃) in 0.4 mL of THF- d_8 in a septum capped NMR tube. An immediate reaction occurred, and an NMR spectrum showed a 30% yield of propionaldehyde (δ 9.68 (t, 1 H), 2.38 (q of d, 2 H), 1.04 (t, 3 H)). Following this the solution turned dark brown, indicating substantial decomposition.

Hydride-Catalyzed Substitution of CpV(CO)₄ by L (L = PPh₃, PMe₃). A 75-mg (0.10-mmol) sample of PPN⁺CpV(CO)₃H⁻, 60 mg (0.23 mmol) of PPh₃, and 58 mg (0.25 mmol) of CpV(CO)₄ were dissolved in 1.0 mL of THF-d₈ and the flask covered to exclude light. NMR spectra were recorded periodically and showed the conversion of CpV(CO)₄ into CpV(CO)₃(PPh₃) (NMR: δ 4.73 (d, J_{PH} = 1.5 Hz)) with no change in the CpV(CO)₃H⁻ resonance ($\tau_{1/2}$ = 1 h).

An identical reaction employing PMe₃ instead of PPh₃ showed complete conversion to CpV(CO)₃PMe₃:¹⁶ ¹H NMR δ 4.90 (5 H, d, J_{PH} = 1.9 Hz); 1.44 (9 H, d, J_{PH} = 8.7 Hz).

1.9 Hz); 1.44 (9 H, d, $J_{PH} = 8.7$ Hz). **Reaction of PPN⁺CpV(CO)**₃H⁻ with CpFe(CO)(PPh₃)(COCH₃) and CO. A 26-mg (0.057-mmol) sample of CpFe(CO)(PPh₃)(COCH₃) and 44 mg (0.058 mmol) of PPN⁺CpV(CO)₃H⁻ were dissolved in 0.5 mL of THF- d_3 and sealed in an NMR tube under 600 mm of CO (0.031 mmol). After 2 days at 25 °C, NMR spectra showed the CpV(CO)₃H⁻ was unchanged, whereas the CpFe(CO)(PPh₃)(COCH)₃ (NMR: 4.38 (5 H, d, $J_{PH} = 2$ Hz), 2.28 (3 H, s)) had been 50% converted (100% yield based on CO) into CpFe(CO)₂(COCH₃)¹¹ (NMR: δ 4.93 (5 H, s), 2.50 (3 H, s)). The solution was heated to 65 °C for 24 h, but no further changes were observed by NMR.

Reaction of CpMo(CO)₃H with CH₃Mn(CO)₅ and CH₃Re(CO)₅. A 27-mg (0.11-mmol) sample of CH₃Mn(CO)₅ was dissolved in 0.48 mg of THF- d_8 in an NMR tube. NMR spectra showed a complete reaction to form CpMo(CO)₃Mn(CO)₅ (δ 5.49²¹), [CpMo(CO)₃]₂ (δ 5.40), [CpMo(CO)₂]₂ (δ 5.27), and CH₃CHO (identified by NMR: δ 2.07 (3 H, d, J = 3 Hz), 9.66 (1 H, q); 50% yield). An equimolar mixture of CpMo(CO)₃H (0.22 M) and CH₃Re(CO)₅ (0.22 M) in THF- d_8 showed no reaction after 3 days at 25 °C.

Reaction of CpMo(CO)₃**H with CpMo(CO)**₃(C₂H₅). A 15-mg (0.061-mmol) sample of CpMo(CO)₃H and 17 mg (0.062 mmol) of CpMo(CO)₃(C₂H₅) were weighed into an NMR tube attached to a ground-glass joint and 0.51 mL of THF- d_8 introduced on a vacuum line. The tube was sealed under vacuum and FT NMR spectra recorded over the next 6 h. The product propionaldehyde (quantitative yield) was identified by NMR (δ 9.68 (1 H, t, J_{ab} = 1.7 Hz), 2.38 (2 H, q of d, J_{bc} = 7.3 Hz), 1.04 (3 H, t)). The dimers [CpMo(CO)₃]₂ and [CpMo(CO)₂]₂, also formed in quantitative yield, were identified by comparison of their NMR spectra with those of authentic samples⁴⁰ (δ 5.40 and 5.27, respectively).

Reaction of CpMo(CO)₃**H with CpMo(CO)**₃(CH₃). A solution of 15 mg (0.061 mmol) of CpMo(CO)₃H and 16 mg (0.065 mmol) of CpMo(CO)₃(CH₃) in 0.43 mL of THF- d_8 was prepared in the drybox in an NMR tube. The tube was heated to 50 °C, and NMR spectra were recorded over the next 40 h, showing the appearance of CH₃CHO (53% yield at completion of reaction) and the molybdenum dimers. A second-order plot of the disappearance of CpMo(CO)₃(CH₃) vs. time gave a second-order rate constant of ~2.5 × 10⁻⁴ M⁻¹ s⁻¹.

Reaction of CpMo(CO)₃(CH₂C₆H₅) with CpMo(CO)₃H. A 15-mg sample of CpMo(CO₃(CH₂Ph) and \sim 11 mg of Cp₂Fe (internal standard) were weighed into each of three NMR tubes. Samples of 44, 88,

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and 132 mg of CpMo(CO)₃H were weighed into the three tubes, respectively. THF- d_8 (0.44 mL) was added to each sample, and the tubes were sealed under vacuum. The tubes were heated to 50 °C in an NMR probe and the relative amounts of benzaldehyde and toluene measured by integration. The dilute hydride solution showed a 3.3:1 ratio of benzaldehyde to toluene, whereas the intermediate and concentrated hydride solutions showed 5:1 and 7.1 ratios of aldehyde to toluene, respectively.

Preparation of (CH₃C₅H₄)Mo(CO)₃(CH₃) and (CH₃C₅H₄)Mo(CO)₃-(CD₃). A 0.75-g (1.5-mmol) sample of $[(CH_3C_5H_4)Mo(CO)_3]_2$ was dissolved in 5 mL of THF and stirred over 20 g of 0.65% Na/Hg amalgam for 1 h. The solution was decanted from the mercury and 0.25 mL of CH₃I added (4.0 mmol). The THF was removed (25 °C (10⁻² mm)) and the products sublimed at 50 °C (10⁻⁴ mm): yield, 0.35 g (45%) of (CH₃C₅H₄)Mo(CO)₃(CH₃); NMR (THF-d₈) δ 5.25 (4 H, m), 1.93 (3 H, s), 0.29 (3 H, s). Anal. Calcd for C₁₀H₀MoO₃: C, 43.45; H, 3.73. Found: C, 43.22; H, 3.64. Substitution of 0.3 mL of CD₃I in place of CH₃I produced 0.52 g (60%) of (CH₃C₅H₄)Mo(CO)₃(CH₃), except for the absence of a methyl resonance at δ 1.93.

The Reaction of CpMo(CO)₃(CH₃) with $(CH_3C_5H_4)Mo(CO)_3(CD_3)$. A solution containing 24 mg each of CpMo(CO)₃(CH₃) and (CH₃C₅-H₄)Mo(CO)₃(CD₃) in 0.38 mL of THF- d_8 was prepared in an NMR tube in the drybox. The tube was heated to 50 °C overnight and an NMR spectrum recorded. No $(CH_3C_5H_4)Mo(CO)_3(CH_3)$ was observed. A control solution containing an authentic mixture of CpMo(CO)₃CH₃ and $(CH_3C_5H_4)Mo(CO)_3CH_3$ demonstrated that the two complexes exhibited distinguishable CH₃ resonances (6 Hz apart), and as little as 1% of the CH₃C₅H₄ complex could have been detected in the mixing experiment.

Preparation of $(CH_3C_4H_4)Mo(CO)_3(CH_2C_6H_5)$ and $(CH_3C_5H_4)Mo(CO)_3(CD_2C_6D_5)$. A 0.60-g (1.16-mmol) sample of $[(CH_3C_5H_4)Mo(C-O)_3]_2$ was reduced with 20 g of 0.65% Na/Hg amalgam in 10 mL of THF. A 0.4-mL (2.53-mmol) sample of $C_6H_5CH_2Br$ was added and the solution stirred for 30 min. The solvent was removed (25 °C (10⁻² mm)) and the solid chromatographed on silica gel (2 cm × 10 cm) by using benzene as eluant. A yellow band was collected and the benzene removed (35 °C (10⁻² mm)), yielding 0.52 g (64%) of (CH_3C_5H_4)Mo(CO)_3-(CH_2C_6H_5): NMR THF- $d_8 \delta$ 7.12 (5 H, m), 5.20 (5 H, s), 2.82 (2 H, s), 1.96 (3 H, s). Anal. Calcd for $C_{16}H_{14}MoO_3$: C, 54.87; H, 4.03. Found: C, 54.66; H, 4.08. Use of $C_6D_5CD_2Br$ (see below) (0.3 mL) in place of $C_6H_5CH_2Br$ produced (CH_3C_5H_4)Mo(CO)_3(CD_2C_6D_5) (mp 49-50 °C), whose NMR was the same as that of (CH_3C_3H_4)Mo(C-O)_3(CH_2C_6H_5) except for the absence of the resonance at δ 7.12 and 2.82.

Reaction of a Mixture of CpMo(CO)₃(CH₃) and (CH₃C₅H₄)Mo(C-O)₃(CD₃) with CpMo(CO)₃H. A 22-mg (0.089-mmol) sample of CpMo(CO)₃H, 24 mg (0.092 mmol) of CpMo(CO)₃(CH₃), and 24 mg (0.086 mmol) of (CH₃C₅H₄)Mo(CO)₃(CD₃) were weighed into an NMR tube, and 0.38 mL of THF- d_8 was introduced on a vacuum line. The tube was sealed and heated to 50 °C, and NMR spectra were recorded over the next 12 h. A total of 48% of the CpMo(CO)₃(CH₃) was consumed vs. 41% of the (CH₃C₅H₄)Mo(CO)₃(CD₃). No (CH₃C₅H₄)Mo(CO)₃(CC)₃ was observed.

A similar experiment with $R = CH_2C_6H_5$ and $CD_2C_6D_5$ also showed no crossover after 72 h, only benzaldehyde (62%, δ 2.89 and 9.56) and toluene (25%; ~2.29) by NMR. Extended heating (192 h) of the benzyl compounds in the absence of hydride showed traces of the crossover product ($CH_3C_5H_4$)Mo(CO)₃($CH_2C_6H_5$) by NMR, a new - CH_2 - resonance appearing 12-Hz upfield from the CpMo(CO)₃($CH_2C_6H_5$) methylene resonance. A small amount of toluene was also formed.

Reaction of CpMo(CO)₃(CH₃) with CH₃COOH and CF₃COOH. A 25-mg (0.096-mmol) sample of CpMo(CO)₃(CH₃) was dissolved in 0.32 mL of THF- d_8 in an NMR tube fitted with a rubber septum. A 5.5- μ L sample of CH₃COOH (0.096 mmol) was introduced with a syringe and the solution heated to 50 °C for 24 h. No changes were observed by NMR. An identical reaction employing CF₃COOH in C₆D₆ showed the formation of CH₄; no aldehyde was observed.

Reaction of CpMo(CO)₂(PMe₃)(H) with CpMo(CO)₃(C₂H₅). A 11mg (0.037-mmol) sample of CpMo(CO)₂(PMe₃)(H) and 8 mg of CpMo(CO)₃(C₂H₅) (0.029 mmol) were sealed in an NMR tube along with 0.42 mL of THF- d_8 . Reaction at 25 °C showed the disappearance of CpMo(CO)₃(C₂H₅) and CpMo(CO)₂(PMe₃)(H) (cis/trans mixture, δ 5.1 (5 H, s), 1.50 (9 H, d, $J_{PH} = 9$ Hz), -6.00 (0.5 H, sharp singlet (cis)), -6.50 (br s, 0.5 H (trans))). Propionaldehyde was the only product observed by NMR (δ 9.68 (1 H, t), 2.38 (2 H, q of d), 1.04 (3 H, t)). The half-life of this reaction was ~100 min, in comparison with the value of ~170 min when CpMo(CO)₃H was employed at the concentration specified in the previously described experiment.

The Synthesis of (MeCp)Mo(CO)₃H (2b). The previously unknown

(MeCp)Mo(CO)₃H (**1b**, MeCp = η^{5} -CH₃C₃H₄) was prepared by the following adaptation of the standard method of synthesis of **2a**. A solution of 1.05 g (3.72 mmol) of Na [(MeCp)Mo(CO)₃] (prepared from NaMeCp and Mo(CO)₆ by the literature method^{2,11}) in 30 mL of THF was treated with 0.7 g (4 mmol) of *p*-toluenesulfonic acid as a THF solution in the glovebox. A copious precipitate formed immediately. After 15 min an IR spectrum of the solution indicated complete conversion of the anion to molybdenum hydride. The yellow solution was distilled at reduced pressure to yield **2b** as a pale yellow, thermally sensitive oil: bp 55–60 °C (0.01mmHg); IR (THF) ν_{CO} 2015 (s), 1930 (s) cm⁻¹; ¹H NMR (THF-*d*₈) δ –5.42 (s, 1 H), 2.12 (s, 3 H), 5.46 (AA'BB' quartets, $J_{AB} = 17$ Hz, $J_{AA'} = 2.1$ Hz, 4 H).

The Reactions of 2b with 6b, 2b with 6a, and 2a with 7b. In all cases the two starting materials were weighed into an NMR tube in the glovebox. Then on a vacuum line $THF-d_8$ was condensed into the tube, and it was sealed off under vacuum. The resulting solutions were heated in a temperature controlled water bath. The reaction progress was monitored by cooling the NMR tubes and recording the NMR spectrum at room temperature. Light was excluded from these solutions by wrapping the NMR tubes in foil. Analysis of the products was achieved by cracking the NMR tubes open in the drybox, removing the solvent, redissolving the resulting residue in CH₃CN, and analyzing by HPLC. High-pressure liquid chromatographic (HPLC) analysis was achieved by using a 1×25 cm Altex Ultrasphere-ODS reversed-phase column, eluting with 20% H₂O/CH₃CN saturated with argon. Injections of $20-50-\mu$ L completely eluted over a 35-min time period at a flow rate of $0.5 \ mL/min.$ Typical pressures at this flow rate were 400–600 psi. The separation achieved under these conditions is demonstrated in the chromatogram of an authentic mixture of 4a-c (prepared by irradiating a mixture of 4a and 4c) and 5a-c (prepared by heating a mixture of 4a and 4c under an N_2 purge⁴⁰) as shown in Figure 1.

(A) A solution of 19 mg (0.077 mmol) of 2a and 20 mg (0.073 mmol) of 7b in 0.4 mL of THF- d_8 was heated to 50 (±0.5) °C for 22 h (approximately 64% reaction) and then analyzed by HPLC. In addition to 7b and products arising from decomposition of 2a in acetonitrile solution,⁴¹ the dimers 4a (see text), 4b and 5b were observed.

(B) A solution of 18 mg (0.07 mmol) of **2b** and 20 mg (0.077 mmol) of **6b** in 0.4 mmol of THF- d_8 was heated to 50 (±0.5) °C for 22 h (approximately 64% reaction) and then analyzed by HPLC. In addition to unreacted **6b** and products from decomposition of **2b** in acetonitrile,⁴¹ significant amounts of the dimers **4b**, **4c**, and **5b** were observed.

(C) A solution of 22 mg (0.085 mmol) of **2b** and 27 mg (0.098 mmol) of **6a** in 0.58 mL of THF- d_8 was allowed to react at room temperature for 48 hours, at which point no unreacted **2b** could be observed by NMR. HPLC analysis gave the chromatogram in Figure 1b. In addition to unreacted **6a** the only other compounds present in significant amounts were the dimers **4b** and **5b**.

(D) A solution of 17 mg (0.065 mmol) of **2b** and 18 mg (0.069 mmol) of **6b** in 0.78 mL of THF- d_8 was heated to 100 °C for 15 h. HPLC analysis showed that all six dimers **4a**-c and **5a**-c were present in significant concentrations.

The products are labeled in these chromatograms. All known compounds were identified by coinjection of authentic samples.

Reaction of CpMo(CO)₃**H with C**₂**H**₄. A solution of 31 mg (0.126 mmol) of CpMo(CO)₃H in 0.4 mL of THF- d_8 was prepared in an NMR tube, 0.245 mmol of C₂H₄ condensed into the tube on a vacuum line, and the tube sealed. The tube was heated to 100 °C, and NMR spectra were recorded over the next 24 h. No propionaldehyde was observed; only resonances due to ethane (36%) and diethyl ketone (15%; δ 2.35 (4 H, q), 0.96 (6 H, t)) were present. The tube was broken open in air and the contents vacuum distilled (30 °C (10⁻² mm)) into a 77 K receiving vessel. One-microliter aliquots were examined by gas chromatography ($^1/_4$ in. × 10 ft 20% Carbowax 20 M/Chrom WAW), confirming the NMR product identification by coinjection with authentic samples.

Reaction of CpMo(CO)₃(CH₃) with Ethylene. A 35-mg (0.135-mmol) sample of CpMo(CO)₃(CH₃) was weighed into a medium-walled NMR tube attached to a ground-glass joint and 21.3 mL of C₂H₄ (25 °C (215 mm)) (0.245 mmol) condensed into the tube (77 K) on a vacuum line. A 0.35 mL sample of THF was also distilled in before sealing the tube. The solution was heated at 100 °C for 4 h over which time the NMR resonances of CpMo(CO)₃(CH₃) (δ 5.41, 0.36) were observed to diminish as resonances of CH₃COCH₂CH₃ (δ 2.37 (4 H, q, *J* = 7.2 Hz), 0.96 (6 H, s), 2.02 (3 H, s)) grew in (50% yield). No CH₄ was observed. The vas broken open and the contents vacuum distilled into a 77 K receiver. GC analysis of a 1-µL aliquot ($^{1}/_{4}$ in. × 10 ft 20% Carbowax

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20 M/Chrom WAW, 90 °C) showed a 55% yield of methyl ethyl ketone and a 5% yield of a component having a retention time equal to that of 1-buten-3-one

Reaction of CpMo(CO)₃(CH₃) with C₂H₄ in the Presence of 1-Buten-3-one. A 36-mg (0.138-mmol) sample of CpMo(CO)₃(CH₃) was weighed into an NMR tube fitted with a ground-glass joint and 2.5 μ L (ca 0.03 mmol) of 1-buten-3-one introduced with a syringe. The tube was quickly attached to a vacuum line, cooled to 77 K, and evacuated. Ethylene (0.25 mmol) and 0.42 mL of THF- d_8 were condensed in and the tube was sealed. The tube was heated to 100 °C, and NMR spectra were recorded over the next 18 h. In 1 h, 46% of the $CpMo(CO)_3(CH_3)$ (0.36 ppm) was consumed and a 25% yield of 2-butanone (δ 0.96 (3 H, t), 2.37 (4 H, q), 2.02 (3 H, s)) observed. A total of 80% of the 1butene-3-one had decomposed. In 6 h, the reaction was 95% complete and a 54% yield of 2-butanone was found. After 18 h all CpMo-(CO)₃(CH₃) had been consumed and a 58% yield of 2-butanone was measured. The tube was broken open, and the volatile contents were

vacuum distilled and analyzed by GC (10 ft \times ¹/₄ in. 20% Carbowax 20M/Chrom WAW, 90 °C). A 55% yield of --butanone was confirmed relative to added internal standard (pentane). Only traces (<5%) of 2-buten-3-one were present.

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Preparation and HeI Photoelectron Spectra of the Halogen Thiocyanates, XSCN (X = Cl and Br)

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Abstract: The unstable chlorine and bromine thiocyanate molecules have been generated in the gas phase by reaction of AgSCN (solid) or (SCN)₂ (gas) with molecular chlorine or bromine, respectively. ISCN does not appear to be formed by this route. The structures are established as nonlinear X-S-C=N molecules, and the observed HeI photoelectron spectra are assigned on this basis with the assistance of minimal basis ab initio calculations. The electronic structures of these molecules lie between those of SX_2 and $S(CN)_2$; the chemical behavior suggests an analogy with the interhalogen compounds.

Simple thiocyanates are rather intriguing compounds, since the SCN group is ambidentate, bonding at either S or N, and forming R-S-C=N (thiocyanate) or R-N=C=S (isothiocyanate) type molecules.^{1,2} The parent acid exists as HNCS in the gas phase,³ whereas both methyl derivatives, CH₃NCS and CH₃SCN, can be isolated.⁴ The halogen thiocyanates, on the other hand, are known only as unstable intermediates in solution, chemical and spectroscopic studies indicating an XSCN rather than an XNCS structure.⁵⁻⁸ This is in contrast to the substituted oxygen analogues, XNCO (X = CN, Cl, Br, and I), which bond only through nitrogen, and which we have investigated previously by ultraviolet photoelectron spectroscopy (UPS).9,10

In this work we present the preparation, detection, and ultraviolet photoelectron spectra of the XSCN molecules (X = Cl and Br). Since these unstable molecules are quite novel in the gas phase, there are several interesting features relevant to such a study. A priori it is uncertain whether the halogen is bonded

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through S or N in the gas-phase molecules, and this we shall attempt to establish. Second, we have previously studied the photoelectron spectrum of the archetypal pseudohalogen, (SC- N_{2} .¹¹ This molecule is the starting point for formation of the halogen thiocyanates, and so we may view all of these molecules as interhalogen compounds with the SCN group possessing an electronegativity somewhere between Br and I. Equilibria between (SCN)₂ and X₂ (compare, e.g., BrCl, ICl, IBr, etc.) may thus be anticipated. Third, as found with the halogen azides and isocyanates,¹⁰ it is of some interest to establish the nature of the interaction between the off-axis substituent and the pseudohalide grouping. By analogy with the structures of the XN_3 and XNCOmolecules we expect a linear, or quasilinear, SCN group. To this end, we have also conducted some ab initio calculations in order to evaluate the electronic and geometric structures. Finally, the XSCN molecules provide the intermediate stage between the $S(CN)_2^{12}$ and $SX_2(X = Cl^{13,14} \text{ and } Br^{15,16})$ molecules previously studied by UPS, and thus an investigation of the XSCN molecules provides an assessment of how the orbital energies change as X is replaced by CN.

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