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### Author

Jones, William D.

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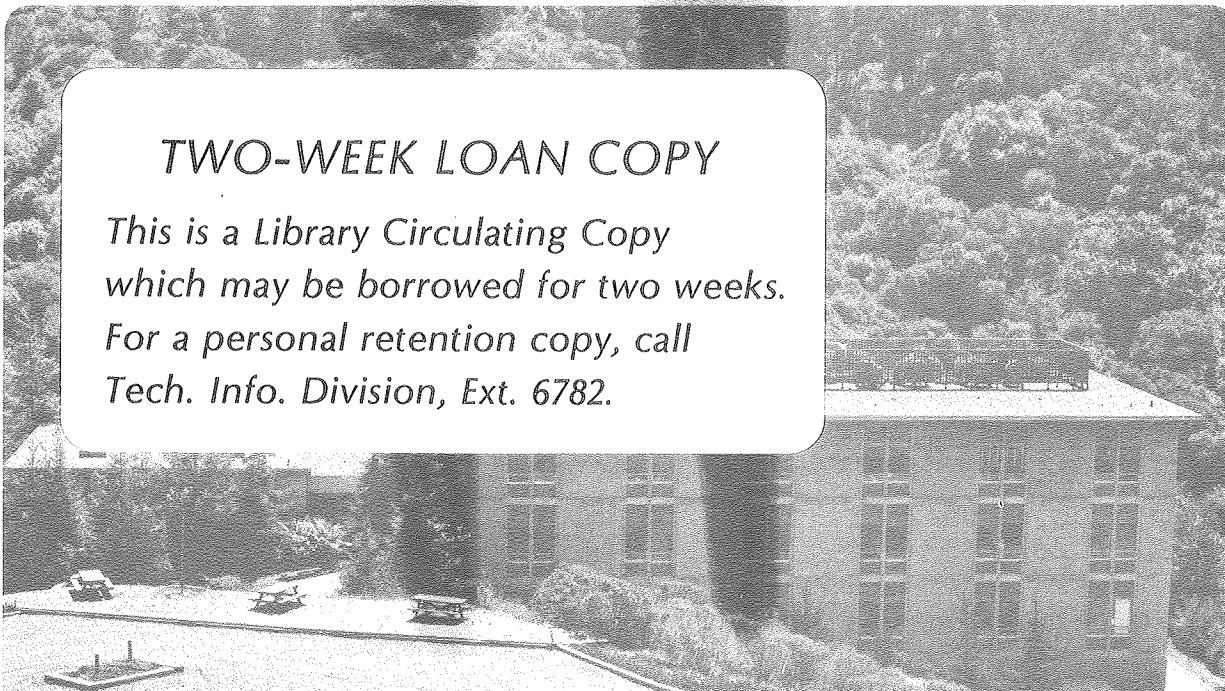
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TRANSITION METAL HYDRIDES WITH TRANSITION METAL  
CARBONYLS AND ALKYL

William D. Jones, John M. Huggins, and  
Robert G. Bergman

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COMPARATIVE REACTIVITIES OF TWO ISOELECTRONIC TRANSITION  
METAL HYDRIDES WITH TRANSITION METAL CARBONYLS AND ALKYL

William D. Jones, John M. Huggins, and Robert G. Bergman

Contribution from the Department of Chemistry, University of  
California, and the Materials and Molecular Research Division,  
Lawrence Berkeley Laboratory, Berkeley, CA 94720

Abstract

The two isoelectronic hydrides  $\text{PPN}^+ \text{CpV}(\text{CO})_3\text{H}^-$  (1) and  $\text{CpMo}(\text{CO})_3\text{H}$  (2) react with a variety of metal carbonyls and alkyls. Treatment of  $\text{Fe}(\text{CO})_5$ ,  $\text{Cr}(\text{CO})_6$ ,  $(\text{CH}_3\text{C}_5\text{H}_4)\text{V}(\text{CO})_4$ ,  $\text{CH}_3\text{Re}(\text{CO})_5$ , and  $(\text{CH}_3\text{CO})\text{Re}(\text{CO})_5$  with 1 produces  $\text{HFe}(\text{CO})_4^-$ ,  $\text{HCr}(\text{CO})_5^-$ ,  $(\text{CH}_3\text{C}_5\text{H}_4)\text{V}(\text{CO})_3\text{H}^-$ ,  $(\text{H})(\text{CH}_3)\text{Re}(\text{CO})_4^-$ , and  $(\text{H})(\text{CH}_3\text{CO})\text{Re}(\text{CO})_4^-$ , respectively, and  $\text{CpV}(\text{CO})_4$  (3). 1 also catalyzes ligand substitution reactions in 3 and  $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{COCH}_3)$ . In comparison 2 reacts only with  $\text{CH}_3\text{Mn}(\text{CO})_5$  and  $\text{CpMo}(\text{CO})_3\text{R}$  ( $\text{R}=\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{CH}_2\text{C}_6\text{H}_5$ ) producing aldehydes and the dimers  $[\text{CpMo}(\text{CO})_3]_2$  (4a) and  $[\text{CpMo}(\text{CO})_2]_2$  (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.

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## Introduction

Our interest in employing organotransition metal compounds in the formation of new carbon-carbon and carbon-hydrogen bonds led us to investigate the reactivity of two isoelectronic transition metal hydrides with metal carbonyl, alkyl, and acyl derivatives. The two hydrides chosen for study were  $\text{PPN}^+ [\text{CpV}(\text{CO})_3\text{H}]^-$ , **1**, the preparation of which we recently reported,<sup>1</sup> and the well known  $\text{CpMo}(\text{CO})_3\text{H}$ , (**2**), first prepared by Piper and Wilkinson in 1956.<sup>2</sup> A comparison of the reactivity patterns of these two hydrides has shown sharp differences in both the types of products observed as well as in the fundamental mechanisms of their reactions.

Examples of the reduction of metal carbonyls with main group hydrides have been reported by other workers. Gladysz has reported<sup>3,4</sup> the triethylborohydride reduction of  $\text{M}_2(\text{CO})_{10}$  ( $\text{M}_2 = \text{Mn}_2, \text{Re}_2, \text{ReMn}$ ),  $\text{CpMn}(\text{CO})_2(\text{NO})^+$ ,  $\text{Re}(\text{CO})_5(\text{PPh}_3)^+$ ,  $\text{Mn}(\text{CO})_4(\text{PPh}_3)_2^+$ ,  $\text{Ir}(\text{CO})_3(\text{PPh}_3)_2^+$ , and  $\text{CpMo}(\text{CO})_3(\text{PPh}_3)^+$ . 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 reported<sup>5</sup> the reduction of several metal carbonyls and of  $\text{CpRe}(\text{CO})_2(\text{NO})^+$  with triisopropoxyborohydride to obtain  $\text{CpRe}(\text{CO})(\text{NO})(\text{CHO})$  and with triethylborohydride to obtain  $\text{CpRe}(\text{NO})(\text{CHO})_2^-$ , in which one and two new carbon-hydrogen bonds are formed, respectively.

In a few cases it has been demonstrated that transition metal hydrides can act as apparent reducing agents towards other transition metal species. The reduction of  $\text{Cp}_2\text{Zr}(\text{CH}_3)_2$  with  $\text{CpMo}(\text{CO})_3\text{H}$  has been reported<sup>6</sup> to form methane and the mixed metal dimer,  $\text{Cp}_2(\text{CH}_3)\text{Zr}-\text{Mo}(\text{CO})_3\text{Cp}$ . Labinger has recently proposed<sup>7</sup> that reduction of  $\text{Fe}(\text{CO})_5$  with  $\text{Cp}_2\text{NbH}_3$  proceeds through an intermediate similar to  $(\text{CO})_4\text{Fe}(\text{CHO})^-$ . Also, Caulton has found<sup>8</sup> that both  $\text{Cp}_2\text{ReH}$  and  $\text{Cp}_2\text{MH}_2$  ( $\text{M} = \text{Mo}, \text{W}$ ) reduce bis-

(cyclopentadienyl)acetylcarbonylzirconium(IV), forming derivatives in which the acetyl functionality has been formally reduced to an alkoxy group. In the hydroformylation of olefins,  $\text{HCo}(\text{CO})_4$  has been proposed<sup>9</sup> to be the species responsible for the reduction of an acyl cobalt complex in the formation of aldehyde.

We report here the comparison of two isoelectronic (but perhaps not isostructural<sup>10</sup>) metal hydrides with transition metal carbonyls, alkyls, and acyls. The major difference found is that **1** can act as an electron transfer agent due to its reduced nature whereas **2** acts as a hydride-ligand, coordinating to the vacant site of an unsaturated metal species.<sup>11</sup>

### Results and Discussion

**A. Reactions of  $\text{PPN}^+ \text{CpV}(\text{CO})_3\text{H}^-$  with metal carbonyls.** In 1958, Fischer reported<sup>12</sup> the reduction of  $\text{CpV}(\text{CO})_4$  (**3**), with sodium metal in liquid ammonia or with sodium amalgam in THF, to give  $\text{Na}^+_2[\text{CpV}(\text{CO})_3]^{2-}$ . More recently, we found that this dianion may be protonated with water and the sodium ion replaced by bistriphenylphosphiniminium ion<sup>1</sup> (Scheme 1). This yellow, microcrystalline hydride is characterized by two <sup>1</sup>H-NMR resonances ( $\delta$  4.60 ppm, 5H; -6.72 ppm, 1H) and two infrared carbonyl stretching frequencies (1887, 1775  $\text{cm}^{-1}$ ) in THF solution.

Reactions of **1** with several metal carbonyls are summarized in Scheme 1. When a 0.14M d<sub>8</sub>-THF solution of **1** is treated with an equivalent of  $\text{Fe}(\text{CO})_5$  at room temperature, new <sup>1</sup>H-NMR resonances are observed at  $\delta$  5.20 ppm and -8.80 ppm, characteristic of **3** and  $\text{PPN}^+\text{HFe}(\text{CO})_4^-$ ,<sup>13</sup> respectively. At this concentration, red crystals of analytically pure  $\text{PPN}^+\text{HFe}(\text{CO})_4^-$  precipitate and can be isolated by decanting the solvent and washing with hexane. The reaction of **1** with  $\text{Cr}(\text{CO})_6$  (0.15 M each) at room temperature produced a solution with <sup>1</sup>H-NMR resonances at  $\delta$  5.20 (characteristic of **3**),  $\delta$  -6.88 (s,

1H, 51% based on 1), and  $\delta$ -19.4 (s, 1H, 15% based on 1), the latter two resonances being assigned<sup>14</sup> to  $\text{HCr}(\text{CO})_5^-$  and  $\text{H}[\text{Cr}(\text{CO})_5]_2^-$ , respectively. An IR spectrum of the solution showed the carbonyl stretching frequencies of  $\text{CpV}(\text{CO})_4$  (2008, 1915  $\text{cm}^{-1}$ ).

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  $(\text{CH}_3\text{C}_5\text{H}_4)\text{V}(\text{CO})_4$  in  $d_8$ -THF is observed by NMR to equilibrate with 3 and  $(\text{CH}_3\text{C}_5\text{H}_4)\text{V}(\text{CO})_3\text{H}^-$  at room temperature over a 12 hour period.

**B. Reaction of  $\text{PPN}^+\text{V}(\text{CO})_3\text{H}^-$  with Metal Alkyls and Acyls.** No reaction is observed between 1 and  $\text{CpFe}(\text{CO})_2(\text{CH}_3)$  (0.10M each) at room temperature in THF solution. However,  $\text{CH}_3\text{Mn}(\text{CO})_5$  reacts instantaneously with 1 (0.17M 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, the reaction of 1 with  $\text{CH}_3\text{Re}(\text{CO})_5$  (0.09M each) in THF was examined 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  $(\text{CO})_4\text{Re}(\text{CH}_3)(\text{H})^-$  on the basis of its  $^1\text{H-NMR}$  ( $\delta$  -0.65 ppm d,  $J = 3$  hz, 3H; -5.56 ppm, broad, 1H) spectrum. Continued thermolysis (50°C) of the solution in the presence of CO produced methane and  $\text{Re}(\text{CO})_5^-$ , providing additional support for the identity of the initially formed complex (Scheme 2). Upon reaction of 1 with  $(\text{CH}_3\text{CO})\text{Re}(\text{CO})_5$  (0.12M each) in  $d_8$ -THF,  $^1\text{H-NMR}$  resonances attributable to 3 ( $\delta$  5.20 ppm) and  $\text{PPN}^+(\text{CO})_4\text{Re}(\text{COCH}_3)(\text{H})^-$  ( $\delta$  2.20, s, 3H; -4.38, br, 1H)<sup>15</sup> appeared (90% yield)

after heating at 50°C for two hours.

Surprisingly, an initial attempt to repeat this reaction using freshly prepared **1** and  $(\text{CH}_3\text{CO})\text{Re}(\text{CO})_5$  under apparently identical conditions showed mostly unreacted starting material and only 5% product by NMR after 2 hours. 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 Na metal caused the reaction to go to completion after 1 hour at 50°C.  $\text{Na}_2\text{CpV}(\text{CO})_3$  (20 mole %) was found to be a most effective catalyst, causing an instantaneous reaction at -20°C. Upon re-examining the reactions of  $\text{Fe}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_6$  with **1**, hydride transfer was observed to occur 3-4 times more rapidly when a trace of  $\text{Na}_2\text{CpV}(\text{CO})_3$  was added to the solution.

Reaction of **1** with  $\text{CpMo}(\text{CO})_3(\text{C}_2\text{H}_5)$  in  $d_8$ -THF at room temperature produced a 30% yield of propionaldehyde (NMR:  $\delta$  9.68 ppm, t,  $J = 1.7$  Hz, 1H; 2.38 ppm, q of d,  $J = 7.3, 1.7$  Hz, 2H;  $\delta$  1.04 ppm, t,  $J = 7.3$  Hz, 3H). 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  $\text{PPh}_3$  (0.23M) and  $\text{CpV}(\text{CO})_4$  (0.25M) was observed in  $d_8$ -THF solution in the absence of light. However, upon introducing 40 mole percent of **1**, a smooth substitution reaction was evident by  $^1\text{H}$ -NMR, producing  $\text{CpV}(\text{CO})_3(\text{PPh}_3)^{16}$  ( $\delta$  4.73 ppm, d,  $J_{\text{ph}} = 1.5$  Hz) as **3** was consumed. No change in the size or shape of the Cp resonance of **1** ( $\delta$  4.60 ppm) was found. Substitution of CO by  $\text{PMe}_3$  is also catalyzed by **1** under similar conditions, producing a quantitative yield (NMR) of  $\text{CpV}(\text{CO})_3(\text{PMe}_3)^{16}$  in 15 min ( $\delta$  4.90 ppm, 5H, d,  $J_{\text{PH}} = 1.9$  Hz; 1.44 ppm, 9H, d,  $J_{\text{PH}} = 8.7$  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.  $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{COCH}_3)$  reacts with neither **1** nor CO (1 atm.) at  $50^\circ\text{C}$  in THF solution. However, addition of **1** to a solution of  $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{COCH}_3)$  under a CO atmosphere induces exchange of CO for  $\text{PPh}_3$  at  $50^\circ$ , producing signals attributable to  $\text{PPh}_3$  and  $\text{CpFe}(\text{CO})_2(\text{COCH}_3)^{17}$  (NMR:  $\delta 4.93$  ppm, s, 5H; 2.50 ppm, s, 3H) as the resonances of  $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{COCH}_3)$  diminish.

**D. Mechanism of Reaction of  $\text{PPN}^+\text{CpV}(\text{CO})_3\text{H}^-$  with Metal Carbonyls.** All of the observed reactions can be explained in terms of the electron transfer process shown in Scheme 3. 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 hydride 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 " $\text{CpV}(\text{CO})_3$ " fragment, which then captures a ligand from solution. The effect of added strong reducing agent (Scheme 2) supports the electron-transfer hypothesis. In this case (Scheme 4), it is our guess that reducing agent X initiates a chain in which further reduction steps are induced by  $\text{CpV}(\text{CO})_3^{\cdot-}$ .

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 3), 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 3 invokes substitution in 17-electron species  $\text{ML}_{n-1}^{\cdot-}$  (Scheme 5), as suggested by Brown for other radical-induced substitutions.<sup>18</sup> 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  $\text{CpV(CO)}_3\text{H}$  regenerates **1** (eq (5-3)) and forms a 16 electron compound that then captures a ligand from solution, forming the substituted product (eq (5-4,5-5)).

However, the experimental evidence speaks against this mechanism due to the required intermediacy of the 16 electron species in equations (5-2) and (5-3). In the case of phosphine substitution in  $\text{CpV(CO)}_4$ , the corresponding intermediate,  $\text{CpV(CO)}_2(\text{PR}_3)$ , should coordinate a second ligand from solution, forming the known<sup>19</sup>  $\text{CpV(CO)}_2(\text{PR}_3)_2$  (eq. (5-4)). However, no disubstituted product is observed (as little as 5% could be detected). Also, in the vanadium catalyzed substitution of phosphine for CO in  $\text{CpFe(CO)(PPh}_3\text{)(COCH}_3\text{)}$ , the corresponding 16 electron intermediate should rapidly decarbonylate to give  $\text{CpFe(CO)}_2(\text{CH}_3)$ , yet none of this latter product is observed. Insertion of CO into the iron-methyl bond in  $\text{CpFe(CO)}_2(\text{CH}_3)$  has been reported<sup>17</sup> to occur at 125°C and 200 psi, suggesting that deinsertion of CO in the intermediate  $\text{CpFe(CO)(COCH}_3\text{)}$  species is facile. However, under our catalytic conditions,  $\text{CpFe(CO)}_2(\text{COCH}_3)$  is formed at 50°C and 1 atm. Both of the above observations tend to argue against the substitution mechanism outlined in Scheme 5.

#### E. Reactions of $\text{CpMo(CO)}_3\text{H}$ with Transition Metal Carbonyls and Alkyls.

We have also examined the reduction capability of the neutral hydride  $\text{CpMo(CO)}_3\text{H}$ , **2**, towards transition metal alkyls and carbonyls. No reaction was observed between **2** (0.2M) and either  $\text{Fe(CO)}_5$  (0.3M) or  $\text{Cr(CO)}_6$  (0.2M) in  $d_8$ -THF solution after 24 hours at 70°C. With the latter carbonyl, thermal decomposition of **2** produced the known<sup>20</sup> dimer  $[\text{CpMo(CO)}_3]_2$ , **4a**, (and presumably hydrogen gas) as previously reported.<sup>2</sup> At no time were any formyl

( $\delta$  10 to 20 ppm) or hydride ( $\delta$  0 to -20 ppm) resonances observed. With  $\text{Fe}(\text{CO})_5$ , metal was observed to form on the walls of the vessel.

Reaction of **2** with  $(\text{CH}_3)\text{Mn}(\text{CO})_5$  (0.23M each) in  $d_8$ -THF was complete after a few hours at room temperature. NMR analysis indicated the formation of dimers **4a** ( $\delta$  5.40 ppm),  $\text{CpMo}(\text{CO})_3\text{-Mn}(\text{CO})_5$  ( $\delta$  5.49 ppm),<sup>21</sup>  $[\text{CpMo}(\text{CO})_2]_2$ , (**5a**, 5.27 ppm),<sup>22</sup> and presumably  $\text{Mn}_2(\text{CO})_{10}$ . Acetaldehyde was also detected by NMR ( $\delta$  2.07, d,  $J = 3$  Hz, 3H,  $\delta$  9.66 ppm, q,  $J = 3$  Hz, 1H) (Scheme 6). The yield of aldehyde was observed to increase to 70%, and then slowly decrease to 50% with longer reaction times. Broadening of the  $^1\text{H}$ -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 analogs, and recalling the successful application of this strategy to the reactions of **1** with  $(\text{CH}_3)\text{M}(\text{CO})_5$  ( $\text{M}=\text{Mn}, \text{Re}$ ), the reduction of  $(\text{CH}_3)\text{Re}(\text{CO})_5$  by **2** (0.22M each) was examined. However, no reaction was observed after several days at room temperature.

The most successful reduction employing **2** was found with the compounds  $\text{CpMo}(\text{CO})_3\text{R}$  (**6a**;  $\text{R}=\text{C}_2\text{H}_5$ ; **6b**,  $\text{R}=\text{CH}_3$ ; **6c**,  $\text{R}=\text{CH}_2\text{C}_6\text{H}_5$ ) (Scheme 6). 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 metal-metal triple bond (**5a**). A  $d_8$ -THF solution of **2** and **6a** (0.12M in each reactant), showed a smooth conversion into propionaldehyde and the dimers  $[\text{CpMo}(\text{CO})_3]_2$  (**4a**) and  $[\text{CpMo}(\text{CO})_2]_2$  (**5a**) (Figs. 1,2) 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 (~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  $d_8$ -THF solution, the quantities of each compound being determined by  $^1\text{H-NMR}$  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  $\text{CpMo}(\text{CO})_3\text{H}$  Reactions.** The drastic change in the reactivity of **2** compared with **1** and the change in the type of products (aldehydes vs. alkanes) suggests that these hydrides react by different mechanisms. The demonstrated propensity of  $\text{RMn}(\text{CO})_5$  and  $\text{CpMo}(\text{CO})_3\text{R}$  to form acyl derivatives<sup>23,24</sup> and the observation of aldehyde products in their reactions with **2** strongly implicates metal acyl intermediates. One possible mechanism, shown in Scheme 7, involves CO insertion followed by homolysis of the molybdenum-acyl bond, the aldehyde being formed in a subsequent step involving hydrogen 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 coworkers for the production of toluene from  $\text{HMn}(\text{CO})_5$  and  $(\text{CO})_5\text{Mn}(\text{CH}_2\text{C}_6\text{H}_5)$ .<sup>25</sup> Alternatively, benzyl radicals could be formed by decarbonylation of the  $\text{PhCH}_2\text{CO}$  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 (eqs. (7-1) and (7-2)) must be rapid and reversible, with hydrogen abstraction from **2** being rate determining, if the mechanism in Scheme 7 is operable. This prediction was tested by heating an equimolar mixture of **6b** and  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3(\text{CD}_3)$  in  $d_8$ -THF to  $50^\circ\text{C}$ . None of the expected crossover product,  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3(\text{CH}_3)$ , (**7b**), was observed by  $^1\text{H}$ -NMR, where as little as 1% could have been detected (Scheme 8)). 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 7.

However, the reaction of the benzyl compound **6c** with **2** is somewhat more complicated. Upon heating a mixture of **6c** and  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3(\text{CD}_2\text{C}_6\text{D}_5)$  at  $50^\circ\text{C}$  in  $d_8$ -THF, a small amount of  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3(\text{CH}_2\text{C}_6\text{H}_5)$ , **7c**, was observed to grow in by  $^1\text{H}$ -NMR. This observation, and the formation of toluene upon reaction with **2**, can be rationalized by assuming that the benzyl radical is stable enough<sup>26</sup> that in this case molybdenum-carbon bond cleavage is competitive with CO-insertion. Consequently, some crossover is observed in the absence of **2**, whereas some toluene is formed 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 9). Evidence for the formation of this intermediate in carbonylation and phosphine-substitution reactions has been available for some time.<sup>27</sup> Unsaturated complex **8** is then trapped by **2** in a rate determining step; subsequent reactions producing aldehyde, **4a**, and **5a** occur rapidly.

The means by which hydrogen is transferred from **2** (i.e., the nature of intermediate(s) **9**) is of some interest.<sup>28</sup> Several possible intermediates are shown in Scheme 10. Because **2** has been found to have a pKa of ~5, one likely path involves **2** acting as an acid, forming  $\text{CpMo(CO)}_3^-$  and a cationic acyl hydride (**9a**) that reductively eliminates aldehyde<sup>29</sup>. 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  $\text{CpMo(CO)}_3^-$  intermediate with a 10-fold excess of  $\text{CH}_3\text{I}$  was unsuccessful (no **6b** was formed). In addition, if **2** is merely acting as an acid in these reactions, then other acids of comparable pKa should also react with **6** to produce aldehydes. However, when **6b** is treated with acetic acid,<sup>30</sup> no reaction occurs. With the stronger acid  $\text{CF}_3\text{COOH}$  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  $\text{PMe}_3$  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,  $\text{CpMo(CO)}_2(\text{PMe}_3)\text{H}$  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  $\text{CpMo(CO)}_3$  and  $\text{CpMo(CO)}_2$ , 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  $\text{CpMo(CO)}_3$  radicals, and two  $\text{CpMo(CO)}_2$  radicals, as well as dimers formed by combination of the two  $\text{CpMo(CO)}_n$  fragments which were present in the initial hydride-acyl solvent

cage.

To test this alternative, the reaction of  $\text{CpMo}(\text{CO})_3\text{H}$  (**2a**) with  $\text{MeCp}(\text{CO})_3\text{CH}_3$  (**7b**) was run, 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 11. This problem has been dealt with earlier using mass spectral techniques;<sup>40</sup> we have found that these materials can be resolved using HPLC on reversed-phase columns (see Fig. 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. A cleaner experiment was achieved by treating  $\text{MeCpMo}(\text{CO})_3\text{H}$  (**2b**) with the more reactive ethylmolybdenum complex  $\text{CpMo}(\text{CO})_3\text{C}_2\text{H}_5$  (**6a**) at room temperature, and employing a deficiency of hydride. As shown in Fig. 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 11; 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  $[\text{CpMo}(\text{CO})_3]^+$  and an anionic hydridoacyl intermediate (**9c** in

Scheme 10). Reductive elimination gives aldehyde and  $[\text{CpMo}(\text{CO})_2]^-$ , which recombines with  $[\text{CpMo}(\text{CO})_3]^+$ . This seems to be the least likely mechanism, due to the generally poor hydride-donating ability of  $\text{Cp}(\text{CO})_3\text{MoH}$  (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  $[\text{Cp}(\text{CO})_3\text{Mo}]^+$  is provided by the fact that running the hydride/alkyl reaction in the presence of 1M LiCl gives no  $\text{Cp}(\text{CO})_3\text{MoCl}$ .<sup>31</sup>

Finally there exists a "concerted" mechanism in which 8 and 2 form a bridging hydride (9d; Scheme 10), 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 oxidative 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<sup>32</sup> 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 1 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<sup>32</sup>; 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** (0.32M) with ethylene (0.61M) did in fact lead to a reaction mixture which exhibited typical ethyl resonances in the proton NMR spectrum, as reported earlier<sup>32</sup>. 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 hrs 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 ethylmolybdenum complex **6a** with ethylene at 100° gave an approximately 10% yield of diethyl ketone. In addition, the corresponding methylmolybdenum complex **6b** reacted with ethylene at 100° to produce methyl ethyl ketone in 50% yield. We conclude from these observations that complex **6b** is formed from **2** and ethylene at 100°, 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<sub>2</sub>D<sub>4</sub> gave completely ethyl-deuterated 2-butanone. 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 to 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° 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 12. 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 10 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, pi-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<sup>33</sup>; ethylene has also been shown to insert in metal acyls formed from alkyltetracarbonylferrates<sup>34</sup>).  $\beta$ -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

Our investigations of the two isoelectronic transition metal hydrides 1 and 2 show drastic differences in their reactivities with metal carbonyls and alkyls. 1 initiates reaction by electron transfer, the ultimate mode of reaction being exchange of hydride in 1 for CO in the metal substrate. When hydride transfer is either thermodynamically or kinetically unfavorable, catalytic ligand substitution in the substrate is observed. On the other hand,  $\text{CpMo}(\text{CO})_3\text{H}$  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  $\text{H}_2$  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  $\text{HCo}(\text{CO})_4$ , was considered many years ago<sup>35</sup>, but it was not until recently<sup>36b,c</sup> that conclusive experimental evidence for the operation of this step in hydroformylation was obtained.<sup>9,36</sup> 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

All solvents were distilled from Na/benzophenone/tetraglyme prior to use and all manipulations performed either in a Vacuum Atmospheres Corporation inert atmosphere box or on a high vacuum line.  $\text{CpV}(\text{CO})_4$ ,  $\text{Na}(\text{diglyme})^+ \text{V}(\text{CO})_6^-$ ,  $[\text{CpMo}(\text{CO})_3]_2$ ,  $[(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3]_2$ ,  $\text{Mn}_2(\text{CO})_{10}$ ,  $\text{Re}_2(\text{CO})_{10}$ ,  $\text{Cr}(\text{CO})_6$ ,  $\text{Fe}(\text{CO})_5$  and  $[\text{CpFe}(\text{CO})_2]_2$  were obtained from the Alfa Corporation or Strem Chemical Company.  $\text{PPN}^+ \text{CpV}(\text{CO})_3\text{H}^-$ ,<sup>1</sup>  $\text{CH}_3\text{Mn}(\text{CO})_5$ ,<sup>37</sup>  $\text{CH}_3\text{Re}(\text{CO})_5$ ,<sup>38</sup> and  $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{COCH}_3)$ <sup>39</sup> were prepared as previously described.  $\text{CpMo}(\text{CO})_3\text{H}$ ,  $\text{CoMo}(\text{CO})_3\text{R}$  ( $\text{R}=\text{CH}_3, \text{C}_2\text{H}_5$ ) and  $\text{CpFe}(\text{CO})_2^-(\text{CH}_3)$  were prepared by the method of Piper and Wilkinson.<sup>2</sup> The methyl-Cp derivatives were prepared analogously from the corresponding methyl-Cp dimer. Deuterated derivatives were prepared using  $\text{CD}_3\text{I}$  or  $\text{C}_6\text{D}_5\text{CD}_2\text{Br}$ .

<sup>1</sup>H-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 PE-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 2mm pathlength 254 nm wavelength kit. Separations were achieved using a 1 x 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  $(\text{CH}_3\text{C}_5\text{H}_4)\text{V}(\text{CO})_4$ .** 2.88g (0.125 mol) sodium and 10g methylcyclopentadiene monomer (0.125 mmol) were dissolved in 50 ml dimethoxyethane (DME). After stirring overnight, the solvent was removed (30°C, 10<sup>-2</sup> mm) and the remaining solid recrystallized from THF/hexane at

-30°C. 1.3g (11.8 mmol) of solid  $\text{Na}^+(\text{CH}_3\text{C}_5\text{H}_4)^-$  was dissolved in 30 ml THF and 3.55g (13.4 mmol)  $\text{HgCl}_2$  added. A solution of 5g (11.8 mmol)  $\text{Na}(\text{DME})_2^+ \text{V}(\text{CO})_6^-$  in 10 ml THF was added slowly as the solution became red-orange. After 1 hr the THF was removed (35°C,  $10^{-2}$  mm) and the remaining material was taken up in 50 ml  $\text{H}_2\text{O}$  plus 50 ml petroleum ether. The  $\text{H}_2\text{O}$  layer was extracted with petroleum ether (2 x 25 ml) and the combined ether layers washed with water (2 x 50 ml) and dried ( $\text{MgSO}_4$ ). The petroleum ether was removed (25°, 20 mm) and the remaining oil chromatographed on a silica gel column (2 x 15 cm) using petroleum ether as eluent. The yellow fraction was collected, the solvent removed (25°C, 20 mm), and the remaining solid sublimed (50°C,  $10^{-2}$  mm) to yield 200 mg (15%)  $(\text{CH}_3\text{C}_5\text{H}_4)\text{V}(\text{CO})_4$  NMR ( $d_8$ -THF):  $\delta$ 5.16 ppm, 2H; 5.05 ppm, 2H; 2.01 ppm, 3H. Mass spectrum: m/e = 242, 214, 186, 158, 130, 51. Anal.: Calcd. for  $\text{C}_{10}\text{H}_7\text{O}_4\text{V}$ : 49.61% C, 2.91% H; Found: 49.38% C, 2.97% H.

**Reaction of  $\text{PPN}^+ \text{CpV}(\text{CO})_3\text{H}^-$  with  $(\text{CH}_3\text{C}_5\text{H}_4)\text{V}(\text{CO})_4$ .** 31 mg (0.054 mmol)  $(\text{CH}_3\text{C}_5\text{H}_4)\text{V}(\text{CO})_4$  and 40 mg (0.054 mmol)  $\text{PPN}^+\text{CpV}(\text{CO})_3\text{H}^-$  were dissolved in 0.47 ml  $d_8$ -THF in an NMR tube. NMR spectra recorded over the next 12 hrs showed the disappearance of  $(\text{CH}_3\text{C}_5\text{H}_4)\text{V}(\text{CO})_4$  and  $\text{CpV}(\text{CO})_3\text{H}^-$  ( $\delta$ 4.60 ppm) and the appearance of  $\text{CpV}(\text{CO})_4$  ( $\delta$ 5.20 ppm) and  $(\text{CH}_3\text{C}_5\text{H}_4)\text{V}(\text{CO})_3\text{H}^-$  ( $\delta$ 4.58 ppm, 2H; 4.42 ppm, 2H; 1.86 ppm, 3H).

**Reaction of  $\text{CpV}(\text{CO})_3\text{H}^-$  with  $\text{Fe}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_6$ .** A similar reaction of 51 mg (0.069 mmol)  $\text{PPN}^+\text{CpV}(\text{CO})_3\text{H}^-$  with 9.3  $\mu\text{l}$  (0.069 mmol)  $\text{Fe}(\text{CO})_5$  in 0.5 ml  $d_8$ -THF produced isolable crystals<sup>13</sup> of  $\text{PPN}^+\text{HFe}(\text{CO})_4^-$  (25 mg, 47%) upon standing for 12 hours. Anal.: Calcd. for  $\text{C}_{40}\text{H}_{31}\text{P}_2\text{NFeO}_4$ : 67.91% C, 4.42% H, 1.98% N; found: 67.51% C, 4.58% H, 1.94% N. No  $(\text{CHO})\text{Fe}(\text{CO})_4^-$  was observed at any time during the reaction.  $\text{Cr}(\text{CO})_6$  (47 mg, 0.21 mmol) reacted with  $\text{PPN}^+\text{CpV}(\text{CO})_3\text{H}^-$  to give a solution containing  $\text{CpV}(\text{CO})_4$ ,  $\text{HCr}(\text{CO})_5^-$  and

$\text{H}[\text{Cr}(\text{CO})_5]_2^-$  (see text), assigned on the basis of data supplied<sup>14</sup> by Professor M.Y. Darensbourg.

**Reaction of  $\text{PPN}^+ \text{CpV}(\text{CO})_3\text{H}^-$  with  $\text{CH}_3\text{Mn}(\text{CO})_5$  and  $\text{CH}_3\text{Re}(\text{CO})_5$ .** A  $d_8$ -THF solution (0.5 ml) of 61 mg (0.082 mmol)  $\text{PPN}^+ \text{CpV}(\text{CO})_3\text{H}^-$  was added to a  $d_8$ -THF solution (0.5 ml) of 18 mg (0.086 mmol)  $\text{CH}_3\text{Mn}(\text{CO})_5$  in an NMR tube. The solution turned brown within 5 min. The  $^1\text{H}$ -NMR showed the disappearance of  $\text{CpV}(\text{CO})_3\text{H}^-$  with the concurrent formation of  $\text{CpV}(\text{CO})_4$ . Traces of  $\text{CH}_4$  (~5%) were observed by NMR and by GC (9' x 1/16 Poropak Q, 80°C).

A similar mixture of 14.3 mg (0.042 mmol)  $\text{CH}_3\text{Re}(\text{CO})_5$  and 30.4 mg (0.041 mmol)  $\text{PPN}^+ \text{CpV}(\text{CO})_3\text{H}^-$  in 0.46 ml  $d_8$ -THF under 1 atm CO showed a slow reaction at 25°C forming methane. Heating this solution to 50°C resulted in a faster reaction rate ( $\tau_{1/2} \cong 2$  hrs), forming a new (unisolable) complex, assigned structure **3** [ $\text{cis}-(\text{CH}_3)(\text{H})\text{Re}(\text{CO})_4^-$ ], on the basis of its NMR spectrum ( $\delta$  -0.65 ppm, 3H, d,  $J_{\text{H-H}} = 3$  Hz;  $\delta$  -5.56 ppm, 1H, br). Eventually all the  $\text{CH}_3\text{Re}(\text{CO})_5$  disappeared and only **3** (plus  $\text{CH}_4$ ) was observed. As the hydride disappeared, the amount of methane increased. A second complex, believed to be  $\text{trans-3}$ , was also observed in 10% yield (NMR: 0.30 ppm, 3H, s;  $\delta$  -4.30 ppm, 1H, s). This solution was treated with 5  $\mu\text{l}$   $\text{CH}_3\text{I}$ , and a large methyl resonance due to  $\text{CH}_3\text{Re}(\text{CO})_5$  ( $\delta$  -0.20 ppm) was observed.

**Preparation of  $(\text{CH}_3\text{CO})\text{Re}(\text{CO})_5$ .** 1.0 g (1.5 mmol)  $\text{Re}_2(\text{CO})_{10}$  was reduced with 1.5 ml 0.65% Na/Hg amalgam in 10 ml THF. The solution was decanted from the mercury and 0.22 ml (3.1 mmol)  $\text{CH}_3\text{COCl}$  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%)  $(\text{CH}_3\text{CO})\text{Re}(\text{CO})_5$ . NMR( $d_8$ -THF):  $\delta$  2.47 ppm. IR (THF): 2125 (w), 2060(w), 2009(s), 1996(sh), 1612(w)  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_7\text{H}_3\text{ReO}_6$ : 22.77% C, 0.82 H; Found: 22.56% C, 0.87% H.

**Reaction of  $\text{PPN}^+ \text{CpV}(\text{CO})_3\text{H}^-$  with  $(\text{CH}_3\text{CO})\text{Re}(\text{CO})_5$ .** 35 mg (0.047 mmol)

$(\text{CH}_3\text{CO})\text{Re}(\text{CO})_5$  and 18 mg (0.049 mmol)  $\text{CpV}(\text{CO})_3\text{H}^-$  were sealed under vacuum in an NMR tube along with 0.4 ml  $d_8$ -THF. Upon heating the solution at  $50^\circ\text{C}$ , new singlets were observed to grow in slowly over 24 hrs at  $\delta 2.20$  ppm (3H) and  $\delta -4.38$  ppm (1H) attributable<sup>15</sup> to  $(\text{H})(\text{CH}_3\text{CO})\text{Re}(\text{CO})_4^-$ . A quantitative yield of  $\text{CpV}(\text{CO})_4$  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  $\text{PPN}^+\text{CpV}(\text{CO})_3\text{H}^-$  with  $(\text{CH}_3\text{CO})\text{Re}(\text{CO})_5$ .**

**A. with Sodium metal.** 35 mg (0.047 mmol)  $\text{PPN}^+\text{CpV}(\text{CO})_3\text{H}^-$  and 18 mg (0.049 mmol)  $(\text{CH}_3\text{CO})\text{Re}(\text{CO})_5$  were weighed into an NMR tube attached to a ground glass joint, 0.4 ml  $d_8$ -THF distilled in, and the tube sealed. The tube was heated to  $50^\circ\text{C}$  for additional 30 min. An NMR spectrum showed 50% yield of the  $\text{H}(\text{COCH}_3)\text{Re}(\text{CO})_4^-$  product.

**B. with  $\text{Na}_2\text{CpV}(\text{CO})_3$ .** 37 mg (0.050 mmol)  $\text{PPN}^+\text{CpV}(\text{CO})_3\text{H}^-$ , 21 mg (0.057 mmol)  $(\text{CH}_3\text{CO})\text{Re}(\text{CO})_5$ , and 5 mg (0.02 mmol)  $\text{Na}_2\text{CpV}(\text{CO})_3$  were weighed into an NMR tube and 0.54 ml  $d_8$ -THF transferred in at  $77^\circ\text{K}$ . The tube was sealed under vacuum, thawed, and the contents mixed. After 5 min. an NMR spectrum was recorded showing a quantitative yield of  $\text{CpV}(\text{CO})_4$  ( $\delta 5.20$  ppm) and  $\text{H}(\text{CH}_3\text{CO})\text{Re}(\text{CO})_4^-$  ( $\delta 2.20$ , s, 3H;  $\delta -4.38$ , br, 1H).

**Catalysis of the Reaction of  $\text{PPN}^+(\text{CpV}(\text{CO})_3\text{H})^-$  with  $\text{Fe}(\text{CO})_5$  and  $\text{Cr}(\text{CO})_6$  by  $\text{Na}_2\text{CpV}(\text{CO})_3$ .** 49 mg (0.066 mmol)  $\text{PPN}^+\text{CpV}(\text{CO})_3\text{H}^-$ , 3 mg (0.01 mmol)  $\text{Na}_2\text{CpV}(\text{CO})_3$ , and 0.78 ml  $d_8$ -THF were placed in a septum-capped NMR tube in the dry box. An NMR spectrum of the heterogeneous solution was recorded ( $\text{Na}_2\text{CpV}(\text{CO})_3$  is insoluble in THF). As 8.7  $\mu\text{l}$  (0.065 mmol) of  $\text{Fe}(\text{CO})_5$  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  $\text{CpV}(\text{CO})_4$  and  $\text{HFe}(\text{CO})_4^-$ . Comparison of the percent completion

(60%) after 10 min. in this reaction to a separate reaction without added  $\text{Na}_2\text{CpV}(\text{CO})_3$  showed that the dianion-catalyzed reaction proceeded ca. 4 times faster.

A similar reaction of 41 mg (0.055 mmol)  $\text{PPN}^+\text{CpV}(\text{CO})_3\text{H}^-$ , 24 mg (0.11 mmol)  $\text{Cr}(\text{CO})_6$ , and 2 mg (.01 mmol)  $\text{Na}_2\text{CpV}(\text{CO})_3$  in 0.53 ml  $d_8$ -THF was examined by NMR after 10 min. Comparison of this reaction to one without added  $\text{Na}_2\text{CpV}(\text{CO})_3$  showed a rate increase of about 3.6.

**Reaction of  $\text{PPN}^+\text{CpV}(\text{CO})_3\text{H}^-$  with  $\text{CpMo}(\text{CO})_3(\text{C}_2\text{H}_5)$ .** A solution of 55 mg (0.074 mmol)  $\text{PPN}^+\text{CpV}(\text{CO})_3\text{H}^-$  dissolved in 0.5 ml  $d_8$ -THF was added by syringe to 21 mg (0.077 mmol)  $\text{CpMo}(\text{CO})_3(\text{C}_2\text{H}_5)$  in 0.4 ml  $d_8$ -THF in a septum capped NMR tube. An immediate reaction occurred, and an NMR spectrum showed a 30% yield of propionaldehyde ( $\delta$  9.68, t, 1H; 2.38, q of d, 2H; 1.04, t, 3H). Following this the solution turned dark brown, indicating substantial decomposition.

**Hydride Catalyzed Substitution of  $\text{CpV}(\text{CO})_4$  by L (L= $\text{PPh}_3$ ,  $\text{PMe}_3$ ).** 75 mg (0.10 mmol)  $\text{PPN}^+\text{CpV}(\text{CO})_3\text{H}^-$ , 60 mg (0.23 mmol)  $\text{PPh}_3$ , and 58 mg (0.25 mmol)  $\text{CpV}(\text{CO})_4$  were dissolved in 1.0 ml  $d_8$ -THF and the flask covered to exclude light. NMR spectra were recorded periodically and showed the conversion of  $\text{CpV}(\text{CO})_4$  into  $\text{CpV}(\text{CO})_3(\text{PPh}_3)$  (NMR:  $\delta$  4.73 ppm, d,  $J_{\text{PH}} = 1.5$  Hz) with no change in the  $\text{CpV}(\text{CO})_3\text{H}^-$  resonance ( $T_{1/2} = 1$  hr).

An identical reaction employing  $\text{PMe}_3$  instead of  $\text{PPh}_3$  showed complete conversion to  $\text{CpV}(\text{CO})_3\text{PMe}_3$ .<sup>16</sup> The ( $^1\text{H}$ -NMR:  $\delta$  4.90 ppm, 5H, d,  $J_{\text{PH}} = 1.9$  Hz; 1.44 ppm, 9H, d,  $J_{\text{PH}} = 8.7$  Hz).

**Reaction of  $\text{PPN}^+\text{CpV}(\text{CO})_3\text{H}^-$  with  $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{COCH}_3)$  and CO.** 26 mg (0.057 mmol)  $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{COCH}_3)$  and 44 mg (0.058 mmol)  $\text{PPN}^+\text{CpV}(\text{CO})_3\text{H}^-$  were dissolved in 0.5 ml  $d_8$ -THF and sealed in an NMR tube under 600 mm CO (0.031 mmol). After 2 days at 25°C, NMR spectra showed the  $\text{CpV}(\text{CO})_3\text{H}^-$  was



unchanged, whereas the  $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{COCH}_3)_3$  (NMR: 4.38, 5H, d,  $J_{\text{PH}} = 2\text{Hz}$ ; 2.28 ppm, 3H, s) had been 50% converted (100% yield based on CO) into  $\text{CpFe}(\text{CO})_2(\text{COCH}_3)^{11}$  (NMR:  $\delta$ 4.93 ppm, 5H, s; 2.50 ppm, 3H, s). The solution was heated to 65°C for 24 hrs, but no further changes were observed by NMR.

**Reaction of  $\text{CpMo}(\text{CO})_3\text{H}$  with  $\text{CH}_3\text{Mn}(\text{CO})_5$  and  $\text{CH}_3\text{Re}(\text{CO})_5$ .** 27 mg (0.11 mmol)  $\text{CH}_3\text{Mn}(\text{CO})_5$  were dissolved in 0.48 mg  $d_8$ -THF in an NMR tube. NMR spectra showed a complete reaction to form  $\text{CpMo}(\text{CO})_3\text{Mn}(\text{CO})_5$  ( $\delta$ 5.49 ppm<sup>21</sup>),  $[\text{CpMo}(\text{CO})_3]_2$  ( $\delta$ 5.40 ppm),  $[\text{CpMo}(\text{CO})_2]_2$  ( $\delta$ 5.27 ppm) and  $\text{CH}_3\text{CHO}$  (identified by NMR:  $\delta$  2.07, 3H, d,  $j=3$  hz; 9.66 ppm, 1H, q; 50% yield). An equimolar mixture of  $\text{CpMo}(\text{CO})_3\text{H}$  (0.22 M) and  $\text{CH}_3\text{Re}(\text{CO})_5$  (0.22 M) in  $d_8$ -THF showed no reaction after 3 days at 25°C.

**Reaction of  $\text{CpMo}(\text{CO})_3\text{H}$  with  $\text{CpMo}(\text{CO})_3(\text{C}_2\text{H}_5)$ .** 15 mg (0.061 mmol)  $\text{CpMo}(\text{CO})_3\text{H}$  and 17 mg (0.062 mmol)  $\text{CpMo}(\text{CO})_3(\text{C}_2\text{H}_5)$  were weighed into an NMR tube attached to a ground glass joint and 0.51 ml  $d_8$ -THF introduced on a vacuum line. The tube was sealed under vacuum and FT-NMR spectra recorded over the next 6 hrs. The product propionaldehyde (quantitative yield) was identified by NMR ( $\delta$ 9.68 ppm, 1H, t,  $J_{\text{ab}} = 1.7$  Hz; 2.38 ppm, 2H, q of d,  $J_{\text{bc}} = 7.3$  Hz; 1.04 ppm, 3H, t). The dimers  $[\text{CpMo}(\text{CO})_3]_2$  and  $[\text{CpMo}(\text{CO})_2]_2$ , also formed in quantitative yield, were identified by comparison of their NMR spectra with those of authentic samples<sup>44</sup> ( $\delta$ 5.40 ppm, 5.27 ppm, respectively).

**Reaction of  $\text{CpMo}(\text{CO})_3\text{H}$  with  $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ .** A solution of 15 mg (0.061 mmol)  $\text{CpMo}(\text{CO})_3\text{H}$  and 16 mg (0.065 mmol)  $\text{CpMo}(\text{CO})_3(\text{CH}_3)$  in 0.43 ml  $d_8$ -THF was prepared in the dry box in an NMR tube. The tube was heated to 50°C and NMR spectra recorded over the next 40 hrs., showing the appearance of  $\text{CH}_3\text{CHO}$  (53% yield at completion of reaction) and the molybdenum dimers. A second order plot of the disappearance of  $\text{CpMo}(\text{CO})_3(\text{CH}_3)$  vs. time gave a second order rate

constant of  $\sim 2.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ .

**Reaction of  $\text{CpMo(CO)}_3(\text{CH}_2\text{C}_6\text{H}_5)$  with  $\text{CpMo(CO)}_3\text{H}$ .** 15 mg of  $\text{CpMo(CO)}_3(\text{CH}_2\text{Ph})$  and  $\sim 11$  mg  $\text{Cp}_2\text{Fe}$  (internal standard) were weighed into each of three NMR tubes. 44 mg, 88 mg, and 132 mg  $\text{CpMo(CO)}_3\text{H}$  were weighed into the three tubes, respectively. 0.44 ml  $d_8$ -THF was added to each sample and the tubes sealed under vacuum. The tubes were heated to  $50^\circ\text{C}$  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  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo(CO)}_3(\text{CH}_3)$  and  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo(CO)}_3(\text{CD}_3)$ .** 0.75 g (1.5 mmol)  $[(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo(CO)}_3]_2$  was dissolved in 5 ml THF and stirred over 20 g 0.65 Na/Hg amalgam for 1 hr. The solution was decanted from the mercury and 0.25 ml  $\text{CH}_3\text{I}$  added (4.0 mmol). The THF was removed ( $25^\circ\text{C}$ ,  $10^{-2}$  mm) and the product sublimed at  $50^\circ\text{C}$  ( $10^{-4}$  mm). Yield 0.35 g (45%)  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo(CO)}_3(\text{CH}_3)$ . Anal. Calcd. for  $\text{C}_{10}\text{H}_{10}\text{MoO}_3$ : 43.45% C, 3.73% H; Found: 43.22% C, 3.64% H. NMR ( $d_8$ -THF):  $\delta$  5.25 ppm, 4H, m; 1.93 ppm, 3H, s; 0.29 ppm, 3H, s. Substitution of 0.3 ml  $\text{CD}_3\text{I}$  in place of  $\text{CH}_3\text{I}$  produced 0.52 g (60%)  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo(CO)}_3(\text{CD}_3)$ , whose NMR was identical to that of  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo(CO)}_3(\text{CH}_3)$  except for the absence of a methyl resonance at  $\delta$  1.93 ppm.

**The Reaction of  $\text{CpMo(CO)}_3(\text{CH}_3)$  with  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo(CO)}_3(\text{CD}_3)$ .** A solution containing 24 mg each of  $\text{CpMo(CO)}_3(\text{CH}_3)$  and  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo(CO)}_3(\text{CD}_3)$  in 0.38 ml  $d_8$ -THF was prepared in an NMR tube in the dry box. The tube was heated to  $50^\circ\text{C}$  overnight and NMR recorded. No  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo(CO)}_3(\text{CH}_3)$  was observed. A control solution containing an authentic mixture of  $\text{CpMo(CO)}_3\text{CH}_3$  and  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo(CO)}_3\text{CH}_3$  demonstrated that the two complexes exhibited

distinguishable  $\text{CH}_3$  resonances (6 Hz apart), and as little as 1% of the  $\text{CH}_3\text{C}_5\text{H}_4$  complex could have been detected in the mixing experiment.

**Preparation of  $(\text{CH}_3\text{C}_4\text{H}_4)\text{Mo}(\text{CO})_3(\text{CH}_2\text{C}_6\text{H}_5)$  and  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3(\text{CD}_2\text{C}_6\text{D}_5)$ .**  
0.60 g (1.16 mmol)  $[(\text{C}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3]_2$  was reduced with 20 g 0.65% Na/Hg amalgam in 10 ml THF. 0.4 ml (2.53 mmol)  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$  was added and the solution stirred for 30 min. The solvent was removed ( $25^\circ\text{C}$ ,  $10^{-2}$  mm) and the solid chromatographed on silica gel (2 cm x 10 cm) using benzene as eluent. A yellow band was collected and the benzene removed ( $35^\circ\text{C}$ ,  $10^{-2}$  mm), yielding 0.52 g (64%)  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3(\text{CH}_2\text{C}_6\text{H}_5)$ . NMR( $d_8$ -THF):  $\delta$  7.12 ppm, 5H, m; 5.20 ppm, 5H, s; 2.82 ppm, 2H, s; 1.96 ppm, 3H, s. Anal: Calcd. for  $\text{C}_{16}\text{H}_{14}\text{MoO}_3$ : 54.87% C, 4.03% H; Found: 54.66% C, 4.08% H. Use of  $\text{C}_6\text{D}_5\text{CD}_2\text{Br}$  (see below) (0.3 ml) in place of  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$  produced  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3(\text{CD}_2\text{C}_6\text{D}_5)$ , m.p.  $49$ – $50^\circ\text{C}$ , whose NMR was the same as that of  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3(\text{CH}_2\text{C}_6\text{H}_5)$  except for the absence of the resonances at  $\delta$  7.12 and  $\delta$  2.82 ppm.

**Reaction of a Mixture of  $\text{CpMo}(\text{CO})_3(\text{CH}_3)$  and  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3(\text{CD}_3)$  with  $\text{CpMo}(\text{CO})_3\text{H}$ .** 22 mg (0.089 mmol)  $\text{CpMo}(\text{CO})_3\text{H}$ , 24 mg (0.092 mmol)  $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ , and 24 mg (0.086 mmol)  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3(\text{CD}_3)$  were weighed into an NMR tube and 0.38 ml  $d_8$ -THF introduced on a vacuum line. The tube was sealed and heated to  $50^\circ\text{C}$ , and NMR spectra recorded over the next 12 hrs. 48% of the  $\text{CpMo}(\text{CO})_3(\text{CH}_3)$  was consumed vs. 41% of the  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3(\text{CD}_3)$ . No  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3(\text{CH}_3)$  was observed.

A similar experiment with  $\text{R} = \text{CH}_2\text{C}_6\text{H}_5$  and  $\text{CD}_2\text{C}_6\text{D}_5$  also showed no crossover after 72 hrs, only benzaldehyde (62%,  $\delta$  2.89 and 9.56 ppm) and toluene (25%;  $\sim$  2.29 ppm) by NMR. Extended heating (192 hrs) of the benzyl compounds in the absence of hydride showed traces of the crossover product  $(\text{CH}_3\text{C}_5\text{H}_4)\text{Mo}(\text{CO})_3(\text{CH}_2\text{C}_6\text{H}_5)$  by NMR, a new  $-\text{CH}_2-$  resonance appearing 12 Hz upfield from the  $\text{CpMo}(\text{CO})_3(\text{CH}_2\text{C}_6\text{H}_5)$  methylene resonance. A small amount of

toluene was also formed.

**Reaction of  $\text{CpMo}(\text{CO})_3(\text{CH}_3)$  with  $\text{CH}_3\text{COOH}$  and  $\text{CF}_3\text{COOH}$ .** 25 mg (0.096 mmol)  $\text{CpMo}(\text{CO})_3(\text{CH}_3)$  was dissolved in 0.32 ml  $d_8$ -THF in an NMR tube fitted with a rubber septum. 5.5  $\mu\text{l}$   $\text{CH}_3\text{COOH}$  (0.096 mmol) was introduced with a syringe and the solution heated to 50<sup>0</sup>C for 24 hrs. No changes were observed by NMR. An identical reaction employing  $\text{CF}_3\text{COOH}$  in  $\text{C}_6\text{D}_6$  showed the formation of  $\text{CH}_4$ ; no aldehyde was observed.

**Reaction of  $\text{CpMo}(\text{CO})_2(\text{PMe}_3)(\text{H})$  with  $\text{CpMo}(\text{CO})_3(\text{C}_2\text{H}_5)$ .** 11 mg (0.037 mmol)  $\text{CpMo}(\text{CO})_2(\text{PMe}_3)(\text{H})$  and 8 mg  $\text{CpMo}(\text{CO})_3(\text{C}_2\text{H}_5)$  (0.029 mmol) were sealed in an NMR tube along with 0.42 ml  $d_8$ -THF. Reaction at 25<sup>0</sup>C showed the disappearance of  $\text{CpMo}(\text{CO})_3(\text{C}_2\text{H}_5)$  and  $\text{CpMo}(\text{CO})_2(\text{PMe}_3)(\text{H})$  (cis/trans mixture,  $\delta$  5.1 ppm, 5H, s; 1.50 ppm, 9H, d,  $J_{\text{PH}} = 9$  Hz; -6.00 ppm, 0.5 H, sharp singlet (cis); -6.50 ppm, broad singlet, 0.5H (trans)). Propionaldehyde was the only product observed by NMR ( $\delta$  9.68 ppm, 1H, t; 2.38 ppm, 2H, q of d; 1.04 ppm, 3H, t). The half life of this reaction was  $\sim$ 100 min, in comparison with the value of  $\sim$ 170 min when  $\text{CpMo}(\text{CO})_3\text{H}$  was employed at the concentration specified in the previously described experiment.

**The Synthesis of  $\text{MeCpMo}(\text{CO})_3\text{H}$ , 2b.** The previously unknown  $\text{MeCpMo}(\text{CO})_3\text{H}$  (1b,  $\text{MeCp} = \eta^5\text{-CH}_3\text{C}_5\text{H}_4$ ) was prepared by the following adaptation of the standard method of synthesis for 2a. A solution of 1.05 g (3.72 mmol) Na  $[\text{MeCpMo}(\text{CO})_3]$  (prepared from NaMeCp and  $\text{Mo}(\text{CO})_6$  by the literature method<sup>2,11</sup>) in 30 ml THF was treated with 0.7 g (4 mmol) p-toluenesulfonic acid as a THF solution in the glove box. A copious precipitate formed immediately. After 15 minutes an IR spectrum of the solution indicated complete conversion of the anion to molybdenum hydride. The yellow solution was filtered and the solvent removed in vacuo to yield a red oil. This oil was distilled at reduced pressure to yield 2b as a pale yellow, thermally sensitive oil; b.p.

55-60°C (0.01 mmHg). IR(THF)  $\nu_{CO}$ : 2015(s), 1930(s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR(THF- $d_8$ ):  $\delta$ -5.42 (s, 1H), 2.12 (s, 3H), 5.46 ppm (AA'BB' quartets,  $J_{AB} = 17$  Hz,  $J_{AA'} = 2.1$  Hz, 4H).

**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 glove box. 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 dry box, removing the solvent, redissolving the resulting residue in  $\text{CH}_3\text{CN}$ , and analyzing by HPLC. High pressure liquid chromatographic (HPLC) analysis was achieved using a 1 x 25 cm Altex Ultrasphere-ODS reversed phase column, eluting with 20%  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  saturated with argon. 20-50  $\mu\text{l}$  injections completely eluted over a 35 minute 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,b,c** (prepared by irradiating a mixture of **4a** and **4c**) and **5a,b,c** (prepared by heating a mixture of **4a** and **4c** under an  $\text{N}_2$  purge<sup>40</sup>) as shown in Figure 1.

A) A solution of 19 mg (0.077 mmol) **2a** and 20 mg (.073 mmol) **7b** in 0.4 ml THF- $d_8$  was heated to 50(+0.5)°C for 22 hours (approximately 64% reaction) and then analyzed by HPLC. In addition to **7b** and products arising from decomposition of **2a** in acetonitrile solution,<sup>41</sup> the dimers **4a** (see text), **4b**, and **5b** were observed.

B) A solution of 18 mg (0.07 mmol) **2b** and 20 mg (0.077 mmol) **6b** in 0.4

mmol THF- $d_8$  was heated to  $50(\pm 0.5)^\circ\text{C}$  for 22 hours (approximately 64% reaction) and then analyzed by HPLC. In addition to unreacted **6b** and products from decomposition of **2b** in acetonitrile,<sup>41</sup> significant amounts of the dimers **4b**, **4c**, and **5b** were observed.

C) A solution of 22 mg (0.085 mmol) **2b** and 27 mg (0.098 mmol) **6a** in 0.58 ml 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) **2b** and 18 mg (0.069 mmol) **6b** in 0.78 ml THF- $d_8$  was heated to  $100^\circ\text{C}$  for 15 hours. HPLC analysis showed that all six dimers **4a,b,c** and **5a,b,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  $\text{CpMo}(\text{CO})_3\text{H}$  with  $\text{C}_2\text{H}_4$ .** A solution of 31 mg (0.126 mmol)  $\text{CpMo}(\text{CO})_3\text{H}$  in 0.4 ml  $d_8$ -THF was prepared in an NMR tube, 0.245 mmol  $\text{C}_2\text{H}_4$  condensed into the tube on a vacuum line, and the tube sealed. The tube was heated to  $100^\circ\text{C}$  and NMR spectra recorded over the next 24 hrs. No propionaldehyde was observed; only resonances due to ethane (36%) and diethyl ketone (15%;  $\delta$  2.35 ppm, 4H, q; 0.96 ppm, 6H, t) were present. The tube was broken open in air and the contents vacuum distilled ( $30^\circ\text{C}$ ,  $10^{-2}$  mm) into a  $-77^\circ\text{K}$  receiving vessel. One- $\mu\text{l}$  aliquots were examined by gas chromatography (1/4" x 10' 20% Carbowax 20M/Chrom WAW), confirming the NMR product identification by co-injection with authentic samples.

**Reaction of  $\text{CpMo}(\text{CO})_3(\text{CH}_3)$  with ethylene.** 35 mg (0.135 mmol)  $\text{CpMo}(\text{CO})_3(\text{CH}_3)$  was weighed into a medium-walled NMR tube attached to a ground glass joint and

21.3 ml  $C_2H_4$  (215 mm,  $25^\circ C$ ) (0.245 mmol) condensed into the tube ( $-77^\circ K$ ) on a vacuum line. 0.35 ml  $d_8$ -THF was also distilled in before sealing the tube. The solution was heated at  $100^\circ C$  for 4 hrs over which time the NMR resonances of  $CpMo(CO)_3(CH_3)$  ( $\delta$ 5.41 ppm, 0.36 ppm) were observed to diminish as resonances of  $CH_3COCH_2CH_3$  ( $\delta$ 2.37 ppm, 4H, q,  $J = 7.2$  Hz; 0.96 ppm, 6H, s; 2.02 ppm, 3H, s) grew in (50% yield). No  $CH_4$  was observed. The tube was broken open and the contents vacuum distilled into a  $-77^\circ K$  receiver. GC analysis of a 1  $\mu$ l aliquot (1/4" x 10' 20% Carbowax 20 M/Chrom WAW,  $90^\circ C$ ) 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  $CpMo(CO)_3(CH_3)$  with  $C_2H_4$  in the presence of 1-buten-3-one.** 36 mg (0.138 mmol)  $CpMo(CO)_3(CH_3)$  was weighed into an NMR tube fitted with a ground glass joint and 2.5  $\mu$ l (ca. 0.03 mmol) 1-buten-3-one introduced with a syringe. The tube was quickly attached to a vacuum line, cooled to  $-77^\circ K$ , and evacuated. Ethylene (0.25 mmol) and 0.42 ml  $d_8$ -THF were condensed in and the tube sealed. The tube was heated to  $100^\circ C$  and NMR spectra recorded over the next 18 hrs. In 1 hr, 46% of the  $CpMo(CO)_3(CH_3)$  (0.36 ppm) was consumed and a 25% yield of 2-butanone ( $\delta$ 0.96 ppm, 3H, t; 2.37 ppm, 4H, q; 2.02 ppm, 3H, s) observed. 80% of the 1-buten-3-one had decomposed. In 6 hrs, the reaction was 95% complete and a 54% yield of 2-butanone was found. After 18 hrs all  $CpMo(CO)_3(CH_3)$  had been consumed and a 58% yield of 2-butanone was measured. The tube was broken open and the volatile contents vacuum distilled and analyzed by GC (10' x 1/4" 20% Carbowax 20M/Chrom WAW,  $90^\circ C$ ). A 55% yield of 2-butanone was confirmed relative to added internal standard (pentane). Only traces (<5%) of 2-buten-3-one were present.

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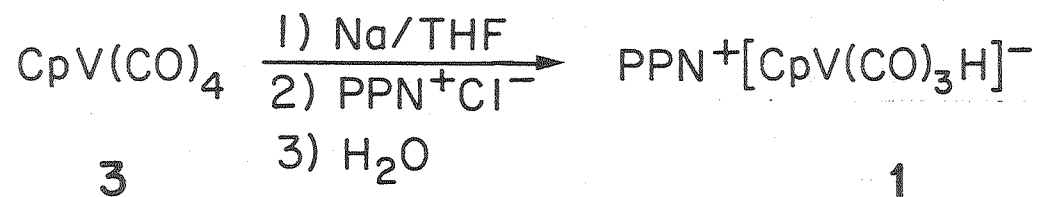
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41.  $\text{CpMo(CO)}_3\text{H}$  decomposes upon dissolving in acetonitrile to form cyclopentadiene and  $\text{Mo(CO)}_3(\text{CH}_3\text{CN})_3$  (R. Jordan and J. Norton, private communication).

Table I. Second order Rate constants for the reaction of  $\text{CpMo(CO)}_3\text{H}$  with  $\text{CpMo(CO)}_3\text{R}$  in  $d_8\text{-THF}$ .

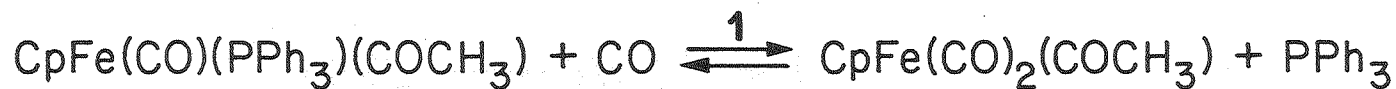
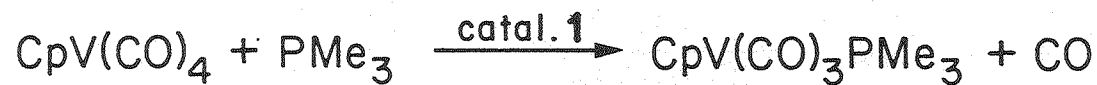
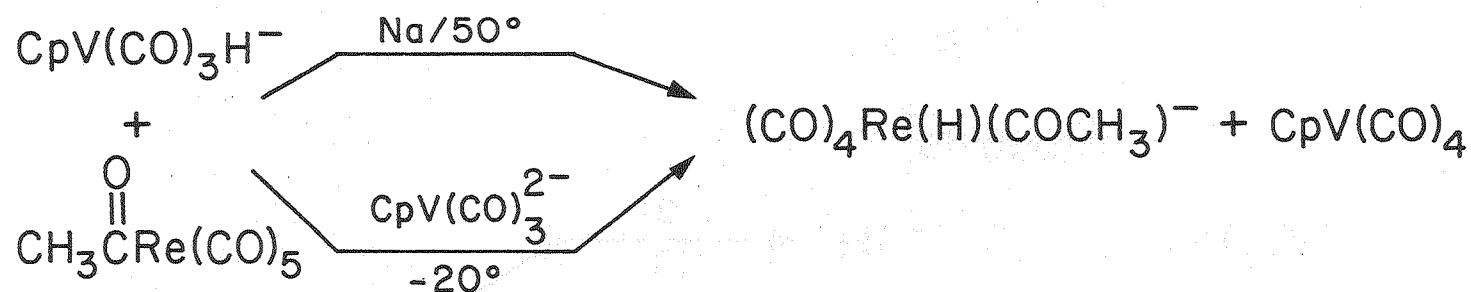
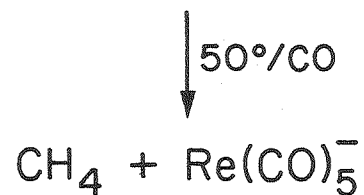
| <u>R</u>                               | <u>T(°C)</u> | <u>k(M<sup>-1</sup>S<sup>-1</sup>)</u> |
|--|--------------|--|
| $\text{C}_2\text{H}_5$ (6a)            | 50           | $4.0 \times 10^{-3}$                   |
| $\text{CH}_3$ (6b)                     | 50           | $2.5 \times 10^{-4}$                   |
| $\text{CH}_2\text{C}_6\text{H}_5$ (6c) | 50           | $2.5 \times 10^{-5}$                   |
| $\text{CH}_3^a$ (7b)                   | 50           | $2.3 \times 10^{-4}$                   |
| $\text{C}_2\text{H}_5$ (6a)            | 25           | $8.5 \times 10^{-4}$                   |

<sup>a</sup>Cp replaced by  $\text{CH}_3\text{C}_5\text{H}_4$

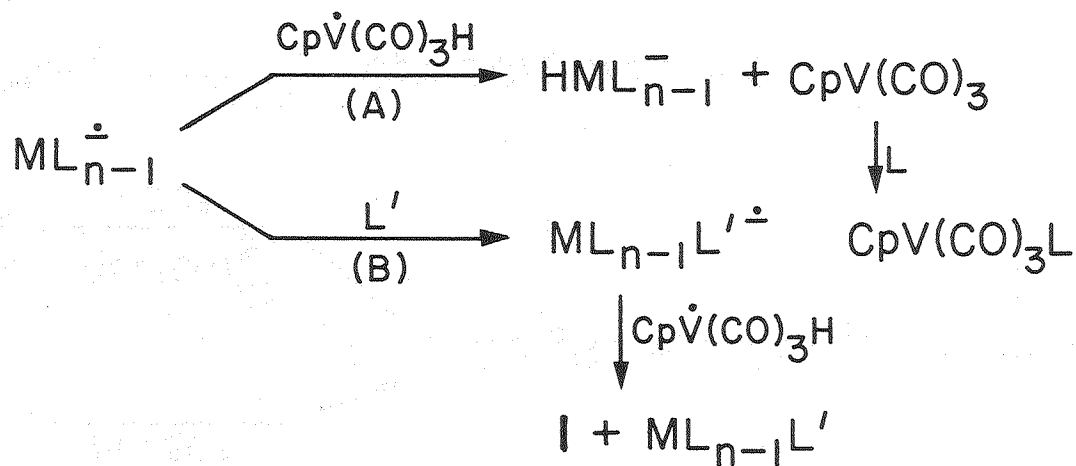
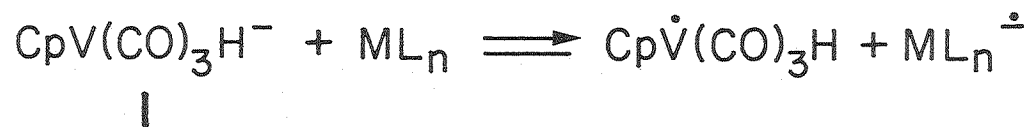
Scheme 1



Scheme 2



Scheme 3

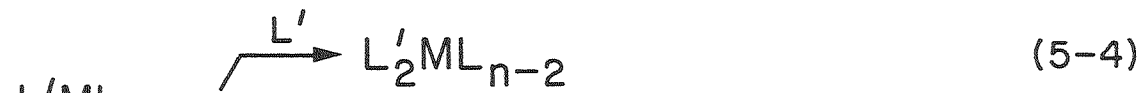


Scheme 4

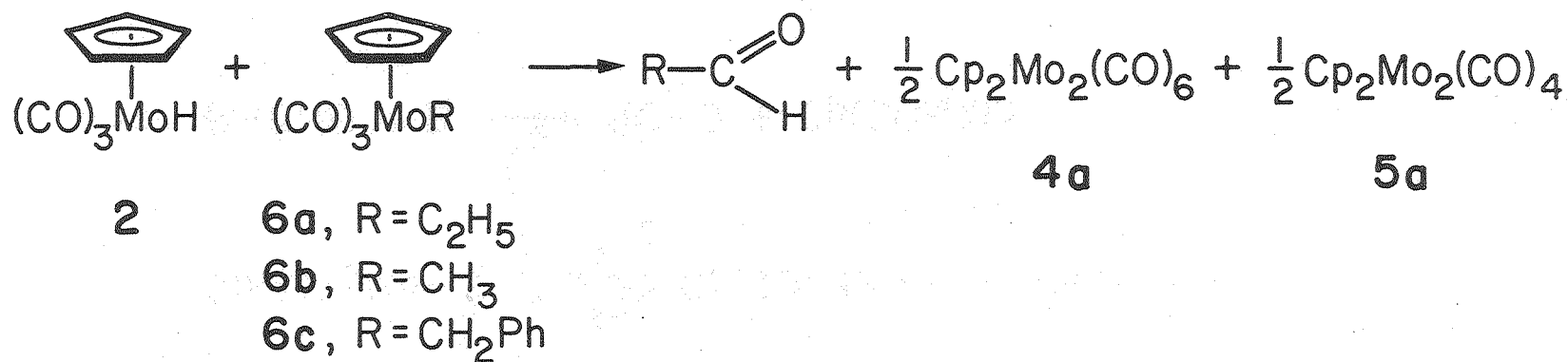
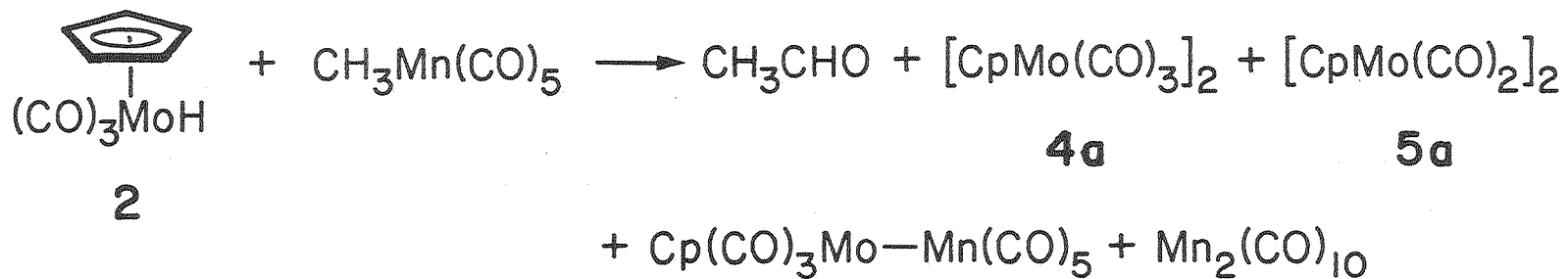




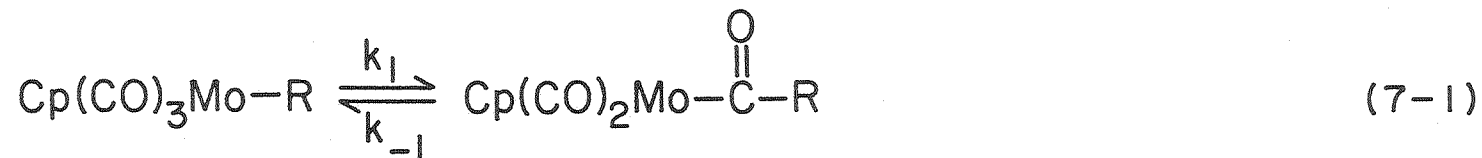
Scheme 5



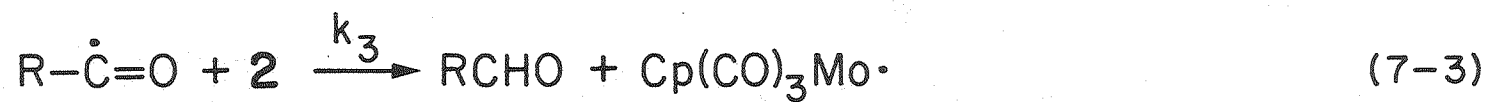
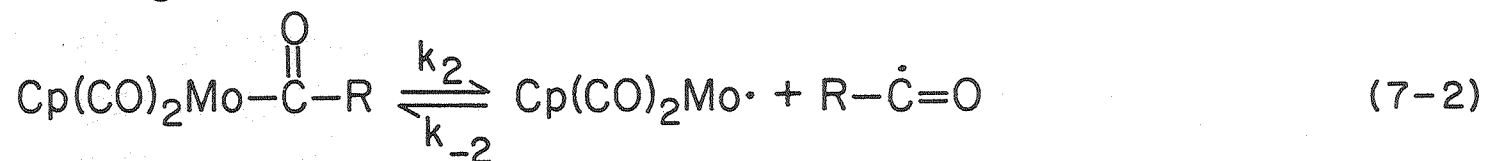
Scheme 6



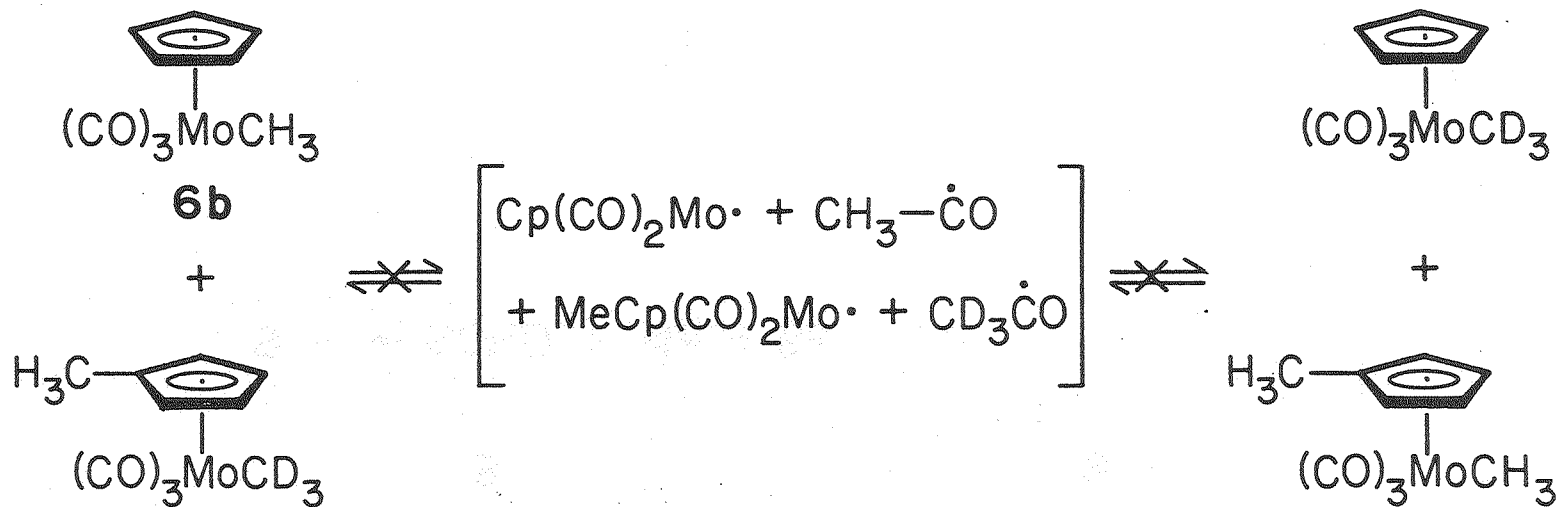
Scheme 7



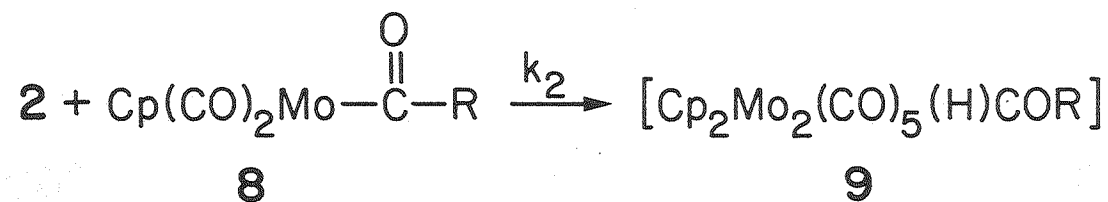
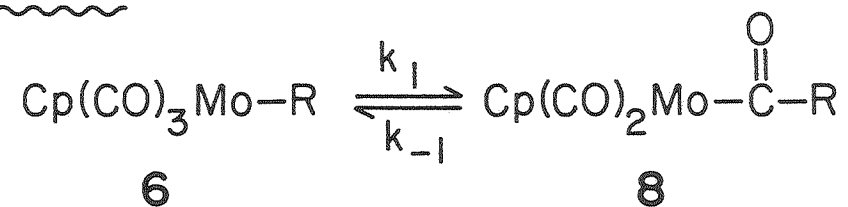
6



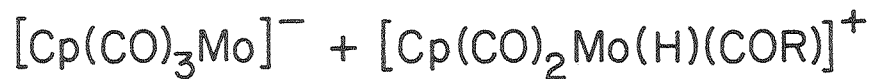
Scheme 8



Scheme 9



Scheme 10



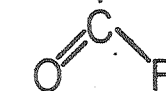
9a



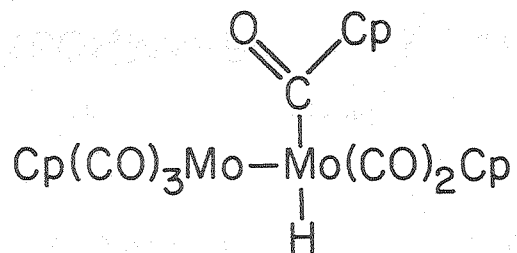
9b



9c

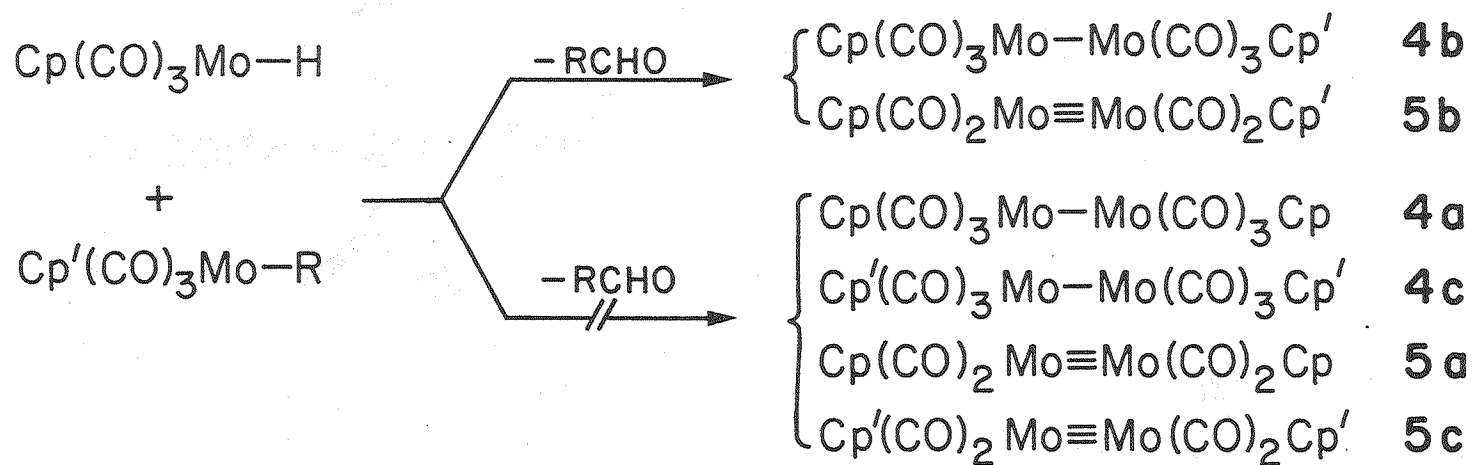


9d



9e

Scheme II



Scheme 12

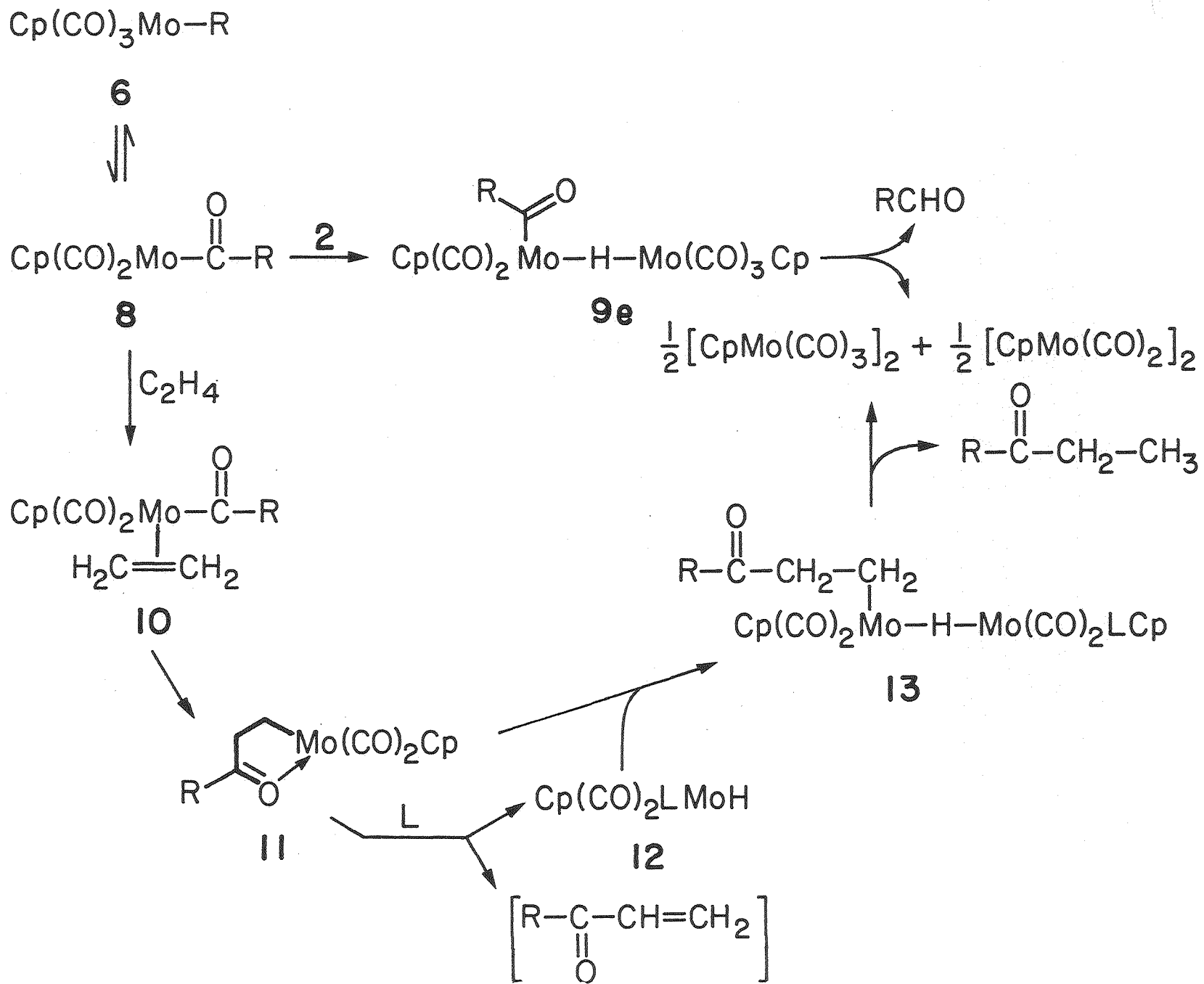




Figure Caption

Figure 1. HPLC traces of mixtures of Cp- and MeCp-substituted molybdenum carbonyl dimers (1 x 25 cm columns packed with Ultrasphere-ODS (Altex) reversed-phase adsorbent; CH<sub>3</sub>CN elution solvent). (a) Synthetic mixture of all six dimers (individual identities of peaks are indicated on figure); (b) Product mixture resulting from reaction of MeCpMo(CO)<sub>3</sub>H (2b) with CpMo(CO)<sub>3</sub>C<sub>2</sub>H<sub>5</sub> (6a) (darkened circles (●) indicate products resulting from decomposition of hydride during chromatography).

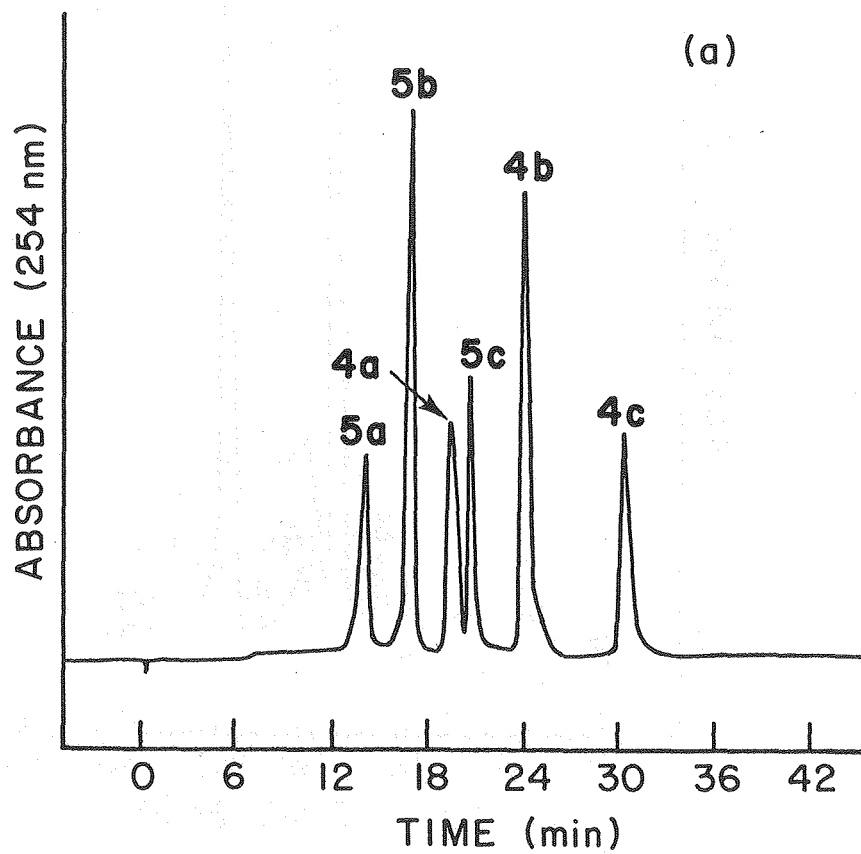


Fig. 1a

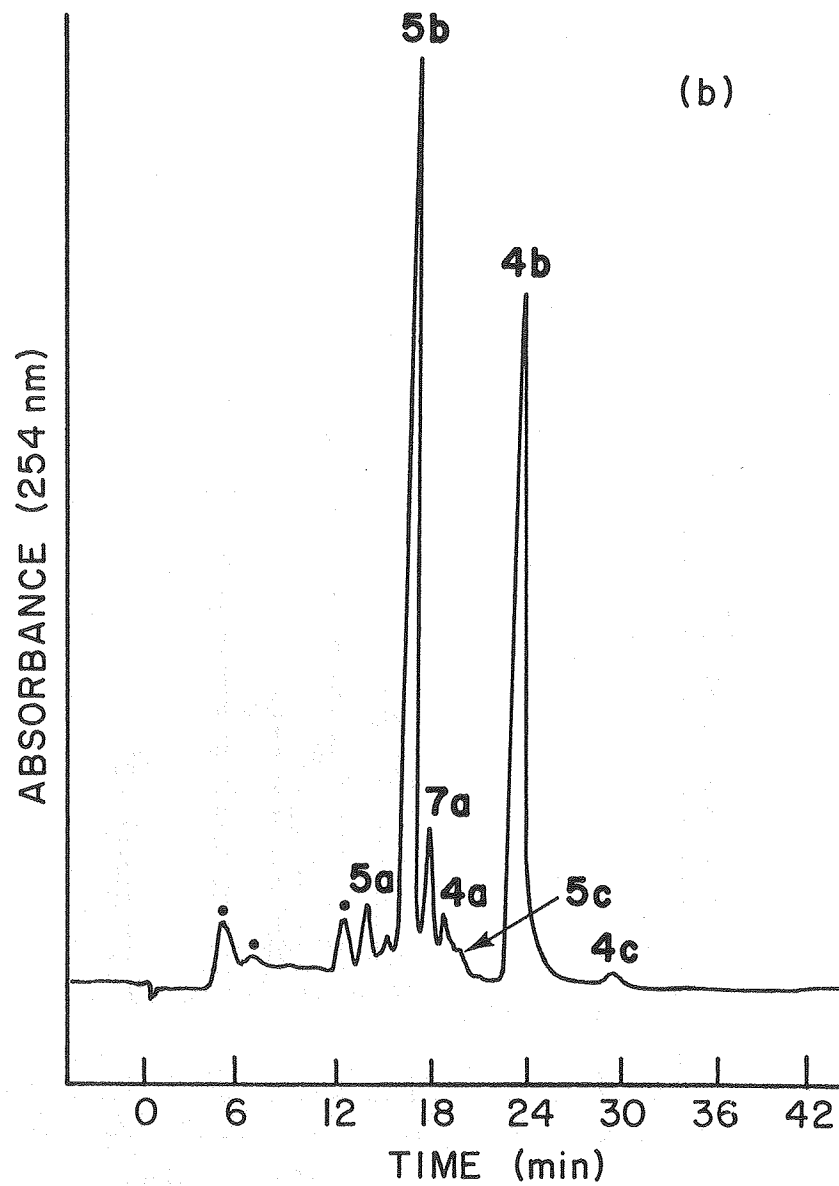


Fig. 1b