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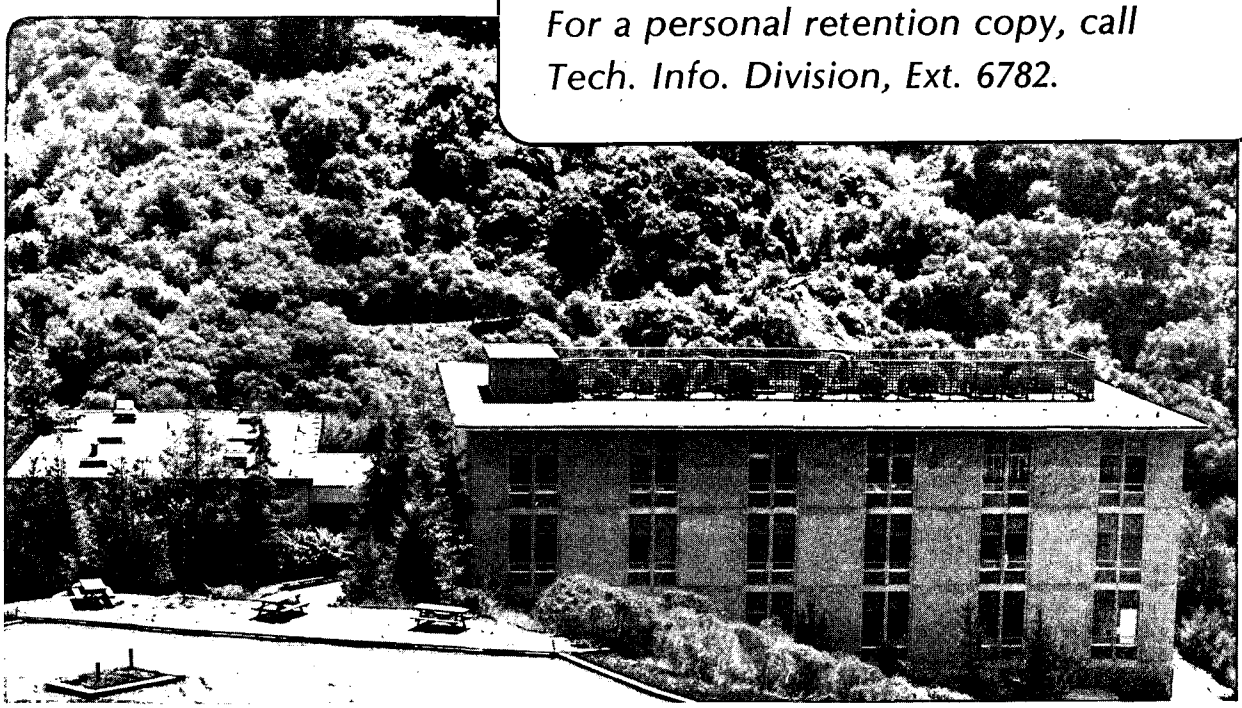

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MECHANISM OF THE REACTION OF MOLYBDENUM CARBONYL ALKYLS WITH MOLYBDENUM HYDRIDES: A MODEL FOR THE ALDEHYDE-PRODUCING STEP OF THE OXO PROCESS

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Abstract

The reaction of $CpMo(CO)_3R$ (1; Cp = η^5-C_5H_5; R = CH_3, C_2H_5) with $CpMo(CO)_3H$ (2), which produces RCHO, $[CpMo(CO)_2]_2$, and $[CpMo(CO)_3]_2$, occurs by way of two competing pathways. One involves reversible solvent-assisted migratory insertion (k_1) to form $CpMo(CO)_2$(solvent)COR (7), followed by attack of metal hydride on this intermediate (k_4). The other route involves the direct reaction of 1 with 2 (k_5). No hydrogen-deuterium kinetic isotope effect is observed on either k_4 or k_5 when $CpMo(CO)_3D$ is substituted for 2. Enhancing the Lewis basicity of the hydride by replacement of a carbonyl ligand with a phosphine to produce $CpMo(CO)_2(PMe_3)H$ increases k_5, while the larger metal-hydrogen bond strength of $CpW(CO)_3H$ is reflected in a decrease in k_4. Qualitative experiments further indicate that ionic intermediates or free radicals are present in neither pathway, and that a metal-metal bond is created prior to or concomitant with aldehyde release. These results suggest the presence of at least some metal-hydrogen bond breaking in the rate-limiting transition state of the reaction of $CpMo(CO)_3H$ with $CpMo(CO)_2$(solvent)COR, (k_4). In contrast with this, rate-determining formation of some dinuclear complex containing an intact Mo-H bond characterizes the direct reaction of 2 with $CpMo(CO)_3R$ (k_5). The structure of this intermediate cannot be determined unambiguously, but may be the datively bound species $Cp(CO)_3HMo$-$Mo(COR)(CO)_2Cp$.

That aldehyde is produced in the reaction of $CpMo(CO)_3H$ with $CpMo(CO)_3R$[1,2] (Scheme 1; Cp = η^5-C_5H_5; R = CH_3, C_2H_5) is noteworthy for several reasons. First, both carbon-carbon and carbon-hydrogen bonds are created under quite mild conditions. Generalization of this process would allow facile homologation of alkyl fragments through addition of a formyl unit.

Second, this transformation is similar to one proposed as the aldehyde-releasing step in cobalt-catalyzed hydroformylation. Although the suggestion of reductive elimination from a dihydridoacyl in the latter case has achieved widespread acceptance,[3,4] evidence for attack of hydridotetracarbonylcobalt(I) on an unsaturated intermediate has been presented (Scheme 2).[5] Study of the oxo process is complicated by the low stability of this cobalt hydride[6] and by the required high pressures of carbon monoxide and dihydrogen. More convenient examination of the related molybdenum system is enabled by its freedom from these difficulties.

A growing interest in the mechanism of dinuclear reductive elimination has provided greatest impetus for investigation of the interaction of $CpMo(CO)_3R$ and $CpMo(CO)_3H$. Several members of this class of reaction have been described,[7] and have displayed a wide variety of mechanisms. Among these have been proton transfer[7i] and M-C bond homolysis followed by hydrogen atom abstraction[7h] (Scheme 3). Reductive elimination of methane from $H(CH_3)Os(CO)_4$ has been postulated to require the intermediacy of a dinuclear hydridoacyl (Scheme 3),[7e] but in this case, as in others where similar proposals have been made, direct study of the hydrocarbon releasing step is not possible. The question thus arises whether reductive elimination can occur in a bimolecular step without prior group transfer (to form an RMH species), or, if not, whether it can occur from a bound H-M-M-R system without an initial 1,2 shift.

The results which are presented here suggest the necessity of forming a dinuclear species, but do not establish the coupling of ligands on adjacent metal centers.

Results

Clean and quantitative production of aldehyde, $Cp_2Mo_2(CO)_4$, and $Cp_2Mo_2(CO)_6$ occurs when solutions of $CpMo(CO)_3H$ (**2**) and $CpMo(CO)_3R$ (**1**) are subjected to mild heating. In the presence of at least an eight-fold molar excess of hydride, metal alkyl is consumed, and aldehyde produced, according to pseudo-first-order kinetics (eq. 1) over more than four half-lives.

$$-\frac{d[1]}{dt} = k_{obs}\,[1] \qquad (1)$$

Kinetics of Phosphine-induced Migratory Insertion. A discussion of migratory carbon monoxide insertion is appropriate at this point in view of its presumed role in the formation of aldehyde from a metal carbonyl alkyl. Because several other pertinent studies have led to the generation of contradictory conclusions,[8] the acyl-producing reaction of $CpMo(CO)_3R$ with methyldiphenylphosphine (Scheme 4) has been examined under carefully controlled conditions. Results of this work, which have been communicated previously,[9] are consistent with the mechanism illustrated in Scheme 5, and are summarized briefly here.

Separation of solvent polarity and donicity effects on migratory insertion has been achieved through the utilization of a series of methyl-substituted tetrahydrofuran media. These compounds allow independent variation of solvent nucleophilicity by virtue of their nearly identical dielectric constants.[9] Results obtained with this technique argue against rate enhancement caused by a generalized solvation effect in the system

studied, and instead indicate the importance of solvent coordination.

In the presence of excess phosphine in tetrahydrofuran (THF) at 60 °C, a pseudo-first-order rate expression describes the disappearance of methyl complex **1a** (Eq. 1). Variation of the ligand concentration results in changes in the observed rate constant (Fig. 1, Eq. 2) which are consistent with the existence of two routes for the transformation of $CpMo(CO)_3CH_3$ and

$$k_{obs} = \frac{k_1 k_2 [PMePh_2]}{k_{-1} + k_2 [PMePh_2]} + k_3[PMePh_2] \qquad (2)$$

methyldiphenylphosphine into $CpMo(CO)_2(PMePh_2)COCH_3$. Coordination of phosphine and migratory insertion may occur simultaneously, in a step which is independent of solvent donicity. In an alternative pathway, reaction with phosphine is preceded by reversible formation of a solvated acyl, **7a**. Alkyl migration in this case occurs at a rate which is a linear function of solvent nucleophilicity.[9,10]

Observation of competing saturation and second-order pathways (Fig. 1) is possible only in a restricted range of values of the ratio k_2/k_{-1}. Any perturbation which affects the partitioning of the intermediate acyl between reaction with phosphine and reversion to starting material thus may alter the measured kinetic order. A change in solvent may be sufficient to do so: the reaction of $CpMo(CO)_3CH_3$ with $PMePh_2$ in 2,5-dimethyltetrahydrofuran (Me_2THF), for example, is governed by superimposed first- and second-order kinetics (Fig. 1, Eq. 3). Replacement of THF with this weakly nucleophilic medium so greatly increases the magnitude of k_2 relative to that of k_{-1} that solvent-assisted migratory insertion becomes irreversible.

$$k_{obs} = k_1 + k_3[PMePh_2] \qquad (3)$$

Acyl production also occurs when $CpMo(CO)_3C_2H_5$ is treated with methyldiphenylphosphine (Scheme 4). While the reaction of **1b** with phosphine is too fast to be measured in THF, solvent-assisted alkyl migration is found to be irreversible in Me_2THF (i.e., Eq. 3 is satisfied; see Table 1). Larger rate constants for acyl formation (k_1 and k_3) in comparison with those associated with **1a** reflect the steric effect imposed by homologation.[11]

Kinetics of the Aldehyde-forming Reaction. An empirical approach to mechanism would suggest that the aldehyde-forming reaction of **1** and $CpMo(CO)_3H$ also occur by way of two avenues (Scheme 6). In both THF and toluene, however, $CpMo(CO)_3CH_3$ is subject to pure second-order disappearance in the presence of hydride. These observations suggest an unfavorable balance between the rates of the forward and reverse processes available to the solvated acyl **7** (i.e., deinsertion (k_{-1}) is much faster than trapping by **2** (k_4)). Consistent with this possibility, the overall velocities of these reactions are diminished relative to those with phosphine in the same solvents.

It seemed possible that more informative kinetic behavior might be obtained by retarding deinsertion from the intermediate acyl, perhaps by substitution of ethyl for methyl. Support for this analysis is provided by a study of the observed rate of reaction of $CpMo(CO)_3C_2H_5$ as a function of hydride concentration in Me_2THF (Fig. 2, Eq. 4, with rate constants indicated in Table 2). Saturation behavior indeed is observed in this case. $CpMo(CO)_3H$ may act directly upon **1b**, or, alternatively, upon some intermediate derived

$$k_{obs} = \frac{k_1 k_4 [2]}{k_{-1} + k_4 [2]} + k_5 [2] \qquad (4)$$

from **1b**. The rate constant ratio, k_4/k_{-1}, which governs consumption of the propionyl intermediate **7b** is very sensitive to the choice of medium. A

pathway which is saturating in hydride operates only in MeTHF and Me_2THF, being supplanted by first- and second-order pathways in toluene and THF, respectively (Eq. 5,6; Fig. 2, Table 2). Thus, k_4/k_{-1} appears to decrease with increasing solvent nucleophilicity.

$$k_{obs}^{toluene} = k_1 + k_5 [2] \quad (5)$$

$$k_{obs}^{THF} = \left(\frac{k_1 k_4}{k_{-1}} + k_5 \right) [2] \quad (6)$$

Implicit in the preceding reasoning and in the arguments which follow is the idea that reaction of $CpMo(CO)_3C_2H_5$ with both hydride and phosphine proceeds in part through the intermediacy of the solvated acyl **7b**. Several pieces of evidence justify this conclusion. Similar rate constants for entry into the saturation pathway in Me_2THF suggest formation of the same species in both cases. Thus, aldehyde is produced more rapidly in solvents which induce migratory insertion more efficiently.[9] Further, $CpW(CO)_3C_2H_5$ (**8b**), which undergoes alkyl migration much less rapidly than **1b**,[12] does not react with hydride. Finally, $CpMo(^{13}CO)_3H$ reacts with **1b** to form unlabelled propanal only,[13] implying the occurrence of migratory insertion in both the k_4 and k_5 pathways.

Kinetic Isotope and Metal Substitution Effects. $CpMo(CO)_3D$ (**2b**) reacts with **1b** to produce propanal-1-d, and the dimers **4** and **5**. Sufficient propanal-d_0 is produced only to account for the isotopic impurity of **2b**; no scrambling (< 5%) of deuterium into cyclopentadienyl groups occurs (quantitative formation of perprotiopropanal from **2a** and **1b** in deuterated media eliminates the possibility of exchange with solvent). Alkyl complex is depleted according to the same rate law and rate constants (Eq. 4, Table 3) which

govern reaction with $CpMo(CO)_3H$ in Me_2THF, i.e., there is no hydrogen-deuterium kinetic isotope effect.

Two group VI hydrides isostructural to **2a** are known, $CpCr(CO)_3H$ and $CpW(CO)_3H$ (**9a**). While the former does not undergo the anticipated reaction with molybdenum alkyls **1**,[14] the latter does, leading to quantitative, albeit slower, formation of aldehyde and of six dimers, four of them produced by disproportionation of the mixed metal species **10** and **11** (Scheme 7). First-order disappearance of $CpMo(CO)_3C_2H_5$ is observed when large excesses of the tungsten hydride are present (Eq. 1). The behavior of the observed rate constant as a function of hydride concentration is indicative of competing second-order and saturation pathways (Fig. 3, Eq. 7, Table 3; see Scheme 5 for definition of analogous rate constants). A molybdenum-tungsten rate ratio of

$$k_{obs} = \frac{k_1 k_4 [9]}{k_{-1} + k_4 [9]} + k_5 [9] \qquad (7)$$

5.7 is reflected in k_4/k_{-1}. Because the rate constant, k_1, for formation of the intermediate in the saturation route is so similar to those obtained for reaction with $PMePh_2$ or **1**, it too must be associated with solvent-assisted CO insertion. A consequence of this conclusion is that any isotope effect observed on k_4/k_{-1} must arise in k_4 alone. Metal substitution causes no change in the rate of direct reaction of hydride with alkyl (k_5).

Production of isotopically pure propanal-1-d results from treatment of **1b** with $CpW(CO)_3D$ (**9b**) in Me_2THF. Equation 7 also is obeyed by this reaction, which occurs without a noticeable hydrogen-deuterium kinetic isotope effect (Table 3).

Reaction with $CpMo(CO)_2(PMe_3)H$ (14). Phosphine substitution has been recognized as a means of perturbing the reactivity of metal carbonyl

complexes.[15] $CpMo(CO)_2(PMe_3)H$, for example, should be less acidic than **2a**[16] and should have a stronger metal-hydrogen bond.[7h] Aldehyde is produced in the reaction of phospine-substituted hydride[2] with **1b** in parallel saturation and second-order pathways (Eq. 8). Rate constants for both these routes are increased relative to those recorded for $CpMo(CO)_3H$ (Table 3).

$$k_{obs} = \frac{k_1 k_4 [14]}{k_{-1} + k_4 [14]} + k_5 [14] \qquad (8)$$

Discussion

An examination of the kinetics of the reaction of $CpMo(CO)_3R$ with $CpMo(CO)_3H$ leads to a simple empirical description of this process (Eq. 4). Complete mechanistic understanding, however, requires assignment of microscopic reaction steps to each of the macroscopic rate constants which has been defined. Two of these, k_1 and k_{-1}, most likely are associated with solvent-assisted migratory insertion and its reverse (Scheme 6), based upon comparisons with the acyl-forming reaction of **1** with methyldiphenylphosphine. Following is a discussion of the nature of the steps which are governed by the remaining rate constants.

Associated with both k_4 and k_5 are product-forming steps, which of necessity include hydrogen transfer from **2a** to the acyl carbon of the incipient aldehyde. Several general mechanisms for this process are shown in rough form in Scheme 8, with ancilliary ligands omitted. Most of these may be ruled out on the basis of qualitative experiments; more exact descriptions of the coordination spheres of those that remain will be presented.

Least complex of the routes to aldehyde is metal-carbon and metal-hydrogen bond breaking in concert with metal-metal and carbon-hydrogen bond formation. Transfer of hydrogen (in one of several oxidation states) may

precede reductive elimination from a hydridoacyl (**15**, **16**, or **17**) thus formed. Sequential Mo-C bond homolysis, yielding a radical pair, and abstraction of hydrogen from **2a** by an acyl radical also would produce aldehyde, as would electron transfer followed by further reacton of the newly-created ion pair, **21** and **22**. Finally, ligature of the two interacting transition metal centers may yield some neutral, diamagnetic species (e.g., **18**, **19**, or **20**) which lies on the reaction coordinate.

Of these alternatives, two may be excluded on the basis of previous results. When heated in both the presence and absence of hydride, mixtures of $CpMo(CO)_3CH_3$ and $(\eta^5\text{-}C_5H_4CH_3)Mo(CO)_3CD_3$ form no $CpMo(CO)_3CD_3$.[1] Such behavior indicates that reversible metal-carbon bond homolysis, leading to acetyl and molybdenum-centered radicals, is not important under the reaction conditions.

Because $CpMo(CO)_3H$ is an acid of moderate strength (pK_a = 13.9 in acetonitrile[17]), it seemed possible that aldehyde was being formed as the result of a proton transfer step. However, treatment of **1a** with acids weaker, of the same strength, and stronger than **2a** (acetic acid,[2] 2,4-dinitrophenol, and trifluoroacetic acid,[2] respectively) in no case resulted in production of ethanal. That the less acidic hydride, $CpMo(CO)_2(PMe_3)H$, reacts more rapidly than does its unsubstituted parent confirms the absence of a proton transfer in the mechanism under study.

Further results argue against the formation of any ionic intermediates in the reaction of **1** with **2**. Proton, hydride, or outer sphere electron transfer processes should produce $CpMo(CO)_n^-$ (n = 2 or 3) either directly or after reductive elimination of aldehyde from some previous intermediate. This anionic moiety should be capable of being trapped by some electrophile.[18] In fact, when $CpMo(CO)_3C_2H_5$ and **2a** are heated in neat methyl iodide-$\underline{d}_3$ (with which $CpMo(CO)_3^-$ should react at > 1 M^{-1} s^{-1}), no $CpMo(CO)_3CD_3$ is observed by

NMR spectroscopy.

The dependence of rates upon reaction medium supports this interpretation. Different solvents favor different partitionings of the acyl intermediate **7b** between reaction with hydride and reversion to starting material. As k_4 and k_{-1} (Scheme 6) both vary simultaneously and kinetically are inseparable, it is impossible to associate changes in the former with solvent properties. This is not true of the rate constant for direct reaction between alkyl and hydride, k_5. Variation of the solvent from MeTHF to toluene, which produces a large change in the ability of the medium to support ion pairs,[19] causes only a five-fold change in k_5 (Table 2). Such a low sensitivity to solvent is inconsistent with an ionic mechanism.

(The origin of the small solvent effect which is observed on k_5 is not obvious. Within experimental error, the analogous rate constant, k_3, for direct attack of $PMePh_2$ on $CpMo(CO)_3CH_3$ is the same in THF and toluene. Thus, in contrast to acyl formation, the bimolecular pathway leading to aldehyde production may involve either some charge separation or solvent reorganization. Because the magnitudes of the measured perturbations are so insubstantial, further interpretation is difficult.)

Two experiments provide evidence that a bond is formed between hydride and solvated acyl intermediate concurrent with or prior to aldehyde release. Only the mixed dimers $(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_5H_4CH_3)Mo_2(CO)_n$ (n = 4, 6) are observed at short reaction times[2,20] when $(\eta^5\text{-}C_5H_4CH_3)Mo(CO)_3H$ and **1b** are heated together (Scheme 9). Similarly, treatment of $CpMo(CO)_3C_2H_5$ with $CpW(CO)_3H$ initially leads to exclusive production of the bimetallic dimers $Cp_2MoW(CO)_n$. If the premise of cage escape competitive with cage recombination is accepted,[22] these findings, together with the results already mentioned, militate against the operation of pathways which produce unbound metal fragments.

Qualitative experiments thus are inconsistent with the operation of pathways containing proton, hydrogen, or electron transfer or homolytic steps. Elimination of these possibilities implicates either a reaction coordinate in which there is no local minimum other than that occupied by the solvated acyl **7**, or formation of one or more intermediates in which both metal centers are joined by a non-electrostatic interaction. These intermediates might arise either through displacement of solvent from $CpMo(CO)_2(S)COR$ (k_4) or induction of CO insertion in $CpMo(CO)_3R$ (k_5) by hydride.

Cleavage of a metal-hydrogen bond is required for the formation of propanal from $CpMo(CO)_3H$ and $CpMo(CO)_3C_2H_5$. Increasing the strength of this bond, e.g., by substituting tungsten for molybdenum,[23] would be expected to result in a decrease in reaction rate if the metal-hydrogen bond order is lowered in or prior to a rate-determining step. Aldehyde release or generation of the hydride-bridged intermediate **23** in a one step process should cause this to occur; creation of some other intermediate followed by fast reductive elimination should not.

Alkyl complex is consumed more slowly in the presence of $CpW(CO)_3H$ than that of $CpMo(CO)_3H$. Careful kinetic analysis, however, reveals that both hydrides display the same bimolecular rate constant, k_5, for direct reaction with $CpMo(CO)_3C_2H_5$ (Table 3). This result is unexpected in view of the higher metal-hydrogen bond energy of the tungsten complex.[23] A plausible explanation for this seeming anomaly is rapid formation of aldehyde subsequent to some slow step. In this case, k_5 would be defined as the rate of production of an intermediate through a transition state in which the metal-hydrogen bond still is intact.

Whereas the rate of bimolecular reaction of $CpMo(CO)_3C_2H_5$ with hydrides (k_5) is insensitive to metal-hydrogen bond dissociation energy, that of the

postulated intermediate $CpMo(CO)_2(Me_2THF)(COC_2H_5)$ (k_4) is not. In this step aldehyde is produced more rapidly in the presence of $CpMo(CO)_3H$ than of $CpW(CO)_3H$ ($k_4^{MoH}/k_4^{WH} = 5.7$). Other properties of the tungsten hydride, for example, its size and basicity (expected to be the same as and greater than those of the molybdenum complex, respectively[25,17]), will not account easily for the observed difference in reactivity. A rate limiting transition state in which tungsten-hydrogen bond order is less than one clearly is implicated.

Two descriptions of the route governed by k_4 are consistent with the data thus far presented. Metal-hydrogen bond breaking may succeed some bimolecular reaction of $CpMo(CO)_2(Me_2THF)COC_2H_5$ and $CpMo(CO)_3H$, or may occur without the intervention of some other step. Use of a hydride with altered reactivity allows for further examination of these eventualities.

Alkyl complex is consumed more rapidly in the presence of $CpMo(CO)_2(PMe_3)H$ than that of its unsubstituted parent. Only the k_5 pathway is accelerated by exchange of a phosphine for a carbonyl, however; k_4 is left unchanged within experimental error (Table 3). If this reaction were to involve only metal-hydrogen bond breaking, a retardation of rate relative to that $CpMo(CO)_3H$ should occur, based upon the difference in hydride M-H bond strengths.[7h] Significant metal-metal bond character might be created at the same time as or prior to metal-hydrogen bond scission in order to explain the lack of effect of phosphine substitution.

Because there is a large difference between Mo-H and Mo-D zero point vibrational energies,[26] a kinetic isotope effect on metal-hydrogen bond breaking might be anticipated. In fact, no effect on either rate constant is observed. Few comparisons of metal hydride and deuteride activity have been communicated, and hence there is little information against which this result might be judged. Dinuclear reductive elimination of methane from

$H(CH_3)Os(CO)_4$ proceeds with a small primary kinetic isotope effect: $k_H/k_D = 1.5$.[29] The lack of any effect in the reaction of $CpMo(CO)_3H$ with $CpMo(CO)_3C_2H_5$ most likely is a consequence of transfer of hydrogen after a rate determining step or in a transition state of low symmetry.[30]

No completely satisfactory mechanism may be constructed based upon the results outlined above. One which is consistent with the data obtained assumes release of aldehyde from two distinct intermediates (Scheme 10). Rate-limiting formation of a metal-metal bond concomitant with alkyl migration to produce the dinuclear species **24** reasonably may be associated with k_5. Mo-Mo and Mo-W bonds are of equal strength,[21] and according to the Hammond postulate[31] should be formed at the same rate in an endothermic reaction. Any disparity in the Lewis basicities of $CpMo(CO)_3H$ and $CpW(CO)_3H$ in this way could be masked by the energetic requirements of CO insertion.

Rate-limiting creation of the hydride-bridged complex **23** through displacement of solvent from $CpMo(CO)_2$(solvent)COR constitutes the alternative pathway (k_4). Because the original metal-hydrogen bond would be weakened in the formation of this adduct, replacement of $CpMo(CO)_3H$ with $CpW(CO)_3H$ would be expected to, and does, retard the rate of reaction. No hydrogen-deuterium kinetic isotope effect is observed, however, possibly as a consequence of the low symmetry of **23**.

Several objections to this proposed mechanism may be raised. It requires two additional intermediates and two transition states for aldehyde production. Further, it is unclear why displacement of solvent from $CpMo(CO)_2$(solvent)COR should entail formation of a hydrogen bridge (**23**), while induction of migratory insertion in $CpMo(CO)_3R$ occurs formation of a metal-metal bond. However, no obvious means of avoiding these objections or similar ones is suggested by the data.

Two distinct modes of dinuclear reductive elimination involving $CpMo(CO)_3H$ now have been uncovered. This hydride may act merely as a protic acid, yielding a mononuclear complex from which alkane release may occur (Scheme 3).[7i] Alternatively, formation of some species in which hydrogen and acyl donor metals are linked may be a prerequisite to aldehyde production. The diversity of dinuclear elimination mechanisms[7] thus is mirrored in the reactions of one transition metal hydride.

Experimental

General. Unless otherwise indicated, reactions and manipulations were carried out at 20 °C under a dinitrogen atmosphere in a Vacuum Atmospheres 553-2 Dri-Lab with attached M60-40-1H Dri-Train. Removal of solvents from reaction mixtures and the preparation of sealed tubes were accomplished using conventional vacuum line techniques.

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian EM-390 spectrometer, or at 200 or 250 MHz on spectrometers built by Mr. Rudi Nunlist of the U.C. Berkeley NMR laboratory, and are reported in parts per million downfield from tetramethylsilane. Infrared (IR) spectra were recorded on a Perkin-Elmer 283 spectrometer using 0.10 mm NaCl solution cells. Melting points were obtained using a Thomas-Hoover capillary apparatus and are uncorrected.

High pressure liquid chromatography (HPLC) was performed on a Beckman 324 gradient chromatograph, which included two computer-controlled two piston pumps, a dual chamber mixer, and a high pressure rotary valve injector with a 10 uL sample loop. Detection of eluted compounds was accomplished using a Hitachi 100-10 UV/Vis spectrophotometer with attached Altex 155-00 flow cell. Peaks were quantified with a Hewlett-Packard 3390A integrator. Compounds were separated on an Altex 4.6 mm X 25 cm stainless steel column prepacked with Ultrasphere-ODS (regular 5 um silica particles treated with an octadecylchlorosilane) and protected with a precolumn packed with Vydac reversed phase adsorbant. Elution was accomplished using a 1.2 mL/m flow of 30% v/v water in acetonitrile (degassed with an argon purge) at a nominal pressure of 1700 psi.

With the following exceptions, reagents were obtained from commercial sources and used as received. Tetrahydrofuran and ether were distilled from

sodium and benzophenone under dinitrogen. Tetrahydrofuran-$\underline{d}_8$, benzene-$\underline{d}_6$, 2-methyltetrahydrofuran, and 2,5-dimethyltetrahydrofuran (equimolar cis and trans) were vacuum distilled from Na/Ph_2CO. Iodomethane, iodoethane, and iodomethane-$\underline{d}_3$ were vacuum distilled onto copper wire and stored in the dark. Trimethylphosphine was vacuum distilled and stored under vacuum. $CpM(CO)_3R$ (M = Mo, W; R = H, D, CH_3, C_2H_5) were synthesized according to published procedures and exhibited satisfactory spectroscopic and physical properties.[28]

Measurement of Reaction Rates. Migratory CO Insertion. Phosphine-induced migratory insertion reactions were followed by monitoring the disappearance of the symmetric CO stretch of **1b** (2020 cm^{-1}). In a typical run, 0.150 mL of a 2.00 M stock solution of $PMePh_2$, 0.120 mL of a stock solution of **1b**, and 2.730 mL of Me_2THF were mixed in a 10 X 75 mm test tube to prepare a solution 0.100 M in phosphine and 0.010 M in alkyl. The tube was capped with a septum and placed in a water bath at 59.9 $\pm$ 0.1 °C under a positive dinitrogen pressure. At regular intervals, a portion of the solution was forced into an IR cell through a syringe needle, and a spectrum recorded.

Aldehyde Formation. Because **1** and **2** have coincident symmetric CO stretching absorptions in the infrared and identical UV/Vis spectra, and because the non-deuterated solvents utilized prevented the use of ^1H NMR spectroscopy, an alternative method was required for the measurement of reaction progress. Analytical reversed phase high pressure liquid chromatography allowed quantification of reactants. A typical experiment involved the mixing of 0.100 mL of a 2.00 M stock solution of **2a**, 0.020 mL of an 0.25 mL stock solution of **1b**, 0.020 mL of isopropylbenzene (internal standard) and 1.80 mL of Me_2THF. The resulting solution was heated at 59.9 $\pm$ 0.1 °C under an atmosphere of dinitrogen. Occasional aliquots were withdrawn with a syringe and injected into the HPLC. The concentration of **1b** was monitored by

measuring its absorbance at 254 nm relative to that of isopropylbenzene. Global rate constants were calculated using a non-linear least squares approach, assuming equal errors in the individual observed rate constants. Small changes were made sequentially in k_1, k_4/k_{-1}, and k_5 while allowing the other two to vary so that a minimum in χ^2 could be attained, and the process repeated until self-consistency was achieved. Standard deviations were estimated by determining the change in each rate constant or rate constant ratio necessary to increase χ^2 by one, given an approximate standard deviation in each k_{obs} of 10 per cent.[32]

Synthesis of $CpMo(CO)_2(PMePh_2)COC_2H_5$ (6b). A 50 mL round-bottomed flask fitted with a magnetic stirring bar was charged with $CpMo(CO)_3C_2H_5$ (0.548 g, 0.200 mmol), THF (20 mL), and methyldiphenylphosphine (0.400 g, 0.200 mmol). After it was stirred for 4.5 h at room temperature, solvent was removed from the resulting mixture, leaving a yellow oil, which was recrystallized from toluene/pentane. After traces of this latter solvent were removed under vacuum, 0.910 g (96.0%) of material was obtained, mp 105.5-107 °C, IR (THF) 1936s, 1855vs, 1626s cm^{-1}, NMR (C_6D_6) δ 7.36 (m, 4H), 4.80 (s, 5H), 3.33 (quartet, J = 7.3 Hz, 2H), 1.78 (d, J = 8.3 Hz, 3H), 1.20 (t, J = 7.3 Hz, 3H). Anal. Calcd for $C_{23}H_{23}MoO_3P$: C, 58.24; H, 4.89. Found: C, 58.41; H, 5.00.

Reaction of $CpMo(CO)_3CH_3$ with 2,4-Dinitrophenol. An NMR tube with attached ground glass joint was charged with **1a** (14 mg, 0.054 mmol) and 2,4-dinitrophenol (40 mg, 0.22 mmol) and capped with a vacuum stopcock. After evacuation, THF-d_8 (0.78 mL) was vacuum transferred into the tube, which then was sealed. No reaction of the resulting solution could be discerned by NMR after 30 m at room temperature or 40 m at 59.9 °C. Prolonged heating (20 h) caused the contents of the tube to turn from yellow to red to black, and also

led to the formation of a black precipitate. No resonances attributable to acetaldehyde were visible in a high field NMR spectrum of the black solution.

Reaction of $CpMo(CO)_3C_2H_5$ with $CpMo(CO)_3H$ in CD_3I. To an NMR tube attached to a ground glass joint were added **1b** (26 mg, 0.095 mmol) and **2a** (23 mg, 0.094 mmol). Iodomethane-$\underline{d}_3$ was vacuum transferred into the tube, now capped with a vacuum stopcock, which then was sealed. Resonances corresponding to **1b** (δ 5.70, 2.04, 1.75) and **2a** (δ 5.83, -5.23), and small amounts of propanal (δ 10.13, 2.80) and **4** (δ 5.60) were visible in the NMR spectrum of the freshly prepared solution. The reaction mixture was stored at room temperature in the dark, and was examined periodically by NMR spectroscopy until no hydride resonance was evident. While the peaks associated with propanal, **4**, and $CpMo(CO)_3I$ (δ 6.04, formed by reaction of **2a** and **5** with CD_3I) increased in area with time, at no point was the cyclopentadienyl resonance of $CpMo(CO)_3CD_3$ (δ 5.72) visible (limit of detectability ca. 5%). Propanal was produced in approximately 67% yield, indicating that one-third of the metal hydride initially present had reacted with solvent.

Reaction of $CpMo(CO)_3D$ with $CpMo(CO)_3C_2H_5$. THF-$\underline{d}_8$ (0.88 mL) was vacuum transferred into a NMR tube attached to a ground glass joint, capped with a vacuum stopcock, and charged with **1b** (23 mg, 0.084 mmol) and **2b** (30 mg, 0.12 mmol). The tube then was sealed and heated to 59.9 °C. In an NMR spectrum recorded after three half-lives (ca. 40 m), the aldehydic proton resonance had sufficient magnitude only to account for the starting protium content of **2b** (6%).

Reaction of $CpW(CO)_3H$ with $CpMo(CO)_3C_2H_5$. An NMR tube fixed to a ground glass joint and closed with a vacuum stopcock was sealed after it had been charged with **1b** (27 mg, 0.10 mmol), **9a** (33 mg, 0.10 mmol), and (by vacuum transfer) THF-$\underline{d}_8$ (0.53 mL). Periodic NMR analysis of the contents of the

tube, which was stored at room temperature in the dark, indicated the disappearance of starting materials ($t_{1/2}$ ca. 1.5 X 10^5 s) and the concurrent quantitative formation of propanal and of a mixture of cyclopentadienyl-containing products. Removal of solvent at the completion of the reaction and dissolution of the resulting red solid in chloroform-d allowed NMR spectroscopic identification of $Cp_2MoW(CO)_6$[21] (δ 5.36, 5.32), $Cp_2MoW(CO)_4$[33] (δ 5.36, 5.30), and minor amounts of **4**, **5**, **12**[34] (δ 5.22), and **13**[21] (δ 5.33).

Reaction of $CpW(CO)_3D$ with $CpMo(CO)_3C_2H_5$. An NMR tube with attached ground glass joint was loaded with **1b** (8.3 mg, 0.030 mmol) and **9b** (10. mg, 0.031 mmol), and then capped with a vacuum stopcock in a dry box. THF-d_8 (0.68 mL) was vacuum distilled into the tube, which subsequently was sealed. Heating at 59.9 °C over a period of 1 d resulted in complete consumption of starting materials. An NMR spectrum of the product solution showed resonances associated with propanal-1-d (< 10% propanal-1-h produced) and the dimers **4**, **5**, and **10-13**.

Synthesis of $CpMo(CO)_2(PMe_3)H$ (14). A procedure analogous to that of Green[35] was used. $CpMo(CO)_3H$ (1.50 g, 6.10 mmol), THF (25 mL), and a magnetic stirring bar were placed in a 100 mL round-bottomed flask, which then was sealed with a vacuum stopcock. The flask was evacuated after its contents were frozen in liquid nitrogen. A known volume of trimethylphosphine vapor (484 mL, 380 Torr, 6.29 mmol) was vacuum transferred into the reaction vessel. After thawing, the resulting mixture was stirred for 1.5 h at room temperature. Removal of solvent under vacuum left a yellow solid, which was sublimed (60 °C, 10^{-2} Torr) to give 1.50 g (80%) of yellow, crystalline, air stable material, mp 78-79 °C, IR (THF) 1940s, 1858s cm^{-1}, NMR (C_6D_6) δ 4.75 (s, 5H), 1.02 (d, J = 9 Hz, 3H), -5.90 (s, br, 1H). Anal. Calcd for $C_{10}H_{15}MoO_2P$: C, 40.83; H, 5.14. Found: C, 40.69; H, 5.21.

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Table 1. Rate constants for reaction of **1a** or **1b** with $PMePh_2$ at 59.9±0.1°C. Rate constants are defined as in Scheme 3.[a]

Complex	Solvent	$10^4k_1(s^{-1})$	$k_2/k_1(M^{-1})$	$10^4k_3(M^{-1}s^{-1})$
1a	THF	7.78±0.14	96±8	1.73±0.16
1a	Me_2THF	0.23±0.06	>500	1.67±0.14
1b	Me_2THF	5.29±0.40	>500	69.1±1.8

[a] Uncertainties listed are 95% confidence limits.

Table 2. Rate constants for reaction of $CpMo(CO)_3C_2H_5$ with $CpMo(Co)_3H$ in various solvents at 59.9±0.1°C. Rate constants are defined as in Scheme 6.[a]

Solvent	$10^4k_1(s^{-1})$	$k_4/k_{-1}(M^{-1})$	$10^4k_5(M^{-1}s^{-1})$
THF[b]	----	----	----
MeTHF	43.4	1.77	7.49
Me_2THF	4.90	19.8	1.48
PhMe	0.21	>500	0.62

[a] Estimated 95% confidence limits are ±10% for k_1 and ±20% for k_4/k_{-1} and k_5; see experimental section.
[b] $(k_1k_4/k_{-1} + k_5) = 71.3 \pm 0.28 \times 10^{-4}\ M^{-1}\ s^{-1}$.

Table 3. Rate constants for reaction of $CpMo(CO)_3C_2H_5$ with various reagents in Me_2THF at 59.9±0.1°C. Rate constants defined as in Scheme 6.[a]

Reagent	$10^4k_1(s^{-1})$	$k_4/k_{-1}(M^{-1})$	$10^4k_5(M^{-1}s^{-1})$
$PMePh_2$	5.29±0.40	>500[b]	69.1±0.18[c]
$CpMo(CO)_3H$	4.90	19.8	1.48
$CpMo(CO)_3D$	4.89	19.5	1.39
$CpW(CO)_3H$	4.97	3.5	1.35
$CpW(CO)_3D$	4.69	3.5	1.42
$CpMo(CO)_2(PMe_3)H$	4.46	28.7	8.31

[a] See footnote b, Table 2.
[b] k_2/k_{-1}.
[c] k_3.

Figure Captions

Figure 1. Dependence of k_{obs} for conversion of $CpMo(CO)_3CH_3$ to $CpMo(CO)_2(PMePh_2)COCH_3$ upon $PMePh_2$ concentration at 59.9 °C in THF (●) and Me_2THF (○).

Figure 2. Dependence of k_{obs} for conversion of $CpMo(CO)_3C_2H_5$ to ethanal upon hydride concentration in Me_2THF at 59.9 °C using the following hydrides: (●) $CpMo(CO)_3H$; (○) $CpMo(CO)_3D$; (■) $CpW(CO)_3H$; (□) $CpW(CO)_3D$.

Figure 1

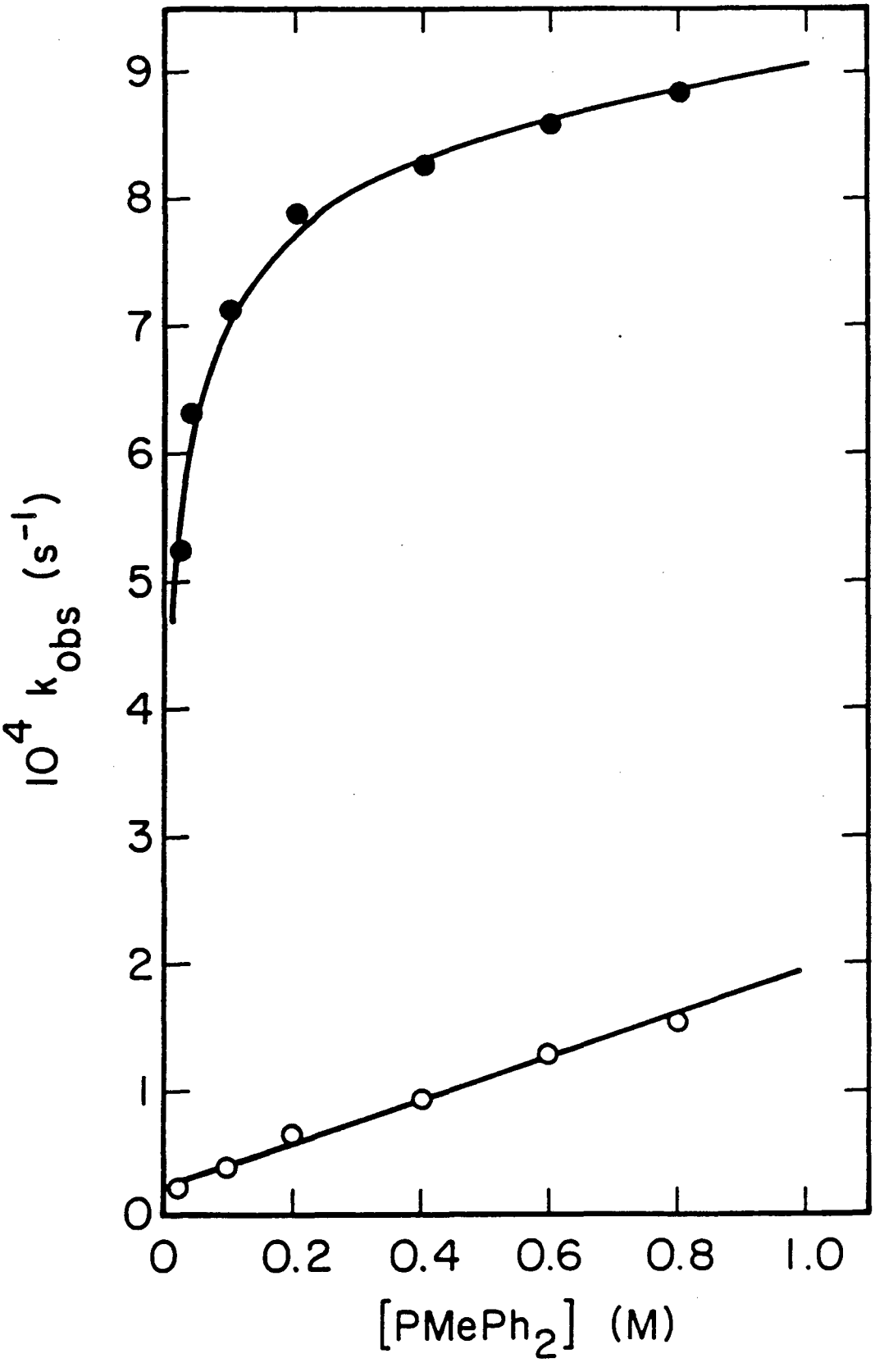
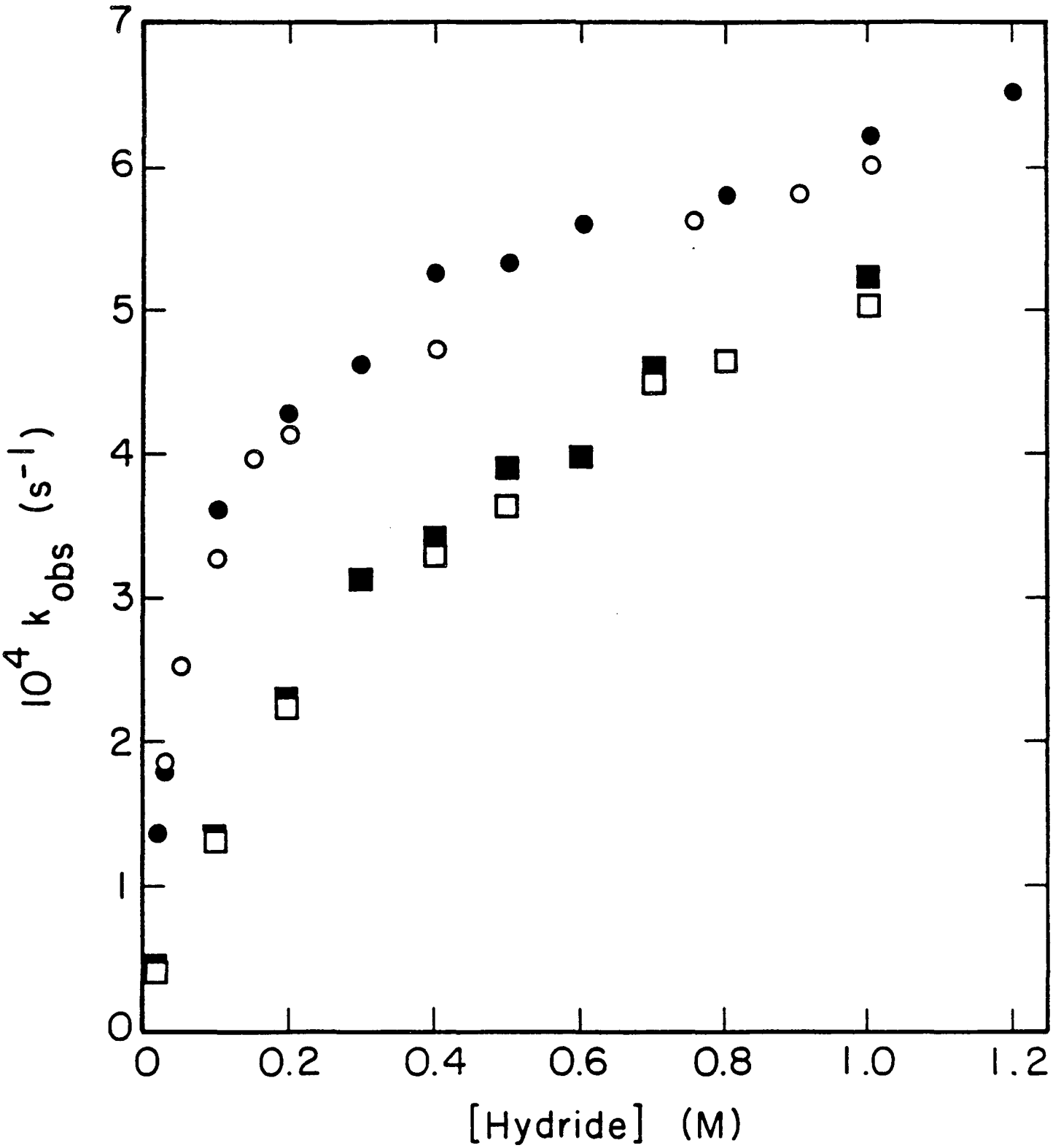
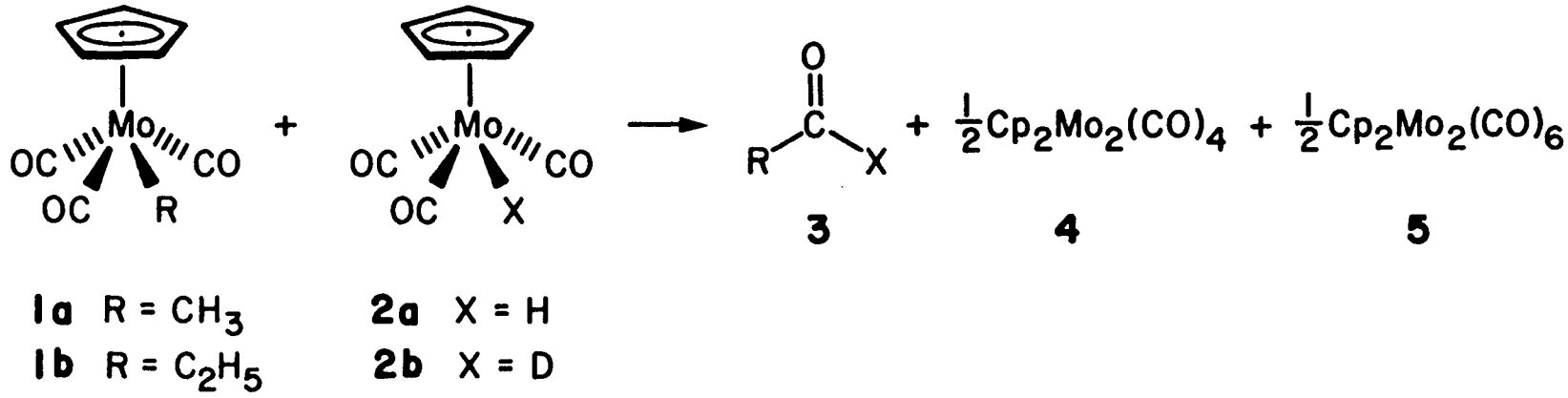


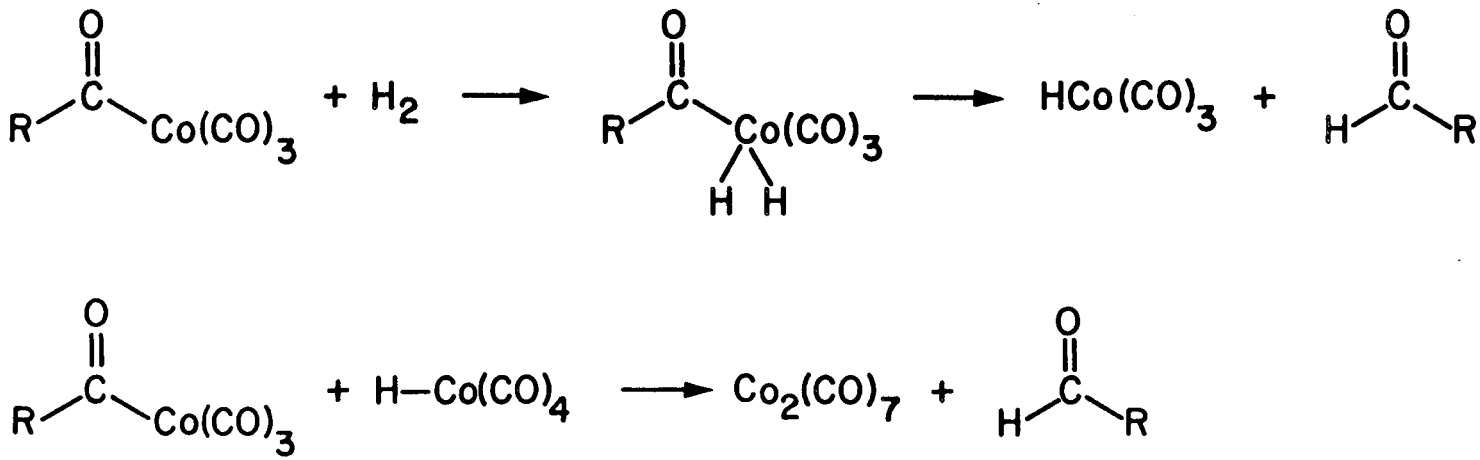
Figure 2



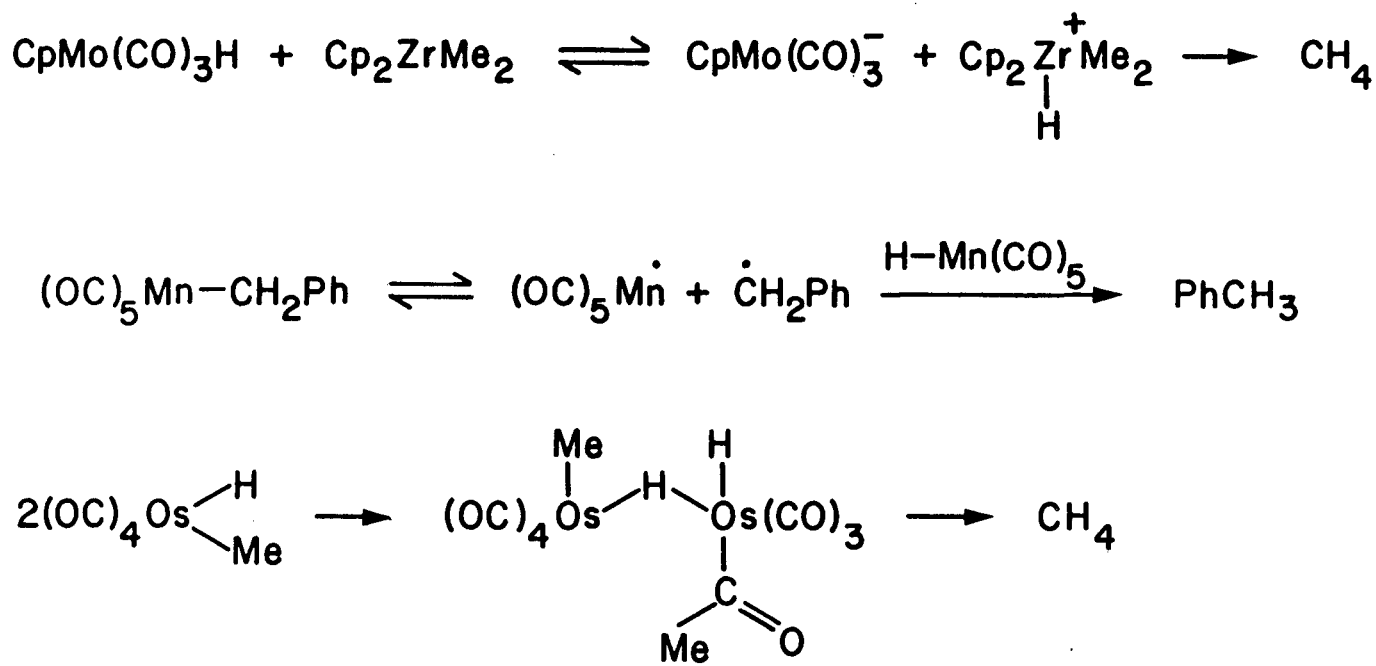
Scheme I


Mo
OC
CO
OC
R
+
Mo
OC
CO
OC
X
O
C
R
X
+ $\frac{1}{2}Cp_2Mo_2(CO)_4$ + $\frac{1}{2}Cp_2Mo_2(CO)_6$
3
4
5
1a R = CH_3
1b R = C_2H_5
2a X = H
2b X = D

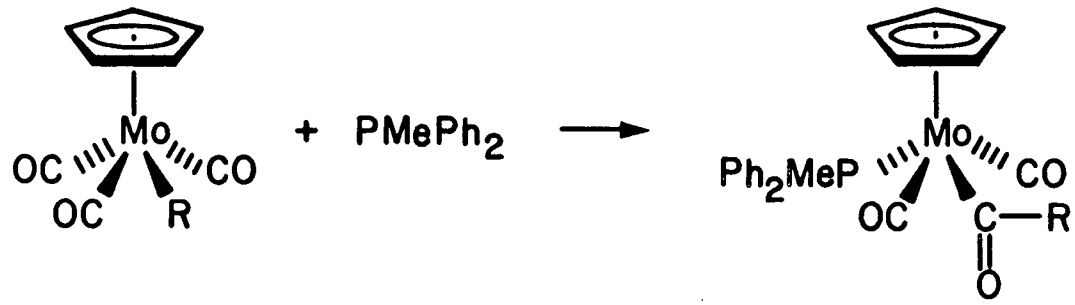
Scheme 2


O
R C Co(CO)3
+ H2
R C Co(CO)3
H H
HCo(CO)3
+
H C R
O
R C Co(CO)3
+ H—Co(CO)4
Co2(CO)7
+
H C R

Scheme 3

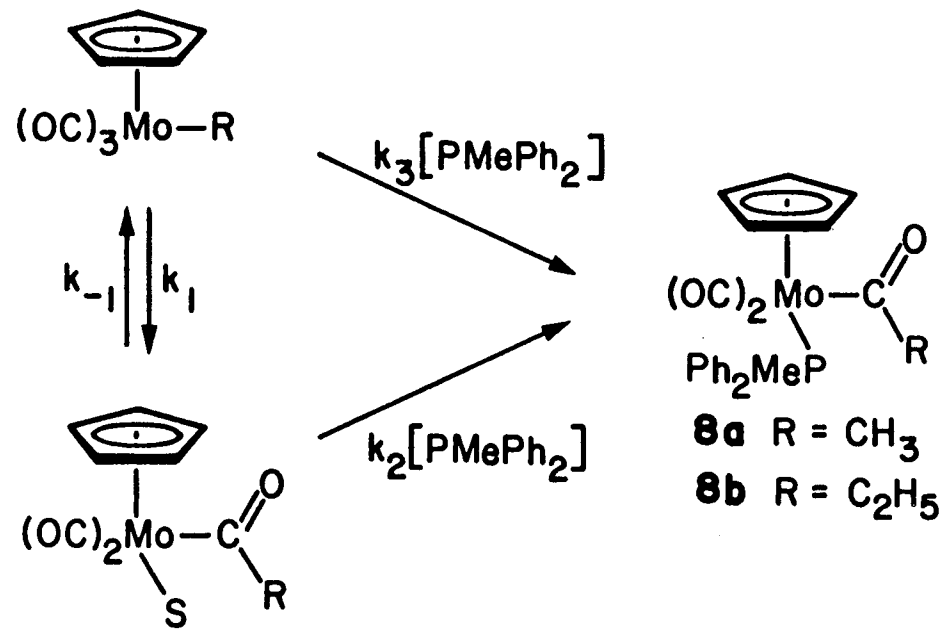

CpMo(CO)3H + Cp2ZrMe2 ⇌ CpMo(CO)3− + Cp2ZrMe2 (Zr+, H) → CH4
(OC)5Mn−CH2Ph ⇌ (OC)5Mn· + ·CH2Ph
H−Mn(CO)5
PhCH3
2(OC)4Os(H)(Me) → (OC)4Os(Me)−H−Os(CO)3(C(Me)=O) → CH4

Scheme 4



6a R = CH_3
6b R = C_2H_5

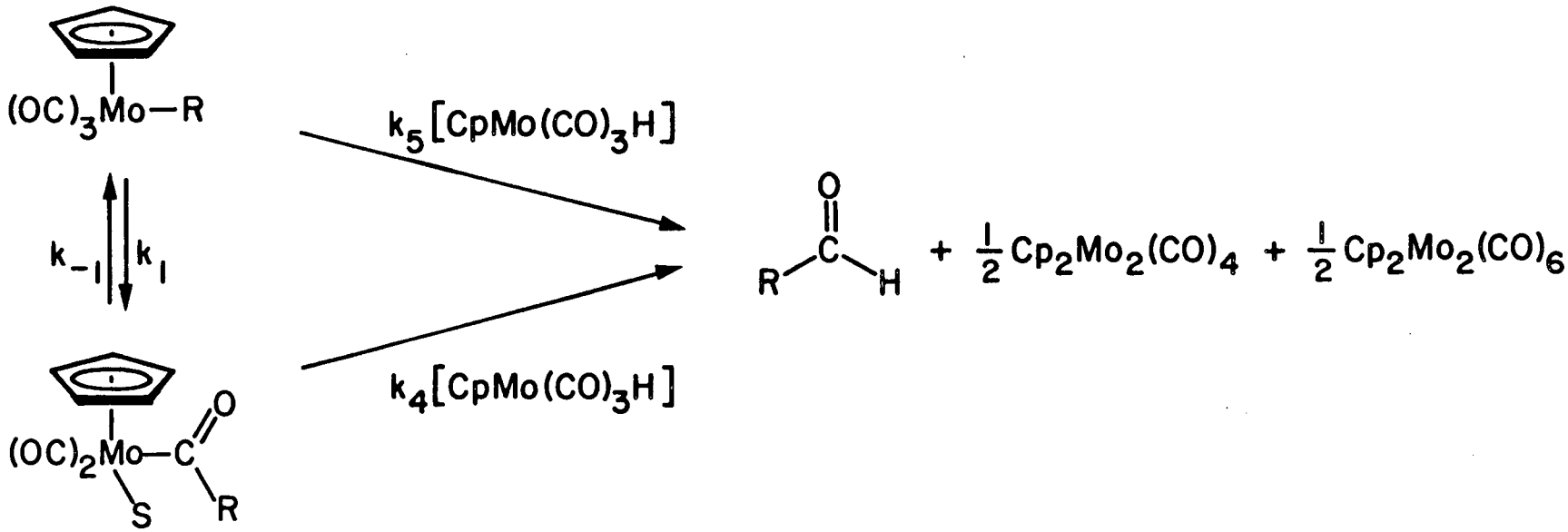
Scheme 5



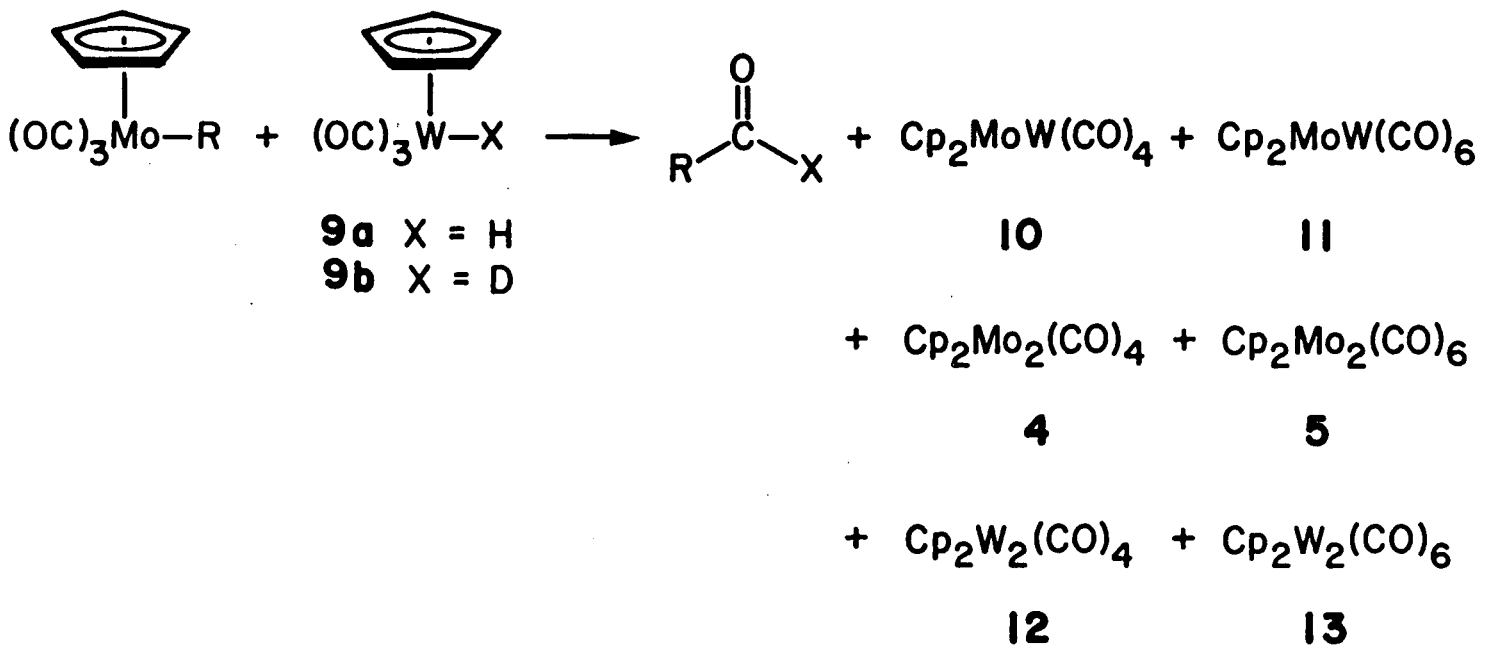
7a R = CH_3
7b R = C_2H_5

S = Solvent

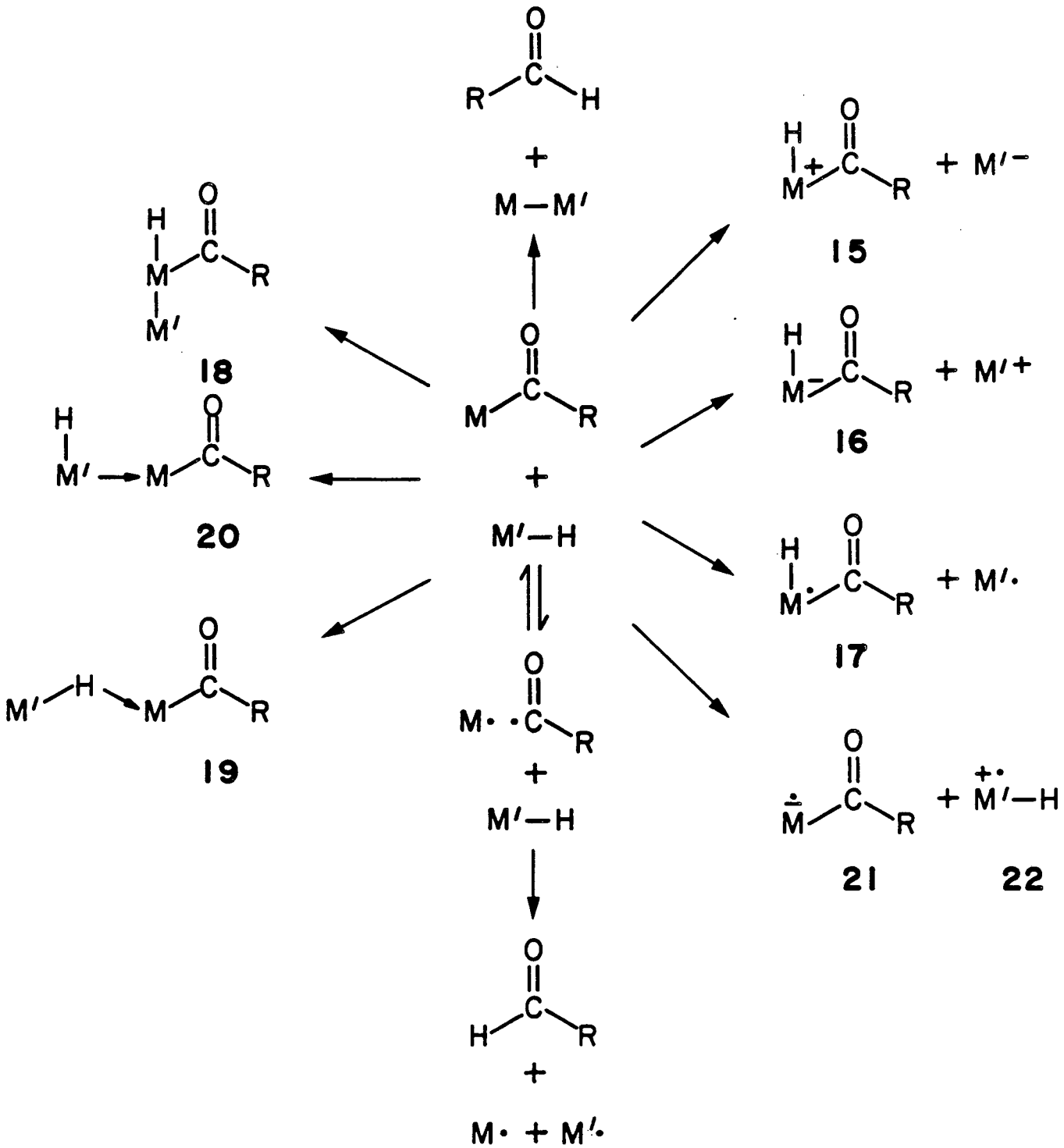
Scheme 6


(OC)3Mo—R
k-1
k1
(OC)2Mo—C
O
S
R
k5[CpMo(CO)3H]
k4[CpMo(CO)3H]
O
C
R
H
+ 1/2 Cp2Mo2(CO)4 + 1/2 Cp2Mo2(CO)6

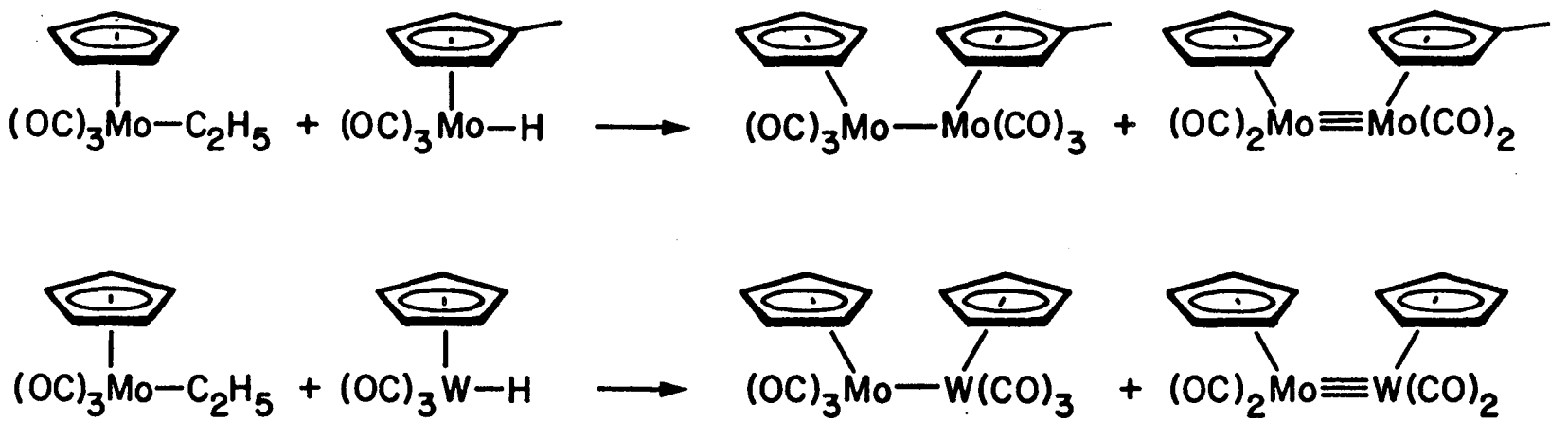
Scheme 7


(OC)3Mo—R
+
(OC)3W—X
9a X = H
9b X = D
O
R
C
X
+ Cp2MoW(CO)4 + Cp2MoW(CO)6
10
11
+ Cp2Mo2(CO)4 + Cp2Mo2(CO)6
4
5
+ Cp2W2(CO)4 + Cp2W2(CO)6
12
13

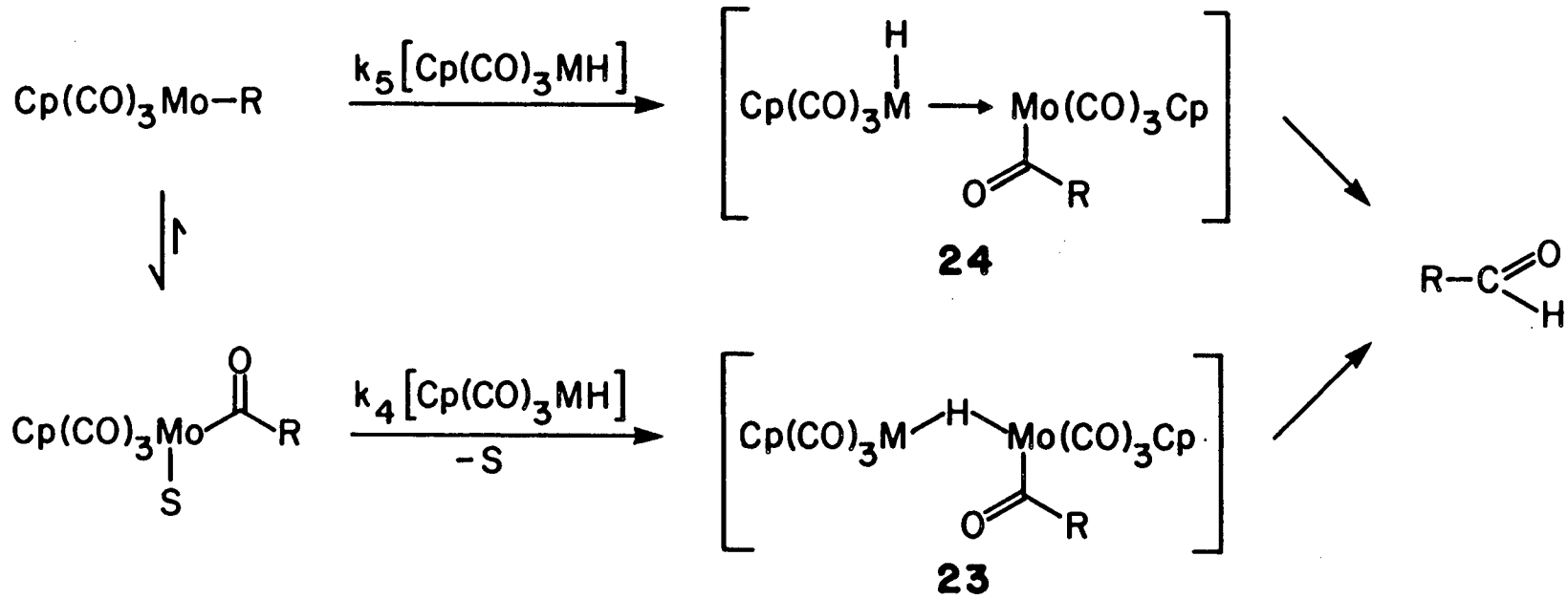
Scheme 8



Scheme 9


(OC)3Mo—C2H5 + (OC)3Mo—H
(OC)3Mo—Mo(CO)3 + (OC)2Mo≡Mo(CO)2
(OC)3Mo—C2H5 + (OC)3W—H
(OC)3Mo—W(CO)3 + (OC)2Mo≡W(CO)2

Scheme 10


Cp(CO)3Mo–R
k5[Cp(CO)3MH]
Cp(CO)3M
H
Mo(CO)3Cp
O
R
24
R–C
O
H
Cp(CO)3Mo
O
R
S
k4[Cp(CO)3MH]
–S
Cp(CO)3M
H
Mo(CO)3Cp
O
R
23

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