Bimetallic Activation of Coordinated Ligands. Attempts at Generating μ_2-Formyl Complexes from μ_2-Hydrides

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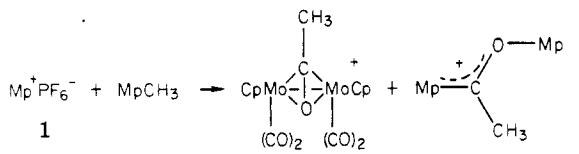
Received September 29, 1983

The Mo hydride complexes $Cp(CO)_3MoH$ and $Cp(CO)_2PPh_3MoH$ react with their respective organometallic Lewis acids $Cp(CO)_3Mo^+PF_6^-$ and $Cp(CO)_2PPh_3Mo^+PF_6^-$ to give exclusively the μ-hydride salts $Cp(CO)_3Mo{-}H{-}Mo(CO)_3Cp^+$ and *trans,trans*-$Cp(CO)_2PPh_3Mo{-}H{-}Mo(CO)_2PPh_3Cp^+$. No evidence for forming μ-formyl complexes, e.g., $[Cp(CO)_2Mo]_2(\mu\text{-}COH)^+$, was indicated. This contrasts with the results of previous studies in which $Cp(CO)_3Mo{-}CH_3$ and $Cp(CO)_3Mo^+$ readily gave the bimetallic μ-(η^2-*C,O*) acetyl $[Cp(CO)_2Mo]_2(COCH_3)^+$ compound. The above μ-hydride salts furthermore do not undergo hydride–CO insertion, which would have afforded bimetallic μ-formyl complexes, by treatment with CO under pressure, with trimethyl phosphite, or with iodide.

Introduction

Alkyl ligand migration to coordinated carbon monoxide on a neutral transition-metal complex is facilitated by main-group Lewis acids (e.g., AlX_3) that can produce adducts with the carbonyl oxygen on the starting $L_nM(R)(CO)$ and/or on the acyl product $L_nM(RCO)$.[1] Attempts at inducing analogous hydride migration, however, have been thwarted by deleterious side reactions arising from the basicity of the metal hydride in the presence of necessarily strong Lewis acids.[2] Continued interest in promoting formation of formyl compounds $L_nM(HCO)$ from neutral metal carbonyl hydrides[3] derives from the purported role of this reaction as an important step in homogeneous CO reduction.[4,5] Accordingly, reports on using a second transition-metal center as a Lewis acid first to activate a CO ligand toward hydride transfer (i.e., one version of bifunctional CO activation)[6] and then to stabilize the formyl product as a bimetallic μ-formyl complex have elicited interest.[7]

We recently reported that $CpMo(CO)_3^+PF_6^-$ (**1**), an extremely reactive organometallic Lewis acid possessing an accessible coordination site,[8] promotes methyl–CO migratory insertion.[9] Thus $MpCH_3$[10] and $Mp^+PF_6^-$ (**1**) when mixed at −20 °C afford mixtures of bimetallic μ-(η^2-*C,O*) (**2**) and μ-(η^1-*C,O*) (**3**) acetyl complexes. Beck et al.[11]



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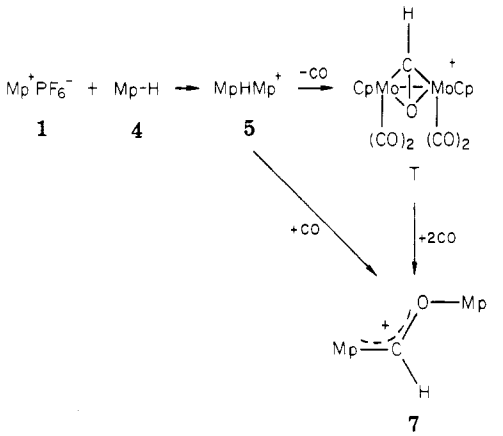
independently have prepared **2** and have determined its structure by X-ray crystallography. Analogous bimetallic μ-formyl compounds accordingly might result from the reaction of **1** and its requisite hydride complex, since the Mp^+ Lewis acid could serve the dual function of both promoting hydride CO migration on either MpH or $MpHMp^+$ (**5**) and then stabilizing the formyl ligand generated as its bimetallic μ-formyl **6** and/or **7**.[12]

Our endeavors toward preparing μ-formyl complexes **6**/**7** were further prompted by a report by Beck and Schloter on the conversion of **1** and **4** to the μ-hydride salt **5**.[8] They isolated a maroon solid whose C, H microanalysis, IR spectrum, and ^1H NMR spectral data (acetone-d_6, −80 °C: Cp singlet δ 6.38) are consistent with **5**; its apparent



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heterolytic cleavage with PPh_3 gave $MpPPh_3^+$ and MpH. These data, however, can be accounted for by μ-formyl

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(5) Note that catalytic homogeneous hydrogenation of carbon monoxide takes place under relatively mild conditions in systems of high Lewis acidicity (e.g., $NaC{-}AlCl_3$ eutectic mixtures). (a) Collman, J. P.; Brauman, J. I.; Tustin, G.; Wann, G. S. *J. Am. Chem. Soc.* **1983**, *105*, 3913. (b) Wang, H.; Choi, H. W.; Mutterties, E. L. *Inorg. Chem.* **1981**, *20*, 2661. Choi, H. W.; Mutterties, W. L. *Ibid.* **1981**, *20*, 2664.

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(9) LaCroce, S. J.; Cutler, A. R. *J. Am. Chem. Soc.* **1982**, *104*, 2312.

(10) Abbreviations: Cp, η-C_5H_5; Mp, (η-C_5H_5)$Mo(CO)_3$.

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(12) It is anticipated that **6** and **7** would result from independent reaction pathways, and that these μ-formyl products could interconvert under the appropriate reaction conditions. Similar conclusions have been arrived at for the μ-acetyl analogues **2** and **3**: LaCroce, S. J.; Markham, J. H.; Tolman, W.; Cutler, A. R., manuscript in preparation.

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structures **6** and/or **7**. Beck and Schloter's microanalytical results, for example, fit either **6** or **7**,[13] and their IR spectral data closely resemble that of the crude mixture of μ-acetyl congeners **2** plus **3** (vide infra). NMR spectral data for the maroon solid unfortunately is incomplete, since a resonance for the single hydrogen that would discern between the μ-H or μ-formyl ligand positions evidently was not detected. We do note, however, that the NMR spectrum of the μ-acetyl analogue **2** in acetone-d_6 (which decomposes **3**) contains an absorption for the Cp ligand at δ 6.19. This study addresses two questions: (1) Does this maroon solid correspond to μ-formyl complexation, and (2) if not, then can treatment of the μ-hydride **5** with CO, phosphite, or iodide induce μ-formyl complexation?

Experimental Section

All synthetic manipulations were performed under a nitrogen atmosphere by using standard Schlenk techniques and glassware suitably modified for inert-atmosphere work.[14] A nitrogen atmosphere was routinely provided for the following four operations: (a) carrying out reactions, (b) handling all solutions of metal complexes, (c) column chromatography, and (d) breaking the vacuum to evacuated vessels, including the Büchi rotovaporator. Solvents for synthetic work and recording of spectral data were deoxygenated by bubbling dinitrogen through the solvents for 20 min. Camag alumina (neutral, activity 3) was used in column chromatography. Carbonylation studies were carried out under conditions of vigorous stirring either in Fischer & Porter bottles (85 psig) or in a Parr Mini-Reactor (800 psig) fitted with an overhead stirrer.

Infrared spectra were taken of CH_2Cl_2 solutions in NaCl amalgam-spaced (0.10-mm) solution cells and were recorded on a Perkin-Elmer Model 297 spectrophotometer. The ν(CO) frequencies (2200–1500 cm^{-1}) were calibrated against the polystyrene 1601-cm^{-1} absorption. ^1H NMR spectra were taken of concentrated $CDCl_3$ or CD_3NO_2 solutions, after centrifugation off of insoluble residues. Varian Models EM-360 and XL-200 NMR spectrometers supplied the NMR spectra, which are reported as δ values in ppm downfield from internal Me_4Si.

Reagent grade solvents and reagents were obtained commercially and used as received. Tetrahydrofuran was additionally distilled under nitrogen from sodium benzophenone ketyl; methylene chloride and nitromethane were likewise procured as needed from P_2O_5. Deuterionitromethane was dried by passage through activated alumina. A modification of Dauben's procedure[15] was used to prepare $Ph_3C^+PF_6^-$. Although stored under nitrogen at +5 °C, trityl salts slowly decompose[16] (as evidenced by appearance of acid fumes), which necessitates periodic reprecipitation from CH_2Cl_2–ethyl acetate and vacuum drying. Metal carbonyl complexes $(C_5H_5)(CO)_3MoH$,[17] $(C_5H_5)_2Mo_2(CO)_6$,[18] $(C_5H_5)(CO)_3MoI$,[19] $(C_5H_5)(CO)_2PPh_3MoH$, and $(C_5H_5)(CO)_2P(OMe)_3MoH$[20] were prepared by literature methods and judged pure by IR and NMR spectroscopy.

$[(C_5H_5)(CO)_3Mo]_2H^+PF_6^-$ (5). MpH (0.984 g, 4.00 mmol) was added to a solution of $Ph_3C^+PF_6^-$ (0.776 g, 2.00 mmol) in 30 mL of CH_2Cl_2 at −78 °C. The resulting brownish-yellow mixture turned purple and deposited a precipitate as it warmed to room temperature (1 h). A dark red microcrystalline solid was filtered, washed with CH_2Cl_2 (4 × 10 mL), and dried in vacuo (<0.05 mm) to obtain spectroscopically pure $Mp_2H^+PF_6^-$ (**5**) (1.139 g, 89.5% yield): IR (CH_3NO_2) 2071 (m), 2055 (m), 1990 (s, br) cm^{-1}; ^1H NMR (CD_3NO_2, 200 MHz) δ 5.93 (s, 10 H, Cp), −20.80 (s, 1 H, Mo_2H). Solutions of **5** in CH_3NO_2 remain stable for several hours at room temperature; crystallization of the above product from CH_3NO_2–ether (60–350 mL) affords unchanged **5** (0.857 g, 67% yield).

Treatment of $[(C_5H_5)(CO)_3Mo]_2$ (0.490 g, 1.00 mmol) in cold (−78 °C) CH_2Cl_2 (50 mL) with $HPF_6{\cdot}OEt_2$, 1.0 mmol or an excess, affords **5** (maximum of 17% yield) and unreacted dimer as ascertained by IR spectroscopy.

Reaction of $[(C_5H_5)(CO)_3Mo]_2H^+PF_6^-$ (5) and $(n\text{-}Bu)_4N^+I^-$. A stirred suspension of **5** (0.064 g, 0.10 mmol) in CH_2Cl_2 (5.0 mL) was treated with $(n\text{-}Bu)_4N^+I^-$ (0.038 g, 0.10 mmol). This immediately produced a pink solution with an IR spectrum consistent with quantitative conversion of **5** to Mp_2. The solution subsequently darkened over a 5-h period, and monitoring of IR spectra of aliquots of the solution indicated the conversion of one-half of the Mp_2 to MpI (45% conversion, 5 h).

Results of the following control experiments (using 0.10 mmol of each of $(n\text{-}Bu)_4N^+I^-$ and CpMo complexes in 2.5 mL of CH_2Cl_2) were ascertained via monitoring of the IR spectra. (a) Neither MpI nor MpH react with I^- (2 h); (b) Mp_2 and $(n\text{-}Bu)_4N^+I^-$ react to give MpI and $(C_5H_5)(CO)_3Mo^-$ $(n\text{-}Bu)_4N^+$:[21] IR (CH_2Cl_2) 1898 (s), 1773 (s, br) cm^{-1} (22% conversion, 20 h); and (c) MpH plus MpI do not react (2 h): IR 2023 (s), 1931 (s, br) and 2043 (s), 1968 (s, br) cm^{-1} respectively.

Reaction of $[(C_5H_5)(CO)_3Mo]_2H^+PF_6^-$ (5) and $(C_2H_5)_3N$. To a stirred suspension of **5** (0.064 g, 0.10 mmol) in CH_2Cl_2 (5.0 mL) was added $(C_2H_5)_3N$ (0.014 mL, 0.10 mmol) via a 100-μL syringe. The suspension immediately dissolved to produce a pink solution; its IR spectrum corresponds to quantitative conversion of **5** to Mp_2: IR (CH_2Cl_2) 2018 (w), 1958 (s), 1913 (s) cm^{-1}. Similar results were obtained in CH_3NO_2.

Reaction of $[(C_5H_5)(CO)_3Mo]_2H^+PF_6^-$ (5) and $P(OCH_3)_3$. Addition of $P(OCH_3)_3$ (0.35 mL, 3.0 mmol) to a dark red CH_3NO_2 solution (30 mL) of **5** (0.636 g, 1.0 mmol) effected immediate gas evolution but no other physical changes. Monitoring of IR spectra established that the reactions were complete after 20 min, with formation of $(C_5H_5)Mo(CO)_3P(OMe)_3^+PF_6^-$ [IR 2073 (s), 2000 (m, sh), 1982 (s, br) cm^{-1}],[22] $(C_5H_5)Mo(CO)_2[P(OMe)_3]_2^+PF_6^-$ [IR 1997 (m), 1920 (s) cm^{-1}],[21c] and $(C_5H_5)(CO)_2[P(OMe)_3]MoH$ [IR 1951 (s), 1872 (s) cm^{-1}].[20] Solvent was then removed in vacuo and a total of 40 mL of CH_2Cl_2 was used to completely extract the crude product and then to precipitate a tan solid by addition of the extract to 300 mL of ether. Filtration, washing with ether (4 × 10 mL), and vacuum drying left 0.353 g of tan solid that assayed (IR and ^1H NMR spectroscopy) as a 3:2 mixture of $(C_5H_5)Mo(CO)_3P(OMe)_3^+PF_6^-$ [NMR (CD_3NO_2) δ 5.91 (s, 5, C_5H_5), 3.89 (d, J = 12 Hz, 9, $POCH_3$)] and $(C_5H_5)Mo(CO)_2[P(OMe)_3]_2^+PF_6^-$ [NMR (CD_3NO_2) δ 5.60 (t, J = 0.5 Hz, 5, C_5H_5), 3.71 (d, J = 12 Hz, 18, $POCH_3$)].

***trans,trans*-[$(C_5H_5)(CO)_2PPh_3Mo]_2H^+PF_6^-$ (10).** $(C_5H_5)(CO)_2PPh_3MoH$ (1.325 g, 2.76 mmol) was added to a solution of $Ph_3C^+PF_6^-$ (0.536 g, 1.38 mmol) in 35 mL of CH_2Cl_2. The resulting burgundy solution was stirred for 2 h before adding it to petroleum ether (400 mL), filtering the resulting pink precipitate, and washing the precipitate with petroleum ether (4 × 10 mL). This left 1.231 g of pink solid that corresponds to a 1:1 mixture of $(C_5H_5)(CO)_2PPh_3Mo^+PF_6^-$ [IR (CH_2Cl_2) 1982 (s), 1894 (s) cm^{-1};

(13) Anal. Calcd for (**5**) $C_{16}H_{11}Mo_2O_6PF_6$: C, 30.21; H, 1.74; (**6**) $C_{15}H_{11}Mo_2O_5PF_6$: C, 29.63; H, 1.82; (**7**) $C_{17}H_{11}Mo_2O_7PF_6$: C, 30.74; H, 1.67. Found:[8] C, 30.14; H, 2.03.

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^1H NMR (CD_3NO_2) δ 5.77 (C_5H_5, s, CD_3NO_2 adduct)][23] and *trans,trans*-[$(C_5H_5)(CO)_2PPh_3Mo]_2H^+PF_6^-$ (**10**) [IR (CH_2Cl_2) 1972 (s), 1908 (s) cm^{-1}; ^1H NMR (CD_3NO_2) δ 7.49 (m, 30, PPh_3), 5.26 (d, J = 2 Hz), 10 (C_5H_5), −22.42 (t, J = 9.6 Hz, 1, μ-H)]. Treatment of this mixture with $(n\text{-}Bu)_4N^+I^-$ effected partial purification in that only $(C_5H_5)(CO)_2PPh_3Mo^+PF_6^-$ was eliminated as $(C_5H_5)(CO)_2PPh_3MoI$,[20c,24] but we were unsuccessful in obtaining samples of this μ-hydride salt that did not contain substantial amounts (ca. 20%) of $(C_5H_5)Mo(CO)_2PPh_3^+PF_6^-$ and/or $(C_5H_5)Mo(CO)_3PPh_3^+PF_6^-$[8,24a] [IR ($CH_2Cl_2$) 2063 (s), 2000 (s), 1977 (s) cm^{-1}; ^1H NMR (CD_3NO_2) δ 7.55 (m, 30, PPh_3), 5.81 (s, 5, C_5H_5)]. Monitoring these purification attempts by IR spectroscopy sufficed to show that **10** did not dissociate/decompose but rather that the $(C_5H_5)Mo(CO)_3PPh_3^+$ derived from disproportionation of unreacted Lewis acid $(C_5H_5)Mo(CO)_2PPh_3^+$.[23]

Attempted Carbonylation of $[(C_5H_5)(CO)_3Mo]_2H^+PF_6^-$ (5). Nitromethane solutions (10 mL) of **5** (0.128 g, 0.20 mmol) when pressurized with CO at either 85 or 800 psig for 8–12 h (25 °C) effected complete conversion of all starting material to mixtures of $(C_5H_5)Mo(CO)_3^+PF_6^-\cdot CH_3NO_2$ solvate (IR 2076 (s), 1992 (s, br) cm^{-1}) and Mp_2, with varying amounts of insolule blue decomposition materials. No $MpCO^+$[8] was detected: IR (CH_3NO_2) 2122 (s), 2041 (s, br) cm^{-1}. Substitution of nitrogen (1 atm) for CO effects the same decomposition of **5** in nitromethane. With trifluoroethanol, **5** quantitatively converted (after 9 h) to Mp_2 under CO pressure (800 psig), although use of less pressure (85 psig) realized extensive decomposition to insoluble black material. Attempted carbonylation of impure **10** in either CH_2Cl_2 or CH_3NO_2 (800 psig, 12 h at 25 °C) left unreacted starting material.

Results and Discussion

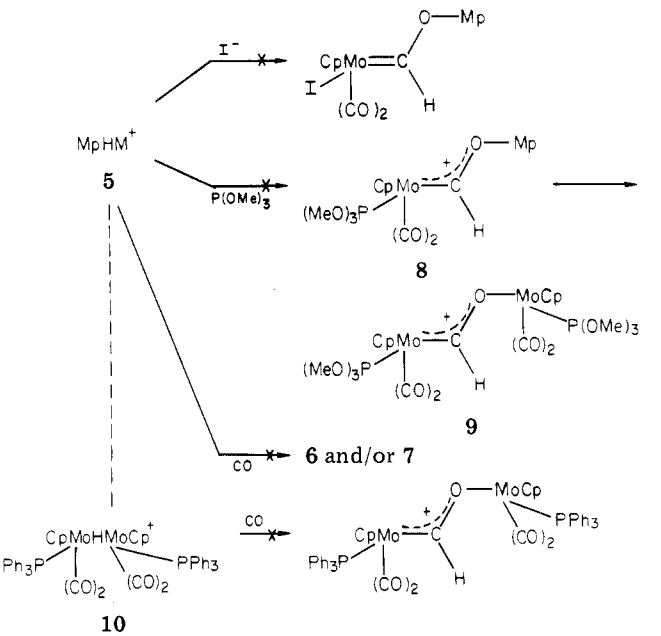
We find, in agreement with Beck and Schloter,[8] that in CH_2Cl_2 with a 2:1 stoichiometry of MpH and Ph_3CPF_6, hydride abstraction affords an air-stable maroon solid.

$$2Mp\text{–}H + Ph_3C^+PF_6^- \xrightarrow[CH_2Cl_2]{} \underset{\mathbf{5}}{MpHMp^+PF_6}$$

This salt is either insoluble in (e.g., CH_2Cl_2) or decomposed by (e.g., acetone, CH_3CN) most solvents useful in dissolving cationic organometallics; nitromethane however readily dissolves **5** with only slow ($\tau_{1/2}$ ca. 4 h, 0.02 M solutions) decomposition and deposition of Mp_2. Otherwise these nitromethane solutions readily precipitate **5** intact (as judged by examining IR and ^1H NMR spectra) upon adding to excess ether. Consideration of NMR spectral data in CD_3NO_2 permits us to unambiguously assign the μ-hydride structure **5**.

The NMR spectrum of **5** exhibits only two sharp singlets integrating 10:1 at δ 5.93 and −20.80, with no absorptions at the δ +26–6 region. Certainly the δ −20.80 resonance presages a metal hydride.[25] We would in contrast have expected a formyl hydrogen of **6** or **7** to resonate in the δ +15–+10 region as observed for neutral[4] and cationic[26] formyl complexes and for alkoxymethylidene salts[27] such as $Cp(CO)_2Fe{=}CH(OCH_3)^+$,[28] although the one known

Scheme I



μ-(η^2-*C,O*) formyl complex $(\eta\text{-}C_5Me_5)_2Cl_4Ta_2(\mu\text{-}H)(\mu\text{-}CHO)$[7b] has its formyl absorption at δ 7.5.

The μ-hydride salt **5** also can be prepared by protonating the Mo–Mo bond in Mp_2.[29]

$$Mp\text{–}Mp \underset{Et_3N\text{ in }CH_2Cl_2}{\overset{HPF_6\cdot OEt_2}{\rightleftharpoons}} \underset{\mathbf{5}}{Mp\text{–}H\text{–}Mp^+PF_6^-}$$

Davison et al.[29a] first reported the solution protonation of Mp_2 (δ −20.99 in H_2SO_4 for μ-H), and we now have isolated **5** in low yield by treating Mp_2 with HPF_6 in CH_2Cl_2. No attempt was made to optimize the yield of this latter reaction. It is also worth noting that triethylamine quantitatively deprotonates **5** as a CH_2Cl_2 suspension or CH_3NO_2 solution back to Mp_2, since such deprotonation of cationic μ-hydrides, e.g., $Cp_3(NO)_4Mo_2H^+$,[29c] is not always possible. Converting MpH to $MpHMp^+$ (**5**) and then deprotonating **5** to Mp_2 amounts to the net two-electron oxidative coupling of MpH.[29e,31]

Compound **5** represents the first example of a bimetallic hydride complex prepared both by protonating a metal–metal bond and by interacting an organometallic Lewis acid with a metal hydride. Whereas protonation of metal–metal bonds is a standard procedure,[25] rather few examples exist for the latter procedure. The Lewis acids $Cp(NO)_2M$ (M = Mo, W),[29c] and $(CO)_5M$ (M = Cr, Mo, W)[30a] or $Cp(CO)_3Nb$[30b] thus react with their metal hydride derivatives to produce cationic and anionic μ-hydride complexes, respectively. Other bridging μ-MoHMo interactions apparently provide a pathway for Mo hydride

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complexes to interact with coordinatively unsaturated organo–Mo species. Thus the transitory intermediate $Cp(CO)_3Mo–H–Mo(CO)_2(COR)Cp$, resulting from interaction of MpH and η^1-alkyl MpR complexes, mediates a binuclear reductive-elimination process that produces aldehyde RCOH.[32]

Given the μ-hydride structure of **5**, we than reacted Lewis bases including CO with it in order to try forcing the hydride CO migration. Four approaches were followed in attempting to promote hydride CO migration on **5** and to form μ-formyl complexes; see Scheme I. The I^- reaction was patterned after the established reaction of CN^- or I^- with η^1-alkyl Mp complexes:[33] $MpCH_3$ and CN^- give $Cp(CO)_2(CN)MoCOCH_3^-$. We also saw potential in phosphite inducing CO insertion on **5** (perhaps facilitated by the associated Mp^+ Lewis acid) and giving the indicated phosphite substituted μ-(η^1-*C*,*O*) formyl compounds **8** and/or **9**, especially since we recently reported the analogous phosphite substituted acetyl compounds.[9] The remaining two approaches entail carbonylating the μ-hydride salts **5** and **10**. None of these procedures when carried out, however, realized the desired hydride CO migration.

One equivalent of iodide instantaneously and cleanly converts **5** to Mp_2; then one-half of the Mp_2 slowly (5 h) forms MpI.

$$\underset{\mathbf{5}}{MpHMp^+} + I^- \xrightarrow[-{}^1/_2H_2]{} Mp–Mp + {}^1/_2I_2 \rightarrow {}^1/_2Mp–Mp + MpI$$

This stoichiometry is consistent with reductive fragmentation of **5** with I^- as the electron donor and subsequent iodination[19] of Mp_2. A previous example of reductive fragmentation of a μ-hydride compound $(Cp_2WH)_2(\mu\text{-}H)^+$ has been observed by Kochi using electrochemical procedures.[29e]

Other mechanisms that were considered for the reaction of iodide and **5** include its direct deprotonation and its unsymmetrical cleavage to MpH plus MpI. Proton transfer would have given Mp_2 and H^+I^- as the final products (5 h), since we have found that I^- and Mp_2 react only very slowly to give MpI and Mp^-. Any Mp^- formed, of course, would then have given MpH[34] under the conditions (i.e., H^+I^- present) of the deprotonation sequence. If MpH had additionally developed from unsymmetrical cleavage of **5**, then it should have been detected in place of Mp_2. In support of this analytical argument are results of several control experiments: I^- does not react with MpH, and neither I^- nor MpH alter MpI in CH_2Cl_2 (25 °C, 5 h). These alternative mechanisms clearly do not account for the observed stoichiometry in transforming **5** plus iodide first to Mp_2 and then to MpI. Although further mechanistic study on the reaction of iodide with **5** is clearly warranted, two conclusions emerge from this study. First, iodide does not induce hydride CO insertion on **5**: the clean conversion of **5** to Mp_2 and MpI precludes this pathway. Second, results of this study are consistent with, but not definitive for, the reductive fragmentation pathway offered.

Three equivalents of $P(OMe)_3$ are required for complete consumption of **5** concomitant with generating the phosphite-substituted hydride **11** and carbonyl salts **12** and **13**. Only these three products and **5** were detected by IR when 1 or 2 equiv of $P(OMe)_3$ were used. Had the bimetallic

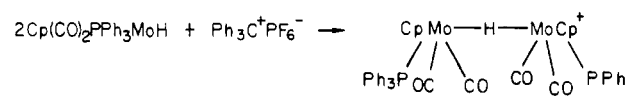
$$\underset{\mathbf{5}}{MpHMp^+} + 3P(OMe)_3 \rightarrow \underset{\mathbf{11}}{Cp((MeO)_3P)(CO)_3MoH} + \underset{\mathbf{12}}{CpMo(CO)_3P(OMe)_3^+} + \underset{\mathbf{13}}{CpMo(CO)_2P(OMe_3]_2^+}$$

μ-formyl **9** formed then it should have been detected (even in the presence of excess phosphite) on the basis of our experience with the stable μ-acetyl analogue.[9] The bis(phosphite) salt **13** observed must result from the interaction of $P(OMe)_3$ with **5** and not from a subsequent CO replacement on **12**, since in agreement with others,[22] we found that excess phosphite does not transform (25 °C) **12** into **13**.

These phosphite products **11–13** can be arrived at by a mechanism analogous to one established for dimer disruption of $[(CO)_5Mo]_2(\mu\text{-}H)^{-1}$ with phosphines to give neutral disubstituted $Mo(CO)_4P_2$.[35] This requires at least one substitution of CO by P on the intact dimer prior to unsymmetric cleavage. A similar CO substitution by $P(OMe)_3$ on **5**, which is probably facilitated by cis labilization adjacent to the μ-hydride ligand,[36] would generate $Mp–H–Mo(CO)_2P(OMe)_3Cp^+$. Unsymmetric cleavage of **5** (to MpH and **12**) and $Mp–H–Mo(CO)_2P(OMe)_3Cp^+$ (to MpH and **13**) in the presence of phosphite then accounts for the observed products.

At first glance our carbonylation approaches seem unfounded in view of the great difficulty reported in carbonylating η^1-alkyl Mp complexes.[37] In unrelated studies, however, we have demonstrated that a variety of alkyl complexes $Cp(CO)_xLM–R$ (M = Fe (x = 1) or Mo (x = 2); L = CO, PPh_3) do carbonylate under extremely mild conditions (≤85 psig CO at 20–50 °C) when the appropriate solvent (CH_3NO_2, CF_3CH_2OH, or $(CF_3)_2CHOH$) is used.[38] Moreover, for the Fe methyl complexes we also found that the presence of ancillary phosphine ligand enhances the methyl CO migration in CH_3NO_2 (85 psig of CO): $Cp(CO)_2FeCH_3$ requires 24 h at 60 °C, whereas $Cp(CO)PPh_3FeCH_3$ needs only 1 h at 25 °C for 95% conversion to their respective acetyl complexes.

Our preparation of **10** thus was part of an attempt at using PPh_3 ligands on the μ-hydride structure to promote H–CO migration. Reaction of the Lewis acid $Cp(CO)_2PPh_3MoH$ with $Ph_3C^+PF_6^-$ gives



10

$(CO)_2PPh_3Mo^+PF_6^-$[23] and its hydride $Cp(CO)_2PPh_3MoH$ does provide **10**, albeit impure. Structural assignment of this μ-hydride (defined according to the Ph_3P–Mo–H stereochemical array on the square base of the square-pyramidal Mo centers)[20c,39] rests on interpretation of the ^1H NMR spectrum.

The ^1H NMR spectrum of **10**, comprising a doublet (J_{P-H} = 2 Hz) for the Cp ligands and a triplet (J_{P-H} = 9.6 Hz) upfield of Me_4Si for the bridging hydride, clearly supports a symmetrical μ-hydride complex with coupling to both ligating phosphorus centers.[25] Moreover, the

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presence of one doublet resonance for both Cp groups established the trans stereochemistry at both Mo sites. According to the same well-established NMR criterion,[20,24] the cis,cis stereoisomer of **10** would exhibit a singlet, and the cis,trans isomer would provide separate NMR absorptions (singlet downfield of doublet by ca. 0.2 ppm) for the Cp ligands. A similar argument has been used to assign the stereochemistry on *trans,trans*-$[Cp(CO)_2LMo]_2Hg$, L = $P(OMe)_3$, PPh_3.[20b] Supporting evidence for the trans,trans-stereochemical assignment for **10** results from comparing the magnitude of the μ-H to ligating phosphorus spin–spin coupling interaction with related J_{PH} values involving the terminal hydride ligand on *cis*- and *trans*-$Cp(CO)_2PPh_3MoH$ (65 and 21 Hz, respectively).[20c] As expected,[40] J_{PH} for **10** is slightly less than one-half the value for the *trans*-$Cp(CO)_2PPh_3MoH$. The magnitude of this J_{PH} on **10** also precludes its stereochemical nonrigidity (fast averaging of the cis- and trans-Mo centers on the NMR time scale), since the presence of any reasonable concentration of cis-Mo centers on **10** would effect an averaged J_{PH} substantially greater than 10 Hz.[20c] (Also, a broadened singlet resonance for the Cp ligand would probably result.) Taken together, these NMR data for **10** are in accord with the presence of only the trans,trans stereoisomer.

(40) (a) The NMR of *cis,cis*-$[(Ph_2MeP)(CO)_4Mo]_2H^-$ exhibits a triplet (δ −11.75) for its μ-hydride with a cis J_{PH} = 16.6 Hz; an analogous trans J_{PH} would be expected to be significantly lower, see ref 35. (b) Compare analogous J_{PH} values of 28 and 74 Hz for $[Cp(CO)_2Fe]_2(\mu\text{-H})(\mu\text{-dppe})^+$ and $[Cp(CO)_2FeH]_2(\mu\text{-dppe})$, respectively, where dppe = $Ph_2PCH_2CH_2PPh_2$: LaCroce, S. J.; Menard, K. P.; Cutler, A. R. *J. Organomet. Chem.* **1980**, *190*, C79.

Attempts at carbonylating **5** and **10** at 85 and 800 psig of CO did not lead to CO addition and generation of μ-formyl complexes. Rather, the μ-hydride salt **5** decomposed under CO pressure to mainly Mp_2 plus small amounts of the nitromethane adduct of Mp^+ but not $MpCO^+$. This decomposition in nitromethane or trifluoroethanol effectively was independent of CO, as similar solutions under 1 atm of nitrogen gave identical results. The phosphine-substituted μ-hydride **10** was recovered unchanged after similar carbonylation attempts, although any residual $(C_5H_5)(CO)_2PPh_3Mo^+$ converted to its saturated carbonyl salt $(C_5H_5)(CO)_3PPh_3Mo^+$.

Conclusions

MpH interacts with the organometallic Lewis acid $Mp^+PF_6^-$ and generates a stable μ-hydride complex Mp–H–$Mp^+PF_6^-$ (**5**). Attempts at converting this μ-hydride salt to bimetallic μ-formyl complexes by using CO, $P(OMe)_3$, or I^- were unsuccessful as other reaction pathways were instead followed. That **5** does not provide a kinetic pathway for hydride–CO insertion contrasts with the pronounced ease for generating analogous μ-acetyl complexes from the interaction of $MpCH_3$ and Mp^+.

Acknowledgment. Support from the Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged.

Registry No. **5**, 68868-70-2; **10**, 89303-04-8; MpH, 12176-06-6; Mp_2, 12091-64-4; MpI, 12287-61-5; $(C_5H_5)(CO)_2PPh_3MoH$, 33519-69-6; $(C_5H_5)(CO)_2[P(OMe)_3]MoH$, 61950-48-9; $(C_5H_5)Mo(CO)_3P(OMe)_3^+PF_6^-$, 68868-07-5; $(C_5H_5)Mo(CO)_2[P(OMe)_3]_2^+PF_6^-$, 89303-02-6; $(C_5H_5)(CO)_2PPh_3Mo^+PF_6^-$, 89303-05-9.

Kinetics and Mechanism of Substitution Reactions of $Mn(\eta^5\text{-}C_9H_7)(CO)_3$ and $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$

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Received November 7, 1983

The reactions of $Mn(\eta^5\text{-}C_9H_7)(CO)_3$ and $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ with phosphines and phosphites proceed readily in decalin at elevated temperatures to form monosubstituted products. For $Mn(\eta^5\text{-}C_{13}H_9)(CO)_3$ a second substitution takes place with P-*n*-Bu_3 and P-c-Hx_3[1] which proceeds via an η^1-fluorenyl species, $Mn(\eta^1\text{-}C_{13}H_9)(CO)_3(P\text{-}n\text{-}Bu_3)_2$. All these reactions take place by a second-order process, first order in metal complex and first order in nucleophile. Reaction rates depend on both size and basicity of the entering ligand. Substitution reactivity of these compounds contrasts the observed[2] thermal substitution inertness of $Mn(\eta^5\text{-}C_5H_5)(CO)_3$. This difference in reactivity is discussed in terms of the *indenyl ligand effect* of the indenyl and fluorenyl ligands vs. the cyclopentadienyl ligand.

Introduction

Although indenyl analogues of many cyclopentadienyl transition-metal compounds are known, kinetic studies comparing substitution at the metal center for cyclopentadienyl vs. indenyl are rare. In 1969 Hart-Davis and Mawby[3] found that the methyl migration in $Mo(\eta^5\text{-}C_9H_7)(CO)_3CH_3$ was ligand assisted. The S_N2 nature of this reaction was attributed to the ability of indenyl ligands to undergo an η^5 to η^3 migration allowing associative attack on the metal center. They believed that the benzene of the indenyl ring provided stabilization of the η^3-allyl intermediate; the cyclopentadienyl analogue reacted 10 times slower. White, Mawby, and Hart-Davis[4] also compared CO substitution by phosphines for the compounds $Mo(\eta^5\text{-}C_5H_5)(CO)_3X$ and $Mo(\eta^5\text{-}C_9H_7)(CO)_3X$ (X = Cl, Br, I). They found that CO substitution for the cyclopentadienyl compound proceeds by a purely dissociative (S_N1) pathway

(1) Abbreviations: P-*n*-Bu_3 = tri-*n*-butylphosphine; P-c-Hx_3 = tricyclohexylphosphine; $P(OEt)_3$ = triethyl phosphite; PPh_3 = triphenylphosphine; P(O-*i*-$Pr)_3$ = triisopropyl phosphite; P-*i*-Bu_3 = triisobutylphosphine; PMe_2Ph = dimethylhenylphosphine.

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