Our results are also at variance with yet another possible alternative mechanism, depicted by eq 10–12, which merits consideration in view of the recent demonstration of analogous mechanisms for the reactions of certain cobalt(II) Schiff's base complexes with nitrobenzyl halides.[22] This mechanism involves an outer-sphere electron transfer to the organic halide from a *six-coordinate* cobalt(II) complex formed in a prior association step. Three features of our results are at variance with this mechanism, namely (i) the observed second-order rate law (in contrast to the third-order rate law,[22] k'[Co(DH)$_2$B][RX][B], expected for this mechanism); (ii) the large dependence on halide variation, *i.e.*, $k_{RI}/k_{RBr} \sim k_{RBr}/k_{RCl} \sim 10^3$, which is characteristic of the halogen atom transfer (eq 1),[11-13] in contrast to the much smaller dependence (*i.e.*, $k_{RI}/k_{RBr} \sim k_{RBr}/k_{Cl} \sim 1$–10) characteristic of the electron-transfer mechanism;[22] and (iii) the discrepancy of the overall stoichiometry.

The only feature of our results which does not find a ready explanation in terms of the mechanism that we have adopted relates to the large negative $\Delta S^{\ddagger}$ values

$$Co(DH)_2B + B \rightleftharpoons Co(DH_2)B_2 \quad (10)$$

$$Co(DH)_2B_2 + RX \longrightarrow Co(DH)_2B_2^+ + X^- + R\cdot \quad (11)$$

$$Co(DH)_2B + R\cdot \longrightarrow RCo(DH)_2B \quad (12)$$

of the reaction (*ca.* −30 eu). An explanation in terms of solvent electrostriction reflecting a highly polar transition state is not readily reconciled with the rather modest dependence of the rate on solvent polarity. It is, however, noteworthy that comparably large negative activation entropies have been observed for atom- or radical-transfer reactions to cobalt(II) complexes from other neutral substrates (*e.g.*, $Co(CN)_5^{3-} + H_2O_2 \rightarrow Co(CN)_5OH^{3-} + OH\cdot$; $\Delta S^{\ddagger} = -31$ eu).[23] Further investigation of this pattern, for which we cannot presently offer a convincing explanation, is warranted.

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Reaction of Transition Metal Dihydrides. I. Insertion and Substitution at the Metal–Hydride Bonds in Dihydridobis(π-cyclopentadienyl)molybdenum[1]

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Abstract: Reactivity of (π-C_5H_5)$_2$MoH$_2$ toward various olefins and acetylenes was investigated. An unsaturated bond having electron-attracting groups such as –CN, –CO_2CH_3, or –CF_3 undergoes monoinsertion into one of the Mo–H bonds. Hydrido-σ-alkyl or -σ-alkenyl complexes of formula (π-C_5H_5)$_2$MoH(R) were isolated and characterized for R = CH(CN)CH_3, CH(CN)CH_2CN, CH(CO_2CH_3)CH_3, CH(CO_2CH_3)$CH_2CO_2CH_3$, *cis*-C(CO_2CH_3)=$CHCO_2CH_3$, and *trans*-C(CF_3)=$CHCF_3$. Some of these, when treated with excess olefins or acetylenes, produced substitution products of formula (π-C_5H_5)$_2$Mo(Un); Un = CH_2=CHCN, CH_2=$CHCO_2CH_3$, *cis*- and *trans*-CH_3O_2CCH=$CHCO_2CH_3$, *trans*-PhCH=$CHCO_2CH_3$, and PhC≡CPh. One of the hydrido-σ-alkenyl complexes, (π-C_5H_5)$_2$MoH[σ-*trans*-C(CF_3)=$CHCF_3$], containing a sterically demanding side chain, emerges in two conformational isomers; possible mechanisms for the observed isomerization were discussed on the basis of the temperature-dependent ^{19}F nmr.

In olefin catalysis such as isomerization and related reactions a metal monohydride species plays an important role. The reversible insertion reactions of olefins into metal–hydrogen bonds have been studied extensively.[2-7] Recently a number of transition metal complexes were found to be able to coordinate molecular hydrogen[8,9] leading to dihydrides. Reactions of the isolated metal–dihydride complexes with olefins have not been studied albeit the importance in catalytic hydrogenations,[10,11] the reason being apparently the elusive nature generally encountered with catalytically active complexes. Exceptions may be Wilkinson's

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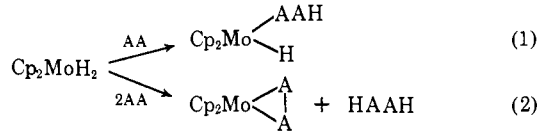
$RhCl(H_2)(PPh_3)_2S$ (S = solvent)[12] and Vaska's $IrX(H_2)(CO)(PPh_3)_2$.[13a,b]

The well-known nitrogen-reducing ability of some molybdenum-containing enzymes[14] suggests the importance of group VI metal hydrides in the hydrogenation of molecular nitrogen or other unsaturated bonds.[15] We have undertaken a systematic study on the reactions of unsaturated compounds with group VI metal dihydrides which are relatively unexplored.

The primary object is to describe in detail the reactions relevant for a discussion of correlations between homogeneous and heterogeneous catalysis. The known dicyclopentadienyldihydridomolybdenum, Cp_2MoH_2[16] (**1**), or -tungsten, Cp_2WH_2[16] (**2**), has several features favorable for this type of study: (1) their adequate thermal stability, (2) a reasonable reactivity toward electrophilic olefins or like compounds leading to a variety of reactions including formation of stable hydrido-σ-alkenyl compounds[1] and the catalytic activity for hydrogenations, and (3) the geometry of molecular structure, in particular the alignment of the two hydrido ligands adjacent to the filled nonbonding metal orbital. The exposed filled orbital is considered to be responsible for the remarkable Lewis basicity[17] and offers a site for approach of an electrophilic olefin. We are interested in factors governing the stability of hydrido-σ-alkyl complexes and those determining the observed reaction pathways 1 and 2. These aspects should have



(1)

(2)

bearing on the recent controversy regarding hydrogenation mechanisms; simultaneous transfer of two hydrido ligands to a coordinated olefin was proposed for a rhodium(I)-catalyzed hydrogenation[12] and for a chromium(0)-catalyzed hydrogenation,[18] whereas an intermediacy of hydrido-σ-alkyl species was proposed for the rhodium(I)-catalyzed hydrogenation of some olefins.[19-21] Another interesting aspect is the conformational isomerism found for a hydrido-σ-alkenyl complex, $Cp_2Mo(H)[C(CF_3)=CHCF_3]$. Possible mechanisms for the equilibration will also be discussed.

Experimental Section

Materials. Dihydridobis(π-cyclopentadienyl)molybdenum and -tungsten were prepared by essentially the same method as that described in the literature.[22] Hexafluorobutyne-2,[23] diphenylacetylene,[24] and dimethyl acetylenedicarboxylate[25] were prepared by the established methods. All the other reagents were commercial products.

Instruments. Infrared spectra were measured by a Hitachi Perkin-Elmer Model 225 and nmr spectra by a Jeol JNM 4H-100 or JNM C-60 HL. Molecular weights were determined in benzene by a Hitachi vapor pressure osmometer Model-115. Melting points were obtained in a sealed capillary under nitrogen. Mass spectra were taken by a Hitachi RMS-4 at 80 eV. Analysis of complex ^1H nmr spectra was performed by a Neac 2200 with a computer program written by Professor T. Fueno and Dr. O. Kazimoto of Osaka University.

Preparation of Complexes. All reactions and manipulations involving organometallic compounds were carried out under pure nitrogen. The solvents were degassed by distillation under nitrogen.

$Cp_2MoH[\sigma$-$C(CO_2CH_3)=CHCO_2CH_3]$. A stirred solution of **1** (165 mg, 0.72 mmol) in 15 ml of tetrahydrofuran was mixed with dimethyl acetylenedicarboxylate (103 mg, 0.72 mmol) slowly by dropwise addition at 0°. The color changed to red immediately. After 1 hr of stirring to ensure completeness of the reaction, the solvent was removed under reduced pressure and the residual solid was dissolved in ether. The ether solution yielded the σ-alkenyl complex as deep red crystals (mp 103–105°, yield 44%) upon concentration and chilling to −20°. From the ether-insoluble part, pale red crystals (mp 150°) were obtained through recrystallization from chloroform. This product was identified as $Cp_2Mo(trans$-$CH_3O_2CCH=CHCO_2CH_3)$ by comparison of its ir and nmr spectra (see below).

$Cp_2MoH[\sigma$-$C(CF_3)=CHCF_3]$. To a tetrahydrofuran solution (10 ml) of **1** (435 mg, 1.91 mmol) was added gaseous hexafluoro-2-butyne (*ca.* 50 ml, 22 mmol) at −78°. Immediate reaction occurred with a concomitant change of color to red. After warming to room temperature and standing overnight the solvent was removed under reduced pressure to leave a red residue which was dissolved in ether. The ether solution was chilled to −20° with addition of some pentane to give the σ-alkenyl complex as red needles (mp 112–113°, yield *ca.* 50%).

$Cp_2WH[\sigma$-$C(CO_2CH_3)=CHCO_2CH_3]$. To a stirred tetrahydrofuran solution (15 ml) of **2** (544 mg, 1.72 mmol) was added dropwise dimethyl acetylenedicarboxylate (186 mg, 1.72 mmol) at room temperature. The mixture was stirred for 1.5 hr at the same temperature. Removal of the solvent gave a dark residue which was mostly dissolved in ether. Filtration of the ether solution followed by concentration and chilling to −20° gave dark red crystals of the insertion product.

Thermal Decomposition of $Cp_2MoH[\sigma$-$C(CO_2CH_3)=CHCO_2CH_3]$. The hydrido-σ-alkenyl complex (73 mg, 0.2 mmol) was heated gradually in a small flask under vacuum up to *ca.* 500°. The trapped volatile material was dissolved in chloroform (0.5 ml). The chloroform solution was examined by glc using an Apiezon GL column at 120° to yield dimethyl acetylenedicarboxylate as the sole volatile product.

Reaction of $Cp_2MoH[\sigma$-$C(CO_2CH_3)=CHCO_2CH_3]$ with Dry HCl. The complex (170 ml, 0.46 mmol) dissolved in ether (10 ml) was slowly mixed with an ether solution (1.0 ml) of hydrogen chloride (108 mg, 3.0 mmol) at room temperature. Purple precipitates formed immediately. The supernatant liquid being removed by a syringe, the precipitates were washed with ether and dissolved in a mixture of CH_2Cl_2–ether. Upon chilling, the solution gave purple crystals (mp 154–156°) of formula $(C_5H_5)_2Mo[\sigma$-$CH(CO_2CH_3)CH_2CO_2CH_3]Cl$. *Anal.* Calcd for $C_{16}H_{19}O_4ClMo$: C, 47.25; H, 4.71; Cl, 8.72. Found: C, 47.52; H, 4.73; Cl, 7.85. ^1H nmr ($CDCl_3$): δ 2.1–3.3 (complex, 3 H), 3.60 (singlet, 3 H, OCH_3), 3.67 (singlet, 3 H, OCH_3), 5.20 (singlet, 5 H, Cp), 5.33 (singlet, 5 H, Cp). Ir (Nujol): 1705 (C=O), 1664 (C=O), 290 cm^{-1} (MoCl).

$Cp_2Mo(PhC\equiv CPh)$. A mixture of **1** (207 mg, 0.91 mmol) and diphenylacetylene (378 mg, 2.12 mmol) in toluene (20 ml) was re-

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fluxed for 3 hr to result in a reddish-brown solution. Concentration and addition of some hexane or ether followed by standing at −20° overnight yielded the acetylene complex as deep red, well-formed needles (mp 164–165°, yield *ca.* 50–60%). The mother liquor was evaporated *in vacuo* and the residue was sublimed [120° (3 mm)] to give a mixture of *cis*- and *trans*-stilbene. The same reaction at room temperature gave almost exclusively *cis*-stilbene. A benzene solution of the acetylene complex was air-sensitive as indicated by a color change to orange yellow in 1 min.

$Cp_2MoH[\sigma$-CH(CN)$CH_3]$. **1** (331 mg, 1.46 mmol) was allowed to react with an equimolar amount of acrylonitrile (77 mg, 1.45 mmol) in toluene (10.0 ml) at room temperature for 4 hr. During this period, the color of the solution turned brownish red. As no crystallization occurs on chilling, the reaction mixture was concentrated under reduced pressure. Brown crystals (314 mg, 77%) were obtained on standing at room temperature, followed by filtration and washing with cold toluene and *n*-hexane. The complex decomposed on brief contact with air and also on heating to *ca.* 100° under nitrogen.

$Cp_2MoH[\sigma$-CH(CN)CH_2CN]. Fumaronitrile (150 mg, 0.96 mmol) and **1** (220 mg, 0.97 mmol) were dissolved in 10 ml of benzene. The mixture was heated at gentle reflux for 1 hr. Upon cooling and standing well-formed crystals of the insertion product separated (210 mg, 57%). The crystals were stable in air for a few hours and only slightly soluble in chloroform and in dichloromethane. The orange solution was quite unstable in air changing its color to deep brown. The presence of a hydride ligand was shown by formation of chloroform in the reaction with carbon tetrachloride.

The complex dissolves in concentrated aqueous hydrochloric acid to give an air-stable wine red solution. Concentrated hydrobromic acid also dissolves it giving a deep red solution whose color turns into very deep blue violet in 10–20 min at room temperature. Owing to the instability of the complex in deuteriochloroform, the ^1H nmr spectrum showed only complex signals at δ 1–4 ppm (TMS) due to partial decomposition. The spectrum in dichloromethane revealed the presence of a hydride proton at δ −8.95 ppm (TMS) and again complex signals δ 1.5–3 ppm (TMS). It does not show adequate solubility in usual nmr solvents.

$Cp_2Mo(CH_2$=CHCN). **1** (212 mg, 0.93 mmol) was dissolved in acrylonitrile (1.7 ml) and toluene (8.0 ml). The solution was refluxed for 3 hr to afford a red solution with a small amount of solid. The solvent being removed partially, the concentrate gave after filtration and chilling at −20° reddish brown crystals (88 mg, 34%). The complex was decomposed in a few minutes in air even in the crystalline state. Another crop (*ca.* 12 mg) may be obtained from the filtrate by an addition of *n*-hexane. Analysis of the filtrate by glc indicated the presence of propionitrile together with unreacted acrylonitrile.

$Cp_2Mo(CH_2$=CH$CO_2CH_3)$. A mixture of **1** (215 mg, 0.95 mmol), methyl acrylate (860 mg, 10 mmol), and toluene (10.0 ml) was stirred overnight at room temperature. The dark red solution after the stirring yielded brown precipitates. After chilling at −20° the precipitates were collected, washed, and dried (102 mg, 32%). Concentration of the mother liquor gave a further crop of the acrylate complex (42 mg, total yield 46%). The complex was very air-sensitive. Its color turned in 1 min to dark green on contact with air in its solid state. Its solution in benzene was even more sensitive, deep blue color being immediately developed in air. It was sublimable at 140–160° (1 mm).

$Cp_2Mo($*trans*-CH_3O_2CCH=CH$CO_2CH_3)$. A solution of **1** (221.1 mg, 0.97 mmol) and dimethyl fumarate (279 mg, 1.88 mmol) in toluene (14 ml) was stirred at room temperature to develop a deep orange color. Then, the solution was refluxed for 4 hr to change the color to dark red. Upon cooling and standing at room temperature overnight, reddish brown, well-formed crystals of the complex separated (264 mg, 73.5%). The crystalline complex was reasonably stable in air for several hours.

$Cp_2Mo($*cis*-CH_3O_2CCH=CH$CO_2CH_3)$. Dimethyl maleate (377 mg, 2.62 mmol) was used in the reaction with **1** (299 mg, 1.31 mmol). The procedure and color change were similar to that described above for dimethyl fumarate. After refluxing for 1 hr, the reaction mixture was cooled and stood overnight. Reddish brown crystals (218 mg, 45%) formed and were separated by filtration and the solution was refluxed again for further 3 hr to obtain pale brown needles upon cooling (65 mg, 13%). The reddish brown crystals were identical with the fumarate complex by their melting point and ir spectrum. The pale brown needles were characterized by ir, nmr, and mass spectra to be a maleate complex (*cf.* Tables I and II). The maleate complex was more soluble in methanol or chloroform than the fumarate complex and had a lower melting point. On heating at or above the melting point the maleate complex rearranged to the fumarate complex.

The same reaction of **1** (294 mg, 1.39 mmol) using an excess of dimethyl maleate (567 mg, 3.94 mmol) in toluene (10 ml) at reflux (bath temperature at 130°) for 1.5 hr gave 215 mg (0.58 mmol) of the fumarate complex on cooling. From the mother liquor, 157 mg (0.43 mmol) of the maleate complex was obtained. The relative yield of the maleate complex was further improved by conducting the same reaction with the same stoichiometry at lower temperature (50–55°) for 9 hr. Almost equal amounts of both products were isolated.

$Cp_2Mo($*trans*-PhCH=CH$CO_2CH_3)$. **1** (190 mg, 0.83 mmol) and *trans*-methyl cinnamate (270 mg, 1.67 mmol) were mixed in toluene (10 ml) and heated at reflux for 3.5 hr. The color turned to red. After filtration of a small amount of dark brown precipitates, the red solution yielded on chilling to −20° pale brown microfine crystals which were filtered, washed with cold toluene, and dried *in vacuo* (150 mg, 47%). A further crop (*ca.* 50 mg) of the complex was obtained by partial removal of the solvent followed by chilling. Presence of a hydrogenation product, methyl 3-phenylpropionate, was shown in the filtrate by the nmr spectrum.

Kinetics of Isomer Equilibration of $Cp_2MoH[\sigma$-C(CF_3)=CH$CF_3]$. The sample prepared at −78° contained the conformational isomers in a ratio of *ca.* 4:1. The ratio, as determined by the relative areas of the Cp proton resonances of the two isomers at 100 MHz, approached 1:1 on overnight standing at or above room temperature (*cf.* Table III). The change of the ratio with time was measured at 20.5, 38.0, and 54.0° in perdeuterioacetone. The decrease of the more abundant isomer was analyzed by an assumption of a process

$$A \underset{k_{-1}}{\overset{k}{\rightleftharpoons}} B$$

where $k_1 = k_{-1}$. The rate constants ($k_1 \times 10^{-3}$ mol^{-1} min^{-1}) obtained are 3.9 at 20.5°, 11.1 at 38°, and 69.0 at 54°. From these data, an approximate activation energy of 16.8 kcal mol^{-1} was derived with $\Delta S^{\ddagger}$ of 1.9 eu mol^{-1}.

Mass Spectra. A direct-inlet system should be used with adequate oven temperature to ensure a good result. As the further fragmentation scheme of a very abundant ion, $(C_5H_5)_2Mo^+$, is nearly the same for all the complexes examined here, the peaks due to the fragments such as $C_5H_5(C_3H_3)Mo^+$, $(C_3H_3)_2Mo^+$, $(C_5H_5)_2Mo^{2+}$, $C_5H_5(C_3H_3)Mo^{2+}$, and Mo^+ are omitted for brevity except in one representative case. Each of the data is listed in order of oven temperature, *m/e* value, relative abundance in parentheses, and probable assignment. Only important or relatively abundant peaks above *m/e* 50 are shown. Cp stands for C_5H_5. For the molybdenum-containing species, only peaks corresponding for ^{96}Mo are listed.

$Cp_2MoH[C(CO_2CH_3)$=CH$CO_2CH_3]$: 100°, 370 (29) M^+, 369 (18) $M^+ - 1$, 339 (2.9) $M^+ - OCH_3$, 338 (2.9) $M^+ - HOCH_3$, 311 (2.9) $M^+ - CO_2CH_3$, 250 (6) $Cp_2MoC_2^+$, 226 (100) Cp_2Mo^+, 200 (3) $CpMo(C_3H_3)^+$, 174 (9) $(C_3H_3)_2Mo^+$, 148 (21) $C_5H_5MoCH^+$, 110 (21) $MoCH_2^+$, 92 (19) $C_7H_8^+$, 77 (22) $C_6H_5^+$, 66 (21) $C_5H_6^+$, 65 (18) $C_5H_5^+$, 57 (46) $C_4H_9^+$.

$Cp_2MoH[C(CF_3)$=CH$CF_3]$: 80°, 390 (9.2) M^+, 371 (0.1) $M^+ - F$, 370 (0.3) $M^+ - HF$, 326 (0.3) $Cp_2Mo(CF_2)_2^+$, 264 (0.2) $Cp_2MoF_2^+$, 245 (25) Cp_2MoF^+, 226 (100) Cp_2Mo^+, 180 (21) ?, 153.5 (9) $Cp_2MoC_2F_3^{2+}$, 132 (2.5) $Cp_2MoF_2^{2+}$, 122.5 (1.9) Cp_2MoF^{2+}, 95 (7.5) $C_2H_2CF_3^+$, 77 (4.8) $C_6H_5^+$, 75 (9.9) $C_2H_5CF_2^+$, 69 (3.6) CF_3^+, 66 (89) $C_5H_6^+$.

$Cp_2Mo(CH_2$=CHCN): 120°, 279 (3) M^+, 226 (26) Cp_2Mo^+, 92 (75) $C_7H_8^+$, 91 (100) $C_7H_7^+$, 66 (6.4) $C_5H_6^+$, 65 (17) $C_5H_5^+$, 53 (4.7) CH_2=CHCN$^+$, 51 (8.2) CH≡CCN$^+$.

$Cp_2MoH[CH(CN)CH_3]$: 80°, 281 (0.1) M^+, 279 (4.8) $M^+ - 2H$, 266 (4.3) $M^+ - CH_3$, 264 (3.8) $Cp_2MoC_2N^+$, 254 (3.7) $Cp_2MoC_2H_4^+$, 252 (2.8) $Cp_2MoC_2H_2^+$, 226 (96) Cp_2Mo^+, 133 (53) $Cp_2MoC_2NH_2^{2+}$, 93 (36) $C_7H_9^+$, 92 (66) $C_7H_8^+$, 91 (100) $C_7H_7^+$, 67 (47) $C_5H_7^+$, 66 (45) $C_5H_6^+$, 65 (32) $C_5H_5^+$, 54 (69) $C_2H_4CN^+$.

$Cp_2Mo(PhC{\equiv}CPh)$: 100°, 404 (26) M^+, 238 (1) Cp_2MoC^+, 226 (100) Cp_2Mo^+, 180 (11) $Ph_2C_2H_2^+$, 179 (11) $Ph_2C_2H^+$, 178 (20) $Ph_2C_2^+$, 91 (10) $C_7H_7^+$, 84 (8) $C_6H_{12}^+$, 78 (2.4) $C_6H_6^+$, 77 (2.3) $C_6H_5^+$, 76 (2.4) $C_6H_4^+$, 69 (7.2), 56 (15) $C_4H_8^+$.

$Cp_2Mo(CH_2$=CH$CO_2CH_3)$: 100°, 312 (8.5) M^+, 281 (1.0) $M^+ - OCH_3$, 253 (1.4) $M^+ - CO_2CH_3$, 240 (1.4) $M^+ - CHCO_2CH_3$, 226 (100) Cp_2Mo^+, 98 (7.1) ?, 92 (5.7) $C_7H_8^+$, 91 (5.3) $C_7H_7^+$, 85 (5.5) $C_4H_5O_2^+$, 66 (44) $C_5H_6^+$, 57 (6.3) $C_4H_9^+$, 55 (32) $C_4H_7^+$.

$Cp_2Mo($*trans*-CH_3O_2CCH=CH$CO_2CH_3)$: 100°, 370 (5.4) M^+, 339 (1.6) $M^+ - OCH_3$, 311 (2.3) $M^+ - CO_2CH_3$, 250 (1.7) Cp_2-

Table I. Analytical and Some Physical Data

Compd	Color	Mp,[a] °C	C, %[b]	H, %[b]	N, %[b]	Mol wt[c]	Characteristic ir frequency (in cm^{-1}) with provisional assignment
$Cp_2MoH(\sigma\text{-}C(CO_2CH_3)=CHCO_2CH_3)$	Dark red	103–105	51.84 (51.90)	4.82 (4.87)		370	1845 (MoH), 1717, 1692 (C=O), 1568 (C=C)
$Cp_2WH(\sigma\text{-}C(CO_2CH_3)=CHCO_2CH_3)$	Dark red	103–105	42.43 (41.94)	4.19 (3.96)			1890 (WH), 1695, 1665 (C=O), 1555 (C=C)
$Cp_2MoH(\sigma\text{-}C(CF_3)=CHCF_3)$	Red	112–113	43.41 (43.09)	3.33 (3.10)		390 360[d]	1905 (MoH), 1610, 1600 (C=C), 1100 (CF)
$Cp_2Mo(PhC{\equiv}CPh)$	Dark red	164–165	70.93 (71.29)	4.97 (4.99)		404	1774 (MoC_2), 1580, 1481, 1439 (Ph), 887, 827 (Cp), 761, 696 (Ph)
$Cp_2MoH(\sigma\text{-}CH(CN)CH_3)$	Brownish orange	87–88	55.68 (55.54)	5.24 (5.34)	4.76 (4.98)	281	2170 (CN), 1860 (MoH), 1410, 1005, 840, 810, 770 (Cp)
$Cp_2MoH(\sigma\text{-}CH(CN)CH_2CN)$	Brownish orange	165–166	54.83 (54.91)	4.66 (4.61)	9.06 (9.15)		2230, 2190 (CN), 1841 (MoH), 1110, 1008, 998, 844, 786 (Cp)
$Cp_2Mo(CH_2{=}CHCN)$	Reddish brown	139–140	56.53 (55.93)	5.20 (4.66)	4.94 (5.02)	279	2170 (CN), 1405, 1145, 1020, 990, 840, 825, 780 (Cp)
$Cp_2Mo(CH_2{=}CHCO_2CH_3)$	Pale brown	190–191	53.91 (53.86)	5.25 (5.13)		312	1658 (C=O), 1437, 1375 (CO), 1155 (CO), 810 (Cp)
$Cp_2Mo(trans\text{-}CH_3O_2CC(H){=}CCO_2CH_3)$	Reddish brown	223–224	51.87 (51.90)	4.84 (4.87)		370	1665 (C=O), 1295, 1157, 1016, 878, 840
$Cp_2Mo(cis\text{-}CH_3O_2CC(H){=}CCO_2CH_3)$	Pale brown	191	51.39 (51.90)	4.82 (4.87)		370	1705 (C=O), 1437, 1143, 1050, 837
$Cp_2Mo(PhCH{=}CHCO_2CH_3)$	Pale pink	196–197	61.81 (61.86)	5.28 (5.15)		388	1653 (C=O), 1589, 1488 (Ph), 1262, 1155 (CO), 696 (Ph)

[a] Measured under nitrogen. [b] Calculated values in parentheses. [c] Measured by mass spectrometry (peaks due to ^{96}Mo are listed). [d] Cryoscopic in benzene.

Table II. ^1H Nmr Spectra[a]

Compd	π-Cyclopentadienyl protons	Other protons[b]	Solvent
$Cp_2MoH(\sigma\text{-}C(CO_2CH_3)=CHCO_2CH_3)$	4.68 (10 H)	−10.4 (1 H, MoH, s), 3.49 (3 H, OCH_3, s), 3.54 (3 H, OCH_3, s), 6.17 (1 H, =CH, s)	CS_2
$Cp_2WH(\sigma\text{-}C(CO_2CH_3)=CHCO_2CH_3)$	4.60 (10 H)	−13 (1 H, WH, s), 3.40 (3 H, OCH_3, s), 3.50 (3 H, OCH_3, s), 6.00 (1 H, =CH, s)	CS_2
$Cp_2MoH(\sigma\text{-}C(CF_3)=CHCF_3)$	4.84 (10 H, isomer I) 4.87 (10 H, isomer II)	−8.51 (1 H, MoH (isomer I), s), −8.90 (1 H, MoH (isomer II), broad s), 6.7 (2 H, =CH (both isomers), m)	CS_2
$Cp_2Mo(PhC{\equiv}CPh)$	4.45 (10 H)	7.05–7.30 (6 H, Ph, m), 7.55, 7.63 (4 H, Ph, m)	CS_2
$Cp_2MoH(\sigma\text{-}CH(CO_2CH_3)CH_3)$	4.32 (5 H), 4.38 (5 H)	1.44 (3 H, CH_3, d, J = 7.5 Hz), 2.24 (1 H, >CH, q, J = 7.5 Hz), 3.45 (3 H, OCH_3, s)	C_6D_6
$Cp_2MoH(\sigma\text{-}CH(CN)CH_3)$	4.18 (5 H), 4.33 (5 H)	−7.9 (1 H, MoH, s), 1.14 (3 H, CH_3, d, J = 6.0 Hz), 1.48 (1 H, >CH, dq, J = 6.0 Hz, J_{HCMoH} = 1.5 Hz)	C_7D_8
$Cp_2Mo(H_2C{=}CHCO_2CH_3)$	3.92 (5 H), 4.33 (5 H)	1.46 (1 H, H_AC=, dd, J_{AB} = 5.9 Hz, J_{AC} = 9.3 Hz), 1.91 (1 H, H_BC=, dd, J_{BC} = 12.0 Hz), 2.56 (1 H, H_CC=, dd), 3.53 (3 H, OCH_3, s)	C_6D_6
$Cp_2Mo(H_2C{=}CHCN)$	4.47 (5 H), 4.59 (5 H)	1.12–1.65 (3 H, H_{A-C}, complex ABC pattern)	$CDCl_3$
$Cp_2Mo(trans\text{-}CH_3O_2CCH{=}CHCO_2CH_3)$	4.61 (10 H)	2.72 (2 H, =CH, s), 3.61 (6 H, OCH_3, s)	$CDCl_3$
$Cp_2Mo(cis\text{-}CH_3O_2CCH{=}CHCO_2CH_3)$	4.65 (10 H)	2.47 (2 H, =CH, s), 3.60 (6 H, OCH_3, s)	$CDCl_3$
$Cp_2Mo(trans\text{-}PhCH{=}CHCO_2CH_3)$	4.19 (5 H), 4.57 (5 H)	2.92 (1 H, $=CH_A$, d, J = 12.4 Hz), 3.64 (3 H, OCH_3, s), 3.75 (1 H, $=CH_B$, d, J = 12.4 Hz), 6.91, 7.23 (5 H, Ph, m)	$CDCl_3$

[a] Chemical shifts measured downfield from internal TMS. [b] Parentheses indicate intensity, assignment, multiplicity, and coupling constant when available: s, singlet; d, doublet; dd, double doublet; q, quartet; m, complex multiplet.

MoC_2^+, 239 (1.6) Cp_2MoCH^+, 226 (100) Cp_2Mo^+, 113 (24) $CH_3O_2CCH{=}CHCO^+$, 92 (26) $C_7H_8^+$, 91 (37) $C_7H_7^+$, 85 (10.5) $C_4H_5O_2^+$, 59 (13) $C_2H_3O_2^+$.

$Cp_2Mo(cis\text{-}CH_3O_2CCH{=}CHCO_2CH_3)$: 100°, 370 (5.5) M^+, 339 (1.4) $M^+ - OCH_3$, 311 (2.1) $M^+ - CO_2CH_3$, 250 (1.0) $Cp_2MoC_2^+$, 238 (1.2) Cp_2MoC^+, 226 (100) Cp_2Mo^+, 115 (32) CH_3O_2-

Table III. ^{19}F Nmr Data of $Cp_2MoH(\sigma\text{-}C(CF_3)=CHCF_3)$

Sample	Solvent (temp of measurement)	Chemical shift[a]	Rel area	Splitting (coupling constant)	Assignment[b]
Fully equilibrated sample	Toluene (at room temperature)	58.3	1	Double quartets (J_{CF_3-H} = 9 Hz) ($J_{CF_3-CF_3}$ = 2 Hz)	β-CF_3 } isomer I
		59.0	1	Quintet (J_{CF_3-H} = 2 Hz) ($J_{CF_3-CF_3}$ = 2 Hz)	α-CF_3 } isomer I
		59.6	1	Double quartets[c]	β-CF_3 } isomer II
		63.9	1	Quintet[c]	α-CF_3 } isomer II
Immediately after preparation at −78°	THF (at −77°)	58.4	4[d]	Doublet quartets[c]	β-CF_3, isomer I
		59.7	1	Double quartets[c]	β-CF_3, isomer II
		60.6	4	Quintet[c]	α-CF_3, isomer I
		64.8	1	Quintet[c]	α-CF_3, isomer II
	THF (at 22.5°)	58.5[e]	4	Double quartets[c]	β-CF_3 } isomer I
		58.8[e]	4	Quintet[c]	α-CF_3 } isomer I
		59.7[e]	1	Double quartets[c]	β-CF_3 } isomer II
		63.9[e]	1	Quintet[c]	α-CF_3 } isomer II

[a] Chemical shift in parts per million from internal $CFCl_3$. [b] Assignment is based on the data obtained in THF at −77 and 22.5°. [c] The same splitting pattern and coupling constants as above. [d] Relative area changes on overnight standing at room temperature. [e] Note changes in chemical shifts. The sample was measured before appreciable conformational change.

$CCH_2CH_2CO^+$, 114 (47) $CH_3O_2CCH{=}CHCHO^+$, 113 (81) $CH_3O_2CCH{=}CHCO^+$, 85 (17.6) $C_4H_5O_2^+$, 66 (24) $C_5H_6^+$, 65 (13) $C_5H_5^+$, 59 (48) $C_2H_3O_2^+$.

$Cp_2Mo(PhCH{=}CHCO_2CH_3)$: 185°, 388 (1.9) M^+, 329 (0.2) $M^+ - CO_2CH_3$, 261 (2.5) ?, 226 (26) Cp_2Mo^+, 162 (67) $PhCH{=}CHCO_2CH_3^+$, 131 (100) $PhCH{=}CHCO^+$, 103 (49) $PhCH{=}CH^+$, 102 (12) PhC_2H^+, 91 (4.8) $C_7H_7^+$, 77 (28) $C_6H_5^+$, 66 (5.8) $C_5H_6^+$, 65 (5.3) $C_5H_5^+$.

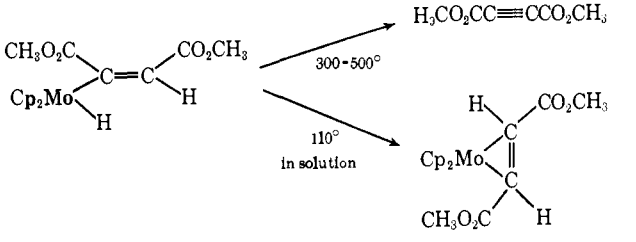
Results

A. Reaction with Acetylenic Compounds. Reactivities of various acetylenic compounds toward **1** or **2** were found sensitive on substitutent effects. While acetylenes having electron-attracting groups such as $-CF_3$ or $-CO_2CH_3$ gave rise to the insertion reactions (eq 1), diphenylacetylene led to the substitution reaction accompanied by the partial hydrogenation (eq 2). Hexafluoro-2-butyne reacted with **1** rapidly; the reaction with an excess of the acetylene at −78° went to completion within 10 min. The reaction with diphenylacetylene proceeded at ambient temperature or above. Di-*tert*-butylacetylene did not react with **1** in refluxing toluene; both of the electronic and steric effects of the substituent may be responsible for the lack of reactivity.

Hydrido-σ-alkenyl Complexes. The analytical and physical properties are summarized in Table I–III. Insertion of an acetylenic triple bond into a metal–hydrogen bond leading to a σ-alkenyl–metal complex has been known for rhenium,[26] manganese,[27,28] iridium,[29,30] and platinum[22] hydride complexes. Hexafluoro-2-butyne gave exclusively a trans adduct, as was the case for $HMn(CO)_5$[27] or $HRe(CO)_5$,[28] as evidenced by the ^{19}F nmr spectrum (Table III). Surprisingly, the cis adduct was completely absent in this case. The exclusive trans addition contrasts with the cis addition (cis insertion) reported for the reaction of hexafluoro-2-butyne with $PtHCl(PR_3)_2$.[31] The stereochemistry of trans insertion appears to favor a nonconcerted, multistep mechanism. However, as will be discussed separately, a concerted mechanism can also accommodate the trans insertion of acetylenic bonds.

The geometry around the double bond of the product from dimethyl acetylenedicarboxylate and **1** or **2** was inferred to be cis on the basis of the ^1H nmr spectrum (Table II), whose pattern resembles that of the known cis adduct, $Cp_2Re[\sigma\text{-}C(CO_2CH_3){=}CHCO_2CH_3]$.[26]

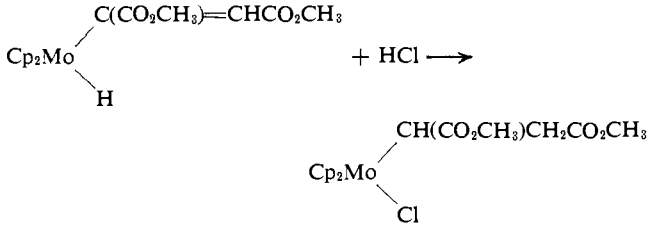
The stability of hydrido-σ-alkenyl compounds from hexafluoro-2-butyne and acetylene dicarboxylate suggests that they lie in relatively deep potential wells. It would than be of interest to examine the thermal reactions as to whether the alkene formation or alkyne formation (reverse reaction of (1)) would prevail. A typical hydrido-σ-alkenyl complex, $Cp_2MoH[\sigma\text{-}C(CO_2CH_3){=}CHCO_2CH_3]$, was heated in refluxing toluene to find a dimethyl fumarate complex, $Cp_2Mo[trans\text{-}CH(CO_2CH_3){=}CHCO_2CH_3]$, no acetylene dicarboxylate being detected. When the solid sample was heated *in vacuo* at elevated temperature (300–500°), the acetylene was released from the complex as the sole product. When the thermal reaction of the σ-alkenyl complex in refluxing toluene was carried out in the presence of excess acetylene dicarboxylate, one finds only the fumarate complex; this indicates the absence of ligand exchange and is suggestive of the inertness of the olefin complex. The reaction involves geometrical isomerization of the *cis*-alkene derived from the disubstituted



acetylene. The result seems reasonable in view of the isomerization observed in the reaction of *cis*-alkene with **1** (*vide infra*). The hydrido–alkenyl complex when

(26) M. Dubeck, *Inorg. Chem.*, **3**, 1757 (1964).
(27) P. M. Treichel, E. Pitcher, and F. G. A. Stone, *ibid.*, **1**, 511 (1962).
(28) J. B. Wilford and F. G. A. Stone, *ibid.*, **4**, 93 (1965).
(29) J. Trocha-Grimshaw and H. B. Henbest, *Chem. Commun.*, 757 (1968).
(30) W. H. Baddley and M. S. Fraser, *J. Amer. Chem. Soc.*, **91**, 3661 (1969).
(31) H. C. Clark and W. C. Tsang, *ibid.*, **89**, 533 (1967).

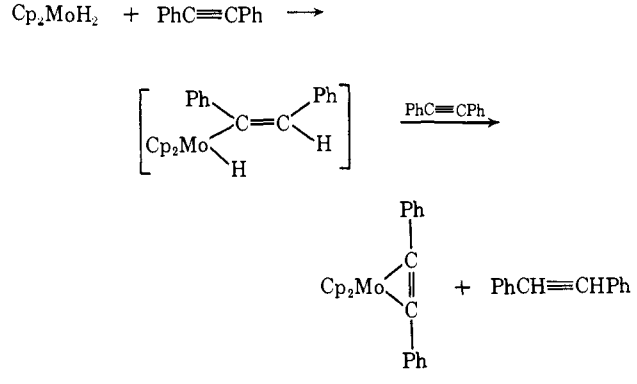
treated with dry hydrogen chloride in ether produced a purple complex which can be assigned a structure as the chloro complex $Cp_2MoCl[\sigma\text{-}CH(CO_2CH_3)CH_2CO_2CH_3]$ on the basis of the nmr spectrum (see Experimental Section). The resistance of the σ-alkyl metal bond



against protolysis is remarkable.

Acetylene Complexes. Attempts to obtain an acetylene complex $Cp_2Mo(RC{\equiv}CR)$ from hexafluoro-2-butyne have been unsuccessful, the outstanding inertness of the hydrido-σ-alkenyl product preventing further reaction. The same reaction with dimethyl acetylenedicarboxylate produced the fumarate complex (foregoing section) but failed to give the expected acetylene complex in any appreciable quantity. The reaction path will be discussed later in terms of the stability of the olefin complex.

An acetylene complex was obtained when **1** was treated with an excess of diphenylacetylene. Although, monitoring the reaction with ^1H nmr, we have failed to detect the existence of the expected hydrido-σ-alkenyl compounds, the intermediacy of a monohydrido complex is quite likely in view of the results described so far. However, a concerted mechanism involving a simultaneous transfer of two hydrido ligands to the



acetylene cannot be excluded. The discussion on the mechanism will be deferred to a future publication. The stereoselectivity of the hydrogenation was quite high; *cis*-stilbene was produced exclusively when the reaction was carried out at 25°. The stereochemical purity was impaired with increase in temperature; the *trans*-stilbene yield increased to 20% at 110°. The absence of the olefin complex in this case is apparently accounted for in terms of the inability of stilbene to form a strong coordination bond to the Cp_2Mo moiety.

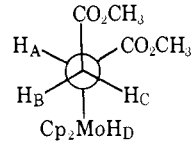
It may be added that only a binuclear diphenylacetylene complex, $Cp_2Mo_2(CO)_6(PhC{\equiv}CPh)$, has been known for molybdenum.[32,33] The same reaction of diphenylacetylene with the tungsten congener, Cp_2WH_2, was attempted in refluxing toluene to find no reaction after 6 hr. Despite of the comparable Lewis basicity, the chemical inertness of metal–hydride bond is prominent for the tungsten compound.

B. Reactions with Olefinic Compounds. Olefins carrying no strongly electron-attacting group lack the reactivity toward **1**, *e.g.*, 1,5-cyclooctadiene or *trans*-stilbene. Typical activated olefins such as methyl acrylate, acrylonitrile, or dimethyl fumarate readily react at room temperature. The reactivity depends not only on the electronic effect but also on the steric effect. Thus, methyl cinnamate or dimethyl citraconate reacts only upon heating at 80–100° and tetrasubstituted ethylenes, *e.g.*, 2,3-dimethyl maleic anhydride, do not react. Tetracyanoethylene reacts readily with **1**, but the product was an unidentifiable insoluble substance.

Hydrido-σ-alkyl Complexes. Acrylonitrile and fumaronitrile provide thermally stable insertion products whose stability permits isolation and full characterization (Tables I and II). They are fairly inert too; in particular the product from fumaronitrile, $Cp_2MoH[\sigma\text{-}CH(CN)CH_2CN]$, is perhaps the most stable hydrido-σ-*sec*-alkyl compound, being resistent to further transformation. For example, when heated at 110° in toluene it is recovered unchanged. The product from acrylonitrile, $Cp_2MoH[\sigma\text{-}CH(CN)CH_3]$, treated with excess acrylonitrile, was transformed into a stable acrylonitrile complex, $Cp_2Mo(CH_2{=}CHCN)$ (*vide infra*).

The insertion products of methyl acrylate and dimethyl fumarate are not stable enough at ambient temperature to allow purification through crystallization but are detectable by ^1H nmr. A reaction solution prepared by dissolving a 1:1 mixture of **1** and fumarate in C_6D_6 at 22° showed a complex nmr spectrum which can be interpreted in terms of the hydrido-σ-alkyl species, $Cp_2MoH[\sigma\text{-}CH(CO_2CH_3)CH_2CO_2CH_3]$. The spectrum contains a typical ABC pattern in the 2–3-ppm region (TMS) indicating that the methylene protons constitutes a diastereotopic pair. A computer analysis of this pattern led to an unequivocal assignment with the parameters shown in Table IV; the chemical shifts and coupling constants are reasonable and compare with the data[34] reported for the related σ-alkyl complex, $Co(CN)_5[\sigma\text{-}CH(CO_2CH_3)CH_2CO_2\text{-}$

Table IV. Nmr Spectrum of $Cp_2MoH[\sigma\text{-}CH(CO_2CH_3)CH_2CO_2CH_3]$



Proton	Chemical shift,[a] ppm	Coupling constants, Hz
H_A	2.69	J_{AB} 5.5
H_B	2.51	J_{AC} 10.5
H_C	2.94	J_{BC} −17.0
H_D	−18.4	
CH_3	3.39	
	3.43	
Cp	4.32, 4.43	

[a] Measured in C_6D_6. Downfield from internal TMS.

(32) A. Nakamura, *Mem. Inst. Sci. Ind. Res., Osaka Univ.*, **19**, 81 (1962).

(33) A. Nakamura and N. Hagihara, *Nippon Kagaku Zasshi*, **84**, 344 (1963).

(34) L. M. Jackman, J. A. Hamilton, and J. M. Lawlor, *J. Amer. Chem. Soc.*, **90**, 1914 (1968).

$CH_3]^{3-}$. The two cyclopentadienyl groups also form a diastereotopic pair due to the asymmetric center at the α-carbon atom, giving rise to two sharp singlets for the protons.

Olefin Complexes. Labile hydrido-σ-alkyl compounds afford the corresponding olefin complexes, Cp_2Mo(olefin), and alkanes upon treatment with excess olefins. The process was followed by ^1H nmr for the reaction between **1** and dimethyl fumarate or dimethyl maleate at 22° in toluene. An identical ABC pattern was observed in the ^1H nmr for both esters indicating the formation of the same hydrido-σ-alkyl species. Then the reaction mixture of **1** and the maleate was heated at 110° for 1 hr to give two isomeric products differing in color and solubility. The less soluble one with a higher melting point was identical with the fumarate complex, Cp_2Mo(*trans*-$CH_3O_2CCH{=}CHCO_2CH_3$), in its ir data (Table I) and the more soluble one with the lower melting point was then assigned as the maleate complex. The higher the reaction temperature, the lower is the yield of the maleate complex. A maximum yield of about 50% was obtained from the reaction of **1** and maleate at 50–55° in toluene for 8 hr.

Acrylonitrile and methyl acrylate afforded at higher temperature (60°) the alkanes and the corresponding olefin complexes *via* the hydrido-σ-alkyl species as detected by the ^1H nmr. These monosubstituted ethylenes being prochiral, the two cyclopentadienyl groups form a diastereotopic pair upon the formation of the olefin complexes. The splitting into two sharp signals of the cyclopentadienyl proton resonance is ascribable to this effect.

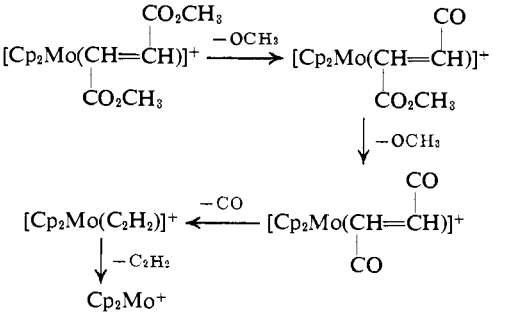
Methyl cinnamate, a prochiral disubstituted ethylene, reacting with **1** only slowly in toluene at 110°, produced the olefin complex, Cp_2Mo(*trans*-$PhCH{=}CHCO_2CH_3$), and the alkane $PhCH_2CH_2CO_2CH_3$, but the hydrido-σ-alkyl species could not be detected by spectral means.

C. Mass Spectra. The mass spectra of the new molybdenum complexes described in this papr serve not only to confirm their molecular structure but also provide valuable information on the nature of the bonds involved. The presence of a molybdenum atom in the parent or fragment ions is readily recognizable by the characteristic isotopic pattern of the atom (isotopic distribution: ^{92}Mo, 15.84; ^{94}Mo, 9.04; ^{95}Mo, 15.72; ^{96}Mo, 16.53; ^{97}Mo, 9.46; ^{98}Mo, 23.78; and ^{100}Mo, 9.63%).

The hydrido-σ-alkyl complexes generally show very weak molecular ions and the spectra are not reproducible. In contrast, the spectra of hydrido-σ-alkenyl complexes contain relatively abundant molecular ions suggesting their greater stability compared to the hydrido-σ-alkyl complexes. This may be due to the transformation into the corresponding olefin complexes as described above for $Cp_2MoH[C(CO_2CH_3){=}CHCO_2CH_3]$.

A very abundant molecular ion peak was observed for the diphenyl acetylene complex, $Cp_2Mo(PhC{\equiv}CPh)$, suggesting stabilization due to an electronic delocalization. Fragmentation to Cp_2Mo^+ and $PhC{\equiv}CPh$ then occurs which was followed by further fragmentations. The mass spectra of the olefin complexes reveal interesting fragmentation patterns which reflect the strength of the molybdenum–olefin bonding. A typical fragmentation scheme is illustrated (Scheme I) for Cp_2Mo(*trans*-$CH_3O_2CCH{=}CHCO_2CH_3$). Elimination of CH_3O groups and CO groups rather than the dimethyl fumarate molecule as a whole may be taken as evidence for the relatively strong metal–olefin or the metal–acetylene bonds.

Scheme I

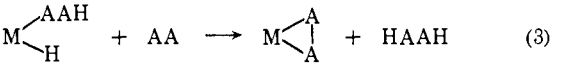


A feature common to all these complexes examined here is the very high abundance of peak at *m/e* 226 corresponding to Cp_2Mo^+. Appearance of peaks at *m/e* 115–111 shows formation of dipositive species Cp_2Mo^{2+}. The result is in accord with the well-known stability of $Cp_2Mo(II)$ complexes. The abundant peak at *m/e* 91 observed in the most of the spectra may be due to $C_7H_7^+$ formed by recombination of $C_5H_5^+$ and C_2H_2.

Discussion

Here we discuss the observed reaction paths with an emphasis on the reactivity and structure based on physical data of the hydrido-σ-alkyl or -σ-alkenyl complexes. The detailed reaction mechanisms as well as the bond nature of the novel molybdenum–acetylene or –olefin complexes will be discussed separately.

Reaction Paths. For the stoichiometric reactions between Cp_2MoH_2 (**1**) and unsaturated compounds we have observed previously two reactions (1 and 2) and confirmed in this paper a path from an insertion product to an olefin complex (reaction 3).



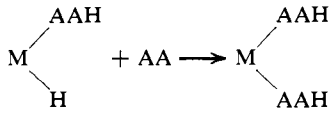
(3)

Many electrophilic olefins and acetylenes produced the hydrido-σ-alkyl (or -σ-alkenyl) compounds (reaction 1). The thermal stability of the hydrido-alkyl compounds appears to increase with the increase in electron-attracting properties of substituents of the alkyl group, a trend commonly observed[35] for metal–carbon bond stabilities. The C≡N stretching band in $Cp_2MoH[\sigma\text{-}CH(CN)CH_2R]$ (R = H, CN) or the CO stretching band in $Cp_2MoH[\sigma\text{-}CH(CO_2CH_3)CH_2\text{-}CO_2CH_3]$ shows a shift to lower frequency with an increase in intensity[36] implying an electron-donating nature of the Cp_2MoH moiety. The enhanced stability of a hydrido-σ-alkenyl compound compared to the corresponding hydrido-σ-alkyl compound is accounted for in terms of the dπ accepting property of an alkenyl group. Qualitatively, these stabilities run parallel with the rate of formation. For example, the most stable hydrido-σ-alkenyl derivative, $Cp_2MoH[\sigma\text{-}C(CF_3){=}CHCF_3]$, was formed from the components within a

(35) P. M. Treichel and F. G. A. Stone, *Advan. Organometal. Chem.*, 1, 178 (1964).
(36) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1968, p 72.

few minutes at −78°, while a sluggish reaction between diphenylacetylene and **1** at room temperature produced only the complex $Cp_2Mo(PhC{\equiv}CPh)$, mainfesting no indication for the existence of the hydrido-σ-alkenyl species in the ^1H nmr. The fact, however, does not invalidate a kinetic intermediacy of the σ-alkenyl species. We may say that in a practical sense[20] the σ-alkenyl species is absent. The above results merely indicate strong dependence of the free energy of activation ($\Delta F^{\ddagger}$) on the potential energy of the hydrido-alkenyl species. The previous observation that a stronger electrophile prefers reaction 1 and a weaker one follows reaction 2 is now understandable. However, a question still remains as to the reason for failure to isolate complexes of strongly electron-accepting acetylenes, *e.g.*, $Cp_2Mo(CF_3C{\equiv}CCF_3)$ or $Cp_2Mo(CH_3O_2CC{\equiv}CCO_2CH_3)$.

Another conceivable reaction path of the hydrido-σ-alkyl complexes is reaction 4. The diinsertion reaction has never been observed here, however. Steric effects due to the alkyl (or alkenyl) and two cyclopentadienyl groups may be responsible for the reluctance of the hydride species to undergo reaction 4, since the spectroscopic data (Tables II and III) of the hydrido-σ-alkyl complexes can be considered to be comparable to the data of Cp_2MoH_2 (ν_{Mo-H} 1847 cm^{-1}; ^1H nmr at δ −8.76 ppm (TMS))[37] for the hydride ligand. The hydride ligand in $Cp_2MoH[\sigma\text{-}CH(CO_2CH_3)CH_2CO_2CH_3]$ retains the usual hydridic character as indicated by the reaction with hydrogen chloride leading to the chloro-σ-alkyl compound.



(4)

The observed stabilities of the hydrido-σ-alkyl compounds described here are remarkable. Prior to the present study, transition metal *cis*-hydrido–alkyl complexes have been regarded to be very thermally unstable and only postulated as intermediates. A few *trans*-hydrido–alkyl or –aryl complexes stabilized with chelated diphosphines are known,[38-40] *e.g.*, *trans*-$HRu(CH_3)(Me_2PCH_2CH_2PMe_2)_2$. In some cases[41-44] interaction of side chain groups of a coordinated phosphine with a coordinatively unsaturated central metal leads to hydrido complexes, *e.g.*, $HRu[\sigma\text{-}CH_2P(CH_3)CH_2CH_2P(CH_3)_2][(CH_3)_2PCH_2CH_2P(CH_3)_2]$. A hydrido–diethylcobalt complex stabilized by a tridentate phosphine, $HCo(C_2H_5)_2[(Ph_2PCH_2)_1C]$, has been reported.[45] Finally, closely related hydrido–aryl complexes of formula, $(\pi\text{-}C_5H_5)_2W(H)Ar$, were reported only recently.[46] The reactivities of these complexes, however, are virtually unknown at present. The molybdenum hydrido–alkyl or –alkenyl complexes are the first example of its class prepared by an insertion reaction.

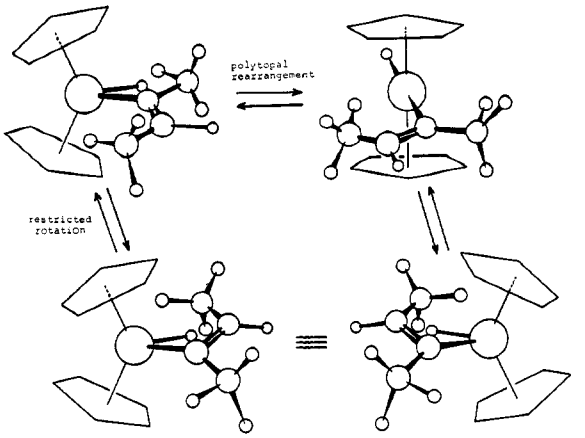


Figure 1. Isomerization schemes.

Conformational Isomerism. Although the elemental analysis and melting behavior of the hexafluorobutyne adduct $Cp_2MoH[\sigma\text{-}C(CF_3){=}CHCF_3]$ proved the chemical purity, the ^1H (Table II) and ^{19}F (Table III) nmr spectra were very complex; every type of protons emerges as a pair of resonances, indicating the presence of two isomeric species. The ^1H and ^{19}F nmr data excluded a geometrical isomerism with respect to the double bond or a valence tautomerism involving, *e.g.*, the hydride shift. The molecular model constructed on the basis of the established molecular structure for Cp_2MoH_2[47,48] suggested the possibility for a conformational isomerism; the steric requirements of the ligands create a barrier for rotation around the σ-alkenyl–metal bond leading to two conformers shown in Figure 1.

The ^1H nmr of a sample prepared at −78° and measured at −77° shows an isomer ratio of 4:1, the maximum value we have achieved so far. Equilibration to the 1:1 mixture was slow at room temperature. The nmr spectrum measured at 22° immediately after preparation at −78° showed approximately the same isomer ratio of 4:1 (Table III). The full equilibration required about 24 hr at room temperature but it was complete within 2 hr at 54°. It is of interest to observe that while the ^{19}F chemical shift of α-CF_3 shows a considerable downfield shift on raising the temperature, the other β-CF_3 remains nearly constant in chemical shift. Two equilibration mechanisms are possible, a restricted rotation or a polytopal rearrangement[49] through a quasi-square-planar intermediate (see Figure 1). Although the temperature dependence of the ^{19}F nmr and the energetics derived therefrom support the existence of conformational isomerism, the available data are insufficient to differentiate between the two mechanisms.

Green and Lindsell observed a doublet for the hydride proton in $(C_5H_5)(C_6F_5C_5H_4)MoH(C_6F_5)$[50] and interpreted it in terms of a through-space coupling with the nearest one of the ^{19}F nuclei in a C_6F_5 group, assuming a hindered rotation of the σ-pentafluorophenyl–metal bond. In the present system one of the conformers (the less abundant isomer II in Table III)

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shows the 1:3:3:1 quartet resonance (J_{HF} = 2 Hz) for the hydride proton which is ascribable to the through-space coupling with the nearest three equivalent ^{19}F nuclei. However, it is worth pointing out that each of the two pathways shown in Figure 1 has its own energy barrier for the equilibration. Let us refer to the rotational barrier as A which is to be overcome when the wedge-type orientation of the two cyclopentadienyl groups is maintained. A stereochemically nonrigid molecule would prefer to proceed along the alternative path, the polytopal rearrangement with barrier B; this molecule when it comes to a top of barrier B will witness an elevation of barrier A due to the increase in steric crowding at the quasisquare-planar transition state.

The energy barrier of *ca.* 17 kcal mol^{-1} suggests the possibility of separating the conformers. The configurational stability of $Cp_2MoH(R)$ is remarkable in view of the stereochemical nonrigidity[51] or the lability[52-54] of the group VIII metal–hydride complexes. A chiral pseudotetrahedral complex, *e.g.*, $(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_4X)MoH(R)$, if it were prepared, should in principle be resolvable into optical isomers as was the case for, *e.g.*, $[CpMn(CO)(NO)(PPh_3)]^+$.[55,56]

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Coenzyme B_{12} Model Studies. Equilibria and Kinetics of Axial Ligation of Methylaquocobaloxime by Thiols[1,2]

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Abstract: The reactions of thiols with methylaquocobaloxime have been shown to involve only axial ligation and not cleavage of the carbon–cobalt bond at 25°, ionic strength 1.0 *M*, and pH values less than 13. The rate constants for ligation by neutral thiol are twofold greater than those for thiolate anion. Mechanisms which account for the apparent reactivity of neutral thiols on the basis of general or specific catalysis by protons of the attack by thiolate anions on methylaquocobaloxime have been ruled out by (i) calculation of rate constants which are greater than the diffusion-controlled limit, (ii) structure–reactivity correlations, and (iii) the similarities of equilibrium and kinetic constants for ligation by neutral thiol and an *S*-methyl sulfide. The small effects of variations in thiolate anion basicity on the rate and equilibrium constants for ligation reactions of methylaquocobaloxime may be due to contributions to the stabilization of transition states and thiol-liganded products by π bonding between the cobalt and sulfur atoms. The data are consistent with a detailed mechanism for ligation which is SN1 in nature.

The similarities of numerous chemical and physical properties of cobaloximes with those of various derivatives of coenzyme B_{12} have recently been emphasized, especially by Schrauzer and coworkers.[4-14]

The cobaloximes are octahedral cobalt complexes with a planar ligand field (Figure 1) provided by two bidentate dimethylglyoxime anion ligands, and in at least one case the glyoxime nitrogens and the cobalt atom have been shown to be coplanar by X-ray crystallography.[15] A variety of alkylcobaloximes have been formed, isolated, and characterized, and either organic or inorganic neutral and anionic Lewis bases may act as axial ligands.

Several papers dealing with the ligand-substitution reactions of cobaloximes[16-19] and cobalamins[20-23]

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(2) Abbreviations: Bicine, *N,N*-bis(2-hydroxyethyl)glycine; EDTA, ethylenediaminetetraacetic acid; HEPES, *N*-2-hydroxyethylpiperazine-*N'*-2-ethanesulfonic acid; MA, mercaptoacetic acid; ME, 2-mercaptoethanol; $Me(D_2H_2)HOH$, methylaquocobaloxime; MMA, methyl mercaptoacetate; py, pyridine; SMME, *S*-methyl-2-mercaptoethanol.
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