Reaction of Transition Metal Dihydrides. III.[1] Stereochemistry and Mechanism of Stoichiometric Hydrogenation of Olefins by Dihydridobis(π-cyclopentadienyl)molybdenum

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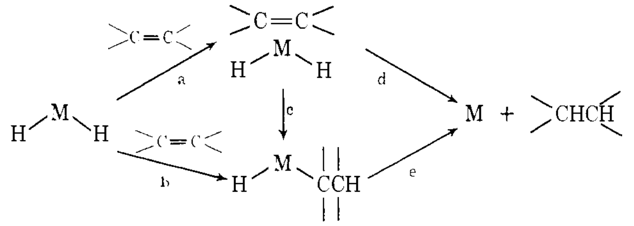
Abstract: The reaction of Cp_2MoH_2 (Cp = h^5-C_5H_5) with some activated olefins was studied as a model system for homogeneous hydrogenation catalysis. Stereochemical studies employing Cp_2MoD_2 and dimethyl fumarate or maleate established that the addition (insertion) produces selectively the cis adduct, threo- or erythro-σ-alkyl compound, $Cp_2MoD[CH(CO_2CH_3)CHD(CO_2CH_3)]$ and that the unimolecular elimination of the alkane from the σ-alkyl compound produces racemic or *meso*-dimethyl 1,2-dideuteriosuccinate with retention of configuration at the σ-bonded α-carbon atom. The elimination reaction, constituting a rate-determining step in the stoichiometric hydrogenation, produces the reactive species "Cp_2Mo" which reacts with a free olefin (if present) giving Cp_2Mo(π-olefin). Formation of a trans olefin π-complex observed in the reaction of Cp_2MoH_2 with a cis olefin (*e.g.*, dimethyl maleate) implies reversible nature of the insertion reaction. The complicated kinetic feature of the insertion step characterized with a considerable induction period suggested that $\sigma\pi$-electron donor-accepter ($\sigma\pi$-EDA) and σ-donor acceptor (σ-DA) interactions are side equilibria retarding the rate. The olefin substituent effect for the rate as well as the kinetics leads to a reasonable assumption that a π-olefin complex with parallel Cp rings (Cp_2MoH_2(olefin)) is an intermediate leading to the observed cis insertion.

In part I of this series,[2] we described the stoichiometric hydrogenation of activated olefins and acetylenes with dihydridobis(π-cyclopentadienyl)molybdenum (Cp_2MoH_2, **1**) which proceeds stepwise through hydrido σ-alkyl or σ-alkenyl complexes, $Cp_2MoH(R)$. Since the stoichiometric hydrogenation can be converted into a catalytic process[3] for some olefins, *e.g.*, methyl acrylate (at 120°, 60 atm), detailed mechanistic studies of the stoichiometric reaction with the dihydride should contribute to understanding of the catalytic reaction. In general, possible reaction pathways starting from a cis dihydride complex may be depicted schematically as shown in Scheme I. The practical difficulties in characterizing the thermally labile active catalysts and intermediates involved in these pathways have so far precluded a complete investigation of the mechanism. Thus, despite numerous reports on various facets of catalytic hydrogenation,[4] none of them provides detailed information of the stereochemistry and mechanism in each elemental step involved in one hydrogenation system.

Scheme I



Scattered information of some of these steps and of intermediates are now available. For example, step a, which has been frequently assumed,[5-10] is recently verified by the preparation of labile cationic trans hydrido olefin complexes,[11,12] $[HPt(PR_3)_2(C_2H_4)]^+$.

Insertion of an olefin into a metal–hydrogen bond most likely creates an intervening complex where the hydrido ligand and the olefin are both coordinated mutually in the cis position. Cis hydrido olefin complexes, *e.g.*, $IrH(CO)(PR_3)_2$(*trans*-NCCH=CHCN)[13] or $IrH(1,5\text{-}C_8H_{12})X_2L$,[14] are known where the stability may be due to its rigid geometry unfavorable to insertion. Further examples,[15,16] $[Cp_2MoH(C_2H_4)]^+$ and $Cp_2NbH(C_2H_4)$, were also recently reported. However, there has been no report detecting dihydrido olefin complexes which serve as a relevant model for the metal-assisted synchronous hydrogen transfer to olefins (*cf.* step d). An intermediate dihydridoolefin complex, $RhH_2Cl(Un)(PPh_3)_2$ (Un = olefin), has been postulated in a kinetic

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[1] A part of this paper was presented at the 5th International Conference on Organometallic Chemistry (Moscow), Abstracts, Vol. 2, 1971, p 550.

[2] Part I: A. Nakamura and S. Otsuka, *J. Amer. Chem. Soc.*, **94**, 1886 (1972); Part II: A. Nakamura and S. Otsuka, *ibid.*, **95**, 5091 (1973).

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study[5] of catalytic olefin hydrogenation with RhCl$(PPh_3)_3$. In the initial stage of interaction of electron-rich low-valent metal complexes with π-acidic olefin, it is not unlikely that electron donor–acceptor (EDA) complexes are formed instead of π complexes. Some bis(cyclopentadienyl)metal complexes are known to form EDA complexes[17] such as $[Cp_2Co]^+[TCNE]^-$, but none is so far found with hydrido complexes.

A one-step concerted insertion (step b) without intervention of a π complex is conceivable as a possible mechanism which formally belongs to a category of symmetry restricted reactions[18] in the absence of d-orbital participation. For distinction between these pathways, a kinetic investigation will be required. So far kinetic investigation of the olefin insertion step (step a–c) of cis dihydrido complexes of rhodium[5] or iridium[9] has been seriously hampered by instability of the resulting hydrido σ-alkyl species. The thermal stability of the species derived from **1** allows the investigation, and we studied olefin substituent effects in this step which should provide some information on the geometry and polarity of the transition state.

Both of the two possible pathways of hydrogen transfer, *i.e.*, the synchronous (step d) and stepwise one (step c–e), could lead to an overall cis addition of hydrogen in catalytic hydrogenation. However, the stereochemistry and kinetics of the alkane-elimination step of cis hydrido σ-alkyl complexes (step e) have not been studied because of the paucity of such complexes of adequate stability. During the period of our research, bis-π-cyclopentadienyls and hydride complexes of early transition metals have attracted interest. Green, *et al.*,[19] reported an analogous hydrido σ-alkyl intermediate in the reaction of Cp_2WH_2 (**2**) with activated olefins. Through an elusive intermediate, Cp_2W, thermally stable hydrido σ-aryls, $Cp_2W(H)Ar$, are formed.[20] Some interesting reactions of highly reactive metallocenes, Cp_2Mo[21] and Cp_2Ti,[22] and of metallocene hydrides, Cp_2NbH_3[16] and Cp_2ZrH_2,[23,24] are also reported. Studies of the olefin hydrogenation with **1** are of interest, both in their own right and for their pertinence to more general questions concerning the mechanism and stereochemistry of the transition metal catalyzed hydrogenation catalysis. In this paper we describe interactions of various olefins with **1** or **2** prior to insertion and the kinetics and stereochemistry of each step. Also discussed is the symmetry consideration of the valency orbitals of Cp_2MH_2 rationalizing the various experimental features observed.

Experimental Section

Materials and apparatus used were described in part I[2] of the series. All the reactions and physical measurements involving organometallic compounds were performed under pure nitrogen.

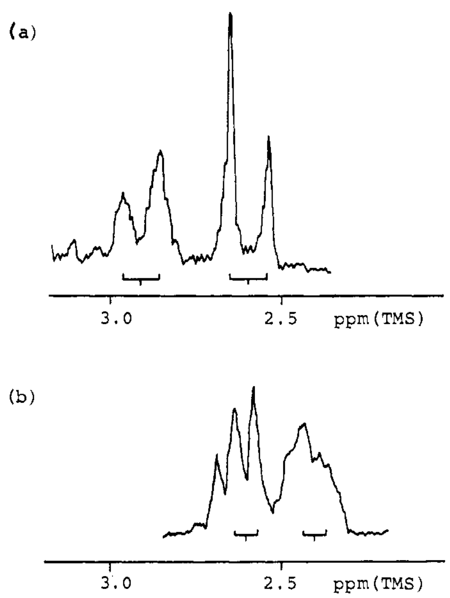

Figure 1. ^1H nmr spectra (measured in C_6D_6 under nitrogen, chemical shift from internal TMS standard at 100 MHz, only a part of peaks assigned to the metal alkyl proton is shown) of isomeric deuterated hydrido alkyl complexes: (a) prepared from Cp_2MoD_2 and dimethyl fumarate, J_{HH} (vicinal) = 10.5 Hz; (b) prepared from Cp_2MoD_2 and dimethyl maleate, J_{HH} (vicinal) = 5.5 Hz.

(a) Stereochemistry of Olefin Insertion. Stereochemical pathways of the insertion are investigated by means of deuterium labeling. A deuteriobenzene solution (0.5 ml) of dimethyl fumarate (58 mg, 0.4 mmol, concentration 0.8 mol/l.) and Cp_2MoD_2 (23 mg, 0.1 mmol, 0.2 mol/l.) was prepared at *ca.* 0° and immediately examined by ^1H nmr spectroscopy at room temperature (Figure 1). A similar experiment was repeated using dimethyl fumarate as the olefin. The results are also shown in the Figure 1.

(b) Stereochemistry of Alkane Elimination from the Hydridoalkyl Complex, $Cp_2MoH(R)$. Thermal decomposition of a deuterio alkyl complex formed *in situ* from Cp_2MoD_2 and dimethyl maleate or fumarate was investigated.

(i) Cp_2MoD_2 (87 mg, 0.381 mmol) was mixed with a benzene solution (3 ml) of dimethyl maleate (114 mg, 0.695 mmol) at room temperature. A color change to red-orange occurred in a few minutes. After being allowed to stand at the temperature for 1.5 hr, the mixture was heated at 60° for 15 min. A mixture of the maleate and the fumarate complexes, $Cp_2Mo(CH_3O_2CCH{=}CHCO_2CH_3)$, crystallized on cooling. The pale brown solution was taken out and evaporated to give a liquid. The presence of ir peaks at 781 and 847 cm^{-1} indicated *meso*-dimethyl 1,2-dideuteriosuccinate, and a peak at 865 cm^{-1} shows the presence of unreacted dimethyl maleate by comparison of the spectrum with the reported data[25] of authentic samples. The nmr spectrum ($CDCl_3$, singlet signals at δ (TMS) 2.60, 3.66, 6.80 ppm) also confirmed the above result although no distinction between the meso and the racemic isomers was made.

(ii) A similar reaction was performed with dimethyl fumarate at 100° for 1 hr. After removal of the fumarate complex and the solvent, the remaining liquid was examined by ir spectroscopy to reveal the presence of racemic dimethyl 1,2-dideuteriosuccinate (a peak at 812 cm^{-1}) and unreacted fumarate (a peak at 884 cm^{-1}).

(c) Kinetics of Insertion Reaction of Activated Olefins into the Mo–H Bond. Rate of formation of hydrido σ-alkyl complexes, $Cp_2MoH(R)$, in toluene solutions prepared at -40 to $-70°$ from **1** and activated olefins, *e.g.*, diethyl fumarate, was measured by following spectral changes in the visible region at 10–40°. An isosbestic point was observed at 380 nm with an increase in absorption at 400–500 nm for the reaction of dimethyl or diethyl fumarate. As the increment in absorption at 450 nm was found proportional to the concentration of the hydrido σ-alkyl species, the time–conversion

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Table I. Comparison of Observed Kinetic Data of Reaction of Cp_2MoH_2 with Diethyl Fumarate (DEF) in Toluene[a]

No.	Molar ratio (Cp_2MoH_2: DEF)	Concn of Cp_2MoH_2 (mmol/l.)	Temp, °C	Max rate (mmol/(l. sec))	Induction period (min)	Time at max rate (min)	Time at 90% conversion (min)	Pseudo-1st-order[b] rate const, sec^{-1}
1	1:18	11.9	10.2	0.0077	34	39	54	0.0020
2			16.0	0.0108	12	18	31	0.0031
3			23.0	0.027	5	7	10	0.0067
4		2.91	16.3	0.0015	28	38	60	0.0015
5			25.1	0.0053	7	11	24	0.0058
6[a]			31.1	0.0095	3	8.5	11	0.0076
7	1:1	26.4	16.5	0.069	6	10	13	0.07[c]
8			25.1	0.12	4	6	8	0.12[c]

[a] Use of dimethyl succinate as solvent in experiment No. 6 lengthened the induction period (13 min) and lowered the maximum rate (0.0042 mmol/(l. sec)). [b] Pseudo-first-order rate constants were obtained from the last half of the reaction by using a large excess of the olefin. [c] Second-order rate constant (mol $l.^{-1}$ sec^{-1}), obtained from the last quarter of the reaction.

curves were continuously plotted by following the increase in absorption at 450 nm. S-shaped time–conversion curves were generally obtained for the reaction of activated olefins (*cf.* Table I). Only the last quarter of the equimolar reaction obeyed second-order rate law. The rates at pseudo-first-order conditions using a 20-fold excess of the olefin, were analyzable after *ca.* 60–70% reaction by a first-order treatment. The induction period persists even when a large excess of olefins are used and even at 31.1°. The pseudo-first-order rate constants (*cf.* Table I) depend on the initial concentration of **1** in fractional order. Pseudo-first-order rate constants at large excess olefin concentrations, temperature, and induction periods are listed below: methyl acrylate ($[\mathbf{1}]_0$, 3.0 mmol/l., molar ratio 1:33), k_1 = 0.0082 sec^{-1}, 16.0°, 13 min; k_1 = 0.012 sec^{-1}, 23.0°, 6 min; acrylonitrile ($[\mathbf{1}]_0$, 3.2 mmol/l., molar ratio 1:35) k_1 = 0.0030 sec^{-1}, 30.3°, 6 min.

(d) **Thermal Decomposition of a Hydrido Alkyl Complex, $Cp_2MoH[CH(CO_2CH_3)CH_2CO_2CH_3]$.** An equimolar mixture of **1** (139 mg, 0.61 mmol) and dimethyl fumarate (87 mg, 0.61 mmol) was dissolved in toluene (5 ml) and allowed to stand at room temperature for 6 hr. During this period, the initially formed hydrido alkyl complex slowly decomposed and the reddish orange solution turned dark reddish brown. The solution gave on cooling $Cp_2Mo($*trans*-$CH_3O_2CCH{=}CHCO_2CH_3)^2$ as brown crystals (22 mg). The mother liquor was evaporated *in vacuo* and the dark brown residue was sublimed (5 mm) to give firstly a small amount of dimethyl succinate at 80°, then **1** (20 mg) at 110°, and finally the fumarate complex (5 mg) at 200°.

(e) **Relative Thermal Stability of Hydrido σ-Alkyl Complexes, $Cp_2Mo(H)R$.** Hydrido σ-(α-carbomethoxy)alkyl complexes, prepared from methyl acrylate, dimethyl fumarate, or dimethyl maleate, show comparable thermal stability. The stability is measured by the first-order rate constant in thermal decomposition of the complexes as described below. $Cp_2MoH[CH(CN)CH_3]$ was stable at room temperature decomposing at 80° in solution and $Cp_2MoH[CH(CN)CH_2CN]$ did not show appreciable decomposition even at 100° in solution.

(f) **Kinetics of the Elimination of Alkanes from the Hydrido σ-Alkyl Complexes.** A benzene-d_6 solution of the hydrido alkyl molybdenum complex (concentration 0.05 mol/l.), $Cp_2MoH[CH(CO_2CH_3)CH_2CO_2CH_3]$, prepared *in situ* by mixing **1** and dimethyl fumarate was kept at 22.5° in the presence of varying amounts (1–3 molar equiv) of dimethyl fumarate. The rate of the elimination was measured by observing an nmr peak at δ 2.72 ppm assigned to the methylene protons of dimethyl succinate. In the later part of the reaction the rate was obscured by precipitation of the olefin complex. The rate of increase of the peak was first order on the concentration of the hydrido alkyl complex with $k = 1.34 \times 10^{-4}$ sec^{-1} to 40–60% reaction. A fourfold increase in the initial concentration (0.2 mol/l.) both of the hydrido alkyl complex and the fumarate did not change the rate constant.

A similar kinetic study was done in the thermal decomposition of the hydrido alkyl complex, $Cp_2MoH[CH(CO_2CH_3)CH_3]$, prepared from **1** and methyl acrylate. The rate was followed by the increase of area of an nmr peak at δ 0.90 ppm assigned to methyl protons of methyl propionate, and the first-order rate constant of $k = 3.4 \times 10^{-4}$ sec^{-1} was similarly obtained at 22.5°.

(g) **$Cp_2Mo[$*trans*-$CN \cdot CH{=}CH \cdot CN]$.** The hydrido σ-alkyl complex $Cp_2MoH[CH(CO_2CH_3)CH_2CO_2CH_3]$, prepared *in situ* by an equimolar reaction of **1** with dimethyl fumarate in benzene was mixed with an excess of fumaronitrile. The mixture was allowed to stand at room temperature 2 days to allow thermal decomposition of the hydrido σ-alkyl complex. Deep brown crystals together with some powdery brown precipitates formed from the red solution. The crystals were well washed and dried (mp 220° dec in air). *Anal.* Calcd for $C_{14}H_{12}N_2Mo$: C, 55.28; H, 3.97; N, 9.21. Found: C, 54.61; H, 3.74; N, 9.04. Ir(Nujol) ν_{CN} 2202 cm^{-1}. The complex was only sparingly soluble in acetonitrile and almost insoluble in benzene. The solubility precluded nmr measurement.

Results

The stoichiometric olefin hydrogenation with **1** or **2** can be divided into the following elemental steps: (1) interaction of olefins with the basic metal atom (*cf.* step a in Scheme I), (2) insertion[26] into the metal–hydrogen bond (step c), (3) elimination of alkanes from hydrido σ-alkyl complexes (step e), and (4) reaction of "Cp_2Mo" with olefins. Stereochemistries of the insertion step and of the elimination step are described first and mechanisms in each step are proposed based mainly on the kinetics and substituent effect of olefins.

(A) **Stereochemistry. (1) Olefin Insertion Step.** The stereochemistry of insertion was examined for the reaction of Cp_2MoD_2 with dimethyl maleate or fumarate. These olefins were chosen because of their reactivity coupled with the propensity for producing reasonably stable hydrido alkyl intermediates.

Dimethyl fumarate or maleate reacts readily with Cp_2MoD_2 upon mixing at room temperature. The ^1H nmr spectrum of a mixture of dimethyl fumarate and Cp_2MoD_2 (4:1) in C_6D_6 prepared at *ca.* 20° was measured at room temperature soon after the preparation. Figure 1(a) illustrates part of the spectrum which indicates formation of the insertion product $Cp_2MoD[CH(CO_2CH_3)CHDCO_2CH_3]$. The broad doublet at δ 2.9 ppm is assigned as owing to the β proton of the alkyl group; the signal is broadened by the geminal coupling with deuterium (I = 1). The sharp doublet at 2.6 ppm is then due to the α-proton. These resonances form an AB pattern with J_{AB} = 10.5 Hz. A similar AB pattern is also observed in the spectrum of the sample prepared from **1** and dimethyl maleate (Figure 1(b)). Here the signal owing to the β-proton emerges as a complex broad peak owing to a weaker vicinal coupling (J_{AB} = 5.5 Hz) overlapped with a comparable geminal one (J_{HD} = 2.6 Hz). In a similar compound such as $(NC)_5CoCHR \cdot CHDR$ (R = CO_2-

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[26] The process of insertion may also be termed as addition of hydrogen and metal to the olefinic double bond (hydrometalation). We prefer to use insertion here because our main interest lies in the reaction of the metal–hydrogen bond.

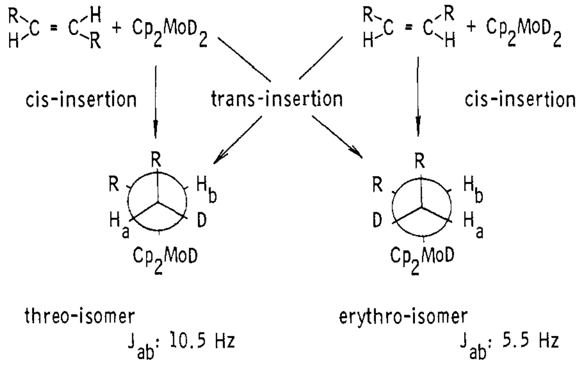

Figure 2. Stereochemistry of olefin insertion into the Mo–D bond.

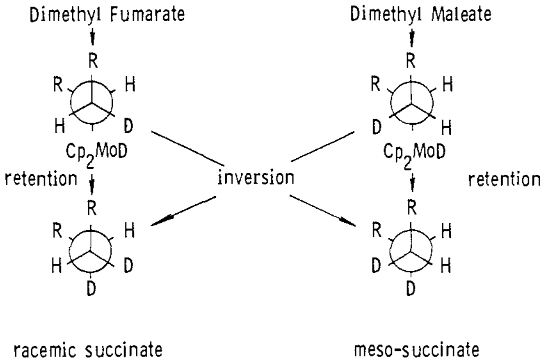

Figure 3. Stereochemistry of the alkane elimination.

$CH_3)^{27}$ the vicinal coupling constant J_{AB} generally ranges from 10 to 13 Hz for threo compounds while the value for erythro compounds falls within a range of 5–7 Hz. The observed J_{AB} values clearly indicate cis insertion (*cf.* Figure 2) of the activated olefin into the metal–hydride bond in **1**. The absence of deuterium scrambling in the reaction implies its essentially irreversible nature at room temperature.

(2) Alkane Elimination Step. The product analysis of thermal decomposition of deuterio-σ-alkyl complexes should distinguish between the two stereochemical pathways, retention or inversion at the α-carbon as illustrated in Figure 3. The deuterium distribution should give important evidence for reversibility of olefin insertion.

A benzene solution of dimethyl maleate and Cp_2MoD_2(1.3:1) was prepared and heated at 60° to ensure the completion of reaction. From the reaction mixture was obtained a mixture of the maleate and the fumarate complexes, $Cp_2Mo(CH_3O_2CCH{=}CHCO_2CH_3)$, upon cooling. The mother liquor was found by ir spectroscopy[26] to contain *meso*-dimethyl 1,2-dideuteriosuccinate and unreacted dimethyl maleate. Similarly, a reaction mixture of Cp_2MoD_2 and dimethyl fumarate (1:4) at 100° produced a good yield (85%) of the fumarate complex and a racemic mixture of dimethyl 1,2-dideuteriosuccinate, together with the unreacted fumarate and a small amount of monodeuteriosuccinate (see Discussion). The deuterium content in the alkane was determined by the mass and nmr spectrum to find some scrambling (~30%). It is worthwhile to note that virtually no deuterium was incorporated into the fumarate complex.

(B) Mechanism of Insertion. (1) Interaction of 1 or 2 with Olefins Prior to Insertion. Although methyl acrylate or dimethyl fumarate undergoes rapid insertion into the Mo–H bond of **1** in toluene at 25°, fumaronitrile or maleic anhydride did not enter into insertion at that temperature, but the solution was colored red or dark violet when concentrated. The infrared and ^1H nmr spectra of the fresh solution preclude the formation of an olefin π-complex, $Cp_2MoH_2(Un)$, Un = olefin, and of any insertion product. On chilling a red toluene solution containing fumaronitrile and **1**, the starting materials were recovered as crystals with disappearance of the red color. This fact suggests that electron donor–acceptor ($\sigma\pi$-EDA) complexes are formed from the σ-basic hydride **1** and π-acidic olefins. As reported already,[2] visible absorption maxima were observed with maleic anhydride and its methyl derivatives or with polynitrobenzenes as the electron acceptors. The frequencies of the maxima parallel those observed using the same acceptors and *N*,*N*-dimethylaniline as the donor. The electron donating ability of **1** or **2** was found similar to *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine.[28] Consistently, reaction of **1** or **2** with tetracyanoethylene or tetracyanoquinodimethane in acetonitrile gives anion radicals of these acceptors as revealed by their electronic spectra.[29]

Besides the $\sigma\pi$-EDA interaction, the dihydrides also interact with σ-acidic reagents (Lewis acid). Protonation leading to $[Cp_2MH_3]^-$ is known and some σ-acidic reagents, *e.g.*, boron trifluoride, readily form stable σ-donor–acceptor (σ-DA) complexes. Therefore, a labile interaction with a σ-acidic carbon center such as $>C{=}O$ is expected. Experimentally, no adducts with ketones or esters are stable enough to be isolated, but the interaction is exhibited in the kinetics of the olefin insertion as will be described later. ^1H nmr spectra of **1** in various solvents gives an indication of the interaction. Thus the hydride nmr signal of **1** in $(CD_3)_2CO$ appears at δ −9.5 ppm (TMS) which is significantly higher field than that observed in C_6D_6(δ −8.8 ppm). When a preferential association of the σ-base **1** with the partially positive carbon of $(CD_3)_2CO$ occurs, the hydride nuclei would be involved in the shielding zone of the magnetic anisotropy of the C=O bond resulting in the diamagnetic shift of the hydride nuclei. The Cp protons, on the contrary, suffer the paramagnetic shift in $(CD_3)_2CO$ (δ 4.6) rather than in C_6D_6 (δ 4.3).

(2) Insertion of Activated Olefins. Since olefins activated by conjugation with electron-attracting groups such as CO_2R or CN insert into the Mo–H bond of **1** near room temperature, kinetic order and relative reactivity using different olefins in this step were investigated. Rates of the olefin insertion step were monitored by following the concentration of the hydrido σ-alkyl complex by means of the visible absorption spectra. For convenience in rate measurements, diethyl fumarate was chosen as the olefin for most cases. The typical results are listed in Table I. Observed time–conversion curves in toluene generally experience a considerably long induction period and are S shaped

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with a turning point at the 40–60% reaction. Even at higher temperatures (31.1°) the induction period does not disappear. This conspicuous feature suggests the presence of a consecutive reaction. Computer simulation of the observed time–conversion curves on an assumption of the cases such as eq 1 or 2, however,

$$\mathrm{A} + \mathrm{B} \rightleftarrows \mathrm{C} \longrightarrow \mathrm{D} \tag{1}$$

$$\left.\begin{array}{l} \mathrm{A} \rightleftarrows \mathrm{B} + \mathrm{C} \\ \mathrm{B} + \mathrm{C} \longrightarrow \mathrm{D} \end{array}\right\} \tag{2}$$

failed, an indication for existence of a more complicated situation. Therefore, the effects of solvents and of additives were briefly examined. A remarkable solvent effect was observed when acetonitrile or methanol was used. The rate in acetonitrile was as little as one-tenth of that in toluene and the shape of the time–conversion curves did not show a clear turning point. In methanol, the reaction occurred only at about 70°. The use of dimethyl succinate as a solvent lengthened the induction period and slowed the reaction. Addition of about tenfold excess of an organic compound containing a CN or CO_2CH_3 group, *e.g.*, C_6H_5CN or $CH_3CO_2CH_3$, into the reaction mixture of **1** with dimethyl fumarate significantly shortened the induction period.

Since the σ-base strength of **1** is comparable with organic amines, **1** would interact with a σ-acidic center of the solvents or additives. Besides these, the $\sigma\pi$-EDA complex formation remarkably influences the rate. Thus, addition of an excess of fumaronitrile to a toluene solution of **1** before the addition of excess methyl acrylate virtually inhibits the insertion of the acrylate which is the most reactive olefin examined. These observations suggest the importance of σ-DA and $\sigma\pi$-EDA interactions. On the basis of the kinetic data and these effects, the following equilibria (eq 3–5) are proposed (*cf.* Discussion Scheme VI).

$$\mathbf{1} + \text{olefin} \rightleftarrows \mathrm{A} \tag{3}$$

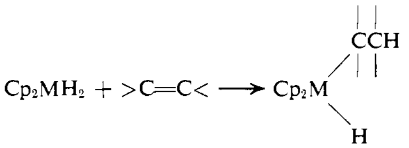
$$\mathbf{1} + \text{olefin} \rightleftarrows \mathrm{B} \tag{4}$$

$$\mathbf{1} + \text{olefin} \rightleftarrows \mathrm{C} \tag{5}$$

$$\mathrm{C} \longrightarrow \text{product}$$

Species A represents a σ-DA complex, species B a $\sigma\pi$-EDA complex, and species C an activated π-complex leading to the insertion product. Owing to the complexity of the reaction, a quantitative numerical analysis is difficult, and we must limit ourselves to a qualitative interpretation of the observed trend in rate profile. Inspection of Table I shows that a large increase in the olefin concentration accompanies neither a corresponding increase in the maximum rate nor a substantial decrease in the induction period. Thus, equilibrium 3 or 4 does not directly lead to the product. Consistently, pseudo-first-order rate constants (*cf.* Table I) obtained by using excess olefin concentrations also show the absence of a simple second- or first-order reaction. Only the last quarter of the reaction of the equimolar reaction follows a second-order rate process, where a rate-determining step would be the formation of an olefin π-complex C. Similar time–conversion curves observed for methyl acrylate and acrylonitrile suggest a similar reaction scheme. Dimethyl maleate shows a different behavior, *i.e.*, *ca.* ten times longer induction period (2.5 hr) at the similar condition (at 25°) as used for diethyl fumarate. The induction period is shortened to only 10 min at 33°. In contrast to the behavior of these activated olefins, no induction period is observed in the reaction with diphenylacetylene or with azobenzene where no evidence for the presence of EDA complex exists. The result supports the hindering effect of $\sigma\pi$-EDA and σ-DA complex formation.

(3) Substituent Effect on the Olefin Insertion. Electronic and steric effects, of the attacking olefin in the monoinsertion (eq 6) into the metal dihydrides **1** or **2**,



$$\mathrm{Cp_2MH_2} + {>}\mathrm{C{=}C}{<} \longrightarrow \mathrm{Cp_2M}\begin{array}{l} \diagup \mathrm{CCH} \\ \diagdown \mathrm{H} \end{array} \tag{6}$$

are surveyed. Ethylene or its alkyl derivatives are inert to **1** or **2** below 100°. The reactivity increases in conjugated diolefins. Isoprene reacts with **1** slowly at room temperature to give a brown complex which is not fully characterized. Sterically more hindered dienes, *e.g.*, 2,4-hexadiene mixture, are almost inert at 80°. Olefins activated with C=O or C≡N groups react with **1** near or above room temperature. Pseudo-first-order rate constants in the insertion of methyl acrylate and diethyl fumarate are about 8 and 2 times, respectively, larger than the value of acrylonitrile in comparable conditions (*cf.* Experimental Section). The apparent relative reactivity order, acrylonitrile > fumaro- or maleonitrile, dimethyl maleate > maleic anhydride, reflects the absence of a simple linear correlation with the π-acidity.

Apparent reactivity of various activated olefins also depends on steric crowding around the double bond. In general, lesser substituted activated olefins react faster or at lower temperature. Disubstituted ones, *e.g.*, methyl *trans*-crotonate, methyl methacrylate, methyl sorbate, or methyl cinnamate, react with **1** at 60–100°, but tri- or tetrasubstituted ones, *e.g.*, dimethyl citraconate or 2,3-dimethylmaleic anhydride, are inert even at 100°. The corresponding reaction with **2** requires significantly higher temperatures. Thus, insertion to **2** of dimethyl fumarate begins to occur only above 100° to give $Cp_2W(CH_3O_2CCH{=}CHCO_2CH_3)$.[19]

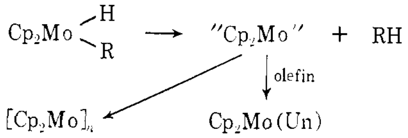
Perfluoroolefins are another class of olefins with high π-acidity. The observed behavior here is quite different from that of activated olefins. Tetrafluoroethylene, perfluorobutene-2, or perfluoroheptene-1 do not give the corresponding hydrido σ-fluoroalkyl complexes by the reaction with **1** at room temperature. Instead, a slow reaction of **1** occurs to form a deep brown hygroscopic solid. Chloroolefins such as tetra- or trichloroethylene also cause oxidation of **1** to Cp_2MoCl_2. These oxidation reactions are similar to those observed with alkyl iodides or bromides already described by Cooper and Green.[30]

(C) Thermal Decomposition of the Hydrido σ-Alkyl Complexes to Alkane and "Cp_2Mo." As described in our previous paper,[2] the hydrido σ-alkyl complexes, $Cp_2MoH(R)$, thermally decompose to give the corresponding alkane and they give, in the presence of a π-acidic olefin (Un), an alkane and an olefin complex, $Cp_2Mo(Un)$. The rate of decomposition was measured by ^1H nmr spectra in the presence of an excess of an

(30) R. L. Cooper and M. L. H. Green, *J. Chem. Soc. A*, 1155 (1967).

olefin and was found independent on the olefin concentration (*cf.* Experimental Section). The kinetics can be well interpreted by a unimolecular reaction, and the first-order rate constants for $Cp_2MoH[CH(CO_2CH_3)CH_3]$ and $Cp_2MoH[CH(CO_2CH_3)CH_2CO_2CH_3]$ are 3.4 × 10^{-4} and 1.34 × 10^{-4} sec^{-1}, respectively, at 22.5° in C_6D_6. The reactive intermediate "Cp_2Mo" can be trapped by the reaction of **1** with, *e.g.*, π-acidic olefins or acetylenes.[21] For example, addition of an excess of fumaronitrile into a solution of $Cp_2MoH[CH(CO_2CH_3)CH_2CO_2CH_3]$ gave air-stable deep red crystals of $Cp_2Mo[C_2H_2(CN)_2]$ after standing overnight. These results indicate the following pathways (Scheme II).

Scheme II



(D) Formation of Molybdenum–Olefin Complexes. The reactive species, "Cp_2Mo," reacts with an activated olefin existing in the reaction mixture. This step is kinetically fast and the geometry of the olefin conserved during the complex formation step. When the hydrido alkyl complex is decomposed in the presence of an excess of dimethyl maleate at 70–100° in toluene, a mixture consisting of Cp_2Mo(*cis*-$CH_3O_2CCH{=}CHCO_2CH_3$) and Cp_2Mo(*trans*-$CH_3O_2CCH{=}CHCO_2CH_3$) results.[2] If only just an equivalent amount of dimethyl maleate ($CpMoD_2$:olefin = 1:1) is used at 35°, Cp_2Mo(*trans*-$CH_3O_2CCH{=}CHCO_2CH_3$) is the major product isolated.[2] Use of a large excess of dimethyl maleate at 60–70° leads to an increased amount of the cis olefin complex over the trans olefin complex. The cis olefin complex did not isomerize to the trans olefin complex below 180° in solution and therefore no isomerization seems to occur at *ca.* 100° in the olefin complex. Substitution of coordinated dimethyl maleate with dimethyl fumarate or with dimethyl acetylenedicarboxylate did not occur below 100°. These results imply that a mixture of the olefin complexes was formed by the reaction of "Cp_2Mo" with activated olefins present in solution after partial cis–trans isomerization. The cis–trans isomerization probably occurred *via* a reversible insertion at *ca.* 80° of dimethyl maleate to **1**. Support for the reversibility was obtained. A deuteriobenzene solution of the hydrido alkyl complex formed *in situ* from **1** and dimethyl fumarate at room temperature was heated at 100° until a complete decomposition of the hydrido alkyl complex is ensured. The products isolated were dimethyl succinate (25%), Cp_2Mo(*trans*-$CH_3O_2CCH{=}CHCO_2CH_3$) (30%), and **1** (15%). The fumarate complex is formed by the reaction of "Cp_2Mo" with free dimethyl fumarate present in an equilibrium amount (Scheme III). The equilibrium was then shifted to regenerate Cp_2MoH_2. No deuterium abstraction from the solvent by the reactive intermediate "Cp_2Mo" occurred.

Discussion

Here we firstly discuss the mechanisms of olefin insertion into the Mo–H bond. σ-Basicity of **1** at the ground state and π-basicity at a somewhat excited state play an important role in the insertion. Distinction of the metal basicity is stressed. Then is discussed the thermal stability which influences the pathways of the hydrido σ-alkyl complexes, $Cp_2MoH(R)$. Finally, the stereochemistry of stoichiometric hydrogenation of olefins with **1** is discussed from a viewpoint of symmetry of frontier orbitals of the participating reactants.

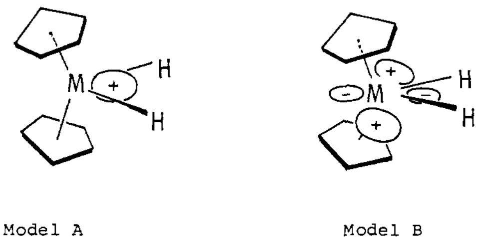
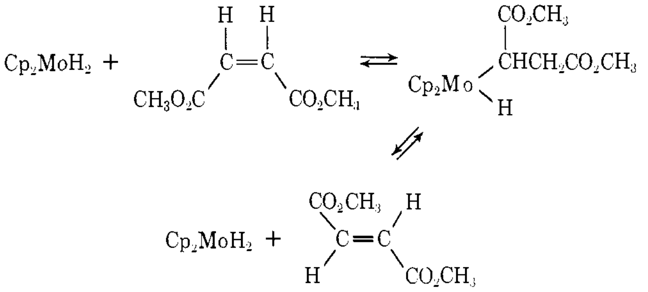


Figure 4. Proposed models for spacial extension of the nonbonding metal orbital in Cp_2MH_2 (M = Mo, W).

Scheme III



Mechanism of Insertion. Investigation of reactivity of low-valent transition metal complexes toward various π-acidic reagents is an important research target which has bearing on the olefin catalysis that takes place through activation on coordination. Some low-valent group VIII metal complexes receive a variety of small molecules as one- or two-center ligands. When a π-acidic two-center ligand interacts with a so-called "metal base," *e.g.*, $Pt(PPh_3)_3$, a π-complex usually forms. A primary step here may involve an electron donor acceptor ($\sigma\pi$-EDA) complex formation with the σ-basic metal atom by a "vertical process."[31–33] Detection of the charge transfer stage of most low-valent d^8 or d^{10} complexes has been virtually impossible by rapid response leading to rehybridization accompanied by structural or configurational change. When these changes are hindered sterically or electronically by some ligands, the process may be detectable by spectroscopic means. Bis(*pentahapto*cyclopentadienyl)metal hydrides, Cp_2MH_n (M = Mo, W, n = 2; M = Re, n = 1), in which the metal is characterized by its σ-donor ability,[34] are now found to be the case where charge transfer absorption is observable.[2] In its interaction with some organic π-acids, the filled nonbonding metal orbital in **1** or **2** does not have suitable spacial extension for π back-bonding. Thus, two proposals[35] unani-

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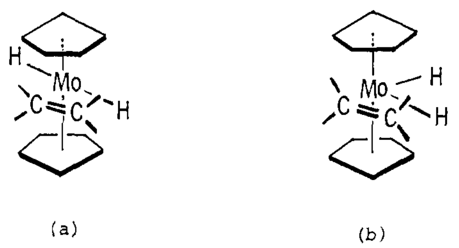
(31) A process without change of the geometry of the atoms in the metal complex, which is essentially identical with "vertical process" defined by Traylor, *et al.*[32]

(32) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem., Soc.*, **92**, 829 (1970).

(33) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Amer. Chem. Soc.*, **93**, 5715 (1971).

(34) J. C. Kotz and D. G. Pedrotti, *Organometal. Chem. Rev., Sect. A*, **4**, 479 (1969).

(35) J. P. Dahl and C. Ballhausen, *Acta Chem. Scand.*, **15**, 1333 (1961); N. W. Alcock, *J. Chem. Soc. A*, 2001 (1967); J. C. Green, M. L. H. Green, and C. K. Prout, *Chem. Soc., Chem. Commun.*, 42 (1972); W. E. Douglas and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1796 (1972).



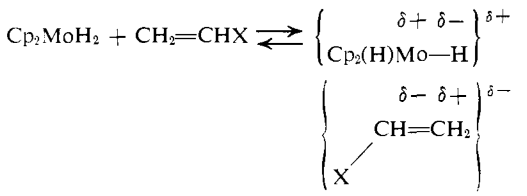
(a) (b)

Figure 5. Suggested structures for intermediate A in olefin insertion.

mously indicate a_1 symmetry for the shape of the nonbonding orbital as shown in Figure 4. When the hybridization of the nonbonding orbital remains, only electron transfer by "vertical process" occurs at ambient temperature for interaction with π-acids. The outcome is then charge transfer or, in a limiting case, complete electron transfer to form an ion pair depending on the strength of π-acidity. For example,[2] TCNE or TCNQ readily forms with **1** or **2** ionized species in CH_3CN even from a dilute solution as has already been observed for $Cr^0(C_6H_6)_2$[36] or Cp_2Co.[36] Fumaro- or maleonitrile forms a $\sigma\pi$-EDA complex in a saturated or in a neat solution. When the π-acidity is further lowered as in dimethyl fumarate, no distinct spectral maximum save a shoulder is observable. However, an analysis of the kinetic time–conversion curves obtained for the formation of the hydrido σ-alkyl complex suggests the $\sigma\pi$-EDA complex formation to be a kinetically important stage (see Results).

Intervention of $\sigma\pi$-EDA complexes in the reaction of organic amines with various π-acids has been well recognized.[37,38] β-Cyanoethylation of primary amines by acrylonitrile involves a $\sigma\pi$-EDA complex[37,38] in a very primary stage where the symmetry of the lone pair obviously does not allow π complexation. Complex **1** thus resembles organic primary amines in this respect, but an important difference is revealed by its reaction with olefins containing a polar double bond (*cf.* Scheme IV). The insertion of acrylonitrile occurs unexpectedly slowly leading to the α-metalated product, $Cp_2MoH[CH(CH_3)CN]$. The direction is opposite to that of the β-cyanoethylation of amines. The observed difference in direction implies hydridic character of the hydride ligand in **1** in contrast to the protic nature of amine hydrogen. The partial positive charge in the incipient $\sigma\pi$-EDA complex, $[Cp_2MoH_2]^{\delta+}[CH_2{=}CHCN]^{\delta-}$, must tighten the metal–hydride bond retarding the hydride transfer to the partially negative olefin as illustrated in Scheme IV.

Scheme IV



$$Cp_2MoH_2 + CH_2{=}CHX \rightleftarrows \left\{\overset{\delta+\quad\delta-}{Cp_2(H)Mo{-}H}\right\}^{\delta+} \left\{\overset{\delta-\quad\delta+}{CH{=}CH_2}\ \ X\right\}^{\delta-}$$

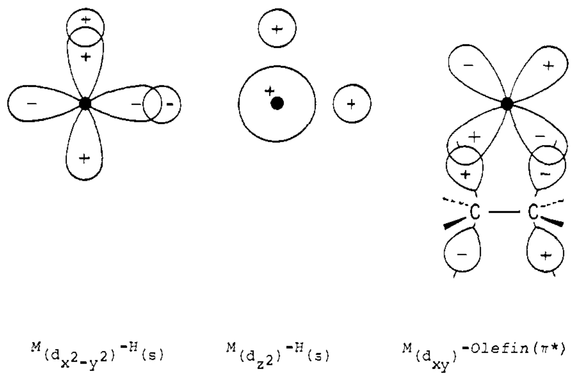


Figure 6. Orbitals used for the bonding of hydrogen and olefin in the intermediate (A). A top view. Cp rings are not shown.

The observed selective cis insertion of dimethyl fumarate indicates intermediacy of a multicentered transition state but it is not a bimolecular one-step reaction between the hydride and the olefin as revealed by our kinetic data. The kinetic evidence suggests that a cis hydrido π-olefin complex is involved as an intermediate. As noted, the π-olefin complex formation *via* $d\pi$–$p\pi$ overlap is not expected for **1** in its ground state, the rigidity of which is assumed as in Cp_2TaH_3.[39] Furthermore, the steric requirements of **1** do not accommodate an olefin in side-on coordination; two Cp rings and two hydrogen ligands in pseudotetrahedral arrangement prevent access of an olefin. Then a question arises how the assumed cis hydrido olefin complex forms. If the two Cp rings become parallel, the dihydrido olefin π-complex may be formed (*cf.* Figure 5). The process requires some excitation of the metal side. Of the two possible geometries (a or b) of the intermediate (A) in Figure 5, the nonrigidity of metal–hydrogen bonds in the excited molecule would make the distinction meaningless at room temperature. When symmetry properties of the metal valence orbitals are considered, the bonding scheme (Figure 6) for isomer (b) (*cf.* Figure 5) is favored over that for isomer (a). The basicity appearing in this way may be designated as a latent π-basicity. When a metal is sandwiched by two parallel Cp rings, three nonbonding metal orbitals emerge mainly by hybridization of d_{xy}, $d_{x^2-y^2}$, d_{z^2} and s orbitals.[40] Attachment of two hydride ligands to the metal is now accomplished by using a_1 and b_1 orbitals, *e.g.*, $d_{x^2-y^2}$ (b_1 symmetry in C_{2v} structure) and d_{z^2} mixed with s (a_1 symmetry) (*cf.* Figure 6). Then the remaining d_{xy} orbital can interact with the π^* orbital of olefins. The d_{xy} orbital constitutes a filled and highest nonbonding orbital of an "excited Cp_2MoH_2" molecule with parallel Cp rings. A strong π back-bonding with an olefin is then possible and the olefin will be sufficiently activated to insertion. At the same time, the metal–hydride bond is weakened in this structure as compared with the original "wedge" structure as suggested by a recent paper[41] on protonation of alkyl ferrocenes to give the wedge-shaped species, $[Cp_2FeH]^+$.

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(36) J. W. Fitch and J. J. Lagowski, *Inorg. Chem.*, 4, 864 (1965); R. L. Brandon, J. H. Osiecki, and A. Ottenberg, *J. Org. Chem.*, 31, 1214 (1966).

(37) E. M. Kosower, *Progr. Phys. Org. Chem.*, 3, 81 (1965).

(38) T. Yamaoka and S. Nagakura, *Bull. Chem. Soc. Jap.*, 44, 1780 (1971); T. Nogami, T. Yamaoka, K. Yoshihara, and S. Nagakura, *ibid.*, 44, 380 (1971); T. Nogami, K. Yoshihara, and S. Nagakura, *ibid.*, **45**, 122 (1972).

(39) L. M. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

(40) S. E. Anderson, Jr., and R. S. Drago, *Inorg. Chem.*, 11, 1564 (1972); H. H. Brintzinger and L. S. Bartell, *J. Amer. Chem. Soc.*, **92**, 1105 (1970).

(41) T. E. Bitterwolf and A. C. Ling, *J. Organometal. Chem.*, 40, 197 (1972).

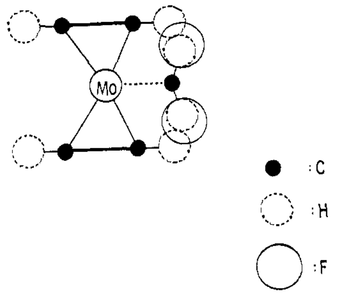


Figure 7. Steric crowding around the metal in a hypothetical olefin π-complex, $Cp_2Mo(\pi\text{-}C_2H_2F_2)$, with parallel π-cyclopentadienyl rings.

As described above a structural change accompanied by rehybridization is a prerequisite process for observed cis insertion to give hydrido σ-alkyl or σ-alkenyl complexes. Postulation of this intermediate (A) readily offers a reasonable explanation for observed steric and electronic effects in olefin insertion when substituted olefins are used. In a series of olefins of similar π-acidity, the least substituted one reacts fastest. Tri- or tetrasubstituted ones, *e.g.*, dimethyl citraconate or dimethylmaleic anhydride, are not reactive even above 100°. Even when π-acidity is strong enough at the carbon center, perfluoroethylenes remain unreacted owing to its steric hindrance to π coordination by the presence of fluoro groups surrounding the double bond (*cf.* Figure 7).

Although the wedge-shaped dihydride molecule would allow the approach of an olefin from the open side, side-on coordination *via* π back-bonding is unlikely in the intermediate (B) (Figure 8). The olefin ligand in the loose complex can assume a geometry favorable for cis insertion. However, the H–Mo–H bond angle is probably near 90°[42] and does not allow π coordination of an olefin between the two H ligands unless the angle opens to *ca.* 180°. Our observation that a π-olefin complex is required as an intermediate clearly rules out this intermediate in stereoselective cis insertion.

As discussed above, three distinct modes of interaction are discernible between **1** and an olefin (π-acidic center), *i.e.*, σ-DA, $\sigma\pi$-EDA, and π complexes. Protonation of **1** with strong acids, *e.g.*, CF_3CO_2H, virtually suppresses the insertion and weaker proton donors, *e.g.*, acetic acid or methanol significantly retard the reaction. The retarding or inhibiting effect of $\sigma\pi$-EDA complex formation was already described in our kinetic study. In particular, about a fivefold increase in concentration of the two reactants, **1** and diethyl fumarate (*cf.* Table I), neither greatly increases the pseudo-first-order rate constant nor drastically decreases the induction period. If only one intermediate, Cp_2MoH_2 (olefin), is present, the induction period would virtually disappear. These results strongly suggest that the σ-DA and $\sigma\pi$-EDA interactions are in side equilibria (see eq 3–5). Thus only the π-complex intermediate leads to the insertion product.

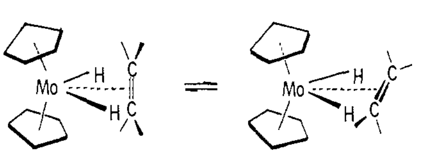
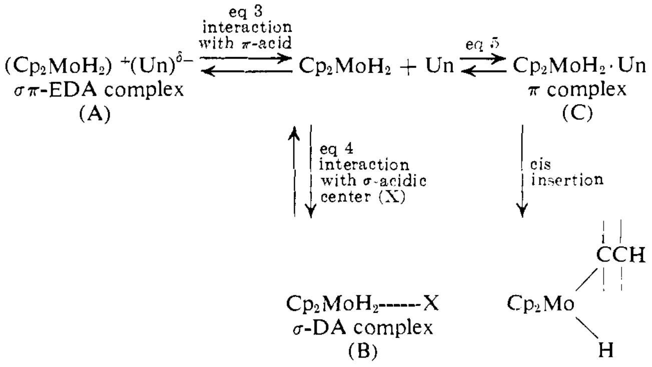


Figure 8. Suggested structures for intermediate B formed by interaction of an olefin through the open side of Cp_2MoH_2.

Scheme V



All our results in olefin insertion can now be summarized in Scheme V. Apparently a delicate balance of equilibria (eq 3–5) influences the overall rate of the insertion; it is premature to determine rate constants in each step only from the observed overall time–conversion curves. The observed difference in the curves for various activated olefins should be traced to each elemental steps where electronic and steric effects are operative in varying degrees.

The recovery of part of the cost of bond breaking by bond making should contribute to the free energy difference. When the energy of participating bonds in the olefin insertion reactions is considered, the process leading to the hydrido σ-alkyl and ultimately to dialkyl complexes is an energetically favored process since the sum of the C–H and M–C bond energies (100 and about 60–70 kcal mol^{-1}) will exceed the sum of an M–H bond (about 60–70 kcal mol^{-1}) and C=C double bond energy (62 kcal mol^{-1}). The thermodynamical aspect is not a sole factor for the reaction to proceed thermally. Since the reaction is not one-step bimolecular and an intermediate π-complex (Figure 5) is suggested, stabilization of the intermediate will lower the activation energy to allow the insertion near room temperature. This stabilization is achieved by the back-bonding, which is enhanced with π-acidic olefins. The trend that only electronegative olefins react with **1** contrasts to that reported for cationic metal hydrides, *e.g.*, [*trans*-$PtH(L)_2L']^+$ where electron-donating olefins react.[12] Importance of metal basicity in the reaction with π-acidic unsaturation is further confirmed by the inertness of $[Cp_2MoH_3]^+$ to hexafluorobutyne-2. Removal of electron density from the hydrido σ-alkyl complex is therefore expected to reverse the insertion. In fact, the oxidation of $Cp_2MoH[CH(CO_2CH_3)CH_2CO_2CH_3]$ with bromine gave the original olefin (dimethyl fumarate) and $[Cp_2MoBr_2]^+Br_3^-$. By contrast, bromination of ordinary metal alkyls gives alkyl bromides.[43]

Although the olefin insertion does not follow pure second-order kinetics, the most important pathway contains a "bimolecular" transition state comprised of a metal hydride complex and an olefin. Then an increase in coordination number around the metal is a prerequisite for ready insertion. For example, even when

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(42) S. C. Abrahams and A. P. Ginsberg, *Inorg. Chem.*, **5**, 501 (1966).

(43) For example, R. G. Pearson and W. R. Muir, *J. Amer. Chem. Soc.*, **92**, 5519 (1970); R. F. Jensen, V. Madan, and D. H. Buchanan, *ibid.*, **93**, 5283 (1971).

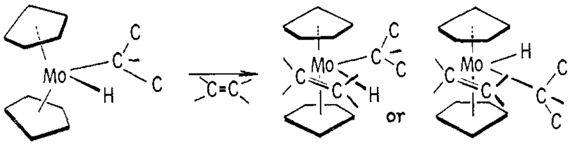
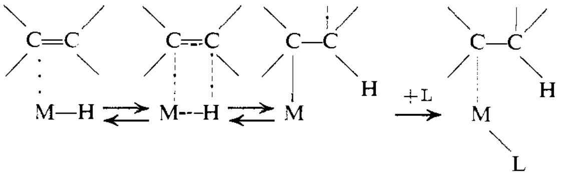


Figure 9. Suggested intermediates for diinsertion or successive insertion of an olefin.

the geometry is suitable as in $[Cp_2MoH(C_2H_4)]^+$[15] or in $Cp_2NbH(C_2H_4)$,[16] only after an attack of triphenylphosphine or ethylene will the formation of an ethyl complex, $[Cp_2MoEt(PPh_3)]^+$ or $Cp_2NbEt(C_2H_4)$, respectively, follow. The attack will bring about a supersaturation of coordination which is relieved by the insertion. Alternatively, the attack may occur after the formation of the coordinatively unsaturated insertion product; the role of the ligand may be to stabilize the product rather than to initiate insertion (*cf.* eq 7). In the present system, coordinative supersaturation in the assumed intermediate (*cf.* Figure 5), $Cp_2MoH_2(Un)$, provides a sufficient driving force for insertion.

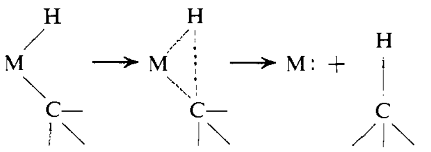


(7)

Although diinsertion or successive insertion into **1** is energetically favored, observed failure[2] can now be understood by assumption of the π-complex intermediate. The bulk of an alkyl group in a hydrido σ-alkyl complex, $Cp_2MoH[CH(X)R]$, would prevent the structural change to the excited molecule required for the π-complex formation and hinders the further insertion (*cf.* Figure 9). Thus, the hydrido σ-alkyl complexes are virtually not π-bases but are σ-bases as experimentally shown by facile protonation of $Cp_2MoH[CH(CN)CH_2CN]$ in aqueous sulfuric acid or in aqueous HBr.

The observation by Wailes, *et al.*,[24] of diinsertion in Cp_2ZrH_2 to give Cp_2ZrR_2 may be ascribed to the vacancy of the nonbonding metal orbital (Lewis acidity) facilitating nucleophilic attack of electron-donating olefins, *e.g.*, ethylene. The vacancy is caused by shortage of two electrons in isostructural Cp_2ZrH_2 as compared with Cp_2MoH_2.

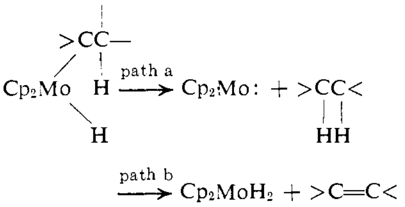
Thermal Reaction of the Hydrido σ-Alkyl Complexes, $Cp_2MoH(R)$. Cis hydrido σ-alkyl complexes of transition metals have been generally regarded as thermally unstable, and its intermediacy is suggested in catalytic hydrogenation of olefins with some metal complexes. The thermal instability of transition metal hydrido alkyls is explicable by a three-centered interaction which is "allowed" when participation of d orbitals to the bonding occurs, but it is "partially forbidden"[18] in nontransition metal complexes. For the reaction (eq 8) to proceed to the right side, the sum of bond energies of M–H and M–C together with the energy of rehybridization at the metal must be smaller than bond energy of C–H. Assuming that other complications owing to structural change, ligand dissociation, and solvation are absent, the observed facile thermal reaction of the most of d^{6-8} hydrido σ-alkyl complexes of group VIII metals implies weakness of M–H and M–C bonds and unimportance of the rehybridization energy relative to C–H bonds. In contrast to the labile metal hydrido σ-alkyl complexes, most of which are coordinatively unsaturated, $Cp_2MoH(R)$ has kinetic stability toward an attack of olefins. The stability contrasts to the observed failure[24] of isolation of $Cp_2ZrH(R)$ from Cp_2ZrH_2 and an olefin. The Mo–C bond energy increases by the stabilizing effect of electron-attracting substituents especially on the α-carbon. In addition to these factors, the high reactivity of "Cp_2Mo" suggests a considerable energy must be paid for its generation. These combined effects contribute to the thermal stabilization of $Cp_2MoH(R)$ and are considered to be responsible for its ready isolation, in particular, when the alkyl is $CH(CN)CH_3$ or $CH(CN)CH_2CN$.



(8)

Thermal instability of transition metal alkyls is generally associated with the presence of β-hydrogen.[44] Two competing reactions, *i.e.*, (a) alkane elimination or (b) alkene elimination, are possible (*cf.* Scheme VI).

Scheme VI



Experiments with $Cp_2MoH[CH(CO_2CH_3)CH_2CO_2CH]_3$ showed path a is favored at 40–50° but path b gains importance on raising the temperature.

Thus, $Cp_2MoH[CH(CO_2CH_3)CH_2CO_2CH_3]$ decomposed at 80° to give Cp_2MoH_2, $Cp_2Mo[$*trans*-$CH_3O_2CCH{=}CHCO_2CH_3]$, and dimethyl succinate. Similar results were obtained in decomposition of $Cp_2MoH[CH(CN)CH_3]$ at 100°. It is important to note that path a is virtually irreversible owing to deactivation of "Cp_2Mo" by polymerization to $[Cp_2Mo]_x$, and also owing to formation of kinetically inert alkanes. The reversibility of path b is also indicated by formation of $Cp_2Mo($*trans*-$CH_3O_2CCH{=}CHCO_2CH_3)$ from **1** and a cis olefin, dimethyl maleate, at higher temperatures.[2]

The species "Cp_2Mo" is probably the same as the one proposed by reduction of Cp_2MoCl_2 as reported by Thomas and Brintzinger.[21] Its high reactivity toward various small molecules such as H_2, CO, N_2, or olefins makes it an intriguing substrate for complex formation. The observed potentiality is due to the presence of two singly occupied or one vacant and one occupied metal orbital of high energy. Both schemes are very suitable for bonding with π-acidic two-center carbon ligands as well as a two-center nitrogen ligand[2] (*e.g.*, azobenzene). The olefin complexes thus obtained may be described by a molybdenacyclopropane limiting structure. "Cp_2Mo" is then characterizable by its strong π-basicity in contrast to the σ-basicity of **1**. Strength of the π-basicity,

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as measured by the ir and ^{1}H nmr spectra[2] of its olefin complexes Cp$_2$Mo(Un), is the highest ever observed among various known d^8- or d^{10}-metal complexes. This π-basic property makes Cp$_2$Mo another important class of metal complexes receiving π-acidic small molecules for coordination.

Stereochemistry of Stoichiometric Hydrogenation. The observed cis insertion of an olefin into a metal–hydride bond has already been found for various metal compounds, *e.g.*, boron,[45] aluminum,[46] and cobalt.[47] Transition metal catalyzed hydrosilation of olefins or acetylenes has also been found to occur in a cis manner.[48–50] The reaction probably involves a similar cis insertion of an olefin into a metal–hydride bond formed by addition of a hydrosilane. Hydroformylation[51] and hydrocarboxylation[52,53] similarly occur cis to the double bond. Now it seems quite general that olefin insertion into the metal–hydrogen bond occurs in a cis manner. A four-centered transition state is, therefore, probable for this reaction. A concerted four-center thermal reaction classifiable as a [$_{\sigma}2_s + {}_{\pi}2_s$] reaction, is "partially forbidden"[18] by orbital symmetry. Although the following two factors loosen the forbiddeness of the bimolecular [$_{\sigma}2_s + {}_{\pi}2_s$] reaction, *i.e.*, participation of d orbitals (*cf.* Figure 10) and of ionicity[54] in the transition state, our result does not agree with a one-step bimolecular reaction. Instead, π complexation of an olefin adjacent to the metal–hydrogen bond is, we believe, a prerequisite for the reaction. Geometry of olefin π complexation is also important. When olefinic double bond and the metal–hydrogen bond are perpendicular as in IrH(CO)(NCCH=CHCN)(PPh$_3$)$_2$[13] and when olefin rotation is inhibited by strong π backbonding, no insertion is observed.

Coplanar arrangement of four participating atoms, *i.e.*, two olefinic carbons, hydrogen, and metal, in the transition state is the most favored geometry (*cf.* Figures 5 and 10). The geometry of the assumed dihydrido π-olefin complex (*cf.* Figure 5) is thus very suitable for the observed cis insertion. Consideration of the geometry alone is not sufficient for the observed ready insertion. Coordination number around the metal is also important as already mentioned in conjunction with stable hydrido olefin complexes, *e.g.*, $[Cp_2MoH(C_2H_4)]^+$.

The timing of M–H bond breaking and M–C bond making in coplanar arrangement of four participating atoms (eq 4) may not be necessarily simultaneous. The step can proceed in two stages without destructing the observed stereoselectivity.

Thermal elimination of an alkane to form the well-defined hydrido σ-alkyl complex, Cp$_2$MoH(R), is found to be unimolecular and stereoretentive at the α-carbon.

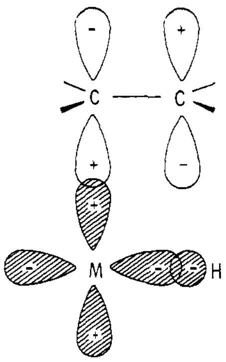

Figure 10. Interaction of a bonding M–H orbital (dσ–sσ) with an antibonding olefin π* orbital (pπ–pπ).

These results seems relevant for us to discuss concertedness of the reaction. A concerted loss of two geminal groups in some carbon compounds ($R_2CX_2 \rightarrow R_2 + CX_2$) is an excited-state reaction.[55] Although the symmetry is lowered, a concerted elimination of the alkane from a hydrido σ-alkyl metal complex (*cf.* eq. 8) belongs to the same category and its stereochemistry deserves investigation. The stereochemistry at the α-carbon atom in hydrogenolytic cleavage of an metal–alkyl bond giving alkane has previously been investigated for ruthenium[56] and cobalt.[57] Without isolation of metal–alkyl species, Halpern, *et al.*,[56] have shown retention of configuration in their protolytic cleavage at the ruthenium–alkyl bond. A formally related cleavage of alkyl pentacyanocobalt was reported to be nonstereospecific.[57] A radical mechanism has been proposed for this case. The elimination described in this paper is the first example where the formation of an alkane occurs *via* a well-characterized hydrido alkyl complex and stereochemistry at the α-carbon atom was determined. Although our result at first sight may appear similar to the case of the ruthenium complex, a definite difference, however, is the intervention of a relatively thermally stable hydrido alkyl complex in our case.

It is important to note that the stereochemistry of the elimination described in this paper is mechanistically related to some reactions of transition metal complexes such as carbonyl insertion and oxidative addition of silicon hydrides. Retention of configuration at the α-carbon is proposed in carbonyl insertion into a metal–carbon bond of CpFe(CO)$_2$CHR$_1$R$_2$ (or Mn(CO)$_5$CHR$_1$R$_2$).[58,59] Nearly complete retention at asymmetric silicon has been found in transition metal catalyzed hydrosilation, chlorination, and hydrogen–deuterium exchange of R$_1$R$_2$R$_3$SiH.[60,61] In the present stereoretentive alkane elimination also, the bond weakening at the Mo–H and Mo–C bonds and bond making at the C–H bond are perhaps not exactly con-

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current. The bond weakening at the Mo–C bond may precede because the observed thermal stability is very strongly dependent on not only the α but also β substituents on the alkyl.

In summary, the stereochemistry of the present stoichiometric hydrogenation is comprised of cis insertion and stereoretentive alkane elimination. A four-center transition state is probable for the insertion which implies concertedness. When participation of d orbitals occurs in the process, thermal forbiddenness of a concerted four-center ($_\sigma 2_s + {_\pi 2_s}$) reaction is loosened. Similar forbiddenness of the observed stereoretentive three-center alkane elimination is also loosened by d-orbital participation. Then overall cis hydrogenation of olefins is one of the important consequence of bonding through d orbitals.

Acknowledgments. The authors express their acknowledgment for experimental assistance to Mr. J. Izawa, Mr. Y. Terawaki, and Mr. H. Okuda in some preparative works and spectral measurements. We also thank Professor T. Fueno and Dr. O. Kazimoto for the computer programs.

Stereochemical Rigidity in ML_5 Complexes. I. A Detailed Line-Shape Analysis for $Rh[P(OCH_3)_3]_5{}^+B(C_6H_5)_4{}^-$ and Other Rhodium(I) Complexes

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Wilmington, Delaware 19898. *Received June 22, 1973*

Abstract: The temperature-dependent nmr spectra for several complexes of the type $RhL_5{}^+X^-$ where L is a phosphite and X^- is a noncoordinating anion are reported. The low-temperature limit proton noise decoupled ^{31}P nmr spectra can be analyzed using an A_2B_3X model indicating that these complexes have D_{3h} symmetry on the nmr time scale at low temperatures. As the temperature is raised, the spectra broaden and coalesce into a symmetric doublet (A part of an A_5X spectrum). The maintenance of ^{31}P–^{103}Rh coupling in the high-temperature limit indicates that this process is intramolecular. At still higher temperatures (above 0°) the spectra again broaden and eventually coalesce into a single line. The higher temperature process involves loss of the ^{103}Rh–^{31}P coupling indicating an intermolecular exchange. A complete density matrix line-shape analysis has been carried out to simulate the temperature-dependent $^{31}P\{^1H\}$ nmr spectra for the intramolecular case. The most detailed analysis has been carried out for the complex $Rh[P(OCH_3)_3]_5{}^+B(C_6H_5)_4{}^-$ where a comparison of the observed line shapes with those calculated assuming both simultaneous exchange of the two axial ligands with two of the equatorial ligands and single axial–equatorial exchanges indicates that the simultaneous exchange process dominates. The barriers to the intramolecular mutual exchange process are observed to increase with ligand size and cover the range 7.5–12 kcal/mol. The invariance of the exchange rates to concentration and nature of the anion demonstrates that the barrier height is a property of the cation alone and is not strongly influenced by ion-pairing effects.

In two recent communications,[1,2] we have presented nmr evidence for stereochemical rigidity in a class of five-coordinate d^8 transition metal complexes of the type $ML_5{}^+X^-$ (M = Co, Rh, Ir) and $ML_5{}^{2+}(X^-)_2$ (M = Ni, Pd, Pt), with X representing a variety of noncoordinating anions. All previous nmr investigations have indicated that the barriers to intramolecular rearrangement in ML_5 complexes are very low (<5 kcal/mol) resulting in a rapid exchange of the five ligands (on the nmr time scale) at all temperatures attainable in solution.

Earlier studies have included complexes which are isoelectronic with those discussed in the present paper. A single resonance was observed for the natural abundance ^{13}C nmr spectrum of $Fe(CO)_5$ at room temperature.[3] No change was observed in this spectrum on cooling a solution in ether.[4] We have observed that the ^{13}C nmr spectrum of a solution of $Fe(CO)_5$ in 90% chlorodifluoromethane–10% methylene chloride remains a sharp single line down to *ca.* −170°. The ^{19}F nmr spectra of $Fe(PF_3)_5$, $Ru(PF_3)_5$, and $Os(PF_3)_5$ have been recorded down to −160° in chlorodifluoromethane; again, all five ligands were observed to be equivalent on the nmr time scale.[5] More recently, we have recorded the ^{31}P nmr spectra of $Fe(PF_3)_5$ and $Ru(PF_3)_5$ over a similar temperature range in the same solvent; there is no evidence for a slowing down of the exchange process to a rate comparable with the nmr time scale.

It has been widely assumed, without direct experimental evidence, that the Berry process[6] is the most probable rearrangement mechanism in ML_5 systems. The nmr line-shape analysis of Whitesides and Mitchell[7] for $(CH_3)_2NPF_4$ does establish a process involving

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