Kinetics and Stereochemistry of CO Substitution Reactions of Half-Open Chromocene Carbonyls (II): Reactions of Cp(η^5-2,4-Me$_2$C$_5$H$_5$)CrCO and Phosphines

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The CO substitution reactions of the complex, Cp(S-2,4-Me$_2$C$_5$H$_5$)CrCo with PR$_3$(PR$_3$=PMePh$_2$, P(OCH$_3$)$_3$, PMe$_2$Ph) were investigated spectrophotometrically at various temperatures. From the reaction rates, it was suggested that the CO substitution reaction took place by first-order (dissociative) pathway. Activation parameters in decaline were $\Delta H^{\neq}$ = 22.0 kcal·mol^{-1}, $\Delta S^{\neq}$ = −3.8 cal·mol^{-1}·K^{-1}. Unusually low value of $\Delta S^{\neq}$ suggests an η^5-S→η^5-U conversion of the pentadienyl ligand. This suggestion was confirmed by the Extended-Hückel molecular orbital (EHMO) calculations, which revealed that the total energy of Cp(S-2,4-Me$_2$C$_5$H$_5$)CrCO is about 0.42 kcal/mol more lower than that of Cp (U-2,4-Me$_2$C$_5$H$_5$)CrCO and the energy of [Cp(U-2,4-Me$_2$C$_5$H$_5$)Cr···CO]$^{\neq}$ transition state is about 2.43 kcal/mol lower than that of [Cp(S-2,4-Me$_2$C$_5$H$_5$)Cr···CO]$^{\neq}$ transition state.

Introduction

The area of metal-pentadienyl chemistry has recently been attracting growing attention,[1-4] and a number of reviews covering various aspects of this field have appeared. While a number of reports dealing with metal pentadienyl complexes had appeared prior to 1980 (vide infra), there was little, if any, indication or recognition that pentadienyl ligands by themselves might lead to a variety of potentially useful carbon-carbon bond formation. However, a close comparison of the pentadienyl fragment, and particularly its molecular orbitals,[5] to the related cyclopentadienyl and allyl fragments, has suggested that the pentadienyl ligand should be capable of imparting thermal stability to a wide variety of metal complexes and that pentadienyl complexes should readily undergo "allyl-like" transformations (*e.g.*, $\eta^5\leftrightarrow\eta^3\leftrightarrow\eta^1$ interconversions) and reactions (coupling and naked metal chemistry). It was also proposed that in some cases metal-pentadienyl bonding might actually be stronger than the renowned metal-cyclopentadienyl bonding,[6-10] even though earlier publications had explicitly pointed out that metal-cyclohexadienyl bonding appeared weaker than metal-cyclopentadienyl bonding.[11]

We reported the kinetic studies and EHMO calculation of reaction between Cp(C$_5$H$_7$)CrCO and PR$_3$ (PR$_3$=PMe$_2$Ph, P(OCH$_3$)$_3$, PMePh$_2$).[19] In that paper, the 18-electron half open carbonyl complex, Cp(S-C$_5$H$_7$)CrCO undwent predominantly CO substitution at various temperatures by a dissociative mechanism and involved η^5-S↔η^5-U interconversions of pentadiene. These results were confirmed by EHMO calculations.

R. M. Kowaleski, *et al.* reported synthesis, kinetics, and mechanism of ligand substitution reactions of 17-electron-half-open vanadium carbonyl complex, Cp(pdl)VCO, where Cp is cyclopentadienyl and pdl is pentadienyl.[18] They reported that carbonyl substitution reactions of the vanadocene carbonyl, Cp$_2$VCO, and decamethyl vanadocene carbonyls, Cp*$_2$VCO, proceeded by an associative mechanism, but the mixed η^5-ligand complexes, Cp(pdl)VCO, reacted at elevated temperature by a CO-dissociative pathway. This reactivity

difference must be attributed to the structural and electronic features which prohibit the pentadienyl complexes to undergo associative reaction which is allowed for Cp$_2$VCO and Cp*$_2$ VCO.

The goal of the present study has been to elucidate the mechanism, the orientation and role of pentadienyl, and the effect of the two methyl groups on the Pdl ligand in reactions between Cp(2,4-Me$_2$C$_5$H$_5$)CrCO and PR$_3$(PR$_3$=PMe$_2$Ph, P(OCH$_3$)$_3$, PMePH$_2$). Kinetic studies and EHMO calculation reported in this work, allow us to characterize the mechanism of CO substitution reaction for 18-electron half open chromocene carbonyls. In order to get further insight into the CO substitution reactions between Cp(2,4-Me$_2$C$_5$H$_5$)CrCO and PR$_3$, we have analyzed the electronic structure, the overlap population, and the orientation preference of (2,4-Me$_2$C$_5$H$_5$ and the role of 2,4-Me$_2$C$_5$H$_5$ in the reaction of Cp(2,4-Me$_2$C$_5$H$_5$)CrCO and PR$_3$ by extended Hückel molecular orbital calculations.

Experimental

General Procedures. The half-open chromocene carbonyls are very air sensitive and sometimes pyrophoric. All compounds were, therefore, prepared, handled and stored under nitrogen in a glove box, while solutions were generally manipulated under a high vacuum or in a Schlenk tube under N$_2$ Ar and CO. Half-open chromocene carbonyl, Cp(2,4-Me$_2$C$_5$H$_5$)CrCO, was prepared by the pulished procedures.[13] The various dienes and phosphines were purchased from Aldrich and Fluca.

Kinetics of CO Substitution Reaction Between Cp (2,4-Me$_2$C$_5$H$_5$)CrCO and PR$_3$. Solution of Cp(2,4-Me$_2$C$_5$H$_5$) CrCO of about 5×10^{-4} mol was prepared undr N$_2$ or Ar gas. The absorption at 430 nm was monitored wich time by Shimadzu 265 UV-spectrophotometer at various temperatures. Plots of ln A *vs.* time were linear for at least three half-live and k_{obsd} was determined by the least-squares method from the slope of this line. Activation parameters, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were calculated by the least-squares method from the plot of ln(k/T) *vs.* $1/T$, where T is temperature and k
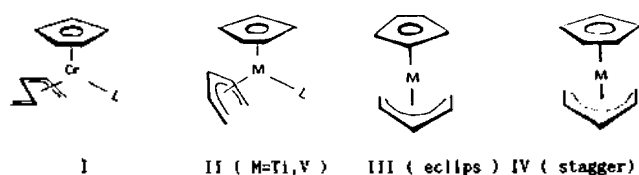
Scheme 1.

Scheme 2.

Table 1. Effect of PR₃ concentration on, Kobsd of CO Substitution Reaction Cp(S-2,4,Me₂C₅H₅)CrCO in Decaline

Temp(°C)	Concentration of PR₃(M)		
	5.0×10^{-3}	7.0×10^{-3}	10.0×10^{-3}
a. PMe₂Ph			
25	6.02×10^{-5}	6.02×10^{-5}	6.00×10^{-5}
35	2.32×10^{-4}	2.20×10^{-4}	2.34×10^{-4}
45	7.26×10^{-4}	7.31×10^{-4}	7.23×10^{-4}
55	1.86×10^{-3}	2.05×10^{-3}	1.90×10^{-3}
65	5.70×10^{-3}	5.63×10^{-3}	5.70×10^{-3}
b. P(OCH₃)₃			
25	6.03×10^{-5}	5.96×10^{-5}	5.99×10^{-5}
35	2.30×10^{-4}	2.34×10^{-4}	2.29×10^{-4}
45	7.06×10^{-4}	7.27×10^{-4}	7.21×10^{-4}
55	1.87×10^{-3}	1.89×10^{-3}	1.95×10^{-3}
65	5.61×10^{-3}	5.71×10^{-3}	5.69×10^{-3}
c. PMePh₂			
25	6.05×10^{-5}	6.10×10^{-5}	6.03×10^{-5}
35	2.33×10^{-4}	2.37×10^{-4}	2.29×10^{-4}
45	7.17×10^{-4}	7.31×10^{-4}	7.27×10^{-4}
55	1.88×10^{-3}	1.97×10^{-3}	1.99×10^{-3}
65	5.77×10^{-3}	5.69×10^{-3}	5.77×10^{-3}

[Cp(S-2,4-Me₂C₅H₅)CrCO] ≒ 5×10⁻⁴ M

Table 2. Rate constants, kobsd of CO Substitution Reactions for Half-Open Chromocene Carbonyls and PR₃ at various Temperatures in Decaline. (where PR₃ = PMe₂Ph, P(OMe)₃, PMePh₂)

Complexes	Temp(°C)	Concentration of PR₃(M)		
		5.0×10^{-3}	7.0×10^{-3}	10.0×10^{-3}
Cp(C₅H₇)CrCO[19]	25	5.69×10^{-6}	5.72×10^{-6}	5.63×10^{-6}
	35	2.00×10^{-5}	2.03×10^{-5}	2.00×10^{-5}
	45	1.01×10^{-4}	1.10×10^{-4}	1.01×10^{-4}
	55	2.73×10^{-4}	2.83×10^{-4}	2.80×10^{-4}
	65	8.53×10^{-4}	8.58×10^{-4}	8.51×10^{-4}
Cp(2,4-Me₂C₅H₅) CrCO	25	6.02×10^{-5}	6.02×10^{-5}	6.00×10^{-5}
	35	2.32×10^{-4}	2.20×10^{-4}	2.34×10^{-4}
	45	7.26×10^{-4}	7.31×10^{-4}	7.23×10^{-4}
	55	1.86×10^{-3}	2.05×10^{-3}	1.90×10^{-3}
	65	5.70×10^{-3}	5.63×10^{-3}	5.70×10^{-3}

[Cp(Pdl)CrCO] ≒ 5×10⁻⁴ M

$$Cp(2,4\text{-}Me_2C_5H_5)CrCO + PR_3 \rightarrow Cp(2,4\text{-}Me_2C_5H_5)CrPR_3 + CO$$
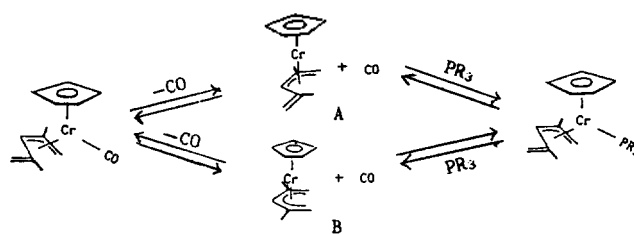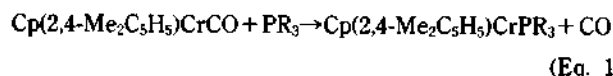
(Eq. 1)

is a first-order rate constant.

Molecular Orbital Calculation. The calculations were carried out with extended Hückel MO calculations with weighted Hij's.[14-15] The Cr parameters given by Summervilled and Hoffmann were used.[16]

Results and Discussion

Kinetic Studies. In general, one might expect that cyclodienyl complexes should exhibit a greater preference toward η⁵-coordination than would pentadienyl complexes, as the former with be held relatively rigid in the U conformation, while pentadienyl fragments tend to prefer W and S(sickle) configurations.[13-16] In fact, a good illustration of this may be found in some chromium chemistry. The half-open chromocene adducts were therefore assigned to be in the highly unusual η⁵-S(S=sickel) configuration (*e.g.*, I), which was opposite to the normal configuration for the titanium and vanadium analogues (*e.g.*, II)[16] in Scheme 1. But half-open chromocene existed in a normal half-open metallocene structure (similar to III or IV vide infra) in Scheme 1.

Kinetic parameters for the reactions of Cp(2,4-Me₂C₅H₅)CrCO with PR₃, where PR₃=PMe₂Ph, P(OCH₃)₃ and PMePh₂, were obtained (Eq. 1)

All of these reactions are first order in the substrate metal complex and zero order in nuclephiles regardless of initial concentration of phosphine. The observed rate constants, k_{obsd}, for the substitution reaction of Cp(2,4-Me₂C₅H₅)CrCO with PR₃ for various concentrations of PR₃ are given in Table 1. As shown in Table 1, the rate constants tended to be almost the same regardless of concentrations and kinds of nucleophiles, which meant that they were independent of nuclophile concetration and nature of nucleophile. The kinetic data suggested that CO substitution reaction of Cp(2,4-Me₂C₅H₅) CrCO with PR₃ proceeded by a dissociative mechanism.

To determine the activation enthalphy (ΔH^*) and the activation entropy (ΔS^*), linear of ln (k_{obsd}/T) *vs.* $1/T$ were and ΔH^* and ΔS^* were calculated to be 22.0± 1.0 kcal/mol and −3.8± 1.9 cal/mol·K, respectively. The observed values could be the evidence of the classic dissociative type of process, like those of vanadium analogues (ΔH^*=27.9± 0.8 kcal/mol, ΔS^*=9.0 cal/mol·K) and Cp(C₅H₇)CrCO (ΔH^*= 24.6± 1.1 kcal/mol, ΔS^*=3.1± 2.8 cal/mol·K) which were reported in previous papers.[19] Thus, the 18-electron half-open complex, Cp(2,4-Me₂C₅H₅)CrCO, undergoes CO substitution at various temperatures predominantly by a dissociative mechanism.

Mechanism of Co Substitution Reaction. A possible dissociative mechanism of CO substitution reaction Cp(2, 4-C₇H₁₁)CrCO with PR₃ is given in Scheme 2.

Table 3. Coordination Geometry of Cr-Pentadienes Complexes.

		S-conformation	U-conformation
Cr-CCP^a	Å	1.838 Å	1.838 Å
Cr-M1^b	Å	1.444 Å	1.444 Å
C(1)-(2)	Å	1.390 Å	1.390 Å
C(2)-(3)	Å	1.412 Å	1.425 Å
C(3)-(4)	Å	1.437 Å	1.425 Å
C(4)-(5)	Å	1.390 Å	1.390 Å
Cr-C(CO)	Å	1.850 Å	1.850 Å
Cr-CO	Å	1.160 Å	1.160 Å
$\angle C_1C_2C_3$	deg	119.55°	122.7°
$\angle C_2C_3C_4$	deg	116.85°	125.3°
$\angle C_3C_4C_5$	deg	113.85°	122.7°
ϕ_1°	deg	156.7°	156.7°
ϕ_2	deg	96.6°	95.6°
ϕ_3	deg	107.7°	107.7°
δ^d	deg	23.3°	24.5°
ϵ^e	deg	56.6°	0.0°

^{a}CCP; centroid of Cyclopentadienyl ligand, ^{b}M1; M1 midpoint of C(1) and C(5), $^d\delta$; dihedral angle between Cp ring and the pdl plane, $^c\phi_{1-3}$; angle formed by the bonds between CCP, M1 and CO, $^e\epsilon$; dihedral angle between C_3-C_5 plane and C_1-C_4 plane

Scheme 3.

Figure 1. The energy profile for S-(φ=18.5° and U-(φ=23.3°) conformers of Cp(2,4-Me$_2$C$_5$H$_5$)CrCO as a function of L.

Table 2 shows the reactivity order of Cp(2,4-Me$_2$C$_5$H$_5$)CrCO>Cp(C$_5$H$_7$)CrCO for the reaction given in Eq. 1, which can be attributed to the usual streic acceleration for the ligand substitution of metal complexes.

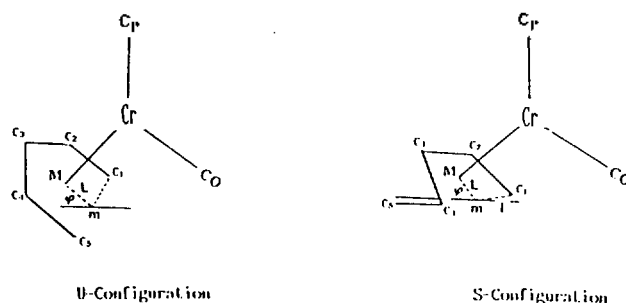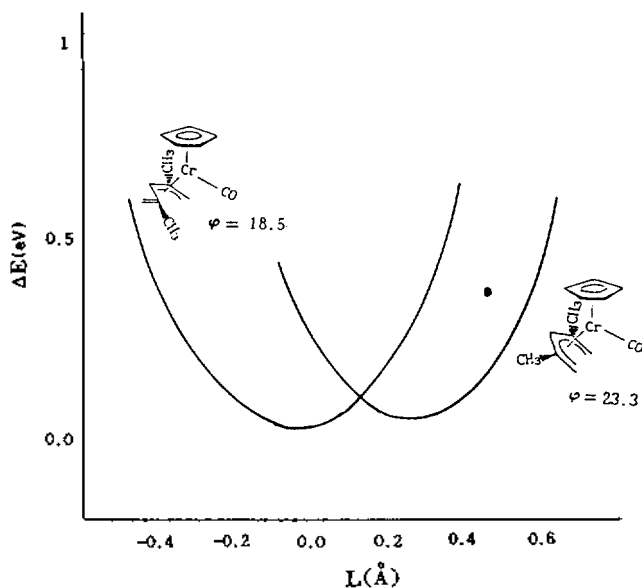The presence of methyl groups at both 2-and 4-positions of 2,4-Me$_2$C$_5$H$_5$ oentadienyl ligand suggests that one of them points toward and weakens the metal-CO bond. Thus, Cp(S-2,4-Me$_2$C$_5$H$_5$)CrCO is more prone to loss of CO and ΔH^* of Cp(S-2,4-Me$_2$C$_5$H$_5$)CrCO is lower than that of Cp(C$_5$H$_7$)CrCO, and the rates for Cp(S-2,4-C$_7$H$_{11}$)CrCO are faster than those for Cp(C$_5$H$_7$)CrCO as shown in Table 2.

To get further insight into the role of pentadiene in Co substitution reaction, the activation parameters (ΔH^*, ΔS^*) of Cp(2,4-Me$_2$C$_5$H$_5$)CrCO were compared to those of Cp(2,4-Me$_2$C$_5$H$_5$)VCO. The value of ΔH^*(22.0 kcal/mol) for Cp(2,4-Me$_2$C$_5$H$_5$)CrCO complex is similar to that of the 17-electron vanadium analogue(27.9 kcal/mol) which undergoes simple dissociative mechanism(A pathway in Scheme 2).

Notably, the ΔS^* values of the Cp(2,4-Me$_2$C$_5$H$_5$)CrCO complex do unusually seem smaller than that of V analogue (9.0 cal/mol·K). Unusually low value of ΔS^* suggested that loss of CO from the Cp(2,4-Me$_2$C$_5$H$_5$)CrCo complex would lead to η^5-S to η^5-U conversion (B pathway in Scheme 2) accompanied by an increase in order and symmetry and a decrease in entropy.

Molecular Orbital Calculations. Here we describe the electronic structure and bonding of Cp(2,4-Me$_2$C$_5$H$_5$)CrCO, focusing mainly on the orientation and the role of pentadiene, based on the extended Hückel MO calculations.

All the bond lengths and the bond angles are listed in Table 3 from the crystallographic data of Cp(2,4-Me$_2$C$_5$H$_5$)CrCO.[6] For both the η^5-U-and η^5-S-isomers, the coordination

geometry of the pentadiene was optimized by using the three variables l, L and φ, as defined in Scheme 3. l is the distance between the C$_1$ atom of C$_5$H$_7$ and "m" and the line of C(1)-C(5). L is the distance between the point "M", and the "m" on the line of C(1)-(5) and the angle φ defines the swing of inner carbons away from Cr.

The other key geometrical parameters that are fixed include the following: Cp(centroid)-Cr=1.838 Å; Cr-C(CO)= 1.85 Å; Cr-M=1.444 Å; Cp(centroid)-Cr-C(CO)=95.6°

The potential energy calculations on Cp(2,4-Me$_2$C$_5$H$_5$)CrCO as a function of the above three variables gave a minimum at l=1.800 Å, L=0.01 Å and φ=18.5° for η^5-S-conformer and a minimum at l= the middle of C(1)-C(5), L=0.290 Å and φ=23.3° for η^5-U coordination isomer. The theoretically optimized geometry of Cp(s-2,4-Me$_2$C$_5$H$_5$)CrCO is very close to the observed one. The optimized geometry is given in Table 3.

The total energy curves show that stability of the limiting pentadiene orientations is well balanced, where the calculated energy difference is only 0.4 kcal/mol, very slightly in favor of η^5-S coordination. As will be discussed shortly, the population analysis for Cp(2,4-Me$_2$C$_5$H$_5$)CrCO proves that the Cr-(S-2,4-Me$_2$C$_5$H$_5$) bond is somewhat stronger than the Cr-(U-2,4-Me$_2$C$_5$H$_5$) bond in the magnitude of the bonding inte-

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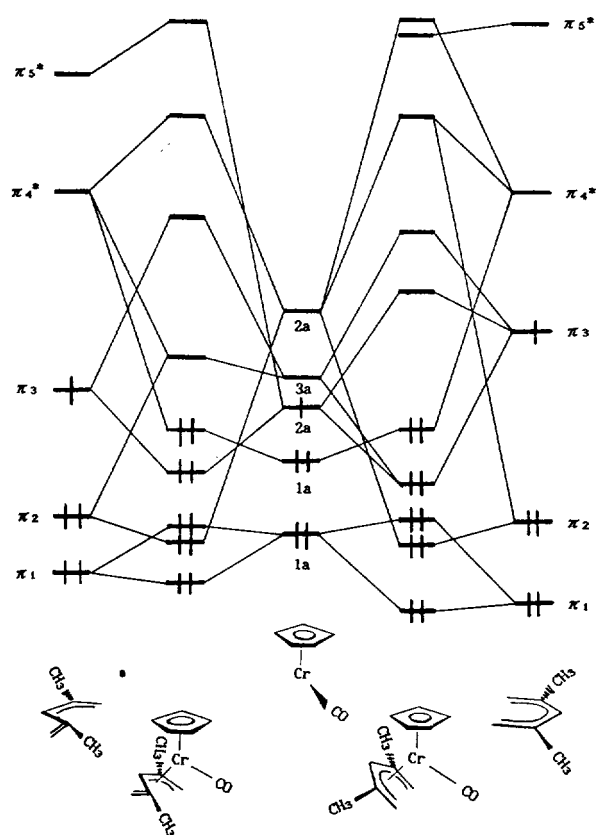
Figure 2. Interaction diagram for the S-and U-conformers of Cp(2,4-Me$_2$C$_5$H$_5$)CrCO.

Table 4. The Results of Population Analysis for Cp(S-2,4-C$_7$H$_{11}$)CrCO and Cp(U-2,4-C$_7$H$_{11}$)CrCO

	S-conformation	U-conformation
P(Cr-C^1)	0.179	0.220
P(Cr-C^2)	0.119	0.072
P(Cr-C^3)	0.169	0.062
P(Cr-C^4)	0.192	0.073
P(Cr-C^5)	0.102	0.217
ΔP	−0.099	0.230
P(Cr-C$_{all}$)	0.661	0.644
P(II$_1$-1a')	0.000	0.000
P(II$_2$-2a'')	0.138	0.188
P(II$_3$-2a')	0.284	0.262
P(II$_4$*-1a'')	0.066	0.125
Q(C^1)	−0.241	−0.259
Q(C^2)	+0.085	+0.139
Q(C^3)	−0.203	−0.108
Q(C^4)	−0.126	+0.140
Q(C^5)	−0.065	−0.258

P: Overlap population, ΔP: P(Cr-C$_{(terminal)}$)-P(Cr-C$_{(inner)}$), P(Cr-C$_{all}$): the sum of all the Cr-C$_{(all)}$)overlap populations., Q: Charge of carbons

ractions between the Cr and 2,4-Me$_2$C$_5$H$_5$ orbitals. The orbital interaction diagram for Cp(S-2,4-Me$_2$C$_5$H$_5$)CrCO and Cp(U-2, 4-Me$_2$C$_5$H$_5$)CrCO is shown in Figure 2.

The bonding between Cr and S-2,4-Me$_2$C$_5$H$_5$ is achieved primarily through the donation-type π_2-2a'', the back-donation-type π_4*-1a'', mixed type π_3-2a', and π_1-1a' interactions. The 1a'' and 2a'' orbitals are essentially d_{xy} and d_{yz} orbitals of Cr, respectively, while the 2a' orbital consists of admixture of $d_{x^2-y^2}$ and d_{z^2} of Cr. It is obvious from Figure 2 that both bonding pictures of U-and S-conformers seem to be alike to each other and that the amount of stabilization of the resulting bonding MO for η^5-S-conformation is also very similar to that for the η^5-U conformation structure.

In order to gain an insight into the Cr-(2,4-Me$_2$C$_5$H$_5$) bonding and CO-substitution reaction of 18-electron Cp(2,4-Me$_2$C$_5$H$_5$) CrCO, a population analysis is performed. The results are summarized in Table 4, which includes overlap populations arising from π_2-2a'', π_4*-1a'', π_3-2a' and π_1-1a' interactions and Cr-C(1 and 5) (terminal) and Cr-C(2, 3 and 4) (inner) bond overlap poplations together with charges on pentadiene carbon atoms. Note that the major contributions to the total Cr-C(2,4-Me$_2$C$_5$H$_5$) overlap population which may be represented by P(Cr-C$_{all}$) come from the above mentioned donation and back-donation and mixed orbital interactions. It appears that the π_1-1a' overlap populations for the two isomers are very similar to each other and seem to be very slightly antibonding. And for the donation interaction P(π_2-2a'') is 0.138 (S-conformation) and 0.188 (U-conformation), and for the back-donation interactions, P(π_4*-1a'') is 0.066 (S-confor-

mation) and 0.125 (U-conformation). But in mixed-orbital interaction, P(π_3-2a') is 0.284 (S-conformation) and 0.262 (U-conformation).

In S-configuration, the back donation interaction is smaller than other interactions. The greater back donation interaction may help stabilize a 20-electron transition state or intermediate. Thus, the small back donation interaction seems to make the chromium center less susceptible to nucleophilic attack. The overlap population between Cr and the carbon of CO, P(Cr-CO) is 0.843. Compared with the value of P(Cr-CO) for Cp(C$_5$H$_7$)CrCO, 0.852, P(Cr-CO) of Cp(S-2,4-Me$_2$C$_5$H$_5$) CrCO is smaller than that of Cp(S-C$_5$H$_7$)CrCO - ordering : Cp (S-2,4-Me$_2$C$_5$H$_5$)CrCO<Cp(S-C$_5$H$_7$)CrCO.

On the otherhand, the order for the reaction rate constants for Scheme 2 is Cp(S-2,4-Me$_2$C$_5$H$_5$)CrCO>Cp(S-C$_5$H$_5$)CrCO in Table 2. It is suggested that Cr-CO bond of the complex S-2,4-Me$_2$C$_5$H$_5$ ligand is weaker than that of the complex with S-C$_5$H$_7$ ligand. Hence, the presence of a 2-methyl substitutent on the handle of the η^5-sickle does lead to significant destabilization. As a result, the value of P(Cr-CO) for Cp(S-2,4-Me$_2$C$_5$H$_5$)CrCO is lower than that of Cp(C$_5$H$_7$)CrCO and the rate of substitution reactions between Cp(S-2,4-Me$_2$C$_5$H$_5$) CrCO and PR$_3$ is faster than that of Cp(S-C$_5$H$_7$)CrCO. The opposite arrangments of these two orderings supports that the rate acceleration caused by the substituents on pentadienyl ligand is steric effect rather than electronic one.

One should not put too much meaning on this small difference in overlap population between S-and U-configurations. But this small difference actually parallels the trend of P(Cr-C$_{all}$). The Cr-(S-2,4-Me$_2$C$_5$H$_5$) bond may be in fact slightly stronger than the Cr-(U-2,4-Me$_2$C$_5$H$_5$) bond, and the total one-electron energies may contribute to the relative stability of the U-conformation isomer.

Another interesting aspect of the Cr-(2,4-Me$_2$C$_5$H$_5$) bond is to see how large or small the contribution of the σ-bonding
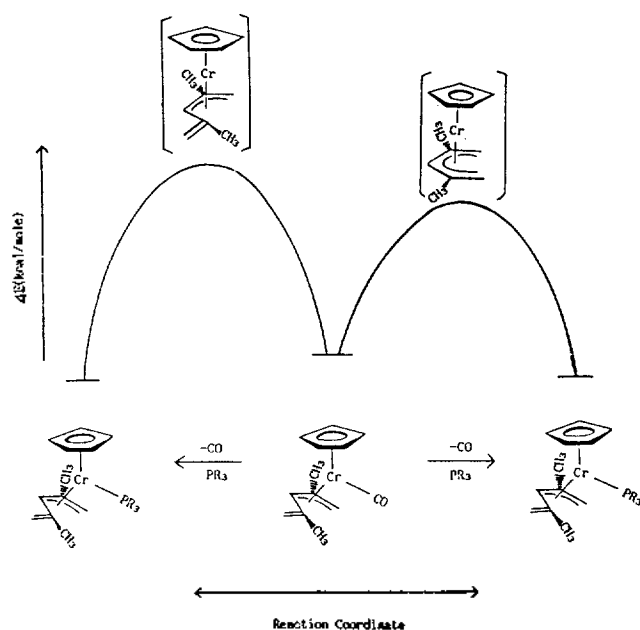
Figure 3. Proposed reaction profile for Cp(2,4-Me₂C₅H₅)CrCO.

is for 1,5-carbons of 2,4-Me₂C₅H₅. The differences of overlap population between Cr-terminal (1,5-) carbons and Cr-inner (2,3,4-) carbons of 2,4-Me₂C₅H₅ $\Delta P (= P(Cr-C_{terminal}) - P(Cr-C_{inner}))$ are -0.099 for the S-conformation compound and 0.230 for the U-conformation compound. The population structure of Cp(S-2,4-Me₂C₅H₅)CrCO is different from that of Cp (U-2,4-Me₂C₅H₅)CrCO. Here, the large ΔP means a greater contribution of 1,5-σ-bonding to the pentadiene coordination. The theoretically optimized structure is very close to the one observed by crystallography. In U-conformer, the population analysis shows that the terminal pentadiene carbons interact with Cr much more strongly than the inner carbons. But in the case of S-conformer, the interaction between Cr and terminal pentadiene carbons is very similar to the interaction between Cr and inner carbons. Therefore it is expected that Cr-(S-2,4-C₇H₁₁) bond is better described as η^5-π-bonding, but the Cr-(U-2,4-Me₂C₅H₅) bond is better described as σ, π-bonding. $P(Cr-C_{all})$, ΔP, and the negative charges accumulated on the pentadiene carbons may be reflected in the orientation and the role of pentadiene.

A proposed reaction profile for Cp(2,4-Me₂C₅H₅)CrCp is shown in Figure 3. This proposed reaction profile determined for CO substitution reaction mechanism of Cp(2,4-Me₂C₅H₅) CrCO is allowed by the contemporaneous quantitative changes of the reaction coordination, *i.e.*, bond length, cone angle, and dihedral angle. The enery of [Cp(2,4-Me₂C₅H₅) Cr···CO]⁺ transition state, and no significant energy barrier

is found in the η^5-S↔η^5-U interconversion. The [Cp(U-2,4-C₇H₁₁)Cr···CO]⁺ path will be favored over [Cp(U-2,4-C₇H₁₁) Cr···CO]⁺ path, and this result agrees with the experimental result. Therefore, it is suggested that the 18-electron Cp(2,4-Me₂C₅H₅)CrCO undergoes CO substitution predominantly by a dissociative mechanism involving η^5-S↔η^5-U interconversion.

References

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