

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

Jong-Jae Chung* and Byung-Gill Roh

Department of Chemistry, College of Natural Sciences, Kyungpook National University, Taegu 702-701

Received September 21, 1992

The CO substitution reactions of the complex, $\text{Cp}(\text{S-2,4-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ with PR_3 ($\text{PR}_3 = \text{PMePh}_2$, $\text{P}(\text{OCH}_3)_3$, PMe_2Ph) 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 $\Delta H^\ddagger = 22.0 \text{ kcal}\cdot\text{mol}^{-1}$, $\Delta S^\ddagger = -3.8 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. Unusually low value of ΔS^\ddagger suggests an $\eta^5\text{-S} \rightarrow \eta^5\text{-U}$ conversion of the pentadienyl ligand. This suggestion was confirmed by the Extended-Hückel molecular orbital (EHMO) calculations, which revealed that the total energy of $\text{Cp}(\text{S-2,4-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ is about 0.42 kcal/mol more lower than that of $\text{Cp}(\text{U-2,4-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ and the energy of $[\text{Cp}(\text{U-2,4-Me}_2\text{C}_5\text{H}_5)\text{Cr}\cdots\text{CO}]^\ddagger$ transition state is about 2.43 kcal/mol lower than that of $[\text{Cp}(\text{S-2,4-Me}_2\text{C}_5\text{H}_5)\text{Cr}\cdots\text{CO}]^\ddagger$ 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 $\text{Cp}(\text{C}_5\text{H}_7)\text{CrCO}$ and PR_3 ($\text{PR}_3 = \text{PMe}_2\text{Ph}$, $\text{P}(\text{OCH}_3)_3$, PMePh_2).¹⁹ In that paper, the 18-electron half open carbonyl complex, $\text{Cp}(\text{S-C}_5\text{H}_7)\text{CrCO}$ underwent predominantly CO substitution at various temperatures by a dissociative mechanism and involved $\eta^5\text{-S} \leftrightarrow \eta^5\text{-U}$ 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, $\text{Cp}(\text{pdl})\text{VCO}$, where Cp is cyclopentadienyl and pdl is pentadienyl.¹⁸ They reported that carbonyl substitution reactions of the vanadocene carbonyl, Cp_2VCO , and decamethyl vanadocene carbonyls, Cp^*_2VCO , proceeded by an associative mechanism, but the mixed η^5 -ligand complexes, $\text{Cp}(\text{pdl})\text{VCO}$, reacted at elevated temperature by a CO-dissociative pathway. This reactivity

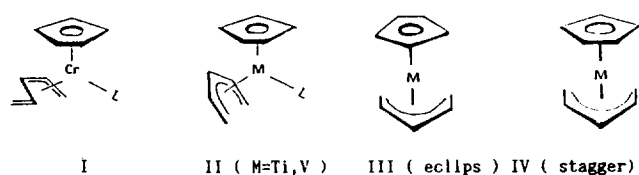
difference must be attributed to the structural and electronic features which prohibit the pentadienyl complexes to undergo associative reaction which is allowed for Cp_2VCO and Cp^*_2VCO .

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 PdI ligand in reactions between $\text{Cp}(\text{2,4-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ and PR_3 ($\text{PR}_3 = \text{PMe}_2\text{Ph}$, $\text{P}(\text{OCH}_3)_3$, 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 $\text{Cp}(\text{2,4-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ and PR_3 , we have analyzed the electronic structure, the overlap population, and the orientation preference of $(\text{2,4-Me}_2\text{C}_5\text{H}_5)$ and the role of $\text{2,4-Me}_2\text{C}_5\text{H}_5$ in the reaction of $\text{Cp}(\text{2,4-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ 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, $\text{Cp}(\text{2,4-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$, was prepared by the published procedures.¹³ The various dienes and phosphines were purchased from Aldrich and Fluka.

Kinetics of CO Substitution Reaction Between $\text{Cp}(\text{2,4-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ and PR_3 . Solution of $\text{Cp}(\text{2,4-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ of about 5×10^{-4} mol was prepared under N_2 or Ar gas. The absorption at 430 nm was monitored with time by Shimadzu 265 UV-spectrophotometer at various temperatures. Plots of $\ln A$ vs. time were linear for at least three half-lives and k_{obsd} was determined by the least-squares method from the slope of this line. Activation parameters, ΔH^\ddagger and ΔS^\ddagger 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.

Table 1. Effect of PR_3 concentration on, k_{obsd} of CO Substitution Reaction $\text{Cp}(\text{S-2,4-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ in Decaline

Temp(°C)	Concentration of $\text{PR}_3(\text{M})$		
	5.0×10^{-3}	7.0×10^{-3}	10.0×10^{-3}
<i>a. PMe_2Ph</i>			
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}
<i>b. $\text{P}(\text{OCH}_3)_3$</i>			
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}
<i>c. PMePh_2</i>			
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}

$[\text{Cp}(\text{S-2,4-Me}_2\text{C}_5\text{H}_5)\text{CrCO}] \approx 5 \times 10^{-4} \text{ M}$

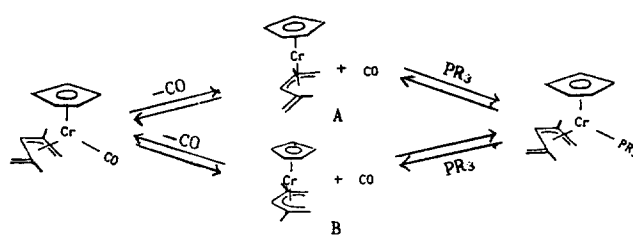
is a first-order rate constant.

Molecular Orbital Calculation. The calculations were carried out with extended Hückel MO calculations with weighted Hiji's.¹⁴⁻¹⁵ The Cr parameters given by Summerville and Hoffmann were used.¹⁶

Results and Discussion

Kinetic Studies. In general, one might expect that cyclopentadienyl complexes should exhibit a greater preference toward η^5 -coordination than would pentadienyl complexes, as the former will 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 η^5 -S(S=sickle) 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 $\text{Cp}(2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ with PR_3 , where $\text{PR}_3 = \text{PMe}_2\text{Ph}$, $\text{P}(\text{OCH}_3)_3$ and PMePh_2 , were obtained (Eq. 1)

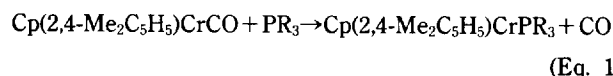


Scheme 2.

Table 2. Rate constants, k_{obsd} of CO Substitution Reactions for Half-Open Chromocene Carbonyls and PR_3 at various Temperatures in Decaline. (where $\text{PR}_3 = \text{PMe}_2\text{Ph}$, $\text{P}(\text{OMe})_3$, PMePh_2)

Complexes	Temp(°C)	Concentration of $\text{PR}_3(\text{M})$		
		5.0×10^{-3}	7.0×10^{-3}	10.0×10^{-3}
$\text{Cp}(\text{C}_5\text{H}_7)\text{CrCO}^{19}$	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}
$\text{Cp}(2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$	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}

$[\text{Cp}(\text{Pd})\text{CrCO}] \approx 5 \times 10^{-4} \text{ M}$



All of these reactions are first order in the substrate metal complex and zero order in nucleophiles regardless of initial concentration of phosphine. The observed rate constants, k_{obsd} , for the substitution reaction of $\text{Cp}(2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ with PR_3 for various concentrations of PR_3 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 nucleophile concentration and nature of nucleophile. The kinetic data suggested that CO substitution reaction of $\text{Cp}(2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ with PR_3 proceeded by a dissociative mechanism.

To determine the activation enthalpy (ΔH^\ddagger) and the activation entropy (ΔS^\ddagger), linear of $\ln(k_{\text{obsd}}/T)$ vs. $1/T$ were and ΔH^\ddagger and ΔS^\ddagger 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 ($\Delta H^\ddagger = 27.9 \pm 0.8$ kcal/mol, $\Delta S^\ddagger = 9.0$ cal/mol·K) and $\text{Cp}(\text{C}_5\text{H}_7)\text{CrCO}$ ($\Delta H^\ddagger = 24.6 \pm 1.1$ kcal/mol, $\Delta S^\ddagger = 3.1 \pm 2.8$ cal/mol·K) which were reported in previous papers.¹⁹ Thus, the 18-electron half-open complex, $\text{Cp}(2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$, undergoes CO substitution at various temperatures predominantly by a dissociative mechanism.

Mechanism of Co Substitution Reaction. A possible dissociative mechanism of CO substitution reaction $\text{Cp}(2,4\text{-C}_7\text{H}_{11})\text{CrCO}$ with PR_3 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 δ ; dihedral angle between Cp ring and the pdl plane, ^e ϵ ; angle formed by the bonds between CCP, M1 and CO, ^e ϵ ; dihedral angle between C₃-C₅ plane and C₁-C₄ plane

Table 2 shows the reactivity order of Cp(2,4-Me₂C₅H₅)CrCO > Cp(C₅H₇)CrCO for the reaction given in Eq. 1, which can be attributed to the usual steric acceleration for the ligand substitution of metal complexes.

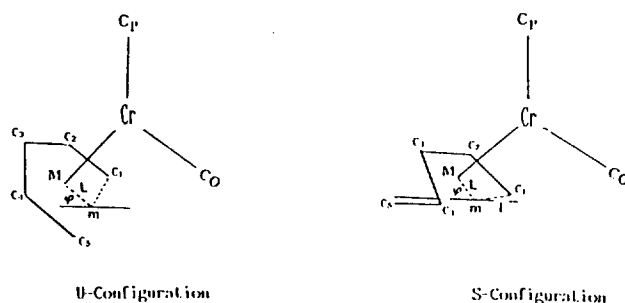
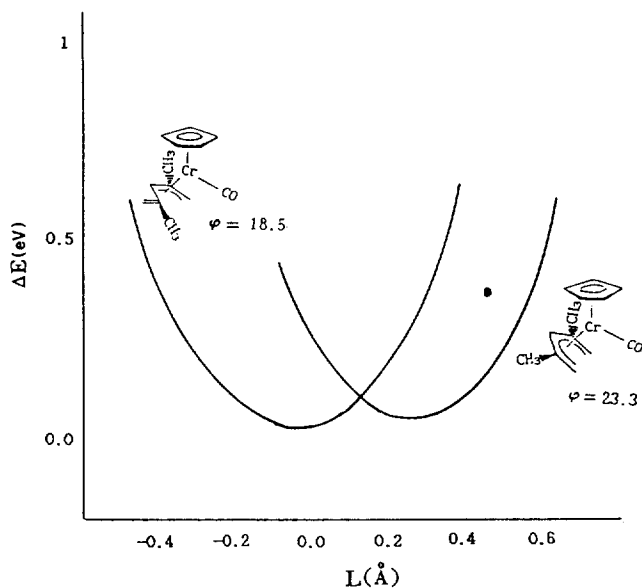
The presence of methyl groups at both 2-and 4-positions of 2,4-Me₂C₅H₅ pentadienyl ligand suggests that one of them points toward and weakens the metal-CO bond. Thus, Cp(S-2,4-Me₂C₅H₅)CrCO is more prone to loss of CO and ΔH^\ddagger of Cp(S-2,4-Me₂C₅H₅)CrCO is lower than that of Cp(C₅H₇)CrCO, and the rates for Cp(S-2,4-C₇H₁₁)CrCO are faster than those for Cp(C₅H₇)CrCO as shown in Table 2.

To get further insight into the role of pentadiene in Co substitution reaction, the activation parameters (ΔH^\ddagger , ΔS^\ddagger) of Cp(2,4-Me₂C₅H₅)CrCO were compared to those of Cp(2,4-Me₂C₅H₅)VCO. The value of ΔH^\ddagger (22.0 kcal/mol) for Cp(2,4-Me₂C₅H₅)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^\ddagger values of the Cp(2,4-Me₂C₅H₅)CrCO complex do unusually seem smaller than that of V analogue (9.0 cal/mol·K). Unusually low value of ΔS^\ddagger suggested that loss of CO from the Cp(2,4-Me₂C₅H₅)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-Me₂C₅H₅)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-Me₂C₅H₅)CrCO.⁶ For both the η^5 -U and η^5 -S isomers, the coordination

**Scheme 3.****Figure 1.** The energy profile for S- ($\phi=18.5^\circ$) and U- ($\phi=23.3^\circ$) conformers of Cp(2,4-Me₂C₅H₅)CrCO as a function of L.

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 C₁ atom of C₅H₇ 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-Me₂C₅H₅)CrCO as a function of the above three variables gave a minimum at $l=1.800$ Å, $L=0.01$ Å and $\phi=18.5^\circ$ for η^5 -S-conformer and a minimum at $l=$ the middle of C(1)-C(5), $L=0.290$ Å and $\phi=23.3^\circ$ for η^5 -U coordination isomer. The theoretically optimized geometry of Cp(s-2,4-Me₂C₅H₅)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-Me₂C₅H₅)CrCO proves that the Cr-(S-2,4-Me₂C₅H₅) bond is somewhat stronger than the Cr-(U-2,4-Me₂C₅H₅) bond in the magnitude of the bonding inte-

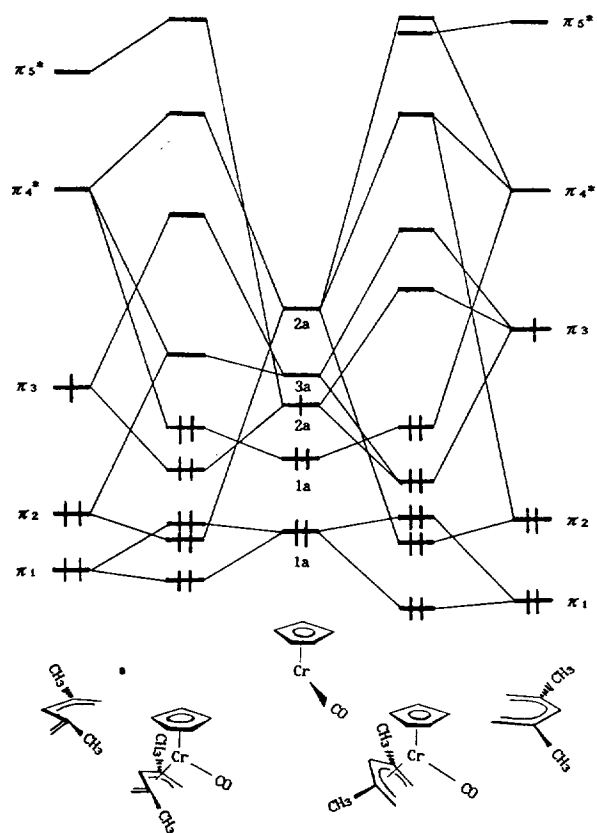


Figure 2. Interaction diagram for the S- and U-conformers of Cp(2,4-Me₂C₅H₅)CrCO.

ractions between the Cr and 2,4-Me₂C₅H₅ orbitals. The orbital interaction diagram for Cp(S-2,4-Me₂C₅H₅)CrCO and Cp(U-2,4-Me₂C₅H₅)CrCO is shown in Figure 2.

The bonding between Cr and S-2,4-Me₂C₅H₅ 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_{z^2} and $d_{x^2-y^2}$ 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-Me₂C₅H₅) bonding and CO-substitution reaction of 18-electron Cp(2,4-Me₂C₅H₅)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 populations together with charges on pentadiene carbon atoms. Note that the major contributions to the total Cr-C(2,4-Me₂C₅H₅) 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-

Table 4. The Results of Population Analysis for Cp(S-2,4-C₇H₁₁)CrCO and Cp(U-2,4-C₇H₁₁)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_(pdt) overlap populations, Q: Charge of carbons

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(C₅H₇)CrCO, 0.852, P(Cr-CO) of Cp(S-2,4-Me₂C₅H₅)CrCO is smaller than that of Cp(S-C₅H₇)CrCO - ordering: Cp(S-2,4-Me₂C₅H₅)CrCO < Cp(S-C₅H₇)CrCO.

On the otherhand, the order for the reaction rate constants for Scheme 2 is Cp(S-2,4-Me₂C₅H₅)CrCO > Cp(S-C₅H₇)CrCO in Table 2. It is suggested that Cr-CO bond of the complex S-2,4-Me₂C₅H₅ ligand is weaker than that of the complex with S-C₅H₇ ligand. Hence, the presence of a 2-methyl substituent 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-Me₂C₅H₅)CrCO is lower than that of Cp(C₅H₇)CrCO and the rate of substitution reactions between Cp(S-2,4-Me₂C₅H₅)CrCO and PR₃ is faster than that of Cp(S-C₅H₇)CrCO. The opposite arrangements 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-Me₂C₅H₅) bond may be in fact slightly stronger than the Cr-(U-2,4-Me₂C₅H₅) 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-Me₂C₅H₅) bond is to see how large or small the contribution of the σ -bonding

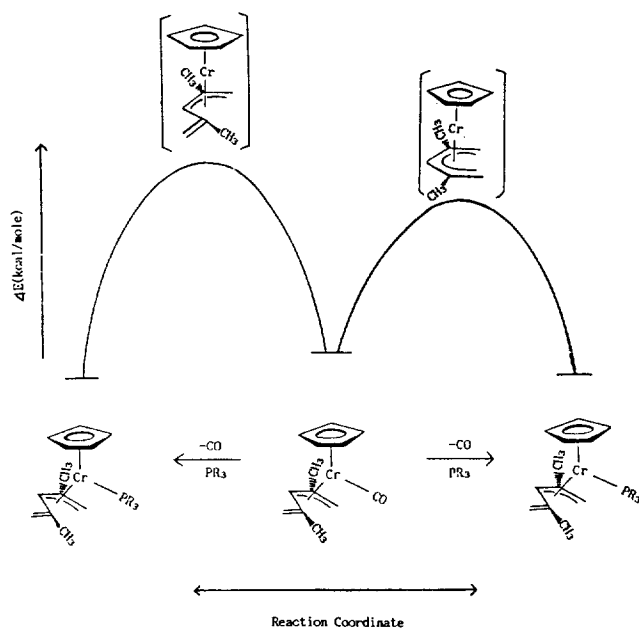


Figure 3. Proposed reaction profile for $\text{Cp}(2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$.

is for 1,5-carbons of $2,4\text{-Me}_2\text{C}_5\text{H}_5$. The differences of overlap population between Cr-terminal (1,5-) carbons and Cr-inner (2,3,4-) carbons of $2,4\text{-Me}_2\text{C}_5\text{H}_5$ $\Delta P(=P(\text{Cr-C}_{\text{terminal}}) - P(\text{Cr-C}_{\text{inner}}))$ are -0.099 for the S-conformation compound and 0.230 for the U-conformation compound. The population structure of $\text{Cp}(S\text{-}2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ is different from that of $\text{Cp}(U\text{-}2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$. 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- C_7H_{11}) bond is better described as $\eta^5\text{-}\pi$ -bonding, but the Cr-(U-2,4- $\text{Me}_2\text{C}_5\text{H}_5$) bond is better described as σ , π -bonding. $P(\text{Cr-C}_{\text{all}})$, 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 $\text{Cp}(2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{CrCp}$ is shown in Figure 3. This proposed reaction profile determined for CO substitution reaction mechanism of $\text{Cp}(2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ is allowed by the contemporaneous quantitative changes of the reaction coordination, *i.e.*, bond length, cone angle, and dihedral angle. The energy of $[\text{Cp}(2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{Cr}\cdots\text{CO}]^\ddagger$ transition state, and no significant energy barrier

is found in the $\eta^5\text{-S}\leftrightarrow\eta^5\text{-U}$ interconversion. The $[\text{Cp}(U\text{-}2,4\text{-C}_7\text{H}_{11})\text{Cr}\cdots\text{CO}]^\ddagger$ path will be favored over $[\text{Cp}(U\text{-}2,4\text{-C}_7\text{H}_{11})\text{Cr}\cdots\text{CO}]^\ddagger$ path, and this result agrees with the experimental result. Therefore, it is suggested that the 18-electron $\text{Cp}(2,4\text{-Me}_2\text{C}_5\text{H}_5)\text{CrCO}$ undergoes CO substitution predominantly by a dissociative mechanism involving $\eta^5\text{-S}\leftrightarrow\eta^5\text{-U}$ interconversion.

Acknowledgement. This research was financially supported by the Basic Science Research Institute Program of the Ministry of Education, Republic of Korea.

References

1. R. D. Ernst, *Chem. Rev.*, **88**, 1255 (1988).
2. P. Powell, in *Advances in Organometallic Chemistry*; West, R. Stone, F. G. A, Eds., Academic, New York, 1986, Vol. 26, p. 125.
3. H. Yasuda and A. Nakamura, *J. Organomet. Chem.*, **285**, 15 (1985).
4. J. R. Bleeke, R. J. Wittenbrink, T. W. Clayton, and M. Y. Chiang, *J. Am. Chem. Soc.*, **112**, 6539 (1990).
5. A. Streitwieser, Jr. *Molecular Orbital Theory for Organic Chemists*, Wiley, New York, 1961.
6. M. C. Böhm, M. Eckert-Maksic, R. D. Ernst, D. R. Wilson, and R. Gleiter, *J. Am. Chem. Soc.*, **104**, 2699 (1982).
7. M. S. Kralik, J. P. Hutchinson, and R. D. Ernst, *J. Am. Chem. Soc.*, **107**, 8296 (1985).
8. M. S. Kralik, A. L. Rheingold, and R. D. Ernst, *Organometallics*, **6**, 2612 (1987).
9. S. J. Severson, J. H. Crmbaluk, R. D. Ernst, J. M. Higashi, and R. W. Parry, *Inorg. Chem.*, **22**, 3833 (1983).
10. J. R. Bleek, and W. J. Peng, *Organometallics*, **6**, 5766 (1987).
11. M. R. Churchill, and F. R. Scholer, *Inorg. Chem.* **20**, 2353 (1981).
12. G. T. Palmer, F. basolo, L. B. Kool, and M. D. Rausch, *J. Am. Chem. Soc.*, **108**, 4417.
13. J. W. Freeman, N. Mallinan, A. M. Arif, R. W. Gedridge, R. D. Ernst, and Fred Basolo, *J. Am. Chem. Soc.* **113**, 6509 (1991).
14. R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).
15. J. H. Ammeter, H. B. Bürg, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 3686 (1978).
16. R. H. Summerville, and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 7240 (1976).
17. L. Stahl, J. P. Hutchinson, and D. R. Wilson, *J. Am. Chem. Soc.*, **107**, 5016 (1985).
18. R. M. Kowaleski, W. C. Troglor, T. D. Newbound, and R. D. Ernst, *J. Am. Chem. Soc.*, **109**, 4860 (1987).
19. J. J. Chung, and B. G. Roh, *Bull. Kor. Chem. Soc.* **2**, 207, 1993.