Kinetics and Stereochemistry of CO Substitution Reactions of Half-Open Chromocene Carbonyls (III): Reactions of $Cp^*(\eta^5\text{-}C_5H_7)CrCO$ and Phosphines

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The CO substitution reactions in the complex, $Cp^*(C_5H_7)CrCO$ with PR_3(PR_3 = $PMePh_2$, $P(OCH_3)_3$, PMe_2Ph) were investigated spectrophotometrically at various temperatures. For the reaction rates, it was suggested that the CO substitution reaction took place by first-order (dissociative) pathway. Activation parameters in decaline are $\Delta H^{\neq} = 21.99 \pm 2.4$ kcal/mol, $\Delta S^{\neq} = -8.9 \pm 7.1$ cal/mol·k. Unusually low value of $\Delta S^{\neq}$ suggested an η^5-S→η^5-U conversion of the pentadienyl ligand. At various temperature, the rates of reaction for the Cp(pdl)CrCO complexes increase in the order $Cp^*(C_5H_7)$-CrCO<$Cp(C_5H_7)CrCO$<$Cp(2,4\text{-}C_7H_{11})CrCO$, which can be attributed to the usual steric acceration or electronic influence for the ligand substitution of metal complexes. This suggestion was confirmed by the extended-Hückel molecular orbital (EHMO) calculations, which revealed that the energy of $[Cp^*(U\text{-}C_5H_7)Cr]^{\neq}$ transition state is about 4.93 kcal/mol lower than that of $[Cp(S\text{-}C_5H_7)Cr]^{\neq}$ transition state, and the arrangement of the overlap populations between Cr and the carbon of CO is $Cp^*(C_5H_7)CrCO$>$Cp(C_5H_7)CrCO$>$Cp(2,4\text{-}C_7H_{11})CrCO$.

Introduction

The area of metal-pentadienyl chemistry has recently been attracting growing attention, and a number of reviews covering various aspects of this field have appeared.[1-4]

The cyclopentadienyl ligand is well-renowned for its utility as a "stabilizing ligand", as it has yielded many very thermally stable compounds. Most notable among these are the metallocenes or bis (cyclopentadienyl) metal complexes.[5-9] While a number of reports dealing with metal-pentadienyl complexs had appeared prior to 1980 (cide 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-forming (coupling) reactions.

We reported the kinetics studies and EHMO calculation of reaction between $Cp(C_5H_7)CrCO$ and PR_3 (PR_3 = PMe_2Ph, $P(OCH_3)_3$, $PMePh_2$) and $Cp(S\text{-}2,4\text{-}C_7H_{11})CrCO$. In this reports,[17] the 18-electron half open complexes, $Cp(S\text{-}C_5H_7)CrCO$, and $Cp(S\text{-}2,4\text{-}C_7H_{11})CrCO$ underwent predominantly CO substitution at various temperatures by a dissociative mechanism and involved the role of the pentadienes (C_5H_7 and $2,4\text{-}C_7H_{11}$). This results were conformed by EHMO calculations.

R. M. Kowaleski, etc. reported synthesis, kinetics, and mechanism of ligand substitution of reactions 17-electron-half-open Vanadium carbonyl complexes Cp(pdl)VCO, where Cp is cyclopentadienyl and pdl is pentadienyl.[16] They reported that carbonyl substitution reactions of the Vanadocene, Cp_2 VCO and decamethyl vanadocene carbonyls, Cp^*_2VCO proceeded by an associative mechanism, but the mixed η^5-ligand complexes, Cp(pdl)VCO reacted at elevated temperture by a CO-dissociative pathway. The difference of these mechanisms must be attributed to the structural and electronic features which prohibit associative reaction pathway for the pentadienyl complexes, but allow it for Cp_2VCO and Cp^*_2 VCO.

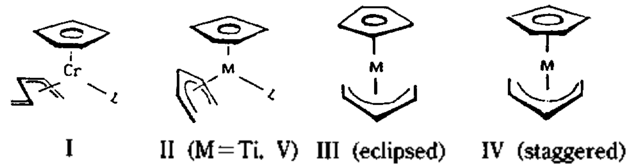
The goal of the present study has been to elucidate the mechanism and the effect of the five methyl groups on the Cp^* ligand for reactions between $Cp^*(C_5H_7)CrCO$ and PR_3(PR_3 = PMe_2Ph, $P(OCH_3)_3$, $PMePh_2$). Kinetics studies and EHMO calculation reported in this work, allow us to characterize the mechanism and the effect of the five methyl group on the Cp^* ligand of CO substitution reaction for 18-electron half open chromocene carbonyl. In order to get further insight into the CO substitution reactions between $Cp^*(C_5H_7)$ CrCO and PR_3, we have analyzed the electronic structure, the overlap population, the orientation preference of C_5H_7, the role of C_5H_7, and the effect of the five methyl groups on the Cp^* ligand in the reaction of $Cp^*(C_5H_7)CrCO$ and PR_3 by extended Hückel molecular orbital calculations.

Experiment

General Procedures. The half-open chromocenes are very air sensitive and sometimes pyrophoric. All compounds were therefore prepared, handled and stored under nitrogene gas in a glove box, while solutions were generally manipulated on a high vacuum or Schlenk tube under N_2, Ar and CO. The synthesis of half-open chromocenes were prepared by published procedures.[11] The various dienes and phosphines were purchased from Aldrich and Fluca.

Kinetics CO substitution reation between $Cp^*(C_5H_7)$ CrCO and PR_3. Solution of $Cp^*(C_5H_7)CrCO$ of about 5×10^{-4} mol was prepared under N_2 and Ar gas. The absorption at 490 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 parameter, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were respectively calculated by the least-squares method from the plot of $\ln(k/T)$ *vs.* $1/T$, where T is temperature and k is a first-order rate constant.

Molecular Orbital Calculation. The calculations were carried out with extended Hückel MO calculations with weighted Hij's.[12,13] The Cr parameters given by Summerville and Hoffmann were used.[14]



Scheme 1.

Table 1. Rate Constants, k_{obsd} of CO Substitution Reaction for $Cp^*(C_5H_7)CrCO$ and PR_3 at Various Temperatures in Decaline

Temp(℃)	Concentration of PR_3 (M)		
	5.0×10^{-3}	7.0×10^{-3}	10.0×10^{-3}
	PMe_2Ph		
25	4.66×10^{-6}	4.72×10^{-6}	4.60×10^{-6}
35	1.59×10^{-5}	1.62×10^{-5}	1.64×10^{-5}
45	5.72×10^{-5}	5.73×10^{-5}	5.67×10^{-5}
55	1.49×10^{-4}	1.58×10^{-4}	1.50×10^{-4}
65	4.43×10^{-4}	4.45×10^{-4}	4.39×10^{-4}
	$P(OCH_3)_3$		
25	4.77×10^{-6}	4.59×10^{-6}	4.67×10^{-6}
35	1.61×10^{-5}	1.60×10^{-5}	1.64×10^{-5}
45	5.70×10^{-5}	5.66×10^{-5}	5.61×10^{-5}
55	1.66×10^{-4}	1.62×10^{-4}	1.59×10^{-4}
65	4.37×10^{-4}	4.44×10^{-4}	4.39×10^{-4}
	$PMePh_2$		
25	4.64×10^{-6}	4.65×10^{-6}	4.60×10^{-6}
35	1.65×10^{-5}	1.70×10^{-5}	1.63×10^{-5}
45	5.68×10^{-5}	5.66×10^{-5}	5.67×10^{-5}
55	1.53×10^{-4}	1.57×10^{-4}	1.60×10^{-4}
65	4.49×10^{-4}	4.44×10^{-4}	4.42×10^{-4}

$[Cp^*(C_5H_7)CrCO] \fallingdotseq 5\times10^{-4}$ M

Results and Discussion

Kinetic Studies. As the neutral pentadienyl fragment may donate five electrons to a metal and possesses molecular orbitals quite similar in nodal properties to the cyclopentadienyl fragment, it is natural that there should be some relationships between their analogous compounds with respect to stoichiometry, structure, and bonding. However, such similarities should not be expected to carry over to reaction chemistry given the arometic nature of the cyclopentadienyl anion and the much different π-orbital energies of the two dienyl fragments. In this key respect, the pentadienyl unit is much more similar to the allyl group, as both are nonaromatic, but have odd alternant delocalized π systems, resulting in a Single Occupied Molecular Orbital (SOMO) for the radical which is nonbinding.

The half-open chromocene adducts were assigned in the highly unusual η^5-S (S=sickel) configuration (*e.g.* I)[11], which were opposite the normal configuration for the titanium and vanadium analogues (*e.g.* II)[11,14] in Scheme 1. The structure for half-open chromocenes exist in normal compounds (*e.g.* III and IV).

Kinetic parameters for the reactions of $Cp^*(C_5H_7)CrCO$ with PR_3, where Cp^*=1,2,3,4,5,pentamethyl-cyclopentadiene and PR_3=PMe_2Ph, $P(OCH_3)_3$ and $PMePh_2$ were obtained (Eq. 1).

$$Cp^*(C_5H_7)CrCO + PR_3 \rightarrow Cp^*(C_5H_7)CrPR_3 + CO \quad (1)$$

All of these reaction are first order for substrates and zero order for nucleophiles in various concentrations of phosphine. The observed rate constants, k_{obsd}, for the substitution reaction of $Cp^*(C_5H_7)CrCO$ with PR_3 at various concentrations are given in Table 1.

As shown in Table 1, the rate constants in not only the various concentrations, but also various nucleophiles tended to be almost the same, which meant that they were independent to nuclophile concentrations and nucleophile species. This kinetic data suggested that the rate-determing stap is a bond-breaking step of Cr-CO bond in transition state.

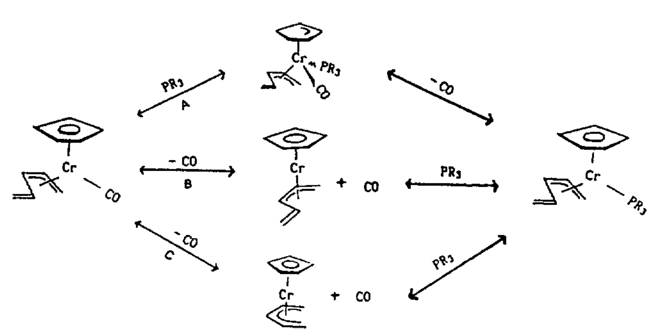
The activated enthalphy ($\Delta H^{\neq}$) and the activated entropy ($\Delta S^{\neq}$) from linear plots of ln (k_{obsd}/T) *vs.* $1/T$ were obtained. $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are listed in Table 2.

Table 2. Activation Parameters of CO Substitution Reaction in the η^5-S-Half-Open Chromocene Carbonyls in Decaline

Complexs	$\Delta H^{\neq}$, (kcal/mol)	$\Delta S^{\neq}$, (cal/mol·k)
$Cp(C_5H_7)CrCO$	24.3± 1.1	3.1± 3.2
$Cp(2,4\text{-}C_7H_{11})CrCO$	22.0± 0.7	−3.8± 1.9
$Cp^*(C_5H_7)CrCO$	21.2± 2.4	−8.1± 7.1
$Cp(3\text{-}C_6H_9)CrCO$	25.7± 0.6	3.7± 1.8
$Cp(C_5H_7)VCO$[16]	28.8	11
$Cp(2,4\text{-}C_7H_{11})VCO$[16]	27.9	9
$Cp_2Ti(CO)_2$[14]	27.9± 1.8	15.0± 5.6
$Cp_2Zr(CO)_2$[14]	12.0± 0.4	−31.2± 1.4
$Cp_2Hf(CO)_2$[14]	15.2± 0.6	−31.0± 1.2

The observed values could be the evidence of the classic dissociative type of process, like those of $Cp(C_5H_7)CrCO$ and $Cp(2,4\text{-}C_5H_7)CrCO$, which was reported in previous papers. Thus, the 18-electron half-open complexe, $Cp^*(C_5H_7)CrCO$, undergoes predominantly CO substitution at various temperatures by the dissociative mechanism.

Mechanism of CO Substitution Reaction. A possible mechanism of CO substitution reactions for half-open chromocene carbonyl is given by following scheme.



The order of rates of reaction for Cp(Pdl)CrCO and PR_3 is given by $Cp^*(C_5H_7)CrCO < Cp(C_5H_7)CrCO < Cp(2,4\text{-}C_7H_{11})$ in Table 3. It is suggested that the major effects of CO substitution reaction are steric repulsion and electronic influences.

For the $Cp(2,4\text{-}C_7H_{11})CrCO$ compound, the major effects of CO substitution reactions are sterric repulsion between one of 2- or 4-methyl groups on pentadienyl and metal-CO

Table 3. Rate Constants, k_{obsd} of CO Substitution Reactions for Half-Open Chromocenes and PR_3 at Various Temperatures in Decaline

Complexes	Temp(℃)	Concentration of PR_3(M)		
		5.0×10^{-3}	7.0×10^{-3}	10.0×10^{-3}
$Cp(C_5H_7)CrCO$	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}
$Cp(2,4-C_7H_{11})CrCO$	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}
$Cp^*(C_5H_7)CrCO$	25	4.66×10^{-6}	4.72×10^{-6}	4.60×10^{-6}
	35	1.59×10^{-5}	1.62×10^{-5}	1.64×10^{-4}
	45	5.72×10^{-3}	5.73×10^{-5}	5.67×10^{-5}
	55	1.49×10^{-4}	1.58×10^{-4}	1.50×10^{-4}
	65	4.43×10^{-4}	4.45×10^{-4}	4.39×10^{-4}

[Cp(PdI)CrCO] ≒ 5×10^{-4} M.

bond. While for the $Cp^*(C_5H_7)CrCO$ compound, a retardation of rate for CO substitution reactions may be attributed to the electronic influences of five methyl substitutients on cyclopentadienyl ligand.

To get further insight into the role of pentadiene in the mechanism of CO substitution reaction, the activated parameters ($\Delta H^{\neq}$, $\Delta S^{\neq}$) of Cp(PdI)CrCo (Cp=Cp and Cp*) were compared to those of Vanadium and Titanium analogues in Table 2. The values of $\Delta H^{\neq}$ for the Cp*(PdI)CrCO complexs are similar to those of Vanadium and Titanium analogue which unergo by dissociative pathway, but different from those of Zr and Hf compounds[19] which undergo by associative pathway (A mechanism).

Kinetic data for CO substitution reactions of the chromium compounds could be the evidence of the classic dissociative pathway. An unusually low value of $\Delta S^{\neq}$ indicates that CO substitution between Cp(PdI)CrCO and PR_3 is not simple dissociative mechanism (B mechanism) and is dissociative mechanism involving the conformation change: η^5-*S* ↔ η^5-U interconversion (C mechanism) accompanied by an increase in order and symmetry and a decrease in entropy.

Molecular Orbital Calculations

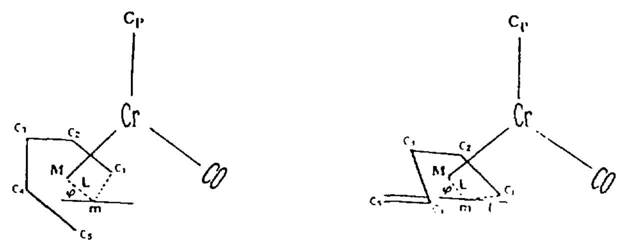
Here we describe the electronic structure and bonding of $Cp^*(C_5H_7)CrCO$, focusing mainly on the orientation and the role of pentadiene and Cp* based on the extended Hückel MO calculations.

All the bond lengths and the bond angles are listed in Table 2 from the crystallographic data of $Cp^*(C_5H_7)CrCO$.[5] For both the η^5-U conformation and η^5-S conformation isomers, the coordination geometry of the pentadiene was optimised by using the three variables l, L and φ as defined is Scheme 3. l is the distance between the atom C_1 of C_5H_7 and "m" on the line of C(1)-C(5). L is the distance between

Table 4. 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[c]	deg	156.7°	156.7°
ϕ_2	deg	95.6°	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; midpoint of C(1) and C(5)
[d]δ; dihedral angle between Cp ring and the PdI plane
[c]ϕ_{1-3}; angle formed by the bonds between CCP, M1 and CO
[e]ε; dihedral angle between C_3-C_5 plane and C_1-C_4 plane.



U-Coordination S-Coordination

Scheme 2.

the point "M", and the "m" on the line of C(1)-C(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 Å.

The potential energy calculations on $Cp^*(C_5H_7)CrCO$ as a function of the above three variables gave a minium at l=1.935 Å, L=0.281 Å and φ=17.0° for η^5-S coordination and a minimum at l=the middle of C(1)-C(5), L=0.650 Å and φ=22.3° for η^5-U coordination isomer. We should mention that the theoreticallly optimized geometry of $Cp^*(C_5H_7)$ CrCO (S-conformation) is very close to the observed one. The optimized geometry is given in Table 4.

The total energy curves show that stability of the limiting pentadiene orientations is well balanced, where the calculated energy difference is only 3.57 kcal/mol, very slightly in favor of η^5-S coordination. Therefore, the S-orientation of the pentadiene is electronically accessible for 18-electron Cp* (C_5H_7)CrCO and the geometrical choice would be determined by small steric and eletronic perturbation. Indeed the X-ray

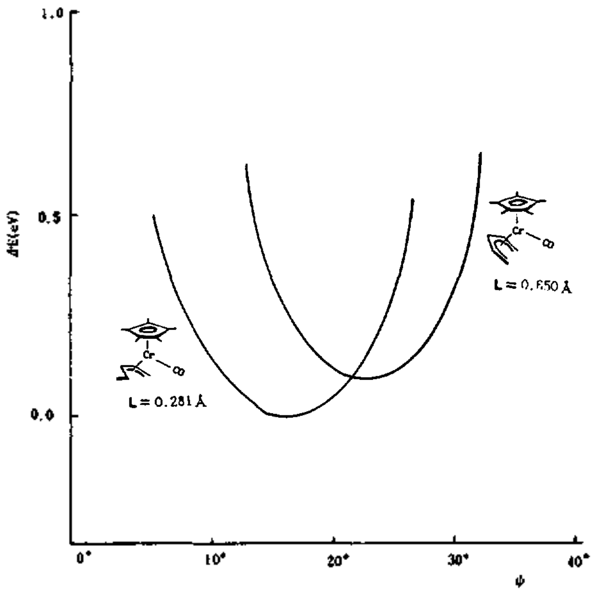


Figure 1. The profile for S-(L=0.281 Å) and U-(L=0.650 Å) conformations of Cp*(C_5H_7)CrCO as a function of L.

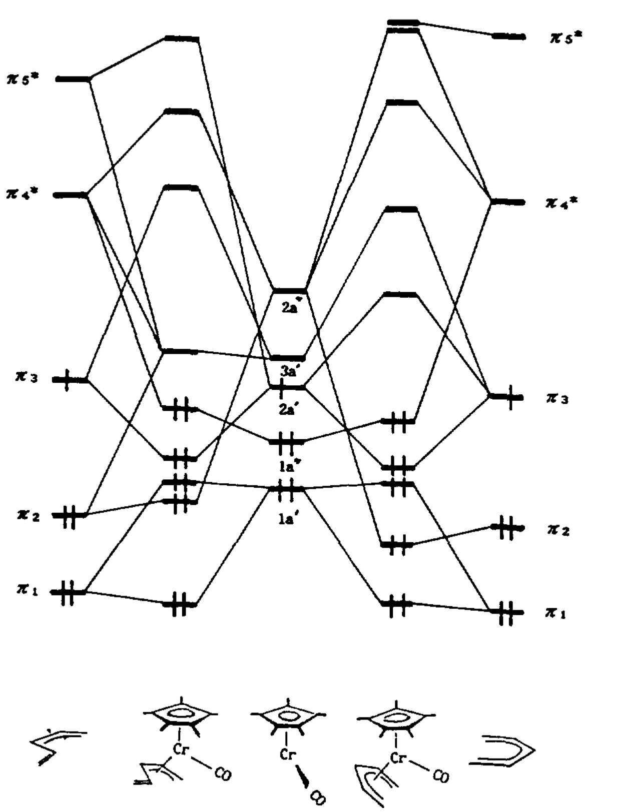


Figure 2. Interaction diagram for the S-and U-conformations in Cp*(C_5H_7)CrCO.

structures of Cp*(C_5H_7)CrCO exhibit the η^5-S-pentadiene orientation. The orbital interaction diagram for Cp*(S-C_5H_7)CrCO and Cp*(U-C_5H_7)CrCO is shown in Figure 2. The bonding between Cr and C_5H_7 is achieved primarily through the donation-type π_2-2a", the back-donation-type π_4^*-1a" and 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,

Table 5. The Results of Population Analysis between Cr and Pentadienyl Cp*(S-C_5H_7)CrCO and Cp*(U-C_5H_7)CrCO

	S-conformation	U-conformation
P(Cr-C^1)	0.155	0.165
P(Cr-C^2)	0.121	0.120
P(Cr-C^3)	0.178	0.127
P(Cr-C^4)	0.087	0.121
P(Cr-C^5)	0.101	0.165
ΔP	−0.129	−0.038
P(Cr-C_{all})	0.652	0.693
P(Π_1-1a')	0.000	0.000
P(Π_2-2a")	0.131	0.200
P(Π_3-2a')	0.264	0.190
P(Π_4^*-1a")	0.072	0.189
Q(C^1)	−0.237	−0.249
Q(C^2)	−0.013	+0.001
Q(C^3)	−0.195	−0.138
Q(C^4)	+0.020	+0.001
Q(C^5)	−0.004	−0.247

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

while the 2a' orbital consists of $d_{x^2-y^2}$ of Cr with an admixture of d_{z^2}. It is obvious from Figure 2 that both bonding pictures between U-conformation and S-conformation compound seem to be alike 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-(C_5H_7) bonding and CO-substitution reaction of 18-electron Cp*(C_5H_7)CrCO, a population analysis is performed. The results are summarized in Table 5, which includes overlap populations arising from π_2-2a", π_4-la", 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 which charges on pentadiene carbon atoms. Note that the major contributions to the total Cr-C(C_5H_7) 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 so happened that the π_1-1a' overlap populations for the two isomers are much alike and seem to be very slightly antibonding. And as for the donation interaction P(π_2-2a') is 0.131 (S-conformation) and 0.200 (U-conformation), and as for the back-donation interactions, P(π_4^*-la") is 0.072 (S-conformation) and 0.189 (U-conformation). But in mixed-orbital interaction, P(π_3-2a') is 0.264 (S-conformation) and 0.190 (U-conformation).

In S-configuration of half-open chromocenes, the back donation interactions 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.

This small difference of overlap population between S-and U-configuration should not be put too much meaning, but this small difference actually parallels the trend of P(Cr-C_{all}). But the Cr-(U-C_5H_7) bond may be in fact slightly stronger

Table 6. Overlap Population between Cr and the Carbon of CO for η⁵-S-Half-Open Chromocene Carbonyls

Complexes	P(Cr-CO)
$Cp(C_5H_7)CrCO$	0.852
$Cp(2,4\text{-}C_7H_{11})CrCO$	0.843
$Cp^*(C_5H_7)CrCO$	0.861

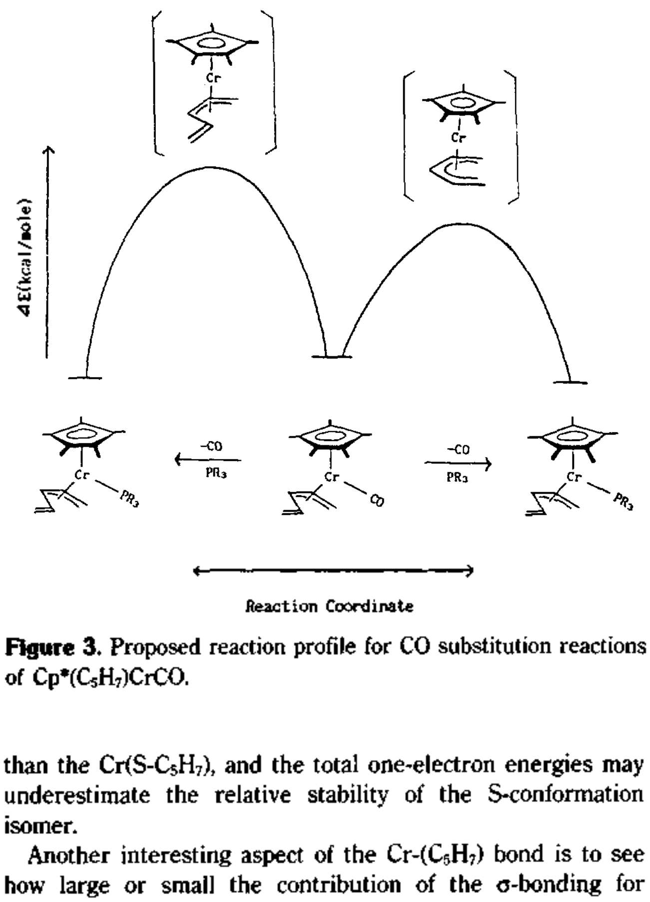


Figure 3. Proposed reaction profile for CO substitution reactions of $Cp^*(C_5H_7)CrCO$.

than the $Cr(S\text{-}C_5H_7)$, and the total one-electron energies may underestimate the relative stability of the S-conformation isomer.

Another interesting aspect of the $Cr\text{-}(C_5H_7)$ bond is to see how large or small the contribution of the σ-bonding for 1,5-carbons of C_5H_7 is. The difference of overlap population between Cr-terminal (1,5-) carbon and Cr-inner (2,3,4-) carbon of $2,4\text{-}C_7H_{11}$. $\Delta P(=P(Cr\text{-}C_{terminal})\text{-}P(Cr\text{-}C_{inner}))$ are −0.099 for the *S*-conformation compound and 0.230 for the U-conformation compound, respectively. The population structure of $Cp^*(S\text{-}C_5H_7)CrCO$ is different form that of $Cp^*(U\text{-}C_5H_7)CrCO$. 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 observed one by crystallography. In U-conformation, 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-conformation, the Cr-terminal pentadiene carbons interaction is very similar to the Cr-inner carbons interaction. Therefore it is expected that $Cr\text{-}(S\text{-}C_5H_7)$ bond is better described as η^5-π-bonding, but the $Cr\text{-}(U\text{-}C_5H_7)$ bond is better descrived as σ,π-bonding. The $P(Cr\text{-}C_{all})$, ΔP and the negative charges accumulated on the pentadiene carbons may be reflected in the reactivity of pentadiene. In order to get further insight into the relation between rate constants, k_{obsd} and overlap population P(Cr-CO) for η^5-S-conformation, the overlap population between Cr and the carbon of CO, P(Cr-CO) is listed in Table 6. Arranging the η^5-S-half-open chromocene carbonyls according to P(Cr-CO) gives the following ordering: $Cp(2,4\text{-}C_7H_{11})CrCO < Cp(C_5H_7)CrCO < Cp^*(C_5H_7)CrCO$. If the η^5-S-half-open chromocene carbonyls are ordered according to reaction rate constants for Scheme 1 at various concentrations of PR_3 and temperatures, the opposite arrangements as for the overlap population of Cr and the carbon of CO is obtained: $Cp^*(C_5H_7)CrCO < Cp(C_5H_7)CrCO < Cp(2,4\text{-}C_7H_{11})CrCO$. The opposite arrangements of these two orderings supports the supposition that substitution on the pentadienyl ligand may cause steric acceleration of the rate of dissociation, while substitutions on the cyclopentadienyl ligand appear to exert electronic influences that result in a retardation in rate.

A proposed reaction profile for $Cp^*(S\text{-}C_5H_7)CrCO$ is shown in Figure 3. This proposed reaction profile determined for CO substitution reaction mechanism of $Cp^*(S\text{-}C_5H_7)CrCO$ is allowed by the quantitative changes of the reaction coordination. The energy of $[Cp(U\text{-}C_5H_7Cr]^*$ transition state is about 4.93 kcal/mole lower than that of $[Cp^*(S\text{-}C_5H_7)Cr]^*$ transition state, and no significant energy barrier is found in the η^5-S↔η^5-U interconversions. The $[Cp^*(U\text{-}C_5H_7)Cr]^*$ mechanism will be favored over $[Cp^*(S\text{-}C_5H_7)Cr]^*$ mechanism, and this result is agreed with the experimental result. Therefore, it is suggested that the 18-electron $Cp^*(C_5H_7)CrCO$ undergoes CO substitution by a predominantly dissociative mechanism, involving the following conformation change: η^5-S↔η^5-U interconversions.

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12-Hydroxyamoorastatone, a New Limonoid from *Melia azedarach* var. *Japonica*

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A chemical investigation of the stem bark of *Melia azedarach* var. *Japonica* (Meliaceae) has led to a new limonoid, 12-hydroxyamoorastatone (**1**), whose structure has been elucidated by spectroscopic measurements including 2D-NMR. The 2D-NOESY experiment on its di-*p*-bromobenzoate derivative (**1a**) has established the relative configuration of **1**.

Introduction

Melia azedarach var. *Japonica* (Meliaceae) is a large tree found commonly in southern Korea and Japan. The bark decoction of this plant has been used for intestinal worms and skin ailments in Korea.[1] As the result of an extensive study[2,3] of plants of this family, a large number of bitter principles have been isolated and classified as limonoids. As part of our continuing search for novel antitumor agents of medicinal plant origin, *Melia azedarach* var. *Japonica* was found to exhibit significant cytotoxicities against human tumor cell lines. Bioassay-directed chromatographic fractionation led to the isolation of a new cytotoxic limonoid, 12-hydroxyamoorastatone (**1**). This paper describes the isolation and structural elucidation of the new compound.

Results and Discussion

The MeOH extract of the stem bark of *M. azedarach* var. *Japonica* was fractionated by a combination of column chromatography on silica gel and LiChroprep RP-18 and finally purified by recycling preparative HPLC to give compound 1 (Figure 1).

Compound 1, $C_{28}H_{36}O_{10}$, IR ν_{max}^{KBr} cm^{-1}: 3600-3200 (-OH), 1720br (C=O), 1242, 1057 (-OAc), 875 (furan) has resonances in its ^{1}H-NMR spectrum for three tertiary methyls (δ 0.82, 0.93 and 1.15), one acetyl (δ 2.04) and the characteristic β-substituted furan (δ 6.35, 7.30 and 7.40). These assignments were supported by its ^{13}C-NMR spectrum (Table 1), which in addition showed two ketonic carbon signals (δ 213.8 and 220.6), six oxygenated carbons (δ 65.0, 70.1, 71.4, 74.9, 78.9 and 97.3) and four quaternary carbons (δ 41.0, 42.7, 43.7 and 47.4). The 2D ^{1}H-^{1}H and ^{13}C-^{1}H COSY spectra of 1 were extensively examined to clarify the connectivity of each proton in **1**, and showed the presence of the partial structures A-

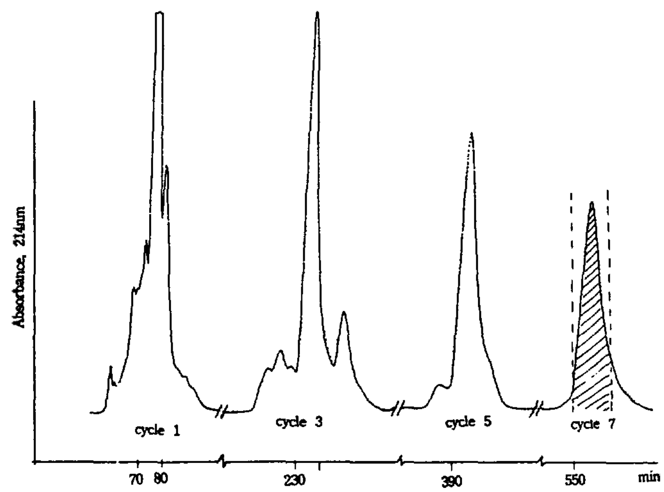

Figure 1. Recycling preparative HPLC of the compound 1. Column: JAIGEL-GS 320 (20×500 mm), Mobile phase: MeOH, flow rate: 5ml/min.

C. Furthermore the methine proton at δ 4.88 (H-24) showed long-range coupling to the non-equivalent methylene proton at δ 4.11 (H-19). This result led to the partial structure D. The ^{1}H-^{1}H COSY spectrum also showed W-coupling between C-26 methyl proton (δ 1.15) and each of two methine protons at δ 3.71 (H-9) and 3.42 (H-14). The gross structure of **1** was determined by analysis of the long-range ^{13}C-^{1}H COSY (Figure 2) and by reference to the data of related limonoids, amoorastatone and 12-hydroxyamoorastatin.[4] The hydroxy group at C-1 and the acetoxy group at C-3 were axial judging from the doublet signals with J=3.7 Hz of H-1 and with J=4.1 Hz of H-3, respectively. The double doublet signal (J=14.9 and 1.8 Hz) assignable to H-5 established that the H-5 was directed anti *trans* to the H-6β.