Kinetics and Stereochemistry of CO Substitution Reactions of Half-Open Chromocene Carbonyls(I): Reactions of Cp(C5H7)CrCO and Phosphines

Jong-Jae Chung*, Byung-Gill Roh, and Yu-Chul Park

Department of Chemistry, College of Natural Sciences,
Kyungpook National University, Taegu 702-701. Received September 15, 1992

The CO substitution reactions in the complex, $Cp(S\text{-}C_5H_7)CrCO$ with $PR_3(PR_3 = PMePh_2, P(OCH_3)_3, PMe_2Ph)$ were investigated spectrophotometrically at various temperatures. From the reaction rates, it was suggested that the CO substitution reaction takes place by first-order (dissociative) pathway. Activation parameters in decaline are $\Delta H^\times = 24.58$ kcal·mol^{-1}, $\Delta S^\times = 3.05$ cal·mol^{-1}·K^{-1}. Unusually low value of $\Delta S^\times$ suggests an $\eta^5\text{-}S \rightarrow \eta^5\text{-}U$ conversion of the pentadienyl ligand. This was confirmed by the extended-Hückel molecular orbital (EHMO) calculations, which revealed that the total energy of $Cp(S\text{-}C_5H_7)CrCO$ is about 6.84 kcal/mol more stable than that of $Cp(U\text{-}C_5H_7)CrCO$ and the energy of $[Cp(U\text{-}C_5H_7)Cr]^\times$ transition state is about 4.25 kcal/mol lower than that of $[Cp(S\text{-}C_5H_7)Cr]^\times$ transition state.

Introduction

Open metallocenes have only recently attracted attention[1-4], while the metallocenes have attracted intense interest since their discovery in 1951. It has already become clear that the open (or halp-open) metallocenes differ dramatically from their fully cyclic analogues in the chemical, spectroscopic and structural aspects. The open metallocenes exhibit rich conformational behaviors, much greater degrees of metal-ligand orbital mixing and much higher degrees of chemical reactivity, even though the metal-ligand bonding in open metallocenes showed stronger than their fully cyclic metallocenes.[5-9]

Kinetics and mechanism of carbonyl substitution reactions between $Cp_2M(CO)_2$ and PR_3 have been reported by G. T. Palmer in 1986, where M is Ti, Zr and Hf, and PR_3 is PEt_3, PMe_3, PPh_3 and $P(OMe)_3$.[10] In their reports, carbonyl substitution reaction of 18-electron $Cp_2Ti(CO)_2$ appears to take place by a CO dissociative (S_N1) mechanism. In marked contrast, the substitution reactions of 18-electron $Cp_2Zr(CO)_2$ and $Cp_2Hf(CO)_2$ proceed by an associative (S_N2) mechanism. The associative pathway probably involves $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ ring slippage in order to maintain an 18-electron count around the metal centers. The distinct difference between the substitution mechanisms of $Cp_2Ti(CO)_2$ vs. $Cp_2Zr(CO)_2$ and $Cp_2Hf(CO)_2$ may be at least partially explained by the smaller size of the titanium atom.

R. M. Kowaleski, etc. reported synthesis, kinetics, and mechanism of ligand substitution reactions of 17-electron-half-open vanadium carbonyl complexes Cp(pdl)VCO, where Cp is cyclopentadienyl and pdl is pentadienyl and 2,4-dimethyl pentadienyl.[16] They reported that carbonyl substitution reactions of the vanadocene carbonyl, Cp_2VCO and decamethyl vanadocene carbonyl, Cp^*_2VCO proceeded by an associative mechanism, but the mixed η^5-ligand complexes, Cp(pdl)VCO reacted at elevated temperature by a CO-dissociative pathway. The difference of these mechanisms must by attributed to the structural and electronic features which prohibit associative reaction pathway for the pentadienyl complexes,

but allow it for Cp_2VCO and Cp^*_2VCO.

The goal of the present study has been to elucidate the the mechanism for reactions between $Cp(C_5H_7)CrCO$ and PR_3-(PR_3PMe_2Ph, $P(OCH_3)_3$, $PMePh_2$). Kinetics studies and EHMO calculation reported in this work allow us to characterize the mechanism 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 and the role of C_5H_7 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 in a glove box, while solutions were generally manipulated using Schlenk technique under N_2, Ar gas. The synthesis of half-open chromocenes were prepared by published procedures.[11] The various dienes and phosphines were purchased from Aldrich and Fluca.

Kinetics of CO Substitution Reaction Between Cp(C5H7)CrCO and PR3. Soltion of $Cp(C_5H_7)CrCO$ of 5×10^{-4} mol decaline was prepared under N_2 and Ar. The absorption at 560 nm was monitored with time by Simadzu 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, $\Delta H^\times$ and $\Delta S^\times$ were calculated by the least-sequares 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 H_{ij}'s.[12,13] The Cr parameters given by Summerville and Hoffmann were used.[14]

I   II (M=Ti, V)   III (eclipsed)   IV (staggered)
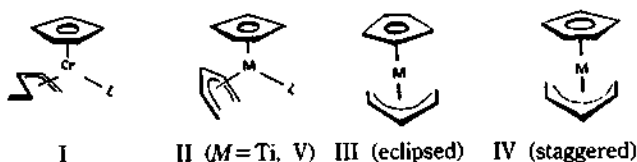
Scheme 1.

Results and Discussion

Kinetic Studies. All half-open chromium carbonyl complexes have higher CO stretching frequencies (1910-1918 cm⁻¹) than the parent Cp_2CrCO (1900 cm⁻¹), indicating that the pentadienyl group appeared to withdraw more electron density from Cr than the cyclopentadienyl ligand.

The 18-electron half-open chromocene ligand adducts are diamagnetic, and their ¹H and ¹³C-NMR spectra revealed that these species were unusual, as the pentadienyl ligands displayed no symmetry, unlike the related complexes of titanium and vanadium.[1,14] The half-open chromocene adducts were therefore assigned in the highly unusual η^5-S (S=sickel) configuration (I), which were opposite to the normal configuration for the titanium and vanadium analogues (II)[14] in Scheme 1. But half-open chromocene exists in a normal half-open metallocene structure (similar to III or IV, vide infra.)[11] in Scheme 1.

Kinetic parameters for the reactions of $Cp(C_5H_7)CrCO$ with PR_3, where $PR_3=P(Me_2)Ph$, $P(OCH_3)_3$ and $PMePh_2$ were obtained Eq. (1).

$$Cp(C_5H_7)CrCO+PR_3 \rightarrow Cp(C_5H_7)CrPR_3+CO \qquad (1)$$

All of these reactions 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 concentration 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 internal bond change was not important in these systems but the significant M-CO bond cleavage in the transition state seemed to be occuring.

To determine the activation enthalphy ($\Delta H^\ast$) and the activation entropy ($\Delta S^\ast$), linear plots of $\ln(k_{obsd}/T)$ vs. $1/T$ were obtained: $\Delta H^\ast$ and $\Delta S^\ast$ were calculated to be 24.6 ± 1.1 kcal/mol and 3.1 ± 2.8 cal/mol K, respectively. The obsreved values could be the evidence of the classic dissociative type of process, like those of vanadium analogues ($\Delta H^\ast=28.8\pm 0.3$ kcal/mol, $\Delta S^\ast=11.0$ cal/mol·K) and $Cp_2Ti(CO)_2$ ($\Delta H^\ast=27.9\pm 1.8$ kcal/mol, $\Delta S^\ast=15.0\pm 5.6$ cal/mol·K). Thus, the 18-electron half-open complex, $Cp(C_5H_7)CrCO$, undergoes predominantly CO substitution by a dissociative mechanism.

Mechanism of Substitution Reaction of $Cp(C_5H_7)$ CrCO with PR_3. Kinetic reactions for the 18-electron half-open chromocene carbonyl, $Cp(C_5H_7)CrCO$ with phosphorus ligands indicated a dissociation mechanism similar to that of 17-electron analogues, $Cp(pdl)VCO$ and 18-electron Cp_2Ti $(CO)_2$. To get further insight into the role of pentadiene in the mechanism of CO substitution reactions, the activation

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

Temp(°C)	Concentration of PR_3 (M)		
	5.0×10^{-3}	7.0×10^{-3}	10.0×10^{-3}
a. PMe_2Ph			
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}	1.00×10^{-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}
b. $P(OCH_3)_3$			
25	5.70×10^{-6}	5.71×10^{-7}	5.70×10^{-7}
35	2.01×10^{-5}	2.00×10^{-5}	2.00×10^{-5}
45	1.03×10^{-4}	1.03×10^{-4}	1.03×10^{-4}
55	2.75×10^{-4}	2.75×10^{-4}	2.73×10^{-4}
65	8.52×10^{-4}	8.58×10^{-4}	8.57×10^{-4}
c. $PMe(Ph)_2$			
25	5.68×10^{-6}	5.70×10^{-6}	5.69×10^{-6}
35	2.00×10^{-5}	2.00×10^{-5}	2.01×10^{-5}
45	1.01×10^{-4}	1.01×10^{-4}	1.01×10^{-4}
55	2.73×10^{-4}	2.74×10^{-4}	2.74×10^{-4}
65	8.53×10^{-4}	8.58×10^{-4}	8.52×10^{-4}

$[Cp(C_5H_5)CrCO]=5\times10^{-4}$ M
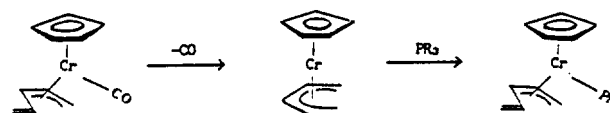
Scheme 2.
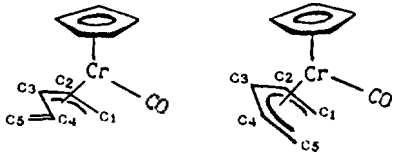
parameters ($\Delta H^\ast$, $\Delta S^\ast$) of $Cp(pdl)CrCO$ were compared to those of $Cp(pdl)VCO$ and $Cp_2Ti(CO)_2$.

It can be noted that the value of $\Delta H^\ast$ (24.6 kcal/mol) for the $Cp(C_5H_7)CrCO$ complex are small, compared with 17-electron vanadium analogues (28.8 kcal/mol) and $Cp_2Ti(CO)_2$ (27.9 kcal/mol). The smaller size of chromium and the presence of η^5-S conformation for its pentadienyl ligands should both lead to enhanced steric constraints in the chromium compound.

The greater steric constraints of the Cr relative to the analogues V or Ti systems would weaken the Cr-CO bond and result in lower $\Delta H^\ast$ values of Cr relative of V or Ti.

Notably the $\Delta S^\ast$ value observed here do seem smaller than that of V analogues (11.0 cal/mol·K) and $Cp_2Ti(CO)_2$ (15.0 cal/mol·K). A low value of $\Delta S^\ast$ could well arise from the fact that loss of CO from a half-open chromocene carbonyl complex would lead to η^5-S to η^5-U conversion (Scheme 2) accompanied by an increase in order and symmetry and a decrease in entropy. The η^5-S to η^5-U change must be quite advanced in the transition state for reaction and probaly promotes the CO release. Thus, the observed values of $\Delta H^\ast$ and $\Delta S^\ast$ may still be attributed to a classic dissociative type of process.

Molecular Orbital Calculations. Here describe the electronic structure and bonding of $Cp(C_5H_7)CrCO$, focusing

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Table 2. Coordination Geometry of Cr-Pentadienes Complexes

		S-configuration	U-configuration
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-CO	Å	1.850 Å	1.850 Å
$<C_1C_2C_3$	deg	119.55°	122.7°
$<C_2C_3C_4$	deg	116.85°	125.3°
$<C_3C_4C_5$	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; M1 midpoint of C(1) and C(5). [c]ϕ_{1-3}; angle formed by the bonds between CCP, M1 and CO. [d]δ; dihedral angle between Cp ring and Pdl plane. [e]ε; dihedral angle between C_3-C_5 plane an C_1-C_4 plane.

U-Configuration   S-Configuration

Scheme 3.
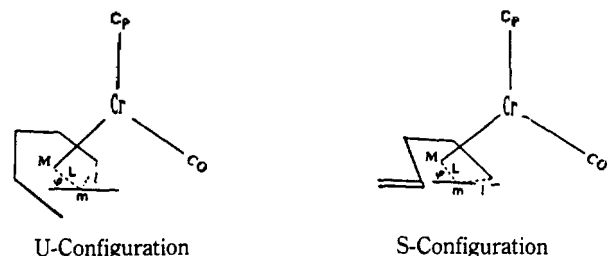
mainly on the orientation and the role of pentadiene, based on the extended Hückel MO calculations.

All the bond lengths and the bond angles are listed in Table 2 from the crystallographic data of Cp(C₅H₇)CrCO.[5] For both the η⁵-U conformation and η⁵-S conformation isomers, the coordination geometry of the pentadiene was optimised by using the three variables l, L and ψ, as defined in 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 the point "M", and the "m" on the line of C(1)-C(5) and the angle ψ 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)= 1.850 Å; Cr-M=1.444 Å; Cp(centroid)-Cr-C(CO)=95.6°; Cp (centroid)-Cr-M=156.7°.

The potential energy calculations on Cp(C₅H₇)CrCO as a function of the above two variables gave a minimum at l =1.9851 Å, L=0.01 Å and ψ=24.5° for η⁵-S coordination
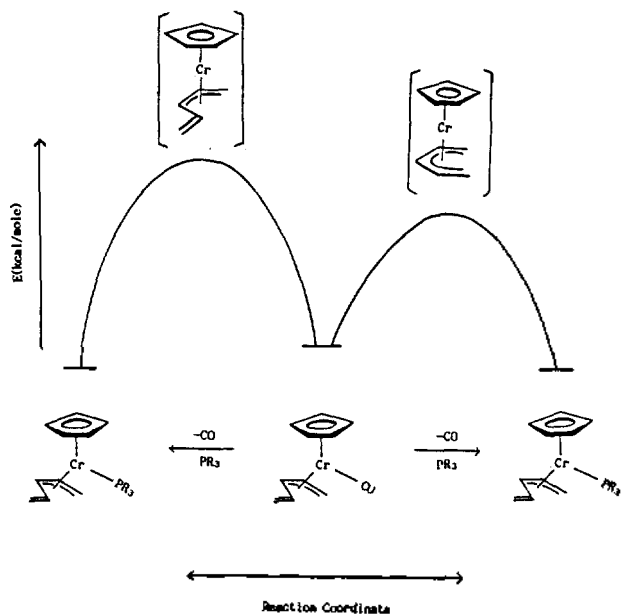
Figure 1. The energy profile for S-(ψ=24.5°) and U-(ψ=23.3°) conformations of Cp(C₅H₇) CrCO as a function of L.
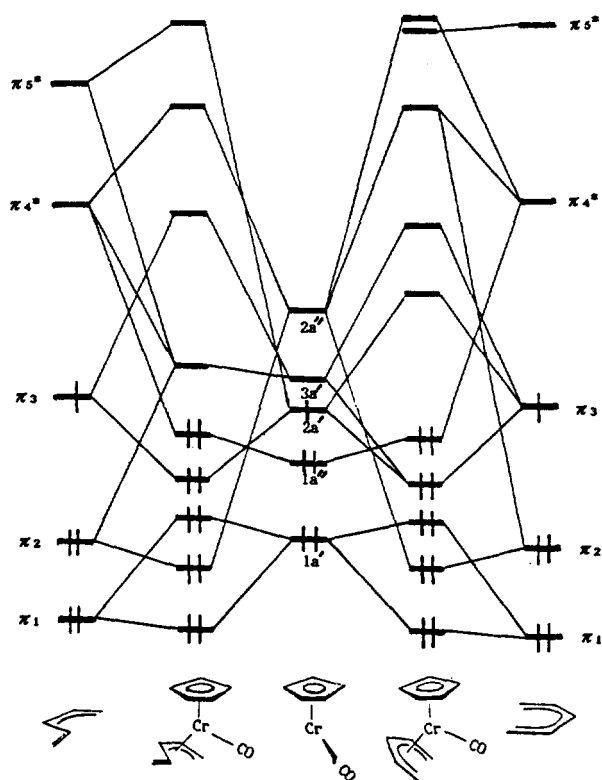
Figure 2. Interaction diagram for the S- and U- conformations in Cp(C₅H₇)CrCO.

and a minimum at l=the middle of C(1)-C(5), L=0.3875 Å and ψ=23.3° for η⁵-U coordination isomer. We should mention that the theoretically optimized geometry of Cp(C₅H₇)-CrCO (S-conformation) is very close to the observed one. The optimized geometry is given in Table 2.

The total energy curves show that stability of the limiting pentadiene orientations is well balanced, where the calcu-

Table 3. The results of population analysis for Cp(S-Pdl)CrCO and Cp(U-Pdl)CrCO
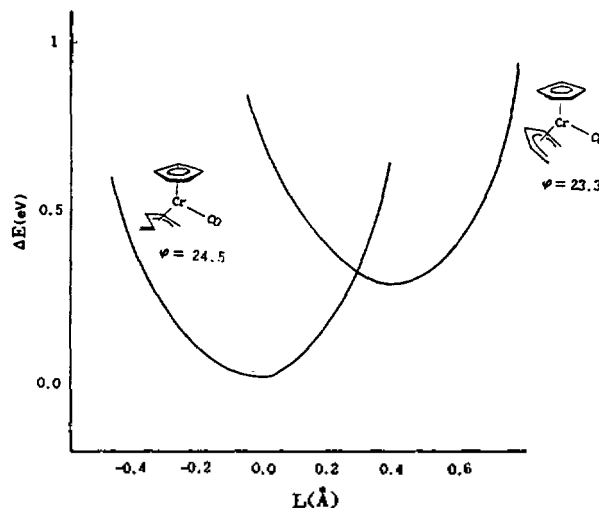
	S-configuration	U-configuration
$P(Cr-C^1)$	0.164	0.208
$P(Cr-C^2)$	0.097	0.084
$P(Cr-C^3)$	0.155	0.701
$P(Cr-C^4)$	0.101	0.084
$P(Cr-C^5)$	0.110	0.205
ΔP	−0.078	0.714
$P(Cr-C_{all})$	0.627	0.651
$P(II_1-1a')$	−0.001	−0.002
$P(II_2-2a'')$	0.110	0.190
$P(II_3-2a')$	0.288	0.255
$P(II_4{}^*-1a'')$	0.088	0.149
$Q(C^1)$	−0.141	−0.235
$Q(C^2)$	−1.357	+0.038
$Q(C^3)$	−1.553	−0.083
$Q(C^4)$	−0.455	+0.039
$Q(C^5)$	−0.034	−0.234

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

lated energy difference is only 6.84 kcal/mol, very slightly in favor of η^5-S coordination. As will be discussed shortly, the population analysis for Cp(C$_5$H$_7$)CrCO proves that the Cr-(U-C$_5$H$_7$) bond is somewhat stronger than the Cr-(S-C$_5$H$_7$) bond in the magnitude of the bonding interations between the Cr and C$_5$H$_7$ orbitals. The orbital interaction diagram for Cp(S-C$_5$H$_7$)CrCO and Cp(U-C$_5$H$_7$)CrCO is shown in Figure 2.

The bonding between Cr and S-C$_5$H$_7$ is achieved primarily through the donation-type π_2-2a″, the back-donation-type $\pi_4{}^*$-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, 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 the same 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$_5$H$_7$ bonding and CO-substitution reaction of 18-electron Cp(C$_5$H$_7$)CrCO, a population analysis is performed. The results are summarized in Table 3, which includes overlap populations arising from π_2-2a″, $\pi_4{}^*$-1a″, $\pi_3{}^*$-2a′ and $\pi_1{}^*$-1a′ interatctions and Cr-C(1 and 5) (terminal) and Ti-C(2, 3, and 4) (inner) bond overlap pouplations together with charges on pentadiene carbon atoms. Note that the major contributions to the total Cr-C (C$_5$H$_7$) 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 0.1100 (S-conformation) and 0.1895 (U-conformation), and as for the back-donation

Figure 3. Proposed reaction profile for Cp(C$_5$H$_7$)CrCO.

interactions, P($\pi_4{}^*$-1a″) is 0.0884 (S-conformation) and 0.1487 (U-conformation). But in mixed-orbital interaction, P(π_3-2a′) is 0.2880 (S-conformation) and 0.2547 (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.

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$_{all}$). The Cr-(U-C$_5$H$_7$) bond may be in fact slightly stronger than the Cr(S-C$_5$H$_7$), but the total one-electron energies may underestimate the relative stability of the U-conformation isomer.

Another interesting aspect of the Cr-C$_5$H$_7$ bond is to see how large or small the contribution of the σ-bonding for 1,5-carbons for C$_5$H$_7$ is. The difference of overlap population between Cr-terminal (1, 5-) carbon and Cr-inner (2, 3, 4-) carbon of C$_5$H$_7$. ΔP (=P(Cr-C$_{terminal}$)−P(Cr-C$_{inner}$)) are −0.078 for the S-conformation compound and 0.174 for the U-conformation compound, respectively. The population structure of Cp(S-C$_5$H$_7$)CrCO is different from that of Cp(U-C$_5$H$_7$)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-conformations, the Cr-terminal pentadiene carbons interaction is very similar to the Cr-inner carbons interaction. Therefore it is expected that Cr-(S-C$_5$H$_7$) bond is better descrived as η^5-π-bonding, but the Cr-(U-C$_5$H$_7$) bond is better descrived as σ,π-bonding. The 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. From η^5-π-bonding between Cr and C$_5$H$_7$, the stronger Cr-(U-C$_5$H$_7$) bond than Cr-(S-C$_5$H$_7$) bond by P(Cr-C$_{all}$) and the negative charges on the all carbons of C$_5$H$_7$, it is expected that η^5-S $\longleftrightarrow$ η^5-U interconversion of the pentadiene prefers

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to a change in electronic configuration ($\eta^5 \rightarrow \eta^3$ transformation) which might be required to be associative mechanism.

A proposed reaction profile for $Cp(C_5H_7)CrCO$ is shown in Figure 3. This proposed reaction profile determined for CO substitution reaction mechanism of $Cp(S-C_5H_7)CrCO$ is allowed by the quantitative changes of the reaction coordination. The energy of $[Cp(U-C_5H_7)Cr]^*$ transition state is about 4.25 kcal/mole lower than the of $[Cp(S-C_5H_7)Cr]^*$ transition state, and no significant energy barrier is found in the η^5-S $\longleftrightarrow$ η^5-U interconversions. The $[Cp(U-C_5H_7)Cr]^*$ mechanism will be favored over $[Cp(S-C_5H_7)Cr]^*$ 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: η^5-S $\longleftrightarrow$ η^5-U interconversions.

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A Linear Photodiode Array Detector System for Multichannel Spectroscopic Applications

Haidong Kim* and Seunghee Han

Advanced Analysis Center, Korea Institute of Science and Technology,
P.O.Box 131 Cheongryang, Seoul 130-650. Received September 23, 1992

A multichannel optical detector system employing a self-scanning linear photodiode array has been developed. The photodiode array detector system is designed for various applications which require fast, multichannel detection of transient signals. The detector system consists of a controller which runs on an IBM personal computer and a detector head connected to the controller through a DB-15 cable. The entire scanning of 1024 detector elements is achieved in 20 ms. By using an on-board 16-bit counter/timer, the operational mode of the photodiode array detector is fully programmable by software. The design considerations and the performance of the photodiode array detector system is presented.

Introduction

Numerous modern analytical techniques are based on detection and quantization of light in the UV to near IR regions of the spectrum. Also, the rapid acquisition of spectral data continues to be an important objective of the spectroscopist, not only for reasons of efficiency but also for enhanced information. For instance, spectral data obtained in a minute is of no kinetic value if the half-life of the monitored reaction is a millisecond. Recently, revolutionary developments in multichannel detectors have greatly expanded and improved the capabilities of current spectrochemical techniques[1].

Solid state image sensors such as photodiode array (PDA)[2], charge-coupled device (CCD)[3], and charge-injection device (CID)[4] have been regarded as highly-technical, expensive, and difficult to use optical detectors. However, recent advances in solid state technology and computer science made these devices find their ways more and more into various scientific instruments. The advantages of solid state image sensors compared to other detectors are that they are high speed, multichannel, and integrating detectors. Many hundreds of data points can be recorded in one single reading,