Effect of Electron-Withdrawing Substituents on the Cobalt(I)-Coordinated Cyclopentadienyl Ring. Spectra and Diene Substitution Kinetics of [Co(C_5H_4X)(1,5-cyclooctadiene)]

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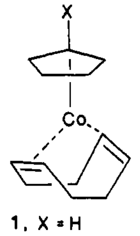
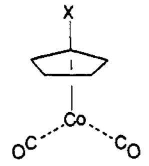
^{13}C NMR chemical shifts of coordinated olefinic carbons in [Co(C_5H_4X)(cod)] (X = H, CO_2Me, Co-*i*-Pr, CHO, $COCF_3$; cod = 1,5-cyclooctadiene) were found to have good correlation with field parameters (σ_F) of X but not with their electronegativity parameters (σ_X). Being easily computable value, σ_F provides a useful scale for the estimation of the electronic effect of X on the central metal. Photoelectron spectroscopy of [Co(C_5H_4X)(cod)] (X = H, CO_2Me, $COCF_3$) showed the HOMO responsible for back-donation was stabilized by ca. 0.5 eV on changing X from H to $COCF_3$. The assignments of the four low-energy bands are discussed. Infrared CO stretching vibrations in [Co(C_5H_4X)$(CO)_2$] (X = H, CO_2Me, $COCF_3$) were analyzed to give force constants of the C≡O stretching: the substitution effect of $COCF_3$ is about two times larger than that of CO_2Me. The kinetic study on replacement of coordinated cod ligand in [Co(C_5H_4X)(cod)] with nbd (nbd = norbornadiene) in acetonitrile solution suggested a mechanism in which the two C=C groups of the cod were displaced stepwise. The detachment of the first C=C group of cod is of S_N1 nature when X = H, but an S_N2 path, which involves the solvent, is dominant when X = $COCF_3$. The same reaction in benzene showed that both S_N1 and S_N2 pathways were also involved, but the nbd-dependent S_N2 path was much more important when X = $COCF_3$ than when X = H. For the transition state of these bimolecular pathways, [Co(η^3-C_5H_4X)(η^4-cod)L] (L = MeCN or η^2-nbd) is proposed. Calculated energy difference between [Co(η^5-C_5H_4X)$(C_2H_4)_2$] and [Co(η^3-C_5H_4X)$(C_2H_4)_2$] is ca. 4 kcal/mol smaller when X = $COCF_3$ than when X = H.

One of the practical ways of modifying the reactivity of transition-metal complexes and catalysts is to introduce a substituent into their ligand. While complexes with a variety of phosphine ligands are known, cyclopentadienyl ligands (Cp) are less variable, only methyl- and pentamethyl-substituted cyclopentadienyls being commonly studied. The replacement of a cyclopentadienyl ligand in transition-metal complexes by a pentamethylcyclopentadienyl ligand often leads to large changes in their chemistry. The changes in properties of these complexes are believed to be due to an increase of electron density along the metal–Cp bond axis together with the steric effects by the methyl groups. The electronic effect induced by the five methyl groups makes the basicity of the $C_5Me_5^-$ anion very much greater than the $C_5H_5^-$ anion.[1] However, when these anions are coordinated to transition metals, a rather small difference in the electronic effect is suggested by photoelectron spectroscopy,[2] MO calculation,[3] and ^{59}Co NQR spectroscopy.[4] The observed difference in properties between C_5H_5- and C_5Me_5-coordinated complexes might therefore be due largely to steric reasons. An ESCA study on metallocenes showed somewhat greater electronic effect: the substitution of two pentamethylcyclopentadienyl groups for the cyclopentadienyl ligands is equivalent to a one-electron reduction of the central metal.[5]

In contrast to the effect of methyl group substitution on the cyclopentadienyl ligand, the electronic effect induced by an electron-withdrawing substituent has scarcely been studied.[6] We have recently found that co-oligomerization of methylacetylene with acetonitrile to give trimethylpyridine is greatly enhanced by use of the [Co($C_5H_4CO_2Me$)L_2] species instead of the [Co(C_5H_5)L_2] catalyst (L_2 = 1,5-cyclooctadiene (cod) or cyclooctatetraene).[7] This and similar findings by others[8] promoted us to investigate the effect of electron-withdrawing substituents on the cyclopentadienyl ring coordinated to cobalt. In this paper we compare the spectra and reactivity of [Co(C_5H_4X)L_2] (**1**–**9**) where X is mainly restricted to H, ester, and acyl in order to minimize any steric problem (in particular the bulkiness of *i*-Pr (**4**) and CF_3 (**6**) is nearly equal). In addition, through the excellent procedure developed by Rausch and co-workers, introduction of an ester or acyl group to a cyclopentadienyl ring is farily easy.[9]



1, X = H
2, X = CO_2Me
3, X = COMe
4, X = CO-*i*-Pr
5, X = CHO
6, X = $COCF_3$



7, X = H
8, X = CO_2Me
9, X = $COCF_3$

Experimental Section

Compounds. Sodium cyclopentadienide, Na[C_5H_4(COR)] (R = OMe, Me, *i*-Pr, H, and CF_3), were prepared by the reaction reported by Rausch.[9] The reaction for Na[$C_5H_4(COCF_3)$] was carried out at 0 °C. Compounds **2**–**6** were prepared by adding the sodium cyclopentadienides to benzene solutions of [CoCl-

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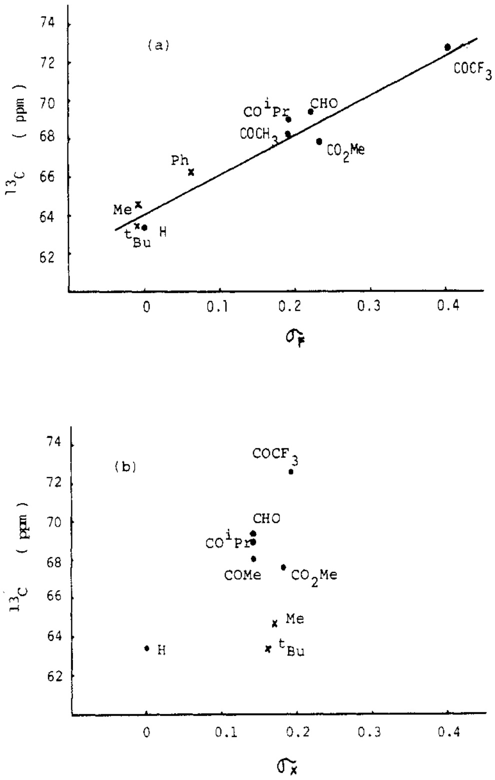


Figure 1. Plot of ^{13}C chemical shifts of the cod olefinic carbons in [Co(C_5H_4X)(cod)] vs. (a) field parameters of X and (b) electronegativity parameters of X. The chemical shifts for X = Me, Ph, or *t*-Bu are from ref 8.

(PPh_3)$_3$] at room temperature followed by addition of 1,5-cyclooctadiene. Detailed procedure for the preparation of **2** has been described elsewhere.[7] **3** has been prepared by a different route.[8]

Complex **4**: yield 24%; yellow-brown crystals; mp 68–70 °C. Anal. Calcd for $C_{17}H_{23}OCo$: C, 67.54; H, 7.67. Found: C, 67.71; H, 7.61.

Complex **5**: yield 46%; dark red-brown crystals; mp (under N_2) 158–160 °C dec. Anal. Calcd for $C_{14}H_{17}OCo$: C, 64.62; H, 6.59. Found: C, 64.61; H, 6.62.

Complex **6**: yield 31%; dark brown crystals; mp 100–101 °C. Anal. Calcd for $C_{15}H_{16}F_3OCo$: C, 54.89; H, 4.91. Found: C, 54.94, H, 4.93.

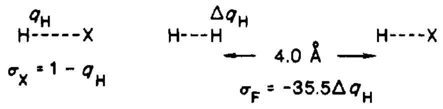
Complexes **7**–**9** were prepared according to Rausch's method and purified by chromatography on alumina.

Spectral Measurements. For IR measurements a Nicolet 5DXB FT-IR spectrometer was used. ^{13}C NMR spectra were recorded on a JEOL FX-100 spectrometer. ^{1}H NMR spectra used for kinetic study were recorded on a JEOL GX-400 spectrometer.

Gas-phase photoelectron spectra of **1**, **2**, and **6** were obtained with the He I photoelectron spectrometer described formerly.[10] The sample inlet and target chamber systems were heated and kept at 144 °C for **1** and **6** and at 147 °C for **2** during the measurements by circulating hot silicone oil.

Kinetics. A sample of the diene complex (15–20 mg, 0.065 mmol) was placed in a NMR tube and connected to a vacuum line. Into this tube a mixture of benzene-d_6–nbd or acetonitrile-d_3–nbd (0.5 mL), which had been degassed by three freeze–pump–thaw cycles, was distilled. After the NMR tube was sealed under vacuum, it was heated in a thermostated oil bath and periodically subjected to ^{1}H NMR measurement. The reaction was monitored by the peak intensities of the cyclopentadienyl protons (in the case of X = CO_2Me, the methyl peak was used) of the starting (cod) and product [nbd] complexes (δ): X = H, (4.60) [4.64] in CD_3CN, (4.36) [4.45] in C_6D_6; X = CO_2Me, (3.88) [3.78] in CD_3CN; X = CO-*i*-Pr, (4.21) [4.55] in CD_3CN, (3.99) [4.45] in C_6D_6; X = CHO, (4.18) [4.46] in CD_3CN; X = $COCF_3$, (4.27) [4.44] in CD_3CN, (3.86) [4.17] in C_6D_6. To ensure independency of the rate in acetonitrile solution on the concentration of nbd, 0.26, 0.52, and 0.78 mol/L solutions of nbd were checked for each sample of complexes.

Scheme I



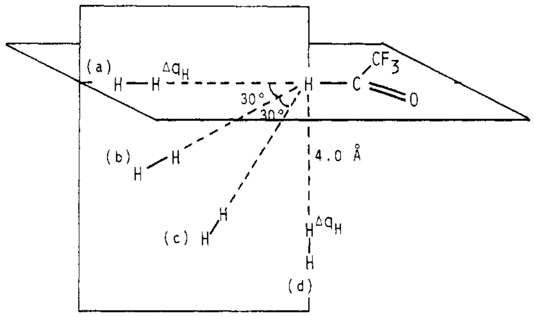


Figure 2. The geometries used for the calculations of charge densities (Δq_H) on hydrogen.

MO Calculations. Ab initio calculations were performed by using the program package PSHONDO. In Hartree–Fock calculations the [Ar] core of Co was replaced by the effective core potential from Barthelat et al.[11] 4s and 4p orbitals of Co were three-term GTO's evaluated by Topiol et al.[12] To represent 3d-valence orbitals, five-term GTO's of Hay were contracted to [2d].[13] The standard STO-3G set was used for other atoms. Throughout the calculations η^5-C_5H_5–Co distance was 1.8 Å with C–C and C–H distances for the cyclopentadienyl ring of 1.42 and 0.98 Å, respectively. The geometries of the substituents were (Å) C(Cp)–C(substituent) = 1.469, C=O = 1.191, C(sp^2)–H = 0.98, C(sp^3)–H = 1.09, and C–F = 1.32. The ethylene C=C and C—H distances were 1.388 and 1.0 Å, respectively.

Results and Discussion

The ^{13}C NMR Spectra. ^{13}C chemical shifts of a series of [Co(C_5H_4X)(cod)] are summarized in Table I. We have noted that the ^{13}C chemical shift of the coordinated olefinic carbons in cod correlates with the field parameter σ_F[14a] for the substituent X as shown in Figure 1a, but not with the electronegativity parameter[14b] σ_X (Figure 1b). The field parameter σ_F is a scale for direct through-space transmission of the substituent dipole to the reaction center while the electronegativity paramater σ_X is a measure for substituent electronegativity which is transmitted to the reaction center by a progressive but diminishing relay along a chain of σ-bonds. It appears therefore that the transmission of the electronic character of substituent X, which causes the observed chemical shift change, is largely through-space in nature. However, some contribution of the through-bond effect may not be neglected since the substituents in our case are bonded to the π-system (Cp ring) and there must be certain conjugation between them.

Topsom and co-workers have proposed a simple and clear-cut way of calculating σ_F and σ_X parameters. It is based on charge density of the hydrogen atom (Scheme I) computed by means of ab initio MO calculations, leading to parameters with good agreement to experimental values.[14] Since the σ_X value for $COCF_3$ has not been reported,

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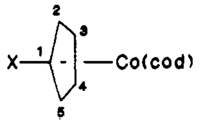
Table I. Carbon-13 Chemical Shifts (δ) for $[Co(C_5H_4X)(cod)]$ in CD_2Cl_2



	X					
	H (1)	CO_2CH_3 (2)	$COCH_3$ (3)	$COCH(CH_3)_2$ (4)	CHO (5)	$COCF_3$ (6)
C(1)	83.924	*a*	97.552	96.5	97.992	*a*
C(2), C(5)		84.314	83.047	80.015	82.781	82.559
C(3), C(4)		87.774	88.895	88.923	89.860	91.965
cod ($-CH_2-$)	32.166	31.922	31.073	32.117	31.924	31.922
cod ($=CH-$)	63.406[b]	67.695	68.064[c]	69.033	69.442	72.763
X ($-CH_3$)		51.514	27.243	20.241		
X ($-CH-$)				37.266		
X ($-CO-$)		167.56	*a*	201.5	185.746	*a*

[a] Not observed. [b] Lit.[8] (toluene-d_8) δ 63.37. [c] Lit.[8] (toluene-d_8) δ 68.33.

it was computed by the procedure indicated in the literature to be 0.19.

We checked further if the substituent dipole, which is responsible for σ_F, is transmitted through space to the direction other than position a (Figure 2). The value of Δq_H for each position calculated by the STO-3G basis set were (a) −0.0122, (b) −0.0123, (c) −0.0132, and (d) −0.0151. We conclude that the substituent dipole can well be transmitted to the direction vertical to the H–X axis and therefore the dipole of the substituent on the Cp ring can also affect the d electrons of the cobalt atom. The ^{59}Co NMR spectra of 1 and 3 reported by Bönnemann et al. indicate that the Co in 3 is more deshielded than that in 1.[8] The larger the σ_F value of the substituent, the more the cloud of d electrons, which include those used for back-donation from the metal to the olefinic carbons, will be pulled up toward the Cp ring. This will most likely result in less back-donation to and deshielding of the coordinating olefinic carbons of cod (Figure 1a). Although the substituent dipole should be transmitted directly to the coordinating carbons of cod also, such a transmission will not be efficient because there exists in between a large and a soft cloud of the metal d electrons. It is important that parameter σ_F can be calculated easily for any groups, and so it works as a convenient scale for the substituent electronic effect even in coordination compounds. The validity of σ_F is further exemplified below.

Photoelectron Spectra. Gas-phase He I photoelectron (PE) spectra of **1**, **2**, and **6** were measured as shown in Figure 3. Our PE spectrum of **1** agrees well with that reported formerly by Green and co-workers.[15] The low ionization energy (IE) region (up to 10 eV) of the PE spectra of these complexes show four bands labeled as A, B, C, and D (see Figure 3).

The rotational barrier of a coordinated cyclopentadienyl ring is very small,[16] but for the sake of convenience we are limiting the discussion to only the most stable conformers. According to the X-ray structures of $[Co(C_5H_4COCF_3)(nbd)]$ (nbd = norbornadiene)[17] and $[Rh(\eta^5\text{-}C_5H_4CO_2Me)(cod)]$,[18] the carbonyl group in each complex lies in the cyclopentadienyl plane and the C(Cp)–C(carbonyl) bond is parallel to the coordinated C=C bonds of nbd or cod. Therefore we assumed that the frameworks (except that of X) of **1**, **2**, and **6** were of C_s symmetry in their most preferred conformations. The schematic orbital interaction diagram for **1** is given in Figure 4, where the notations are the same as in the paper by Green and co-

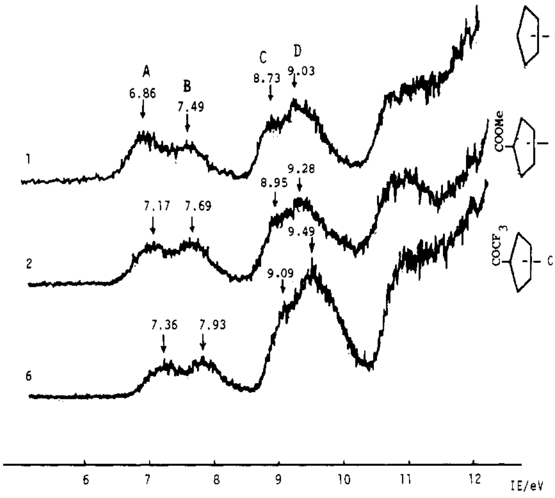


Figure 3. He I photoelectron spectra of **1**, **2**, and **6**.

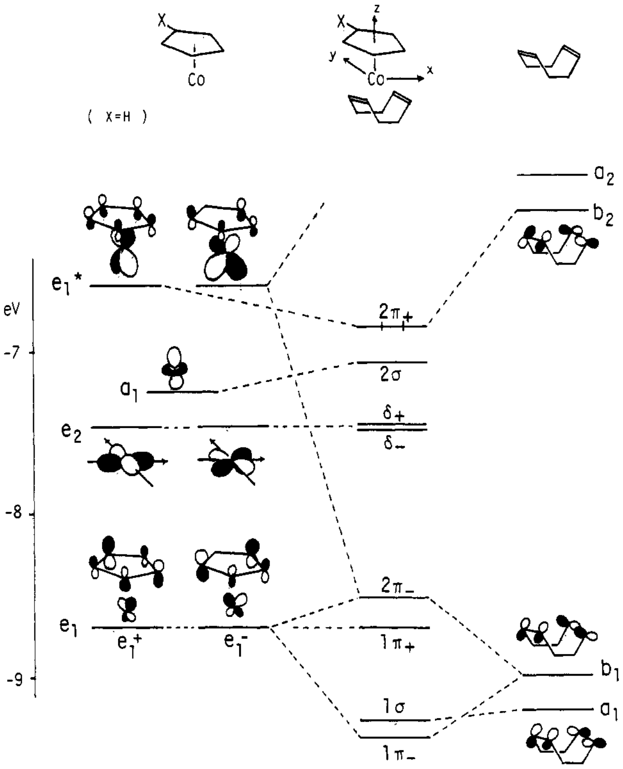


Figure 4. Interaction diagram of $[Co(C_5H_5)]$ with [cod] fragment.

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workers;[15] the subscripts + and − denote symmetry and antisymmetry with respect to the mirror plane (yz). The free cod is known to have π-ionization band at 9.06 eV.[19] In the case of complex **1** Green and co-workers have assigned band A to the ionizations from the $2\pi_+$ and 2σ orbitals, band B to those from the δ_- and δ_+ orbitals, band C to those from the $2\pi_-$ and 1σ orbitals, band D to those from the $1\pi_+$ and $1\pi_-$ orbitals, respectively. That is, each of these apparent four bands have been assigned to a pair of highly overlapping bands. According to their data, peralkylation of the cyclopentadienyl ring in **1** leads to large shifts of band C compared to those of the other three bands. This fact indicates that band C has significant cyclopentadienyl ring character. It seems reasonable to us, therefore, to assign band C to the ionizations from the $2\pi_-$ and $1\pi_+$ orbitals which are mainly localized on the Cp ligand and band D to those from the 1σ and $1\pi_-$ orbitals which are mainly contributed by the cod π orbitals.

On introduction of $COCF_3$ or CO_2Me to the Cp ring, the four bands are shifted toward the higher IE side (Figure 3). As the first IE's of trifluoroacetic acid and methyl acetate are 12.0[20] and 10.48 eV,[21] respectively, the four bands, A, B, C, and D, in **2** or **6** do not originate from their substituents. The close similarity of the band shapes between the complexes suggests that the components of each band in **2** and **6** are the same as those of **1**. The shifts of the bands in **2** and **6** to higher IE region relative to those of **1** are ascribed to the electron-withdrawing effect of the CO_2Me or $COCF_3$ group, the former being about one half less effective than the latter. This electron-withdrawing effect must be associated with the parameter σ_F (cf. Figure 1).

The shift of band C warrants discussion. It shows the least shift of the four bands on going from **1** to **2** and to **6** although the tendency is not pronounced between **1** and **2**. The shifts between **1** and **6** were (in eV) as follows: band A, 0.50; band B, 0.44; band C, 0.36; band D, 0.46. This is in marked contrast to the case of peralkylation of the Cp ring, where all the four bands shift to a lower IE region and the shift of band C is the largest.[15] Our MO calculation on hypothetical noncoordinating cyclopentadienyl anions showed that both e_1^+ and e_1^- orbitals of $[C_5Me_5]^-$ are 0.14 eV higher and those of $[C_5H_4COCF_3]^-$ are ca. 1.0 eV lower in energy (in the latter case e_1^- and e_1^+ are nondegenerate but the energy difference is small) than that of the parent $[C_5H_5]^-$. Accordingly the e_1 orbitals of the [CpCo] fragment, which is mainly contributed by orbitals of the Cp ring (see Figure 4), will be lowered significantly when one of the hydrogens in $[Co(C_5H_5)]$ is replaced by a $COCF_3$ group. This will result in an increase of the repulsive interaction between an e_1-like orbital of the [CpCo] fragment and the b_1 orbital of the [cod] fragment, pushing back the $2\pi_-$ orbital to a higher energy. Hence band C, which is a superposition of the ionizations from $2\pi_-$ and $1\pi_+$, remains rather insensitive to substitution of a Cp ring hydrogen for an electron-withdrawing group. The same argument applies to the shift of band D, which is rather sensitive to the Cp substituent in spite of its cod character, i.e. effective pushing down of the $1\pi_-$ orbital by an e_1-like orbital of a [substituted CpCo] complex.

So far we have discussed only on the C_S conformers. In reality, however, there exist many other conformers because the Cp ring is expected to be rotating almost freely under the experimental conditions. This must be one of the reasons why the components of each peak were not observed split.

Table II. CO Stretching Frequencies (cm^{-1}) and Force Constants (mdyn/Å) for 7, 8, and 9

	7	8	9
ν(CO)	2031.4, 1971.0	2039.9, 1982.4	2049.8, 1996.4
k	16.17	16.34	16.53
k_i	0.488	0.463	0.436

It should be remarked that the $2\pi_+$ HOMO of $[Co(C_5H_5)(olefin)_2]$ is an orbital responsible for back-donation from Co to the olefin as has been suggested by Albright et al. on the basis of extended Hückel calculations.[22] According to Green the $2\pi_+$ orbital has much metal d character[15] in contrast to its counterpart, $2\pi_-$. Nevertheless, introduction of a $COCF_3$ group causes stabilization of the $2\pi_+$ orbital by as much as 0.5 eV. These observations suggest that back-donative interaction between metal d and olefin π^* orbitals will be significantly decreased when one of the hydrogens of the C_5H_5 unit is replaced with a $COCF_3$ group. Replacement by a CO_2Me group should be about half as effective.

Infrared CO Stretching Vibrations of Dicarbonyl Complexes. The stretching vibrations of coordinated CO ligand have been known to be a measure of metal–CO π-bonding order which may be perturbed by other ligands. The CO stretching frequencies of $[Co(C_5H_5)(CO)_2]$ (**7**), $[Co(C_5H_4CO_2Me)(CO)_2]$ (**8**), and $[Co(C_5H_4COCF_3)(CO)_2]$ (**9**) in hexane are listed in Table II. The diagonal (k) and interaction (k_i) force constants were calculated in the Cotton–Kraihanzel's approximation[23] and listed together. When the metal d to CO π^* back-donation decreases, the CO bond order increases and at the same time the interaction between the two CO groups through the Co d orbitals become less effective. As expected the CO stretching force constant k in **9** is the largest while the interaction force constant k_i is the smallest of the three. We concluded that the substituent effect of $COCF_3$ on the decrease in metal to CO back-donation is twice as large as that of CO_2Me, and this is consistent with the results deduced from NMR (Figure 1a) and photoelectron spectra.

Diene Substitution Reaction. The displacement of the cod ligand in **1**–**6** by norbornadiene (nbd) was studied in benzene and acetonitrile, because these were the solvent and the reactant in the catalytic system for the preparation of pyridines reported previously and the phenomenon which has promoted our present study.[7] The displacement reaction was conveniently monitored by changing NMR spectra. In acetonitrile, the exchange reaction rate was first-order with respect to the complex and independent of the nbd concentration. A remarkable feature of the reaction in acetonitrile is the very large dependency of the rate on the substitutents of the cyclopentadienyl ring. In order for the reaction of **1** to proceed at an appreciable rate, the reaction mixture had to be heated above 100 °C, while the displacement of cod in **6** could be performed at room temperature. The observed rate constants and activation parameters in acetonitrile solution are given in Table III.

The diolefin exchange in benzene solutions were examined for **1**, **4**, and **6**. Figure 5 displays plots of k_{obsd} vs. nbd concentration at 129.4 °C. The electron-withdrawing substituent on the cyclopentadienyl ring does not accel-

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Table III. Rate Constant and Activation Parameters for the Displacement of cod from [Co(C_5H_4X)(cod)] in Acetonitrile

	X	T, °C	$10^5 k_{obsd}$, s^{-1}	ΔH^*, kcal/mol	ΔS^*, eu
1	H	118.8	7.92	37.7 ± 0.8	19.2 ± 2.1
		111.0	3.47		
		90.4	0.19		
		83.8	0.076		
2	CO_2Me	99.4	14.83	29.1 ± 0.8	2.2 ± 2.1
		90.6	5.56		
		78.0	1.42		
		72.2	0.60		
		61.6	0.15		
4	Co-*i*-Pr	101.0	13.44	29.4 ± 0.5	2.5 ± 1.4
		95.9	6.75		
		85.9	2.53		
		72.4	0.49		
		61.6	0.12		
5	CHO	88.0	11.94	25.3 ± 0.4	-6.4 ± 1.2
		81.1	5.83		
		69.0	1.76		
		57.5	0.45		
6	$COCF_3$	39.0	17.22	18.4 ± 0.8	-17.0 ± 2.7
		31.6	6.39		
		23.0	3.06		
		0.0	0.23		

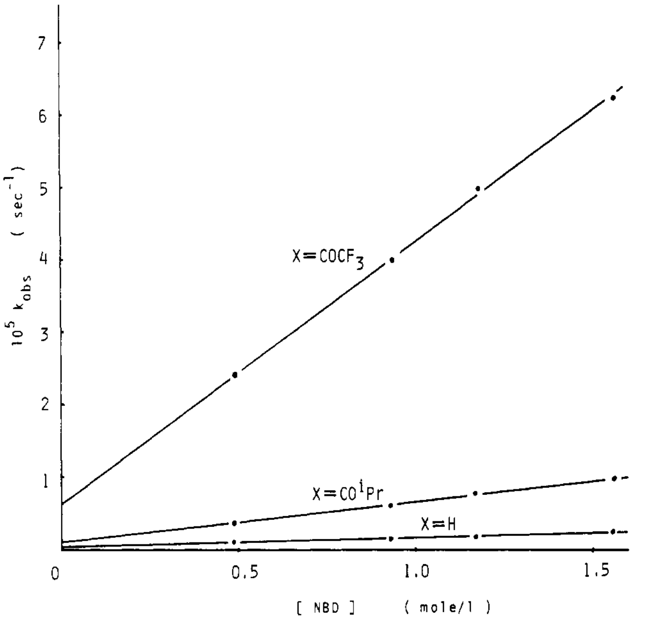


Figure 5. Plot of k_{obsd} vs. nbd concentrations in benzene solution.

erate the rate in benzene as much as in acetonitrile. For instance the reaction of **6**, which was observed at room temperature in acetonitrile, took place only when heated above 100 °C in benzene solution. Although the difference is smaller, the order of the reaction rates, i.e. **6** > **4** > **1**, still holds true. Figure 5 also shows the relationship $k_{obsd} = k_1 + k_a[\text{nbd}]$, where k_a is the slope of line and k_1 is the intercept.

The proposed mechanism deduced from these observations is shown in Scheme II. For the reaction in benzene solution the two intermediates B and C are assumed. Application of the steady-state hypothesis to B and C gives the rate equation (1).

$$\frac{-\mathrm{d}[\mathrm{A}]}{\mathrm{d}t} = \frac{k_1 k_2[\text{nbd}][\mathrm{A}]}{k_{-1} + k_2[\text{nbd}]} + k_a[\text{nbd}][\mathrm{A}] \qquad (1)$$

If the approximation $k_2[\text{nbd}] \gg k_{-1}$ holds true even in the cases of the lowest concentrations of nbd (0.49 mol/L nbd vs. 0.1 mol/L of [A]), eq 1 reduces to

$$\frac{-d[\mathrm{A}]}{\mathrm{d}t} = (k_1 + k_a[\text{nbd}])[\mathrm{A}] \qquad (2)$$

Scheme II

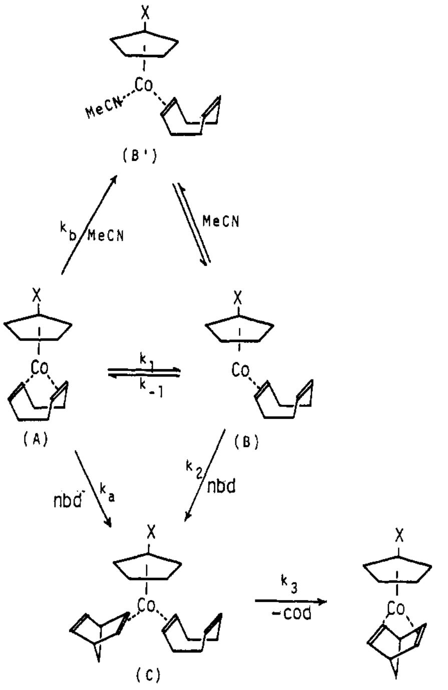


Table IV. The First- and Second-Order Rate Constants for the Replacement of cod from [Co(C_5H_4X)(cod)] in Benzene Solution at 129.4 °C

compd	X	$10^5 k_1$, s^{-1}	$10^5 k_a$, L/(mol·s)
1	H	0.03 ± 0.02	0.15 ± 0.03
4	CO-*i*-Pr	0.11 ± 0.02	0.58 ± 0.02
6	$COCF_3$	0.67 ± 0.06	3.61 ± 0.06

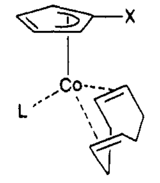
Thus a plot of k_{obsd} vs. [nbd] should give a straight line whose slope and intercept are k_a and k_1, respectively, in accord with the result shown in Figure 5. Calculated values of k_1 and k_a for **1**, **4**, and **6** are listed in Table IV.

In the case of the reaction in acetonitrile, another intermediate (B′) may be taken into consideration. The steady-state assumption for B, B′, and C together with the approximation of $k_2[\text{nbd}] \gg k_{-1}$ as above yields $k_{obsd} = k_1 + k_b[\text{MeCN}] + k_a[\text{nbd}]$. Since the observed rate was independent of [nbd] in acetonitrile, the last term must be negligibly small.

$$k_{obsd} = k_1 + k_b[\text{MeCN}] \qquad (3)$$

As the concentration of acetonitrile does not change during the reaction, k_{obsd} in eq 3 appears as the sum of two first-order rate constants. However, they can be differentiated by entropy of activation: the $\Delta S^{\ddagger}$ responsible for k_b is expected to be smaller than zero because it is actually for the second-order S_N2-type reaction while that for k_1 is greater than zero, being purely for the first-order process. The apparent entropy of activation listed in Table III suggests that in the case of X = H, the unimolecular process (k_1) predominates whereas participation of acetonitrile, the process k_b, is important when X = $COCF_3$. The reactions of **2**, **4**, and **5**, whose apparent entropy of activation values are between those of **1** and **6**, may be situated in between these two extremes. The apparent enthalpies of activation listed in Table III are also consistent with this view; the observed $\Delta H^{\ddagger}$ for X = H is large due to a coordinatively unsaturated 16-electron transition state of path A → B while $\Delta H^{\ddagger}$ for X = $COCF_3$ is relatively small, the mostly contributing transition state being a favorable 18-electron configuration (vide infra) in path A → B′.

In related reactions, Basolo et al. have noted that CO substitutions in $[Rh(C_5H_5)(CO)_2]$ and $[M(C_5Me_5)(CO)_2]$ (M = Co, Rh) by CO, phosphines, and phosphites proceed solely by associative pathways.[24] In contrast, Bergman et al. have found that phosphine substitution in $[Co(\eta^5\text{-}C_5H_5)(PPh_3)_2]$ by PMe_3 takes place by a dissociative route, via a 16-electron $[Co(\eta^5\text{-}C_5H_5)(PPh_3)]$ intermediate.[25] These studies bring out the speculation that the bulkiness of the ligand to be replaced might be a controlling factor in whether the substitution proceeds by an associative or a dissociative mechanism. It is not surprising, therefore, that in our diolefin substitution the reaction takes place via both an associative transition state and a dissociative 16-electron intermediate, because the bulkiness of a η^2-olefin is probably intermediate between those of CO and PPh_3. An important conclusion about the effect of substituent X on the rate-determining step is that X with large σ_F parameters tends to prefer bimolecular pathways, i.e. path A → B′ in acetonitrile and A → C in benzene, over the unimolecular path A → B while the reverse is true for X with small σ_F. The most probable transition state for these bimolecular paths is illustrated below, which includes an η^3-cyclopentadienyl ligand. The slippage or haptotropic shift of a cyclopentadienyl ligand was first suggested by Basolo et al. in the associative transition state such as $[Rh(C_5H_5)(CO)_2L]$ to avoid an unfavorable 20-electron configuration.[24b] Later a complex with a η^3-Cp ligand, $[W(\eta^3\text{-Cp})(\eta^5\text{-Cp})(CO)_2]$ (**10**), was indeed isolated and structurally characterized.[26] According to Basolo the haptotropic shift is promoted by an electron-withdrawing group on the cyclopentadienyl ring because it increases the positive charge on the metal and enhances the attack of a nucleophile by an S_N2 mechanism. The effect of substituent X in our present observation fits with this mechanism.



L = MeCN or η^2-nbd

We further postulated that without considering the attack by a nucleophile, the barrier for the slippage of the Cp ring from η^5 to η^3 coordination might be smaller when an electron-withdrawing group is present on the Cp ring. Such a substituent should ease the localization of charge in the Cp ring caused by the deformation into allyl and ene components. Recent reports on the structures of $[Rh(C_5H_4\text{–}X)(diene)]$ (X = CO_2Me, diene = cod; X = CHO, diene = 2,4-dimethylpenta-1,4-diene) indicate that although the bonding of the Cp ring to the metal is predominantly of the type expected for the η^5-Cp, there is a small but significant contribution of the allyl–ene-type coordination.[6,18] The energy barrier for the slippage of η^5-Cp → η^3-Cp in $[Co(C_5H_4X)(C_2H_4)_2]$ (X = H, CHO, $COCF_3$) was studied by ab initio MO calculations. The geometry of η^3-Cp was taken from the structural data of **10**, and the result is shown in Figure 6. Since we did not perform geometry optimization, the absolute values for the energy barriers are not reliable, but the tendency that the barrier decreases in the order X = H > X = CHO > X = $COCF_3$ by a few kilocalories per mole may be true, since the calculated models have a different X but the geometry of the rest of the molecule being held the same as each other.

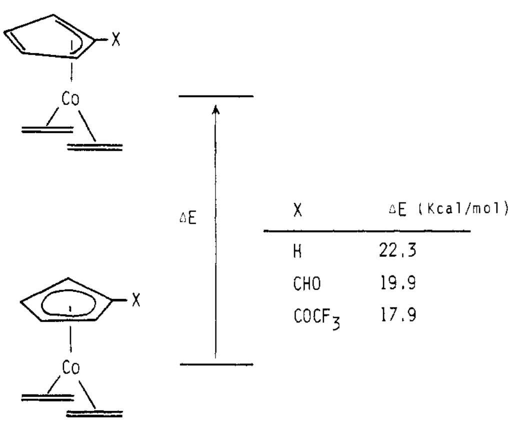


Figure 6. Calculated energy differences between η^5-C_5H_4X and η^3-C_5H_4X.

Conclusion

When an electron-withdrawing substituent is introduced into the cyclopentadienyl group in $[Co(C_5H_5)L_2]$ system, its electronic effect is transmitted to the cobalt atom propably via the direct through-space mechanism. An immediate consequence is a decrease in the metal to L back-donative interaction, which has been evidenced by (1) NMR chemical shifts of coordinating olefinic carbons in L (L_2 = 1,5-cyclooctadiene), (2) the orbital energy of HOMO observed in the photoelectron spectroscopy (L_2 = 1,5-cyclooctadiene), and (3) IR CO stretching force constants (L = CO). The other result of the substitution on the cyclopentadienyl ring becomes important in the displacement reaction of L: the η^5 to η^3 slippage of the cyclopentadienyl ligand in the transition state is facilitated by an electron-withdrawing substituent, promoting an S_N2 mechanism.

All of these phenomena have surprisingly good correlations with the field parameters of the substituents. For example substitution of one of the hydrogens at the cyclopentadienyl ring by $COCF_3$ (σ_F = 0.40) has an effect about twice as large as that by CO_2Me (σ_F = 0.23) on all the spectral results and even on extent of the haptotropic shift of the cyclopentadienyl ring during the reaction.

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