Substituent Effects on the Rates of CO Substitution of (η^5-C_5H_4X)Rh(CO)$_2$

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The syntheses and characterization of the new compounds (η^5-$C_5H_4CF_3$)Rh(CO)$_2$ and (η^5-$C_5H_4N(CH_3)_2$)Rh(CO)$_2$ are reported. The compounds (η^5-C_5H_4X)Rh(CO)$_2$ and (η^5-C_5H_4X)Rh(CO)PPh$_3$ (where X = H, NO_2, CF_3, Cl, CH_3, or $N(CH_3)_2$) show a good linear correlation between the values of CO stretching frequencies, ν_{CO}, and the Hammett σ values of the X ring substituents. This may be the first time such a correlation has been reported, and it is believed to mirror the electron density on the metal which in turn results in greater or lesser π-back-bonding, M→CO. In spite of this the rates of CO substitution of these compounds show strong deviations from linear correlation with Hammett σ values. This is rationalized in terms of resonance stabilization of the transition state for reaction by certain ring substituents.

Introduction

Investigations of associative ligand substitution reactions of 18-electron transition-metal organometallic compounds that were reported 2 decades ago[1] have been revisited, and a rule formulated[1d] that states "substitution reactions of 18-electron metal complexes may proceed by an associative mechanism provided the metal complex can delocalize a pair of electrons onto one of its ligands and make available a vacant low-energy orbital on the metal to permit nucleophilic attack on the metal."

Recent studies[2] show that this process of localizing a pair of electrons on the cyclopentadienyl ligand of its metal complex to allow associative substitution reactions is accelerated by having electron-withdrawing substituents on the cyclopentadienyl ligand. The substituent effects on the reactivity of aromatic molecules have been studied by organic chemists for decades. They have shown that substituent effects can be treated quantitatively by use of a linear free energy relationship, and the most commonly used variant of such an empirical treatment involves use of the Hammett equation (eq 1).[3] In this classical equation,

$$\log (k_x/k_0) = \rho\sigma_x \qquad (1)$$

k_x is the rate constant for a compound substituted by a group x, k_0 is the rate constant for the unsubstituted compound, σ_x is a substituent constant, and ρ is the proportionality factor called reaction constant. Data for literally hundreds of reactions have been successfully correlated by means of this empirical treatment. However, these have been little exploited by the organometallic chemists, although the few examples reported have shown it to be applicable to inorganic reactions.[4]

Equilibrium constants can be treated in a similar way, and even physical properties such as chemical shifts in NMR, frequencies in IR spectra, and polarographic half-wave potentials[5] have been successfully correlated by using the Hammett equation. Egger and Nikiforov[6] have shown nice linear relationships between the α and ortho and between the β and meta, respectively, substituents on the cyclopentadienylmanganese tricarbonyls and benzene ring by using ^{1}H NMR spectra.

No example in the literature of the application of Hammett relationship to CO substitution reactions of substituted cyclopentadienyl metal carbonyls was found. In order to test the applicability of the Hammett relationship on these reactions, we decided to investigate the effects of substituents on the rates of CO substitution of the compounds (η^5-C_5H_4X)Rh(CO)$_2$.

Kinetic studies on the unsubstituted compound (η^5-C_5H_5)Rh(CO)$_2$[1a] and the substituted compound (η^5-$C_5H_4NO_2$)Rh(CO)$_2$[2] (σ_p = 0.78) have been reported. Considering a wide range of Hammett σ values and spacings between them, we decided to study trifluoromethyl (0.54), chloro (0.23), methyl (−0.17), and dimethylamino (−0.60) compounds (η^5-C_5H_4X)Rh(CO)$_2$ (σ_p values[7] are in parentheses). Unfortunately (η^5-C_5H_5)Rh(CO)$_2$ does not undergo aromatic substitution reactions to yield functionally substituted derivatives.[8] As a consequence the syntheses and subsequent chemistry of functionally substituted (η^5-cyclopentadienyl)rhodium compounds have been severely limited in scope. Alternative methods are necessary for the formation of functionally substituted cyclopentadienylmetal compounds, and these generally involve the reaction of substituted cyclopentadienyl reagents such as TlC_5H_4X, NaC_5H_4X, or LiC_5H_4X with metal halide fragments. Fortunately the compounds (η^5-C_5H_4Cl)Rh(CO)$_2$[9] and (η^5-$C_5H_4CH_3$)Rh(CO)$_2$[10] had been synthesized earlier, and thallium (trifluoromethyl)cyclopentadienide[11] and lithium (dimethylamino)cyclopentadienide[12] are known. We report here a new synthesis of the (chlorocyclopentadienyl)rhodium carbonyl (I) and what we believe are the first reported syntheses of II and IV. All four compounds were studied kinetically for CO substitution reactions, and the Hammett relationship observed is discussed for the mechanisms proposed.

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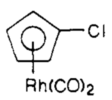

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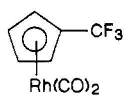

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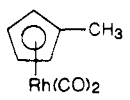

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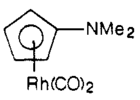

IV

Experimental Section

Compounds and Solvents. All manipulations were routinely carried out by using standard Schlenk techniques under an atomosphere of N_2, excluding oxygen and moisture. Hexane, tetrahydrofuran, and Decalin were dried and distilled over Na in the presence of benzophenone under N_2 atmosphere. The hexane and Decalin were stored over concentrated H_2SO_4 and washed with KOH before distillation. Chlorodicarbonylrhodium(I) dimer[13] and 5-diazo-1,3-cyclopentadiene[14] were prepared by published procedures. PPh_3 (Aldrich) was recrystallized from methanol prior to use.

(η^5-Chlorocyclopentadienyl)dicarbonylrhodium(I), (η^5-C_5H_4Cl)Rh(CO)$_2$ (I). To a solution of $[RhCl(CO)_2]_2$ (0.17 g) in THF (30 mL) in a nitrogen-filled 50-mL Schlenk flask connected to a nitrogen line equipped with a bubbler was added a portion of 1.8 M pentane solution of 5-diazo-1,3-cyclopentadiene (0.5 mL). Bubbles of gas were evolved. The reaction was allowed to proceed overnight, and then the solvent was removed under vacuum. The product was dissolved in 20 mL of hexane and filtered. The solvent was removed from the filtrate to yield 0.07 g (31% yield) of a yellow oil: IR (Decalin) ν(CO) 2053, 1991; IR (hexane) ν(CO) 2055, 1994 cm^{-1}; ^{1}H NMR (C_6D_6) δ 5.42 (t, 2 H), 4.82 (t, 2 H); mass spectrum, m/e, M$^+$ 258. The ^{1}H NMR and mass spectra agree with literature results.[9]

[η^5-(Trifluoromethyl)cyclopentadienyl]dicarbonylrhodium(I), (η^5-$C_5H_4CF_3$))Rh(CO)$_2$ (II). In a 50-mL Schlenk flask was placed 1.9 g of $TlC_5H_4CF_3$,[11] 0.5 g of $[RhCl(CO)_2]_2$, and 30 mL of THF. The resultant mixture was stirred for 2 h. The solvent was removed under vacuum, 40 mL of hexane added, and the mixture suction filtered through a medium frit. Hexane was removed from the filtrate to yield 0.19 g (32% yield) of a yellow oil: IR (Decalin) ν(CO) 2060, 1999 cm^{-1}; ^{1}H NMR ($CHCl_3$-d) δ 5.51 (s, 2 H), 5.76 (s, 2 H); mass spectrum, m/e (relative intensity) M$^+$ 292 (33.9), (M-CO)$^+$ 264 (45.3), (M − 2CO)$^+$ 236 (100).

(η^5-Methylcyclopentadienyl)dicarbonylrhodium(I), (η^5-$C_5H_4CH_3$)Rh(CO)$_2$ (III). This compound was prepared in a similar manner to II, using $NaC_5H_4CH_3$ to give the product as a yellow oil: IR (Decalin) ν(CO) 2041, 1978; IR (THF) ν(CO) 2036, 1970 cm^{-1}; ^{1}H NMR ($CDCl_3$-d) δ 2.03 (s, 3 H), 5.20 (t, 2 H), 5.39 (t, 2 H); mass spectrum, m/e (relative intensity) M$^+$ 238 (45.7), (M − CO)$^+$ 210 (52.1), (M − 2CO)$^+$ 182 (100).

[η^5-(Dimethylamino)cyclopentadienyl]dicarbonylrhodium(I), (η^5-$C_5H_4N(CH_3)_2$)Rh(CO)$_2$ (IV). *N*,*N*-Dimethyl-1,3-cyclopentadienylamine was prepared by reacting NaC_5H_5 with *N*,*N*-dimethyl-*O*-(toluenesulfonyl)hydroxylamine in THF at −20 °C. Compound IV was synthesized in manners analogous to those used for II. The orange crystalline product was purified by sublimation under vacuum (ca. 40 °C): IR (Decalin) ν(CO) 2030, 1965; IR (THF) 2020, 1955 cm^{-1}; ^{1}H NMR (CH_3Cl_3-d) δ 2.41 (s, 6 H), 4.96 (t, 2 H), 5.10 (t, 2 H); mass spectrum, m/e (relative intensity) M$^+$ 267 (42.2), (M − CO)$^+$ 239 (48.3), (M − 2CO)$^+$ 211 (100). Anal. Calcd for $C_9H_{11}NO_2Rh$: C, 40.47; H, 3.77; N, 5.24. Found: C, 40.55; H, 3.71; N, 5.26.

[(η^5-Trifluoromethyl)cyclopentadienyl]carbonyl(triphenylphosphine)rhodium(I), (η^5-$C_5H_4CF_3$)Rh(CO)PPh$_3$ (V). To a 5-mL hexane solution of II (0.095 g) was added PPh_3 (0.085 g) (1:1) by ampule transfer. The solution was stirred at room temperature for ca. 3 days, during which time a yellow precipitate formed. This was filtered and dried to afford the product as a yellow powder: IR (hexane) ν(CO) 1972 cm^{-1}; mass spectrum, m/e (relative intensity) M$^+$ 526 (13.4), M − CO)$^+$ 498 (100), (M − CO − PPh$_3$)$^+$ 236 (23.7). Anal. Calcd: C, 57.05; H, 3.64. Found: C, 57.12; H, 3.84.

PPh_3 derivatives for the (chlorocyclopentadienyl)-, (methylcyclopentadienyl)-, or [(dimethylamino)cyclopentadienyl]rhodium carbonyls were synthesized in manners analogous to those used for V. The IR carbonyl stretches of all products agree closely with those obtained in kinetic measurements.

Table I. Rate Constants and Activation Parameters for the CO Substitution Reactions of (η^5-C_5H_4X)Rh(CO)$_2$ with PPh$_3$ in Decalin (Eq 2)

X	T, °C	k_{CO}, M^{-1} s^{-1}	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, eu
NO_2[a]	25	1.26	+12.0 (±0.2)	−17.9 (±0.6)
	37	2.58		
	49	6.14		
CF_3	15	6.16×10^{-3}	+10.2 (± 1.3)	−30 (±3)
	25	1.58×10^{-2}		
	35	2.17×10^{-2}		
Cl	25	5.18×10^{-2}		
H[b]	25	1.3×10^{-4}[c]	+15[d]	−26[d]
CH_3	25	9.98×10^{-5}	+15.6 (±2.0)	−27 (±4)
	35	1.89×10^{-4}		
	45	5.20×10^{-4}		
$N(CH_3)_2$	25	1.05×10^{-3}	+9.5 (±1.4)	−40 (±3)
	35	1.73×10^{-3}		
	45	3.10×10^{-3}		

[a] Reference 2. [b] Reference 1a. [c] Estimated from rate of reaction with PPh_3 at 40 °C and activation parameters of reaction with P(n-OC_4H_9)$_3$. [d] For the reaction with P(n-OC_4H_9)$_3$.

Table II. Carbonyl Stretching Frequencies of the (η^5-C_5H_4X)Rh(CO)$_2$ and (η^5-C_5H_4X)Rh(CO)PPh$_3$ in Decalin

R	dicarbonyl	ν_{CO}, cm^{-1}	monocarbonyl	ν_{CO}, cm^{-1}
NO_2	1	2067, 2011	7	1980[a]
CF_3	2	2060, 1999	8	1969
Cl	3	2053, 1991	9	1963
H	4	2051, 1987[b]	10	1957[a]
CH_3	5	2041, 1978	11	1950
$N(CH_3)_2$	6	2030, 1965	12	1941

[a] Hexane. [b] Cyclohexane.

Instrumentation. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer. Deuteriated solvents were dried and degassed. IR spectra were recorded on a Nicolet 7199 FT-IR spectrometer using either a Specac P/N 20.500 variable-temperature IR cell which contained a 0.5-mm AgCl cell or 0.2-mm CaF_2 cells. Mass spectra were obtained by Dr. D. Hung of Northwestern University Analytical Services Laboratory on a HP 5985 A spectrometer using 70 eV ionization. Elemental analyses for solid samples were carried out by Galbraith Laboratories, Inc. (Knoxville, TN).

Kinetic Measurements. Rate data for the disappearance of rhodium dicarbonyls were obtained by monitoring spectral changes in the ν(CO) region of the IR. In a typical experiment, the solutions were approximately 5 mM in rhodium dicarbonyls, and the reactions were carried out under pseudo-first-order conditions with at least a 10-fold excess of PPh_3. The IR cells were sealed with rubber septa and flushed with N_2 prior to use. Decalin solutions were placed in the constant temperature bath. Constant temperature was maintained by an external circulating bath (Neslab RTE-8). After thermal equilibrium the two solutions were mixed and placed into the IR cell. During the reaction, temperature was maintained within ±0.05 °C. IR spectra changes for the disappearance of the highest carbonyl absorption band were monitored. Plots of −ln A vs time for the disappearance of reactant rhodium dicarbonyl and plots of −ln ($A_\infty - A$) vs time for the appearance of product rhodium monocarbonyl were linear over 3–4 half-lives (linear correlation coefficient >0.99). The slopes of these lines yielded k_{obsd}. Both methods for monitoring the reaction rates yielded similar k_{obsd} values of a given reaction.

Results

The reaction of I, II, III, or IV with PPh_3 yields a monosubstituted product as shown in eq 2. Typical IR

$$(\eta^5\text{-}C_5H_4X)Rh(CO)_2 + PPh_3 \rightarrow (\eta^5\text{-}C_5H_4X)Rh(CO)PPh_3 + CO \quad (2)$$

$$X = CF_3,\ Cl,\ CH_3,\ N(CH_3)_2$$

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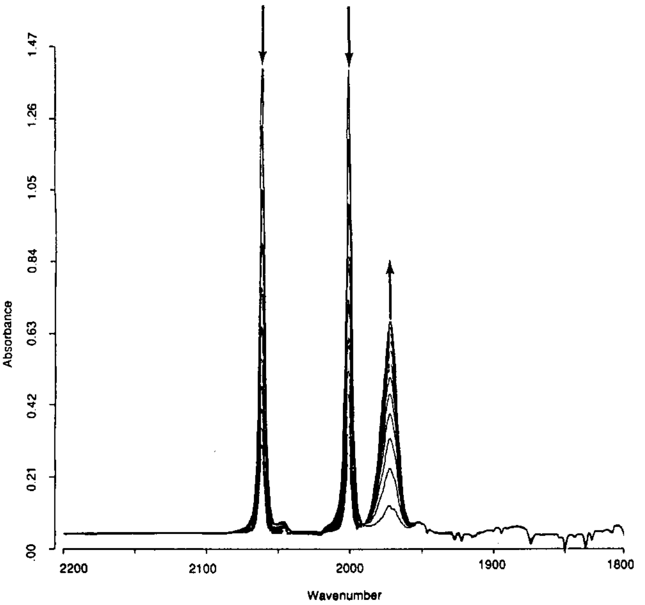

Figure 1. Infrared spectral changes for the reaction $(\eta^5\text{-}C_5H_4CF_3)Rh(CO)_2 + PPh_3 \rightarrow (\eta^5\text{-}C_5H_4CF_3)Rh(CO)PPh_3 + CO$ in Decalin at 25.0 °C.

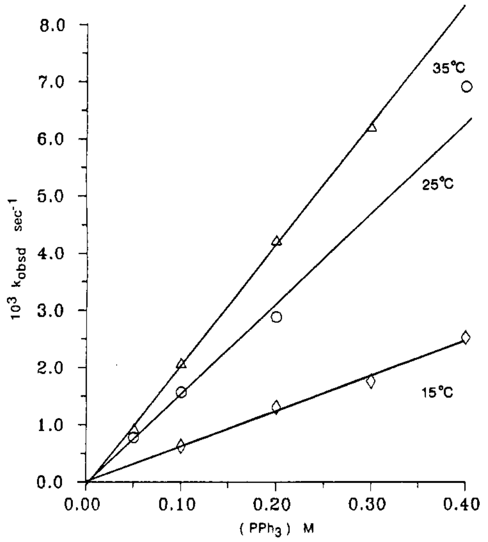

Figure 2. Plot of k_{obsd} vs PPh_3 for the reaction $(\eta^5\text{-}C_5H_4CF_3)Rh(CO)_2 + PPh_3 \rightarrow (\eta^5\text{-}C_5H_4CF_3)Rh(CO)PPh_3 + CO$ in Decalin at various temperatures.

spectral changes in the carbonyl region for the CO substitution reaction of II with PPh_3 in Decalin at 25 °C are shown in Figure 1. Rate constants and activation parameters for CO substitution reactions of I, II, III, or IV with PPh_3 appear in Table I. Kinetic results for the CO substitution reactions support an associative mechanism. The rates of reactions are first order in complex and first order in PPh_3 for all compounds, with activation parameters of $\Delta H^{\ddagger} < 20$ kcal/mol and $\Delta S^{\ddagger} < -15$ eu. No evidence for a dissociative pathway was obtained. Figure 2 shows plots of observed CO substitution rate constants at different temperatures vs PPh_3 concentrations for the reaction of II with PPh_3. Table II contains the carbonyl stretches of the various substrates and their substituted products.

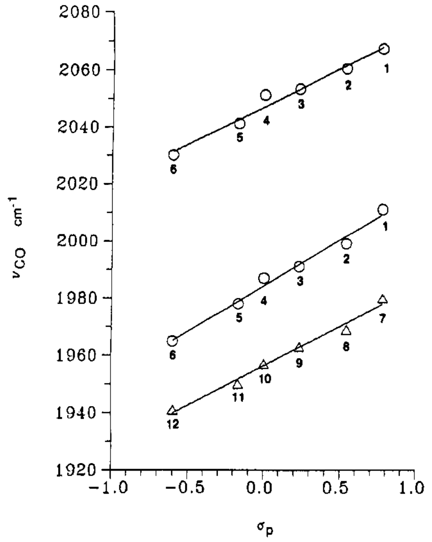

Figure 3. Plot of Hammett σ_p values vs ν_{CO}'s for the cyclopentadienylrhodium carbonyls (see Table II for identity of specific compounds): ○, $(\eta^5\text{-}C_5H_4X)Rh(CO)_2$; △, $(\eta^5\text{-}C_5H_4X)Rh(CO)PPh_3$.

Discussion

Most of the substituted cyclopentadienylrhodium carbonyls synthesized are compounds with electron-withdrawing substituents, such as $CH{=}CH_2$,[15] CHO,[8] $COCH_3$,[8] or $COOCH_3$.[8] Cyclopentadienylrhodium carbonyls substituted with electron-donating groups are compounds with pentamethyl[16] or pentaphenyl[17] substituents. Although it is known[2] that the electron-withdrawing group NO_2 on the cyclopentadienyl ring of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ increases its rate of CO substitution reaction by 10^4, no systematic study of the effect of ring substituents on the rates of CO substitution of such metal carbonyls has been reported. The effect of electron-donating groups is limited to $(\eta^5\text{-}C_5(CH_3)_5)Rh(CO)_2$ which decreases the rate of CO substitution by 10^{-2} relative to the parent compound, but some of this decrease is surely due to steric factors.

For associative reactions of 18-electron organometallic compounds, an η^5 to η^3 rearrangement mechanism has been proposed[1,18] (see eq 3). By putting electron-donating as well as electron-withdrawing substituents on the cyclopentadienyl ring, we now are able to consider the $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ ring slippage in greater detail. Figure 3 shows the dependence of the CO stretching frequencies ν_{CO} for the cyclopentadienylrhodium carbonyls on the Hammett σ_p values. The plot is reasonably linear, with no marked deviation for any substituent. This suggests consistent effects for substituents of the cyclopentadienyl ring on the CO frequencies of rhodium carbonyls, be they the reactant carbonyls $(\eta^5\text{-}C_5H_4X)Rh(CO)_2$ or the product carbonyls $(\eta^5\text{-}C_5H_4X)Rh(CO)PPh_3$. It is well-known[19] that for such systems the values of ν_{CO} increase when the electron density on the metal decreases and they decrease when the electron density on the metal increases. That is exactly what happens here; for positive values of σ_p (electron-withdrawing groups) the ν_{CO} values increase, whereas for negative values of σ_p (electron-donating groups) the ν_{CO} values decrease. This may be the first time such a good linear correlation between values of ν_{CO} and Hammett σ values for metal carbonyls have been reported.

On the basis of such a good correlation between ν_{CO} and σ values, perhaps reflecting variations in electron densities

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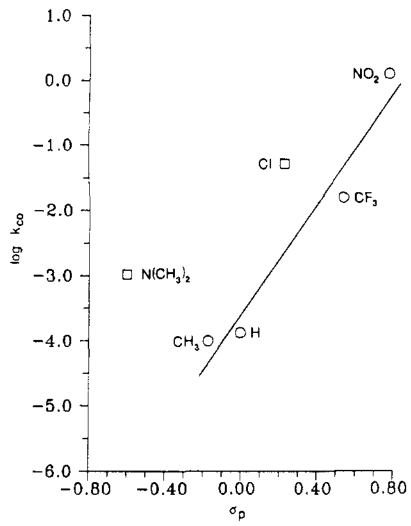
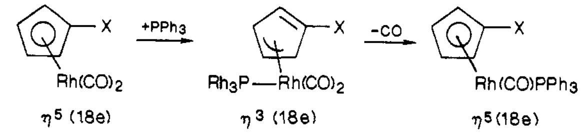


Figure 4. Plot of Hammett σ_p values vs log k_{CO} for CO substitution reactions of cyclopentadienylrhodium carbonyls in Decalin at 25 °C.

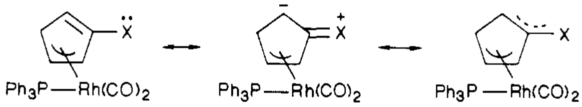
on the metal, it was expected that a similar correlation would be found between the Hammett σ values of the substituents and the rates of CO substitution of the metal carbonyls. This is expected on the basis of the associative $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ mechanism[1,2] which involves delocalization of electron density from the metal to the ring ligand. However, Figure 4 shows there are strong deviations from linearity of a plot of log k_{CO} vs Hammett σ_p values. Four of the substituents (H, CH_3, CF_3, and NO_2) give a satisfactory correlation, but two of the substituents ($N(CH_3)_2$ and Cl) on this basis give compounds that react much faster than expected.

One difference between the groups $N(CH_3)_2$ and Cl and the other four ring substituents is that these contain one or more nonbonding electron pairs that may get involved to help stabilize the transition state for reaction. The associative $\eta^5 \rightarrow \eta^3 \rightarrow \eta^5$ mechanism for CO substitution (eq 3) is also supported by X-ray[20a] and core and valence



(3)

ionization studies[20b] that show allyl–ene distortion in such ring-substituted cyclopentadienyl compounds of the cobalt triad of elements. The η^3-allyl–ene ring structure is believed to be the structure of the transition state or active intermediate for CO substitution reactions, and it may be that this structure can be resonance stabilized by ring substituents with nonbonding pairs of electrons, as shown by (4). Such resonance stabilization of the transition state



(4)

for reaction may account for the electron donor group $N(CH_3)_2$ increasing the rate of substitution by 8 times over the unsubstituted parent compound, when the mechanism proposed (eq 3) suggests it should decrease the rate of reaction. The fact that in the ground-state good linearity of the Hammett plot (Figure 3) is observed for all substituents and the failure to see a similar linearity of the Hammett plot for rates of reaction (Figure 4) resides in how substituents affect the transition state. Also a poor fit of log k with σ^+ or σ^- values indicates the substituent does not enter into direct resonance interaction with the reaction site in the transition state. Instead, stabilization of the transition state comes from stabilization of the localized double bond away from the reaction site of the transition state.

The ρ value (= +4.0) for this reaction series, excluding Cl and $N(CH_3)_2$, is quite large. The magnitude of ρ is a measure of the amount of charge developed at the reaction center and the extent to which the substituents are able to interact with developing charge. Therefore, very large ρ values for CO substitution of cyclopentadienylrhodium carbonyls indicate that substituents on the cyclopentadienyl ring can interact extensively with an electron pair from the 18-electron rhodium center, stabilizing or destabilizing the electron-rich transition state.

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Registry No. **1**, 75862-04-3; **2**, 115406-90-1; **3**, 94890-74-1; **4**, 12192-97-1; **5**, 63544-85-4; **6**, 115406-91-2; **7**, 91842-67-0; **8**, 115406-92-3; **9**, 115406-93-4; **10**, 12203-88-2; **11**, 115406-94-5; **12**, 115406-95-6; $[RhCl(CO)_2]_2$, 14523-22-9; $TlC_5H_4CF_3$, 102649-16-1; $NaC_5H_4CH_3$, 55562-83-9; NaC_5H_5, 4984-82-1; 5-diazo-1,3-cyclopentadiene, 1192-27-4; *N,N*-dimethyl-1,3-cyclopentadienylamine, 75812-62-3; *N,N*-dimethyl-*O*-(toluenesulfonyl)hydroxylamine, 32884-91-6.

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