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Systematic Ligand Effects on the Rates of CO Substitution of $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2$

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The reaction of $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2$ with phosphines and phosphites gives the monosubstituted products $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)L$. The reaction proceeds solely by a second-order process, first order in metal complex and first order in the nucleophile. The effects of phosphorus(III) ligands on the kinetics of this reaction have been studied. The electronic profile shows the division of ligands into one group that shows no steric effects and another group that shows steric effects. The former includes alkylphosphines and mixed alkylarylphosphines as well as triaryl phosphites. The intrinsic reactivity and steric properties of $(\eta^5\text{-}C_5Me_5)Co(CO)_2$ and $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2$ are compared. The carbomethoxy complex shows higher intrinsic reactivity and greater steric threshold (θ_{st}) and is more flexible than the pentamethyl complex.

Introduction

Since creation of a vacant coordination site is fundamental to catalytic processes, an understanding of how coordinatively saturated organometallic compounds react by associative mechanisms is relevant to synthetic and catalytic transformations.

Substitution reactions of cyclopentadienylmetal compounds with P-donor nucleophiles have been of special interest ever since Schuster-Woldan and Basolo[1] studied the reactions of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ and proposed that the cyclopentadienyl ligand prompted an associative pathway for carbonyl substitution reactions, attributed to the ability of the cyclopentadienyl ligand to accept an electron pair from the metal, thus creating a vacant orbital susceptible to nucleophilic attack. 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 ligands.[2,3]

The study of such reactions in cobalt cyclopentadienyl complexes is confined to the $(\eta^5\text{-}C_5Me_5)Co(CO)_2$ derivative, showing that the rate of associative substitution in this complex is slower than in the analogous rhodium complex.[4]

Herein we report the kinetics of CO substitution by P-donor nucleophiles in the compound $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2$ in order to measure the influence of the electron-withdrawing carbomethoxy substituent on the reaction rate.

On the other hand, because of the central role played by phosphorus(III) compounds in the study of organometallic chemistry, and in catalysis in general,[5] there has been considerable interest in the stereoelectronic factors that influence metal–phosphorus bonding.[6,7] These properties can be parameterized into electronic and steric components. The most commonly used measures of the steric requirements are the cone angles (θ)[8] of the free ligands. The separation of the electronic parameter into σ and π components is complicated by the concept of synergic bonding, which requires the electronic factors to be mutually dependent.[9]

Over the past 5 years Giering and co-workers have been exploring the quantification of σ,π and steric properties of phosphorus(III) ligands through the development of an analytical method—the quantitative analysis of ligand effects (QALE).[10-12] The phosphorus(III) ligands appear to be divided into at least two different classes (σ-donors and σ-donors/π-acceptors), depending on the stereoelectronic nature of the metal fragment and the phosphorus(III) ligand. This analysis leads to satisfying results, but as the authors say, unfortunately only a few of the scores of papers that they examined report the required data. pK_a values have been used as measures of σ-donicity of the ligands. However, as the authors have reported recently,[13] the pK_a values appear to contain a steric component and the χ values,[14] which reflect no steric influences, for $LNi(CO)_3$ (L = trialkylphosphines, mixed alkylarylphosphines, and triaryl phosphites) are better measures of the σ-donicity when restricted to this group of ligands. Unfortunately, χ values cannot generally be used as measures of the σ-donicity of the ligand since χ may also contain a π component. Accordingly, these authors use eq 1 to calculate the new set of χ values (χ_d)[13] that would be expected for the π-acids where they behave as only σ-donor ligands.

$$pK_a = -[0.68\ (\pm0.03)]\chi - [0.047\ (\pm0.010)]\theta + 18.9\ (\pm1.6) \quad (1)$$

The application of this method to a suitable combination of P-donor nucleophiles has allowed us to evaluate systematically the influence of σ,π and steric components on the $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2$ CO substitution reaction.

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(14) Bartik, T.; Himmler, T.; Schulte, H.-G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29. χ is defined as the difference between the A_1 terminal carbonyl band of $LNi(CO)_3$ and 2056.1 cm^{-1} (the A_1 band for $(t\text{-}Bu)_3PNi(CO)_3$).

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Table I. Carbonyl Stretching Frequencies (cm^{-1}, Toluene) and Force Constants (mdyn/Å) for $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)L$

compd no.	L	ν_{CO}	k_{CO}
	CO	2073, 2034	16.22
1	P(*n*-Bu)$_3$	1924.2	14.95
2	PMe$_3$	1927.3	15.00
3	PMe$_2$Ph	1932.8	15.08
4	PMePh$_2$	1936.7	15.15
5	PPh$_3$	1938.3	15.17
6	P(*m*-tolyl)$_3$	1938.6	15.18
7	P(*p*-tolyl)$_3$	1938.6	15.18
8	P(*p*-MeOPh)$_3$	1936.7	15.15
9	PCy$_3$	1921.2	14.90
10	P(OMe)$_3$	1949.2	15.34
11	P(OEt)$_3$	1946.9	15.31
12	P(OPh)$_3$	1962.5	15.55

Experimental Section

Compounds and Solvents. All manipulations were carried out by using standard Schlenk tecniques under an atmosphere of oxygen-free N_2. The solvents toluene, benzene, hexane, and tetrahydrofuran were dried and distilled over Na in the presence of benzophenone under an N_2 atmosphere and then bubbled with N_2 for 1 h after distillation and stored under nitrogen.

The reagents PCy$_3$, PMe$_3$, PMe$_2$Ph, PMePh$_2$, P(*m*-tolyl)$_3$, P(*p*-tolyl)$_3$, and P(*p*-MeOPh)$_3$ were obtained from Strem or Aldrich Chemicals and were used without further purification. PPh$_3$ (Aldrich) was recrystallized from methanol prior to use. The phosphine P(*n*-Bu)$_3$ and the phosphites P(OMe)$_3$, P(OEt)$_3$, and P(OPh)$_3$ were also obtained from Aldrich Chemicals, but these were distilled from Na under N_2 before use.

The compound $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2$[15] was prepared by methods described in the literature and characterized by its IR and NMR spectra.

Product Identification. The monosubstituted complexes $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)L$ [L = P(*n*-Bu)$_3$, PMe$_3$, PMe$_2$Ph, PMePh$_2$, PPh$_3$, P(*m*-tolyl)$_3$, P(*p*-tolyl)$_3$, P(*p*-MeOPh)$_3$, PCy$_3$, P(OMe)$_3$, P(OEt)$_3$, and P(OPh)$_3$] were prepared by stirring a mixture of $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2$ (2 g, 8.40 mmol) and L (8.40 mmol) in 20 mL of benzene until the ν_{CO} band of the parent complex had disappeared. The solution was cooled to room temperature and filtered, and then the solvent was removed under vacuum. The products were recrystallized from benzene–hexane in a 1:4 ratio. With L = PPh$_3$, P(*m*-tolyl)$_3$, P(*p*-tolyl)$_3$, P(*p*-MeOPh)$_3$, and PCy$_3$ red-brown crystals were separated and these products were dried at room temperature under high vacuum. When L = P(*n*-Bu)$_3$, PMe$_3$, PMe$_2$Ph, PMePh$_2$, P(OMe)$_3$, P(OEt)$_3$, and P(OPh)$_3$ the products were again filtered and the solvents were removed from the filtrate to yield a red oil. The yields were approximately 95%. The ν_{CO} stretching frequencies and NMR spectral data, in toluene and CDCl$_3$ solutions, respectively, for these complexes $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)L$ are listed in Tables I and II, and the analyses (calculated and found) are listed in Table III. The amount of cobalt was determined by titration of the Co–EDTA complex in the presence of Eriochrome Black T as indicator.

Instrumentation. For IR measurements a Nicolet 5DX FT-IR spectrometer was used. For kinetic measurements the absorbance mode was used. ^{1}H NMR spectra were recorded on a Bruker WM-200-SY FT mode spectrometer. The deuteriated solvent CDCl$_3$ was dried and degassed.

Kinetic Measurement. Rate constants were determined by monitoring the disappearance of the highest frequency carbonyl stretching band of the complex $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2$. The absorbance mode was used. The toluene solutions of both the ligand and the compound $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2$ were placed under nitrogen in an aluminum-foil-wrapped Schlenk flask and thermostated in a constant-temperature bath (±0.2 °C). No detectable change in the infrared spectrum of a 8.5 × 10^{-3} M toluene solution of $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2$ occurred during 1 week in the dark at 30 °C. Tetrahydrofuran and dichloromethane solutions of the compound showed about a 12% decrease in the intensity of the carbonyl absorption after storing for 2 days at 30 °C in the dark.

At zero time the solution of phosphine or phosphite was added via a syringe to the cobalt compound to give between 5 and 8 cm^3 of the reaction mixture. Aliquots were subsequently withdrawn through a rubber septum with the use of a syringe at intervals to obtain 5–10 readings during 1–3 half-lives of the reaction and transferred to a 0.5-mm NaCl cell. The IR cell was flushed with N_2 and sealed with rubber septa before use.

Plots of log A vs time were linear for more than 3 half-lives, and values of k_{obs} were determined from the slope of this line by the least-squares method. The correlation of the least-squares line (R^2 > 0.997) was very good.

Approximately 8.5 × 10^{-3} M solutions of complex were used, and all kinetic experiments were carried out under pseudo-first-order conditions with a least a 10-fold excess of nucleophile. The reactions went to completion to give the corresponding monocarbonyl product $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)L$.

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Table II. ^{1}H NMR Chemical Shifts (δ) for $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)L$ in CDCl$_3$

L	chem shift
P(*n*-Bu)$_3$	0.94 (s, br, 9 H, CH$_3$); 1.40 (s, br, 12 H, CH$_2$); 1.57 (s, br, 6 H, CH$_2$); 3.73 (s, 3 H, CO$_2$CH$_3$); 4.96 (s, br, 2 H, H(3,4), C$_5$H$_4$); 5.08 (s, br, 2 H, H(2,5), C$_5$H$_4$)
PMe$_3$	1.48 (d, J_{PH} = 10, 3 Hz, 9 H, CH$_3$); 3.66 (s, 3 H, CO$_2$CH$_3$); 4.87 (s, br, 2 H, H(3,4), C$_5$H$_4$); 5.06 (s, br, 2 H, H(2,5), C$_5$H$_4$)
PMe$_2$Ph	1.55 (d, J_{PH} = 10.2 Hz, 6 H, CH$_3$); 3.60 (s, 3 H, CO$_2$CH$_3$); 4.76 (s, br, 2 H, H(3,4), C$_5$H$_4$); 4.94 (s, br, 2 H, H(2,5), C$_5$H$_4$); 7.26 (m, *m*- and *p*-H, 3 H, C$_6$H$_5$); 7.40 (m, *o*-H, 2 H, C$_6$H$_5$)
PMePh$_2$	1.60 (d, J_{PH} = 10, 2 Hz, 3 H, CH$_3$); 3.56 (s, 3 H, CO$_2$CH$_3$); 4.64 (s, br, 2 H, H(3,4), C$_5$H$_4$); 4.80 (s, br, 2 H, H(2,5), C$_5$H$_4$); 7.24 (m, *m*- and *p*-H, 6 H, C$_6$H$_5$); 7.42 (m, *o*-H, 4 H, C$_6$H$_5$)
PPh$_3$	3.51 (s, 3 H, CO$_2$CH$_3$); 4.59 (s, br, 2 H, H(3,4), C$_5$H$_4$); 4.82 (s, br, 2 H, H(2,5), C$_5$H$_4$); 7.24 (m, *m*- and *p*-H, 9 H, C$_6$H$_5$); 7.36 (m, *o*-H, 6 H, C$_6$H$_5$)
P(*m*-tolyl)$_3$	2.21 (s, 3 H, CH$_3$); 3.55 (s, 3 H, CO$_2$CH$_3$); 4.59 (s, br, 2 H, H(3,4), C$_5$H$_4$); 4.76 (s, br, 2 H, H(2,5), C$_5$H$_4$); 7.38 (m, 12 H, C$_6$H$_4$)
P(*p*-tolyl)$_3$	2.26 (s, 3 H, CH$_3$); 3.55 (s, 3 H, CO$_2$CH$_3$); 4.61 (s, br, 2 H, H(3,4), C$_5$H$_4$); 4.77 (s, br, 2 H, H(2,5), C$_5$H$_4$); 7.36 (m, 12 H, C$_6$H$_4$)
P(*p*-MeOPh)$_3$	3.63 (s, 3 H, CO$_2$CH$_3$); 3.80 (s, 9 H, CH$_3$OPh); 4.79 (s, br, 2 H, H(3,4), C$_5$H$_4$); 4.96 (s, br, 2 H, H(2,5), C$_5$H$_4$); 7.28 (m, 12 H, C$_6$H$_4$)
PCy$_3$	1.31 (m, H$_{ax}$, 18 H, C$_6$H$_{11}$); 1.81 (m, H$_{eq}$, 15 H, C$_6$H$_{11}$); 3.72 (s, 3 H, CO$_2$CH$_3$); 4.88 (s, br, 2 H, H(3,4), C$_5$H$_4$); 5.06 (s, br, 2 H, H(2,5), C$_5$H$_4$)
P(OMe)$_3$	3.60 (d, J_{PH} = 10, 2 Hz, 9 H, OCH$_3$); 3.75 (s, 3 H, CO$_2$CH$_3$); 5.08 (s, br, 2 H, H(3,4)); 5.12 (s, br, H(2,5), C$_5$H$_4$)
P(OEt)$_3$	1.25 (s, br, 9 H, CH$_3$); 3.72 (s, 3 H, CO$_2$CH$_3$); 3.97 (s, br, 6 H, OCH$_2$); 5.06 (s, br, 2 H, H(3,4), C$_5$H$_4$); 5.25 (s, br, 2 H, H(2,5), C$_5$H$_4$)
P(OPh)$_3$	3.64 (s, 3 H, CO$_2$CH$_3$); 5.02 (s, br, 2 H, H(3,4), C$_5$H$_4$); 5.25 (s, br, 2 H, H(2,5), C$_5$H$_4$); 7.33 (m, 15 H, C$_6$H$_5$)

Results

The substitution of the electron-withdrawing carbomethoxy group in the cyclopentadienyl ring results in a shift of ν_{CO} to higher frequency with respect to that band in the parent complex $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (2037, 1965 cm^{-1}). This is attributed to the reduced nature of back-bonding between cobalt and carbon, making the CO bond closer to the triple bond in free CO, and indicates that the cobalt

Table III. Analytical Data for (η^5-$C_5H_4CO_2Me$)Co(CO)L[a]

L	yield, %	Co, % found	Co, % calcd	C, % found	C, % calcd	H, % found	H, % calcd
P(*n*-Bu)$_3$	94	14.08	14.29	58.14	58.22	8.30	8.25
PMe$_3$	95	20.24	20.60	46.04	46.15	5.62	5.59
PMe$_2$Ph	95	16.83	16.93	55.10	55.21	5.04	5.17
PMePh$_2$	95	14.27	14.37	61.41	61.50	4.79	4.88
PPh$_3$	90	12.28	12.47	65.97	66.05	4.56	4.66
P(*m*-tolyl)$_3$	92	11.33	11.46	67.70	67.75	5.41	5.44
P(*p*-tolyl)$_3$	90	11.49	11.46	67.68	67.75	5.38	5.44
P(*p*-MeOPh)$_3$	93	10.36	11.48	61.88	61.96	4.86	4.98
PCy$_3$	92	11.95	12.02	63.42	63.62	8.08	8.16
P(OMe)$_3$	91	17.42	17.64	39.49	39.52	4.83	4.79
P(OEt)$_3$	96	15.11	15.67	44.61	44.67	5.80	5.85
P(OPh)$_3$	94	10.96	11.33	59.94	59.97	4.29	4.23

[a] The microanalyses were performed by the Microanalytical Laboratory of the Departamento de Química at the Universidad Autónoma de Madrid.

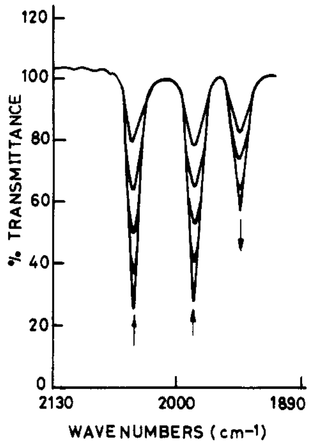

Figure 1. Infrared spectral changes for the reaction (η^5-$C_5H_4CO_2Me$)Co(CO)$_2$ + P(*n*-Bu)$_3$ → (η^5-$C_5H_4CO_2Me$)Co(CO)P(*n*-Bu)$_3$ + CO in toluene at 35.0 °C.

is less electron-rich in the carbomethoxycyclopentadienyl complex. Because of this the compound should be more susceptible to nucleophilic attack.

The reaction of (η^5-$C_5H_4CO_2Me$)Co(CO)$_2$ with phosphines or phosphites yields a monosubstituted product, as shown in eq 2.

$$(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2 + L \rightarrow (\eta^5\text{-}C_5H_4CO_2Me)Co(CO)L + CO \quad (2)$$

L = P(*n*-Bu)$_3$, PMe$_3$, PMe$_2$Ph, PMePh$_2$, PPh$_3$, P(*p*-tolyl)$_3$, P(*p*-MeOPh)$_3$, P(*m*-tolyl)$_3$, PCy$_3$, P(OMe)$_3$, P(OEt)$_3$, P(OPh)$_3$

All the compounds were characterized by means of elemental analysis and IR and ^{1}H NMR spectra.

Typical IR spectral changes in the carbonyl region for the CO substitution reaction with P(*n*-Bu)$_3$ in toluene at 35 °C are shown in Figure 1. Table I contains the carbonyl stretches of the substituted products as well as the force constants, k_{CO} (calculated by the method of Cotton and Kraihanzel[16]). Table II contains the ^{1}H chemical shifts for (η^5-$C_5H_4CO_2Me$)Co(CO)L.

The second-order rate constants for the reaction shown in eq 2, as well as cone angle (θ) and basicity data (pK_a,[17] χ_d[13]) for the ligands, are listed in Table IV. The activation parameters appear in Table V. Kinetic results for the CO

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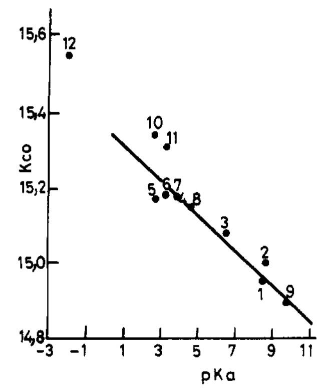

Figure 2. Plot of k_{CO} values of (η^5-$C_5H_4CO_2Me$)Co(CO)L vs pK_a of the phosphine ligands L.

substitution reactions support an associative mechanism. The rates of reactions are first order in complex and first order in ligand with activation parameters of $\Delta H^{\ddagger} < 16$ kcal mol^{-1} and $\Delta S^{\ddagger} < -17$ eu. No evidence for a dissociative mechanism was obtained.

The electronic profile (Figure 4) for the kinetic data shows the division of ligands into one group that shows no steric effects and another group that shows steric effects. The former includes alkylphosphines and mixed alkylarylphosphines as well as trialkyl and triaryl phosphites.

The electronic and steric profiles for (η^5-$C_5H_4CO_2Me$)Co(CO)$_2$ and (η^5-C_5Me_5)Co(CO)$_2$ (Figure 10) show that their powers of electronic discrimination[18] (a measure of the relative amounts of bond making in the transition states) are comparable but the former has a higher intrinsic reactivity and is more flexible than the latter.

Discussion

In all cases the IR spectra show one stretching vibration ν_{CO} for the molecular symmetry C_s.

The stretching vibrations of coordinated CO ligands have been known to be a measure of metal–CO π-bonding order, which may be perturbed by other ligands. When the metal d to CO π^* back-donation decreases, the CO bond order increases. As expected, the CO stretching force constants, k_{CO}, are largest when the nucleophilic basicity of the ligand decreases. Figure 2 shows a good linear correlation of the k_{CO} values with pK_a values. The greater scatter of the linear correlation arises in phosphite complexes and is attributed to the π-acidity of the ligands.

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Table IV. Rate Constants for the CO Substitution Reaction of $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2$ with L in Toluene (Eq 2) (Ratio 1:11.73), pK_a, χ_d, and Cone Angle Data for Phosphorus(III) Ligands

compd no.	L	T, °C	k_{obs}, 10^4 s^{-1}	k_2, 10^3 M^{-1} s^{-1}	θ,[a] deg	pK_a[b]	χ_d[c]
1	$P(n\text{-}Bu)_3$	35	9.84 ± 0.02	9.98	132	8.43	5.25
		45	21.06 ± 0.03	21.36			
		55	40.31 ± 0.03	40.88			
2	PMe_3	25	21.4 ± 0.3	21.7	118	8.65	8.55
		35	47.63 ± 0.02	48.28			
		45	102 ± 2	103			
3	PMe_2Ph	26.4	15.8 ± 0.5	16.0	122	6.50	10.60
		35	25.9 ± 0.2	26.2			
		45	59.8 ± 0.3	60.7			
4	$PMePh_2$	25.8	4.03 ± 0.03	4.09	136	4.57	12.10
		35	9.65 ± 0.02	9.78			
		45	21.2 ± 0.6	21.5			
5	PPh_3	45	2.51 ± 0.08	2.54	145	2.73	13.25
		55	5.70 ± 0.05	5.74			
		65	12.4 ± 0.1	12.6			
6	$P(m\text{-tolyl})_3$	45	2.6 ± 0.08	2.65	165	3.30	
		55	6.6 ± 0.1	6.7			
		65	12.8 ± 0.1	13.0			
7	$P(p\text{-tolyl})_3$	45	4.8 ± 0.1	4.9	145	3.84	11.5
		55	9.75 ± 0.09	9.98			
		65	20.25 ± 0.5	20.6			
8	$P(p\text{-MeOPh})_3$	45	7.23 ± 0.2	7.3	145	4.59	10.50
		55	15.9 ± 0.4	16.1			
		65	34.2 ± 1	35			
9	PCy_3	45	3.94 ± 0.08	4.00	170	9.70	1.40
		55	7.6 ± 0.1	7.7			
		65	16.7 ± 0.5	17.0			
10	$P(OMe)_3$	45	4.4 ± 0.1	4.4	107	2.60	16.7
		55	9.6 ± 0.3	9.7			
		65	19.8 ± 0.3	20.1			
11	$P(OEt)_3$	45	5.9 ± 0.2	5.9	109	3.35	15.51
		55	14.8 ± 0.4	13.4			
		65	25.6 ± 0.3	25.9			
12	$P(OPh)_3$	45	0.38 ± 0.01	0.37	128	−2.00	22.05
		55	0.94 ± 0.03	0.96			
		65	1.83 ± 0.04	1.86			

[a] Cone angles taken from ref 8. [b] pK_a values are taken from ref 17 and 15. [c] χ_d values are taken from ref 13.

Table V. Activation Parameters for the Reaction $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2 + L \rightarrow (\eta^5\text{-}C_5H_4CO_2Me)Co(CO)L + CO$

L	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu
$P(n\text{-}Bu)_3$	14.14 ± 0.5	−21.8 ± 1.6
PMe_3	14.7 ± 0.1	−17.0 ± 0.3
PMe_2Ph	13.6 ± 1.5	−21.6 ± 4.6
$PMePh_2$	15.3 ± 0.5	−18.2 ± 1.5
PPh_3	14.6 ± 0.1	−24.1 ± 0.3
$P(m\text{-tolyl})_3$	14.5 ± 1.4	−24.4 ± 4.3
$P(p\text{-tolyl})_3$	13.1 ± 0.3	−28.0 ± 1
$P(p\text{-MeOPh})_3$	14.2 ± 0.5	−23.5 ± 1.4
PCy_3	13.2 ± 0.5	−27.9 ± 1.4
$P(OMe)_3$	13.7 ± 0.2	−25.2 ± 0.6
$P(OEt)_3$	13.5 ± 0.7	−26.1 ± 2.1
$P(OPh)_3$	14.7 ± 1.1	−27.9 ± 3.8

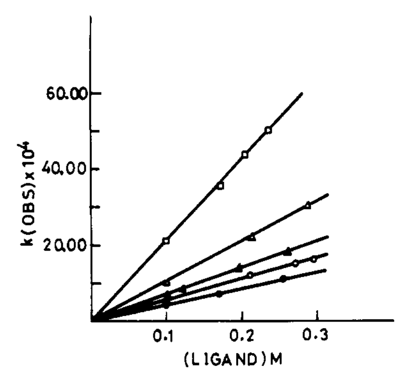


Figure 3. Plot of k_{obs} (s^{-1}) vs ligand concentration (M) for reaction 1: (□) T = 25.0 °C, L = PMe_3; (○) T = 45.0 °C, L = PPh_3; (▲) T = 45.0 °C, $P(MeOPh)_3$; (●) T = 55.0 °C, L = PCy_3; (△) T = 55.0 °C, $P(OMe)_3$.

Although it is known that the electron-withdrawing substituents in the cyclopentadienyl ring of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ increase the rate of its CO substitution reaction,[2-4] no systematic study of the effect of these groups in cobalt cyclopentadienyl complexes has been reported. As is shown in Table I, ν_{CO} bands of $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2$ appear at higher frequency than in the analogous $(\eta^5\text{-}C_5H_5)Co(CO)_2$ (2037, 1965 cm^{-1}), indicating that the cobalt is less electron-rich in the former complex. Thus, substitution is expected to proceed faster for the carbomethoxycyclopentadienyl complex. This was observed experimentally. For example, when L = PPh_3, the rate of reaction of $(\eta^5\text{-}C_5H_4CO_2Me)Co(CO)_2$ in toluene at 40 °C (extrapolated from an Arrhenius plot) is 64 times faster than that for $(\eta^5\text{-}C_5H_5)Co(CO)_2$, while $(\eta^5\text{-}C_5Me_5)Co(CO)_2$ does not react.[4a]

The rate of reaction is directly proportional to the concentration of the incoming ligand. Furthermore, the zero intercept shows there is no detectable contribution from a ligand-independent (first-order) process under these experimental conditions, as is shown in Figure 3 for some of the ligands.

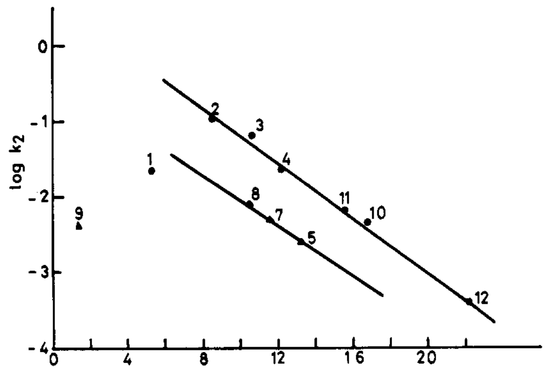
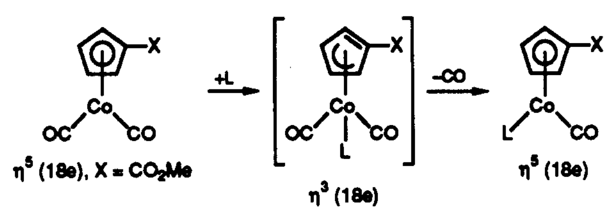


Figure 4. Electronic profile for reaction 2: (●) small ligands ($\theta < 145°$); (▲) ligands with cone angle ≥145°. The numbers correspond to those in Table IV.

These observations together with the activation parameters, relatively small values of $\Delta H^{\ddagger}$, and high negative values of $\Delta S^{\ddagger}$ (Table V) support an associative (S_N2) substitution process for the carbomethoxycyclopentadienyl systems.

These results are consistent with a S_N2 mechanism similar to that first proposed by Basolo and co-workers[1] for $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ with various phosphines and can be represented by eq 3, where the η^3-allyl–ene ring structure is believed to be the structure of the transition state or active intermediate for CO substitution reactions.



(3)

It is assumed that log k is divisible into steric (log k_{st}), electronic (log k_{el}), and intrinsic (C, independent of the stereoelectronic properties of PR_3) components[19] such that

$$\log k = \log k_{el} + \log k_{st} + C \quad (4)$$

Construction of electronic and steric profiles allows the separation of the two effects. An electronic profile is a plot of log k for a series of isosteric ligands (or small ligands that do not exhibit steric effects) versus a measure of the σ-donicity (commonly pK_a values) of the phosphorus(III) ligands. log k_{st} is the difference (at the same pK_a) between data points for the remaining ligands and the electronic profile. The steric profile is generated by plotting log k_{st} versus the cone angle (θ) of the ligand.

We used χ_d values, instead of pK_a, as a measure of the σ-donicity of the ligands to generate the electronic profile. Figure 4 clearly shows the linear relationship between log k and χ_d for the ligands with cone angle values less than 145° and that for the isosteric (θ = 145°) triarylphosphine ligands. The graph shows the division of ligands into one group (small ligands, ●) that shows no steric effects and another group (▲) that shows steric effects. The data for $P(n\text{-}Bu)_3$ are problematic. Giering and co-workers find that this often is the case for this ligand with long-chain alkyl groups. Thus, we will not take it into account in this analysis.

The group that shows no steric effects include alkylphosphines and mixed alkylarylphosphines as well as

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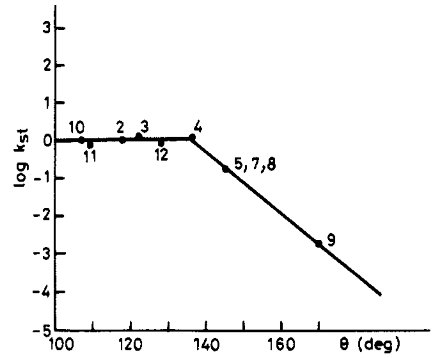

Figure 5. Steric profile based on χ_d values for reaction 2. The numbers correspond to those in Table IV.

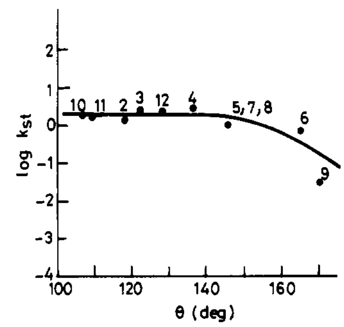

Figure 6. Steric profile based on pK_a values for reaction 2. The numbers correspond to those in Table IV.

trialkyl phosphites. The last compounds are potentially strong π acids, and yet their rate constants correlate with a σ-donor parameter (χ_d). This suggests that these ligands also behave as σ-donors. This is also observed from an analysis of kinetic and thermodynamic data for several reactions involving phosphorus(III) ligands where, in some cases, the phosphites behave as π-acids[11,20] and, in other cases, appear to behave as σ-donors.[21] There is accumulating evidence that phosphorus(III) ligands may act as pure σ-donors, depending on the nature of the pendent groups, the length of the M–P bond, and the crowding about the metal.

By a plot of log k_{st} versus θ the steric profile is generated (Figure 5). It shows a plateau region until a cone angle value of ca. 136° (θ_{st}, steric threshold), after which it declines as the cone angles increases to 170°. The steric threshold (θ_{st})[10] is the value of the cone angle of the ligands above which steric effects become evident and is a measure of the congestion about the metal in the transition state. The slope (steric sensitivity) of the steric profile after θ_{st} is related to the flexibility of the transition-state complex. A large slope indicates a stiff complex, whereas a smaller slope indicates a more flexible complex.

The analysis of the data with use of pK_a values to generate the steric profile (Figure 6) gives a less clearly defined threshold (140–150°) and changes the steric sensitivity ($d(\log k_{st})/d\theta$), as was also shown by Giering and co-workers[13] from reported kinetic and thermodynamic data. The change is attributed to the steric dependence of the pK_a values.

The apparent existence of a sharp threshold when χ_d values are used allows a quantitative analysis of the data via linear equations shown in eq 5, where the coefficient a reflects the degree of entering-ligand–metal bonding in

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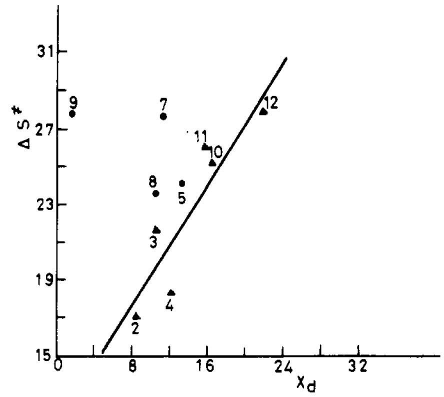


Figure 7. Electronic profile for the activation entropy of reaction 2: (▲) ligands with θ < 136°; (●) ligands with θ > 136°. The numbers correspond to those in Table IV.

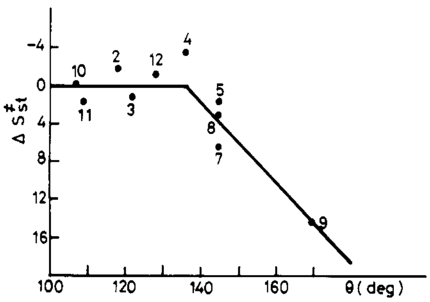


Figure 8. Steric profile for the activation entropy of reaction 2. The numbers correspond to those in Table IV.

the transition state (also known as the electronic discrimination parameter, β[18]). The coefficient b is related to the

$$\log k = a(\chi_d) + b(\theta - \theta_{st})\lambda + C \quad (5)$$

relative flexibility of the ground and transition states, and λ is a switching function that turns on the steric effect when the size of the ligand exceeds the steric threshold; i.e. $\lambda = 0$ when $\theta < \theta_{st}$ and $\lambda = 1$ when $\theta > \theta_{st}$. The constant term C is related to the "intrinsic reactivity", i.e. the intrinsic susceptibility of the complex to nucleophilic attack.

The analysis of the data obtained by us gives the relationship between log k, χ_d, and θ shown in eq 6.

$$\log k = -0.184\chi_d - 0.078(\theta - 136) + 0.657 \qquad r = 0.999,\ \sigma = 0.02 \quad (6)$$

On the other hand, from an analysis of the enthalpy and entropy data it is possible to shed light on the origins of the steric effects and steric threshold. Thus, we will consider the electronic and steric profiles for the activation parameters. From a plot of ΔH^* versus χ_d and θ scattering diagrams are obtained. However, there is a significant correlation between ΔS^* and χ_d (electronic profile for ΔS^*) for ligands with cone angles smaller than 136° (θ_{st}) (Figure 7). The steric profile generated by plotting ΔS^*_{st} (difference between data points for the remaining ligands and the electronic profile at the same χ_d) versus θ (Figure 8) shows the threshold (θ_{st} = 136°) for the onset of the steric effects in the transition state of the reaction. The relationship between ΔS^* and the stereoelectronic parameters is shown in eq 7.

$$\Delta S^* = -0.75\chi_d - 0.42(\theta - 136°) - 12.47 \qquad r = 0.932,\ \sigma = 2.5 \quad (7)$$

After the steric threshold the negative values of ΔS^* rise rapidly, leading to an increasing destabilization of the transition state, and so the rate of the reaction drops rapidly (Figure 5). The origin of the steric effects on ΔS^*

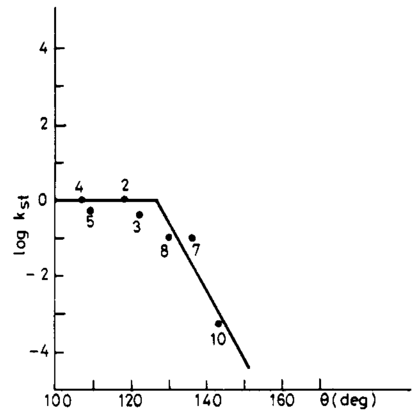


Figure 9. Steric profile for the CO substitution reaction of (η^5-C_5Me_5)Co(CO)$_2$. Data are taken from ref 4a.

of the reaction perhaps could be attributed to the fact that, for ligands with cone angles values greater than the threshold ($\theta \approx$ 136°), the five possible positions in the cyclopentadienyl ring for the carbomethoxy substituent, which in the absence of steric effects could be assumed to be equivalent, will be restricted to those where the steric interaction between the carbomethoxy group and the phosphine is less unfavorable. On this basis we would be expect an increase of the order in the transition state as the cone angle of the ligands increases above the threshold.

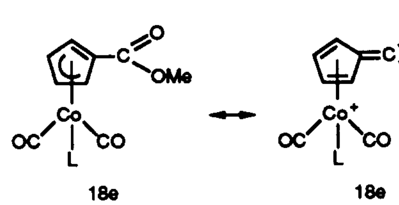
Since kinetic data for associative substitution reactions of (η^5-C_5Me_5)Co(CO)$_2$ with P-donors in toluene at 70 °C have been reported,[4a] we can compare them with those for (η^5-$C_5H_4CO_2Me$)Co(CO)$_2$ obtained by us in this work, extrapolated to this temperature.

Since in the paper by Basolo and co-workers[4a] no data are available for at least two nucleophiles with the same cone angle, we used the data points for the small nucleophiles P(OMe)$_3$ and PMe$_3$ to establish the electronic profile. The steric profile of the pentamethyl complex is given in Figure 9. The quantitative analyses of the kinetics of the reactions for carbomethoxy and pentamethyl complexes at 70 °C give the relationships between log k, χ_d, and θ shown in eqs 8 and 9, respectively.

$$\log k = -0.184\chi_d - 0.078(\theta - 136°) + 1.25 \qquad r = 0.999,\ \sigma = 0.02 \quad (8)$$

$$\log k = -0.16\chi_d - 0.18(\theta - 126°) - 1.34 \qquad r = 0.998,\ \sigma = 0.11 \quad (9)$$

The analysis shows that the electronic discrimination is similar for the two complexes, thereby indicating that the degrees of bond making in the transition states are comparable. (η^5-$C_5H_4CO_2Me$)Co(CO)$_2$ has a higher intrinsic reactivity (+1.25) than (η^5-C_5Me_5)Co(CO)$_2$ (−1.34), which may be ascribed to a resonance stabilization of the transition state owing to the presence of the electron-withdrawing carbomethoxy group on the ring. This effect may be ilustrated by writing two resonance structures as shown in (10).



(10)

The steric profiles for the two compounds also differ appreciably. The steric threshold for (η^5-C_5Me_5)Co(CO)$_2$ is smaller (126°) than that for (η^5-$C_5H_4CO_2Me$)Co(CO)$_2$

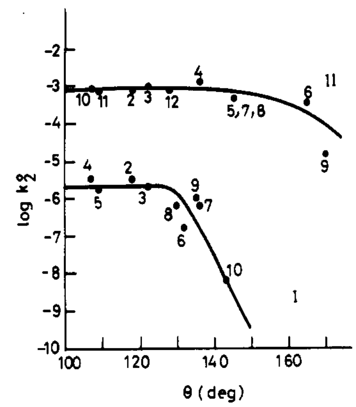


Figure 10. Steric profile for (η^5-C_5Me_5)Co(CO)$_2$ (I) and (η^5-$C_5H_4CO_2Me$)Co(CO)$_2$ (II) at 70.0 °C. The numbers correspond to those in the paper reported by Basolo and co-workers[4a] and to those in Table IV, respectively.

(136°); thus, as expected, the transition state is more congested in the former complex.

On the other hand, the smaller steric sensitivity (0.078) for the carbomethoxy complex indicates that its ability to sterically accommodate the incoming ligand is higher; that is, (η^5-$C_5H_4CO_2Me$)Co(CO)$_2$ is more flexible than (η^5-C_5Me_5)Co(CO)$_2$, which can be attributed to a greater degree of ring slippage $\eta^5 \rightarrow \eta^3$ in the former caused by the electron-withdrawing carbomethoxy substituent in the ring.

These results about the steric properties and intrinsic reactivity of both complexes are qualitatively similar to those obtained when the analysis of kinetics data is based on pK_a values. The intrinsic reactivity is log k_2 for a particular small nucleophile corrected to what it would be for a standard nucleophile with pK_a = 0.[22,23] Pöe[18] has proposed that it is useful to use a less basic hypothetical nucleophile as a reference standard, on the grounds that the rate for a less basic nucleophile is determined more by the complex itself than by the nucleophile.

He has chosen to use as a standard a hypothetical very weak nucleophile with pK_a = −4. This is less basic than any of the P-donors available[11] and will provide reasonable estimation of intrinsic reactivities.

The plot of log $k_2 - a(pK_a + 4) = \log k_2°$ against θ (Figure 10) allows us to obtain the value of $[\log k_2°]_{\theta \to 0}$ (intrinsic reactivity) after the a value has been determined.

We use the value a = 0.22 obtained by Giering[10] for the (η^5-C_5Me_5)Co(CO)$_2$ complex and the value a = 0.25 for the (η^5-$C_5H_4CO_2Me$)Co(CO)$_2$ obtained from the electronic profile generated from the isosteric (θ = 145°) triarylphosphine data points. As is shown in Figure 10, the difference ($\Delta \simeq 2.5$) in the intrinsic reactivity of both complexes is similar to that obtained above.

The steric effects for (η^5-C_5Me_5)Co(CO)$_2$ become evident at a cone angle (θ_{st} = 120–125°) smaller than that for (η^5-$C_5H_4CO_2Me$)Co(CO)$_2$ (θ_{st} = 140–145°). Above this cone angle range, the sharp and gradual changes for the pentamethyl and carbomethoxy complexes respectively indicate that the latter is more flexible than the former.

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Transition-Metal-Substituted Diphosphenes. 21.[1] [2 + 2] Cycloaddition of a Diphosphene to Maleimide and *N*-Methylmaleimide. X-ray Structure Analysis of a 4,5-Diphospha-2-azabicyclo[3.2.0]hepta-1,3-dione

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The reaction of [(η^5-C_5Me_5)(CO)$_2$FeP=P—aryl (aryl = 2,4,6-t-$Bu_3C_6H_2$) with maleimide and *N*-methylmaleimide in benzene at 75 °C afforded the transition-metal-functionalized orange-red 1,2-diphosphetanes (η^5-C_5Me_5)(CO)$_2$Fe-P[C(H)C(O)N(R)C(O)CH]P-aryl, **3** (R = H) and **4** (R = CH_3), as a mixture of diastereoisomers. They result from an endo and/or exo [2 + 2] cycloaddition of the P=P double bond of **1** to the C=C functionality of the imides. The novel compounds were characterized by elemental analyses and spectroscopic methods (IR, ^{1}H, ^{13}C, and ^{31}P NMR, and mass spectroscopy). The molecular structure of the major isomer of 1,2-diphosphetane (η^5-C_5Me_5)(CO)$_2$Fe-P[C(H)C(O)N(CH_3)C(O)CH]P-aryl·0.5(C_2H_5)$_2$O (**4b**) was elucidated by a complete single-crystal diffraction study [$C2/c$ space group; Z = 8, a = 31.465 (7) Å, b = 14.131 (3) Å, c = 17.277 (3) Å, β = 94.850 (15)°].

Introduction

Low-coordinated phosphorus compounds as, e.g., diphosphenes $R^1P{=}PR^2$, are potential candidates for ambident reactivity, because they possess two high-lying molecular orbitals [π and n(P)] of similar energy.[2] The introduction of an electron-releasing metal fragment at the phosphorus center raises the energy of the n(P) orbital considerably and thus renders a nucleophilic low-coordinated P atom. In keeping with this, diphosphene **1** un-

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