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Carbonyl substitution reactions of carbomethoxycyclopentadienyldicarbonylcobalt(I) with bidentate phosphines. A kinetic and mechanistic study

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Abstract

The reactions of $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)_2$ with nucleophiles such as dppm, dppa, Ph_2Ppy and *t*-dppv [dppm = bis(diphenylphosphino)methane; dppa = bis(diphenylphosphino)amine; Ph_2Ppy = 2-(diphenyl)phosphino)pyridine; *t*-dppv = *trans*-1,2-vinylenebis(diphenylphosphine] give the monosubstituted products $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)L$, whereas when the ligand is dppe [bis(diphenylphosphino)ethane] the chelate compound is formed. The reactions are of first order in the metal complex and first order in the nucleophile.

Introduction

Substitution reactions of cyclopentadienylmetal compounds have been of special interest ever since Basolo and co-workers [1–4] studied the reactions of $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ and suggested that the presence of the cyclopentadienyl ligand promoted an associative pathway for carbonyl substitution reactions. This was attributed to the ability of the ligand to accept an electron pair from the metal, thus creating a vacant orbital susceptible to nucleophilic attack. This localization of a pair of electrons on the cyclopentadienyl ligand of a metal complex to allow associative substitution reactions is enhanced by the presence of electron-withdrawing substituents on the cyclopentadienyl ligand [4,5]. The cause of these associative substitution reactions of metal carbonyls with P-donor nucleophiles is known to depend on the basicity of the entering nucleophiles [1,6].

Tertiary diphosphine ligands have played a major role in coordination chemistry [7]; in particular, bis(diphenylphosphino)methane (dppm) has been much used [8,9]. In contrast, related systems such as, for instance, the isoelectronic bis(diphenylphosphino)amine (dppa), have received little attention [10–12].

We report here the synthesis of $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)_2$ and the kinetics of its reactions with nucleophiles such as dppm, dppe, dppa, Ph_2Ppy, and *t*-dppv that can behave as mono- or bidentate ligands. Some of these phosphines such as dppm and dppe have been used previously in carbonylcyclopentadienyl complexes such as $[(\eta^5\text{-}C_5Me_5)Co(dppm)I]I$ [13], $[(\eta^5\text{-}C_5H_5)Co(dppe)I]I$ [13], and $[(\eta^5\text{-}C_5H_4CO_2CH_3)\text{-}Co(diphos)I]I$ [14] (diphos = dppm and dppe), but the reactivity of potentially bidentate phosphines with carbonyicyclopentadienyl cobalt(I) complexes has been little studied.

Discussion

The presence of the electron-withdrawing carbomethoxy group on the cyclopentadienyl ring results in a shift of the $\nu(CO)$ bands (2034, 1974 cm^{-1}) to higher frequency with respect to those (2029, 1968 cm^{-1}) for the parent complex $(\eta^5\text{-}C_5H_5)Co(CO)_2$. This is attributed to a reduction in the backbonding between cobalt and carbon, making the CO bond more like the triple bond in free CO, and indicates that the cobalt is less electron-rich in the carbomethoxycyclopentadienyl complex, and because of this the compound is more reactive.

The reaction of $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)_2$ with dppm, dppa, Ph_2Ppy and *t*-dppv yields a monosubstituted product, as shown in eq. 1; the $\nu(CO)$ values are listed in Table 1; these $\nu(CO)$ bands appear at lower frequency than for the parent complex, and this is attributed to the better σ-donor character of these ligands. When the ligand is dppe the chelate is formed, and this can be attributed to the greater stability of a five-membered ring (eq. 2).

$$(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)_2 + L \rightarrow (\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)L + CO \qquad (1)$$

$$(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)_2 + dppe \rightarrow (\eta^5\text{-}C_5H_4CO_2CH_3)Co(dppe) + 2\ CO \qquad (2)$$

All the compounds were characterized of elemental analysis, and IR, ^1H and ^{31}P NMR spectroscopy. Table 1 lists IR spectral data for the substituted products. As usual in neutral complexes containing dppa the band due to $\nu(NH)$ (3320 cm^{-1}) is shifted to higher energies relative to that for the free ligand [12,15] (3225 cm^{-1}). In the Ph_2Ppy complex the bands due to $\nu(CN)$ (1568 and 1559 cm^{-1}) and $\delta(py)$ (619 cm^{-1}) are not shifted to higher energies with respect to the free ligand, showing that

Table 1

IR data for the complexes (cm^{-1}, Nujol)

Complex	$\nu(NH)$	$\nu(CO)$ [a]	$\nu(CO)(CO_2CH_3)$	$\nu(C{=}N)$	$\gamma(NH)$	$\nu(PC)$
Cp′Co(CO)(dppm)		1937.5 vs	1698 vs			692 vs 676 sh
Cp′Co(CO)(dppa)	3320 m	1941.2 vs	1714 vs		917 vs	695 vs 674 sh
Cp′Co(CO)(t-dppv)		1938.3 vs	1704 vs			694 vs 675 w
Cp′Co(CO)(Ph_2PPy)		1937.3 vs	1699 vs	1568 m 1559 m		694 vs 679 sh
Cp′Co(dppe)		–	1701 s			695 vs 675 w

Cp′ = $\eta^5\text{-}C_5H_4CO_2CH_3$. [a] In toluene.

Table 2

^{1}H and ^{31}P chemical shifts (δ) for (η^5-$C_5H_4CO_2CH_3$)Co(CO)L and (η^5-$C_5H_4CO_2CH_3$)Co(dppe) in $CDCl_3$

L	(δ) ppm
dppm	^{1}H: 3.24 (d, J(PH) = 15.0 Hz, 2H, CH_2); 7.25 (m, *m*- and *p*-H, 12H, C_6H_5); 7.43 (m, *o*-H, 8H, C_6H_5)
	^{31}P: 18.9 (d, P); −25.5 (d, P*); J(PP) = 180 Hz
dppa	^{1}H: 3.30 (s, br, 1H, NH); 7.24 (m, *m*- and *p*-H, 12H, C_6H_5); 7.36 (m, *o*-H, 8H, C_6H_5)
	^{31}P: 63.4 (d, P); −14.7 (d, P*); J(PP) = 100 Hz
t-dppv	^{1}H: 6.38 (m, 2H, CH=CH); 7.37 (m, *m*- and *p*-H, 12H, C_6H_5); 7.48 (m, *o*-H, 8H, C_6H_5)
	^{31}P: 61.0 (d, P); −0.9 (d, P*); J(PP) = 120 Hz
Ph_2Ppy	^{1}H: 7.13 (m, 5-py, 1H); 7.23 (m, 10H, C_6H_5); 7.52 (m, 3- and 4-py, 2H); 8.61 (m, 6-py, 1H)
	^{31}P: 65.5 (s, P)
dppe	^{1}H: 3.40 (m, 4H, CH_2); 7.35 (m, 2H, C_6H_5)
	^{31}P: 74.4 (s, P)

P = coordinated P; P* = uncoordinated P.

the Ph_2Ppy functions as a monodentate ligand and that the coordination takes place through the P-atom, whose base strength is lower than that of the N-atom. This is in accord with the fact that cobalt is a class b, or soft, metal.

The ^{31}P NMR data for these complexes are summarized in Table 2. The usual down-field (high frequency) shift of the ^{31}P resonance is observed when the phosphorus is coordinated to a metal [16]. For the (η^5-$C_5H_4CO_2CH_3$)Co(CO)-$(\overset{\frown}{P\ \ P^{\star}})$ $(\overset{\frown}{P\ \ P^{\star}}$ = dppm, dppa and *t* = dppv) two signals are observed in the ranges for coordinated, P, and uncoordinated, P*, phosphorus atoms. P* may either be shifted to higher field with respect to the free phosphine (as in dppa and dppm), to lower field (as in *t*-dppv), or may remain at the same position as the P resonance for the free phosphine [17]. For (η^5-$C_5H_4CO_2CH_3$)Co(dppe) the spectrum shows a singlet, due to the equivalence of the two P atoms.

Substitution reaction

The rate of reaction (eq. 1) is directly proportional to the concentration of the incoming ligand. Furthermore, as Fig. 1 shows, for L = dppm, dppa, Ph_2Ppy, and *t*-dppv there is a zero intercept of the plots for all ligands, indicating there is no detectable contribution from a ligand-independent (first-order) process under these conditions.

The second-order constants for the reaction (eq. 1) as well as the activation parameters calculated from an Arrhenius plot are shown in Table 3. The low activation enthalpies and high negative activation entropies provide further evidence for an associative, S_N2, mechanism. The mechanism for such reactions proposed by Basolo [1] is depicted in eq. 3.

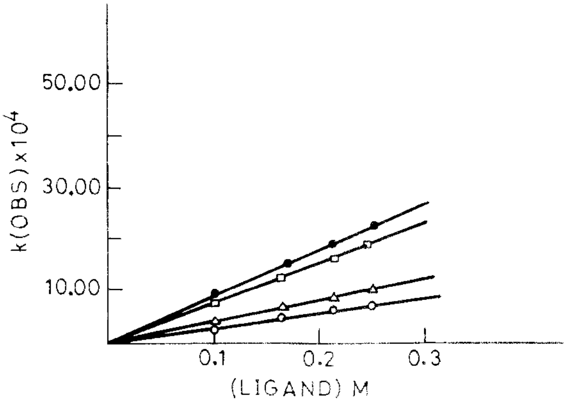
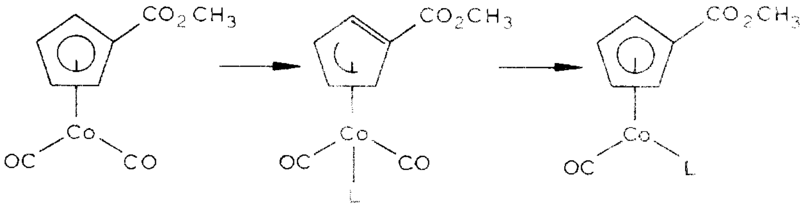


Fig. 1. Plot of k_{obs} (s^{-1}) vs. ligand concentration (M) for reaction 1 [T = 35.0 °C, L = dppa (●); T = 45.0 °C, L = dppm (△); T = 35.0 °C, L = T-dppv (□); T = 45.0 °C, L = Ph_2Ppy (○)].



(3)

It involves a transition state in which a rearrangement of the ring from a delocalized to an allyl-ene structure takes place, and the cobalt is bound only to the allyl portion.

The reaction with dppe proceeds in two consecutive steps to form the chelate (η^5-$C_5H_4CO_2CH_3$)Co(dppe) (eq. 4). The formation of the proposed intermediate is indicated by the appearance of a band at 1934.4 cm^{-1} during the reaction, a

Table 3

Rate constants and activation parameters (at 45 °C) for the CO-substitution reactions of (η^5-$C_5H_4CO_2CH_3$)Co$(CO)_2$ with L in toluene (eq. 1) (1 : 11.73, 1 : 25, 1 : 30 ratio)

L	T (°C)	$k_2 \times 10^3$ (M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)
dppm	45	3.98 ± 0.08	14.0 ± 0.5	−25 ± 1.7
	55	8.23 ± 0.02		
	65	14.8 ± 0.3		
dppa	35	9.41 ± 0.5	13.6 ± 0.9	−23 ± 3.0
	45	21.78 ± 0.05		
	55	38.3 ± 0.9		
t-dppv	45	7.8 ± 0.2	16.4 ± 0.7	−17 ± 2.2
	55	18.2 ± 0.3		
	65	36.5 ± 0.1		
Ph_2Ppy	45	2.77 ± 0.08	15.9 ± 0.7	−20 ± 2.1
	55	6.25 ± 0.01		
	65	12.4 ± 0.3		

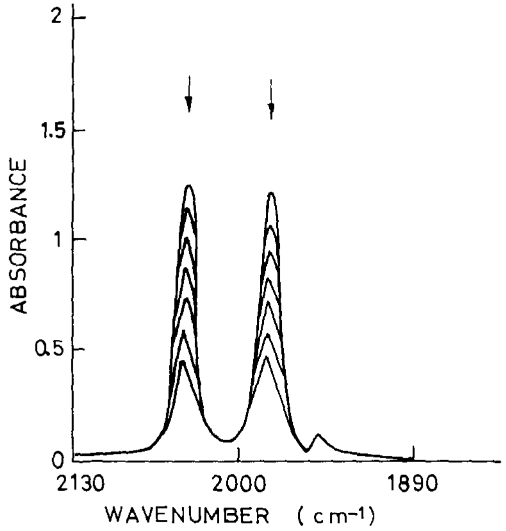


Fig. 2. Changes in infrared spectra for reaction 2 in toluene at 35.0 °C.

position similar to that observed after reaction with monodentate ligands (Table 1). As shown in Fig. 2 the absorbance for this band remains constant during the reaction, whereas those for the bands of $(\eta^5\text{-C}_5H_4CO_2CH_3)Co(CO)_2$ (2034, 1974 cm^{-1}) decrease.

$$Cp'Co(CO)_2 \xrightarrow[\substack{-CO\\+\,dppe}]{k_{obs}} Cp'Co(CO)(\eta^1\text{-dppe}) \xrightarrow[-CO]{k_1} Cp'Co(dppe) \tag{4}$$

$$Cp' = (\eta^5\text{-C}_5H_4CO_2CH_3)$$

The rate constant of the first stage is dependent on, and that of the second stage independent of [dppe] and both rate constants are independent of [CO], indicating an associative mechanism without a contribution from a dissociative mechanism (Table 4).

The rate law for formation of $(\eta^5\text{-C}_5H_4CO_2CH_3)Co(CO)(\eta^1\text{-dppe})$ is shown in eq. 5:

$$\frac{d[Cp'Co(CO)(\eta^1\text{-dppe})]}{dt} = k_{obs}[Cp'Co(CO)_2] - k_1[Cp'Co(CO)(\eta^1\text{-dppe})] \tag{5}$$

$$Cp' = (\eta^5\text{-C}_5H_4CO_2CH_3)$$

Since $(\eta^5\text{-C}_5H_4CO_2CH_3)Co(CO)(\eta^1\text{-dppe})$ is a very reactive intermediate and its concentration remains low and constant during the reaction (Fig. 2) we adopt the steady-state approximation [18], i.e. $d[Cp'Co(CO)(\eta^1\text{-dppe})]/dt = 0$, at steady state, and

$$k_{obs}[Cp'Co(CO)_2]_{ss} = k_1[Cp'Co(CO)(\eta^1\text{-dppe})]_{ss} \tag{6}$$

$$k_1 = \frac{k_{obs}[Cp'Co(CO)_2]_0\, e^{-k_{obs}t}}{[Cp'Co(CO)(\eta^1\text{-dppe})]_{ss}} \tag{7}$$

Table 4

Rate constants and activation parameters (at 45 °C) for the CO-substitution reaction of (η^5-$C_5H_4CO_2CH_3$)Co(CO)$_2$ with dppe in toluene

T (°C)	[L]	$k_{obs} \times 10^4$ (s^{-1})		$k_1 \times 10^4$ (s^{-1})	
		N_2 (100%)	CO (100%)	N_2 (100%)	CO (100%)
35	0.098	7.62 ± 0.01		11 ± 1	
35	0.169	13.0 ± 0.4		11 ± 1.2	
35	0.247	18.8 ± 0.5		11 ± 1.8	
45	0.098	13.8 ± 0.2	13.8 ± 0.1	28.7 ± 0.9	27 ± 1.7
55	0.098	29.2 ± 0.5		54 ± 1.2	

Activation parameters

$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (e.u.)
13 ± 1.5 [a]	−29 ± 4.5 [a]
16 ± 1.8 [b]	−20 ± 5.6 [b]

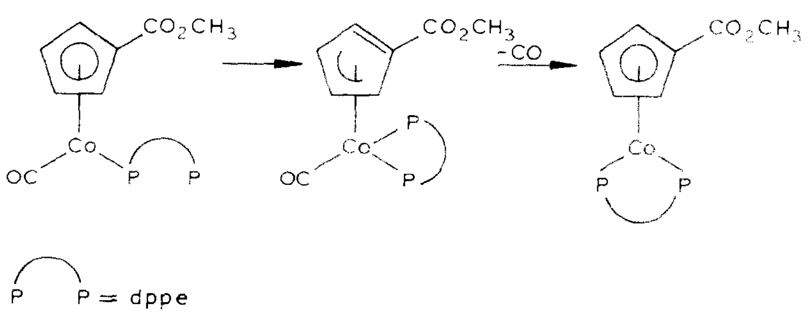
[a] $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)_2 + dppe \xrightarrow[-CO]{k_{obs}} (\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)(\eta^1\text{-dppe})$

[b] $(\eta^5\text{-}C_5H_4CO_2CH_3)Co(CO)(\eta^1\text{-dppe}) \xrightarrow{k_1} (\eta^5\text{-}C_5H_4CO_2CH_3)Co(dppe) + CO$

The observed pseudo first-order rate constant (k_{obs}) and the derived first-order constant (k_1) for the reaction, along with the activation parameters calculated from an Arrhenius plot, are shown in Table 4.

The k_2 values for L = dppm and dppe (k_{obs}/[dppe]) are comparable, as expected since the two ligands contain the same bonding atoms and the adjacent groups are similar (Tables 3 and 4). The activation parameters for this first stage of the reaction (Table 4) are characteristic of an associative mechanism. The activation parameters show that the chelate formation also takes place by an associative mechanism. This second stage of the reaction with the dppe ligand may be represented as follows (eq. 8):

The difference between the values $\Delta S^{\ddagger} = -29$ cal K^{-1} mol^{-1} for the intermolecular associative attack of dppe on (η^5-$C_5H_4CO_2CH_3$)Co(CO)$_2$ in the first stage and $\Delta S^{\ddagger} = -20$ cal K^{-1} mol^{-1} for chelate formation must reflect the much higher effective concentration of the uncoordinated P-atom in the intermediate, which



(8)

makes the second stage faster than the first, as is shown by the values of k_{obs} and k_1 (Table 4), although in terms of the values of $\Delta H^{\ddagger}$ the intermediate (η^5-$C_5H_4CO_2CH_3$)Co(CO)(η^1-dppe) is less susceptible to nucleophilic attack owing the presence of a coordinated P-donor atom.

Experimental

All operations were carried out by standard Schlenk techniques under oxygen-free N_2. Toluene, benzene, hexane, and tetrahydrofuran were dried and distilled from Na in the presence of benzophenone under N_2, then N_2 was bubbled through for 1 h and the purified solvents stored under nitrogen.

The reagents dppm [19], dppe [19], dppa [20], Ph_2Ppy [21], and *t*-dppv [22] were prepared by published methods and characterized by their IR, ^1H and ^{31}P NMR spectra. The melting points and elemental analyses were in good agreement with reported values.

The complex (η^5-$C_5H_4CO_2CH_3$)Co$(CO)_2$ was prepared as previously described [23] and characterized by its IR and ^1H NMR spectra.

^1H and ^{31}P NMR spectra were recorded on a Bruker WH-200-SY (200 MHz) FT mode spectrometer. Deuteriated $CDCl_3$ was dried and degassed. All ^1H NMR chemical shifts are relative to TMS. Values of $\delta(^{31}P)$ are relative to 85% H_3PO_4. IR spectra were recorded on a Nicolet 5DX FT-IR spectrometer; for kinetic measurements the absorbance mode was used.

Analyses were carried out by the Microanalytical Laboratory of this department. The cobalt was determined by titration of the Co-EDTA complex in the presence of NET as indicator.

Preparation of (η^5-$C_5H_4CO_2CH_3$)Co(CO)L (I) (L = dppm, dppa, Ph_2Ppy and t*-dppv) and (η^5-$C_5H_4CO_3CH_3$)Co(dppe) (II)*

To a 30 ml benzene solution of (η^5-$C_5H_4CO_2CH_3$)Co$(CO)_2$ (2 g, 8.40 mmol) in a nitrogen-filled 100 ml Schlenk flask a solution of L (8.40 mmol) in the same solvent was slowly added by ampoule transfer. The mixture was stirred and then, refluxed for ca. 12 h, then allowed to cool to room temperature. The solution was filtered and the solvent removed under vacuum. The product was recrystallized from 1/4 benzene–hexane. The red-brown crystals obtained were dried at room temperature under high vacuum; the yields were ca. 85%. The more relevant IR (benzene) and

Table 5

Analytical data for (η^5-$C_5H_4CO_2CH_3$)Co(CO)L and (η^5-$C_5H_4CO_2CH_3$)Co(dppe) [a]

L	Yield (%)	Co (%)		C (%)		H (%)		N (%)	
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
dppm	82	9.87	9.91	66.23	66.63	4.64	4.48	–	–
dppa	78	9.86	9.90	64.04	64.50	4.58	4.70	2.34	2.35
t-dppv	84	9.79	9.72	61.35	61.40	4.15	4.29	–	–
dppe	89	10.26	10.16	67.83	68.29	4.97	5.34	–	–
Ph_2Ppy	92	12.28	12.45	63.04	63.39	4.36	4.46	3.02	2.96

[a] The microanalyses were performed by the Microanalytical Laboratory of this department.

^{1}H, ^{31}P NMR ($CDCl_3$) spectroscopic data for the complexes (η^5-$C_5H_4CO_2CH_3$)Co(CO)L and (η^5-$C_5H_4CO_2CH_3$)Co(dppe) are listed in Tables 1 and 2. The elemental analyses are shown in Table 5.

Kinetic measurements

Toluene solutions of both the ligand and the compound (η^5-$C_5H_4CO_2CH_3$)-$Co(CO)_2$ were placed under nitrogen in an aluminium foil-wrapped Schlenk flask which was kept in a constant-temperature (±0.2°C) bath. At zero time the solution of phosphine was added from a syringe to the cobalt compound to give between 5 and 8 cm^3 of reaction mixture. Aliquots were subsequently withdrawn through a rubber septum with a syringe at intervals allowing 5–10 analyses during 1–3 half-lives of reaction and transferred to a 0.5 mm NaCl cell. The IR cell was flushed with N_2 and sealed with rubber septum before use.

The progress of the reaction was monitored by observing the disappearance of the highest frequency carbonyl stretching band of the complexes (η^5-$C_5H_4CO_2CH_3$)$Co(CO)_2$; the absorbance mode was used. Plots of log A vs. time were linear for more than three half-lives, and k_{obs} was determined from the slope of this line by the least-squares method. The correlation coefficient for the least-squares line ($R^2 > 0.996$) was very high.

Approximately 8.5×10^{-3} M solutions of complex were used, and all kinetic experiments were carried out under pseudo first-order conditions with at least a ten-fold excess of ligand present. The reactions went to completion to give the corresponding monocarbonyl products (η^5-$C_5H_4CO_2CH_3$)Co(CO)L when the ligand was dppm, dppa, Ph_2Ppy or t-dppv, and the chelate product when the ligand was dppe.

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