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Kinetics of nucleophilic attack on coordinated organic moieties

XXVII *. Kinetics and mechanism of addition of tertiary phosphines and phosphites to $[Co(C_5H_5)(\eta^5\text{-}C_8H_{11})]^+$ and related cobalt cations

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Abstract

Kinetic data are reported for the addition of a range of tertiary phosphines and phosphites to the dienyl cation $[Co(C_5H_5)(\eta^5\text{-}C_8H_{11})]$ (I) (eq. 1). The rate law depends on the nature of the nucleophile. For example, the reactions with PBu^n_3 and $P(OBu^n)_3$ obey the expression $k_{obs} = k_1\,[PR_3]$, while the two-term equation $k_{obs} = k_1\,[PR_3] + k_{-1}$ is followed for the reversible addition of PPh_3. The low enthalpies of activation ($\Delta H_1^{\#}$ 15–36 kJ mol^{-1}) are consistent with bimolecular addition of PR_3 to the C_8H_{11} ligand, as are the large negative entropies of activation ($\Delta S_1^{\#}$ -91 to -124 J K^{-1} mol^{-1}). The basicity of the phosphorus nucleophiles is shown to be important (Bronsted slope, α, ca. 0.5) in determining the nucleophilicity towards cation I. An excellent linear free energy relationship is found between reactions 1 and the related additions of phosphines and phosphites to the cation $[Fe(CO)_3(1\text{–}5\text{-}\eta\text{-}C_6H_7)]^+$, suggesting similar transition states for each process.

$$I + PR_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Co(C_5H_5)(R_3PC_8H_{11})]^+ \qquad (1)$$

The analogous additions of PBu^n_3 to the cations $[Co(C_5H_5(1\text{–}5\text{-}\eta\text{-}C_6H_7)]^+$ (IIIa) and $[Co(C_5H_5)(1\text{–}5\text{-}\eta\text{-}C_7H_9)]^+$ (IIIb) are very much slower. The relative electrophilicities of the cations I ≫ IIIa ≫ IIIb (rel. rates $4 \times 10^4/2.5 \times 10^2/1$) are found to be enthalpy controlled ($\Delta H_1^{\#}$ 15, 31 and 38 kJ mol^{-1}, respectively).

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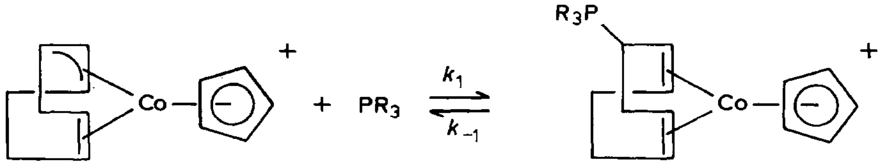
* For part XXVI see ref. 14.

Introduction

Considerable kinetic information has been accumulated in recent years on the addition of nucleophiles to transition metal-coordinated π-hydrocarbons. As a result, our understanding of the factors controlling reactivity in such systems has grown considerably, and has been the subject of a recent review [1].

However, almost all the quantitative data obtained to date have involved metals from the chromium, manganese, and especially iron triads. Apart from one brief report [2], there have been no quantitative studies of nucleophile attack on π-hydrocarbons coordinated to cobalt moieties.

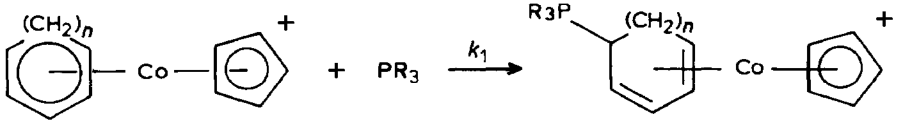
In this paper we describe detailed kinetic studies of the addition of a range of phosphorus nucleophiles to the enyl cation $[Co(C_5H_5)(\eta^5\text{-}C_8H_{11})]^+$ (I) (eq. 1; R = Ph, 4-MeC_6H_4, 2-CNC_2H_4, Bu^n, OBu^n, OEt, OMe).



(1)

(I) (II)

Kinetic data are also reported for the additions of tri-η-butylphosphine to the cyclohexadienyl and cycloheptadienyl complexes $[Co(C_5H_5)(1\text{-}5\text{-}\eta\text{-}C_6H_7)]^+$ (IIIa) and $[Co(C_5H_5)(1\text{-}5\text{-}\eta\text{-}C_7H_9)]^+$ (IIIb) (eq. 2, $n = 1$ or 2). This allows direct comparison with results for the thoroughly studied dienyliron cations $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-dienyl})]^+$.



(2)

(III) (IV)

Experimental

Materials

The salts $[Cp(C_5H_5)(\eta^5\text{-}C_8H_{11})][PF_6]$ (I), $[Co(C_5H_5)(1\text{-}5\text{-}\eta\text{-}C_6H_7)][PF_6]$ (IIIa), and $[Co(C_5H_5)(1\text{-}5\text{-}\eta\text{-}C_7H_9)]$ $[PF_6]$ (IIIb) were prepared and purified by published procedures [3–5].

The phosphorus nucleophiles were purchased in the purest grades available (Strem Ltd. or Aldrich Ltd.) and used as supplied. Tri-n-butylphosphine was stored under dinitrogen. Acetone solvent was analytical grade, and was deoxygenated by passage of a stream of dinitrogen for 20 min. Solutions of the appropriate phosphorus nucleophile were prepared under dinitrogen immediately before use.

Kinetic studies

All reactions **1** and **2** in acetone were rapid and were monitored at 380 nm by use of a thermostatted (±0.1° C) stopped-flow spectrophotometer. At this wavelength a large decrease in absorbance was observed for each reaction.

The reactions were generally studied under pseudo-first-order conditions, involving a large excess of phosphorus nucleophile. Pseudo-first-order rate constants, k_{obs}, were calculated from the slopes of plots of log $(A_t - A_\infty)$ vs. time. Such plots were generally linear for at least two half-lives. Each k_{obs} is the average of at least three separate runs, with an average reproducibility of ±5%.

In the case of PBu^n_3 attack on cation I, equimolar conditions ($[Co] = [PBu^n_3] = 5 \times 10^{-4}$ mol dm^{-3}) were employed. Second order rate constants, k_1, for this reaction were obtained directly from the slope of plots of $x/a(a-x)$ vs. time, where a is the initial concentration of I and x is the concentration of the phosphonium adduct at time t. These runs were carried out in quadruplicate, with a reproducibility of ±5%.

Results and discussion

Nature of the reactions

It was previously established by one of us [5] that cationic complexes of cobalt of the general type $[Co(C_5H_5)(dienyl)]^+$ (dienyl = C_8H_{11}, C_6H_7 and C_7H_9) are remarkably stable, as is evident from the fact that all the cations can be recrystallised from hot water without hydrolysis. Addition of PPh_3 and PPr^i_3 to the cation I has been shown [2,5,6] to occur at the enyl fragment of the C_8H_{11} ligand, as in eq. 1. Analogous regiospecificity is assumed in each of the reactions 1 examined here.

Similarly, exclusive addition of trialkylphosphines to the C(1) site on the dienyl ligands in complexes IIIa and IIIb has been unequivocally established from ^{13}C NMR spectroscopy, and the phosphonium adducts (IV, $R = Pr^i$) isolated in quantitative yield [5]. It is now generally accepted that in most cases additions of this type give *exo*-products. In the case of the related cobalticenium salt, $[Co(C_5H_5)_2]^+$, this has been clearly demonstrated by an X-ray structure determination [7].

Kinetics and mechanism

Kinetic results for the reactions of various phosphorus nucleophiles with $[Co(C_5H_5)(\eta^5\text{-}C_8H_{11})]^+$ (I) are summarised in Tables 1 and 2. For the nucleophiles PBu^n_3 and $P(OBu^n)_3$, the second-order rate law 3 was confirmed at each of the temperatures employed.

$$Rate = k_1[Co][PR_3] \quad (3)$$

With PPh_3, this rate law is also obeyed within experimental error for temperatures up to 6.2° C. However, at temperatures ≥ 19° C, plots of k_{obs} vs. $[PPh_3]$ reveal small but non-zero intercepts, indicating the two-term rate law 4. This may be

$$Rate = k_{obs}\,[Co]$$

$$k_{obs} = k_1[PPh_3] + k_{-1} \quad (4)$$

rationalised in terms of an equilibrium process in which k_1 is the second-order rate constant for addition of PPh_3 to the enyl ligand in reaction 1, and k_{-1} is the first-order rate constant for the reverse dissociation of the phosphonium adduct II. Combination of the k_1 and k_{-1} values gives an equilibrium constant K_1 ($= k_1/k_{-1}$)

Table 1

Kinetic data for the reaction of $[CoCp(\eta^5\text{-}C_8H_{11})]PF_6$ with PPh_3 in acetone

Temperature (°C)	$10^3[PPh_3]$ (mol dm^{-3})	k_{obs} (s^{-1})	k_1[a] (dm^3 mol^{-1} s^{-1})	k_{-1}[a] (s^{-1})
0.15	3.0	2.20		
	5.0	3.49		
	10.0	6.51	696(6)	–[b]
	28.5	19.4		
	50.0	34.9		
6.2	3.0	2.79		
	5.0	4.70		
	10.0	8.92	776(26)	0.48(0.69)
	30.0	21.8		
	50.0	40.3		
19.4	3.0	6.20		
	5.0	9.82	1150(40)	3.82(0.64)
	10.0	16.5		
	30.0	37.7		
23.9	3.0	8.90		
	5.0	10.7		
	10.0	19.3	1329(19)	5.10(0.50)
	30.0	45.7		
	50.0	71.0		
27.0	2.9	11.9		
	5.0	14.8		
	10.0	22.7	1560(7)	7.24(0.18)
	30.0	54.6		
	50.0	85.0		

[a] Calculated by a least squares analysis of eq. 4. [b] Too small for accurate measurement.

Table 2

Kinetic data for the reaction of $[CoCp(\eta^5\text{-}C_8H_{11})]PF_6$ with other P nucleophiles in acetone

Nucleophile	Temperature (°C)	$10^3[PR_3]$ (mol dm^{-3})	k_{obs} (s^{-1})	k_1 (dm^3 mol^{-1} s^{-1})
$P(4\text{-}MeOC_6H_4)_3$	0.0	5.5	23.7	4310
$P(2\text{-}CNC_2H_4)_3$	0.0	17.0	0.55	32.4
$P(Bu^n)_3$	0.0			27100[a]
	22.1			49700[a]
	31.0			57100[a]
	40.0			73800[a]
$P(OBu^n)_3$	0.0			9.80[b]
	15.5			23.9[b]
	24.4			40.6[b]
	33.1			62.0[b]
$P(OMe)_3$	0.0			3.02

[a] From equimolar ($[Fe] = [PBu^n_3] = 5 \times 10^{-4}$ mol dm^{-3}) experiment. [b] Rate law $k_{obs} = k_1\,[P(OBu^n)_3]$ obeyed at each temperature.

for reaction 1 (R = Ph) varying between 301 (19.4 °C) and 215 (27.0 °C). For the other phosphorus nucleophiles employed, the simple rate law 3 has been assumed.

Activation parameters determined for reactions 1 (R = Ph, Bu^n, OBu^n) are listed in Table 3. The low enthalpies of activation calculated for each of these reactions ($\Delta H_1^{\#}$ 15–36 kJ mol^{-1}) are consistent with bimolecular addition (k_1) to the enyl ligand, as are the large negative entropies of activation ($\Delta S_1^{\#}$ −91 to −124 J K^{-1} mol^{-1}). In contrast, the reverse k_{-1} step exhibits a positive $\Delta S^{\#}_{-1}$ value (+72 J K^{-1} mol^{-1}), as expected for a dissociative process. Also consistent with cleavage of the carbon-phosphorus bond in the phosphonium adduct II is the relatively large $\Delta H^{\#}_{-1}$ (90 kJ mol^{-1}).

For substrate I the nucleophilicity order $PBu^n_3 > PPh_3 > P(OBu^n)_3$ (rel. rates 2800/70/1) is seen to be enthalpy controlled, with the reaction of the very reactive PBu^n_3 showing one of the lowest $\Delta H_1^{\#}$ values yet determined for addition to a coordinated η-hydrocarbon.

As previously noted [8] for related reactions on $[Fe(CO)_3(dienyl)]^+$ substrates, the rate of phosphine addition to the enyl cation I is strongly influenced by the nucleophile basicity. Separate two-point plots of log k_1 vs. pK_a (H_2O) for both tris(-aryl)- and tris(-alkyl)-phosphines give Brönsted slopes of ca. 0.5 in each case. For the weakly basic $P(OPh)_3$ no reaction with I could be detected.

A close parallel between reaction I and the well-studied [8] phosphine/phosphite additions to the dienyl cation $[Fe(CO)_3(1\text{–}5\text{-}\eta\text{-}C_6H_7)]^+$ is revealed by the excellent linear free energy relationship shown in Fig. 1 ($r = 0.99$). The slope of 0.98 (0.04) suggests a similar transition state for both sets of reactions.

Kinetic data for the related additions of PBu^n_3 to the cations $[Co(C_5H_5)(1\text{–}5\text{-}\eta\text{-}dienyl)]^+$ (dienyl = C_6H_7 or C_7H_9) (eq. 2) are collected in Table 4. The second-order rate constants, k_1, for addition to the dienyl rings were calculated assuming relationship 3. Table 5 summarises rate and activation parameters thus calculated for PBu^n_3 addition to each of the $[Co(C_5H_5)(\pi\text{-hydrocarbon})]^+$ cations studied here. At 20 °C, k_1 is seen to decrease markedly down the target π-hydrocarbon series $C_8H_{11} \gg C_6H_7 \gg C_7H_9$ (relative rates ca. $3.8 \times 10^4/2.5 \times 10^2/1$). This cation electrophilicity order is enthalpy controlled, the more reactive C_8H_{11} substrate having a very low $\Delta H_1^{\#}$ of 15 kJ mol^{-1}, and the least reactive C_7H_9 cation having the highest $\Delta H_1^{\#}$ of 38 kJ mol^{-1}. The large negative $\Delta S_1^{\#}$ values observed for each reaction are consistent with general bimolecular addition to the π-hydrocarbon ligands.

Table 3

Rate and activation parameters for the reactions of $[Co(C_5H_5)(\eta^5\text{-}C_8H_{11})]^+$ with phosphorus nucleophiles in acetone

PR_3	k_1(0 °C) (dm^3 mol^{-1} s^{-1})	$\Delta H_1^{\#}$ (kJ mol^{-1})	$\Delta S_1^{\#}$ (J K^{-1} mol^{-1})	$\Delta H^{\#}_{-1}$ (kJ mol^{-1})	$\Delta S^{\#}_{-1}$ (J K^{-1} mol^{-1})
PBu^n_3	27100	14.9(0.9)	−104(4)		
$P(4\text{-}MeOC_6H_4)_3$	4310				
PPh_3	690	17.6(1.6)	−124(6)	89.5(8.1)	72(16)
$P(2\text{-}CNC_2H_4)_3$	32.4				
$P(OBu^n)_3$	9.8	36.4(0.7)	−91(3)		
$P(OMe)_3$	3.0				

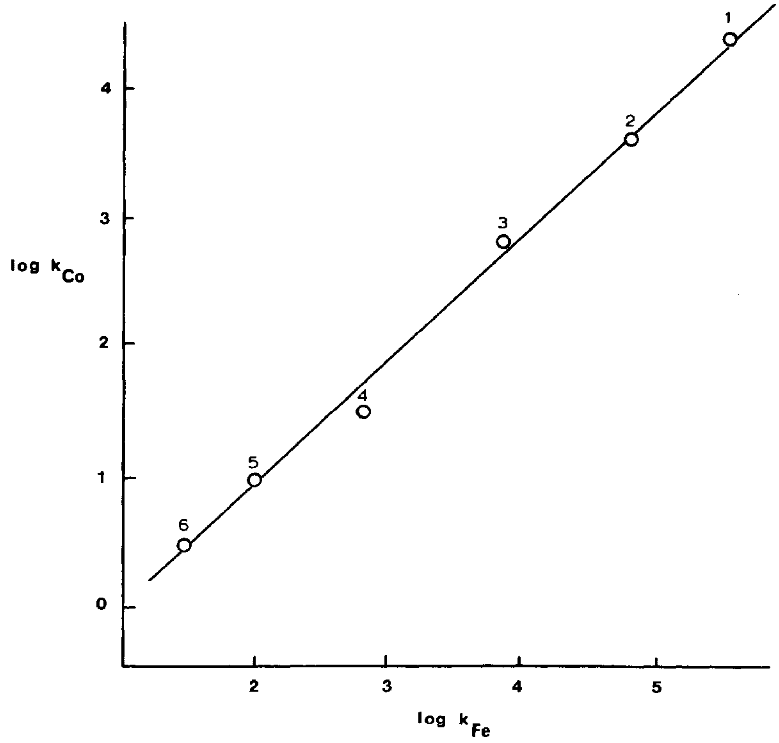


Fig. 1. Plot of values of log k_1 for I at 0 °C against those for $[Fe(CO)_3(1\text{–}5\text{-}\eta\text{-}C_6H_7)]^+$ at 20 °C for reactions with phosphorus nucleophiles in acetone: 1, PBu^n_3; 2, $P(4\text{-}MeOC_6H_4)_3$; 3, PPh_3; 4, $P(2\text{-}CNC_2H_4)_3$; 5, $P(OBu^n)_3$; 6, $P(OMe)_3$.

The rate sequence $C_6H_7 \gg C_7H_9$ supports direct addition of PBu^n_3 from above the dienyl ring. As discussed in previous studies [8] of phosphine addition to related $[Fe(CO)_3(dienyl)]^+$ cations, the additional methylene group in the C_7H_9 ligand is expected to markedly enhance steric hindrance to the vertical approach of a

Table 4

Kinetic data for the reactions of $[CoCp(\eta^5\text{-dienyl})]^+$ cations with PBu^n_3 in acetone

Complex	Temperature (°C)	k_{obs} (s^{-1})	k_1 ($dm^3\ mol^{-1}\ s^{-1}$)
$[CoCp(\eta^5\text{-}C_6H_7)]^+$ [a]	0.0	28.5	113
	5.9	40.1	159
	10.5	49.9	198
	18.2	72.8	289
	20.2	77.9	309
$[CoCp(\eta^5\text{-}C_7H_9)]^+$ [b]	23.7	0.031	1.51
	36.2	0.059	2.92
	40.3	0.073	3.61
	45.2	0.095	4.66
	49.3	0.112	5.50

[a] [Co] 3.4×10^{-4} mol dm^{-3}, [PBu^n_3] 0.252 mol dm^{-3}. [b] [Co] 1.1×10^{-4} mol dm^{-3}, [PBu^n_3] 2.03×10^{-2} mol dm^{-3}.

Table 5

Rate and activation parameters for the addition of PBu^n_3 to $[Co(C_5H_5)(\pi\text{-hydrocarbon})]^+$ cations in acetone

Cation	k_1(20 °C) (dm^3 mol^{-1} s^{-1})	$\Delta H_1^{\#}$ (kJ mol^{-1})	$\Delta S_1^{\#}$ (J K^{-1} mol^{-1})
$[Co(C_5H_5)(\eta^5\text{-}C_8H_{11})]^+$	46000	14.9(0.9)	−104(4)
$[Co(C_5H_5)(\eta^5\text{-}C_6H_7)]^+$	305	30.6(1.6)	−92(6)
$[Co(C_5H_5)(\eta^5\text{-}C_7H_9)]^+$	1.22	38.0(0.5)	−113(2)

Table 6

Relative electrophilicities of $[ML_n(\pi\text{-hydrocarbon})]^+$ cations towards PBu^n_3 at 20 °C

Cation	Solvent	k_1 (20 °C) (dm^3 mol^{-1} s^{-1})	Relative k_1	Ref.
$[Fe(CO)_3(C_6H_7)]^+$	acetone	340000	2.8×10^5	8
$[Fe(CO)(NO)(PPh_3)(C_4H_4)]^+$	CH_3NO_2	120000 [a]	9.8×10^4	10
$[CoCp(C_8H_{11})]^+$	acetone	46000	3.8×10^4	This work
$[Cr(CO)_3(C_7H_7)]^+$	acetone	41000	3.4×10^4	1
$[Fe(CO)_3(C_7H_9)]^+$	acetone	11100	9.1×10^3	13
$[Mn(CO)(NO)(PPh_3)(C_6H_7)]^+$	CH_3CN	4500 [a]	3.7×10^3	11
$[FeCp(C_7H_8)]^+$	acetone	2200 [a]	1.8×10^3	1
$[Mn(CO)_3(C_6H_6)]^+$	CH_3NO_2	2000 [a]	1.6×10^3	12
$[Re(CO)_3(C_6H_6)]^+$	CH_3NO_2	1800 [a]	1.5×10^3	12
$[Mn(CO)_3(MeC_6H_5)]^+$	CH_3NO_2	1500 [a]	1.2×10^3	1
$[Mn(CO)_2(NO)(6\text{-}PhC_6H_6)]^+$	CH_3NO_2	1000 [a]	8.2×10^2	1
$[Re(CO)_3(MeC_6H_5)]^+$	CH_3NO_2	750 [a]	6.1×10^2	1
$[CoCp(C_6H_7)]^+$	acetone	305	2.5×10^2	This work
$[FeCp(CO)_2(CH_2CH_2)]^+$	acetone	82	67	1
$[CoCp(C_7H_9)]^+$	acetone	1.22	1	This work

[a] Temperature 25 °C.

nucleophile to the C(5) carbon atom of the dienyl ring (Fig. 2). In a recent communication, one of us suggested [9] that $k(C_6H_7)/k(C_7H_9)$ ratios may be a useful measure of the extent of C(5)–nucleophile bond formation in additions to $[ML_n(\text{dienyl})]$ substrates. The $k(C_6H_7)/k(C_7H_9)$ ratio of 250 recorded here for the cobalt reactions 2 is the highest yet reported, being considerably larger than the quotient of ca. 50 described for the additions of PBu^n_3 to $[Fe(CO)_3(\text{dienyl})]^+$ cations. This suggests a relatively "late" transition state for reactions 2, involving considerable carbon–phosphorus bond formation.

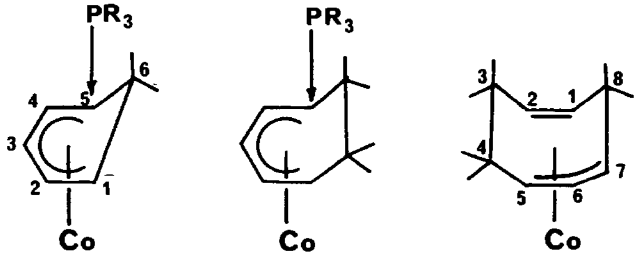


Fig. 2. Approach of PR_3 from above the dienyl rings of $[CoCp(C_6H_7)]^+$, $[CoCp(C_7H_9)]^+$ and $[CoCp(C_8H_{11})]^+$.

Similar steric considerations would readily explain why nucleophilic attack on $[Co(C_5H_5)(\eta^5\text{-}C_8H_{11})]^+$ occurs exclusively at the enyl C(7) atom rather than at the more blocked C(5) centre (Fig. 2). The origin of the much greater reactivity of the C_8H_{11} ligand compared to C_6H_7 is uncertain, and may be associated with differences in the σ- and π-bonding interactions of the two hydrocarbons with the $Co(C_5H_5)$ moiety. Consideration of an alternative explanation, based on only a small bending of the C(8) methylene group away from the C(5)–C(7) plane, must await an X-ray crystallographic study of I.

Finally, combination of the present results with previous data [1,8] for PBu^n_3 addition to other organometallic substrates, gives rise to the relative electrophilicity order shown in Table 6 for $[ML_n(\pi\text{-hydrocarbon})]^+$ cations.

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