Kinetics and Mechanism of Addition of Tertiary Phosphines and Phosphites to the Dicarbonyl(η^5-cyclopentadienyl)(η-ethene)iron Cation†

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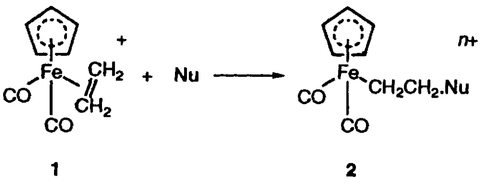
Kinetic studies of the addition of a range of tertiary phosphine and phosphite nucleophiles PR_3 to the cation $[Fe(cp)(CO)_2(\eta\text{-}C_2H_4)]^+$ **1** (cp = η^5-C_5H_5) [equation (i)] revealed the general rate law, Rate = $k_1[Fe][PR_3]$. The second-order rate constants k_1 decrease markedly down the order $P(C_6H_4OMe\text{-}2)_3$ > PBu^n_3 > $P(C_6H_4OMe\text{-}4)_3$ > $P(C_6H_4Me\text{-}4)_3$ > $P(C_6H_4Me\text{-}4)Ph_2$ > PPh_3 > $P(C_2H_4CN\text{-}2)Ph_2$ > $P(C_2H_4CN\text{-}2)_3$ > $P(C_6H_4Cl\text{-}4)_3$ > $P(OBu^n)_3$. This reactivity order parallels that of decreasing electron availability at the phosphorus centre, as shown quantitatively by the good correlation between log k_1 and the Tolman $\Sigma\chi$ values. An excellent fit to the Hammett and Brønsted equations is also observed for reaction (i) with the nucleophiles $P(C_6H_4X\text{-}4)_3$. The moderate Brønsted slope α of

$$[Fe(cp)(CO)_2(\eta\text{-}C_2H_4)]^+ + PR_3 \longrightarrow [Fe(cp)(CO)_2(C_2H_4PR_3)]^+ \qquad \text{(i)}$$

0.46 establishes the importance of phosphine basicity in determining nucleophilicity towards the ethene ligand in cation **1**. These results, together with the large negative entropy of activation with PPh_3 ($\Delta S^\ddagger_1 = -103$ J K^{-1} mol^{-1}), are interpreted in terms of direct addition (k_1) of the phosphorus nucleophiles to the ethene ligand in **1** and suggest a transition state in which there is build-up of positive charge on the phosphorus centre and considerable phosphorus–carbon bond formation.

The addition of nucleophiles to metal-co-ordinated alkenes is a reaction widely encountered in organometallic chemistry and has significant potential in organic synthesis.[2–4] Industrially important examples include the Pd^{2+}-catalysed conversion of ethene into acetaldehyde in the Wacker Process. Surprisingly, apart from the Wacker Process which has been extensively studied,[5] very few kinetic studies have been reported[6–10] for such processes and little quantitative information is available concerning the factors controlling co-ordinated alkene reactivity.

A particularly attractive substrate for such a systematic investigation is the ethene complex $[Fe(cp)(CO)_2(\eta\text{-}C_2H_4)]BF_4$ **1** (cp = η^5-C_5H_5). This cation has been shown[3,4,11,12] to react with a wide range of anionic and neutral nucleophiles according to Scheme 1 (nucleophile, Nu = RO^-, RS^-, RNH_2, C_5H_5N, PR_3, *etc.*; n = 0 or 1), establishing it as a useful stoichiometric reagent in organic synthesis. In the present study we report detailed kinetic and spectroscopic studies for the addition of a wide range of tertiary phosphines and phosphites to cation **1** where Nu = $P(C_6H_4X)_3$ (X = H, 4-MeO, 4-Me or 4-Cl), $PPh_2(C_6H_4Me\text{-}4)$, $PPh_2(C_2H_4CN\text{-}2)$, $P(C_2H_4CN\text{-}2)_3$, PBu^n_3 or $P(OBu^n)_3$. Formation of the phosphonium adduct **2** with Nu = PPh_3 has been previously reported by Rosenblum and coworkers.[4] Synthetic and spectroscopic studies described here confirm the formation of analogous adducts with each of the other phosphorus nucleophiles. The kinetic results are consistent with direct bimolecular addition to the ethene ligand and establish quantitatively the importance of electronic factors (*e.g.* nucleophile basicity) in the reactions where Nu = PR_3 or $P(OR)_3$. Structure–reactivity relationships provide useful information as to the nature of the transition states in these reactions. Comparison with kinetic data previously obtained[13–16] for the related additions of tertiary phosphines and phosphites to other π-hydrocarbon metal complexes indicates that the relative nucleophilicities of phosphorus nucleophiles are independent of the nature or reactivity of the organometallic substrate. A preliminary report of the kinetics of the reactions of PPh_3 and PBu_3 with cation **1** has appeared.[6]



Scheme 1

Experimental

Materials.—The tertiary phosphines were used as supplied from Strem Chemicals Inc. Tri-*n*-butyl phosphite (Aldrich) was freshly distilled and stored under dinitrogen prior to use. Acetone solvent (ANALAR grade) was deoxygenated by bubbling a stream of dinitrogen through it for 30 min, and solutions for the kinetic runs were prepared under dinitrogen immediately prior to use. The substrate complex $[Fe(cp)(CO)_2(\eta\text{-}C_2H_4)]BF_4$ **1** was prepared according to published procedures,[4b] recrystallised from light petroleum (b.p. 40–60 °C)–acetone and stored in the dark (Found: C, 36.8; H, 3.0; O, 18.9. Calc. for $C_9H_9BF_4FeO_2$: C, 37.0; H, 3.1; O, 19.1%).

Preparation of Phosphonium Adducts.—Representative examples of the new phosphonium adducts with $[Fe(cp)(CO)_2(\eta\text{-}C_2H_4)]BF_4$ **1** were isolated and purified using procedures similar to those reported previously[4] for the triphenylphosphine adduct. Each of the other phosphonium adducts with **1** were prepared *in situ* and characterised by their ^1H NMR and/or IR spectra (Table 1).

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† Kinetics of nucleophilic attack on co-ordinated organic moieties. Part 30.[1]

Dicarbonyl(η-cyclopentadienyl){2-[tris(2-methoxyphenyl)-phosphonio]ethyl}iron tetrafluoroborate **2a**. Tris(2-methoxyphenyl)phosphine (36 mg, 0.10 mmol) was added to a solution of the salt $[Fe(cp)(CO)_2(\eta-C_2H_4)]BF_4$ **1** (30 mg, 0.10 mmol) in dry acetone (1 cm^3) under dinitrogen and the solution stirred at room temperature for 15 min. Dropwise addition of an excess of diethyl ether and cooling in an ice-bath gave a yellow precipitate of the product (52 mg, 81%), which was recrystallised from dichloromethane–diethyl ether (Found: C, 56.6; H, 4.7. Calc. for $C_{30}H_{30}BF_4FeO_5P$: C, 55.9; H, 4.7%). ^{1}H NMR [$(CD_3)_2CO$]: δ 7.85–7.25 (aryl), 5.06 (s, 5 H, cp), 3.81 (s, 9 H, OMe), 3.39 [dd, 2 H, CH_2P, J(P–H) = 18, J(H–H) = 11], and 1.29 [dd, 2 H, CH_2Fe, J(P–H) = 18, J(H–H) = 10 Hz]. Electrospray mass spectrum: m/z 557, $[M]^+$.

Dicarbonyl(η-cyclopentadienyl){2-[tris(4-methoxyphenyl)-phosphonio]ethyl}iron tetrafluoroborate **2b**. A similar procedure to the above gave complex **2b** in 90% yield (Found: C, 55.1; H, 4.7. Calc. for $C_{30}H_{30}BF_4FeO_5P$: C, 55.9, H, 4.7%). ^{1}H NMR [$(CD_3)_2CO$]: δ 7.85–7.55 (aryl), 5.09 (s, 5 H, cp), 3.82 (s, 9 H, OMe), 3.52 (m, 2 H, CH_2P) and 1.38 (m, 2 H, CH_2Fe).

Dicarbonyl(η-cyclopentadienyl){2-[tris(4-tolyl)phosphonio]-ethyl}iron tetrafluoroborate **2c**. A similar procedure to the above employing equimolar (0.10 mmol) tris(4-tolyl)phosphine and complex **1** in acetone (3 cm^3) gave no precipitate upon addition of dry diethyl ether to the reaction mixture. Rotary evaporation to dryness yielded golden needles of the product, which were washed with diethyl ether and dried *in vacuo* (47 mg, 82%) (Found: C, 60.7; H, 5.1. Calc. for $C_{30}H_{30}BF_4FeO_2P$: C, 60.4; H, 5.1%). ^{1}H NMR. [$(CD_3)_2CO$]: δ 7.85–7.55 (aryl), 5.10 (s, 5 H, cp), 3.53 [dd, 2 H, CH_2P, J(P–H) = 17.5, J(H–H) = 11], 2.50 (s, 9 H, Me) and 1.38 [dd, 2 H, CH_2Fe, J(P–H) = 17.5, J(H–H) = 9 Hz]. Electrospray mass spectrum: m/z 509, $[M]^+$.

Dicarbonyl(η-cyclopentadienyl){2-[tris(4-chlorophenyl)phosphonio]ethyl}iron tetrafluoroborate **2d**. A similar procedure to the above using equimolar (0.10 mmol) tris(4-chlorophenyl)-phosphine and complex **1** in acetone (2 cm^3) gave the product as a yellow solid (58 mg, 87%) (Found: C, 48.3; H, 3.3. Calc. for $C_{27}H_{24}BCl_3F_4FeO_2P$: C, 49.0; H, 3.6%). ^{1}H NMR [$(CD_3)_2CO$]: δ 8.05–7.8 (aryl), 5.11 (s, 5 H, cp), 3.71 [dd, 2 H, CH_2P, J(P–H) = 17.5, J(H–H) = 11], and 1.39 [dd, 2 H, CH_2Fe, J(P–H) = 17.5, J(H–H) = 9.5 Hz]. Electrospray mass spectrum: m/z 571 $[M]^+$ (^{37}Cl); 569, $[M]^+$ (^{35}Cl); 205, $[M - P(C_6H_4Cl\text{-}4)_3]^+$; 177, ($[M - P(4\text{-}ClC_6H_4)_3 - CO]^+$).

Dicarbonyl(η-cyclopentadienyl)[2-(triphenylphosphonio)-ethyl]iron tetrafluoroborate. This was prepared and purified using the published procedure.[9] ^{1}H NMR [$(CD_3)_2CO$]: δ 7.95–7.25 (aryl), 5.11 (s, 5 H, cp), 3.65 [dd, 2 H, CH_2P, J(P–H) = 17.5, J(H–H) = 11] and 1.40 [dd, 2 H, CH_2Fe, J(P–H) = 17.5, J(H–H) = 9 Hz]. Electrospray mass spectrum: m/z 467, $[M]^+$; 205, $[M - PPh_3]^+$.

In situ *preparation of other phosphonium adducts.* The other new phosphonium adducts with cation **1** were obtained *in situ* and characterised by their ^{1}H NMR and/or IR and electrospray mass spectra. Proton NMR spectra were recorded using [**1**] = [PR_3] = 0.08 mol dm^{-3}.

Dicarbonyl(η-cyclopentadienyl){2-tris[(2-cyanoethyl)phosphonio]ethyl}iron tetrafluoroborate. ^{1}H NMR [$(CD_3)_2CO$]: δ 5.11 (s, 5 H, cp), 3.19 (overlapping m, 12 H, CH_2CH_2CN), 2.87 [dd, 2 H, CH_2P, J(P–H) = 18, J(H–H) = 11] and 1.50 [dd, 2 H, CH_2Fe, J(P–H) = 18.3, J(H–H) = 8.9 Hz].

Dicarbonyl(η-cyclopentadienyl)[2-(tributoxyphosphonio)-ethyl]iron tetrafluoroborate. ^{1}H NMR [$(CD_3)_2CO$]: δ 5.10 (s, 5 H, cp), 4.56 (dd, 6 H, OCH_2), 2.74 (m, 2 H, CH_2P), 1.80 (m, 6 H, OCH_2CH_2), 1.48 (m, 6 H, $OCH_2CH_2CH_2$), 1.30 (m, 2 H, CH_2Fe) and 0.96 (t, 9 H, CH_2CH_3).

Dicarbonyl(η-cyclopentadienyl)[2-(tributylphosphonio)ethyl]-iron tetrafluoroborate. ^{1}H NMR [$(CD_3)_2CO$]: δ 5.08 (s, 5 H, cp), 2.50 [m, 2 H, CH_2P, J(P–H) = 18, J(H–H) = 11], 2.37 (m, PBu_3), 1.75–1.46 (multiplets, PBu_3), 1.42 [m, 2 H, CH_2Fe, J(P–H) = 18, J(H–H) = 8] and 0.95 [t, 3 H, CH_3 of PBu_3, J(H–H) = 7.3 Hz].

Table 1 Infrared spectral data for phosphonium adducts formed in the reaction of phosphorus nucleophiles with cation **1** in acetone at 20 °C

PR_3	ν(CO)/cm^{-1}
$P(C_6H_4OMe\text{-}2)_3$	2007, 1950
$P(C_6H_4OMe\text{-}4)_3$	2008, 1952
$P(C_6H_4Me\text{-}4)_3$	2007, 1953
$P(C_6H_4Me\text{-}4)Ph_2$	2009, 1953
PPh_3	2010, 1950
$P(C_2H_4CN\text{-}2)Ph_2$	2009, 1953
$P(C_2H_4CN\text{-}2)_3$	2012, 1956
$P(C_6H_4Cl\text{-}4)_3$	2011, 1954
PBu^n_3	2007, 1950
$P(OBu^n)_3$	2008, 1953

Spectroscopic Studies.—Infrared spectra were recorded using a Perkin-Elmer 783 spectrophotometer and matched 0.5 mm CaF_2 solution cells, ^{1}H NMR spectra (referenced to $SiMe_4$) on either a JEOL GX400 or a Varian Unity 400 MHz spectrometer and electrospray mass spectra using a Fisons/VG Biotech Quattro (Altrincham, UK) mass spectrometer. For the latter the complexes were dissolved in acetonitrile and 10 μl injected. The electrospray probe-tip potential was 3.5 kV, and a skimmer voltage of 20 V was employed.

Kinetic Studies.—All of the reactions were rapid and were monitored at 390 nm using a thermostatted (±0.1 °C) stopped-flow spectrophotometer. At this wavelength a large decrease in absorbance was observed during the reaction associated with the disappearance of the original alkene complex **1**.

The reactions were studied under pseudo-first-order conditions, using a large excess of phosphine or phosphite nucleophile {[Fe] = 1 × 10^{-3} mol dm^{-3}; [PR_3] = (5–850) × 10^{-3} mol dm^{-3}}. Pseudo-first-order rate constants, k_{obs}, were calculated from the slopes of plots of log ($A_t - A_\infty$) *vs.* time using a least-squares analysis. These plots were normally linear for at least two half-lives. The k_{obs} values quoted are the averages from at least three separate runs, having an average reproducibility of ±2%. Least-squares analyses of log k_{obs} *vs.* [PR_3] were carried out to obtain the second-order rate constants, k_1. Enthalpies of activation and associated standard errors of estimate were calculated from least-squares analyses of Arrhenius plots of ln k_1 *vs.* T^{-1}. Entropies of activation were calculated by standard procedures using the second-order rate constants, k_1.

Results and Discussion

Nature of the Reactions.—The products from the reactions in Scheme 1 with Nu = $P(C_6H_4X)_3$ (X = 2-MeO, 4-MeO, 4-Me or 4-Cl) have been unequivocally characterised as the phosphonium adducts **2a**–**2d** on the basis of elemental analyses and their IR, ^{1}H NMR and electrospray mass spectra (see Experimental section). Similarly, the rapid (< 1 min) formation of analogous phosphonium adducts with each of the other phosphorus nucleophiles has been confirmed by their *in situ* IR and ^{1}H NMR spectra, which are very similar to those previously reported[4] for the triphenylphosphine adduct $[Fe(cp)(CO)_2(C_2H_4PPh_3)]BF_4$. Thus, each of the new phosphonium species exhibits two sharp, intense ν(CO) bands at *ca.* 2010 and 1950 cm^{-1} in acetone solvent (Table 1). These bands are at substantially lower frequency than those observed for the initial ethene complex (2080 and 2040 cm^{-1}), indicating partial relocation of the positive charge in the adducts onto the phosphorus atom. Similarly, *in situ* ^{1}H NMR studies of equimolar mixtures of **1** and the various phosphorus nucleophiles ([**1**] = [PR_3] = 0.08 mol dm^{-3}) in $(CD_3)_2CO$

Table 2 Kinetic results for the addition of tertiary phosphines and phosphites to cation **1** in acetone at 20.0 °C

Phosphorus nucleophile	10^3[PR$_3$]/ mol dm^{-3}	k_{obs}/s^{-1}	$k_1{}^a$/dm^3 mol^{-1} s^{-1}
P(C$_6$H$_4$OMe-2)$_3$	5.1	33.9	6680 (26)
	10.3	69.1	
P(C$_6$H$_4$OMe-4)$_3$	2.5	1.0	408 (8)
	5.1	2.0	
P(C$_6$H$_4$Me-4)$_3$	10.0	2.2	220 (2)
	19.5	4.3	
P(C$_6$H$_4$Me-4)Ph$_2$	5.0	0.361	102 (1)
	10.0	0.884	
	30.0	2.87	
	50.0	4.89	
	100	10.2	
PPh$_3$	10.0	0.709	82.2 (1.2)
	20.0	1.33	
	40.0	2.87	
	60.0	5.10	
	79.7	6.91	
	100	8.15	
	120	9.73	
	151	12.0	
P(C$_2$H$_4$CN-2)Ph$_2$	9.9	0.352	37.6 (0.5)
	15.0	0.546	
	25.1	0.924	
P(C$_2$H$_4$CN-2)$_3$	10.1	0.137	21.1 (0.4)
	15.0	0.312	
	21.0	0.340	
	29.9	0.548	
	49.8	1.10	
	105	2.13	
P(C$_6$H$_4$Cl-4)$_3$	9.9	0.094	9.6 (0.2)
	14.9	0.127	
	20.0	0.191	
	40.0	0.366	
	50.0	0.483	
PBu$^n{}_3$	9.0	6.0	636 (40)^b
	22.0	15.2	
	36.0	25.0	
	45.0	34.1	
	89.0	56.9	
P(OBu^n)$_3$	200	0.117	0.48 (0.01)
	250	0.156	
	303	0.175	
	413	0.215	
	498	0.251	
	850	0.442	

[a] Values in parentheses are the standard errors of estimate from the least-squares analyses. [b] At 0.0 °C.

Table 3 Temperature dependence of k_1 for the reaction of complex **1** with PPh$_3$ in acetone

T/°C	$k_1{}^a$/dm^3 mol^{-1} s^{-1}
0.0	30.0
7.9	47.7
8.1	50.8
14.0	63.0
15.5	77.4
20.0	82.2^b
25.0	108

[a] Runs were carried out with [PPh$_3$] = 0.10 mol dm^{-3}, and rate law (1) was assumed to calculate k_1. [b] Calculated from a plot of k_{obs} *vs.* [PPh$_3$].

Table 4 Relative reactivities of phosphorus nucleophiles toward cation **1** in acetone at 20.0 °C

Nucleophile	k_1 (20.0 °C)/dm^3 mol^{-1} s^{-1}	Relative rate
P(C$_6$H$_4$OMe-2)$_3$	6680	13 900
P(C$_6$H$_4$OMe-4)$_3$	408	850
P(C$_6$H$_4$Me-4)$_3$	220	458
P(C$_6$H$_4$Me-4)Ph$_2$	102	213
PPh$_3$	82.2	174
P(C$_2$H$_4$CN-2)Ph$_2$	37.6	78
P(C$_2$H$_4$CN-2)$_3$	21.1	44
P(C$_6$HCl-4)$_3$	9.6	20
P(OBu^n)$_3$	0.48	1

have confirmed the quantitative formation of adducts **2** in each case, except for the weakly nucleophilic P(C$_6$H$_4$Cl-4)$_3$ where *ca.* 20% unreacted **1** was observed at equilibrium. For each phosphonium adduct **2**, a singlet was observed at *ca.* δ 5.1 for the cp ligand (*cf.* δ 5.85 for substrate **1**). The alkyl protons on the carbon atom adjacent to the phosphorus centre (CH$_2$P) in adducts **2** generally appear as a double doublet in the region δ 3.4–3.7, while the CH$_2$Fe protons resonate further upfield at *ca.* δ 1.3–1.4. In contrast to the previously reported[4] spectrum of [Fe(cp)(CO)$_2$(C$_2$H$_4$PPh$_3$)]$^+$ in CD$_3$NO$_2$, no P–H coupling was observed for any of the P(C$_6$H$_4$X)$_3$ adducts **2** (including X = H) in (CD$_3$)$_2$CO. This indicates rapid exchange between adduct-bound and free P(C$_6$H$_4$X)$_3$ in acetone, while this exchange is slow on the NMR time-scale in nitromethane. However, phosphorus coupling to each of the alkyl protons was observed in (CD$_3$)$_2$CO for the phosphonium adducts **2** with tri-*n*-butylphosphine and tri-*n*-butyl phosphite.

Kinetics and Mechanism.—Kinetic results for addition of each of the phosphorus nucleophiles to cation **1** in acetone at 20.0 °C are summarised in Table 2, while temperature-dependence data for the PPh$_3$ reaction are collected in Table 3. Each of the reactions is seen to obey the general rate law (1)

$$\text{Rate} = k_{obs}[\text{Fe}] \qquad (1)$$

where $k_{obs} = k_1[\text{PR}_3]$. This rate law is most readily explained in terms of direct addition (k_1) of the phosphorus nucleophiles to the ethene ligand in **1**. No spectroscopic evidence was found for the presence of an intermediate during any of the reactions. Direct addition (k_1) to the ethene ligand is also supported by the very low enthalpy of activation [$\Delta H^{\ddagger}{}_1$ = 30.8(0.6) kJ mol^{-1}] and large negative entropy of activation [$\Delta S^{\ddagger}{}_1$ = −103(2.3) J K^{-1} mol^{-1}] calculated for the PPh$_3$ reaction. These activation parameters are similar to those previously reported[13–16] for the addition of tertiary phosphines and phosphites to other π-hydrocarbon metal complexes. The values for $\Delta H^{\ddagger}{}_1$ and $\Delta S^{\ddagger}{}_1$ found here for reaction of **1** with PPh$_3$ are different to those briefly reported[6] previously for this reaction. The present data are considered more reliable because of their excellent reproducibility and the internal consistency apparent in the linear free-energy relationships discussed below.

Electronic Effects.—From the k_1 values in Table 2 the relative nucleophilicity of the phosphorus nucleophiles towards cation **1** is seen to decrease in the order P(C$_6$H$_4$OMe-2)$_3$ > PBu$^n{}_3$ > P(C$_6$H$_4$OMe-4)$_3$ > P(C$_6$H$_4$Me-4)$_3$ > P(C$_6$H$_4$Me-4)Ph$_2$ > PPh$_3$ > P(C$_2$H$_4$CN-2)Ph$_2$ > P(C$_2$H$_4$CN-2)$_3$ > P(C$_6$H$_4$-Cl-4)$_3$ > P(OBu^n)$_3$ (overall reactivity range of 1.4 × 10^4, see Table 4). This reactivity order parallels that of decreasing electron availability at the phosphorus centre, as shown quantitatively by the excellent correlation (r = 0.99) between log k_1 and the nucleophile Σχ values (Fig. 1). These Σχ values have been proposed by Tolman[17] as a measure of the relative σ-donating and π-accepting ability of phosphorus nucleophiles. The slope (−0.19) of the Tolman plot in Fig. 1 is similar to those previously found for the addition of PR$_3$ to a range of other substrates (Table 5), indicating similar electronic demands in each of the reactions.

Bodner *et al.*[22] have alternatively used δ values obtained from the ^{13}C NMR chemical shifts of [Ni(CO)$_3$(PR$_3$)] complexes to quantify electron donor/acceptor properties of phosphorus

Table 5 Slopes of Tolman, Hammett and Brønsted plots for the reactions of various substrates with phosphorus nucleophiles

Substrate	Solvent	Slope			Ref.
		Tolman	Hammett	Brønsted	
			ρ	α	
EtI	Me_2CO	−0.21	−1.1	0.49	18
$PhCH_2Cl$	C_6H_6–MeOH	−0.20	−1.08		18, 19
$[Mn(CO)_2(NO)(C_6H_6Me\text{-}6)]^+$	MeCN			0.47	20
$[Fe(CO)(NO)(PPh_3)(C_4H_4)]^+$	$MeNO_2$	−0.27	−1.0	0.47	21
$[Fe(CO)_3(C_6H_7)]^+$ **3**	Me_2CO	−0.23	−1.32	0.50	13
$[Fe(CO)_3(C_7H_9)]^+$ **4**	Me_2CO	−0.19	−1.08	0.49	14
1	Me_2CO	−0.19	−1.09	0.46	This work

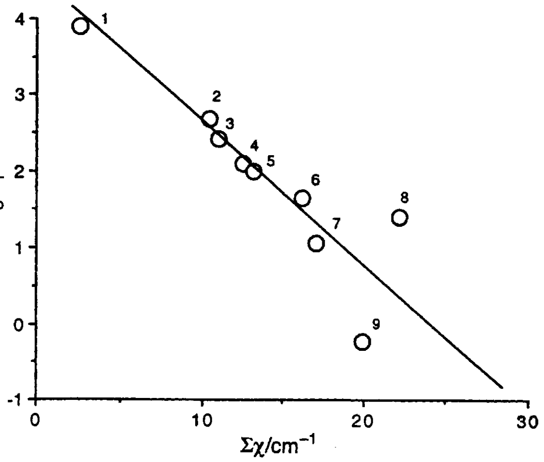


Fig. 1 Plot of log k_1 *vs.* Tolman $\Sigma\chi$ values for the addition of tertiary phosphines and phosphites to $[Fe(cp)(CO)_2(\eta\text{-}C_2H_4)]^+$ in acetone at 20.0 °C: 1, $P(C_6H_4OMe\text{-}2)_3$; 2, $P(C_6H_4OMe\text{-}4)_3$; 3, $P(C_6H_4Me\text{-}4)_3$; 4, $P(C_6H_4Me\text{-}4)Ph_2$; 5, PPh_3; 6, $P(C_2H_4CN\text{-}2)Ph_2$; 7, $P(C_6H_4Cl\text{-}4)_3$; 8, $P(C_2H_4CN\text{-}2)_3$; 9, $P(OBu^n)_3$

ligands. We also observe a good linear relationship (r = 0.97) when the log k_1 values for the reaction in Scheme 1 are plotted against these δ values. The only phosphorus nucleophiles that do not fit closely the Tolman and Bodner-type plots are $P(OBu^n)_3$ and $P(C_2H_4CN\text{-}2)_3$. Deviation of the latter from similar plots for the related reactions of the cyclohexadienyl cation $[Fe(CO)_3(\eta^5\text{-}C_6H_7)]^+$ **3** has also been previously noted.[13] The reason for the deviation of $P(OBu^n)_3$ is uncertain.

An excellent fit (r = 0.99) to the Hammett equation (2) is

$$\log(k/k_H) = \rho\sigma_p \quad (2)$$

also observed for attack by $P(C_6H_4X\text{-}4)_3$ nucleophiles on cation **1** (Fig. 2). The slope, ρ, of −1.09 is similar to those found for analogous reactions with other organic and organometallic substrates listed in Table 5, indicating similar sensitivity to the electronic effects of arene ring substituents. However, $\log(k/k_H)$ values correlate poorly with the $\Sigma\sigma^+$ parameter, suggesting only a small demand for resonance stabilisation of the transition state.

The above observations, together with the strong dependence of rate on phosphine basicity (see below) for the reaction, suggest a transition state in which there is a build-up of positive charge on the phosphorus atom and considerable, but incomplete, phosphorus–carbon bond formation. A similar transition state has been proposed[13,14] for the reaction of phosphorus nucleophiles with the dienyl rings of the cations $[Fe(CO)_3(\eta^5\text{-}C_6H_7)]^+$ **3** and $[Fe(CO)_3(\eta^5\text{-}C_7H_9)]^+$ **4**. This similarity in mechanism is further supported by the excellent correlation (r = 0.99) and slope of 1.02 found when the log k_1 values for the reactions in Scheme 1 are plotted against log k_1 values for the related reactions with cation **3** (Fig. 3).

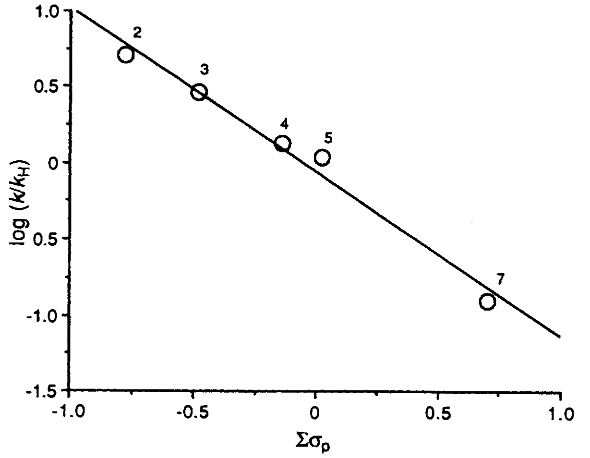


Fig. 2 Hammett plot of $\log(k/k_H)$ *vs.* $\Sigma\sigma_p$ values for the addition of triarylphosphines to $[Fe(cp)(CO)_2(\eta\text{-}C_2H_4)]^+$ in acetone at 20.0 °C; key as in Fig. 1

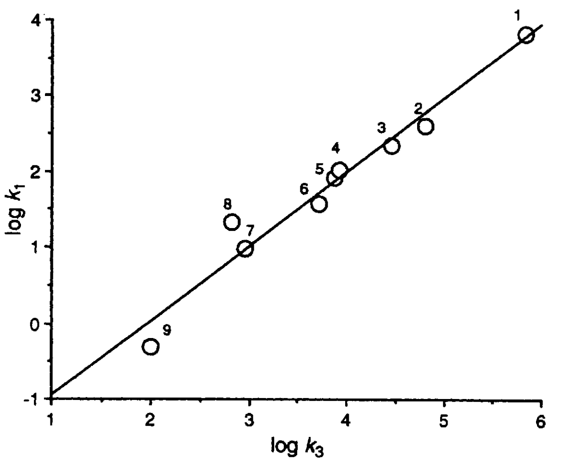


Fig. 3 Correlation plot of log k values for the reactions of cations $[Fe(cp)(CO)_2(\eta\text{-}C_2H_4)]^+$ **1** (k_1) and $[Fe(CO)_3(\eta^5\text{-}C_6H_7)]^+$ **3** (k_3) with phosphorus nucleophiles in acetone at 20.0 °C; key as in Fig. 1

Influence of Nucleophile Basicity.—For the $P(C_6H_4X\text{-}4)_3$ nucleophiles, which have similar steric demands, the Brønsted equation (3) is seen to be closely obeyed (Fig. 4; r = 0.99). The

$$\log k_1 = \alpha pK_a + \text{constant} \quad (3)$$

moderate slope α of 0.46 establishes the importance of phosphine basicity in determining nucleophilicity towards the ethene ligand in cation **1**. Once again, the similarity of this Brønsted slope to those observed for the other substrates listed in Table 5 suggests a similar position for the transition state along the reaction coordinate in each case. This indicates that the π-hydrocarbon complexes, like the well studied organic

Table 6 Anchimeric effect in the reactions of $P(C_6H_4X)_3$ with various substrates

Substrate	$k_{2\text{-MeO}}/k_{4\text{-MeO}}$	$k_{2\text{-MeO}}/k_H$	Solvent	Ref.
$PhCH_2Cl$[a]	4	27	C_6H_6–MeOH (3:2)	23
m-$NCC_6H_4CHBrSO_2Ph$[b]	2	446	$HCONMe_2$–water (9:1)	24
$[Fe(CO)_3(\eta^5\text{-}C_6H_7)]^+$[c]	11	91	Me_2CO	13
1[d]	16	80	Me_2CO	This work

[a] At 31.0 °C. [b] At 25.0 °C. [c] At 0.0 °C. [d] At 20.0 °C.

Table 7 Relative rates and activation parameters for the reaction of PPh_3 with various substrates

Complex	k_1 (20.0 °C)/ $dm^3\ mol^{-1}\ s^{-1}$	Relative rate	$\Delta H^\ddagger_1$[a]/ $kJ\ mol^{-1}$	$\Delta S^\ddagger_1$[a]/ $J\ K^{-1}\ mol^{-1}$	Ref.
$[Fe(C_6H_6)_2]^{2+}$	320 000[b]	3 900	17.6 (3.8)	−80 (13)	25
$[Fe(CO)_2(NO)(C_4H_4)]^+$	44 000[c]	540	24.2 (9.3)	−73 (10)	21
$[Fe(CO)_3(C_6H_7)]^+$	16 000[d]	195	33.6 (8.8)	−50 (26)	26
$[Ru(C_6H_6)_2]^{2+}$	8 400[b]	102	30.1 (8.3)	−67 (33)	25
$[Fe(CO)_3(C_6H_6OMe\text{-}2)]^+$	1 900[d]	23	26.5 (5.2)	−91 (18)	26
$[Os(C_6H_6)_2]^{2+}$	1 800[b]	22	36.8 (6.3)	−59 (21)	25
$[Co(cp)(C_8H_{11})]^+$	1 200[c]	15	21.0 (3.3)	−110 (14)	27
$[Cr(CO)_3(C_7H_7)]^+$	890[c]	11			16, 28
$[Fe(CO)_3(C_7H_9)]^+$	215[d]	2.6	41.1 (2.8)	−60 (8)	26
$[Fe(CO)_2(PPh_3)(C_6H_7)]^+$	123[b]	1.5	40.0 (9.6)	−68 (32)	16, 29
1	82[c]	1	30.8 (1.5)	−103 (6)	This work

[a] Errors quoted are 95% confidence limits. [b] Solvent MeCN. [c] Solvent acetone. [d] Solvent $MeNO_2$.

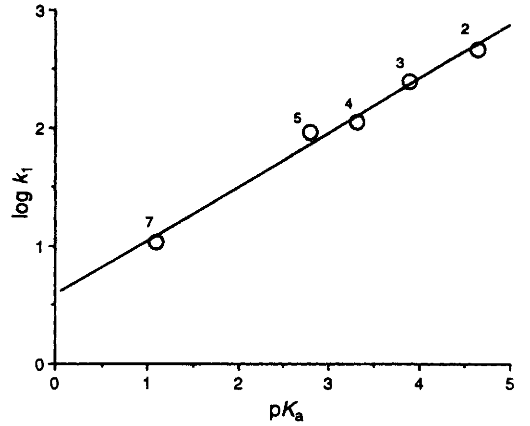
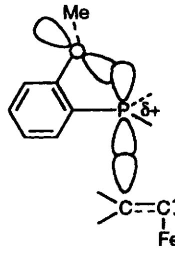


Fig. 4 Brønsted plot of log k_1 vs. pK_a (of conjugate acid) for the addition of triarylphosphines to $[Fe(cp)(CO)_2(\eta\text{-}C_2H_4)]^+$ in acetone at 20.0 °C; key as in Fig. 1

substrates EtI[18] and $PhCH_2Cl$,[19] have only partial phosphorus–carbon bond formation in the transition state.

Anchimeric Effect.—Further support for the transition-state structure proposed above for the reactions in Scheme 1 comes from the exceptionally rapid addition of $P(C_6H_4OMe\text{-}2)_3$ to cation **1**. From Tables 4 and 6, this sterically blocked phosphine is seen to be *ca.* 80 times more nucleophilic than PPh_3 and some 16 times more reactive than the related *p*-substituted $P(C_6H_4OMe\text{-}4)_3$. The exceptional reactivity of $P(C_6H_4OMe\text{-}2)_3$ may be rationalised in terms of anchimeric assistance similar to that proposed for related activations previously observed[23,24] with organohalide substrates, in which a pair of 2p electrons on the methoxy group overlap with a vacant 3d orbital on the phosphorus. This helps to delocalise the positive charge built up on the phosphorus centre in the transition state **I**, causing stabilisation and a rapid reaction. The $k_{2\text{-MeO}}/k_H$ ratio of 80:1 for the reaction in Scheme 1 is significantly larger than that previously found[23] for the analogous reactions with benzyl chloride ($k_{2\text{-MeO}}/k_H = 27:1$, Table 6). This suggests more advanced phosphorus–carbon bond formation in the transition state than in the related reactions with $PhCH_2Cl$ as substrate. However, a very similar $k_{2\text{-MeO}}/k_H$ ratio of 91:1 has been reported[13] for triarylphosphine addition to the dienyl cation $[Fe(CO)_3(\eta^5\text{-}C_6H_7)]^+$, again supporting a close similarity in transition-state structure.



I

Relative Electrophilicities of Organometallic Cations.—Rate and activation parameters for the reactions of a range of π-hydrocarbon complexes with triphenylphosphine are summarised in Table 7. The ethene complex **1** is seen to be the least electrophilic cation examined to date. A similar reactivity order is also observed for the analogous reactions with PBu^n_3. The relatively low electrophilicity of cation **1** compared with the other organometallic substates is seen from Table 7 to arise from its large negative $\Delta S^\ddagger_1$ value of −103 J K^{-1} mol^{-1}. For example, although cations $[Fe(CO)_3(\eta^5\text{-}C_6H_7)]^+$ and $[Ru(\eta\text{-}C_6H_6)_2]^{2+}$ have similar $\Delta H^\ddagger_1$ values to those of complex **1** (34 and 30 kJ mol^{-1}, respectively), their reaction rates (k_1) are 100–200 times faster due to much less negative $\Delta S^\ddagger_1$ values. In general, each of the complexes in Table 7 exhibits quite low activation enthalpies ($\Delta H^\ddagger_1$ = 18–41 kJ mol^{-1}) for their reactions with PPh_3, and their relative electrophilicities appear to be largely entropy controlled. The only significant exception is $[Co(cp)(\eta^5\text{-}C_8H_{11})]^+$ which has the most negative $\Delta S^\ddagger_1$ value (−110 J K^{-1} mol^{-1}) of the substrates examined. Its considerably higher reactivity towards PPh_3 compared with the ethene complex **1** arises from its exceptionally low $\Delta H^\ddagger_1$ value of 21 kJ mol^{-1}.

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