Kinetics of Nucleophilic Attack on Co-ordinated Organic Moieties. Part 21.[†] Factors governing the Nucleophilicity of Phosphorus Nucleophiles towards $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ [‡]

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Synthetic and kinetic studies are reported for the addition of a wide range of tertiary phosphines and phosphites to the dienyl ring of $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ (1). All the reactions obey the expression $k_{obs.} = k_1[PR_3]$, except for the reversible additions of $P(CH_2CH_2CN)_3$ and $P(C_6H_4Me\text{-}2)_3$ which follow the two-term equation, $k_{obs.} = k_1[PR_3] + k_{-1}$. A good correlation ($r = 0.98$) is found between log k_1 and the Tolman ΣX values of the phosphorus nucleophiles. The Brönsted slope of 0.5 derived from a linear plot of log k_1 *vs.* pK_a for triarylphosphines demonstrates the importance of basicity in controlling nucleophilicity towards (1). Nucleophile polarisability is shown to play a minor role. Steric factors, quantified by negative deviations from the above plots by $P(C_6H_4Me\text{-}2)_3$ and $P(C_6H_{11})_3$, are shown to be much more important than in related reactions with ethyl iodide. The Hammett slope ρ of −1.32 observed for the additions of triarylphosphines to (1) suggests moderate, but far from complete, phosphorus–carbon bond formation in the transition states. A similar conclusion is drawn from the novel anchimeric assistance observed in the unexpectedly rapid reaction with $P(C_6H_4OMe\text{-}2)_3$ ($k_{2\text{-MeO}}/k_H = 91$). Finally, comparison with other results provides an electrophilicity order for an extended series of organometallic cations covering a reactivity range of *ca.* 10^6 between $[Mn(CO)_3(1—6\text{-}\eta\text{-}C_7H_8)]^+$ and $[Co(\eta\text{-}C_5H_5)(1—5\text{-}\eta\text{-}C_7H_9)]^+$.

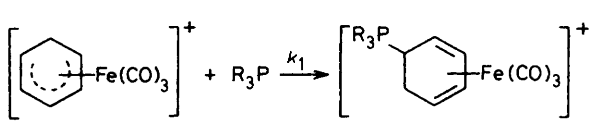
As part of a programme investigating the factors controlling the reactivity of co-ordinated π-hydrocarbons, we recently reported [1] some synthetic and kinetic studies of the addition of tertiary phosphines and phosphites to $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ (1) and related dienyl cations. The results supported direct attack by the phosphorus nucleophiles upon the dienyl ligands. Furthermore, a preliminary examination of the variation of nucleophilicity with the basicity of the phosphorus nucleophiles suggested an anomalously high reactivity for triphenylphosphine. In order to elucidate the source of this apparent anomaly and to delineate more clearly the mechanism of these novel phosphonium adduct formations, a much wider range of tertiary phosphines and phosphites has now been investigated [equation (i); R_3 = $Bu^n{}_3$, $(C_6H_{11})_3$, $(CH_2CH_2CN)_3$, Et_2Ph, Ph_3, $(4\text{-}MeC_6H_4)Ph_2$, $(4\text{-}MeC_6H_4)_3$, $(4\text{-}MeOC_6H_4)_3$, $(4\text{-}ClC_6H_4)_3$, $(4\text{-}FC_6H_4)_3$, $(2\text{-}MeC_6H_4)_3$, $(2\text{-}MeOC_6H_4)_3$, $(EtO)_3$, and $(MeO)_3$]

The importance of steric factors and of electronic contributions such as nucleophile basicity in reactions (i) have been determined. Structure–reactivity relationships have helped to define the position and nature of the transition states. Finally, during the course of these studies an unusual example of anchimeric assistance has been found in the unexpectedly rapid reaction with $P(C_6H_4OMe\text{-}2)_3$.

EXPERIMENTAL

Materials.—The salt $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]BF_4$ (1) was prepared and purified using established procedures.[2] The phosphorus nucleophiles were purchased in the purest grades available (Strem Ltd. or Aldrich Ltd.) and used as supplied. Acetone solvent was analytical grade, and was deoxygenated by passing through it a stream of nitrogen for 20 min. Solutions of the appropriate phosphorus nucleophile were prepared under dinitrogen immediately prior to use.

Isolation of New Phosphonium Adducts.—*Tricarbonyl-*[1—4-η-5-(*tri*-p-*methoxyphenylphosphonio*)*cyclohexa*-1,3-*diene*]*iron tetrafluoroborate* (2a). This salt was prepared in an analogous fashion to that used previously for the triphenylphosphine and tri-*p*-tolylphosphine adducts.[1,3] The salt $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]BF_4$ (0.061 g, 0.20 mmol) was dissolved in acetone (2 dm³) containing tri-*p*-methoxyphenylphosphine (0.070 g, 0.20 mmol) at room temperature.



(1) (2) (i)

Addition of sodium-dried diethyl ether (20 cm³) and cooling in ice yielded the phosphonium adduct as a pale yellow oil. Rotary evaporation gave a cream solid which was dried over silica gel (0.041 g, 36%), m.p. 113—115 °C (Found: C, 55.0; H, 4.5. Calc. for $C_{30}H_{28}BF_4FeO_6P$: C, 54.8; H, 4.3%). A solution in nitromethane exhibited two intense i.r. carbonyl bands at 2 062 and 1 998 cm⁻¹ as expected. ¹H N.m.r.: (CD_3NO_2) 2.1—2.9 (12 H, multiplets, aromatic), 4.54 (1 H, m, H^2 or H^3), 4.86 (1 H, m, H^2 or H^3), 5.7 (partly masked by CH_3NO_2 resonance, $H^{5'}$), 6.07 (9 H, s, CH_3), 6.74 (2 H, overlapping resonances, H^1 and H^4), and 7.71 (2 H, overlapping resonances, H^6 and $H^{6'}$); (CD_3COCD_3) 1.90—3.40 (12 H, multiplets, aromatic), 4.54 (1 H, m, H^2 or H^3), 4.87 (1 H, m, H^2 or H^3), 5.71 (1 H, m, $H^{5'}$), 6.24 (9 H, s, CH_3), 6.73 (2 H, overlapping resonances, H^1 and H^4), 7.42 (1 H, m, $H^{6'}$), and 7.82 (1 H, m, H^6).

Tricarbonyl[1—4-η-5-(*tri*-o-*methoxyphenylphosphonio*)-*cyclohexa*-1,3-*diene*]*iron tetrafluoroborate* (2b). A similar procedure to the above employing equimolar tri-*o*-methoxyphenylphosphine and (1) gave no precipitate upon addition of sodium-dried diethyl ether to the reaction mixture. Rotary evaporation yielded a cream solid (0.072 g, 63%) which was dried over silica gel, m.p. 194—196 °C (Found: C, 52.3; H,

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[†] Part 20, J. G. Atton and L. A. P. Kane-Maguire, *J. Organomet. Chem.*, 1982, **226**, C43.

[‡] Tricarbonyl(1—5-η-cyclohexadienyl)iron(1+).

4.3. Calc. for $C_{30}H_{28}BF_4FeO_6P$: C, 54.8; H, 4.3%). A solution in nitromethane exhibited strong i.r. carbonyl bands at 2 060 and 1 998 cm^{-1}. ^1H N.m.r.: (CD_3NO_2) 2.05—3.30 (12 H, multiplets, aromatic), 4.51 (1 H, m, H^2 or H^3), 5.10 (1 H, m, H^2 or H^3), 5.8 (partly masked by CH_3NO_2 resonance, $H^{5'}$), 6.22 (9 H, s, CH_3), 6.65 (1 H, m, H^1), 6.86 (1 H, m, H^4), 7.71 (1 H, m, $H^{6'}$), and 7.86 (1 H, m, H^6); (CD_3COCD_3) 1.80—3.20 (12 H, multiplets, aromatic), 4.41 (1 H, m, H^2 or H^3), 5.04 (1 H, m, H^2 or H^3), 5.85 (1 H, m, $H^{5'}$), 6.23 (9 H, s, CH_3), 6.72 (2 H, overlapping resonances, H^1 and H^4), 7.57 (1 H, m, $H^{6'}$), and 7.76 (1 H, m, H^6).

In situ Preparation of Other Phosphonium Adducts.—The other new phosphonium adducts were obtained quantitatively *in situ*, and characterised by their ^1H n.m.r. and/or i.r. spectra. Proton n.m.r. spectra were recorded in CD_3NO_2 using [Fe] = 0.2 mol dm^{-3} and $[PR_3]$ = 0.4 mol dm^{-3}.

Tricarbonyl[1—4-η-5-(*diphenyl*-p-*tolylphosphonio*)*cyclohexa*-1,3-*diene*]*iron tetrafluoroborate* (2c). ^1H N.m.r. (CD_3NO_2): 2.00—2.85 (14 H, overlapping resonances, aromatic), 4.70 (1 H, m, H^2), 4.94 (1 H, m, H^3), 5.80 (1 H, m, $H^{5'}$), 6.73 (2 H, overlapping multiplets, H^1 and H^4), 7.20 (1 H, m, $H^{6'}$), 7.4 (1 H, m, H^6), and 7.54 (3 H, s, CH_3). ν(CO) in CH_3NO_2: 2 061 and 2 002 cm^{-1}.

Tricarbonyl[1—4-η-5-(*tri*-p-*chlorophenylphosphonio*)*cyclohexa*-1,3-*diene*]*iron tetrafluoroborate* (2d). ^1H N.m.r. (CD_3NO_2): 2.00—2.85 (12 H, overlapping resonances, aromatic), 4.63 (1 H, m, H^2), 4.85 (1 H, m, H^3), 5.77 (1 H, m, $H^{5'}$), 6.82 (2 H, overlapping multiplets, H^1 and H^4), and 7.34 (2 H, overlapping multiplets, $H^{6'}$ and H^6). ν(CO) in CH_3NO_2: 2 063 and 2 004 cm^{-1}.

Tricarbonyl[1—4-η-5-(*diethylphenylphosphonio*)*cyclohexa*-1,3-*diene*]*iron tetrafluoorbroate* (2e). ^1H N.m.r. (CD_3NO_2): 4.45 (1 H, m, H^2), 4.72 (1 H, m, H^3), 5.6 (m, partly masked by CH_3NO_2 resonance), 6.85 (2 H, overlapping multiplets, H^1 and H^4), 7.86 (1 H, m, $H^{6'}$), and 8.06 (1 H, m, H^6). ν(CO) in CH_3NO_2: 2 060 and 2 000 cm^{-1}.

Tricarbonyl[1—4-η-5-(*tricyclohexylphosphonio*)*cyclohexa*-1,3-*diene*]*iron tetrafluoroborate* (2f). ^1H N.m.r. (CD_3NO_2): 4.14 (2 H, overlapping multiplets, H^2 and H^3), 5.6 (m, partly masked by CH_3NO_2 resonances), 6.72 (1 H, m, $H^{6'}$), 7.00 (1 H, m, H^6), and 7.9—8.0 (*ca*. 30, m, aliphatic). ν(CO) in CH_3NO_2: 2 065 and 2 000 cm^{-1}.

Tricarbonyl[1—4-η-5-(*tricyanoethylphosphonio*)*cyclohexa*-1,3-*diene*]*iron tetrafluoroborate* (2g). ^1H N.m.r. (CD_3NO_2): 4.26 (2 H, overlapping multiplets, H^2 and H^3), 5.7 (m, partly obscured by CH_3NO_2 resonance), 6.52 (2 H, overlapping multiplets, H^1 and H^4), 6.7—7.6 (overlapping resonances, $H^{6'}$, H^6, and CH_2), and 8.12 (9 H, t, CH_3). ν(CO) in CH_3NO_2: 2 062 and 2 003 cm^{-1}.

Adducts (2; R = $4\text{-}FC_6H_4$ and $2\text{-}MeC_6H_4$) were characterised by their ν(CO) bands in nitromethane at 2 065, 2 004 cm^{-1} and 2 063, 1 997 cm^{-1}, respectively. The phosphite adducts (2; R = EtO and MeO) similarly exhibited only two intense ν(CO) bands at *ca*. 2 055 and 1 980 cm^{-1} in acetone.

Spectroscopic Studies.—Infrared spectra were recorded on a Pye Unicam SP3 200 spectrophotometer using matched 0.5-mm NaCl cells, ^1H n.m.r. spectra (90 MHz) on a Perkin-Elmer R32 spectrophotometer.

Equilibrium Studies.—Equilibrium constants for reactions (i) (R = NCC_2H_4 or $2\text{-}MeC_6H_4$) were determined as follows. Solutions of (1) and the appropriate phosphine in acetone were thermostatted at 20.0 °C for 15 min prior to mixing, and the i.r. spectra of the mixtures recorded immediately over the region 1 900—2 200 cm^{-1}. The equilibrium concentrations of unreacted (1) were calculated from the absorption at 2 120 cm^{-1}, using its known[4] absorption coefficient. From the known starting concentrations, the equilibrium concentration of the products (2) could then be estimated, allowing calculation of the equilibrium constants K_{eq} using equation (ii).

$$K_{eq} = \frac{[Fe(CO)_3(1\text{—}4\text{-}\eta\text{-}5\text{-}R_3P{\cdot}C_6H_7)^+]}{[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)^+][PR_3]} \qquad \text{(ii)}$$

Kinetic Studies.—All reactions (i) in acetone were rapid and were monitored at 370 nm with a thermostatted (±0.1 °C) stopped-flow spectrophotometer using techniques which have been previously described.[1] At this wavelength a large decrease in absorbance was observed associated with the disappearance of the original cation (1).

Reactions (i) [R_3 = $(4\text{-}FC_6H_4)_3$, $(4\text{-}ClC_6H_4)_3$, $(2\text{-}MeC_6H_4)_3$, $(4\text{-}MeC_6H_4)Ph_2$, $(CH_2CH_2CN)_3$, $(EtO)_3$, and $(MeO)_3$] were studied under pseudo-first-order conditions employing a large excess of nucleophile ([Fe] = 1.0×10^{-4}—3.0×10^{-4} mol dm^{-3}, $[PR_3]$ = 1.0×10^{-3}—50×10^{-3} mol dm^{-3}). Pseudo-first-order rate constants, $k_{obs.}$, were calculated from the slopes of plots of log $(A_t - A_\infty)$ *versus* time. Such plots were generally linear for at least two half-lives. Each $k_{obs.}$ is the average from at least three separate runs, with an average reproducibility of ±5%.

On the other hand, reactions (i) [R_3 = $(2\text{-}MeOC_6H_4)_3$, Bu^n_3, Et_2Ph, $(4\text{-}MeOC_6H_4)_3$, and $(C_6H_{11})_3$] were investigated under equimolar conditions ([Fe] = $[PR_3]$ = 3.0×10^{-4} mol dm^{-3}). Second-order rate constants, k_1, for these processes were obtained directly from the slope of plots of $x/a(a - x)$ *versus* time, where a is the initial concentration of (1) and x is the concentration of phosphonium adduct at time t. These runs were also carried out in triplicate, the plots generally being linear for at least 65% completion of reaction. The reproducibility was *ca*. ±6%.

RESULTS AND DISCUSSION

The products from reactions (i) (R = $4\text{-}MeOC_6H_4$ and $2\text{-}MeOC_6H_4$) have been unequivocally characterised as the phosphonium adducts (2a) and (2b) on the basis of elemental analyses and their i.r. and ^1H n.m.r. spectra (see Experimental section). Similarly, the formation of analogous phosphonium cations with each of the other tertiary phosphines and phosphites investigated has been confirmed by their *in situ* ^1H n.m.r. and i.r. spectra, which are very similar to those previously reported[1,3] for the tricarbonyl[1—4-η-5-(*exo*-triphenylphosphonio)-cyclohexa-1,3-diene]iron cation and related tri-*p*-tolylphosphonio- and tri-n-butylphosphonio-species.

Kinetic results obtained here for reactions (i) are summarised in Table 1. Except for (R = $NCCH_2CH_2$ and $2\text{-}MeC_6H_4$) all the reactions proceed to completion under the kinetic conditions employed, and obey the relationship (iii). However, the reactions with $P(CH_2CH_2CN)_3$ and $P(C_6H_4Me\text{-}2)$ are equilibrium processes,

$$k_{obs.} = k_1[PR_3] \qquad \text{(iii)}$$

$$k_{obs.} = k_1[PR_3] + k_{-1} \qquad \text{(iv)}$$

and obey the expected two-term expression (iv). The separate k_1(forward) and k_{-1}(reverse) rate constants and their associated standard errors in Table 1 were calculated by least-squares analyses of equation (iv).

The equilibrium constant ($K_{eq} = k_1/k_{-1}$) calculated for reaction (i) ($R = 2\text{-MeC}_6H_4$) from the kinetic data in Table 1 agrees within experimental error with that obtained from static i.r. studies (Table 2). The reason for the poor agreement between the kinetic and static K_{eq} values for the related reaction with $P(CH_2CH_2CN)_3$ is uncertain, but it may reflect complications in the latter process. However, in no instance was kinetic or spectroscopic evidence found for the presence of an intermediate during reactions (i), nor for any subsequent rearrangements prior to recording the i.r. spectra (few minutes). For reasons previously elaborated,[1] the second-order rate constants, k_1, are therefore considered to refer to direct addition of the tertiary phosphines and phosphites to the dienyl ring of (1).

TABLE 1

Kinetic results for the addition of tertiary phosphines and phosphites to $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$ in acetone at 20.0 °C

Phosphorus nucleophile	10^4 [Fe]/ mol dm^{-3}	10^3 [PR$_3$]/ mol dm^{-3}	$k_{obs.}$/s^{-1}	$10^{-2}k_1$[a]/ dm^3 mol^{-1} s^{-1}
$P(C_6H_4OMe\text{-}2)_3$	3.0	0.30		6 800
PBu^n_3	3.0	0.30		3 360
PEt_2Ph	3.0	0.30		1 550
$P(C_6H_4OMe\text{-}4)_3$	3.0	0.30		642
$P(C_6H_{11})_3$	3.0	0.30		1.74
$PPh_2(C_6H_4Me\text{-}4)$	2.0	2.0	16.2	81.0
$P(C_6H_4F\text{-}4)_3$	1.0	1.0	1.83	
	1.0	2.0	3.30	
	1.0	8.0	12.8	15.7(0.13)
$P(C_6H_4Cl\text{-}4)_3$	3.0	3.0	2.32	
	3.0	5.0	4.63	
	3.0	15.0	13.4	9.08(0.39)
$P(CH_2CH_2CN)_3$	1.0	1.0	0.550	
	1.0	2.0	0.690	
	1.0	5.0	1.12	1.43(0.01) [b]
$P(C_6H_4Me\text{-}2)_3$	4.0	5.0	0.159	
	4.0	20.0	0.283	
	4.0	30.0	0.367	
	4.0	50.0	0.504	0.077(0.003) [c]
$P(OEt)_3$	4.35	12.2	0.53	
	4.35	20.0	0.95	
	4.35	52.5	2.37	0.459(0.005)
	4.35	104	4.77	
$P(OMe)_3$	4.35	6.3	0.201	0.297
	4.35	60.1	1.64	

[a] Values in parentheses are standard errors. [b] $k_{-1} = 0.406$ (0.002) s^{-1}. [c] $k_{-1} = 0.127$ (0.009) s^{-1}.

TABLE 2

Equilibrium constants (K_1/dm^3 mol^{-1}) for the addition of tertiary phosphines to $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$ in acetone at 20 °C

Phosphine	K_1(static)	$K_1 = k_1/k_{-1}$
$P(CH_2CH_2CN)_3$	635	352 (17) *
$P(C_6H_4Me\text{-}2)_3$	88	61 (5) *

* Values in parentheses are standard deviations calculated using the standard errors quoted in Table 1 for k_1 and k_{-1}. If 95% confidence limits are employed for k_1 and k_{-1}, then the calculated K_1 values are 352 ± 31 and 61 ± 21 dm^3 mol^{-1}, respectively.

In the reactions of (1) with $P(OMe)_3$ and $P(OEt)_3$ in acetone, the i.r. spectra of the solutions after the stopped-flow kinetic runs showed only two intense ν(CO) bands at *ca.* 2 055 and 1 980 cm^{-1}. Thus, as previously observed[1] with $P(OBu^n)_3$, the phosphonium adducts formed with these tertiary phosphites are stable in solution, and do not undergo ready Arbusov elimination to yield neutral phosphonate derivatives.

Electronic and Steric Effects in Reactions (i).—The results in Table 1, taken together with more limited earlier data,[1] throw considerable light on the factors controlling the nucleophilicity of phosphorus donors towards cation (1). The reactivity of the phosphorus nucleophiles is seen to decrease markedly in the order below (relative rates in brackets). This reactivity order

$$\underset{(1.6\times10^7)}{P(C_6H_4OMe\text{-}2)_3} > \underset{(8.1\times10^6)}{PBu^n_3} > \underset{(3.8\times10^6)}{PEt_2Ph} >$$

$$\underset{(1.6\times10^6)}{P(C_6H_4OMe\text{-}4)_3} > \underset{(6.9\times10^5)}{P(C_6H_4Me\text{-}4)_3} > \underset{(2.0\times10^5)}{PPh_2(C_6H_4Me\text{-}4)}$$

$$> \underset{(1.8\times10^5)}{PPh_3} > \underset{(3.8\times10^4)}{P(C_6H_4F\text{-}4)_3} > \underset{(2.2\times10^4)}{P(C_6H_4Cl\text{-}4)_3} >$$

$$\underset{(4.2\times10^3)}{P(C_6H_{11})_3} > \underset{(3.5\times10^3)}{P(CH_2CH_2CN)_3} > \underset{(2.0\times10^3)}{P(OBu^n)_3} >$$

$$\underset{(1.1\times10^3)}{P(OEt)_3} > \underset{(7.2\times10^2)}{P(OMe)_3} > \underset{(1.9\times10^2)}{P(C_6H_4Me\text{-}2)_3} > \underset{(1)}{P(OPh)_3}$$

parallels that of decreasing electron availability at the phosphorus centres, as shown quantitatively by the excellent correlation between log k_1 and the nucleophile $\Sigma\chi$ values (Figure 1, correlation coefficient $r = 0.98$).

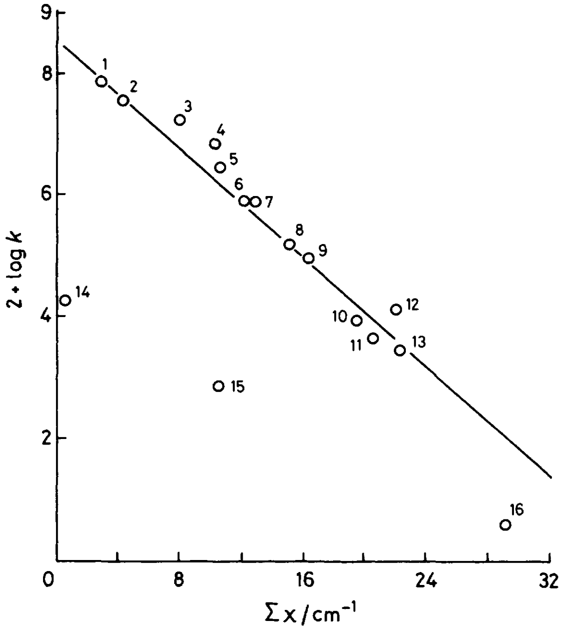


FIGURE 1 Plot of log *k vs.* Tolman $\Sigma\chi$ values for the addition of tertiary phosphines and phosphites to $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$ in acetone at 20 °C: 1, $P(C_6H_4OMe\text{-}2)_3$; 2, PBu^n_3; 3, PEt_2Ph; 4, $P(C_6H_4OMe\text{-}4)_3$; 5, $P(C_6H_4Me\text{-}4)_3$; 6, $PPh_2(C_6H_4Me\text{-}4)$; 7, PPh_3; 8, $P(C_6H_4F\text{-}4)_3$; 9, $P(C_6H_4Cl\text{-}4)_3$; 10, $P(OBu^n)_3$; 11, $P(OMe)_3$; 12, $P(CH_2CH_2CN)_3$; 13, $P(OEt)_3$; 14, $P(C_6H_{11})_3$; 15, $P(C_6H_4Me\text{-}2)_3$; 16, $P(OPh)_3$

The $\Sigma\chi$ values, derived by Tolman,[5] are a measure of the relative σ-donating and π-accepting ability of the various ligands. More recently, Bodner *et al.*[6] have quantified the electron-donor and -acceptor properties of phosphorus ligands in terms of σ values obtained from the ^{13}C n.m.r. chemical shifts of $Ni(CO)_3L$ complexes. We also observe a good linear relationship ($r = 0.96$) between the log k_1 values for reactions (i) and these σ values.

TABLE 3

Slopes of log *k* *vs.* $\Sigma\chi$ plots for the reactions of various substrates with phosphorus nucleophiles

Substrate	No. of data points	Correlation coefficient (r)	Slope	Ref.
EtI	8	0.98	−0.21	8, 9
$PhCH_2Cl$	15	0.95	−0.20	11, 12
Bu^{n}Cl	3	0.99	−0.16	12
(3) $[Fe(CO)(NO)(PPh_3)(\eta\text{-}C_4H_4)]^+$	5	0.98	−0.27	13
(1) $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$	13	0.98	−0.23	This work

The only significant deviations from the correlation line in Figure 1 are the points for $P(C_6H_4Me\text{-}2)_3$, $P(C_6H_{11})_3$, and possibly $P(OPh)_3$. For each of the other phosphorus nucleophiles, the good fit indicates approximately constant steric demands in the transition states along the series. The large negative deviations (Δ) for $P(C_6H_4\text{-}Me\text{-}2)_3$ and $P(C_6H_{11})_3$ undoubtedly arise from major steric hindrance due to their large cone angles ($\theta = 194$ and 179°, respectively).[7] These compare with cone angles of 145 and 130° for PPh_3 and PBu$^n{}_3$, respectively, and much smaller angles (107—121°) for the tertiary phosphites. The cause of the smaller negative deviation by $P(OPh)_3$ is uncertain.

The steric retardation for $P(C_6H_4Me\text{-}2)_3$ and $P(C_6H_{11})_3$ in reactions (i) may be quantified by their Δ values of *ca.* 3.55 and 4.35, respectively. That is, their rates are sterically retarded by factors of *ca.* 10^4 compared with what one would have anticipated on electronic grounds. Steric factors are thus far more important in processes (i) than in the related reactions of tertiary phosphines with ethyl iodide. For the latter reactions, using published rate data in acetone,[8,9] we find a similar correlation (slope $= -0.21$, $r = 0.98$) between log k and $\Sigma\chi$. The negative deviation (Δ) of $P(C_6H_{11})_3$ from this line is only *ca.* 0.75 log units. The intrinsically high steric demands of substrate (1) compared with methyl iodide have been previously commented upon in the related quaternization reactions with substituted pyridines.[10] In addition, we find that published[11] log k data for the reactions of tertiary phosphines with benzyl chloride in benzene–methanol (3 : 2) also correlate reasonably well with $\Sigma\chi$ values ($r = 0.95$), and that the point for $P(C_6H_4Me\text{-}2)_3$ shows a negative deviation (Δ) of *ca.* 2.0. Thus even the relatively sterically demanding benzyl chloride substrate is much less sensitive to steric factors than cation (1).

Table 3 summarises the slopes of plots of log k *vs.* $\Sigma\chi$ calculated from published[8,9,11-13] data for the reactions of phosphorus nucleophiles with various substrates. Quantitative comparison of the slopes is currently hampered by the limited range of nucleophiles studied for substrates other than (1). For example, the only other substrate for which reaction with a tertiary phosphite has been reported is the cation $[Fe(CO)(NO)(PPh_3)(\eta\text{-}C_4H_4)]^+$ (3), for which a P(OBu^n)$_3$ datum point is available.[13] However, the general negative slopes and the relatively small spread in absolute values suggest similar electronic demands in each of the reactions.

Further insight into electronic effects in reactions (i) comes from the Hammett plot ($r = 0.98$) of log (k/k_H) *vs.* $\Sigma\sigma_p$ for the attack of *para*-substituted triarylphosphines on (1) (Figure 2). Interestingly, the slope ($\rho = -1.32$) is larger than those previously found for analogous reactions with benzyl chloride ($\rho = -1.08$ in benzene–methanol),[14] ethyl iodide ($\rho = -1.1$ in acetone),[8] and cation (3) ($\rho = -1.0$ in nitromethane).[13] This suggests a somewhat 'later' transition state for reactions (i) than in these latter processes, for which relatively 'early' transition states have been ascribed.[8-14] This view is consistent with the large steric effects observed above for reactions (i). However, there is only a small demand for resonance stabilisation of the transition state, as shown by the poor correlation of log k_1 with σ^+ values (correlation coefficient = 0.71). Overall, these observations indicate a transition state in which there is moderate, but far from complete, phosphorus–carbon bond formation and positive charge build-up on the phosphorus atom.

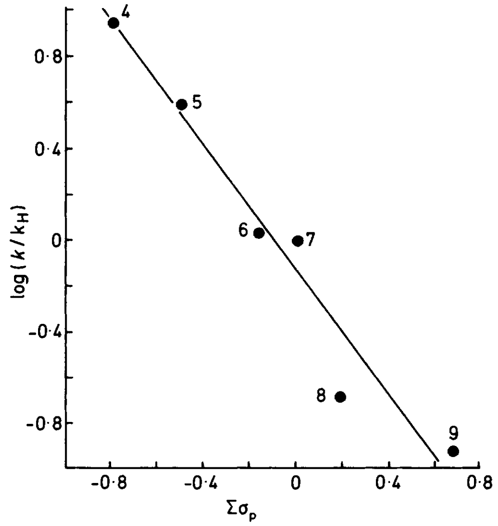


FIGURE 2 Hammett plot of log (k_X/k_H) *vs.* $\Sigma\sigma_p$ values for the addition of triarylphosphines to $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$ in acetone at 20 °C; key as in Figure 1

Further support for a close similarity in the mechanisms of phosphorus-donor addition to cations (1) and (3) comes from the excellent correlation (slope *ca.* 0.9, $r = 0.99$) between their log k_1 values (Figure 3). In contrast, a similar correlation plot for reactions with (1) and EtI reveals marked deviations for $P(C_6H_{11})_3$ and $P(CH_2CH_2CN)_3$. The exceptionally low k_1 for attack by $P(C_6H_{11})_3$ on (1) has already been explained on steric grounds (see above).

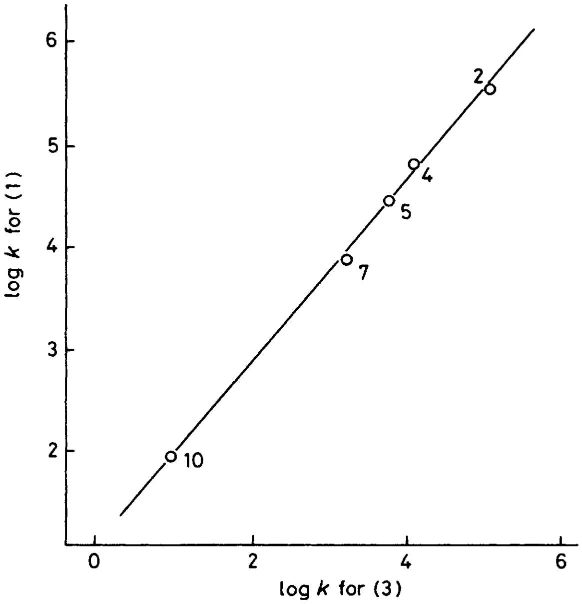


FIGURE 3 Correlation plot of log k values for the reactions of (1) and $[Fe(CO)(NO)(PPh_3)(\eta\text{-}C_4H_4)]^+$ (3) with phosphorus nucleophiles in acetone (20 °C) and CH_3NO_2 (25 °C), respectively; key as in Figure 1

Influence of Nucleophile Basicity.—It has recently been established that the basicity of nitrogen nucleophiles such as pyridines [10] and anilines [15] is an important factor in determining their nucleophilicity towards organometallic cations of the type (1). Figure 4 shows a plot of log k_1 *vs.* pK_a (in water) of the phosphorus nucleophiles for reactions (i). In order to extend the range of available [16,17] pK_a values, we have extrapolated pK_a values for $P(C_6H_4Cl\text{-}4)_3$, $P(C_6H_4F\text{-}4)_3$, and $PPh_2(C_6H_4Me\text{-}4)$ from plots of pK_a *vs.* Tolman's [5] $\Sigma\chi$ and Bodner's [6] σ values. Confidence in these extrapolated values is reinforced by the agreement (usually ± 0.25 pK_a units) between values obtained *via* the two methods. Significantly, the Brönsted equation (v) with a slope of α of *ca.* 0.5 is seen to be obeyed for the reactions of triarylphosphines with (1), clearly establishing the importance

$$\log k_1 = \alpha pK_a + \text{constant} \qquad \text{(v)}$$

of basicity in controlling nucleophilicity. This conclusion contrasts with the reactions of tertiary phosphines with *trans*-$[PtCl_2(py)_2]$ (py = pyridine), where nucleophile basicity has almost no influence on rate constants.[18] The similarity of the Brönsted slope for reactions (i) [PR_3 = triarylphosphines] to α values (0.47—0.49) recently reported [13] for the analogous reactions with EtI, $PhCH_2Cl$, and (3) again suggests only partial phosphorus–carbon bond formation in the transition states for each reaction.

The points for PEt_2Ph, $PBu^n{}_3$, and $P(CH_2CH_2CN)_3$ deviate significantly from the above Brönsted plot, suggesting that trialkylphosphines form a separate plot (of similar slope, as shown by the dashed line in Figure 4). Similarly, the very marked deviation of the tertiary phosphites indicates that they form a third distinct group (dotted line). These observations are not surprising since the pK_a values take no account of possible π-bonding interactions, which are believed from the correlation in Figure 1 to contribute to the k_1 values. Variations in polarisability between the three sets of phosphorus nucleophiles may also contribute to the demarcation apparent in Figure 4.

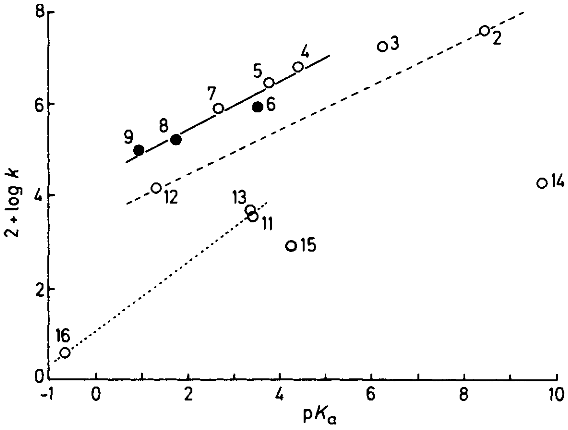


FIGURE 4 Brönsted plot of log k *vs.* pK_a (of conjugate acid) for the addition of tertiary phosphines and phosphites to $[Fe(CO)_3\text{-}(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$ in acetone at 20 °C; key as in Figure 1

The present results reveal the source of the 'anomalously high' reactivity towards (1) previously attributed [1] to PPh_3. In the earlier study, fortuitous linearity occurred in the log k_1 *vs.* pK_a [pK_a = 10.12 − 0.0129 Δ (half-neutralization points)] plot for $PBu^n{}_3$, $P(OBu^n)_3$, and $P(OPh)_3$. The large positive deviation of PPh_3 from this apparent correlation line suggested excessive reactivity. However, the results in Figure 4 show PPh_3 to behave as a typical triarylphosphine towards (1).

The importance of steric effects in reactions (i) is once more confirmed by the large negative deviation (Δ) of $P(C_6H_{11})_3$ from the Brönsted plot in Figure 4 for trialkylphosphines defined by $P(CH_2CH_2CN)_3$ and $PBu^n{}_3$. The steric retardation (Δ) of *ca.* 3.8 log units thus estimated compares favourably with that (Δ = 3.55) previously calculated for this bulky phosphine from Figure 1.

Influence of Nucleophile Polarisability.—In an attempt to define the influence of nucleophile polarisability on the rates of reactions (i), related additions with $AsPh_3$ and $SbPh_3$ were investigated. No reaction was observed between cation (1) and $AsPh_3$ (0.1 mol dm^{-3}) in CH_3NO_2 over 1 week at room temperature, in agreement with an earlier report by Lewis and co-workers.[19] A slow reaction (apparent $k_{obs.}$ *ca.* 5×10^{-5} s^{-1}) was noted between (1) and $SbPh_3$ (0.075 mol dm^{-3}) in CH_3NO_2 at 15 °C. Assuming a rate law analogous to (iii), this indicates a *ca.* 2×10^7 times lower second-order rate constant k_1 than that with PPh_3.[1] However, the triphenylstibine reaction was characterised only on the basis of the appearance of two ν(CO) bands at 2 049 and 1 978 cm^{-1}, and proved difficult to reproduce. It may therefore be an artifact arising from the reaction of (1) with products from the thermal decomposition of $SbPh_3$. What is clear from the extremely slow or non-existent reactions with $AsPh_3$ and $SbPh_3$ is that the polarisability of the donor group in EPh_3 (E = P, As, or Sb) ligands has little influence on their nucleophilicity towards cation (1).

TABLE 4

Relative reactivities of N- and P-nucleophiles towards various substrates at 0 °C

Nucleophile	$\log(k/k_{aniline})$		
	trans-$[PtCl_2(py)_2]$ [a]	MeI [a]	$[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ [b]
PBu^n_3	5.8	3.0	2.0
PPh_3	5.8	1.3	0.4
Imidazole	0.3	0.7	0.3 [c]
Pyridine	0.03	−0.5	0 [d]
Aniline	0	0	0 [d]
$AsPh_3$	3.8	−0.9	No reaction
$SbPh_3$	3.7	$\leqslant -3.7$	$\leqslant -7.1$

[a] Solvent MeOH, ref. 18. [b] Solvent CH_3NO_2, this work and ref. 1. [c] Solvent CH_3CN, D. Evans and L. A. P. Kane-Maguire, *Inorg. Chim. Acta*, in the press. [d] Solvent CH_3CN, refs. 10 and 15.

No reaction was also observed between (1) and NPh_3 (0.007 mol dm^{-3}) in CH_3NO_2 at 15 °C. This can probably be attributed to extreme steric crowding about the nitrogen reaction centre. However, when cation (1) is compared with other substrates such as MeI and *trans*-$[PtCl_2(py)_2]$, non-sterically crowded N-donor nucleophiles such as pyridine and aniline are disproportionately reactive compared with P- and As-nucleophiles (Table 4). For example, whereas PPh_3 is *ca.* 10^6 and 20 times more reactive than aniline when attacking *trans*-$[PtCl_2(py)_2]$ and MeI, respectively, it is only *ca.* twice as reactive as aniline towards (1). Similarly, although $AsPh_3$ is *ca.* 5×10^3 times more reactive than aniline towards *trans*-$[PtCl_2(py)_2]$, it does not react with (1) at all despite the rapid reaction of the latter cation with aniline. These observations are all consistent with a dominant role for basicity in controlling nucleophilicity towards (1). This in turn is consistent with a relatively 'hard' character for cation (1), as expected for a stabilised carbonium ion in which there is significant positive charge residing on the dienyl ring carbon atoms.[20]

TABLE 5

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

Substrate	$k_{4\text{-Me}}/k_{2\text{-Me}}$	$k_{2\text{-MeO}}/k_{4\text{-MeO}}$	$k_{2\text{-MeO}}/k_{2\text{-Me}}$	$k_{2\text{-OMe}}/k_H$	Ref.
$PhCH_2Cl$ [a]	99	4	610	27	11
m-$CNC_6H_4CHBrSO_2Ph$ [b]	660 [c]	2 [d]	10 400 [d]	446 [d]	22
$[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ [e]	3 700	11	89 000	91	This work

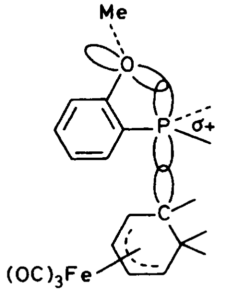
[a] Solvent C_6H_6–MeOH (3 : 2) at 31.0 °C. [b] Solvent dimethylformamide–water (9 : 1). [c] At 50 °C. [d] At 25 °C. [e] Solvent acetone, 0 °C.

Anchimeric Effect in Reactions (i).—A final striking feature of the results in Table 1 is the remarkable reactivity of $P(C_6H_4OMe\text{-}2)_3$. On classical electronic grounds one would expect $P(C_6H_4OMe\text{-}2)_3$ and $P(C_6H_4OMe\text{-}4)_3$ to have similar nucleophilic reactivities. However, more pronounced steric crowding at the phosphorus reaction centre in the former should cause relative retardation. Nevertheless, $P(C_6H_4OMe\text{-}2)_3$ is found to be 11 and 91 times more nucleophilic towards cation (1) than are $P(C_6H_4OMe\text{-}4)_3$ and PPh_3, respectively. Very similar observations have been made by McEwen *et al.*[11,12] in the reactions of $P(C_6H_4X)_3$ nucleophiles with benzyl chloride (Table 5). The unexpected reactivity of $P(C_6H_4OMe\text{-}2)_3$ was explained in terms of anchimeric assistance in which a pair of 2*p* electrons on the methoxyl oxygen overlap with a vacant 3*d* orbital on the phosphorus. This interaction helps to delocalise the positive charge built up on the phosphorus centre in the transition state, thereby decreasing its energy and causing a rapid reaction. Support for this hypothesis included *X*-ray and ^1H n.m.r. evidence [11,12] and the fact that no such effect was seen [21] in analogous reactions of 2-methoxydimethylaniline, 4-methoxydimethylaniline, and dimethylaniline with MeI (relative rates 1.9 : 4.4 : 1).

We propose the presence of analogous anchimeric assistance in reaction (i) to explain the high reactivity of $P(C_6H_4OMe\text{-}2)_3$. A possible transition state for the addition of $P(C_6H_4OMe\text{-}2)_3$ to cation (1) is depicted below (only one aryl group is shown for simplicity). In support of such a through-space interaction is the upfield shift of the $H^{5'}$ proton of (2b) compared with the $H^{5'}$ protons in the related phosphonium adducts with $P(C_6H_4OMe\text{-}4)_3$ and PPh_3 (τ 5.85, 5.71, and 5.32, respectively, in $[^2H_6]$acetone, see Experimental section).

McEwen *et al.*[11] have quantified the anchimeric effect in terms of the ratio $k_{2\text{-MeO}}/k_{2\text{-Me}}$, *i.e.* the relative rate constants for the reactions with $P(C_6H_4OMe\text{-}2)_3$ and

$P(C_6H_4Me\text{-}2)_3$. They further suggested that the magnitude of this ratio may reflect the degree of phosphorus–carbon bond formation and the extent of positive charge build-up on the phosphorus atom in the transition state. This view was reinforced by the observation of a large $k_{2\text{-MeO}}/k_{2\text{-Me}}$ ratio of 10 400 in the reactions with *m*-$CNC_6H_4CHBrSO_2Ph$ for which accumulated evidence [22] suggested a ' late ' transition state, whereas in the related processes with benzyl chloride where an ' early ' transition state was envisaged a smaller $k_{2\text{-MeO}}/k_{2\text{-Me}}$ ratio of 610 was found.[11]



However, we feel that the $k_{2\text{-MeO}}/k_{2\text{-Me}}$ ratio is a hazardous measure of relative anchimeric effects because of its sensitivity to steric effects. Since blocking by a 2-methyl substituent will be far more serious than by a 2-methoxy-group, high $k_{2\text{-MeO}}/k_{2\text{-Me}}$ ratios may arise with certain sterically demanding substrates largely because of major steric retardation of the $P(C_6H_4Me\text{-}2)_3$ reaction rather than from anchimeric assistance of the attack by $P(C_6H_4OMe\text{-}2)_3$. This would appear to be the case in the present reactions with cation (1) ($k_{2\text{-MeO}}/k_{2\text{-Me}} = 8.9 \times 10^4$), in which very significant retardation of the $P(C_6H_4Me\text{-}2)_3$ reaction has been established (see above and Table 5). This potential problem can be considerably reduced by employing the ratio $k_{2\text{-MeO}}/k_H$ as the quantitative measure of anchimeric effects.

TABLE 6

Relative reactivities of π-hydrocarbon complexes towards PBu^n_3 in acetone

Complex	k_1 (20 °C)/ dm³ mol⁻¹ s⁻¹	Rel. k_1	Ref.
$[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$	336 000	1.7×10^7	This work
$[Cr(CO)_3(\eta\text{-}C_7H_7)]^+$	40 900	2.0×10^6	*a*
$[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]^+$	16 100	8.0×10^5	1
$[Fe(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_2H_4)]^+$	861	4.3×10^4	*b*
$[Mn(CO)_3(\eta\text{-}C_6H_6)]^+$	770	3.9×10^4	*c*
$[Fe(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}MeCHCH_2)]^+$	140	7.0×10^3	*b*
$[Co(\eta\text{-}C_5H_5)(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$	87	4.3×10^3	*d*
$[Fe(CO)_2I(1\text{—}5\text{-}\eta\text{-}C_6H_7)]$	1.8	90	*e*
$[Co(\eta\text{-}C_5H_5)(1\text{—}5\text{-}\eta\text{-}C_7H_9)]^+$	1.5	75	*d*
$[Fe(CO)_2I(1\text{—}5\text{-}\eta\text{-}C_7H_9)]$	0.02	1	*e*

[a] G. R. John, L. A. P. Kane-Maguire, and D. A. Sweigart, *J. Organomet. Chem.*, 1976, **120**, C47; J. G. Atton, G. R. John, and L. A. P. Kane-Maguire, unpublished results. [b] L. Cosslett and L. A. P. Kane-Maguire, *J. Organomet. Chem.*, 1979, **178**, C17; and unpublished work. [c] L. A. P. Kane-Maguire and D. A. Sweigart, *Inorg. Chem.*, 1979, **18**, 700. [d] L. A. P. Kane-Maguire, P. D. Mouncher, and A. Salzer, unpublished work. [e] M. Gower, G. R. John, L. A. P. Kane-Maguire, T. I. Odiaka, and A. Salzer, *J. Chem. Soc., Dalton Trans.*, 1979, 2003.

Some $k_{2\text{-MeO}}/k_H$ ratios for various reactions are summarised in Table 5. Interestingly, for attack on cation (1) the $k_{2\text{-MeO}}/k_H$ value of 91 is considerably larger than that (27) with $PhCH_2Cl$ as substrate. Since cation (1) is seen from the $k_{4\text{-Me}}/k_{2\text{-Me}}$ ratios to be much the more sterically demanding substrate, its higher $k_{2\text{-MeO}}/k_H$ ratio can only arise from more significant anchimeric assistance. This in turn suggests somewhat greater phosphorus–carbon bond formation in the transition states for reactions (i) than in the related processes with benzyl chloride (a view supported by their relative Hammett slopes, ρ of −1.32 and −1.08, respectively). The much higher $k_{2\text{-MeO}}/k_H$ ratio of 446 found with *m*-$CNC_6H_4CHBrSO_2Ph$ as substrate (Table 5) is consistent with the very ' late ' transition state established for its reactions. In view of these observations, the potential of employing $k_{2\text{-MeO}}/k_H$ ratios as a sensitive probe of the transition state in the reactions of tertiary phosphines with other π-hydrocarbon metal complexes is currently being explored.

Relative Electrophilicities of Organometallic Cations.—Kinetic data are now available for the addition of PBu^n_3 as a common nucleophile (in acetone solvent) to a wide variety of co-ordinated π-hydrocarbons. The results in Table 6 show a range of relative reactivities for organometallic cations of *ca.* 2.2×10^5 between the most electrophilic, $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$, and the least electrophilic, namely $[Co(\eta\text{-}C_5H_5)(1\text{—}5\text{-}\eta\text{-}C_7H_9)]^+$. If one includes the neutral $[Fe(CO)_2I(1\text{—}5\text{-}\eta\text{-dienyl})]$ substrates in this comparison, an overall reactivity range of *ca.* 1.7×10^7 is seen to be involved. A similar order of electrophilicities is obtained by comparison of available data for addition of PPh_3 to organometallic cations (Table 7). Unfortunately, these latter studies involve changes of solvent. However, various studies suggest that rate constants for phosphines are unlikely to vary by more than a factor of two on changing solvent in the series acetone, nitromethane, and acetonitrile. The results in Table 7 cover a reactivity range of *ca.* 8.4×10^5 between $[Fe(\eta\text{-}C_6H_6)_2]^{2+}$ and $[Fe(CO)_2(\eta\text{-}C_5H_5)(1\text{—}2\text{-}\eta\text{-}MeCHCH_2)]^+$. Considering that other studies [23] with $P(C_6H_4Cl\text{-}4)_3$ show the cycloheptatriene cation $[Mn(CO)_3(1\text{—}6\text{-}\eta\text{-}C_7H_8)]^+$ to be *ca.* 58 times more electrophilic than $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$, it is now clear that

TABLE 7

Relative reactivities of π-hydrocarbon complexes towards PPh_3 at 20 °C

Complex	Solvent	k_1/dm³ mol⁻¹ s⁻¹	Rel. k_1	Ref.
$[Fe(\eta\text{-}C_6H_6)_2]^{2+}$	CH_3CN	320 000	8.4×10^5	*a*
$[Fe(CO)_2(NO)(\eta\text{-}C_4H_4)]^+$	CH_3NO_2	44 000 [b]	1.2×10^5	13
$[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$	CH_3NO_2	16 000	4.2×10^3	1
$[Ru(\eta\text{-}C_6H_6)_2]^{2+}$	CH_3CN	8 400	2.2×10^3	*a*
$[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]^+$	CH_3NO_2	1 870	4.9×10^2	1
$[Fe(CO)(NO)(PPh_3)(\eta\text{-}C_4H_4)]^+$	CH_3NO_2	1 740 [b]	4.5×10^2	13
$[Os(\eta\text{-}C_6H_6)_2]^{2+}$	CH_3CN	1 500	3.9×10^2	*a*
$[Co(\eta\text{-}C_5H_5)(C_8H_{11})]^+$	Acetone	1 180	3.1×10^2	*c*
$[Cr(CO)_3(\eta\text{-}C_7H_7)]^+$	Acetone	890	2.3×10^2	*d*
$[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_7H_9)]^+$	CH_3NO_2	215	57	1
$[Fe(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}C_2H_4)]^+$	Acetone	115	30	*e*
$[Fe(CO)_2(\eta\text{-}C_5H_5)(\eta\text{-}MeCHCH_2)]^+$	Acetone	3.8	1	*e*

[a] P. J. Domaille, S. D. Ittel, J. P. Jesson, and D. A. Sweigart, *J. Organomet. Chem.*, 1980, **202**, 191. [b] Temperature 25 °C. [c] L. A. P. Kane-Maguire, P. D. Mouncher, and A. Salzer, *J. Organomet. Chem.*, 1979, **168**, C42. [d] J. G. Atton, G. R. John, and L. A. P. Kane-Maguire, unpublished work. [e] L. Cosslett and L. A. P. Kane-Maguire, *J. Organomet. Chem.*, 1979, **178**, C17; and unpublished work.

cations varying by more than six orders of magnitude in reactivity are available for study. These should therefore provide an ideal testing ground for recent suggestions [24] that the reactivity–selectivity principle does not apply to the reactions of carbonium ions with nucleophiles. We are currently exploring this question by examining the selectivities of a variety of such cations towards a range of neutral and anionic nucleophiles.

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