Kinetics of Nucleophilic Attack on Co-ordinated Organic Moieties. Part 25.† A Nucleophilic Order for Attack upon the $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_7H_9)]^+$ Cation

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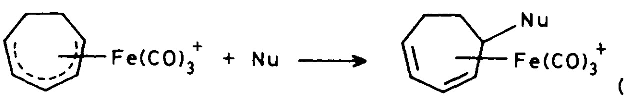
Kinetic studies of the addition of a range of phosphine and phosphite nucleophiles (PR_3) to the cation $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_7H_9)]^+$ to give $[Fe(CO)_3(1—4\text{-}\eta\text{-}R_3P\cdot C_7H_9)]^+$ adducts reveal the general rate law $k_{obs} = k_1[PR_3]$. Combination of these results with analogous data for amine and anionic nucleophiles provides the first comprehensive nucleophilicity order for attack on this cycloheptadienyl substrate. For the neutral phosphorus and nitrogen nucleophiles, this nucleophilicity order quantitatively parallels that found for the related but much more reactive $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ substrate, indicating departure from the reactivity-selectivity principle. However, with N_3^- the C_7H_9 cation reveals exceptional reactivity, suggesting a change in mechanism for this anionic nucleophile.

Kinetic data have been reported for the addition of a wide range of phosphorus, nitrogen, and carbon nucleophiles to the cyclohexadienyl ring of the cation $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ (**1**), and a nucleophilicity order established.[1] For tertiary phosphines,[2] anilines,[3] and pyridines,[4] for which the most extensive information is available, a strong dependence of rate constant on nucleophile basicity was noted. Moderate, but far from complete, nucleophile–carbon bond formation was suggested[2-4] in the transition states for these processes.

Less detailed studies[1-4] of nucleophilic addition to other π-hydrocarbon complexes of lower intrinsic reactivity such as $[Fe(CO)_3(1—5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]^+$ or $[Cr(CO)_3(\eta\text{-}C_7H_7)]^+$ revealed a quantitatively similar nucleophilicity order to that shown by cation (**1**). This suggested that relative nucleophilic reactivities towards organometallic $[M(\pi\text{-hydrocarbon})L_n]^+$ electrophiles may be electrophile independent. Confirmation of this hypothesis would establish a close parallel with related additions to free carbonium ions. Ritchie[5] and more recently Alavosus and Sweigart[6a] have shown that for the addition of oxygen, sulphur, nitrogen, and phosphorus nucleophiles to carbocations, the nucleophilicity (N_+) is independent of the nature or reactivity of the electrophile, being given by relationship (1). Here k_1 is the rate constant for a particular nucleophile

$$N_+ = \log k_1/k_0 \qquad (1)$$

and k_0 is the rate constant for a standard nucleophile (H_2O). This behaviour of free carbonium ions represents a gross departure from the reactivity–selectivity principle. Studies of cationic $[M(\pi\text{-hydrocarbon})L_n]^+$ complexes have revealed[1,2] a very broad range of electrophilicities (factor of *ca.* 10^7) towards nucleophiles (Nu). Such organometallic substrates therefore provide an ideal testing ground for the reactivity–selectivity principle.[6a] As part of a programme examining this question, we report here kinetic data for the addition of tertiary phosphines and phosphites to the cycloheptadienyl complex $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_7H_9)]^+$ (**2**) [equation (2)], which limited earlier studies[2-4] had shown to be intrinsically less reactive than (**1**).



(2)

(**2**) (**3**)

Table 1. Infrared data of $[Fe(CO)_3(1—4\text{-}\eta\text{-}R_3P\cdot C_7H_9)]^+$ adducts in CH_3CN

PR_3	$\nu(CO)/cm^{-1}$
$P(2\text{-}MeOC_6H_4)_3$	2 049, 1 978
$P(4\text{-}MeC_6H_4)_3$	2 054, 1 983
$P(4\text{-}MeC_6H_4)Ph_2$	2 053, 1 983
PPh_3	2 056, 1 984
$P(2\text{-}CNC_2H_4)Ph_2$	2 052, 1 982
$P(2\text{-}CNC_2H_4)_3$	2 058, 1 986
$P(OBu)_3$	2 055, 1 982

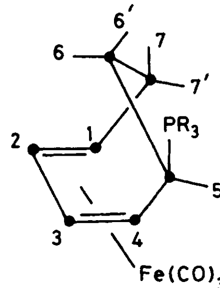


Figure 1. Phosphonium adducts $[Fe(CO)_3(1—4\text{-}\eta\text{-}R_3P\cdot C_7H_9)]^+$ (**3**)

Experimental

Materials.—The salt $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_7H_9)]BF_4$ was prepared and purified using established procedures.[7] The phosphorus nucleophiles were purchased in the purest grades available (Strem or Aldrich) and used as supplied. Acetone solvent was analytical grade, and was deoxygenated by passing through it a stream of dinitrogen for 20 min. Solutions of the appropriate phosphorus nucleophile were prepared under dinitrogen immediately prior to use.

Preparation of Phosphonium Adducts.—Some of the new phosphonium adducts were isolated and characterised, while others were prepared *in situ* and characterised by their ^1H n.m.r. and/or i.r. spectra (Table 1). Proton n.m.r. spectra were

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† Part 24, S. Chapman, L. A. P. Kane-Maguire, and R. Kanitz, *J. Organomet. Chem.*, 1987, **329**, C11.

recorded in CD_3COCD_3 using $[Fe] = [PR_3] = 0.08$ mol dm^{-3}. Refer to Figure 1 for the labelling of atoms.

Tricarbonyl{1—4-η-5-[*tris*(p-*methoxyphenyl*)*phosphonio*]-*cyclohepta*-1,3-*diene*}*iron tetrafluoroborate.* Tris(4-methoxyphenyl)phosphine (28 mg, 0.0079 mmol) was added to a solution of (**2**) (25 mg, 0.0078 mmol) in acetone (1 cm^3). Rotary evaporation and treatment with diethyl ether gave the product as a pale yellow solid (37 mg, 70% yield) (Found: C, 55.4; H, 4.7. Calc. for $C_{31}H_{30}BF_4FeO_6P$: C, 55.4; H, 4.5%). ^1H N.m.r. (CD_3COCD_3): δ 8.0—7.1 (m, aromatic), 5.45 (dd, 1 H, H^2, $J_{2,1}$ 7.5, $J_{2,3}$ 4.9), 5.31 (m, 1 H, H^3, $J_{3,4}$ 7.0, $J_{3,1}$ 2.0), 4.28 (dt, 1 H, $H^{5'}$, $J_{5',6} = J_{5',P}$ 13.0, $J_{5',6'}$ 2.8 Hz), 3.90 (s, 9 H, OCH_3), 3.30 (m, 1 H, H^1, $J_{1,2}$ 7.5, $J_{1,7}$ 6.0), 3.10 (dd, 1 H, H^4, $J_{4,P}$ 15.5, $J_{4,3}$ 7.2, $J_{4,5'}$ 0 Hz), 2.25 (m, 2 H, H^7 and $H^{7'}$), 1.99 (m, 1 H, $H^{6'}$), and 1.25 (m, 1 H, H^6).

Tricarbonyl{1—4-η-5-[*tris*(o-*methoxyphenyl*)*phosphonio*]-*cyclohepta*-1,3-*diene*}*iron tetrafluoroborate.* ^1H N.m.r. (CD_3COCD_3): δ 7.95—7.1 (m, aromatic), 5.58 (dd, 1 H, H^2), 5.40 (m, 1 H, H^3), 4.12 (dt, 1 H, $H^{5'}$, $J_{5',6} \sim J_{5',P} \sim 13$, $J_{5',6'} \sim 3$), 3.90 (s, 9 H, OCH_3), 3.34 (t, 1 H, H^1, $J_{1,2} \sim J_{1,7} \sim 6.5$ Hz), 3.02 (dd, 1 H, H^4), 2.16 (overlapping multiplets, 2 H, H^7 and $H^{7'}$), 1.76 (m, 1 H, $H^{6'}$), and 1.32 (m, 1 H, H^6).

Tricarbonyl[1—4-η-5-(*tri*-p-*tolylphosphonio*)*cyclohepta*-1,3-*diene*]*iron tetrafluoroborate.* This was isolated in a similar manner to the above (Found: C, 58.6; H, 4.9. Calc. for $C_{31}H_{30}BF_4FeO_3P$: C, 59.6; H, 4.8%). ^1H N.m.r. (CD_3COCD_3): δ 7.95—7.1 (m, aromatic), 5.44 (dd, 1 H, H^2), 5.28 (m, 1 H, H^3), 4.40 (dt, 1 H, $H^{5'}$), 3.30 (m, 1 H, H^1), 3.12 (dd, 1 H, H^4, $J_{4,P}$ 15.2, $J_{4,3}$ 7.2, $J_{4,5'}$ 0 Hz), 2.40 (overlapping multiplets, 2 H, H^7 and $H^{7'}$), 2.29 (s, 9 H, CH_3), 2.05 (m, 1 H, $H^{6'}$, partly masked by CH_3COCH_3 resonance), and 1.25 (m, 1 H, H^6).

Tricarbonyl{1—4-η-5-[*tris*(2′-*cyanoethyl*)*phosphonio*]*cyclohepta*-1,3-*diene*}*iron tetrafluoroborate.* This was isolated in a similar manner to the above (Found: C, 44.4; H, 3.8; N, 7.9. Calc. for $C_{19}H_{21}BF_4FeN_3O_3P$: C, 44.5; H, 4.1; N, 8.2%). ^1H N.m.r. (CD_3COCD_3): δ 5.77 (m, 1 H, H^3), 5.65 (dd, 1 H, H^2, $J_{2,1}$ 7.6, $J_{2,3}$ 4.9), 3.49 (dt, 1 H, $H^{5'}$, $J_{5',6} = J_{5',P}$ 13.2, $J_{5',6'}$ 2.7), 3.35 (t, 1 H, H^1, $J_{1,2} = J_{1,7}$ 7.0 Hz), 3.3—3.1 (overlapping multiplets, *ca.* 7 H, CH_2CH_2P and H^4), 2.4—2.1 (overlapping multiplets, 2 H, H^7 and $H^{7'}$), 2.00 (m, 1 H, $H^{6'}$, partly masked by CH_3COCH_3 resonance), and 1.68 (m, 1 H, H^6).

Tricarbonyl[1—4-η-5-(*tributoxyphosphonio*)*cyclohepta*-1,3-*diene*]*iron tetrafluoroborate.* ^1H N.m.r. (CD_3COCD_3): δ 5.72 (m, 1 H, H^3), 5.64 (dd, 1 H, H^2), 4.72 (m, 6 H, OCH_2), 3.35 (t, 1 H, H^1, $J_{1,2} = J_{1,7}$ 6.9 Hz), 3.22 (m, 1 H, $H^{5'}$), 3.03 (dd, 1 H, H^4, $J_{4,P}$ 15.9, $J_{4,3}$ 7.1, $J_{4,5'}$ 0 Hz), 2.35—1.40 (overlapping multiplets, H^7, $H^{7'}$, $H^{6'}$ and $OCH_2CH_2CH_2Me$, partly masked by CD_3COCD_3 resonance), and 0.97 (t, 9 H, CH_3).

Spectroscopic Studies.—Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer using matched 0.5-mm CaF_2 solution cells. ^1H N.m.r. spectra (400 MHz) in [$^2H_6$]-acetone were measured on a JEOL GX 400 spectrometer.

Kinetic Studies.—All of the reactions were rapid and were monitored at 380 nm with a thermostatted (±0.1 °C) stopped-flow spectrophotometer. At this wavelength a large decrease in absorbance occurs during the reaction, associated with the disappearance of the original dienyl salt (**2**).

All the processes were studied under pseudo-first-order conditions using a large excess of phosphorus nucleophile and $[Fe] = 3.0 \times 10^{-4}$—$5.0 \times 10^{-4}$ mol dm^{-3}. Pseudo-first-order rate constants, $k_{obs.}$, were calculated from the slopes of plots of $\log(A_\infty - A_t)$ *vs.* time *t* using a least-squares program. These plots were generally linear for at least 80% of reaction. Each run was carried out in quadruplicate, with $k_{obs.}$ values showing an average reproducibility better than ±5%.

Second-order rate constants, *k*, were generally calculated from

Table 2. Kinetic data for the addition of P-nucleophiles to $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_7H_9)]^+$ (**2**) in acetone at 20.0 °C

Nucleophile	$10^3[PR_3]$/mol dm^{-3}	$k_{obs.}/s^{-1}$	$k_1/dm^3\ mol^{-1}\ s^{-1}$ [a]
$P(2\text{-}MeOC_6H_4)_3$	1.00	28.30	28 300
$P(4\text{-}MeOC_6H_4)_3$	5.00	4.54	
	10.00	8.68	850 (7)
	30.00	25.6	
$P(4\text{-}MeC_6H_4)_3$	3.00	1.12	
	6.00	2.49	435 (14)
	10.00	4.32	
$P(4\text{-}MeC_6H_4)Ph_2$	2.50	0.411	
	5.00	0.891	175 (3)
	10.00	1.74	
PPh_3	5.00	0.624	
	10.00	1.32	120 (3)
	30.00	3.60	
	3.00	0.126 [b]	
	8.00	0.320 [b]	
	15.00	0.658 [b]	41.7 (0.5) [b]
	30.00	1.21 [b]	
	60.00	2.51 [b]	
$P(2\text{-}CNC_2H_4)Ph_2$	5.00	0.377	
	10.00	0.748	76.0 (0.4)
	25.00	1.90	
$P(2\text{-}CNC_2H_4)_3$	10.00	0.100	
	25.00	0.209	8.3 (0.7)
$P(OBu^n)_3$	40.00	0.461	
	100.00	0.930	
	200.00	1.92	7.9 (0.4)
	320.00	2.89	
	500.00	3.92	
$P(OMe)_3$	200.00	0.168	0.84

[a] Derived from equation (3). Estimated standard deviations are given in parentheses. [b] Temperature 0.0 °C.

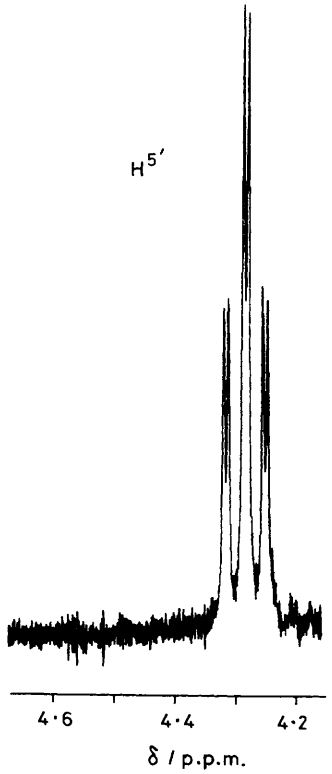

Figure 2. $H^{5'}$ N.m.r. signal for *exo*-$[Fe(CO)_3\{(4\text{-}MeOC_6H_4)_3P\cdot C_7H_9\}]BF_4$

the slopes of plots of $k_{obs.}$ *vs.* $[PR_3]$ using a least-squares analysis.

Results and Discussion

Nature of the Reactions.—Synthetic and spectroscopic studies have established that neutral amine (pyridines,[4] anilines,[2] imidazole,[8] or aliphatic amines[9]) and phosphorus[9] nucleophiles generally add to the cycloheptadienyl ring of cation (**2**) as shown in equation (2). In particular, Brown *et al.*[9] have shown that tertiary aryl and alkyl phosphines add to (**2**) to yield *exo*-phosphonium adducts of type (**3**, Nu = PR_3). Formation of analogous tricarbonyl(1,3-diene)iron products of type (**3**) was confirmed for each of the phosphorus nucleophiles studied here in acetone solvent by the production of typical ν(CO) product bands at *ca.* 2 055 and 1 980 cm^{-1} in each case (Table 1), and from their *in situ* n.m.r. spectra.

In contrast to the complex spectra previously observed[2,9] for related species at 100 MHz, the 400-MHz ^1H n.m.r. spectra of adducts $[Fe(CO)_3(1\text{—}4\text{-}\eta\text{-}R_3P\cdot C_7H_9)]^+$ (**3**) [PR_3 = $P(2\text{-}MeOC_6H_4)_3$, $P(4\text{-}MeOC_6H_4)_3$, $P(4\text{-}MeC_6H_4)_3$, $P(4\text{-}MeC_6H_4)Ph_2$, PPh_3, $P(2\text{-}CNC_2H_4)Ph_2$, $P(2\text{-}CNC_2H_4)_3$, or $P(OBu^n)_3$] show discrete signals for each of the diene ring protons, except H^7 and $H^{7'}$ which appear as overlapping multiplets (see Experimental section). This permitted unequivocal assignment of each of the ring protons *via* a series of spin-decoupling experiments. Details will be reported in a subsequent paper correlating the configurations of a range of substituted diene and triene iron tricarbonyl complexes *via* 400-MHz n.m.r. spectroscopy. Of particular concern to the present study is the unequivocal assignment of an *exo*-configuration to the PR_3 substituent at C(5) (R = $2\text{-}MeOC_6H_4$, $4\text{-}MeOC_6H_4$, $4\text{-}MeC_6H_4$, $2\text{-}CNC_2H_4$, or OBu^n). In each case, the $H^{5'}$ proton appears as a characteristic double triplet (*e.g.* Figure 2). This collapses to a triplet ($J_{5',6} \sim J_{5',P} \sim 13$ Hz) upon irradiation at $H^{6'}$, and to a double doublet ($J_{5',6} \sim 12$, $J_{5',6'} \sim 3$ Hz) upon irradiation at H^6. The signal for $H^{5'}$ is unaffected by irradiation at H^4, confirming no or very weak coupling between H^4 and $H^{5'}$. The near zero $J_{4,5'}$ value is predicted from the CH^4–$CH^{5'}$ dihedral angle determined from a molecular model of the *exo*-adduct (**3**). An *exo* configuration has been similarly assigned[9] to the related phosphonium adduct (**3**, R = Et) on the basis of the magnitude of $J_{4,5'}$. For the alternative *endo* isomers, a model predicts $J_{4,5'} \geqslant 5$ Hz on the basis of the Karplus equation.[10]

With some sterically non-demanding trialkylphosphines and specific solvent conditions, rearrangement of the *exo*-phosphonium adducts to the related *endo* derivatives has been reported.[9] However, no evidence was observed here in acetone for the conversion of any of the pale yellow *exo* adducts to the brown *endo* isomers, either with the bulky triarylphosphines or with the much smaller trialkyl phosphite nucleophiles.

Kinetics and Mechanism.—Kinetic data for the addition of various tertiary phosphines and phosphites to cation (**2**) in acetone at 20 °C are collected in Table 2. The rate law (3) is seen to be generally obeyed. In the case of $P(2\text{-}MeOC_6H_4)_3$, only one phosphine concentration could be conveniently studied because of its high reactivity. For this nucleophile and $P(OMe)_3$, rate law (3) has been assumed. Second-order rate constants, k_1, thus calculated for each phosphorus nucleophile are summarised in Table 2.

$$\text{Rate} = k_{obs.}[\text{complex}]$$

$$k_{obs.} = k_1[PR_3] \qquad (3)$$

The rate law (3) is most readily rationalised in terms of direct addition, k_1, to the cycloheptadienyl ring of (**2**). Direct

Table 3. Nucleophilicity order for addition to $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_7H_9)]^+$ (**2**) at 20 °C

Nucleophile	Solvent	N_{Fe}[a]	k_1/ dm^3 mol^{-1} s^{-1}	Ref.
(*i*) P-nucleophiles				
$P(2\text{-}MeOC_6H_4)_3$	Acetone	3.83	28 300	This work
PBu^n_3		3.52	11 100	
$P(4\text{-}MeOC_6H_4)_3$		2.81	850	
$P(4\text{-}MeC_6H_4)_3$		2.45	435	
$P(4\text{-}MeC_6H_4)Ph_2$		2.13	175	
PPh_3		1.87	120	
$P(2\text{-}CNC_2H_4)Ph_2$		1.72	76	
$P(2\text{-}CNC_2H_4)_3$		0.80	9.2	
$P(OBu^n)_3$		0.00	7.9	
$P(OMe)_3$		−0.53	0.84	
(*ii*) N-nucleophiles				
4-Methylaniline	CH_3CN	2.16	939	3
Imidazole		2.10	374	8
Pyridine		1.79	320	4
2-Methylaniline		1.32	113	3
2-Methylpyridine		1.34	61.3	4
2,6-Dimethylpyridine		−0.55	1.7	4
N_3^-	Water	1.93	2 620	16

[a] Nucleophilicity parameters for reference substrate $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_6H_7)]^+$.

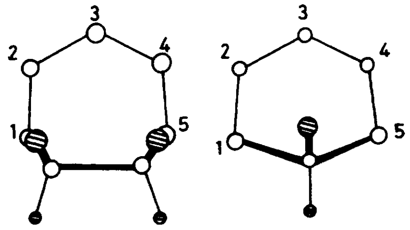

Figure 3. View of co-ordinated C_6H_7 and C_7H_9 rings from above the dienyl planes. Only hydrogen atoms bonded to methylene carbons are shown

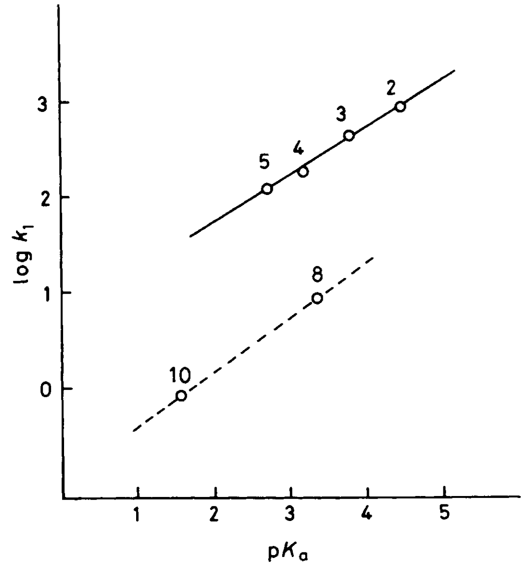

Figure 4. Brønsted plot of log k_1 *vs.* pK_a (of conjugate acid) for the addition of tertiary phosphines and phosphites to $[Fe(CO)_3(1\text{—}5\text{-}\eta\text{-}C_7H_9)]^+$ (**2**) in acetone at 20 °C; key as in Figure 5

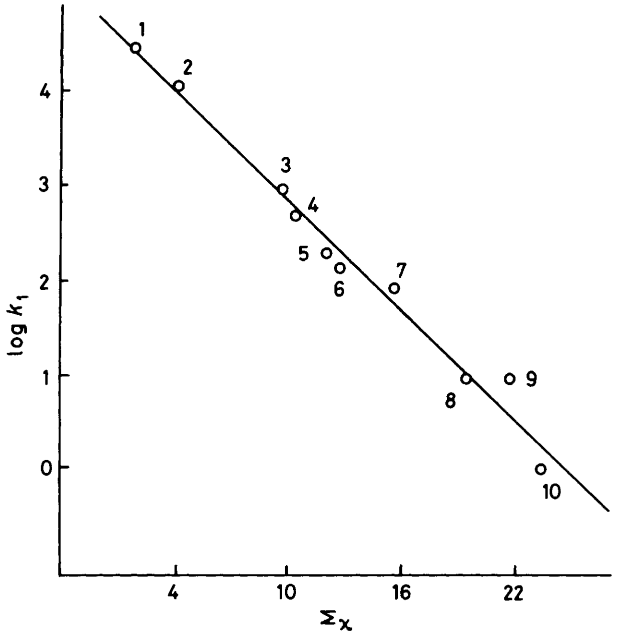

Figure 5. Plot of logk_1 *vs.* Tolman Σχ values for the addition of tertiary phosphines and phosphites to $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_7H_9)]^+$ (**2**) in acetone at 20 °C: 1, $P(2\text{-}MeOC_6H_4)_3$; 2, $PBu^n{}_3$; 3, $P(4\text{-}MeOC_6H_4)_3$; 4, $P(4\text{-}MeC_6H_4)_3$; 5, $P(4\text{-}MeC_6H_4)Ph_2$; 6, PPh_3; 7, $P(2\text{-}CNC_2H_4)Ph_2$; 8, $P(OBu^n)_3$; 9, $P(2\text{-}CNC_2H_4)_3$; 10, $P(OMe)_3$

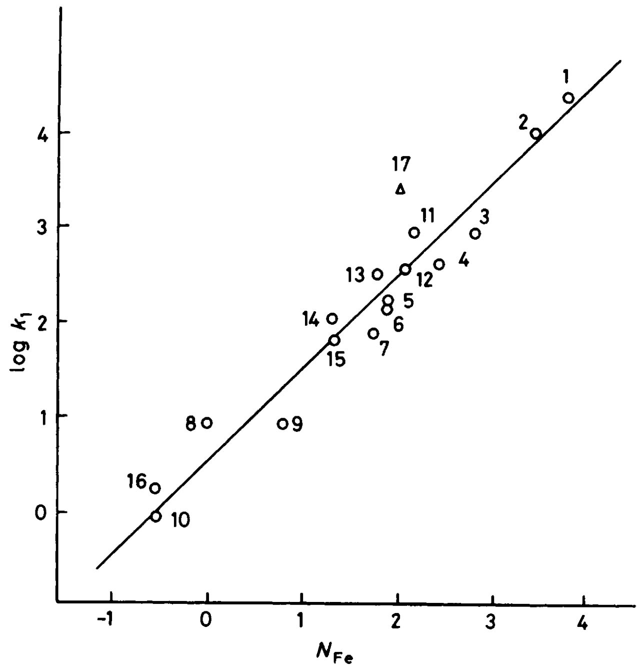

Figure 6. Plot of log k_1 for the reactions of various nucleophiles with $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_7H_9)]^+$ (**2**) *vs.* N_{Fe}; key as in Figure 5 and 11, 4-methylaniline; 12, imidazole; 13, pyridine; 14, 2-methylaniline; 15, 2-methylpyridine; 16, 2,6-dimethylpyridine; 17, N_3^-

approach from above the dienyl ring is supported by the *exo* configuration established above for adducts (**3**, Nu = PR_3). Also consistent with this mechanism is the considerably faster reaction observed[2] for each nucleophile with the related cyclohexadienyl cation $[Fe(CO)_3(1—5\text{-}\eta\text{-}C_6H_7)]^+$ (**1**). For example, rate constant ratios, $k_{C_6H_7}/k_{C_7H_9}$, of *ca.* 60 are observed for addition of triarylphosphines. [The somewhat smaller $k_{C_6H_7}/k_{C_7H_9}$ ratio of 24 for $P(2\text{-}MeOC_6H_4)_3$ is believed to arise from an underestimation[2] of the k_1 value for attack of this highly reactive phosphine on cation (**1**).] As is clear from Figure 3, which gives a view from above the dienyl rings, the C_7H_9 ligand will generate considerably greater steric hindrance to *exo* attack at C(5) than will a C_6H_7 ligand.[11] In the C_7H_9 case, one H atom on each methylene group effectively eclipses the adjacent C(5) [or C(1)] atom. In contrast, the two H atoms on the methylene group of C_6H_7 are symmetrically disposed at considerable distance from C(1) and C(5).

The k_1 values summarised in Table 2 for addition of various phosphorus nucleophiles to cation (**2**) reveal a strong dependence on nucleophile basicity. A Brønsted plot of log k_1 *vs.* pK_a is linear for triarylphosphines with a slope of *ca.* 0.45 (Figure 4). This slope is very similar to that previously reported[2] for the analogous addition to cation (**1**). A separate Brønsted plot is followed by trialkyl phosphites (Figure 4), with a similar strong dependence of k_1 on nucleophile basicity. The trialkylphosphine $P(2\text{-}CNC_2H_4)_3$ does not fit on either of the above linear free-energy relationships.

In general, the reactivity order of the phosphorus nucleophiles towards (**2**), $P(2\text{-}MeOC_6H_4)_3$ (3.4×10^4) > $PBu^n{}_3$ (1.3×10^4) > $P(4\text{-}MeOC_6H_4)_3$ (1.0×10^3) > $P(4\text{-}MeC_6H_4)_3$ (5.2×10^2) > $P(4\text{-}MeC_6H_4)Ph_2$ (2.1×10^2) > PPh_3 (1.4×10^2) > $P(2\text{-}CNC_2H_4)Ph_2$ (90) > $P(2\text{-}CNC_2H_4)_3$ (10) > $P(OBu^n)_3$ (9) > $P(OMe)_3$ (1), parallels that of decreasing electron availability at the phosphorus centres. This is shown by the excellent correlation between logk_1 and the nucleophile Σχ values (Figure 5, correlation coefficient $r = 0.99$). The Σχ values, derived by Tolman,[12] are a measure of the relative σ-donating and π-withdrawing ability of the various phosphorus ligands. A Hammett plot of log (k/k_H) *vs.* $\Sigma\sigma_p$ for the attack of *p*-substituted triarylphosphines on (**2**) gives a slope, ρ, of 1.08 (correlation coefficient $r = 0.99$). This is similar to the Hammett slopes found for analogous reactions with ethyl iodide ($\rho = -1.1$ in acetone)[13] and benzyl chloride ($\rho = -1.08$ in benzene–methanol),[14] and slightly smaller than that reported[2] for the related cyclohexadienyl cation (**1**) ($\rho = -1.32$). However, our log (k/k_H) values correlate poorly with $\Sigma\sigma^+$, showing only a small demand for resonance stabilisation of the transition state. These observations, together with the strong dependence of rate on phosphine basicity suggest a transition state for reactions (2) (Nu = PR_3) in which there is significant, but far from complete, phosphorus–carbon bond formation and build up of positive charge on the phosphorus centre.

Further support for this transition-state structure comes from the exceptionally rapid reaction of (**2**) with $P(2\text{-}MeOC_6H_4)_3$. From Table 2 this sterically blocked phosphine is seen to be *ca.* 230 times more reactive than triphenylphosphine. In keeping with similar observations[15] with organic substrates the unexpected reactivity of $P(2\text{-}MeOC_6H_4)_3$ towards (**2**) may be explained in terms of anchimeric assistance in which a pair of 2*p* electrons on the methoxy oxygen overlap with a vacant 3*d* orbital on the phosphorus. This interaction facilitates the delocalisation of the positive charge built up on the phosphorus centre in the transition state, thereby causing a rapid reaction. Interestingly, the $k_{2\text{-}MeO}/k_H$ ratio of 230 for cation (**2**) is much higher than that observed for analogous reactions with benzyl chloride ($k_{2\text{-}MeO}/k_H = 27$).[15] This suggests significantly greater phosphorus–carbon bond formation in the transition states for reactions (2) (Nu = PR_3) than in the related processes with benzyl chloride. Rate constants have been reported[1—4,8,16] for the addition of a wide range of nucleophiles to the related cyclohexadienyl cation (**1**), and nucleophilicity constants (N_{Fe}) calculated according to equation (5).

$$N_{\mathrm{Fe}} = \log k_1/k_0 \qquad (5)$$

The N_{Fe} values listed in Table 3 differ slightly from those published previously[1] due to a redetermination of k_0 for the reference nucleophile $P(OBu^n)_3$. If, as preliminary observations suggest,[1-4] nucleophilicities towards organometallic $[M(\pi\text{-hydrocarbon})L_n]^+$ substrates are electrophile independent, then plots of $\log k_1$ *vs.* N_{Fe} should be linear with unit slope for *all* electrophiles.

Figure 6 shows such a plot for cation (**2**) using the present results with phosphorus nucleophiles and reported k_1 values for various amines[3,4] and the azide ion.[16] These nucleophiles vary in reactivity by a factor of *ca.* 2×10^4. For the neutral nucleophiles, a satisfactory correlation ($r = 0.98$) is observed with a slope of 1.06 (0.06), confirming a constant nucleophile selectivity for the cations (**1**) and (**2**) despite their differing intrinsic reactivities. However, the log plot disguises some minor differences between the reactivity patterns of cations (**1**) and (**2**). Thus, while $k_{C_6H_7}/k_{C_7H_9}$ ratios of *ca.* 60 are observed for the additions of triarylphosphines, this ratio decreases to *ca.* 20—40 for anilines and pyridines. These differences probably arise from the smaller steric demands of the nitrogen nucleophiles.

The only large deviation from the correlation in Figure 6 is the point (Δ) for the azide ion. In contrast to the behaviour with neutral phosphorus and nitrogen nucleophiles, cations (**1**) and (**2**) have similar reactivities towards the N_3^- anion. This strongly suggests that addition of N_3^- proceeds *via* a different mechanism to that observed for the neutral nucleophiles. It is possible that, as has been suggested elsewhere,[16] addition of N_3^- to cations (**1**) and (**2**) proceeds *via* an 'early' ion-pair like transition state, whereas the present study supports considerable carbon–phosphorus bond formation in reactions (2).

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References

1 L. A. P. Kane-Maguire, E. D. Honig, and D. A. Sweigart, *Chem. Rev.*, 1984, **84**, 525 and refs. therein.

2 G. R. John and L. A. P. Kane-Maguire, *J. Chem. Soc., Dalton Trans.*, 1979, 873; J. G. Atton and L. A. P. Kane-Maguire, *ibid.*, 1982, 1491.

3 L. A. P. Kane-Maguire, T. I. Odiaka, S. Turgoose, and P. A. Williams, *J. Chem. Soc., Dalton Trans.*, 1981, 2489 and refs. therein.

4 T. I. Odiaka and L. A. P. Kane-Maguire, *J. Chem. Soc., Dalton Trans.*, 1981, 1162.

5 C. D. Ritchie, *J. Am. Chem. Soc.*, 1983, **105**, 3573 and refs. therein.

6 (*a*) T. J. Alavosus and D. A. Sweigart, *J. Am. Chem. Soc.*, 1985, **107**, 985; (*b*) C. D. Johnson, *Chem. Rev.*, 1975, **75**, 755 and refs. therein.

7 M. A. Hashmi, J. D. Munro, and P. L. Pauson, *J. Chem. Soc. A*, 1967, 240.

8 D. J. Evans and L. A. P. Kane-Maguire, *Inorg. Chim. Acta*, 1982, **62**, 109; unpublished work.

9 D. A. Brown, S. K. Chawla, W. K. Glass, and F. M. Hussein, *Inorg. Chem.*, 1982, **21**, 2726.

10 M. Karplus, *J. Chem. Phys.*, 1959, **30**, 11.

11 L. A. P. Kane-Maguire, E. D. Honig, and D. A. Sweigart, *J. Chem. Soc., Chem. Commun.*, 1984, 345.

12 C. A. Tolman, *J. Am. Chem. Soc.*, 1970, **92**, 2953.

13 W. A. Henderson and S. A. Buckler, *J. Am. Chem. Soc.*, 1960, **82**, 5794.

14 G. I. Keldsen and W. E. McEwen, *J. Am. Chem. Soc.*, 1978, **100**, 7312.

15 W. E. McEwen, A. B. Janes, J. W. Knapczyk, V. L. Kyllingstad, W-I. Shiau, S. Shore, and J. H. Smith, *J. Am. Chem. Soc.*, 1978, **100**, 7304.

16 J. G. Atton, G. Shaw, and L. A. P. Kane-Maguire, unpublished work.

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