Kinetics of Nucleophilic Attack on Co-ordinated Organic Moieties. Part 7.† Mechanisms of Addition of Tertiary Phosphines and Phosphites to Tricarbonyl(dienyl)iron Cations

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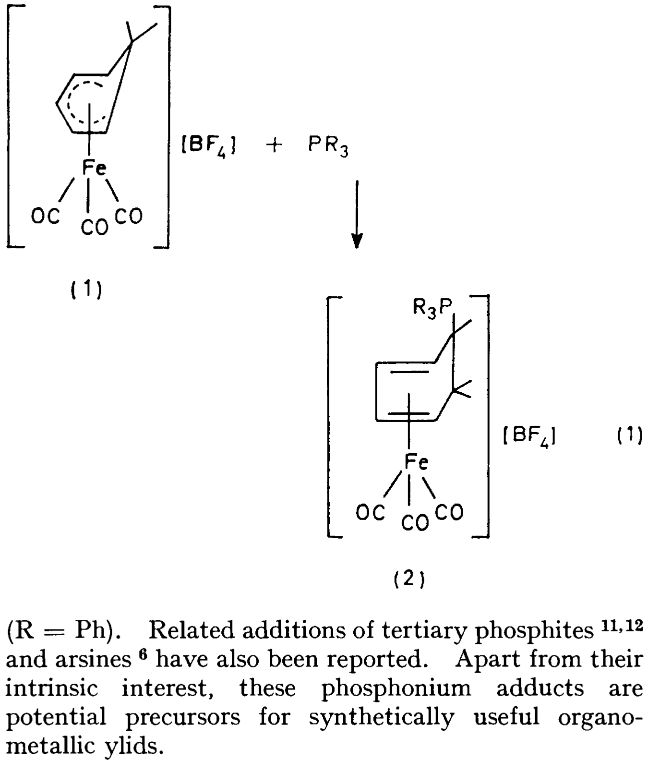
The reaction of tertiary phosphines and phosphites with dienyl complexes such as $[Fe(C_6H_7)(CO)_3][BF_4]$ (1) provides a general route to phosphonium adducts of the type $[Fe(C_6H_7{\cdot}PR_3)(CO)_3][BF_4]$ (R = Ph, *p*-tolyl, Bu^n, OPh, or OBu^n). An analogous reaction with 1,2-bis(diphenylphosphino)ethane leads to the dimeric salt $[Fe_2\{(C_6H_7{\cdot}Ph_2PCH_2)_2\}(CO)_6][BF_4]_2$. The rate law, Rate = *k*[Fe][PR$_3$], is observed for addition of a range of phosphines and phosphites to (1) and the related cations $[Fe(C_6H_6OMe)(CO)_3]^+$ and $[Fe(C_7H_9)(CO)_3]^+$. Rate and activation parameters indicate direct addition at the dienyl rings. The marked dependence of *k* on the basicity of phosphorus nucleophiles suggests significant bond making in the transition states for adduct formation.

Considerable recent interest has centred on the addition of tertiary phosphines to co-ordinated π hydrocarbons to yield stable phosphonium adducts.[1-10] For example, triphenylphosphine has been shown [1] to add to $[Fe(C_6H_7)(CO)_3][BF_4]$ (1) according to equation (1) (R = Ph). Related additions of tertiary phosphites [11,12] and arsines [6] have also been reported. Apart from their intrinsic interest, these phosphonium adducts are potential precursors for synthetically useful organometallic ylids.



(1)

(2)

(1)

As part of a systematic study of the mechanisms of nucleophilic attack on π-hydrocarbon ligands, we recently reported [13] kinetic data for the addition of tri-n-butylphosphine to $[M(arene)(CO)_3][BF_4]$ (M = Mn or Re) complexes to give $[M(arene{\cdot}PBu_3)(CO)_3][BF_4]$, as well as for the analogous reactions of PBu$_3$ with $[M(C_7H_7)(CO)_3][BF_4]$ (M = Cr, Mo, or W).[14] Sweigart and Wilker [15] have also recently investigated the kinetics of addition of $P(C_6H_4Cl\text{-}p)_3$ to the cyclobutadiene group of the cation $[Fe(C_4H_4)(CO)_2(NO)]^+$. The present paper reports further synthetic studies of the reaction of $[Fe(C_6H_7)(CO)_3][BF_4]$ (1) with tertiary phosphines and phosphites, together with detailed kinetic data for reaction (1) (R = Ph, *p*-tolyl, Bu^n, or OBu). Kinetic studies of phosphonium-adduct formation with the related cations $[Fe(C_6H_6OMe)(CO)_3][BF_4]$ (3) and $[Fe(C_7H_9)(CO)_3][BF_4]$ (4) are also described.

EXPERIMENTAL

Materials.—The dienyl salts $[Fe(C_6H_7)(CO)_3][BF_4]$, $[Fe(C_6H_6OMe)(CO)_3][BF_4]$, and $[Fe(C_7H_9)(CO)_3][BF_4]$ were prepared and purified using published methods.[11,12] Nitromethane solvent was distilled under nitrogen and stored over molecular sieves. Acetone was analytical grade. Both solvents were deoxygenated by passing through a stream of nitrogen for 20 min. Solutions of the appropriate phosphorus nucleophile were prepared immediately prior to use.

*Preparation of New Phosphonium Adducts.—Tricarbonyl(5-tri-*p*-tolylphosphoniocyclohexa-1,3-dienide)iron tetrafluoroborate* (2a). This salt was prepared in 74% yield using the procedure reported [1] for the analogous triphenylphosphine adduct (Found: C, 59.0; H, 4.4. Calc. for $C_{30}H_{28}BF_4FeO_3P$: C, 59.0; H, 4.6%). The off-white solid melts with decomposition at 200—205 °C, and in acetone has strong carbonyl bands at 2 052 and 1 985 cm^{-1} as expected. The presence of a strong band at *ca.* 1 060 cm^{-1} (Nujol mull) confirmed the presence of the $[BF_4]^-$ anion.

Tricarbonyl(5-tri-n-butylphosphoniocyclohexa-1,3-dienide)iron tetrafluoroborate (2b). The salt $[Fe(C_6H_7)(CO)_3][BF_4]$ (0.10 g) was dissolved in acetone (1 cm^3), and tributylphosphine added dropwise until the yellow colour disappeared. Addition of sodium-dried diethyl ether and cooling in ice gave a fine off-white precipitate, which was washed several times with light petroleum (60—80 °C) and pentane. The yield of (2b) was 0.140 g (85%), m.p. 80—82 °C (Found: C, 49.4; H, 7.1. Calc. for $C_{21}H_{34}BF_4FeO_3P$: C, 49.6; H, 6.7%). An acetone solution exhibited strong i.r. carbonyl bands at 2 052 and 1 980 cm^{-1}. The presence of the $[BF_4]^-$ anion was confirmed by the strong band (Nujol mull) at 1 060 cm^{-1}.

$[Fe\{C_6H_7{\cdot}P(OBu)_3\}(CO)_3][BF_4]$ (2c). Dropwise addition of tri-n-butyl phosphite (0.082 g, 0.33 mmol) to a solution of $[Fe(C_6H_7)(CO)_3][BF_4]$ (0.10 g, 0.33 mmol) in acetone (1 cm^3) gave a pale yellow solution. Chromatography on an alumina H column with pentane, followed by evaporation, gave a yellow oil. This product (2c) remained as a pale yellow oil (0.124 g, 70%) despite several recrystallisations (Found: C, 45.3; H, 6.3. Calc. for $C_{21}H_{34}BF_4FeO_6P$: C

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† Part 6 is ref. 14.

45.3; H, 6.1%). The presence of i.r. carbonyl bands at 2 055 and 1 980 cm^{-1} (acetone solution) and a strong $[BF_4]^-$ peak at 1 060 cm^{-1} (Nujol mull) also confirm the suggested formulation.

$[Fe\{C_6H_6OMe{\cdot}P(OBu)_3\}(CO)_3][BF_4]$ (2d). Similar treatment of $[Fe(C_6H_6OMe)(CO)_3][BF_4]$ with $P(OBu)_3$ gave the analogous product (2d) in good yield [ν(CO) in acetone at 2 055 and 1 980 cm^{-1}, strong $[BF_4]^-$ band at 1 030 cm^{-1} in Nujol mull].

$[Fe_2(C_6H_7{\cdot}Ph_2PC_2H_4PPh_2{\cdot}C_6H_7)(CO)_6][BF_4]_2$ (2e). To a suspension of (1) (0.200 g) in dry dichloromethane (10 cm^3) was added a large excess of 1,2-bis(diphenylphosphino)ethane (dppe, 1.5 g). The mixture was stirred for 10 min at room temperature giving a clear solution. Sodium-dried diethyl ether was added until the solution became milky, and was then cooled in ice. The fine, pale cream, precipitate of (2e) (0.195 g, 60%) was collected, washed with pentane, and dried *in vacuo* (Found: C, 52.5; H, 3.8; P, 6.2. Calc. for $C_{44}H_{38}B_2F_8Fe_2O_6P_2$: C, 52.3; H, 3.8; P, 6.1%). In acetone its i.r. spectrum showed ν(CO) at 2 055 and 1 985 cm^{-1}, and in CH_2Cl_2 at 2 060 and 1 990 cm^{-1}. A $[BF_4]^-$ band at 1 060 cm^{-1} was observed in Nujol mull.

$[Fe\{C_6H_7{\cdot}PO(OPh)_2\}(CO)_3]$ (5). Triphenyl phosphite (0.2 g) was added dropwise to $[Fe(C_6H_7)(CO)_3][BF_4]$ (0.2 g) in acetone (10 cm^3) until the i.r. spectrum of the reaction mixture showed that all the original dienyl salt had reacted. Extraction of the product as above gave 0.19 g of a yellow low-melting solid (m.p. 15 °C) (Found: C, 56.2; H, 4.0. Calc. for $C_{21}H_{17}FeO_6P$: C, 55.8; H, 3.8%). The i.r. spectrum of the liquid product showed strong carbonyl bands at 2 050 and 1 975 cm^{-1}.

Spectroscopic Measurements.—Infrared spectra were recorded on a Perkin-Elmer 257 spectrometer, ^{1}H n.m.r. (90 MHz) spectra on a Perkin-Elmer R32 spectrophotometer. Field-desorption (f.d.) mass spectra were measured using a Varian combined FD/FI/EI source on a CH5D mass spectrophotometer linked to a Varian 620i data system. Acetone was employed as solvent in all cases. The source temperature was *ca.* 80 °C, and low emitter currents (10—13 mA) were used for desorption of the samples.

Kinetic Studies.—The reactions of $[Fe(C_6H_7)(CO)_3][BF_4]$ (1) and $[Fe(C_6H_6OMe)(CO)_3][BF_4]$ (3) with $P(OPh)_3$ were slow enough to follow by i.r. spectroscopy, using a large excess of the phosphite. Reaction solutions ($[Fe] = 6.0 \times 10^{-3}$ mol dm^{-3}) were prepared in alumina-foil-covered flasks and sealed under nitrogen with Suba seals. Samples were withdrawn by syringe at appropriate intervals, and the reactions monitored by following the disappearance of the carbonyl band of the original dienyl salts at 2 110 cm^{-1}. Pseudo-first-order rate constants were calculated from the gradients of plots of log A_t against time, which were generally linear for at least 60% completion of reaction.

All of the other addition reactions [equation (1)] were very rapid, and were studied using a thermostatted stopped-flow spectrophotometer.[16] Incident light of the desired wavelength was provided by a Bausch and Lomb monochromator fitted with variable slits. All of the additions were accompanied by a large decrease in absorbance in the 370—385 nm region. Reaction traces were monitored on a Tektronix 564 B storage oscilloscope fitted with a log converter, thus giving a direct record of absorbance changes.

Most of the reactions were studied under pseudo-first-order conditions by employing a large excess of phosphorus nucleophile. Values of $k_{obs.}$ were calculated from the gradients of plots of log $(A_t - A_\infty)$ against time, where A_∞ is the absorbance of the solution at infinite time and A_t is the absorbance at time t. Linear first-order kinetics were generally obtained for at least two half-lives. Each $k_{obs.}$ is the average of four separate runs, with an average reproducibility of ±4%.

In some of the runs with triphenylphosphine, equimolar concentrations of iron (dienyl) complex and PPh_3 were employed ($[Fe] = [PPh_3] = 2.0 \times 10^{-3}$ or 3.0×10^{-3} mol dm^{-3}). For these cases second-order rate constants k were calculated directly from the gradients of plots of $x/a(a - x)$ against time, where a = initial concentration of dienyl salt and x = concentration of product at time t. Such rate plots were linear for at least 80% completion of reaction.

Activation enthalpies for the above reactions were obtained from the gradients of Arrhenius plots calculated by a least-squares method. The errors quoted are the standard errors of estimation derived from the least-squares analyses. Entropies of activation were calculated using the second-order rate constants, k.

RESULTS AND DISCUSSION

Synthesis and Characterisation of Phosphonium Adducts.—The present studies show that reaction (1) provides a general route to phosphonium adducts of the type (2) not only with tertiary phosphines (R = *p*-tolyl, Bu^n, or Ph) but also with the analogous tertiary phosphites (R = Bu^n or Ph), although these latter adducts are not always stable. Furthermore, addition of 1,2-bis(diphenylphosphino)ethane, dppe, to $[Fe(C_6H_7)(CO)_3][BF_4]$ leads to the related dimeric adduct $[Fe_2\{(C_6H_7{\cdot}PPh_2CH_2)_2\}(CO)_6][BF_4]_2$ (2e). The phosphine adducts (2a) and (2b) are air-stable microcrystalline solids. They exhibit two strong carbonyl bands in acetone solution at 2 055 and 1 985 cm^{-1}, which are at slightly higher frequency than for neutral $[Fe(diene)(CO)_3]$ complexes. Their ^{1}H n.m.r. spectra are consistent with the proposed formulation, while their f.d. mass spectra show only single peaks due to the molecular ions (Table 1).

The addition of dppe to $[Fe(C_6H_7)(CO)_3][BF_4]$ was investigated as part of a broader study of the synthetic value of employing potentially bidentate ligands as nucleophiles towards co-ordinated π-hydrocarbons. In this particular instance four possible reaction paths are envisaged: (*i*) displacement of a carbonyl ligand to give $[Fe(C_6H_7)(CO)_2(dppe)][BF_4]$, in which the dppe is unidentate; (*ii*) displacement of two carbonyl ligands to yield $[Fe(C_6H_7)(CO)(dppe)][BF_4]$, involving bidentate co-ordination of dppe; (*iii*) addition to the dienyl ring to give $[Fe(C_6H_7{\cdot}Ph_2PC_2H_4PPh_2)(CO)_3][BF_4]$; and (*iv*) stepwise addition to two dienyl rings to yield the dimeric adduct $[Fe_2\{(C_6H_7{\cdot}PPh_2CH_2)_2\}(CO)_6][BF_4]_2$.

The carbonyl-displaced structures (*i*) and (*ii*) were eliminated by the elemental analyses, i.r. spectrum [ν(CO) at 2 055 and 1 985 cm^{-1} in acetone], and ^{1}H n.m.r. spectrum. A broad phenyl resonance is observed at *ca.* τ 2.1, well displaced from the resonance expected at *ca.* τ 2.65 for phenyl groups attached to a free terminal phosphorus as in (*i*) and (*ii*). In addition, phosphorus splitting of the C_6 hydrogens is apparent as expected for structures (*iii*) or (*iv*).

Strong additional support for structure (*iv*) comes

TABLE 1

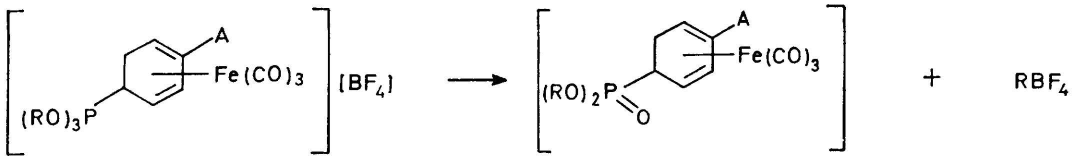
Hydrogen-1 n.m.r. and f.d. mass spectra[a] of diene products

Complex	Proton	Chemical shift, τ [b]	f.d. mass peaks, *m/e*
(2a)	$H^{1,4}$	6.68 (m, 2)	523
	$H^{2,3}$	4.55 (m, 1)	
		4.88 (m, 1)	
	H^5	5.46 (m, 1)	
	$H^{6,6}$	7.1—7.5 (m, 2)	
	aromatic	2.0—2.5 (m, 12)	
	CH_3	7.52 (m, 9)	
(2b)	$H^{1,4}$	6.64 (m, 2)	421
	$H^{2,3}$	4.22 (m, 2)	
	H^5	6.85 (m, 1)	
	$H^{6,6}$	7.4—7.8 (m, 2)	
	alkyl: CH_2	7.96 (m, 6)	
	CH_2CH_2	8.43 (m, 12)	
	CH_3	9.05 (t, 9)	
(2c)	$H^{1,4}$	6.70 (m, 2)	412
	$H^{2,3}$	4.40 (m, 2)	
	H^5	6.44 (m, 1)	
	$H^{6,6}$	7.4—7.8 (m, 2)	
	alkyl: OCH_2	5.08 (m, 6)	
	CH_2	5.94 (m, 6)	
	CH_2	8.4 (br m, 6)	
	CH_3	9.06 (t, 9)	
(2d)			442
(2e)	$H^{1,4}$	6.58 (m, 4)	924, 923, 617, 398, 219
	$H^{2,3}$	4.70 (m, 2)	
		5.10 (m, 2)	
	H^5	5.95 (m, 2)	
	$H^{6,6}$	6.7—7.0 (m, 4)	
	aromatic	1.9—2.3 (m, *ca.* 20)	
	alkyl: CH_2	7.30 (s, 4)	
(5)	$H^{1,4}$	6.73 (m, 2)	452
	$H^{2,3}$	3.70 (m, 1)	
		4.50 (m, 1)	
	H^5	6.62 (m, 1)	
	$H^{6,6}$	7.6—8.0 (m, 2)	
	aromatic	2.80 (d, 2)	
		2.82 (t, 4)	
		3.14 (d, 4)	

[a] In $(CD_3)_2CO$. [b] The multiplicity and intensity are given in parentheses.

from the f.d. mass spectrum of (2e) (Table 1). Although fairly complex, it shows strong peaks at *m/e* 923 and 924 as expected for the molecular M^+ and $[M + 1]^+$ ions of the parent $[Fe_2\{(C_6H_7{\cdot}Ph_2PCH_2)_2\}(CO)_6(BF_4)]^+$. Further peaks at *m/e* 617, 398, and 219 can be assigned to the fragmentation products $[Fe(C_6H_7{\cdot}Ph_2PC_2H_4PPh_2)(CO)_3]^+$, dppe, and $[Fe(C_6H_7)(CO)_3]^+$, respectively. No peaks attributable to products (*i*) and (*ii*) are observed. This example provides another demonstration of the utility of f.d. mass spectrometry in identifying organometallic salts. Stepwise addition of dppe at two π-hydrocarbon ligands contrasts with earlier studies[17] of the reaction of bidentate phosphines with the related tropylium complex $[Mo(C_7H_7)(CO)_2I]$, in which only carbonyl displacement was observed.

The reactions of $[Fe(C_6H_7)(CO)_3][BF_4]$ and $[Fe(C_6H_6OMe)(CO)_3][BF_4]$ with $P(OBu)_3$ are among the first reported examples of phosphite additions to coordinated π-hydrocarbons to yield stable phosphonium salts.[11,12] The i.r. spectra of the adducts (2c) and (2d) in acetone showed two strong carbonyl bands at 2 055 and 1 980 cm^{-1}, which are very similar to those for the analogous tri-n-butylphosphine adduct (2b). It is noteworthy, however, that while (2c) and (2d) are stable for long periods at room temperature in the solid state and give ^1H n.m.r. spectra consistent with their phosphonium-adduct formulation (Table 1), no parent adducts are observed in their f.d. mass spectra. Instead, single strong peaks appear at *m/e* 412 and 442, respectively (Table 1), indicating that Arbusov elimination has occurred in the mass spectrometer to give the corresponding phosphonate derivatives (5) [equation (2)] (A = H or OMe, R = Bu^n).



(2)

(2) (5)

In contrast, the reaction of $P(OPh)_3$ with $[Fe(C_6H_7)(CO)_3][BF_4]$ yielded the diphenyl phosphonate (5; A = H, R = Ph) after work-up, rather than the phosphonium salt. However, the appearance of only two strong i.r. bands at 2 055 and 1 985 cm^{-1} during the reaction confirmed initial phosphonium-adduct formation as in equation (1). The final product after work-up contains no $[BF_4]^-$, and shows two strong i.r. bands at 2 050 and 1 975 cm^{-1} consistent with a neutral species. These apparent differences in adduct stability are a little surprising since aromatic phosphites often form more stable phosphonium salts than aliphatic phosphites.

Kinetics and Mechanisms.—Kinetic data for the addition of PPh_3 to the cations of (1), (3), and (4) in nitromethane solvent are collected in Table 2. For $[Fe(C_6H_6OMe)(CO)_3][BF_4]$ (3) as substrate the second-order rate law (3) is seen to be closely obeyed over the range $[PPh_3] = 2.5 \times 10^{-3} - 15.0 \times 10^{-3}$ mol dm^{-3}. From the gradient of a plot of $k_{obs.}$ against $[PPh_3]$ a second-order rate constant k of 995 dm^3 mol^{-1} s^{-1} is estimated at 0 °C. This agrees well with the value of 1 000 dm^3 mol^{-1} s^{-1} obtained directly from a run carried out under equimolar second-order conditions (Table 2).

Rate law (3) is also established for addition of tri-*p*-tolyl- and tri-n-butyl-phosphine to complex (3) in nitromethane and acetone, respectively (Tables 3 and 4).

$$\text{Rate} = k[\text{Fe}][\text{PR}_3] \qquad (3)$$

Second-order rate constants k of 3 740 and 11 100 dm^3

mol^{-1} s^{-1}, respectively, are estimated at 0 °C from the gradients of the plots of $k_{obs.}$ against $[PR_3]$.

TABLE 2

Kinetic data for the addition of PPh_3 to iron (dienyl) complexes in nitromethane

Complex	θ_c / °C	$10^3[PPh_3]$ / mol dm^{-3}	$k_{obs.}$ / s^{-1}	$10^{-3}k$ / dm^3 mol^{-1} s^{-1}
(1) [a]	0.0	3.0		4.96
	5.0	3.0		6.83
	10.0	3.0		7.54
	15.0	3.0		11.1
	20.0	3.0		16.0
	25.0	3.0		19.0
(3) [b]	0.0	2.0		1.00
	10.0	2.0		1.40
	20.0	2.0		1.87
	30.0	2.0		2.08
	40.0	2.0		3.99
	50.0	2.0		6.52
	0.0	2.5	2.38	0.952
	0.0	5.0	5.14	1.03
	0.0	10.0	10.1	1.01
	0.0	15.0	14.9	0.993
(4) [c]	11.5	15.0	1.90	0.127
	15.0	15.0	2.50	0.167
	20.0	15.0	3.28	0.215
	25.0	15.0	4.46	0.297
	30.0	15.0	5.95	0.397

[a] [Fe] = 3.0×10^{-3} mol dm^{-3}. [b] From equation (3), mean k (0 °C) = 9.95×10^2 dm^3 mol^{-1} s^{-1}; [Fe] = 2.0×10^{-3} mol dm^{-3}. [c] [Fe] = 1.5×10^{-3} mol dm^{-3}.

Similarly, the additions of $P(OBu)_3$ to $[Fe(C_6H_7)(CO)_3][BF_4]$ (1) and of $P(OPh)_3$ to (3) in nitromethane are seen from Table 5 to obey the rate law (3) (R = OBu or OPh). The second-order rate constants k estimated from the plots of $k_{obs.}$ against $[P(OR)_3]$ at 20 °C are given in Table 6. This Table summarises the k values at 20 °C for addition of each of the phosphorus nucleophiles to the cations (1) and (3) in nitromethane and acetone solvents. In the cases where detailed nucleophile-dependence data were not obtained, rate law (3) was assumed in estimating k. Changing the solvent from nitromethane to acetone is seen to have little effect on the k values, indicating similar solvation effects on the dienyl cations and their corresponding transition states.

TABLE 3

Kinetic data for the addition of $P(C_6H_4Me\text{-}p)_3$ to iron (dienyl) complexes in nitromethane. [Fe] = 1.0×10^{-4} mol dm^{-3}, $[P(C_6H_4Me\text{-}p)_3]$ = 1.0×10^{-3} mol dm^{-3}

Complex	θ_c / °C	$k_{obs.}$ / s^{-1}	$10^{-4}k$ / dm^3 mol^{-1} s^{-1}
(1)	0.0	19.5	1.95
	5.0	24.4	2.44
	12.5	31.3	3.13
	20.0	40.9	4.09
(3) [a]	0.0	3.74	0.374
	5.0	4.20	0.420
	10.0	5.30	0.530
	15.0	6.66	0.666
	20.0	7.98	0.798
	0.0 [b]	1.82	0.364
	0.0 [c]	9.65	0.386
	0.0 [d]	15.4	0.385
	0.0 [e]	18.4	0.368

[a] From equation (3), mean k (0 °C) = 3.74×10^3 dm^3 mol^{-1} s^{-1}. [b—e] $[P(C_6H_4Me\text{-}p)_3]$ = 0.50×10^{-3}, 2.50×10^{-3}, 4.00×10^{-3}, and 5.00×10^{-3} mol dm^{-3} respectively.

TABLE 4

Kinetic data for the addition of PBu_3 to iron (dienyl) complexes in acetone. [Fe] = 1.0×10^{-4} mol dm^{-3}

Complex	θ_c / °C	$10^3[PBu_3]$ / mol dm^{-3}	$k_{obs.}$ / s^{-1}	$10^{-4}k$ / dm^3 mol^{-1} s^{-1}
(1) [a]	0.0	0.50	23.5	4.70
	0.0	1.00	46.7	4.67
	20.0	0.50	65.0	13.0
(3) [b]	0.0	0.50	5.44	1.09
	5.0	0.50	5.73	1.14
	10.0	0.50	6.59	1.32
	15.0	0.50	7.70	1.54
	20.0	0.50	8.03	1.61
	0.0	0.25	2.94	1.18
	0.0	1.00	12.1	1.21
	0.0	1.50	17.3	1.15
	0.0	2.00	22.7	1.14
	0.0	3.00	33.5	1.12

[a] From equation (3), mean k (0 °C) = 4.69×10^4 dm^3 mol^{-1} s^{-1}.
[b] From equation (3), mean k (0 °C) = 1.14×10^4 dm^3 mol^{-1} s^{-1}.

TABLE 5

Kinetic data for the addition of tertiary phosphites to iron (dienyl) complexes in nitromethane

Complex	Phosphite	θ_c / °C	10^2 $[P(OR)_3]$ / mol dm^{-3}	$k_{obs.}$ / s^{-1}	k / dm^3 mol^{-1} s^{-1}
(1) [a]	$P(OBu)_3$	0.5	5.0	0.72	14.4
		5.0	5.0	1.37	27.4
		10.0	5.0	2.27	45.4
		15.0	5.0	3.86	77.2
		20.0	5.0	6.73	135
		20.0	3.0	4.04	135
		20.0	2.0	2.71	136
		20.0	1.0	1.38	138
		20.0	0.50	0.650	130
	$P(OPh)_3$	20.0	5.0	1.76×10^{-3}	3.52×10^{-2}
(3) [b]	$P(OBu)_3$	20.0	0.50	0.120	24
	$P(OPh)_3$	20.0	5.0	1.77×10^{-4}	3.54×10^{-3}
		20.0	10.0	3.65×10^{-4}	3.65×10^{-3}
		20.0	15.0	5.43×10^{-4}	3.62×10^{-3}
		20.0	20.0	7.32×10^{-4}	3.66×10^{-3}
		20.0	25.0	9.04×10^{-4}	3.62×10^{-3}

[a] For addition of $P(OBu)_3$, mean k (20 °C) = 135 dm^3 mol^{-1} s^{-1}; [Fe] = 5×10^{-4} mol dm^{-3}. [b] For addition of $P(OPh)_3$, mean k (20 °C) = 3.62×10^{-3} dm^3 mol^{-1} s^{-1}; [Fe] = 6×10^{-3} mol dm^{-3}.

TABLE 6

Effect of solvent on the addition of phosphorus nucleophiles to iron (dienyl) complexes at 20.0 °C

		k/dm^3 mol^{-1} s^{-1}	
Complex	Nucleophile	Acetone *	Nitromethane
(1)	PBu_3	130×10^3	
	$P(C_6H_4Me\text{-}p)_3$	28.3×10^3	40.9×10^3
	PPh_3	7.46×10^3	16.0×10^3
	$P(OBu)_3$	84.4	135
	$P(OPh)_3$	4.13×10^{-2}	3.51×10^{-2}
(3)	PBu_3	16.1×10^3	
	$P(C_6H_4Me\text{-}p)_3$	5.16×10^3 (2.30×10^3)	7.98×10^3
	PPh_3	1.71×10^3 (0.66×10^3)	1.87×10^3
	$P(OBu)_3$	13.5	24.0
	$P(OPh)_3$	7.72×10^{-3}	3.62×10^{-3}

* Values in parentheses refer to 0 °C.

Observation of the simple second-order rate law (3) with each of the phosphorus nucleophiles in reactions of type (1) is most readily rationalised in terms of direct addition at the dienyl rings to give the phosphonium adducts. In support of this one-step mechanism is the observation that addition of phosphines and phosphites to $[Fe(C_6H_6OMe)(CO)_3][BF_4]$ is generally 5—10 times slower than with the parent cation $[Fe(C_6H_7)(CO)_3][BF_4]$ (Table 6). Similar differences have previously been reported [18] for the related additions of pentane-2,4-dione to these dienyl cations. This is in accordance with the mesomeric influence of the methoxide group, which has been shown [19] from INDO molecular-orbital calculations to decrease the positive charge on the dienyl C^5 atom.

Further support for direct addition at the dienyl ring comes from comparison of the *k* values for attack of PPh_3 on $[Fe(C_6H_7)(CO)_3][BF_4]$ and $[Fe(C_7H_9)(CO)_3][BF_4]$ (Table 2). The 200-fold smaller *k* for the cycloheptadienyl cation is readily explicable in steric terms if one assumes approach of PPh_3 from above the dienyl rings, whereas little difference is expected for attack at the iron or carbonyl groups. Interestingly, it has recently been suggested [20] that addition of PBu_3 to $[Fe(C_7H_9)(CO)_3]^+$ proceeds *via* initial attack at the iron centre, followed by rearrangement of the phosphine group to the dienyl ring. The only evidence given in support of this two-stage mechanism was the observation of a transient red colour during the 30-min reaction. Not only have we been unable to observe this red intermediate, but also the data in Table 4 show that when $[Fe] = [PBu_3] = 1.0 \times 10^{-4}$ mol dm^{-3} the addition reaction is complete in <1 s.

Comparison of the data in Tables 2—6 reveals decreasing *k* values in the order $PBu_3 > P(C_6H_4Me\text{-}p)_3 > PPh_3 \gg P(OBu)_3 \gg P(OPh)_3$ for addition to both (1) and (3). Interestingly, although the overall range of nucleophilicities is *ca.* 10^6, the range for the phosphines is not large. Attack by PBu_3 on (1) and (3) is only 10—17 times faster than by PPh_3, despite the much greater basicity of the former nucleophile.

The source of this anomaly is apparent from a plot of log *k* against the half-neutralisation potentials, $-\Delta$ (h.n.p.), which have been used [21,22] as a quantitative measure of basicity for phosphorus nucleophiles (Figure). The reactions of (1) and (3) with PBu_3, $P(OBu)_3$, and $P(OPh)_3$ are seen to give good linear free-energy relations (l.f.e.r.s) of the type previously found by Basolo [21-24] and other workers [25] for substitution at metal centres. The relatively high gradients of *ca.* -8.6 V^{-1} for the l.f.e.r. plots * indicate that the dienyl cations discriminate strongly between the phosphorus nucleophiles, suggesting significant bond formation in the transition states for adduct formation. However, PPh_3 shows a large positive deviation from the l.f.e.r. plots for both (1) and (3). This contrasts with the normal behaviour of bulky nucleophiles such as PPh_3, which generally show large negative deviations attributed [26] to steric effects. It is possible that specific ' stacking ' interactions [27] between the aromatic rings of PPh_3 and the dienyl ligands of (1) and (3) may be responsible for the anomalously high addition rates for PPh_3.

Activation parameters for several of the phosphonium-adduct formations are summarised in Table 7. The rapidity of the phosphine additions is reflected in their low activation enthalpies; the $\Delta H^\ddagger$ value of 11.9 ± 1.5 kJ mol^{-1} for the reaction of PBu_3 with (3) is the lowest yet found in our current survey of nucleophilic addition to co-ordinated π-hydrocarbons. The rate trend $PBu_3 > P(C_6H_4Me\text{-}p) > PPh_3 \gg P(OBu)_3$ correlates well with increasing $\Delta H^\ddagger$ values. Further support for $\Delta H^\ddagger$ control of relative rates comes from the modestly good isokinetic plots of the data in Table 7, with isokinetic

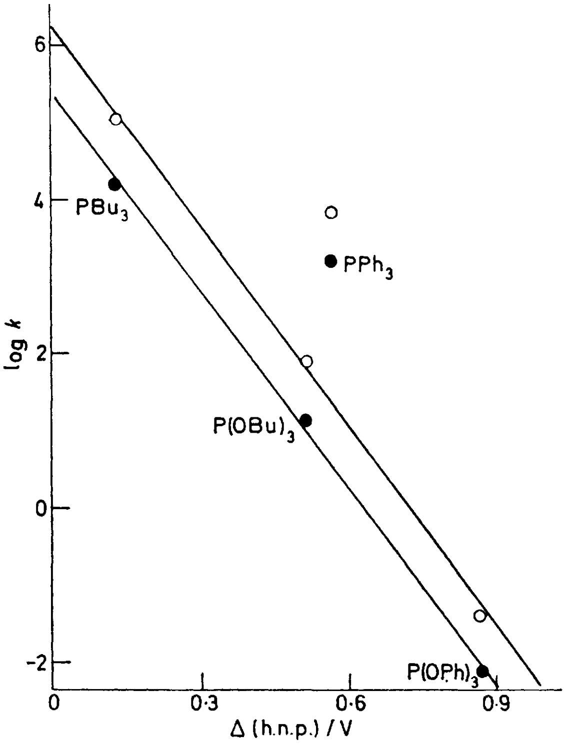


FIGURE Correlation of rate constants with half-neutralisation potentials, Δ(h.n.p.), for the reaction of $[Fe(C_6H_6\cdot Y)(CO)_3][BF_4]$ with phosphines and phosphites in acetone at 20.0 °C. Y = H(○), gradient = -8.72 V^{-1} or OMe (●), gradient = -8.49 V^{-1}

TABLE 7

Activation parameters for reactions of $[Fe(dienyl)(CO)_3][BF_4]$ complexes with phosphorus nucleophiles in nitromethane

Phosphine	Complex	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
PBu_3*	(3)	11.9 ± 1.5	-124 ± 5
$P(C_6H_4Me\text{-}p)_3$	(1)	21.3 ± 0.8	-84 ± 3
	(3)	23.8 ± 1.7	-89 ± 6
PPh_3	(1)	33.6 ± 3.4	-50 ± 10
	(3)	26.5 ± 2.0	-91 ± 7
	(4)	41.1 ± 1.0	-60 ± 3
$P(OBu)_3$	(1)	50.2 ± 1.3	-33 ± 4

* In acetone solvent.

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* These compare with gradients of -1.5 and -2.5 V^{-1} found for bimolecular substitutions by phosphorus-donor ligands on $[M(CO)_6]$ (M = Mo or W) and $[Ru_3(CO)_{12}]$ (ref. 25, and refs. therein).

temperatures in the range 130—290 °C, much above the temperatures at which these kinetic data were obtained. Each of the reactions has a negative entropy of activation as expected for simple addition processes.

The much slower addition of PPh_3 to $[Fe(C_7H_9)(CO)_3][BF_4]$ compared with the corresponding cyclohexadienyl complex is also seen to arise largely from a more unfavourable $\Delta H^\ddagger$. However, both $\Delta H^\ddagger$ and $\Delta S^\ddagger$ appear to contribute to the much smaller rate differences observed between (**1**) and its methoxy-derivative (**3**).

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