Mechanism of Attack by Trialkylphosphines on Dicarbonyl(dienyl)iodoiron Complexes †

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The reactions of $[Fe(1\text{—}5\text{-}\eta\text{-}C_6H_7)(CO)_2I]$ and $[Fe(1\text{—}5\text{-}\eta\text{-}C_7H_9)(CO)_2I]$ with $PBu^n{}_3$ and $PPr^i{}_3$ have been shown to proceed *via* the stepwise process:

$$\begin{tikzcd}[Fe(dienyl)(CO)_2I] + PR_3 \arrow[r, "k_1"] & {[Fe(R_3P.diene)(CO)_2I]} \arrow[d, "PR_3"] \\ & {[Fe(R_3P.diene)(CO)_2(PR_3)]I}\end{tikzcd}$$

Kinetic studies of the rapid first step with $PBu^n{}_3$ in acetone gave the rate law, Rate = $k_1[\text{complex}][PBu^n{}_3]$ for both complexes. The activation parameters $\{\Delta H_1{}^{\ddagger} = 32.2 \pm 1.3$ kJ mol^{-1}, $\Delta S_1{}^{\ddagger} = -130 \pm 3$ J K^{-1} mol$^{-1}\}$ and the much faster (*ca.* 80 times) rate for the C_6H_7 complex support a mechanism involving direct addition to the dienyl ligands. The complex rate law, Rate = $\dfrac{k_2k_3[\text{complex}][PBu^n{}_3]}{k_{-2}[I^-] + k_3[PBu^n{}_3]}$, observed in both cases for the much slower second step, indicates a dissociative mechanism for the iodide replacement. $\Delta H_2{}^{\ddagger} = 91.1 \pm 4.1$ kJ mol^{-1} and $\Delta S_2{}^{\ddagger} = -32 \pm 8$ J K^{-1} mol^{-1} for the iodide dissociation of the C_6H_7 complex.

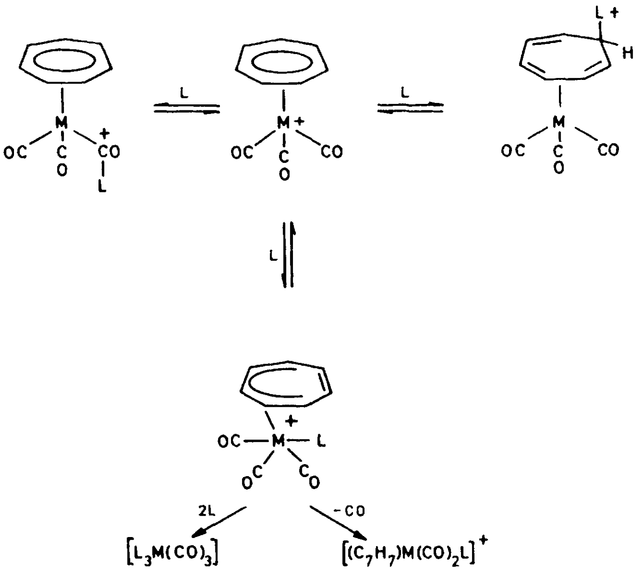
In contrast to an earlier study, $[Fe(1\text{—}3\text{-}\eta\text{-}C_3H_5)(CO)_3I]$ has been shown to react with PPh_3 and $PPr^i{}_3$ at room temperature to give phosphonium salts $[PR_3(C_3H_5)]I$. Comparison with other related reactions suggests that in general addition to the π-hydrocarbon ligands by trialkylphosphines is kinetically favoured over attack at the metal.

THE reactions of Lewis bases, L, *e.g.* tertiary phosphines, with $[M(\pi\text{-hydrocarbon})(CO)_3]^+$ complexes have received considerable attention recently. In such systems several alternative reaction pathways are possible and have in fact been experimentally observed, namely nucleophilic attack at the metal, carbonyl, or hydrocarbon sites. With phosphine nucleophiles in particular, variations of experimental conditions have often led to the exclusive observation of only one reaction path.[1-4] This has led to considerable confusion, with apparently conflicting results within analogous systems.[1-3]

However, from our recent studies [5-7] it has become apparent that all the conflicting observations can be rationalised in terms of one general scheme, shown opposite for the particular case of the reation of $[M(\text{tropylium})(CO)_3]^+$ cations with neutral, monodentate nucleophiles (Scheme 1).

As an extension of these studies we now report the results of a kinetic and mechanistic study of the reactions of trialkylphosphines with $[Fe(1\text{—}5\text{-}\eta\text{-}C_6H_7)(CO)_2I]$ and $[Fe(1\text{—}5\text{-}\eta\text{-}C_7H_9)(CO)_2I]$. These reactions are of particular interest since they provide an unusual example in which nucleophilic attack occurs at both the hydrocarbon ligand and the metal centre. They therefore provide a novel test for the validity of Scheme 1. A further attractive feature of these systems is that they permit a quantitative determination of the kinetic preference of one reaction path over the other. One of us [5] has previously suggested that in general nucleophilic attack at the hydrocarbon moiety should be the most kinetically favoured process under mild conditions.

Also reported are related studies of phosphine additions to $[Fe(1\text{—}3\text{-}\eta\text{-}C_3H_5)(CO)_3I]$, which contrary to a previous report,[8] also conform to Scheme 1.



SCHEME 1

EXPERIMENTAL

Materials.—Tri-n-butylphosphine and tri-isopropylphosphine were purchased in the purest grades available. The tri-n-butylphosphine (B.D.H.) employed in kinetic runs was distilled under nitrogen before use. Its i.r. spectrum was periodically checked to confirm that oxidation had not

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occurred, as indicated by the absence of a PO band at *ca.* 1 250 cm^{-1}. Analytical grade acetone was used as solvent.

Dicarbonyl(cyclohexadienyl)iodoiron.—The literature[9] preparation in our hands generally gave only 45—50% yield of this red-brown compound. An improved synthesis is outlined below. [Fe(1—5-η-C_6H_7)$(CO)_3$][BF_4] (0.20 g) was dissolved in acetone (50 cm^3) and an excess of [NEt_4]I (0.80 g) added. The reaction was allowed to proceed under nitrogen for 30 min at room temperature in the presence of light. Undissolved iodide was removed by passing the reaction mixture down a short alumina-H column. Evaporation of the eluant gave a dark brown solid, which on extraction with acetone–water yielded dark red needles (0.15 g) of the product (74%), m.p. 95—96 °C (lit.,[9] 95—96 °C); i.r. ν_{CO}(liquid film) 2 040 and 1 980 cm^{-1} (Found: C, 30.0; H, 2.5; I, 39.4. Calc. for $C_8H_7FeIO_2$: C, 30.1; H, 2.5; I, 39.8%).

Dicarbonyl(cycloheptadienyl)iodoiron.—This dark brown complex was prepared by the literature method.[9] Its i.r. spectrum in hexane showed two carbonyl bands at 2 039 and 2 004 cm^{-1} (Found: C, 32.0; H, 2.6. Calc. for $C_9H_9FeIO_2$: C, 32.5; H, 2.7%).

Reaction of [Fe(1—5-η-C_6H_7)$(CO)_2$I] *with Tri-n-butylphosphine.*—Tri-n-butylphosphine (0.08 g) was added to a solution of [Fe(1—5-η-C_6H_7)$(CO)_2$I] (0.06 g) in acetone (15 cm^3) and the reaction allowed to proceed for 30 min at room temperature. On evaporation to dryness and washing with cold pentane (3 × 20 cm^3), a yellow-brown oil was obtained. Treatment with light petroleum (b.p. 40—60 °C) and a drop of dichloromethane gave a light yellow-brown solid (0.06 g) which was characterised as the final product [Fe{(Bu^n_3P)C_6H_7}$(CO)_2$(PBu^n_3)]I, m.p. 120—121 °C; i.r. ν_{CO}(liquid film) 1 975 and 1 915 cm^{-1} (Found: C, 53.0; H, 8.7. Calc. for $C_{32}H_{61}FeIO_2P_2$: C, 53.2; H, 8.5%). The ^1H n.m.r. spectrum of the product in [$^2H_6$]acetone showed resonances at τ 4.92, 5.88, 6.55, and 7.3—7.6 with relative intensities 2 : 1 : 2 : 2, assigned to the $H^{2,3}$, H^5, $H^{1,4}$, and $H^{6,6}$ ring protons, respectively. A multiplet centred at *ca.* τ 8.5 and a triplet at τ 9.05 (intensities *ca.* 34 : 18) were assigned to the CH_2 and CH_3 protons of the PBu^n_3 groups.

Reaction of [Fe(1—5-η-C_7H_9)$(CO)_2$I] *with Tri-isopropylphosphine.*—An analogous reaction of [Fe(1—5-η-C_7H_9)$(CO)_2$I] with PPr^i_3 yielded the related final product [Fe{(Pr^i_3P)C_7H_9}$(CO)_2$(PPr^i_3)]I (Found: C, 48.1; H, 8.4; Fe, 8.4; P, 9.4. Calc. for $C_{27}H_{51}FeIO_2P_2$: C, 49.8; H, 7.8; Fe, 8.6; P, 9.5%); i.r. ν_{CO}(CH_2Cl_2) 1 975 and 1 917 cm^{-1}.

Reaction of [Fe(1—5-η-C_7H_9)$(CO)_2$I] *with Tri-n-butylphosphine.*—Similar reactions of [Fe(1—5-η-C_7H_9)$(CO)_2$I] with PBu^n_3 gave the final product [Fe{(Bu^n_3P)C_7H_9}$(CO)_2$(PBu^n_3)]I as a yellow oil. It was characterised by its ν_{CO} bands at 1 960 and 1 915 cm^{-1} in acetone.

In situ *Preparation of* [Fe{(Bu^n_3P)C_6H_7}$(CO)_2$I].—The i.r. spectra of solutions obtained from mixing equimolar amounts of [Fe(η-C_6H_7)$(CO)_2$I] and PBu^n_3 indicated the presence of only the initial product [Fe{(Bu^n_3P)C_6H_7}$(CO)_2$I] (ν_{CO} in acetone at 1 965 and 1 895 cm^{-1}; see Discussion section). However, repeated attempts to isolate this product invariably resulted, after work-up, in only poor yields of the final product [Fe{(Bu^n_3P)C_6H_7}$(CO)_2$(PBu^n_3)]I. Nevertheless, the ^1H n.m.r. spectrum of the initial product was obtained *in situ* in this fashion, showing resonances in [$^2H_6$]acetone at τ 4.55, 6.40, 6.57, and 7.75 (relative intensities 2 : 1 : 2 : 2). These were assigned to the $H^{2,3}$, H^5, $H^{1,4}$, and $H^{6,6}$ ring protons, respectively. A further multiplet and triplet at τ 8.53 and 9.05 (intensities *ca.* 18 : 9) were assigned to the CH_2 and CH_3 protons of the PBu^n_3 group added to the ring.

In situ *Preparation of* [Fe{(Bu^n_3P)C_7H_9}$(CO)_2$I].—[Fe(1—5-η-C_7H_9)$(CO)_2$I] (0.050 g) was reacted with PBu^n_3 (0.13 g, four-fold molar excess) in acetone (5 cm^3) at −10 °C under nitrogen in the dark. After 18 h an i.r. spectrum showed almost quantitative formation of the initial product [Fe{(Bu^n_3P)C_7H_9}$(CO)_2$I] (ν_{CO} bands at 1 950 and 1 895 cm^{-1}). Cooling at −78 °C overnight gave no precipitate. Subsequent addition of an excess of pentane produced an oil. However, attempts to solidify this oil resulted only in the formation of the final product [Fe{(Bu^n_3P)C_7H_9}$(CO)_2$(PBu^n_3)]I, identified by its ν_{CO} bands at 1 960 and 1 915 cm^{-1}.

Although other experiments employing smaller molar excesses of PBu^n_3 also showed the *in situ* formation of largely [Fe{(Bu^n_3P)C_7H_9}$(CO)_2$I] attempts to isolate this intermediate species were unsuccessful.

Reaction of [Fe(1—3-η-C_3H_5)$(CO)_3$I] *with Tri-isopropylphosphine.*—On adding PPr^i_3 to a solution of [Fe(1—3-η-C_3H_5)$(CO)_3$I] in dichloromethane at room temperature an exothermic reaction was observed, the colour of the solution changing from brown to green. Addition of an excess of ether after 10 min gave a white precipitate of the phosphonium salt [P(C_3H_5)Pr^i_3]I in almost quantitative yield. This was filtered off and washed with ether (Found: C, 43.7; H, 7.9, I, 38.7. Calc. for $C_{12}H_{26}IP$: C, 43.8; H, 8.3; I, 38.5%).

Reaction of [Fe(1—3-η-C_3H_5)$(CO)_3$I] *with Triphenylphosphine.*—[Fe(1—3-η-C_3H_5)$(CO)_3$I] was reacted with an excess of PPh_3 in dichloromethane for 5 h at room temperature, during which time a gradual colour change from dark brown to yellow was observed. Addition of ether gave a yellow precipitate, which was then extracted with hot water. On cooling, off-white crystals of the phosphonium salt [P(C_3H_5)Ph_3]I separated out, and were filtered off and dried by suction (yield 45%) (Found: C, 58.5; H, 4.7; I, 29.7. Calc. for $C_{21}H_{20}IP$: C, 58.6; H, 4.7; I, 29.5%).

Spectroscopic Studies.—^1H n.m.r. spectra were recorded on a 90-MHz Perkin-Elmer R32 spectrophotometer. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer.

Kinetic Studies.—(*a*) The reaction of [Fe(1—5-η-C_6H_7)$(CO)_2$I] with PBu^n_3 in acetone occurred in two distinct steps which could be monitored independently. The initial rapid addition of PBu^n_3 to the cyclohexadienyl ring was studied using a thermostatted (±0.1 °C) stopped-flow spectrophotometer of the type described previously.[10] Reactant solutions of the appropriate concentrations were prepared separately in acetone, and were thermostatted in the stopped-flow apparatus for at least 10 min before mixing. The final complex concentration was invariably 1.0 × 10^{-3} mol dm^{-3}, while [PBu^n_3] = 0.05—1.0 mol dm^{-3}. The large decrease in absorbance at 360 nm was followed. Attachment of a log-converter unit[11] to the oscilloscope permitted direct absorbance read-out. Pseudo-first-order rate constants $k_{obs.}$ were estimated from the gradients of plots of log $\{-(A_\infty - A_t)\}$ *vs.* time t. These plots were generally linear for at least 70% completion of reaction. Each rate run was carried out in quadruplicate giving $k_{obs.}$ values with an average reproducibility of ±3%.

The much slower second step, involving replacement of the iodide ligand by PBu^n_3, was studied by the i.r. sampling technique previously described.[12] For these runs, the complex concentration was *ca.* 3 × 10^{-3} mol dm^{-3} and a large

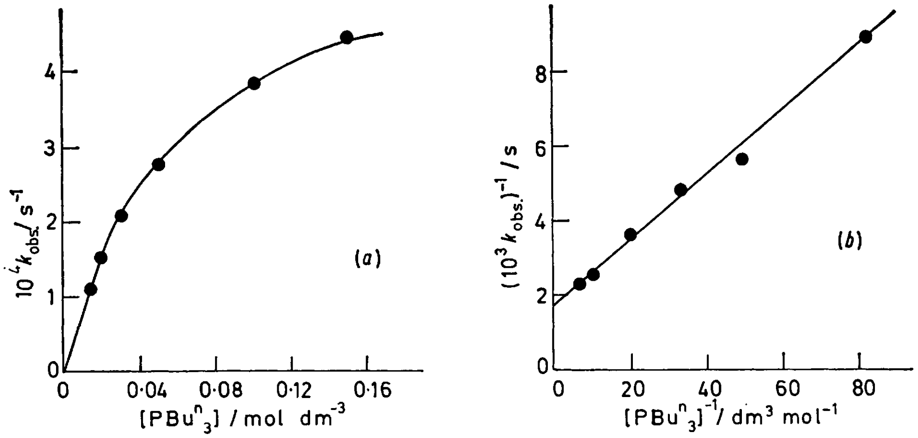


FIGURE 1 Reaction of $[Fe\{(Bu^n_3P)C_7H_9\}(CO)_2I]$ with PBu^n_3 in acetone at 40 °C; $[I^-] = 0.10$ mol dm^{-3}; $I = 0.20$ mol dm^{-3}. (a) Dependence of $k_{obs.}$ on $[PBu^n_3]$; (b) dependence of $1/k_{obs.}$ on $[PBu^n_3]^{-1}$

excess of PBu^n_3 was again always employed. Except for some runs reported in Table 6, all experiments were carried out in the presence of an excess of iodide ion, added as solid tetra(n-butyl)ammonium iodide. The ionic strength, except where otherwise stated, was maintained at 0.20 mol dm^{-3} by the addition of $NaClO_4 \cdot H_2O$. The PBu^n_3 was added by micro-syringe, all solution preparations being carried out in a glove bag under nitrogen.

The initial product $[Fe\{(Bu^n_3P)C_6H_7\}(CO)_2I]$ was formed rapidly under these conditions, and the decrease in its carbonyl band at 1 895 cm^{-1} then monitored. Pseudo-first-order rate constants $k_{obs.}$ were obtained from the slopes of plots of log A_t *vs.* time, these plots being generally linear for at least 70% completion of reaction.

(*b*) In the analogous reaction of $[Fe(1\text{—}5\text{-}\eta\text{-}C_7H_9)(CO)_2I]$ with PBu^n_3 in acetone, both steps were slow enough to follow by the above i.r. sampling technique. Although the separation of the two steps was not as clear-cut as for the cyclohexadienyl complex, at 20 °C the second-step was generally at least ten times slower than the initial ring-addition, allowing independent study of the first step.

This first step was monitored by following the disappearance of the strong carbonyl band of $[Fe(1\text{—}5\text{-}\eta\text{-}C_7H_9)(CO)_2I]$ at 2 025 cm^{-1}. Solutions ([complex] = 3×10^{-3}, $[PBu^n_3]$ = 0.011 7—0.053 mol dm^{-3}) were prepared under nitrogen as above. With the lower phosphine concentrations second-order rate constants, k_1, were obtained from the slopes of plots of $b(a - x)/a(b - x)$ *vs.* time; where a,b = initial concentrations of complex and phosphine, respectively, and x = amount of complex reacted at time t. In the cases where a large excess of PBu^n_3 was employed, pseudo-first-order rate constants, $k_{obs.}$, were obtained from the gradients of plots of log A_t *vs.* t. The kinetic plots were generally linear for 70—80% completion of reaction. Most $k_{obs.}$ values were the average of duplicate determinations (±5%).

Reaction solutions for the slower second step were prepared in an analogous manner to that described above for the related C_6H_7 complex. All runs were carried out in the presence of an excess of PBu^n_3 and I^-, and at a constant ionic strength of 0.20 mol dm^{-3}. The solutions were stored at −10 °C overnight in order to allow the first step to proceed to completion, as shown by the presence of only two ν_{CO} bands at 1 950 and 1 895 cm^{-1} due to $[Fe\{(Bu^n_3P)C_7H_9\}(CO)_2I]$. The reaction flask was then transferred to a thermostatted bath at the desired temperature, and the second step monitored by following the decrease of the strong intermediate carbonyl band at 1 895 cm^{-1}. Values of $k_{obs.}$ were obtained from plots of log A_t *vs.* t, which were generally linear for 70—90% completion of reaction.

(*c*) Activation enthalpies, $\Delta H^\ddagger$, were obtained from the

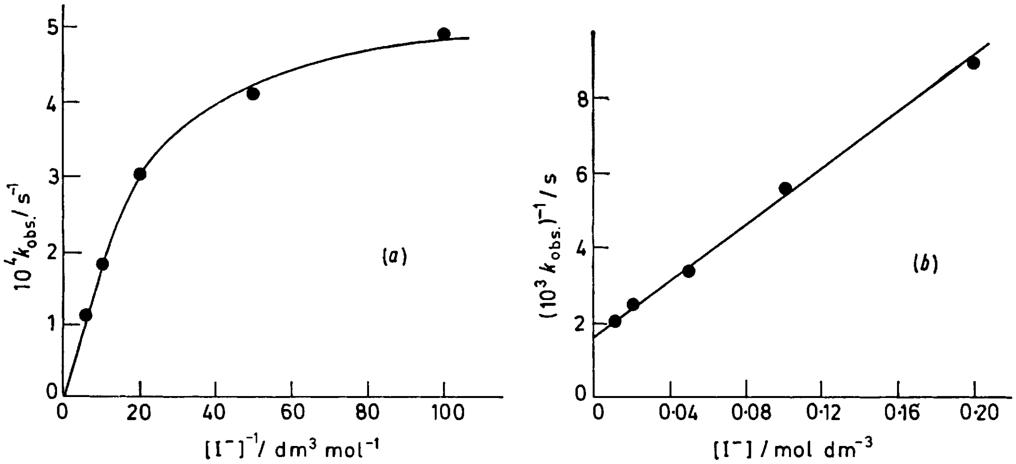
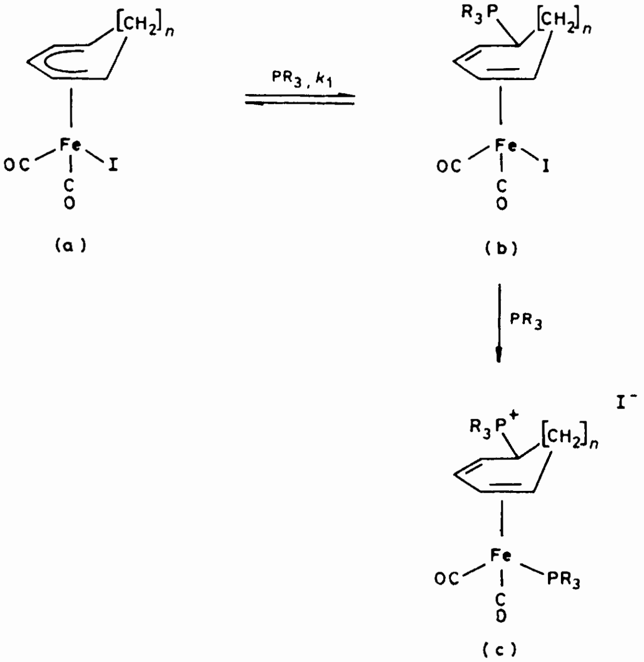


FIGURE 2 Reaction of $[Fe\{(Bu^n_3P)C_7H_9\}(CO)_2I]$ with PBu^n_3 in acetone at 40 °C; $[PBu^n_3] = 0.020$ mol dm^{-3}; $I = 0.20$ mol dm^{-3}. (a) Dependence of $k_{obs.}$ on $[I^-]^{-1}$; (b) dependence of $1/k_{obs.}$ on $[I^-]$

slopes of Arrhenius plots of log $k_{obs.}$ *versus* $1/T$, calculated by a least-squares method. The errors quoted are standard deviations derived from the least-squares analyses. Entropies of activation, $\Delta S^{\ddagger}$, were calculated after conversion of the observed rate constants to second-order rate constants.

RESULTS AND DISCUSSION

Nature of the Reaction of Trialkylphosphines with [Fe(dienyl)$(CO)_2I$].—Elemental analysis of the final products from these reactions clearly establishes that two phosphine molecules have added to the original [Fe(dienyl)$(CO)_2I$] complexes. The i.r. and ^{1}H n.m.r. data (see Experimental section) indicate that one phosphine molecule has added to the dienyl ring, while the second has replaced the iodide ligand giving the salts [Fe{(R_3P)diene}$(CO)_2(PR_3)$]I.



SCHEME 2

In the case of the cyclohexadienyl complex, qualitative i.r. studies in a variety of solvents show that the reaction proceeds in two distinct steps. On addition of PBu^n_3 to a solution of [Fe(η-C_6H_7)$(CO)_2I$] (1a) in acetone two new carbonyl bands rapidly appear at 1 965 and 1 895 cm^{-1}. These are then slowly replaced by the growth of the final product bands at 1 975 and 1 915 cm^{-1}.

Although attempts to isolate the initial product (1b) resulted only in poor yields of the final product (1c), the initial product was identified as [Fe{$(Bu^n_3P)C_6H_7$}$(CO)_2I$] from its ^{1}H n.m.r. and i.r. spectra. Its ^{1}H n.m.r. spectrum (see Experimental section) is fully consistent with the addition of one molecule of PBu^n_3 to the dienyl ring, giving a spectrum similar to that of the related [Fe{$(Bu^n_3P)C_6H_7$}$(CO)_3$][BF_4] complex.[13] Its i.r. spectrum eliminates an alternative allyl formulation [Fe(1—3-η-C_6H_7)$(CO)_2(PBu^n_3)I$] obtained *via* phosphine attack at the metal, since the closely related species [Fe(1—3-η-C_3H_5)$(CO)_2(PPh_3)I$] is reported[8] to have carbonyl bands at 2 018 and 1 970 cm^{-1}. The overall reaction is outlined in Scheme 2.

On the other hand, with the analogous [Fe(η-C_7H_9)$(CO)_2I$] complex (2a) separation of the two steps was not as clear-cut. However, the use of non-polar solvents or low temperatures preferentially slowed down the second step, allowing the first step to be observed independently. In the case of PBu^n_3, bands at 1 950 and 1 895 cm^{-1} appear in acetone due to (2b). An analogous reaction occurs with PPr^i_3, bands appearing at 1 962 and 1 885 cm^{-1} in hexane. Work-up of the final products in both cases shows them to be completely analogous to the species (1c) above.

Kinetics and Mechanisms.—(a) *Step* 1. Kinetic data for the first step of the reactions of [Fe(C_6H_7)$(CO)_2I$] and [Fe(C_7H_9)$(CO)_2I$] with PBu^n_3 in acetone are collected in Tables 1 and 2, respectively. In both cases the linear dependence of $k_{obs.}$ on [PBu^n_3] indicates the simple second-order rate law (1). This behaviour is most

$$\text{Rate} = k_1\,[\text{complex}][PBu^n_3] \qquad (1)$$

readily rationalised in terms of direct addition of PBu^n_3 to the dienyl rings. The low $\Delta H_1^{\ddagger}$ value of 32.2 kJ mol^{-1} and the large negative $\Delta S_1^{\ddagger}$ (-130 J K^{-1} mol^{-1}) calculated for the cyclohexadienyl complex (Table 6) are also consistent with direct addition.

Further support for direct attack of PBu^n_3 on the

TABLE 1

Kinetic data for step 1 of the reaction of [Fe(C_6H_7)$(CO)_2I$] with PBu^n_3 in acetone; [complex] = 1.0×10^{-3} mol dm^{-3}

Temperature (°C)	10[PBu^n_3]/ mol dm^{-3}	$k_{obs.}$/s^{-1}
20.0	0.50	0.103
	1.00	0.184
	2.50	0.450
	5.00	0.801
	10.0	1.51
10.0	2.50	0.288
15.0	2.50	0.367
25.0	2.50	0.586
30.0	2.50	0.764

Mean k_1 (20 °C) = 1.76 dm^3 mol^{-1} s^{-1}.

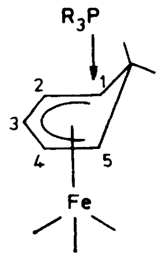
TABLE 2

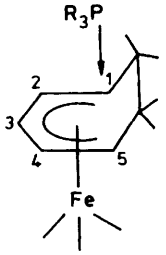
Kinetic data for step 1 of the reaction of [Fe(C_7H_9)$(CO)_2I$] with PBu^n_3 in acetone; [complex] = 3.0×10^{-3} mol dm^{-3}; temperature 20.0 °C

10[PBu^n_3]/ mol dm^{-3}	$10^4k_{obs.}$/s^{-1}	10^2k_1/ dm^3 mol^{-1} s^{-1}
0.117		1.98 *
0.122		2.26 *
0.170		2.02 *
0.231	4.99	2.16
0.298	5.95	2.00
0.364	7.11	1.95
0.398	7.73	1.94
0.406	7.39	1.82
0.444	9.20	2.07
0.534	9.46	1.77

* Calculated from second-order rate plot. Mean k_1 = 2.00 $\times 10^{-2}$ dm^3 mol^{-1} s^{-1}.

dienyl rings comes from the striking observation that step 1 is *ca.* 80 times slower (20 °C) for [Fe(C_7H_9)(CO)$_2$I] than for the analogous C_6H_7 complex (Table 6). The cycloheptadienyl complex would be expected to cause considerably greater steric hindrance to approach of a PBu$^n_3$ molecule from above the ring than would the C_6H_7 complex (see below). On the other hand, these two dienyl ligands would have similar steric influences on alternative mechanisms involving initial nucleophilic attack at the Fe or a carbonyl group. It should be noted, however, that while the ^{1}H n.m.r. spectrum of the [Fe{(Bu$^n_3$P)-C_6H_7}(CO)$_2$I] adduct clearly indicates addition at the C-1 (or C-5) position of the C_6H_7 ring (see Experimental section), we have no direct evidence for the position of ring attachment in the C_7H_9 complex. Nucleophilic addition at the C-2 ring position has been reported [14] for some related C_7H_9 complexes. The large rate differences between the analogous C_6H_7 and C_7H_9 complexes could thus alternatively arise from steric blocking of the electronically favoured [15] C-1 position in the C_7H_9 compound, resulting in a less electronically favoured attack at C-2.





Finally, it is interesting that the mean second-order rate constant, k_1, for addition of PBu$^n_3$ to the dienyl ring of [Fe(C_6H_7)(CO)$_2$I] (k_1 = 1.76 dm^3 mol^{-1} s^{-1} at 20 °C) is *ca.* 10^5 times lower than that previously obtained [13] for addition to the analogous parent cation [Fe(C_6H_7)-(CO)$_3$]$^+$. This large rate difference no doubt arises from the absence of a positive charge on the [Fe(C_6H_7)(CO)$_2$I] substrate.

(b) *Step* 2. Kinetic data for the second step of Scheme 2, *i.e.* the substitution of the iodide ligands by PBu$^n_3$ in [Fe{(Bu$^n_3$P)C_6H_7}(CO)$_2$I] and [Fe{(Bu$^n_3$P)C_7H_9}(CO)$_2$I], are summarised in Tables 3—5. Unless otherwise stated, all results were obtained at a constant ionic strength of 0.20 mol dm^{-3}. In contrast to the first step, the $k_{obs.}$ values show a complex non-linear dependence on [PBu$^n_3$] [*e.g.* Figure 1(*a*)] and are markedly retarded by the addition of iodide ion [*e.g.* Figure 2(*a*)]. All these results may be explained in terms of the mechanism outlined in Scheme 3, *i.e.* dissociation (k_2) of the iodide

TABLE 3

Kinetic data for step 2 of the reaction of [Fe(C_6H_7)(CO)$_2$I] with PBu$^n_3$ in acetone at 40.0 °C; [complex] = 3.01 × 10^{-3} mol dm^{-3}; ionic strength = 0.20 mol dm^{-3}

[PBu$^n_3$]/ mol dm^{-3}	[Bu$^n_4$NI]/ mol dm^{-3}	$10^5k_{obs.}$/s^{-1}
0.051	0.020	3.55
0.101	0	22.1
0.101	0.010	9.17
0.101	0.020	5.80
0.101	0.050	3.00
0.101	0.100	1.57
0.101	0.200	0.99
0.190	0.020	8.34
0.608	0.020	14.9
1.01	0.020	16.5
2.03	0.020	18.2

TABLE 4

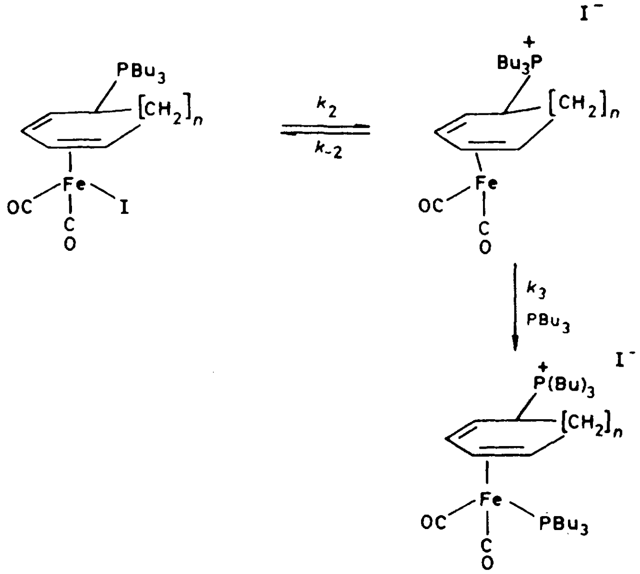
Influence of temperature and ionic strength on step 2 of the reaction of [Fe(C_6H_7)(CO)$_2$I] with PBu$^n_3$ in acetone; [complex] = 3 × 10^{-3} mol dm^{-3}

Temperature (°C)	[PBu$^n_3$]/ mol dm^{-3}	[Bu$^n_4$NI]/ mol dm^{-3}	I/ mol dm^{-3}	$10^5k_{obs.}$/s^{-1}
20.0	1.50	0	0.003	0.746
25.0	1.50	0	0.003	1.61
30.0	1.50	0	0.003	2.71
35.0	1.50	0	0.003	4.49
40.0	1.50	0	0.003	9.26
40.0	1.12	0	0.003	8.92
40.0	0.75	0	0.003	8.46
40.0	0.40	0	0.003	8.12
40.0	0.107	0.005	0.008	2.96
40.0	0.107	0.013	0.103	4.83
40.0	0.107	0.050	0.053	1.77
40.0	0.107	0.050	0.103	3.30
40.0	0.107	0.10	0.103	1.63

TABLE 5

Kinetic data for step 2 of the reaction of [Fe(C_7H_9)(CO)$_2$I] with PBu$^n_3$ in acetone at 40.0 °C; [complex] = 3.01 × 10^{-3} mol dm^{-3}; I = 0.20 mol dm^{-3}

10[PBu$^n_3$]/ mol dm^{-3}	[Bu$^n_4$NI]/ mol dm^{-3}	$10^4k_{obs.}$/s^{-1}
0.122	0.10	1.12
0.203	0.010	4.93
0.203	0.020	4.07
0.203	0.050	3.02
0.203	0.100	1.80
0.203	0.200	1.13
0.304	0.10	2.09
0.507	0.10	2.76
1.01	0.10	3.88
1.50	0.10	4.45



SCHEME 3

ligand to produce a reactive intermediate, $[\mathrm{Fe}\{(\mathrm{PBu^n_3P})\text{-}\mathrm{diene}\}(\mathrm{CO})_2]^+$, which may then either recombine with I^- (k_{-2}) to re-form the starting complex, or add a $\mathrm{PBu^n_3}$ ligand (k_3) to give the final complex.

Assuming a steady-state concentration of the intermediate, this mechanism gives a general rate expression of the form (2,3).

$$\text{Rate} = \frac{k_2k_3[\text{complex}][\mathrm{PBu^n_3}]}{k_{-2}[\mathrm{I}^-] + k_3[\mathrm{PBu^n_3}]} \qquad (2)$$

$$k_{\text{obs.}} = \frac{k_2k_3[\mathrm{PBu^n_3}]}{k_{-2}[\mathrm{I}^-] + k_3[\mathrm{PBu^n_3}]} \qquad (3)$$

Thus, if $k_{-2}[\mathrm{I}^-] \gg k_3[\mathrm{PBu^n_3}]$, equation (3) reduces to expression (4), which explains the approximately linear dependence of $k_{\text{obs.}}$ on $[\mathrm{PBu^n_3}]$ at low $[\mathrm{PBu^n_3}]$ observed for both complexes at constant $[\mathrm{I}^-]$ [Tables 3 and 5; Figure 1(*a*)]. Separate runs carried out at constant $[\mathrm{PBu^n_3}]$

$$k_{\text{obs.}} = \frac{k_2k_3[\mathrm{PBu^n_3}]}{k_{-2}[\mathrm{I}^-]} \qquad (4)$$

(Tables 3 and 5) confirm the inverse dependence of $k_{\text{obs.}}$ on $[\mathrm{I}^-]$ expected from equation (4) at high $[\mathrm{I}^-]$ values [*e.g.* Figure 2(*a*)].

On the other hand, if $k_3[\mathrm{PBu^n_3}] \gg [\mathrm{I}^-]$ then equation (3) simplifies to the first-order form (5). This explains why the $k_{\text{obs.}}$ *vs.* $[\mathrm{PBu^n_3}]$ plots for both complexes become

$$k_{\text{obs.}} = k_2 \qquad (5)$$

curved at higher phosphine concentrations ($[\mathrm{PBu^n_3}]$ >0.10 and 0.03 mol dm^{-3} for C_6H_7 and C_7H_9 compounds, respectively), and tend to a limiting value [*e.g.* Figure 1(*a*)]. For the same reason the related $k_{\text{obs.}}$ *vs.* $1/[\mathrm{I}^-]$ plots become curved at the lower $[\mathrm{I}^-]$ values employed, with $k_{\text{obs.}}$ tending as predicted by equation (5) to the dissociation rate constant k_2 [*e.g.* Figure 2(*a*)].

Further quantitative support for the general rate law (3) is the excellent linearity of plots of $1/k_{\text{obs.}}$ *vs.* $1/[\mathrm{PBu^n_3}]$ observed for both complexes at constant $[\mathrm{I}^-]$ [*e.g.* Figure 1(*b*)], and of $1/k_{\text{obs.}}$ *vs.* $1/[\mathrm{I}^-]$ plots performed at constant $[\mathrm{PBu^n_3}]$ [*e.g.* Figure 2(*b*)]. This behaviour is expected from expression (6), obtained by inverting equation (3).

$$1/k_{\text{obs.}} = 1/k_2 + \frac{k_{-2}[\mathrm{I}^-]}{k_2k_3[\mathrm{PBu^n_3}]} \qquad (6)$$

From the intercept ($1/k_2$) of the plot in Figure 1(*b*) an iodide-dissociation rate constant (k_2) of $(5.71 \pm 0.46) \times 10^{-4}$ s^{-1} was calculated at 40 °C for $[\mathrm{Fe}\{(\mathrm{Bu^n_3P})C_6H_9\}(\mathrm{CO})_2\mathrm{I}]$. In excellent agreement with this, a k_2 value of $(5.92 \pm 0.35) \times 10^{-4}$ s^{-1} is independently derived from Figure 2(*b*). These values are close to the limiting values apparent from the $k_{\text{obs.}}$ *vs.* $[\mathrm{PBu^n_3}]$ or $1/[\mathrm{I}^-]$ plots. In addition, k_{-2}/k_3 values of 0.49 ± 0.05 and 0.43 ± 0.03 are estimated from the slopes of the plots in Figures 1(*b*) and 2(*b*), respectively, after inserting the known values for k_2, $[\mathrm{I}^-]$, and $[\mathrm{PBu^n_3}]$ into equation (6).

Values of k_2 and k_{-2}/k_3 for the related $[\mathrm{Fe}\{(\mathrm{Bu^n_3})C_6H_7\}(\mathrm{CO})_2\mathrm{I}]$ are summarised in Table 6. Iodide-dissociation (k_2) is seen to be about three times faster at 40 °C for the C_7H_9 complex than for the related C_6H_7 species. This may reflect an intrinsically weaker Fe–I bond in the former complex. In contrast, a previous study [16] has shown that carbonyl dissociation from the related $[\mathrm{Fe(dienyl)(CO)_2I}]$ complexes decreases in the order $C_6H_7 > C_7H_9$ in a variety of solvents. It is also interesting that while the intermediate $[\mathrm{Fe}\{(\mathrm{Bu^n_3P})C_6H_7\}(\mathrm{CO})_2]^+$ shows a significant preference for I^- over $\mathrm{PBu^n_3}$ ligands (k_{-2}/k_3 *ca.* 12, Table 6) this preference is reversed for the related C_7H_9 species (k_{-2}/k_3 *ca.* 0.5).

TABLE 6

Activation and rate parameters for steps 1 and 2 of reaction of $\mathrm{PBu^n_3}$ with $[\mathrm{Fe(dienyl)(CO)_2I}]$ complexes

	Dienyl	
Parameter	C_6H_7	C_7H_9
k_1 (20 °C)/mol dm^3 s^{-1}	1.76	0.020
$\Delta H_1^‡$/kJ mol^{-1}	32.2 ± 1.3	
$\Delta S_1^‡$/J K^{-1} mol^{-1}	-130 ± 3	
10^4k_2 (40 °C)/s^{-1}	1.97 ± 0.07 [a]	5.71 ± 0.46 [a]
	(2.08 ± 0.14) [b]	(5.92 ± 0.35) [b]
k_{-2}/k_3	11.8 ± 0.7	0.49 ± 0.05
	(12.3 ± 1.0)	(0.43 ± 0.03)
$\Delta H_2^‡$/kJ mol^{-1}	91.1 ± 4.1	
$\Delta S_2^‡$/J K^{-1} mol^{-1}	-32 ± 8	

[a] Derived from $1/k_{\text{obs.}}$ *vs.* $1/[\mathrm{PBu^n_3}]$ plot. [b] Derived from $1/k_{\text{obs.}}$ *vs.* $[\mathrm{I}^-]$ plot.

Since the temperature-dependence data for the reaction of $[\mathrm{Fe}\{(\mathrm{Bu^n_3P})C_6H_7\}(\mathrm{CO})_2\mathrm{I}]$ with $\mathrm{PBu^n_3}$ were obtained at $[\mathrm{PBu^n_3}] = 1.50$ mol dm^{-3} and $[\mathrm{I}^-]_{\text{initial}} = 0$ (Table 4), the $k_{\text{obs.}}$ values refer to k_2. The relatively high $\Delta H_2^‡$ value thus obtained of 91.1 kJ mol^{-1} (Table 6) is consistent with a dissociative process, while the slightly negative $\Delta S_2^‡$ value of -32 J K^{-1} mol^{-1} may suggest that solvation effects are significant.

The influence of ionic strength on step 2 for the C_6H_7 complex is also consistent with the mechanism in Scheme 3. Comparison of the data for $[\mathrm{PBu^n_3}] \doteqdot 0.1$ mol dm^{-3} in Tables 3 and 4 shows that $k_{\text{obs.}}$ values increase markedly with increasing ionic strength provided $[\mathrm{I}^-]$ is low. Under these conditions $k_{\text{obs.}}$ in equation (3) is dominated by the dissociation k_2, which should be facilitated by higher ionic strengths. The smaller dependence of $k_{\text{obs.}}$ on ionic strength at higher $[\mathrm{I}^-]$ arises from the increasing contribution of the ion association k_{-2} to $k_{\text{obs.}}$.

The above kinetic evidence clearly establishes that, as proposed in the introduction, nucleophilic addition of trialkylphosphines to the dienyl ring is kinetically more favoured than attack at the metal. This is not unexpected in view of the less extensive rearrangement required for a simple addition process. It is also consistent with the considerably lower activation enthalpy observed for the first step (k_1) in the case of the C_6H_7 complex (Table 6).

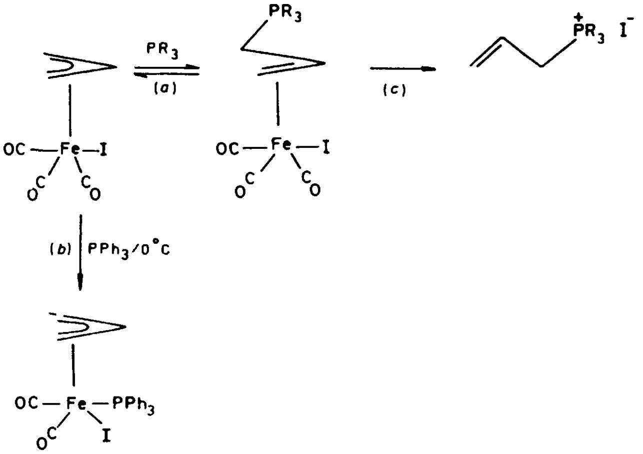
Comparison with Related Reactions.—Interestingly, Lewis and co-workers [14] have prepared a variety of complexes $[\mathrm{Fe}(1\text{—}5\text{-}\eta\text{-}C_7H_9)(\mathrm{CO})_2(\mathrm{L})][\mathrm{PF_6}]$ (L = $\mathrm{PPh_3}$, $\mathrm{SbPh_3}$, $\mathrm{AsPh_3}$, pyridine, or $\mathrm{CH_2CHCN}$) *via* treatment of $[\mathrm{Fe}(C_7H_9)(\mathrm{CO})_2\mathrm{I}]$ with $\mathrm{Ag[PF_6]}$ in acetone–dichloromethane solvent, followed by addition of L. In these cases preferential attack by L at the metal may arise from the lability of the acetone ligand in the intermediate $[Fe(1—5-\eta-C_7H_9)(CO)_2(acetone)]^+$ species. In an earlier study the related $[Fe(\eta-C_5H_5)(CO)_2I]$ species was shown [17] to react with PPh_3 to yield $[Fe(\eta-C_5H_5)(CO)_2(PPh_3)]^+$. The absence of ring-addition in this latter reaction is consistent with the general inertness of co-ordinated cyclopentadienyl groups to nucleophilic addition.

More surprising is the recent report [16] that PPh_3 and $P(OPh)_3$ react with the [Fe(dienyl)(CO)$_2$I] (dienyl $=C_6H_7$ or C_7H_9) complexes to yield the carbonyl-substituted species [Fe(dienyl)(CO)(L)I] as the only products. A dissociative mechanism was proposed for carbonyl substitution. Failure to observe initial ring addition with PPh_3 and $P(OPh)_3$ was probably due to (*i*) the low nucleophilicity of these nucleophiles compared with the trialkylphosphine employed in the present studies, and (*ii*) more significantly, the much higher temperatures employed (44—72 °C) would favour the carbonyl-dissociation path in view of its high activation enthalpy (*ca.* 100 kJ mol^{-1} for both C_6H_7 and C_7H_9 complexes in acetonitrile [16]). Although the carbonyl-dissociation route is obviously also available in the systems studied here, its very slow rate ($k_{obs.}$ *ca.* 6×10^{-4} s^{-1} for both C_6H_7 and C_7H_9 complexes at 51 °C in acetonitrile [16]) prevents it from interfering with the very rapid ring addition by $PBu^n{}_3$.

In more general terms, it is significant that preferential attack of phosphine nucleophiles to π-hydrocarbon ligands occurs in all other related systems we have investigated to date (Scheme 1). For example, contrary to previous reports,[1,3,18] it has been shown that ring-addition is the initial reaction on treating $[Mn(\eta\text{-arene})(CO)_3]^+$ and $[Mo(\eta-C_7H_7)(CO)_3]^+$ complexes with trialkylphosphines.[5,6,19] Furthermore, a recent suggestion [20] that ring addition by $PBu^n{}_3$ on $[Fe(1—5-\eta-C_7H_9)(CO)_3]^+$ occurs *via* initial attack at the metal appears to be erroneous. In support of this mechanism, the authors reported the appearance of an initial red colour which disappeared over 30 min. We have not observed this transient red colour. In addition, kinetic studies [13] of this particular reaction show that with [complex] $= [PBu^n{}_3] = 1 \times 10^{-4}$ mol dm^{-3} the reaction is complete in <1 s at 20 °C.

A further system previously suggested to involve preferential attack by phosphines at the metal, namely the reaction of $[Fe(\eta-C_3H_5)(CO)_3I]$ with PPh_3,[8] has also been reinvestigated here. On treating $[Fe(\eta-C_3H_5)(CO)_3I]$ (3) with PPh_3 at room temperature for 5 h, a 45% yield of the phosphonium salt $[PPh_3(C_3H_5)]I$ was obtained (see Experimental section). This contrasts with the observation by Heck and Boss [8] that (3) is almost quantitatively converted with PPh_3 to $[Fe(\eta-C_3H_5)(CO)_2(PPh_3)I]$ at 0 °C. Since this CO-substitution was observed at a lower temperature than our phosphonium salt formation, this earlier result might suggest that attack at the metal is kinetically favoured over hydrocarbon addition.

However, we believe that in this system also hydrocarbon addition occurs prior to metal attack. The apparently conflicting evidence can be rationalised by Scheme 4, in which a phosphonium adduct complex is formed in an initial rapid reversible process (*a*). The different products obtained at 0 and 20 °C can then be explained if the activation enthalpies for the subsequent irreversible steps (*b*) and (*c*) vary in the order $\Delta H_c^\ddagger \gg \Delta H_b^\ddagger$. The possibility that $[Fe(\eta-C_3H_5)(CO)_2(PPh_3)I]$ reacts with further PPh_3 to give the free phosphonium salt can be excluded, since no such reaction was observed after 2 d.



SCHEME 4

The complex $[Fe(\eta-C_3H_5)(CO)_3I]$ undergoes an analogous reaction with $PPr^i{}_3$ at room temperature, giving a nearly quantitative yield of $[PPr^i{}_3(C_3H_5)]I$ after 10 min.

In conclusion, it appears that with trialkylphosphines such as $PBu^n{}_3$ and $PPr^i{}_3$, addition at π-hydrocarbon ligand (C_3H_5, C_4H_4, C_6H_6, C_6H_7, C_7H_7, or C_7H_9) will be generally favoured kinetically over attack at the metal. With less nucleophilic triarylphosphines such as PPh_3, the situation is complicated by the possibility that dissociation of another ligand (*e.g.* CO, I, acetone) may interfere. However, recent kinetic studies on $[Fe(dienyl)(CO)_3]^+$ and $[Cr(\eta-C_7H_7)(CO)_3]^+$ cations [7,13] indicate that PPh_3 adds to these π-hydrocarbon ligands only *ca.* 20 times more slowly than $PBu^n{}_3$ at 0 °C. It is therefore probable that, unless a particularly labile ligand such as acetone is present, addition to the π-hydrocarbon ligand will still be usually the more favoured route with PPh_3 (especially at low temperatures). However, since phosphonium adduct formation is frequently reversible (Scheme 1) carbonyl- or hydrocarbon-displaced final products may be observed due to subsequent irreversible displacement at the metal.

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