

SYNTHESIS OF CATIONIC INDENYLIRON COMPLEXES: $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{L}]^+$ (L = phosphine, phosphite, CO)

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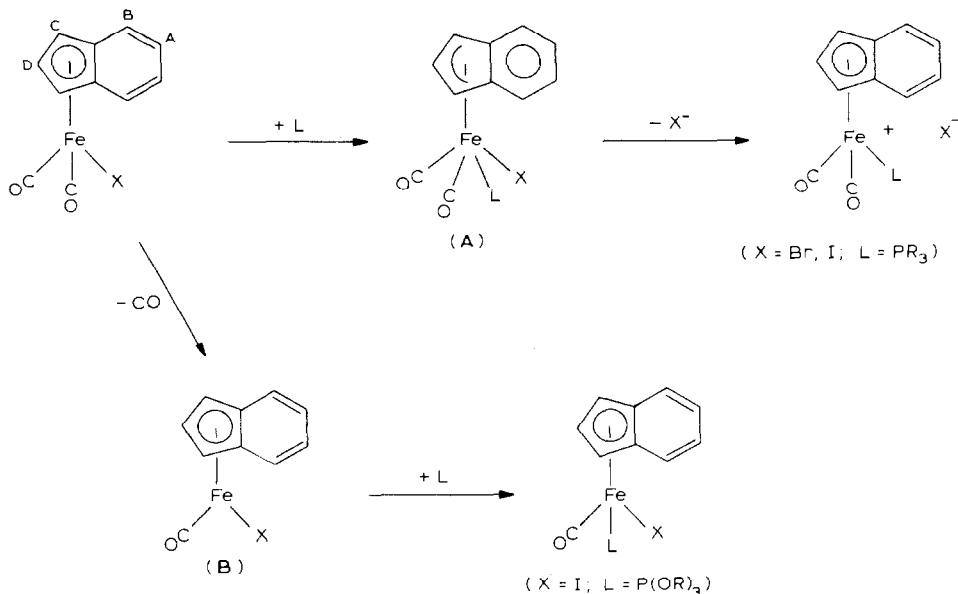
Summary

Synthetic routes to the cationic complexes $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{L}]^+$, (L = CO, phosphine, phosphite, nitrile, pyridine) have been investigated. The most versatile method is oxidation of the dimer $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2]_2$ with ferricinium ion, in the presence of the appropriate ligand. $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_3]^+$ is best prepared by oxidation of the dimer with Ph_3CBF_4 . This tricarbonyl cation readily loses one CO group on reaction with phosphines and $\text{P}(\text{OCH}_3)_3$. The acetonitrile ligand in $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{CH}_3\text{CN}]^+$ can also be replaced by phosphines. Finally, reactions of $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{X}$, (X = Br, I) with phosphines also yield cationic products, isolated as PF_6^- salts.

The cyclopentadienyl complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_n\text{L}_{3-n}]^+$ (where L is a 2-electron donor) have been widely investigated [1]. Recently, a range of pentamethylcyclopentadienyl complexes $[(\eta^5\text{-C}_5\text{Me}_5)\text{Fe}(\text{CO})_n\text{L}_{3-n}]^+$ have also been reported [2]. Comparatively little is known about the related indenyl ($\eta^5\text{-C}_9\text{H}_7$) system, though some olefin complexes $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_2(\eta^2\text{-olefin})]^+$ have been synthesised [3]. The indenyl cations might be expected to be more reactive towards substitution, owing the ability of the indenyl ring to slip to η^3 -coordination [4], allowing associative attack by an incoming ligand. One study of the rate of CO replacement by $\text{P}(\text{OC}_2\text{H}_5)_3$ and $\text{P}(\text{OC}_6\text{H}_5)_3$ in $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{I}$ showed however that a dissociative mechanism operated [5].

We describe here synthetic routes to monosubstituted cations $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{L}]\text{BF}_4$ (or PF_6) for a range of ligands L (Scheme 1). The starting material in all cases is the dimer $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2]_2$ (**1**) [6].

The acetonitrile complex $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{NCCH}_3]\text{BF}_4$ (**2a**), was obtained by protonation of **1** in acetonitrile with HBF_4 /acetic anhydride, a modification of the method reported for the $\eta^5\text{-C}_5\text{H}_5$ analogue [7]. The CH_3CN ligand cannot be displaced by phosphites.



SCHEME 1

In contrast, the more basic alkyl phosphines $P(n\text{-C}_4\text{H}_9)_3$ and $P[\text{CH}(\text{CH}_3)_2]_3$ react rapidly with **2a** at room temperature giving the monosubstituted cations **3a** and **3b** (Table 1). Refluxing conditions are required for substitution of CH_3CN by $P(2\text{-OCH}_3\text{C}_6\text{H}_4)_3$. Similar reactivity is found for $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{NCCCH}_3]^+$ [8].

A more general route to these cations is oxidation of **1** in the presence of the appropriate ligand. Of the oxidation methods available [2,9,10], the ferricinium ion $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}][\text{BF}_4]$ [2] was found to be the most efficient, allowing easy purification of the products. The reaction between **1** and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^+$ in CH_2Cl_2 /acetone at 0°C was successful for a wide range of ligands (L = phosphine, phosphite, nitrile, pyridine), Table 1. It is noteworthy that the oxidation of **1** is very rapid with both $(\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}^+$ and Ph_3C^+ , in contrast to the long reaction times required for the $\eta^5\text{-C}_5\text{H}_5$ [10] and $\eta^5\text{-C}_5\text{Me}_5$ [2] dimers.

Attempts to prepare a solvent coordinated intermediate $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{S}]^+$ (S = THF or acetone) by this method, were unsuccessful. Instead, the tricarbonyl cation $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_3]^+$ (**4**) was isolated from the reaction mixtures in low yields. The optimum synthesis of **4** is reaction of **1** with $[\text{Ph}_3\text{C}][\text{BF}_4]$ in CH_2Cl_2 , giving yields of 55–60% even in the absence of added CO. **4** readily loses one CO ligand on treatment with phosphines and $\text{P}(\text{OCH}_3)_3$, again giving cations **3**. However **4** does not react with $\text{P}(\text{OPh})_3$ even after prolonged reaction times.

The reactions of $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{X}$ (X = Br, I) with phosphorus ligands are of interest, in view of the complex reactivity displayed by their $\eta^5\text{-C}_5\text{H}_5$ counterparts [11–15]. $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{Br}$ (**5**) prepared from **1** and Br_2 , is noticeably less stable than $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{Br}$. Solutions of **5** decompose slowly giving variable amounts of **4**. Reactions of **5** with the arylphosphines $P(4\text{-CH}_3\text{C}_6\text{H}_4)_3$ and $P(2\text{-OCH}_3\text{C}_6\text{H}_4)_3$ in THF at room temperature give the monosubstituted cations **3c** and **3d**, isolated as PF_6^- salts. $P(n\text{-C}_4\text{H}_9)_3$ also reacts with **5** in THF but only gives **3a** in ~15% yield. However, when the solvent was changed to methanol, with NH_4PF_6 added, **3a** was

TABLE 1
PREPARATIVE DETAILS AND ANALYTICAL DATA FOR $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{L}]^+$

Compound		Method ^a	Yield ^b (%)	Analysis (found (calcd.) (%))		
No.	L			C	H	N
2a	CH ₃ CN ^c		68	43.46 (44.00)	2.93 (2.84)	3.84 (3.95)
2b	C ₆ H ₅ CN	III	67	51.02 (51.84)	2.91 (2.90)	3.29 (3.36)
2c	C ₅ H ₅ N	III	63	48.28 (48.88)	3.27 (3.08)	4.10 (3.56)
3a	P(n-C ₄ H ₉) ₃	Ib	68 (44)	53.52 (53.52)	6.69 (6.64)	—
		II	84 (57)			
		III	52			
3b	P(i-C ₃ H ₇) ₃	II	70 (45)	49.15 (50.67)	6.45 (5.96)	—
3c	P(4-CH ₃ C ₆ H ₄) ₃	Ia	50 (33)	55.92 (56.64) ^d	4.26 (4.16)	—
3d	P(2-CH ₃ OC ₆ H ₄) ₃	Ia	48 (31)	57.73 (57.67)	4.34 (4.24)	—
		III	65			
		IV	65 (48)			
3e	P(3-ClC ₆ H ₄) ₃	III	54	50.96 (51.26)	2.93 (2.82)	—
3f	P(OC ₆ H ₅) ₃	III	61	55.84 (55.81)	3.56 (3.55)	—
3g	P(OC ₂ H ₅) ₃	III	71	42.60 (42.54)	5.54 (4.62)	—
3h	P(OCH ₃) ₃ ^c		78 (44)	39.29 (38.38)	3.70 (3.65)	—
4	CO ^c		57	41.97 (41.16)	2.10 (2.06)	—

^a Methods: Ia: L+5 in THF, NH₄PF₆/methanol; Ib: L+5+NH₄PF₆ in methanol; II: L+2 in CH₂Cl₂; III: L+1+Cp₂FeBF₄; IV: L+6, reflux in petroleum ether. ^b Overall yield from 1 in parentheses for methods I, II and IV. ^c See text for preparation. ^d PF₆ salt.

obtained in 68% yield. P(OPh)₃ and P(OCH₃)₃ do not react with 5 at room temperature, while refluxing conditions lead only to decomposition.

Reactions of $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{X}$ with phosphines and phosphites lead to displacement of X ($[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{L}][\text{X}]$) or CO substitution ($\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})\text{LX}$), depending on the nature of X and the basicity of the incoming ligand. Changing the solvent or reaction temperature may also affect the product distribution [11]. In the indenyl system, however, $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{Br}$ gives exclusively cationic products under a variety of experimental conditions. No evidence for the CO-substituted product $\eta\text{-C}_9\text{H}_7\text{Fe}(\text{CO})\text{LBr}$ was found. A possible mechanism involving an η^3 -intermediate (A) is shown in Scheme 1.

In view of the contrasting behaviour found for $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{I}$ (6), which gives $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})\text{LI}$ on reaction with phosphites [5], the reactions of 6 with P(n-C₄H₉)₃ and P(2-OCH₃C₆H₄)₃ were investigated. The cations 3a and 3d were obtained in 65–70% yields on heating 6 with the phosphines in petroleum ether for 1 h. It may be that the less basic phosphites will not add easily to 5 or 6 and under the

strong reaction conditions used for **6** [5], the alternative dissociative mechanism (Scheme 1, B) predominates. The involvement of free radical intermediates has been implicated in substitution reactions of $\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{Br}$ [16] and in $[\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2]_2$ catalysed reactions of $\eta^5\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{I}$ [15] and cannot be ruled out in the present study.

Conclusions

Synthetic routes to a range of cationic indenyliron complexes $[\eta^5\text{-C}_9\text{H}_7\text{Fe(CO)}_2\text{L}]$ have been assessed. As expected the indenyl complexes are generally more reactive than their $\eta^5\text{-C}_5\text{H}_5$ analogues, particularly in the case of the oxidation of the dimer **1**. The reactions of $\eta^5\text{-C}_9\text{H}_7\text{Fe(CO)}_2\text{X}$ (X = Br, I) with phosphines are fast and give exclusively cationic products.

The oxidation of **1** and the reactions of the cations **3** with nucleophiles are under investigation.

Experimental

All reactions were carried out under a nitrogen atmosphere. Solvents were dried by standard procedures. Petrol refers to petroleum ether, boiling fraction 40–60°C. Ligands were obtained commercially and used as received. $\eta^5\text{-C}_9\text{H}_7\text{Fe(CO)}_2\text{I}$ (**6**) was prepared by a literature method [5].

Infrared spectra were run on a Perkin–Elmer 257 or a Perkin–Elmer 398 spectrometer in 0.50 mm cells. Proton NMR spectra were recorded on a Varian EM 360L spectrometer (Table 2). Elemental analyses were performed by the E. Pascher Microanalytical Laboratory, Bonn, W. Germany (Table 1).

TABLE 2
INFRARED AND ^1H NMR DATA

Compound		Infrared ^a and ^1H NMR resonances ^b (δ (ppm))					
No.	L	$\nu(\text{CO})$ (cm^{-1})		Indenyl ^c			
				$\text{H}_\text{A}, \text{H}_\text{B}(\text{m})$	$\text{H}_\text{C}(\text{d})$	$\text{H}_\text{D}(\text{m})$	L
2a	CH_3CN	2067	2023	7.97	6.05	5.95	2.10 (s, CH_3)
2b	$\text{C}_6\text{H}_5\text{CN}$	2071	2025	7.80	5.97	5.60	7.80 (m, Ph)
2c	$\text{C}_5\text{H}_5\text{N}$	2056	2009	7.67–7.50	6.13	5.70	7.67, 8.06, 8.35 ($\text{C}_5\text{H}_5\text{N}$)
3a	$\text{P}(\text{n-C}_4\text{H}_9)_3$	2040	1993	8.04, 7.77	6.30	5.98	1.0(m), 1.56(m) (C_4H_9)
3b	$\text{P}(\text{CH}(\text{CH}_3)_2)_3$	2041	1995	7.97	6.48	6.17	1.35 (dd, CH_3), 2.75 (m, CH)
3c	$\text{P}(\text{4-CH}_3\text{C}_6\text{H}_4)_3$	2046	2005	7.86–7.45	6.26	5.45	2.48 (s, CH_3), 7.45–7.86 (m, C_6H_4)
3d	$\text{P}(\text{2-CH}_3\text{OC}_6\text{H}_4)_3$	2047	2007	7.77–7.00	5.83	5.18	3.85 (s, CH_3), 7.00–7.77 (m, C_6H_4)
3e	$\text{P}(\text{3-ClC}_6\text{H}_4)_3$	2051	2009	7.88–7.37	6.40	5.83	7.37–7.88 (m, C_6H_4)
3f	$\text{P}(\text{OC}_6\text{H}_5)_3$	2065	2025	7.87–7.60	5.87	6.00	7.60 (m, C_6H_5)
3g	$\text{P}(\text{OC}_2\text{H}_5)_3$	2061	2017	7.94	6.40	5.90	1.44 (t, CH_3), 4.32 (q, CH_2)
3h	$\text{P}(\text{OCH}_3)_3$	2060	2015	7.91	6.42	5.91	4.02 (d, CH_3 , $J(\text{HP})$ 12 Hz)
4	CO	2115	2063	8.04	6.76	6.39	–

^a In CH_2Cl_2 . ^b In $(\text{CD}_3)_2\text{CO}$, TMS internal reference. ^c See Scheme 1 for labelling of indenyl protons.

*Preparation of $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2]_2$ (**1**)*

The method of Hallam and Pauson was used [6]. Indene (12 g, 0.1 mol) and $\text{Fe}(\text{CO})_5$ (17.6 g, 0.09 mol) were heated to $124 \pm 2^\circ\text{C}$ for 18 h. After cooling to 0°C , the supernatant red oil was removed. The residue was washed with petrol, extracted with CH_2Cl_2 and filtered through celite. The product was precipitated with petrol and recrystallised (CH_2Cl_2 /petrol) giving $[\text{C}_9\text{H}_7\text{Fe}(\text{CO})_2]_2$ (**1**) (2.5 g, 12.2%).

*Preparation of $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{Br}$ (**5**)*

A solution of Br_2 (0.35 g, 2.2 mmol) in CH_2Cl_2 was added dropwise to a solution of the dimer **1** (1.0 g, 2.2 mmol) in CH_2Cl_2 . After removal of the solvent in vacuo the crude product was washed with petrol and recrystallised (CH_2Cl_2 /petrol) giving a red-brown powder (0.88 g, 65%). Infrared (CH_2Cl_2): $\nu(\text{CO})$: 2039, 1993 cm^{-1} . ^1H NMR (CDCl_3) δ (ppm): 7.60 (m, 4H, H_A , H_B); 5.36 (d, 2H, H_C); 5.21 (q, 1H, H_D).

*Preparation of $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2(\text{CH}_3\text{CN})][\text{BF}_4]$ (**2a**)*

A solution of HBF_4 aq. (~ 8 mmol) in 2 cm^3 acetic anhydride was added dropwise to **1** (1.5 g, 3.3 mmol) in 15 cm^3 acetonitrile. After 15 min the solvent was evaporated, the residue was washed with diethyl ether and recrystallised (CH_2Cl_2 /diethyl ether) giving a red powder (1.585 g, 68%).

*Reaction of **2a** with alkyl phosphines*

2a (0.25 g, 0.7 mmol) was stirred with 2 equivalents of phosphine L, in CH_2Cl_2 at room temperature. The solution rapidly changed from orange to yellow. After 5 min, the solvent and excess phosphine were evaporated in vacuo and the product recrystallised (CH_2Cl_2 /diethyl ether) to give $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{L}][\text{BF}_4]$ as a yellow solid. L = $\text{P}(\text{n-C}_4\text{H}_9)_3$ (**3a**), yield 84%; L = $\text{P}(\text{i-C}_3\text{H}_7)_3$ (**3b**), yield 70%.

*Reaction of **2a** with $\text{P}(2\text{-OCH}_3\text{C}_6\text{H}_4)_3$*

2a (0.15 g, 0.42 mmol) and $\text{P}(2\text{-OCH}_3\text{C}_6\text{H}_4)_3$ (0.50 g, 1.43 mmol) in 20 cm^3 acetone/5 cm^3 THF, were heated to 80°C for 16 h. The solvents were evaporated in vacuo. The residue was washed well with toluene and recrystallised twice from CH_2Cl_2 /diethyl ether, giving $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{P}(2\text{-OCH}_3\text{C}_6\text{H}_4)_3][\text{BF}_4]$ (**3d**) (0.18 g, 64%).

*Preparation of $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{L}][\text{BF}_4]$ by oxidation of **1***

$[\text{Cp}_2\text{Fe}][\text{BF}_4]$ (0.3 g, 1.1 mmol) in 5 cm^3 acetone was added to **1** (0.2 g 0.44 mmol) and 2 equivalents of ligand L in 30 cm^3 CH_2Cl_2 . After 15 min at room temperature the solution was filtered. The filtrate was reduced in volume and petroleum ether was added to precipitate the crude product. Recrystallisation (CH_2Cl_2 /diethyl ether) gave the pure product. Ligands used were $\text{C}_6\text{H}_5\text{CN}$, $\text{C}_5\text{H}_5\text{N}$, $\text{P}(\text{n-C}_4\text{H}_9)_3$, $\text{P}(2\text{-OCH}_3\text{C}_6\text{H}_4)_3$, $\text{P}(3\text{-ClC}_6\text{H}_4)_3$, $\text{P}(\text{OC}_6\text{H}_5)_3$, $\text{P}(\text{OC}_2\text{H}_5)_3$. Yields are given in Table 1.

*Oxidation of **1** in THF or acetone*

Reaction of **1** (0.2 g, 0.44 mmol) with $[\text{Cp}_2\text{Fe}][\text{BF}_4]$ (0.3 g, 1.1 mmol) in CH_2Cl_2 /THF or CH_2Cl_2 /acetone 2/1 and work-up as described above, gave $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_3][\text{BF}_4]$ (**4**) in 22% yield.

*Preparation of $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_3]^+$ (**4**) in CH_2Cl_2*

1 (0.30 g 0.66 mmol in 20 cm³ CH_2Cl_2 was stirred with Ph_3CBF_4 (0.64 g, 2.0 mmol) for 2 h at room temperature. Filtration through celite, concentration of the solution and addition of diethyl ether gave crude **4**. Recrystallisation (CH_2Cl_2 /diethyl ether) gave **4** (0.257 g, 57%).

*Reaction of **4** with phosphines, phosphites*

4 (0.045 g, 0.13 mmol) was stirred with three equivalents of ligand L at room temperature. Concentration of the solution and addition of diethyl ether gave the crude product. Recrystallisation (CH_2Cl_2 , diethyl ether) gave pure product, $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{L}][\text{BF}_4]$. **3a**: L = $\text{P}(\text{n-C}_4\text{H}_9)_3$, reaction time 10 min, yield 73%; **3d**: L = $\text{P}(\text{2-OCH}_3\text{C}_6\text{H}_4)_3$, reaction time 50 min, yield 70%; **3h**: L = $\text{P}(\text{OCH}_3)_3$, reaction time 30 min, yield 78%.

*Reaction of $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{Br}$ (**5**) with phosphines*

(i) in THF: **5** (0.221 g, 0.72 mmol) and two equivalents of phosphine were stirred in THF, for 30 min at room temperature. The solvent was evaporated and the residue washed with petroleum ether. A solution of NH_4PF_6 (0.24 g, 1.5 mmol) in methanol was added. A yellow precipitate formed on stirring, was collected, washed with methanol and recrystallised (CH_2Cl_2 /diethyl ether). Yields: For aryl phosphines ~ 50% (Table 1) for alkyl phosphine $\text{P}(\text{n-C}_4\text{H}_9)_3$ ~ 15%.

(ii) In methanol: **5** (0.1 g, 0.33 mmol), $\text{P}(\text{n-C}_4\text{H}_9)_3$ (0.13 g, 0.64 mmol) and NH_4PF_6 (0.11 g, 0.68 mmol) were dissolved in 15 cm methanol. After 1 h at room temperature a yellow solution containing some precipitate was obtained. Evaporation of the solvent, extraction of the residue with CH_2Cl_2 and recrystallisation (CH_2Cl_2 /diethyl ether) gave $[\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{P}(\text{n-C}_4\text{H}_9)_3][\text{PF}_6]$ (**3a**) (0.116 g, 68%).

*Reaction of $\eta^5\text{-C}_9\text{H}_7\text{Fe}(\text{CO})_2\text{I}$ (**6**) with phosphines*

6 (0.10 g, 0.28 mmol) and 0.60 mmol phosphine in 20 cm³ petroleum ether were refluxed for 1 h. The brown precipitate which formed was washed with petroleum ether and treated with NH_4PF_6 (0.07 g, 0.43 mmol) in methanol. Evaporation of the solvent, extraction with CH_2Cl_2 and recrystallization (CH_2Cl_2 /diethyl ether) gave the cationic products in yields of 60% (L = $\text{P}(\text{n-C}_4\text{H}_9)_3$) and 65% (L = $\text{P}(\text{2-OCH}_3\text{C}_6\text{H}_4)_3$).

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