Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

REACTIONS OF METAL CARBONYL DERIVATIVES
VII*. REACTIONS OF CHLORO- AND IODODICARBONYL-π-CYCLOPENTADIENYLIRON WITH SOME TERTIARY PHOSPHINES AND PHOSPHITES**

R. J. HAINES***

Research and Process Development, South African Iron and Steel Industrial Corporation Limited, P.O. Box 450, Pretoria (Republic of South Africa)

A. L. DU PREEZ AND I. L. MARAIS

Department of Inorganic and Analytical Chemistry, University of Pretoria, Pretoria (Republic of South Africa)

(Received December 1st, 1970)

SUMMARY

The tertiary alkyl phosphites $P(OR)_3$ ($R=CH_3$, C_2H_5, n-C_4H_9 and C_3H_5) react with π-$C_5H_5Fe(CO)_2Cl$ in benzene to give in addition to neutral π-C_5H_5-$Fe(CO)P(OR)_3Cl$ and ionic $[\pi$-$C_5H_5Fe(CO)_2P(OR)_3]Cl$ complexes, neutral phosphonate derivatives of formula π-$C_5H_5Fe(CO)_2[P(O)(OR)_2]$ and π-$C_5H_5Fe(CO)$-$[P(OR)_3][P(O)(OR)_2]$. The corresponding reactions involving the tertiary phosphonite $P(OC_3H_5)_2C_6H_5$ and the tertiary phosphinite $P(OC_3H_5)(C_6H_5)_2$ yield similar type products. In contrast compounds of the type $[\pi$-$C_5H_5Fe(CO)P(OR)_3]I$ are the sole products from the reactions of $P(OR)_3$ ($R=CH_3$ and C_2H_5) with π-$C_5H_5Fe(CO)_2I$. The formation of π-$C_5H_5Fe(CO)_2[P(O)(OR)_2]$ is shown to occur via $[\pi$-C_5H_5-$Fe(CO)_2P(OR)_3]Cl$ as intermediate and to involve a Michaelis–Arbuzov rearrangement. The reactions of π-$C_5H_5Fe(CO)_2X$ ($X=Cl$ and I) with the tertiary phosphines PR_3 ($R=C_2H_5$ and C_4H_9) are also described.

INTRODUCTION

Previous studies have demonstrated that the action of tertiary phosphines PR_3 (R=alkyl and aryl) on π-$C_5H_5Fe(CO)_2X$ (X=Cl, Br and I) results in either the replacement of a carbonyl group or the displacement of the halogen to afford compounds of the type π-$C_5H_5Fe(CO)PR_3X$ or of the type $[\pi$-$C_5H_5Fe(CO)_2PR_3]X$ respectively[3-8]. The tendency for halogen displacement in preference to carbonyl replacement has been established to increase with increasing basicity of the ligand and also along the series $I < Br < Cl$[7,9]. Products formed as a result of both modes of reaction *viz.* $[\pi$-$C_5H_5Fe(CO)L_2]$ Anion (L=ligand) have been reported but their syntheses required the presence of a strong Lewis acid *e.g.* $AlBr_3$[7].

In contrast most reports which describe reactions involving π-$C_5H_5Fe(CO)_2X$ (X=halogen) and tertiary phosphites $P(OR)_3$ (R=alkyl or aryl) refer to the formation of products resulting from carbonyl replacement only. Apart from a reference to an

---

* For Part VI, see ref. 1.

** A preliminary communication of some of this work has been presented[2].

*** To whom correspondence concerning this publication should be addressed.

ionic product formed in the reaction of π-$C_5H_5Fe(CO)_2X$ with $P(OC_6H_5)_3$ and for which no analytical and physical data were given[10], no mention of products of the type $[\pi$-$C_5H_5Fe(CO)_2P(OR)_3]X$ being produced in these reactions has been made. For instance the reactions[10] of π-$C_5H_5Fe(CO)_2X$ (X = Br and I) with $P(OC_6H_5)_3$ in benzene under reflux have been observed to afford π-$C_5H_5Fe(CO)P(OC_6H_5)_3X$ in yields greater than 90% while irradiation[11] of a refluxing benzene solution of π-C_5H_5-$Fe(CO)_2I$ and excess $P(OC_6H_5)_3$ with ultraviolet light has been shown to give π-$C_5H_5Fe[P(OC_6H_5)_3]_2I$. Further the results of a kinetic study of the reactions of π-$C_5H_5Fe(CO)_2I$ with the tertiary alkyl phosphites $P(OC_2H_5)_3$ and $P(OC_6H_{13})_3$ as well as those for the reactions of π-$C_5H_5Fe(CO)_2X$ (X = Br and I) with $P(OC_6H_5)_3$ in solution are consistent with the formation of products of the type π-C_5H_5Fe-$(CO)P(OR)_3X$ by a dissociative mechanism[10].

It is now found that the reactions of π-$C_5H_5Fe(CO)_2Cl$ with tertiary phosphites, phosphonites and phosphinites afford a new type of product which is formed as a result of the degradation of the ligand.

RESULTS AND DISCUSSION

Treatment of π-$C_5H_5Fe(CO)_2I$ with a slight excess of the tertiary phosphites $P(OR)_3$ (R = CH_3, C_2H_5 and C_6H_5) in benzene under reflux was observed to give neutral products characterised as π-$C_5H_5Fe(CO)P(OR)_3I$ in excellent yield*. Similarly π-$C_5H_5Fe(CO)P(OC_6H_5)_3Cl$ was isolated in good yield from the corresponding room temperature reaction involving $P(OC_6H_5)_3$ although a small amount of $[\pi$-$C_5H_5Fe(CO)_2P(OC_6H_5)_3]Cl$ was also formed in this reaction; this latter complex was characterised as the tetraphenylborate. In contrast π-C_5H_5-$Fe(CO)P(OR)_3Cl$ was found to be a minor product (yield ca. 20%) in the reaction of π-$C_5H_5Fe(CO)_2Cl$ with the tertiary alkyl phosphites $P(OR)_3$ (R = CH_3, C_2H_5, n-C_4H_9 and C_3H_5) in benzene at room temperature. These latter reactions afforded as major product a halogen-free derivative shown to be π-$C_5H_5Fe(CO)_2[P(O)$-$(OR)_2]$. Small amounts of π-$C_5H_5Fe(CO)[P(OR)_3][P(O)(OR)_2]$ were also formed in these reactions. The yield of the latter was increased by increasing the ligand to parent compound ratio, by performing the reaction in refluxing benzene and by extending the reaction period. However, in spite of these variations in the reaction conditions, π-$C_5H_5Fe(CO)_2[P(O)(OR)_2]$ was still the major product. π-C_5H_5Fe-$(CO)_2[P(O)(OR)_2]$ and π-$C_5H_5Fe(CO)[P(OR)_3][P(O)(OR)_2]$ were readily separated from π-$C_5H_5Fe(CO)P(OR)_3Cl$ by means of column chromatography but separation of the two phosphonate derivatives was not always successful. Thus while π-$C_5H_5Fe(CO)_2[P(O)(OR)_2]$ (R = C_2H_5 and C_3H_5) and π-$C_5H_5Fe(CO)[P(OC_3$-$H_5)_3][P(O)(OC_3H_5)_2]$ were characterised by elemental analysis and molecular weight measurements, π-$C_5H_5Fe(CO)_2[P(O)(OR')_2]$ (R' = CH_3 and C_4H_9) and π-$C_5H_5Fe(CO)[P(OR'')_3][P(O)(OR'')_2]$ (R'' = CH_3, C_2H_5 and C_4H_9) were identified by means of infrared spectroscopy only. Apart from π-$C_5H_5Fe(CO)P(OCH_3)_3Cl$, the complexes π-$C_5H_5Fe(CO)P(OR)_3Cl$ (R = C_2H_5, n-C_4H_9 and C_3H_5) were also iden-

---

* The syntheses, isolation and characterisation of π-$C_5H_5Fe(CO)P(OCH_3)_3X$ (X = Br and I) have recently been reported in a publication which appeared at the same time as the preliminary communication of the results presented in this paper[12].

tified by means of infrared only. Confirmatory evidence for the formulation π-$C_5H_5Fe(CO)_2[P(O)(OR)_2]$ was obtained by studying the reaction of π-$C_5H_5Fe(CO)_2Cl$ with $NaOP(OC_2H_5)_2$ in THF. The product isolated from this reaction *viz.* π-$C_5H_5Fe(CO)_2[P(O)(OC_2H_5)_2]$ was identical to the unsubstituted phosphonate obtained from the reaction of π-$C_5H_5Fe(CO)_2Cl$ with $P(OC_2H_5)_3$.

By monitoring the reactions of π-$C_5H_5Fe(CO)_2Cl$ with the above tertiary alkylphosphites in benzene at room temperature by means of infrared it was observed that a species, identified as $[\pi\text{-}C_5H_5Fe(CO)_2P(OR)_3]^+$, is initially formed and that this species is an intermediate in the formation of π-$C_5H_5Fe(CO)_2[P(O)(OR)_2]$. The intermediates in the reactions involving $P(OCH_3)_3$ and $P(OC_3H_5)_3$ were isolated by performing the reactions in the presence of $NaB(C_6H_5)_4$ and a little methanol to ensure dissolution of the latter. The compounds which separated from solution were characterised as $[\pi\text{-}C_5H_5Fe(CO)_2P(OR)_3]B(C_6H_5)_4$ ($R=CH_3$ and C_3H_5) and were shown to be 1/1 electrolytes in acetone.

The tertiary phosphonite $P(OC_3H_5)_2(C_6H_5)$ and the phosphinite $P(OC_3H_5)(C_6H_5)_2$ were observed to behave in an analogous manner to tertiary alkyl phosphites on reaction with π-$C_5H_5Fe(CO)_2Cl$ and to afford similar type products. Thus the reaction of π-$C_5H_5Fe(CO)_2Cl$ with excess $P(OC_3H_5)(C_6H_5)_2$ in benzene under reflux afforded as well as a low yield of π-$C_5H_5Fe(CO)P(OC_3H_5)(C_6H_5)_2Cl$, the products π-$C_5H_5Fe(CO)_2[P(O)(C_6H_5)_2]$ and π-$C_5H_5Fe(CO)[P(OC_3H_5)(C_6H_5)_2][P(O)(C_6H_5)_2]$. Similarly π-$C_5H_5Fe(CO)P(OC_3H_5)_2(C_6H_5)Cl$, π-$C_5H_5Fe(CO)_2[P(O)(OC_3H_5)(C_6H_5)]$ and π-$C_5H_5Fe(CO)[P(OC_3H_5)_2(C_6H_5)][P=(O)(OC_3H_5)(C_6H_5)]$ were isolated from the corresponding reaction involving $P(OC_3H_5)_2(C_6H_5)$. Further $[\pi\text{-}C_5H_5Fe(CO)_2L]B(C_6H_5)_4$ [$L=P(OC_3H_5)_2(C_6H_5)$ and $P((OC_3H_5)(C_6H_5)_2$] were also isolated from the reactions of π-$C_5H_5Fe(CO)_2Cl$ with these ligands under the appropriate experimental conditions. The compounds $[\pi\text{-}C_5H_5Fe(CO)_2L]B(C_6H_5)_4$ [$L=P(OC_3H_5)_2(C_6H_5)$ and $P(OC_3H_5)(C_6H_5)_2$], π-$C_5H_5Fe(CO)_2L'$ [$L'=P(O)(OC_3H_5)(C_6H_5)$ and $P(O)(C_6H_5)_2$] and π-$C_5H_5Fe(CO)L''L'''$ [$L''=P(OC_3H_5)_2(C_6H_5)$, $L'''=P(O)(OC_3H_5)(C_6H_5)$; $L''=P(OC_3H_5)(C_6H_5)_2$, $L'''=P(O)(C_6H_5)_2$] were characterised by elemental analysis and molecular weight measurements while in view of their instability π-$C_5H_5Fe(CO)L''''Cl$ [$L''''=P(OC_3H_5)_2(C_6H_5)$ and $P(OC_3H_5)(C_6H_5)_2$] were identified by means of infrared only.

Treatment of π-$C_5H_5Fe(CO)_2Cl$ with the tertiary phosphines PR_3 ($R=C_2H_5$ and C_4H_9) in benzene at room temperature was observed to effect the displacement of the halogen and to afford $[\pi\text{-}C_5H_5Fe(CO)_2PR_3]Cl$, which was isolated as the tetraphenylborate, in high yield. A small amount of π-$C_5H_5Fe(CO)PR_3Cl$ was also formed as established by monitoring the reaction with infrared. The corresponding reaction involving π-$C_5H_5Fe(CO)_2I$ and $P(C_2H_5)_3$ similarly afforded primarily $[\pi\text{-}C_5H_5Fe(CO)_2P(C_2H_5)_3]I$ (yield >80%). However π-$C_5H_5Fe(CO)P(C_2H_5)_3I$ was isolated in a yield of *ca.* 30% by reacting these latter compounds in benzene under reflux for 30 minutes. Further π-$C_5H_5Fe(CO)P(C_4H_9)_3I$ was obtained almost quantitatively from the reaction of π-$C_5H_5Fe(CO)_2I$ with $P(C_4H_9)_3$ under similar experimental conditions. It is thus suggested that $[\pi\text{-}C_5H_5Fe(CO)_2PR_3]I$ ($R=$ alkyl group) is an intermediate in the formation of π-$C_5H_5Fe(CO)PR_3I$.

The infrared spectra of the various compounds synthesised in this study are summarised in Table 2. Strong peaks in the spectra of π-$C_5H_5Fe(CO)_2L'$ and π-$C_5H_5Fe(CO)$ (Ligand)L' ($L'=$phosphonate, phosphinate or phosphine oxide ligand)

TABLE 1

CONDUCTIVITY, ANALYTICAL AND MOLECULAR WEIGHT DATA

Compound[a]	Conductivity[b] (Ohm^{-1}·cm^2·mol^{-1})	Analyses (%)						Mol wt.[c,d]	
		Found			Calcd.			Found	Calcd.
		C	H	Others	C	H	Others		
π-$C_5H_5Fe(CO)P(OCH_3)_3Cl$	2.0	35.3	4.8	11.4 (Cl)	35.0	4.6	11.5 (Cl)	306	308
π-$C_5H_5Fe(CO)P(OC_6H_5)_3Cl$	3.3	57.9	4.1	6.9 (Cl)	58.3	4.1	7.2 (Cl)	N.m.	
π-$C_5H_5Fe(CO)P(C_2H_5)_3I$	6.2	36.5	5.2		36.6	5.1		N.m.	
π-$C_5H_5Fe(CO)P(C_4H_9)_3I$	4.4	44.9	6.8		45.1	6.9		N.m.	
π-$C_5H_5Fe(CO)P(OCH_3)_3I$	1.5	27.0	3.5	31.9 (I)	27.0	3.5	31.7 (I)	N.m.	
π-$C_5H_5Fe(CO)P(OC_2H_5)_3I$	1.9	33.0	4.6		32.6	4.6		N.m.	
π-$C_5H_5Fe(CO)P(OC_6H_5)_3I$	2.6	49.4	3.4	21.8 (I)	49.2	3.4	21.7 (I)	N.m.	
$[\pi$-$C_5H_5Fe(CO)_2P(C_2H_5)_3]B(C_6H_5)_4$	92	72.4	6.6		72.3	6.6			
$[\pi$-$C_5H_5Fe(CO)_2P(C_4H_9)_3]B(C_6H_5)_4$	89	73.9	7.6	7.8 (Fe)	73.9	7.5	8.0 (Fe)		
$[\pi$-$C_5H_5Fe(CO)_2P(OCH_3)_3]B(C_6H_5)_4$	98	66.0	5.4	4.9 (P)	65.8	5.5	5.0 (P)		
$[\pi$-$C_5H_5Fe(CO)_2P(OC_3H_5)_3]B(C_6H_5)_4$	93	69.0	5.6	4.3 (P)	68.8	5.8	4.4 (P)		
$[\pi$-$C_5H_5Fe(CO)_2P(OC_6H_5)_3]B(C_6H_5)_4$	90	72.7	5.0		73.0	5.0			
$[\pi$-$C_5H_5Fe(CO)_2P(OC_3H_5)_2(C_6H_5)]B(C_6H_5)_4$	92	71.8	5.7	4.2 (P)	71.9	5.6	4.3 (P)		
$[\pi$-$C_5H_5Fe(CO)_2P(OC_3H_5)(C_6H_5)_2]B(C_6H_5)_4$	89	75.1	5.7	4.1 (P)	74.8	5.5	4.2 (P)		
π-$C_5H_5Fe(CO)_2[P(O)(OC_2H_5)_2]$	0.1	42.0	4.8	9.5 (P)	42.1	4.8	9.9 (P)	312	314
π-$C_5H_5Fe(CO)_2[P(O)(OC_3H_5)_2]$[e]	0.1	45.5	4.5		46.2	4.5		359	338
π-$C_5H_5Fe(CO)_2[P(O)(OC_3H_5)(C_6H_5)]$[e]	0.3	53.9	4.5		53.7	4.2		379	358
π-$C_5H_5Fe(CO)_2[P(O)(C_6H_5)_2]$	0.2	60.7	4.2	8.1 (P)	60.4	4.0	8.2 (P)	399	378
π-$C_5H_5Fe(CO)[P(OC_3H_5)_3][P(O)(OC_3H_5)_2]$[e]	0.1	49.0	5.8	11.8 (P)	49.2	5.9	12.1 (P)	501	512
π-$C_5H_5Fe(CO)[P(OC_3H_5)_2(C_6H_5)][P(O)(OC_3H_5)(C_6H_5)]$[e]	0.1	58.6	5.3		58.7	5.5		537	552
π-$C_5H_5Fe(CO)[P(OC_3H_5)(C_6H_5)_2][P(O)(C_6H_5)_2]$	2.6	66.8	5.1	10.3 (P)	66.9	5.1	10.5 (P)	558	592

[a] Compounds in general gave poorly defined melting points; all are stable in air in the crystalline state apart from those under e. [b] 1–10×10^{-4} M solutions in acetone. [c] Measured in benzene. [d] Abbreviation: N.m. not measured. [e] Isolated as oils.

TABLE 2

INFRARED AND PROTON MAGNETIC RESONANCE SPECTROSCOPIC DATA

Compound	Stretching frequencies (cm^{-1})[a]			Resonances[c,d,f]	
	ν(C–O)		ν(P–O)[b]	C_5H_5	J(P–H) (Hz)
$\pi\text{-}C_5H_5Fe(CO)P(OCH_3)_3Cl$	1980 ms	1970 s[e]		5.24 d	~1
$\pi\text{-}C_5H_5Fe(CO)P(OC_6H_5)_3Cl$	1986[g]			5.75 s	
$\pi\text{-}C_5H_5Fe(CO)P(C_2H_5)_3I$	1944[g]			5.29 s	
$\pi\text{-}C_5H_5Fe(CO)P(C_4H_9)_3I$	1953[e]			5.42 d	1.4
$\pi\text{-}C_5H_5Fe(CO)P(OCH_3)_3I$	1981 ms	1968 s[e]		5.28 d	1.0
$\pi\text{-}C_5H_5Fe(CO)P(OC_2H_5)_3I$	1972 ms	1964 s[e]		5.30 s	
$\pi\text{-}C_5H_5Fe(CO)P(OC_6H_5)_3I$	1986[e]			5.80 s	
$[\pi\text{-}C_5H_5Fe(CO)_2P(C_2H_5)_3]B(C_6H_5)_4$	2051 s	2008 s[g]		4.16[h] d	1.6
$[\pi\text{-}C_5H_5Fe(CO)_2P(C_4H_9)_3]B(C_6H_5)_4$	2051 s	2008 s[g]		5.81 d	1.4
$[\pi\text{-}C_5H_5Fe(CO)_2P(OCH_3)_3]B(C_6H_5)_4$	2073 s	2032 s[g]		4.36[i] d	1.1
$[\pi\text{-}C_5H_5Fe(CO)_2P(OC_3H_5)_3]B(C_6H_5)_4$	2071 s	2030 s[g]		4.81[i] d	1.2
$[\pi\text{-}C_5H_5Fe(CO)_2P(OC_6H_5)_3]B(C_6H_5)_4$	2075 s	2034 s[g]		5.99 s	
$[\pi\text{-}C_5H_5Fe(CO)_2P(OC_3H_5)_2(C_6H_5)]B(C_6H_5)_4$	2067 s	2028 s[g]		4.88[i] d	1.3
$[\pi\text{-}C_5H_5Fe(CO)_2P(OC_3H_5)(C_6H_5)_2]B(C_6H_5)_4$	2063 s	2023 s[g]		4.62[i] d	1.2
$\pi\text{-}C_5H_5Fe(CO)_2[P(O)(OCH_3)_2]$	2043 s	1989 s[g]	N.m.	N.m.	
$\pi\text{-}C_5H_5Fe(CO)_2[P(O)(OC_2H_5)_2]$	2045 s	1993 s[e]	1180	4.91 s	
$\pi\text{-}C_5H_5Fe(CO)_2[P(O)(OC_4H_9)_2]$	2039 s	1988 s[g]	N.m.	N.m.	
$\pi\text{-}C_5H_5Fe(CO)_2[P(O)(OC_3H_5)_2]$	2044 s	1994 s[e]	1179	4.90 s	
$\pi\text{-}C_5H_5Fe(CO)_2[P(O)(OC_3H_5)(C_6H_5)]$	2039 s	1986 s[e]	1167	5.09 s	
$\pi\text{-}C_5H_5Fe(CO)_2[P(O)(C_6H_5)_2]$	2031 s	1975 s[e]	1126	5.06 s	
$\pi\text{-}C_5H_5Fe(CO)[P(OCH_3)_3][P(O)(OCH_3)_2]$	1964[g]		N.m.	N.m.	
$\pi\text{-}C_5H_5Fe(CO)[P(OC_2H_5)_3][P(O)(OC_2H_5)_2]$	1966[e]		N.m.	N.m.	
$\pi\text{-}C_5H_5Fe(CO)[P(OC_4H_9)_3][P(O)(OC_4H_9)_2]$	*ca.* 1961[g]		N.m.	N.m.	
$\pi\text{-}C_5H_5Fe(CO)[P(OC_3H_5)_3][P(O)(OC_3H_5)_2]$	1970[e]		1159	4.95 t	0.8
$\pi\text{-}C_5H_5Fe(CO)[P(OC_3H_5)_2(C_6H_5)][P(O)(OC_3H_5)(C_6H_5)]$	1961[e]		1140	5.62 t	1.2
$\pi\text{-}C_5H_5Fe(CO)[P(OC_3H_5)(C_6H_5)_2][P(O)(C_6H_5)_2]$	1933[e]		1116	5.53 s	

---

[a] Abbreviations: s, strong; ms, medium strong; N.m., not measured. [b] Measured in CS_2. [c] τ scale (TMS reference). [d] Abbreviations: s, singlet; d, doublet; t, triplet; N.m. not measured. [e] Measured in C_6H_{12}. [f] Measured in $CDCl_3$ at 38°. [g] Measured in CH_2Cl_2. [h] Measured as $[\pi\text{-}C_5H_5Fe(CO)_2P(C_2H_5)_3]I$ in CD_3COCD_3 at 38°. [i] Measured in CD_3COCD_3 at 38°.

in the region 1100–1200 cm^{-1} are assigned to P–O stretching modes on the basis of a comparison with the spectra of the corresponding derivatives $\pi\text{-}C_5H_5Fe(CO)$(Ligand)Cl and $\pi\text{-}C_5H_5Mo(CO)_2$ (Ligand)L′ (refs. 1 and 13). The frequencies of these modes are observed to decrease along the series $\pi\text{-}C_5H_5Fe(CO)_2[P(O)(OR)_2]$ ($R = C_2H_5$ and C_3H_5) $> \pi\text{-}C_5H_5Fe(CO)_2[P(O)(OC_3H_5)(C_6H_5)] > \pi\text{-}C_5H_5Fe(CO)_2[P(O)(C_6H_5)_2]$ and $\pi\text{-}C_5H_5Fe(CO)[P(OC_3H_5)_3][P(O)(OC_3H_5)_2] > \pi\text{-}C_5H_5Fe(CO)[P(OC_3H_5)_2(C_6H_5)][P(O)(OC_3H_5)(C_6H_5)] > \pi\text{-}C_5H_5Fe(CO)[P(OC_3H_5)(C_6H_5)_2][P(O)(C_6H_5)_2]$ and to parallel a corresponding decrease in the C–O stretching frequencies. It is proposed that this decrease is as a result of the replacement of an allyloxy by a less electronegative phenyl group effecting an increase in the electron density on the phosphorus atom which is then redistributed into the P–O anti-bonding orbitals. An alternative possibility that the decrease is due to a mass

(*continued on p.* 412)

TABLE 3

PREPARATIVE DETAILS

Reactants (quantities)	Reaction solvent	Reaction temp. (°C)	Reaction time	Reaction products isolated	Crystallised from	Yield[a] (%)
π-$C_5H_5Fe(CO)_2I$ (0.5 g, 1.6 mmole) $P(C_2H_5)_3$ (0.29 g, 2.4 mmole)	Benzene	80	30 min	$[\pi$-$C_5H_5Fe(CO)_2P(C_2H_5)_3]I$ π-$C_5H_5Fe(CO)P(C_2H_5)_3I$	Not crystallised Petroleum ether	55 30
π-$C_5H_5Fe(CO)_2I$ (0.5 g, 1.6 mmole) $P(C_4H_9)_3$ (0.35 g, 1.9 mmole)	Benzene	80	10 h	π-$C_5H_5Fe(CO)P(C_4H_9)_3I$	Petroleum ether	>85
π-$C_5H_5Fe(CO)_2I$ (0.5 g, 1.6 mmole) $P(OCH_3)_3$ (0.3 g, 2.4 mmole)	Benzene	80	24 h	π-$C_5H_5Fe(CO)P(OCH_3)_3I$	Petroleum ether	70
π-$C_5H_5Fe(CO)_2I$ (0.5 g, 1.6 mmole) $P(OC_2H_5)_3$ (0.4 g, 2.4 mmole)	Benzene	80	16 h	π-$C_5H_5Fe(CO)P(OC_2H_5)_3I$	Petroleum ether	70
π-$C_5H_5Fe(CO)_2I$ (0.5 g, 1.6 mmole) $P(OC_6H_5)_3$ (0.75 g, 2.4 mmole)	Benzene	80	16 h	π-$C_5H_5Fe(CO)P(OC_6H_5)_3I$	Benzene/Pet. ether	>85
π-$C_5H_5Fe(CO)_2Cl$ (0.5 g, 2.4 mmole) $P(C_2H_5)_3$ (0.44 g, 3.6 mmole)	Benzene	25	15 h	$[\pi$-$C_5H_5Fe(CO)_2P(C_2H_5)_3]Cl^c$	Acetone/Pet. ether[d]	>90
π-$C_5H_5Fe(CO)_2Cl$ (0.5 g, 2.4 mmole) $P(C_4H_9)_3$ (0.58 g, 2.8 mmole)	Benzene	25	4 days	$[\pi$-$C_5H_5Fe(CO)_2P(C_4H_9)_3]Cl^c$ π-$C_5H_5Fe(CO)P(C_4H_9)_3Cl^b$	Acetone/Pet. ether[d] Not crystallised	65 N.m.
π-$C_5H_5Fe(CO)_2Cl$ (1.0 g, 4.7 mmole) $P(OCH_3)_3$ (1.2 g, 9.7 mmole)	Benzene	25	16 h	π-$C_5H_5Fe(CO)P(OCH_3)_3Cl$ π-$C_5H_5Fe(CO)_2[P(O)(OCH_3)_2]^b$ π-$C_5H_5Fe(CO)[P(OCH_3)_3][P(O)(OCH_3)_2]^b$	Benzene/Pet. ether Not separated	30 N.m.
π-$C_5H_5Fe(CO)_2Cl$ (1.0 g, 4.7 mmole) $P(OC_2H_5)_3$ (0.94 g, 5.6 mmole)	Benzene	25	4 days	π-$C_5H_5Fe(CO)P(OC_2H_5)_3Cl^b$ π-$C_5H_5Fe(CO)_2[P(O)(OC_2H_5)_2]$ π-$C_5H_5Fe(CO)[P(OC_2H_5)_3][P(O)(OC_2H_5)_2]^b$	Not crystallised Benzene/Pet. ether Oil	N.m. 40 N.m.
π-$C_5H_5Fe(CO)_2Cl$ (1.0 g, 4.7 mmole) $P(OC_3H_5)_3$ (1.58 g, 7.8 mmole)	Benzene	25	90 min	π-$C_5H_5Fe(CO)P(OC_3H_5)_3Cl^b$ π-$C_5H_5Fe(CO)_2[P(O)(OC_3H_5)_2]$ π-$C_5H_5Fe(CO)[P(OC_3H_5)_3][P(O)(OC_3H_5)_2]$	Not crystallised Oil Oil	20 35 20
π-$C_5H_5Fe(CO)_2Cl$ (0.5 g, 2.4 mmole) $P(OC_6H_5)_3$ (1.1 g, 3.6 mmole)	Benzene	25	4 days	$[\pi$-$C_5H_5Fe(CO)_2P(OC_6H_5)_3]Cl^c$ π-$C_5H_5Fe(CO)P(OC_6H_5)_3Cl$	Acetone/Pet. ether[d] Benzene/Pet. ether	7 55

π-$C_5H_5Fe(CO)_2Cl$ (1.0 g, 4.7 mmole) $P(OC_3H_5)_2(C_6H_5)$ (2.0 g, 9.0 mmole)	Benzene	25	1 h	π-$C_5H_5Fe(CO)P(OC_3H_5)_2(C_6H_5)Cl$[b]	Not crystallised	20
				π-$C_5H_5Fe(CO)_2[P(O)(OC_3H_5)(C_6H_5)]$	Oil	35
				π-$C_5H_5Fe(CO)[P(OC_3H_5)_2(C_6H_5)][P(O)(OC_3H_5)(C_6H_5)]$	Oil	25
π-$C_5H_5Fe(CO)_2Cl$ (1.0 g, 4.7 mmole) $P(OC_3H_5)(C_6H_5)_2$ (2.3 g, 9.4 mmole)	Benzene	80	3 h	π-$C_5H_5Fe(CO)P(OC_3H_5)(C_6H_5)_2Cl$[b]	Not crystallised	20
				π-$C_5H_5Fe(CO)_2[P(O)(C_6H_5)_2]$	Benzene/Pet. ether	45
				π-$C_5H_5Fe(CO)[P(OC_3H_5)(C_6H_5)_2][P(O)(C_6H_5)_2]$	Benzene/Pet. ether	15
π-$C_5H_5Fe(CO)_2Cl$ (0.5 g, 2.4 mmole) $P(OCH_3)_3$ (0.35 g, 2.8 mmole) $NaB(C_6H_5)_4$ (1.7 g, 5.0 mmole)	Benzene + methanol	25	5 h	$[\pi\text{-}C_5H_5Fe(CO)_2P(OCH_3)_3]B(C_6H_5)_4$	Acetone/Pet. ether	50
π-$C_5H_5Fe(CO)_2Cl$ (0.5 g, 2.4 mmole) $P(OC_3H_5)_3$ (0.55 g, 2.7 mmole) $NaB(C_6H_5)_4$ (1.7 g, 5.0 mmole)	Benzene + methanol	25	15 h	$[\pi\text{-}C_5H_5Fe(CO)_2P(OC_3H_5)_3]B(C_6H_5)_4$	Acetone/Pet. ether	50
π-$C_5H_5Fe(CO)_2Cl$ (0.5 g, 2.4 mmole) $P(OC_3H_5)_2(C_6H_5)$ (0.63 g, 2.8 mmole) $NaB(C_6H_5)_4$ (1.7 g, 5.0 mmole)	Benzene + methanol	25	3 h	$[\pi\text{-}C_5H_5Fe(CO)_2P(OC_3H_5)_2(C_6H_5)]B(C_6H_5)_4$	Acetone/Pet. ether	60
π-$C_5H_5Fe(CO)_2Cl$ (0.5 g, 2.4 mmole) $P(OC_3H_5)(C_6H_5)_2$ (0.68 g, 2.8 mmole)	Benzene	25	30 min	$[\pi\text{-}C_5H_5Fe(CO)_2P(OC_3H_5)(C_6H_5)_2]Cl$[c]	Acetone/Pet. ether[d]	50

[a] Abbreviation: N.m., not measured. [b] Identified by means of infrared. [c] Characterised as tetraphenylborate. [d] Solvents apply to tetraphenylboron derivative.

effect was eliminated on the basis of the observation that the P–O stretching frequencies for the series of compounds π-$C_5H_5Mo(CO)_2[P(OR)_3][P(O)(OR)_2]$ ($R=CH_3$, C_2H_5, i-C_3H_7 and n-C_4H_9) all occur at *ca.* 1165 cm^{-1} (ref. 13). A similar explanation to that described above may be invoked to account for the decrease in the P–O stretching frequencies from the unsubstituted to the substituted products, *e.g.* from π-$C_5H_5Fe(CO)_2[P(O)(OC_3H_5)_2]$ to π-$C_5H_5Fe(CO)[P(OC_3H_5)_3][P(O)(OC_3H_5)_2]$. The infrared spectra of the compounds of the type π-$C_5H_5Fe(CO)P(OR)_3X$ ($X=Cl$ or I, R = alkyl), measured in cyclohexane, contain two C–O stretching bands. This feature is consistent with the presence of two conformers in solution as recently reported by Brown *et al.*[12].

The chemical shifts of the cyclopentadienyl proton resonances observed in the NMR spectra of a number of compounds discussed above are recorded in Table 2. In general coupling between the cyclopentadienyl protons and the phosphorus nuclei was observed and was of the order 1 Hz. The apparent absence of coupling in a few cases can be related to the broadness of the peaks. The resonances in the spectra of π-$C_5H_5Fe(CO)[P(OC_3H_5)_3][P(O)(OC_3H_5)_2]$ and π-$C_5H_5Fe(CO)[P(OC_3H_5)_2(C_6H_5)][P(O)(OC_3H_5)(C_6H_5)]$ occur as triplets whereas those in the spectra of π-$C_5H_5Mo(CO)_2[P(OR)_3][P(O)(OR)_2]$ ($R=CH_3$, C_2H_5, i-C_3H_7 and n-C_4H_9) occur as 1/1/1/1 quartets[13]. It is thus apparent that for the former derivatives the two phosphorus nuclei of the non-equivalent ligands effect approximately equal coupling with the cyclopentadienyl protons.

Based on the results presented above the mechanism outlined below is proposed for the formation of π-$C_5H_5Fe(CO)_2[P(O)(OR)_2]$ and related compounds from π-$C_5H_5Fe(CO)_2Cl$ and $P(OR)_3$, $P(OR)_2R'$ or $P(OR)R'_2$,

$$\pi\text{-}C_5H_5Fe(CO)_2Cl + P(OR)_3 \rightarrow [\pi\text{-}C_5H_5Fe(CO)_2P(OR)_3]Cl \xrightarrow{Cl^-} \pi\text{-}C_5H_5Fe(CO)_2[P(O)(OR)_2] + RCl$$

This mechanism is similar to that proposed for the formation of π-$C_5H_5Mo(CO)_2[P(OR)_3][P(O)(OR)_2]$ from $[\pi$-$C_5H_5Mo(CO)_3]_2$ and $P(OR)_3$ (refs. 1 and 13) and is analogous to the mechanism for the Michaelis–Arbuzov rearrangement involving tertiary phosphites and alkyl halides[14]. Consistent with the proposed mechanism is the observation that the nucleophilic attack of $[\pi$-$C_5H_5Mo(CO)_3]^-$ on $[\pi$-$C_5H_5Fe(CO)_2P(OCH_3)_3]^+$ yielded π-$C_5H_5Fe(CO)_2[P(O)(OCH_3)_2]$ and π-$C_5H_5Mo(CO)_3CH_3$ albeit in low yield. The major products in the latter reaction were $[\pi$-$C_5H_5Mo(CO)_3]_2$ and $[\pi$-$C_5H_5Fe(CO)_2]_2$ resulting from the cleavage of the Fe–P bond. No reaction was observed between π-$C_5H_5Fe(CO)_2[P(O)(OCH_3)_2]$ and excess $P(OCH_3)_3$ in benzene under reflux over a period of two days. This suggests that π-$C_5H_5Fe(CO)[P(OR)_3][P(O)(OR)_2]$ is formed through $\{\pi$-$C_5H_5Fe(CO)[P(OR)_3]_2\}Cl$ as intermediate.

The results of this study together with those previously reported on the reactions of $[\pi$-$C_5H_5Mo(CO)_3]_2$ with tertiary phosphites, phosphonites and phosphinites[1,13] suggest that the formation of phosphonate and related type products through intermediates of the type $\{M[P(OR)_3]_x\,(\text{Ligand})_y\}$Anion (M = metal, R = alkyl) may well occur for numerous other systems.

EXPERIMENTAL

The ligands $P(OC_3H_5)_3$, $P(OC_3H_5)_2(C_6H_5)$ and $P(OC_3H_5)(C_6H_5)_2$ were synthesised by addition of three moles, two moles and one mole of allyl alcohol to one mole of PCl_3, $P(C_6H_5)Cl_2$ and $P(C_6H_5)_2Cl$ in hexane in the presence of pyridine, respectively. π-$C_5H_5Fe(CO)_2Cl$ and π-$C_5H_5Fe(CO)_2I$ were prepared according to established procedures[15,16]. $[\pi$-$C_5H_5Fe(CO)_2]_2$ and the other ligands employed in this study were obtained commercially. All reactions and operations were performed under a nitrogen atmosphere. The chromatographic separations were effected on an alumina column (50 × 1.5 cm; Merck acid washed alumina, activity III). The infrared and NMR spectra were recorded on a Perkin–Elmer model 21 spectrophotometer and on a Varian A60 respectively. Conductivities were determined using a Metrohm E365B conductoscope. The molecular weights were measured using a Mechrolab vapour pressure osmometer. The elemental analyses (C, H, P, Cl, I and Fe) were obtained by the Alfred Bernhardt Microanalytical Laboratory, Elbach-über-Engelskirchen, West Germany and by Mr. G. J. Roberts, National Chemical Research Laboratory, C.S.I.R., Pretoria.

The experimental details for the synthesis of the derivatives isolated and characterised in this study are summarised in Table 3. Separation of the neutral products from the same reaction was effected by means of column chromatography. In general the order of elution from the column on increasing the polarity of the eluent was π-$C_5H_5Fe(CO)(Ligand)Cl$, followed by π-$C_5H_5Fe(CO)(Ligand)L'$ and finally π-$C_5H_5Fe(CO)_2L'$ (L′ = phosphonate, phosphinate or phosphine oxide ligand). The most convenient synthesis is reported for those derivatives which may be obtained by more than one method.

ACKNOWLEDGEMENTS

The authors express their gratitude to Dr. K. G. R. Pachler, National Chemical Research Laboratory, C.S.I.R., Pretoria for the measurement of the NMR spectra. Two of the authors (A. L. du Preez and I. L. Marais) thank the Industrial Development Corporation, the South African Council for Scientific and Industrial Research and the University of Pretoria for financial support.

REFERENCES

1 R. J. Haines, A. L. du Preez and I. L. Marais, *J. Organometal. Chem.*, 28 (1971) 97.
2 R. J. Haines, A. L. du Preez and I. L. Marais, *J. Organometal. Chem.*, 24 (1970) C26.
3 A. Davison, M. L. H. Green and G. Wilkinson, *J. Chem. Soc.*, (1961) 3172.
4 K. K. Joshi, P. L. Pauson and W. L. Stubbs, *J. Organometal. Chem.*, 1 (1963) 51.
5 R. B. King, *Inorg. Chem.*, 2 (1963) 936.
6 E. O. Fischer and E. Moser, *J. Organometal. Chem.*, 5 (1966) 63.
7 P. M. Treichel, R. L. Shubkin, K. W. Barnett and D. Reichard, *Inorg. Chem.*, 5 (1966) 1177.
8 H. Brunner, H.-D. Schindler, E. Schmidt and M. Vogel, *J. Organometal. Chem.*, 24 (1970) 515.
9 A. L. du Preez, M.Sc. Thesis, University of Pretoria, 1968.
10 D. A. Brown, H. J. Lyons, A. R. Manning and J. M. Rowley, *Inorg. Chim. Acta*, 3 (1969) 346.
11 A. N. Nesmeyanov, Yu. A. Chapovsky and Yu. A. Ustynyuk, *J. Organometal. Chem.*, 9 (1967) 345.
12 D. A. Brown, H. J. Lyons and A. R. Manning, *Inorg. Chim. Acta*, 4 (1970) 428.
13 R. J. Haines and C. R. Nolte, *J. Organometal. Chem.*, 24 (1970) 725.
14 R. G. Harvey and E. R. De Somber, in M. Grayson and E. J. Griffith (Eds.), *Topics in Phosphorus Chemistry*, Vol. 1, Interscience, New York, 1964, p. 57.
15 T. S. Piper, F. A. Cotton and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 1 (1955) 165.
16 T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, 2 (1956) 38.