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REACTIONS OF METAL CARBONYL DERIVATIVES X.* THE SYNTHESIS AND REACTIVITY OF SOME DINUCLEAR DERIVATIVES OF IRON CONTAINING BOTH BRIDGING CARBONYLS AND BRIDGING PHOSPHIDO OR SULPHIDO GROUPS**

R. J. HAINES***
Research and Process Development Department, South African Iron and Steel Industrial Corporation Limited, P.O. Box 450, Pretoria (Republic of South Africa)
C. R. NOLTE
Department of Inorganic and Analytical Chemistry, University of Pretoria, Pretoria (Republic of South Africa)

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SUMMARY

The tertiary phosphine π-$C_5H_5Fe(CO)_2P(C_6H_5)_2$ reacts with a suspension of $Fe_2(CO)_9$ in benzene to give the dinuclear complex π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$. This compound is also obtained by nucleophilic attack of $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ on $Fe(CO)_4$-$[P(C_6H_5)_2Cl]$ in tetrahydrofuran. Irradiation of a benzene solution of π-$C_5H_5Fe_2$-$P(C_6H_5)_2(CO)_6$ with ultraviolet light affords π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ which contains both a bridging carbonyl and a bridging phosphido group. The unstable bridged sulphido derivatives π-$C_5H_5Fe_2SR(CO)_6$ ($R=CH_3$ and C_6H_5) and π-C_5H_5-$Fe_2(t\text{-}C_4H_9S)(CO)_5$ are similarly obtained employing π-$C_5H_5Fe(CO)_2SR$ as ligand. The reactions of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ with tertiary phosphines and phosphites yield three types of products depending on the reaction conditions and the ligand involved. Examples include π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4P(C_6H_5)_3$, a mono-substituted derivative of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$, and π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5P(C_2H_5)_3$ and π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4[P(OCH_3)_3]_2$, mono- and bis-substituted derivatives of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$, respectively. The reaction of π-$C_5H_5Fe_2P(C_6H_5)_2$-$(CO)_5$ with $(C_6H_5)_2PCH_2P(C_6H_5)_2$ in benzene under reflux affords $[\pi\text{-}C_5H_5Fe_2$-$P(C_6H_5)_2(CO)_4](C_6H_5)_2PCH_2P(C_6H_5)_2$ in which the ditertiary phosphine bridges two iron atoms.

INTRODUCTION

Although tertiary phosphines of the type PR′R″R‴ (R′, R″ and R‴ = alkyl or aryl groups) are used extensively as ligands in transition metal chemistry, phosphines of the type $PR^{IV}R^{V}R^{VI}$ in which R^{IV} and R^{V} are alkyl or aryl groups and R^{VI} is an

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* For Part IX see ref. 1.
** A preliminary communication of some of this work has been presented[2].
*** To whom correspondence concerning this publication should be addressed.

organometallic moiety bonded to the phosphorus through a transition metal atom have not been employed in the same role. A few isolated examples in which related sulphur and nitrogen derivatives have been used as donor ligands are known however. For instance it has been established that π-$C_5H_5Ti[N(CH_3)_2]_3$ reacts with $M(CO)_6$ (M=Cr, Mo and W) in cyclohexane on irradiation with ultraviolet light to afford π-$C_5H_5Ti[N(CH_3)_2]_3M(CO)_3$[3]. It has also been observed that treatment of $M(CO)_4$(nor-C_7H_8) and $M(CO)_4(CH_3CN)_2$ (M=Cr, Mo and W) with $(\pi$-$C_5H_5)_2Ti(SR)_2$ (R=CH_3 and C_6H_5) in solution yields the bridged sulphur derivatives $(\pi$-$C_5H_5)_2$-$Ti(SR)_2M(CO)_4$[4-6]. Further $(\pi$-$C_5H_5)_2M(SR)_2$ (M=Mo and W; R=CH_3 and C_6H_5) have been shown to react with a number of transition metal derivatives, *e.g.* $M'(CO)_6$ (M'=Cr, Mo and W) and $(C_8H_{12}RhCl)_2$ to give mixed-metal species, *e.g.* $(\pi$-$C_5H_5)_2M(SC_6H_5)_2M'(CO)_3$ and $[(\pi$-$C_5H_5)_2M(SR)_2RhC_8H_{12}]^+$ (ref. 7). Reactions in which transition metal complexes similar to those discussed above act as "monodentate" ligands have not been reported however.

Transition metal derivatives containing ligands of the type $PR^{IV}R^{V}R^{VI}$ discussed above will have two transition metal atoms in mutually β-positions. A β-effect resulting from a metal–metal interaction is thus possible. As part of a general study of the reactivity of tertiary phosphines of the type $PR^{IV}R^{V}R^{VI}$ towards transition metal complexes and of the influence of metal–metal interactions on the properties of the products so obtained, the reactions of the tertiary phosphine π-$C_5H_5Fe(CO)_2P$-$(C_6H_5)_2$ as well as the sulphides π-$C_5H_5Fe(CO)_2SR$ (R=CH_3, t-C_4H_9 and C_6H_5) with various derivatives have been studied. The results of those involving $Fe_2(CO)_9$ and of the reactions of one of the products isolated from the latter *viz.* π-$C_5H_5Fe_2$-$P(C_6H_5)_2(CO)_5$, with various ligands are reported here.

RESULTS AND DISCUSSION

Treatment of a suspension of $Fe_2(CO)_9$ in benzene at room temperature with $P(C_6H_5)_3$ has been previously shown to afford $Fe(CO)_4P(C_6H_5)_3$[8], a substituted derivative of $Fe(CO)_5$. It is now observed that the ligand π-$C_5H_5Fe(CO)_2P(C_6H_5)_2$, synthesised by addition of $LiP(C_6H_5)_2$ to π-$C_5H_5Fe(CO)_2Cl$, reacts similarly with $Fe_2(CO)_9$ to yield a product characterised as π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$*. This formulation is confirmed by the mass spectrum which exhibits the molecular ion (*m/e* 530 for ^{56}Fe isotope) and peaks corresponding to the stepwise loss of six carbonyl groups. The solution infrared spectrum of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$ in the C–O stretching region is very similar to those of $Fe(CO)_4P(C_6H_5)_3$[10] and $Fe(CO)_4[P$-$(C_6H_5)_2H]$[11] apart from two extra peaks at 2031 (s) and 1991 cm^{-1} (ms) (measured in cyclohexane). The structure represented in Fig. 1 (L'=L''=CO) is thus proposed for this dinuclear derivative; the two abovementioned peaks are assigned to the modes associated with the carbonyls bonded to the same iron atom as the cyclopentadienyl group. The frequencies of these modes are *ca.* 20 cm^{-1} higher than the corresponding bands observed in the spectrum of π-$C_5H_5Fe(CO)_2P(C_6H_5)_2$ [2015 (s) and 1966 cm^{-1}

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* Subsequent to our preliminary communication of the results of this study[2], a publication reporting the synthesis of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$ by reaction of π-$C_5H_5Fe(CO)_2Cl$ with $Fe(CO)_4[P(C_6H_5)_2H]$ in the presence of the base $HN(C_2H_5)_2$, and of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ by irradiation of π-$C_5H_5Fe_2$-$P(C_6H_5)_2(CO)_6$ with ultraviolet light, has appeared[9].

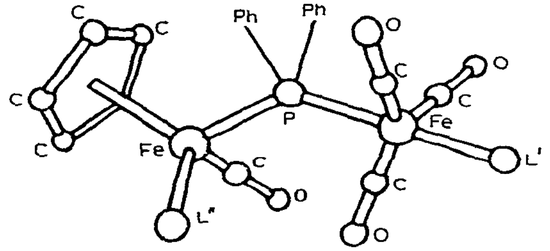

Fig. 1. Proposed structure of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L'L''$ [$L''=CO$, $L'=CO$, $P(C_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$ and $P(OC_6H_5)_3$; $L''=L'=P(C_2H_5)_3$, $P(OCH_3)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$ and $P(OC_6H_5)_3$] showing the stereochemistry of the iron atoms only.

(s), measured in cyclohexane]. This is attributed to a reduction of electron density on the iron adjacent to the cyclopentadienyl group as a result of the bonding of the phosphorus to the iron of the $Fe(CO)_4$ moiety. The NMR spectrum of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$is consistent with the proposed formulation, the ratio of the intensities of the phenyl and cyclopentadienyl proton resonances being 2/1. The latter resonance is broad and thus the expected coupling between the cyclopentadienyl protons and the phosphorus nucleus could not be observed.

Although the most convenient synthesis of π-$C_5H_5Fe(CO)_2P(C_6H_5)_2$ involves the addition of $LiP(C_6H_5)_2$ to π-$C_5H_5Fe(CO)_2Cl$, this compound is also obtained by treating $P(C_6H_5)_2Cl$ with $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ in tetrahydrofuran at 0°. On the basis of the latter reaction, $Fe(CO)_4[P(C_6H_5)_2Cl]$, prepared from $Fe_2(CO)_9$ and $P(C_6H_5)_2Cl$, was reacted with $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ in the above solvent at 0° with a view to synthesising π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$ by an alternative method. The observation that this compound, together with small amounts of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and a product possibly $Fe_2(CO)_8[(C_6H_5)_2PP(C_6H_5)_2]$, is in fact formed in this reaction prompts the suggestion that this type of reaction might be employed as a general method for synthesising mixed metal derivatives.

Irradiation of a benzene solution of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$ with ultraviolet light effects the replacement of a carbonyl group from the parent complex and the formation of a purple product characterised by elemental analysis and mass and NMR spectroscopy as π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$. The mass spectrum contains the parent ion (*m/e* 502) and peaks corresponding to the successive loss of five carbonyl groups. The solid state infrared spectrum of this compound (Table 2) contains both terminal and bridging carbonyl stretching peaks. Based on this infrared evidence and on the known structures of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$[12-14] and $[Fe(CO)_3(SC_2H_5)]_2$[15], the structure represented in Fig. 2A ($L=CO$) is proposed for this derivative in the crystalline state. This structure is analogous to that previously established for π-$C_5H_5Fe_2C_2H_2COCH_3(CO)_5$[16] and similar to that recently suggested for π-$C_5H_5NiFeP(C_6H_5)_2(CO)_4$[17]. The NMR spectrum of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ contains as well as a cyclopentadienyl proton resonance at τ 5.11, a much weaker peak to lower field which is also assigned to the cyclopentadienyl protons*. Both peaks are some-

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* The possibility of the weak peak resulting from impurities in solution was eliminated on the basis that identical NMR spectra to that reported above were obtained for π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ after a number of recrystallisations and that the intensity of this peak did not increase with time.

TABLE 1

COLOURS AND ANALYTICAL AND MOLECULAR WEIGHT DATA

Compound[a,b]	Colour	Analyses, found (calcd.) (%)			Mol.wt.[c,d]
		C	H	P	Found (calcd.)
$CpFe_2PPh_2(CO)_6$	Red	52.2 (52.1)	2.9 (2.9)	5.7 (5.8)	537 (530)
$CpFe_2PPh_2(CO)_5$	Purple	52.9 (52.6)	3.1 (3.0)	6.1 (6.2)	498 (502)
$CpFe_2PPh_2(CO)_4PPh_3$	Olive-green	63.6 (63.7)	4.1 (4.5)	8.4 (8.3)	N.m.
$CpFe_2PPh_2(CO)_4P(OMe)_3$	Green	48.0 (48.2)	4.0 (4.1)	10.3 (10.4)	596 (598)
$CpFe_2PPh_2(CO)_4P(OEt)_3$	Green	50.9 (50.7)	4.7 (4.7)	9.6 (9.7)	N.m.
$CpFe_2PPh_2(CO)_4P(O\text{-}i\text{-}Pr)_3$	Green	52.4 (52.8)	5.5 (5.3)	9.0 (9.1)	653 (682)
$CpFe_2PPh_2(CO)_5PEt_3$	Red	54.1 (54.2)	4.8 (4.9)	9.9 (10.0)	624 (620)
$CpFe_2PPh_2(CO)_5P(O\text{-}i\text{-}Pr)_3$	Red	53.0 (52.8)	5.2 (5.3)	9.0 (9.1)	684 (682)
$CpFe_2PPh_2(CO)_5P(OPh)_3$	Red	59.3 (59.1)	3.9 (3.7)	7.5 (7.6)	N.m.
$CpFe_2PPh_2(CO)_4(PEt_3)_2$	Red	56.0 (55.8)	6.5 (6.4)	13.2 (13.1)	N.m.
$CpFe_2PPh_2(CO)_4[P(OMe)_3]_2$	Red	44.4 (44.1)	4.7 (4.8)	12.9 (13.4)	733 (694)
$CpFe_2PPh_2(CO)_4[P(O\text{-}i\text{-}Pr)_3]_2$	Red	52.3 (52.6)	7.0 (6.5)	10.2 (10.4)	886 (891)
$CpFe_2PPh_2(CO)_4[P(OPh)_3]_2$	Red	62.3 (62.6)	4.1 (4.1)	8.6 (8.5)	1081 (1095)
$[CpFe_2PPh_2(CO)_4]Ph_2PCH_2PPh_2$	Red	64.1 (64.4)	4.3 (4.4)	10.6 (10.8)	I.s.

[a] All compounds are diamagnetic and gave, in general, poorly defined melting points. [b] Abbreviations: Me, CH_3; Et, C_2H_5; i-Pr, iso-C_3H_7; t-Bu, tert-C_4H_9; Ph, C_6H_5; Cp, π-C_5H_5. [c] Abbreviations: N.m., not measured; I.s., insufficiently soluble. [d] Measured in benzene.

what broad and as a result the ratio of their intensities could not be accurately ascertained and coupling between the cyclopentadienyl protons and the adjacent phosphorus nucleus could not be observed. The presence of two cyclopentadienyl resonances in the spectrum is interpreted in terms of more than one isomer being present in solution. A bridging carbonyl stretching mode is observed in the solution infrared spectrum of this derivative consistent with the structure shown in Fig. 2A (L=CO) for the major isomer. A possible structure for the second isomer is that represented in Fig. 2B (L=CO). This structure is analogous to that recently found for $[PdClP(C_6H_5)_2Fe(CO)_4]_2$[18] and proposed for $Co(CO)_3P(C_6H_5)_2Fe(CO)_4$[19]. Significantly an equilibrium between carbonyl-bridged and non-carbonyl-bridged isomers of the type proposed above has been established for $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ and related derivatives in solution[20-23]. Consistent with the above proposal that the second iso-

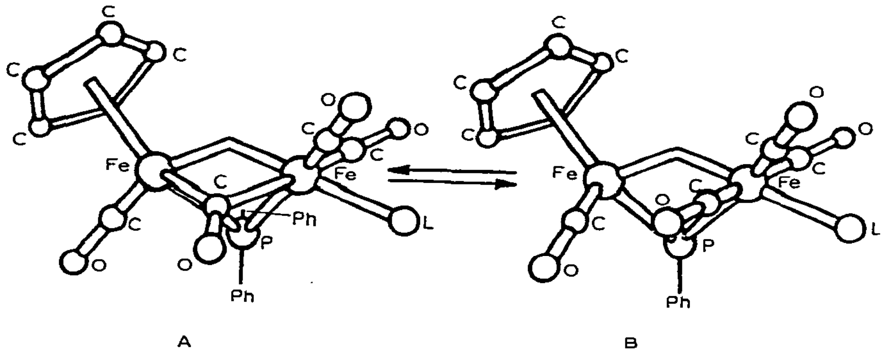


Fig. 2. Proposed structures of the isomers of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$ [L=CO, $P(C_2H_5)_3$, $P(C_6H_3)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$ and $P(OC_6H_5)_3$] existing in solution showing the stereochemistry of the iron atoms only.

mer contains terminal carbonyls only is the observation that the intensity of the bridging carbonyl stretching peak in the solution infrared spectrum of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ is considerably weaker than that of the corresponding band in the solid state spectrum of this derivative.

Similar to that found for π-$C_5H_5Fe(CO)_2P(C_6H_5)_2$, the sulphur ligands π-$C_5H_5Fe(CO)_2SR$ (R=CH_3 and C_6H_5) were observed to react with a suspension of $Fe_2(CO)_9$ in benzene to afford products identified as π-$C_5H_5Fe_2SR(CO)_6$ by means of infrared spectroscopy. These compounds could not be separated from other products owing to their instability in solution and were consequently not fully characterised. Carbonyl replacement was also effected from π-$C_5H_5Fe_2SR(CO)_6$ (R=CH_3 and C_6H_5) on irradiation with ultraviolet light but the expected products π-$C_5H_5Fe_2SR(CO)_5$ could not be detected in the reaction mixtures. [π-$C_5H_5Fe(CO)_2$]$_2$ and [$Fe(CO)_3SR$]$_2$ were found to be formed and it is thus apparent that rearrangement of π-$C_5H_5Fe_2SR(CO)_5$ in solution occurs. Significantly treatment of a suspension of $Fe_2(CO)_9$ in benzene at room temperature with π-$C_5H_5Fe(CO)_2(t\text{-}C_4H_9S)$ led directly to the formation of π-$C_5H_5Fe_2(t\text{-}C_4H_9S)(CO)_5$. This compound was separated from [π-$C_5H_5Fe(CO)_2$]$_2$ and [$Fe(CO)_3(t\text{-}C_4H_9S)$]$_2$, also formed in the reaction, by means of column chromatography and was isolated as an impure green microcrystalline material. The derivative is extremely reactive, decomposing rapidly in solution, and as a consequence was identified by means of infrared spectroscopy only.

The photochemical reactions of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ with excess of the ligands L=$P(C_6H_5)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$ and $P(O\text{-}i\text{-}C_3H_7)_3$ have been studied and shown to afford products characterised as π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$. The compounds π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$ [L=$P(C_2H_5)_3$ and $P(OC_6H_5)_3$] were obtained similarly but owing to their instability were identified by means of infrared only. Bridging carbonyl stretching bands are observed in the solution and solid state infrared spectra of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$ [L=$P(C_2H_5)_3$, $P(C_6H_5)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$ and $P(OC_6H_5)_3$] and it is thus apparent that these compounds are substituted derivatives of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$. No C–O stretching peaks with energy higher than 2000 cm^{-1} are found in the spectra of *cis*- and *trans*-[π-$C_5H_5Fe(CO)P(C_6H_5)_2$]$_2$[24] and *cis*- and *trans*-[π-$C_5H_5Fe(CO)_2$]$_2$[14,22]. On this basis the peak at 2035 cm^{-1} in the spectrum of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ is assigned

TABLE 2

INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC DATA

Compound	C–O stretching frequencies[a] (cm^{-1})	Proton resonances[b,c]	
		C_5H_5	CH_3
$CpFe_2PPh_2(CO)_6$	2045 m, 2031 s, 1991 ms, 1963 ms, 1930 s, 1912 s[d]	4.98 b	
$CpFe_2SMe(CO)_6$	2048 m, 2028 s, 1991 m, 1947 m, 1918 s (b)[e]	N.m.	
$CpFe_2SPh(CO)_6$	2050 m, 2029 s, 1992 m, 1952 m, 1920 s (b)[e]	N.m.	
$CpFe_2PPh_2(CO)_5$	2024 m, 1975 ms, 1938 s, 1758 ms[f] 2035 ms, 1980 s, 1970 ms (sh), 1956 ms, 1797 m[d]	4.19 ; 5.07	
$CpFe_2(t\text{-}BuS)(CO)_5$	2034 ms, 1967 s (b), 1770 w[e]	N.m.	
$CpFe_2PPh_2(CO)_4PEt_3$	1989 m, 1930 s, 1893 ms, 1775 w[d]	N.m.	
$CpFe_2PPh_2(CO)_4PPh_3$	1962 vw, 1938 s, 1932 s (sh), 1890 s, 1772 w (b)[f] 2004 w, 1970 w, 1948 s, 1905 s, 1776 vw[d]	5.00 ; 5.88	
$CpFe_2PPh_2(CO)_4P(OMe)_3$	1977 w, 1944 s, 1910 s, 1749 m[f] 2014 vw, 1980 vw, 1958 s, 1917 ms, 1782 w[d]	4.94 ; 5.33	6.17 q (J_1 11.8; J_2 1 Hz); 6.26 d (J 12.2 Hz)
$CpFe_2PPh_2(CO)_4P(OEt)_3$	1970 w, 1937 s, 1903 s, 1755 m[f] 2013 vw, 1976 vw, 1958 s, 1915 ms, 1779 w[d]	4.99 ; 5.34	8.63 t [J(HH) 7.3 Hz]
$CpFe_2PPh_2(CO)_4P(O\text{-}i\text{-}Pr)_3$	1968 w, 1941 s, 1901 s, 1762 m[f] 2012 vw, 1975 vw, 1955 s, 1913 ms, 1778 w[d]	5.36[g]	8.63 d [J(HH) 6 Hz]
$CpFe_2PPh_2(CO)_4P(OPh)_3$	2016 w, 1982 w, 1960 s, 1921 ms, 1778 w[d]	N.m.	
$CpFe_2PPh_2(CO)_4Ph_2PCH_2PPh_2$	2015 w, 1945 s, 1900 m, 1770 w[e]	N.m.	
$CpFe_2PPh_2(CO)_5PEt_3$	2032 ms, 1983 ms, 1949 vw, 1872 s, 1855 s[d]	4.95 d (J 1.5 Hz)	8.68 t[J(HH) 6 Hz]; 8.95 t[J(HH) 7 Hz]
$CpFe_2PPh_2(CO)_5P(O\text{-}i\text{-}Pr)_3$	2030 ms, 1980 ms, 1963 vw, 1879 s, 1865 s (sh)[d]	5.01 d (J 1.5 Hz)	8.72 d [J(HH) 6 Hz]
$CpFe_2PPh_2(CO)_5P(OPh)_3$	2033 ms, 1983 ms, 1897 s, 1878 s[d]	N.m.	N.m.
$CpFe_2PPh_2(CO)_4(PEt_3)_2$	1951 m, 1930 ms, 1859 s, 1839 s[d]	5.19 t (J 1.9 Hz)[h]	9.2 mt[h]
$CpFe_2PPh_2(CO)_4[P(OMe)_3]_2$	1972 m, 1953 ms, 1878 s, 1867 s (sh)[i]	5.12 b	6.28 d [J(PH) 12.6 Hz]; 6.58 d [J(PH) 10.8 Hz]
$CpFe_2PPh_2(CO)_4[P(O\text{-}i\text{-}Pr)_3]_2$	1963 m, 1944 ms, 1869 s, 1857 s (sh)[d]	5.42 b[h]	8.63 d [J(HH) 6 Hz]; 9.12 d [J(HH) 6.2 Hz][i]
$CpFe_2PPh_2(CO)_4[P(OPh)_3]_2$	1980m, 1960 ms, 1892 s, 1873 s[d]	5.49 b	
$[CpFe_2PPh_2(CO)_4]Ph_2PCH_2PPh_2$	1971 s, 1950 ms (sh), 1891 ms, 1869 ms[e]	I.s.	

[a] Abbreviations: s, strong; ms, medium strong; m, medium; w, weak; vw, very weak; (sh), shoulder; (b), broad. [b] τ scale measured in $CDCl_3$ at 38° (TMS reference). [c] Abbreviations: d, doublet; t, triplet; q, quadruplet; mt, multiplet; b, broad; N.m., not measured; I.s., insufficiently soluble. [d] Measured in cyclohexane. [e] Measured in CH_2Cl_2. [f] Measured as nujol mull. [g] If a weak C_5H_5 resonance is present it is obscured by the $-OC(H)<$ resonance. [h] Measured in C_6D_6. [i] Measured in CCl_4.

to carbonyl groups associated with the $Fe(CO)_3$ moiety; the peak associated with the carbonyl bonded to the same iron atom as the cyclopentadienyl group is assigned to that at 1980 cm^{-1} based on the infrared spectrum of π-$C_5H_5NiFeP(C_6H_5)_2(CO)_4$ [ν(C–O) 2035 (s), 1990 (s), 1978 (s) and 1840 cm^{-1} (s), measured in hexane][17]. Substitution of a carbonyl in the $Fe(CO)_3$ moiety of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ by a tertiary phosphine or phosphite is expected to decrease the frequencies of the stretching modes associated with the remaining carbonyls of this group considerably [*cf.* π-$C_5H_5Mn(CO)_3$: ν(C–O) 2028 (s) and 1946 cm^{-1} (s), measured in cyclohexane[25] and π-$C_5H_5Mn(CO)_2P(C_6H_5)_3$: ν(C–O) 1940 (s) and 1864 cm^{-1} (s), measured in carbon disulphide[26]]. The corresponding decrease on replacement of the carbonyl bonded to the iron atom adjacent to the cyclopentadienyl group by the above ligands is expected to be much less however. The presence of the highest energy band in the region 1960–1980 cm^{-1} in the solid state infrared spectra of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$ [$L=P(C_6H_5)_3$, $P(OCH_3)_3$, $P(OC_2H_5)$ and $P(O\text{-}i\text{-}C_3H_7)_3$] is thus interpreted in terms of substitution of a carbonyl in the $Fe(CO)_3$ moiety (Fig. 2A) [$L=P(C_6H_5)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$ or $P(O\text{-}i\text{-}C_3H_7)_3$]. The Mössbauer spectra of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$ [$L=P(OCH_3)_3$ and $P(C_6H_5)_3$] are also consistent with this structure in the solid state[27]. The solution infrared spectra of the compounds π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$ [$L=P(C_2H_5)_3$, $P(C_6H_5)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$ and $P(OC_6H_5)_3$] contain five peaks in the terminal carbonyl stretching region. This is explained in terms of more than one isomer being present in solution. The presence of a peak in the region 1990–2020 cm^{-1} in these spectra is not inconsistent with the structure suggested for the second isomer (Fig. 2B) and the isomeric equilibrium represented in Fig. 2. This equilibrium is analogous to that proposed above for π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$. The NMR spectra of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$ [$L=P(C_6H_5)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$ and $P(O\text{-}i\text{-}C_3H_7)_3$] are summarised in Table 2. Two cyclopentadienyl proton resonances are observed in each of these spectra while two methyl resonances are also found in the spectrum of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4P(OCH_3)_3$. This is consistent with the above proposal that these derivatives exist in more than one isomeric form in solution. Based on the relative intensities of the cyclopentadienyl peaks the second isomer (Fig. 2B, L = tertiary phosphine or phosphite) is present in very small amount however. Interestingly the strong methyl resonance in the spectrum of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4P(OCH_3)_3$ is split into a 1/1/1/1 quartet as a result of coupling of the methyl protons with both phosphorus nuclei.

The products π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5L$ and π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L_2$ as well as π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$ were found to be formed on reaction of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ with tertiary phosphines and phosphites L in benzene under reflux. The relative yields of the three depended on the ligand L and the parent to ligand molar ratio. For instance the reaction of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ with an equimolar amount of $P(OCH_3)_3$ under the above reaction conditions yielded primarily π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4P(OCH_3)_3$ whereas a similar reaction involving a four-fold excess of the ligand gave π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4[P(OCH_3)_3]_2$. Further while the reaction of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ with the latter amount of $P(C_2H_5)_3$ afforded mainly π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5P(C_2H_5)_3$, the corresponding reaction involving $P(C_6H_5)_3$ yielded π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4P(C_6H_5)_3$.

The infrared spectra of the mono-substituted derivatives π-$C_5H_5Fe_2P(C_6H_5)_2$-

$(CO)_5L$ [L$=P(C_2H_5)_3$, $P(O\text{-i-}C_3H_7)_3$ and $P(OC_6H_5)_3$] contain C–O stretching peaks corresponding to terminal carbonyls only (Table 2), suggesting that these compounds are substituted derivatives of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$. Compounds of the type $Fe(CO)_3LL'$, in which the two axial carbonyls of $Fe(CO)_5$ have been replaced by the ligands L and L', belong to the molecular point group D_{3h} for $L=L'$. One infrared-active C–O stretching mode (E_u) is predicted for this symmetry. Thus the presence of a single C–O stretching peak at 1886 cm^{-1} in the spectrum of $Fe(CO)_3[P(C_6H_5)_3]_2$, measured in carbon disulphide[28], is consistent with *trans* disposition of the phosphine ligands in this derivative. The molecular symmetry of $Fe(CO)_3LL'$ is lowered from D_{3h} to C_{3v} for $L\neq L'$, for which two infrared-active C–O stretching modes (A_1+E) are predicted. However, for those derivatives in which L is only slightly dissimilar to L', the intensity of the A_1 mode is expected to be very weak. The infrared data for π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5L$ [L$=P(C_2H_5)_3$, $P(O\text{-i-}C_3H_7)_3$ and $P(OC_6H_5)_3$] are thus readily explained in terms of a structure of the type $Fe(CO)_3LL'$ and in which a carbonyl *trans* to the $P(C_6H_5)_2$ group in π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$ has been replaced by the ligand L [Fig. 1; $L'=P(C_2H_5)_3$, $P(O\text{-i-}C_3H_7)_3$ or $P(OC_6H_5)_3$; $L''=CO$]. The weak peak observed in the region 1950–1975 cm^{-1} is assigned to the A mode and the strong band between 1850 and 1900 cm^{-1} to the E mode. The splitting of the latter is attributed to a slight deviation of the P–Fe–P' grouping from linearity. The remaining peaks at *ca.* 2030 and 1980 cm^{-1} in the spectra of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5L$ [L$=P(C_2H_5)_3$, $P(O\text{-i-}C_3H_7)_3$ and $P(OC_6H_5)_3$] are assigned to the carbonyls bonded to the same iron atom as the cyclopentadienyl group.

The NMR spectrum of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5P(C_2H_5)_3$ contains two triplets of comparable intensity assigned to the ligand methyl protons suggesting that this derivative is present in two isomeric forms in solution. In contrast a single methyl doublet is found in the spectrum of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5P(O\text{-i-}C_3H_7)_3$, consistent with this compound occurring as either a single isomer or as two or more isomers in dynamic equilibrium in solution. The band patterns in the C–O stretching region in the infrared spectra of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5P(C_2H_5)_3$ and π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5P(O\text{-i-}C_3H_7)_3$ are very similar and it is thus proposed that the above isomerism results from restricted rotation about the "cyclopentadienyl" iron-bridging phosphorus bond.

Compounds of the type π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5L$ are readily converted to π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$ on irradiation with ultraviolet light which is interpreted as demonstrating that the ligands L are bonded to equivalent iron atoms in both types of compounds. The proposed structures for π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5L$ and π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$ (L$=$tertiary phosphine or phosphite) are thus internally consistent.

The frequencies of the C–O stretching modes observed in the infrared spectra of the bis-substituted derivatives π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L_2$ [L$=P(C_2H_5)_3$, $P(OCH_3)_3$, $P(O\text{-i-}C_3H_7)_3$ and $P(OC_6H_5)_3$] are recorded in Table 2. On the basis of the assignments of the peaks at 2045 and 2031 cm^{-1} in the spectrum of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$ and on the arguments employed in the structural assignments of the compounds of the type π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$ and π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5L$ (L$=$tertiary phosphine or phosphite), these data are readily explained in terms of a structure in which the ligands L are bonded to both iron atoms. Although a unique structure for these bis-substituted compounds cannot be established from this infrared evidence, it is suggested that similar to that proposed for the mono-substituted derivatives π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5L$ discussed above, a carbonyl *trans* to the $P(C_6H_5)_2$ group is replaced by one of the ligands [Fig. 1; $L'=L''=P(C_2H_5)_3$, $P(OCH_3)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$ or $P(OC_6H_5)_3$]. The methyl resonances in the NMR spectrum of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4[P(C_2H_5)_3]_2$ occur as complex multiplets indicative of this derivative existing in more than one isomeric form in solution. Significantly displacement of a tertiary phosphine or phosphite L and not a carbonyl group is effected on irradiation of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L_2$ with ultraviolet light.

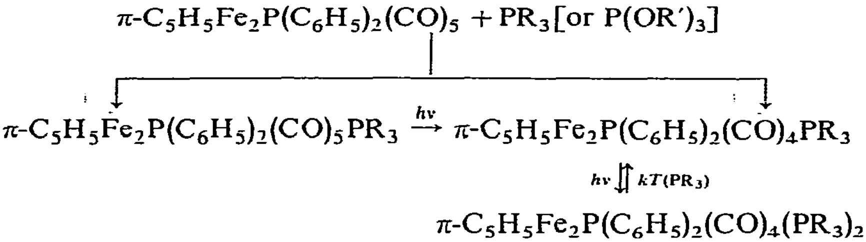
The reaction of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ with an equimolar amount of the ditertiary phosphine $(C_6H_5)_2PCH_2P(C_6H_5)_2$ in benzene under reflux afforded as product a compound characterised as $[\pi$-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4](C_6H_5)_2PCH_2P(C_6H_5)_2$. The frequencies of the C–O stretching peaks observed in the infrared spectrum of this derivative are very similar to those of the corresponding modes in the spectra of the compounds of the type π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L_2$. A structure analogous to that proposed for the latter derivatives but in which the diphosphine ligand bridges the two iron atoms, is suggested.

Irradiation of a benzene solution of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ and an equimolar amount of $(C_6H_5)_2PCH_2P(C_6H_5)_2$ led to the formation of a product shown by means of infrared to be of the type π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$ (Fig. 2A). This compound rearranges to $[\pi$-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4](C_6H_5)_2PCH_2P(C_6H_5)_2$ in solution and as a consequence could not be isolated. This rearrangement is interpreted as demonstrating that the derivative is dinuclear with the diphosphine behaving as a monodentate rather than tetranuclear with the ligand bridging two dinuclear units.

Previous studies have established that the ditertiary phosphine $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ shows less tendency to act as a bridging ligand than $(C_6H_5)_2PCH_2P(C_6H_5)_2$[1,29]. Consistent with this is the observation that the reaction of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ with an equimolar amount of $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ in benzene at room temperature affords as sole product a compound shown by means of infrared to be a mono-substituted derivative of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$ [ν(C–O): 2024 (ms), 1974 (ms), 1943 (vw), 1870 (s) and 1856 cm^{-1} (s), measured in dichloromethane]. The compound decomposes in solution and thus could not be isolated pure. Extensive decomposition occurred in the corresponding reaction in benzene under reflux.

Pyridine, carbon monoxide and the dienes, 1,5-cyclooctadiene and bicyclo[2.2.1]hepta-2,5-diene proved to be unreactive towards π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ under the conditions employed in the reactions discussed above. Further, treatment of the latter with iodine led to the formation of $[Fe(CO)_3P(C_6H_5)_2]_2$.

In contrast to π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$, π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$ and π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5L$ (L=tertiary phosphine or phosphite) were found not to react with tertiary phosphines and phosphites in benzene under reflux. It is thus apparent that the bis-substituted derivatives π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L_2$ are formed via the bridging carbonyl compounds π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$ (L= tertiary phosphine or phosphite) as intermediates and that the overall reaction scheme for π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ with tertiary phosphines and phosphites is that outlined below. Consistent with this scheme is the observation that the reaction of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4P(C_2H_5)_3$, prepared *in situ* photochemically from π-$C_5H_5Fe_2$-



$P(C_6H_5)_2(CO)_5$ and $P(C_2H_5)_3$, with excess of this ligand in benzene under reflux gives π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4[P(C_2H_5)_3]_2$ in high yield whereas the reaction of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ with a similar amount of $P(C_2H_5)_3$ under these conditions affords primarily π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5P(C_2H_5)_3$.

It is suggested that the ready formation of the metal–metal bonded derivatives π-$C_5H_5Fe_2(t\text{-}C_4H_9S)(CO)_5$ and π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4L$ [$L = CO$, $P(C_2H_5)_3$, $P(C_6H_5)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$ and $P(OC_6H_5)_3$], by stirring of a solution of π-$C_5H_5Fe_2(t\text{-}C_4H_9S)(CO)_6$ in benzene at room temperature and irradiation of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5L$ with ultraviolet light respectively, results from the intramolecular interaction of the iron atoms, in mutually β-positions, in the latter derivatives.

EXPERIMENTAL

The compounds $Fe_2(CO)_9$ and π-$C_5H_5Fe(CO)_2Cl$ were synthesised according to established procedures[30,31]. All experiments were performed under a nitrogen atmosphere. The photochemical reactions employed a Hanovia medium pressure arc photochemical reactor. 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 and on the Varian A60A and HA 100 instruments respectively. The mass spectra were obtained by Dr. R. Greatrex, University of Newcastle, Great Britain. The elemental analyses and the molecular weights were obtained by the Alfred Bernhardt Micro-analytical Laboratory, Elbach-über-Engelskirchen, West Germany and by Mr. G. J. Roberts, National Chemical Research Laboratory, C.S.I.R., Pretoria.

Synthesis of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$

(*i*). *From* π-$C_5H_5Fe(CO)_2P(C_6H_5)_2$ *and* $Fe_2(CO)_9$. A suspension of $Fe_2(CO)_9$ (0.36 g, 1.0 mmole) and π-$C_5H_5Fe(CO)_2P(C_6H_5)_2$ (0.72 g, 2.0 mmole), prepared *in situ* by addition of $LiP(C_6H_5)_2$ to π-$C_5H_5Fe(CO)_2Cl$, in benzene (*ca.* 60 ml) was stirred for 90 min. The solution was filtered, concentrated to a small volume and transferred to an alumina column. Elution with benzene/petroleum ether (1/1) afforded a red band which was collected. The solvent was removed under reduced pressure and the residue crystallised from benzene/petroleum ether. Yield *ca.* 40%.

(*ii*). *From* $Na[$π-$C_5H_5Fe(CO)_2]$ *and* $Fe(CO)_4[P(C_6H_5)_2Cl]$. A solution of $Na[$π-$C_5H_5Fe(CO)_2]$ (0.80 g, 4.0 mmole) in THF (*ca.* 50 ml) was added dropwise to a stirred solution of $Fe(CO)_4[P(C_6H_5)_2Cl]$ (1.55 g, 4.0 mmole), prepared from $Fe_2(CO)_9$ and $P(C_6H_5)_2Cl$, in THF (*ca.* 30 ml) at −80° and the resultant solution allowed to slowly reach room temperature. The solvent was removed under reduced pressure and the residue extracted with a minimum of benzene and transferred to an alumina column. The compound was isolated pure as described above. Yield *ca.* 40%.

Synthesis of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$

A solution of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_6$ in benzene was irradiated with ultraviolet light for *ca.* 45 min. The solution was concentrated and transferred to an alumina column. Elution with benzene/petroleum ether (1/3) afforded a purple band which was collected. The solvent was removed under reduced pressure and the residue crystallised from benzene/petroleum ether. Yield *ca.* 70%.

Synthesis of π-$C_5H_5Fe_2(t\text{-}C_4H_9S)(CO)_5$

A suspension of $Fe_2(CO)_9$ (0.72 g, 2.0 mmole) and π-$C_5H_5Fe(CO)_2(t\text{-}C_4H_9S)$ (1.06 g, 4.0 mmole), prepared from π-$C_5H_5Fe(CO)_2Cl$ and $Na(t\text{-}C_4H_9S)$[32], in benzene (*ca.* 60 ml) was stirred for 90 min. The solution was filtered, concentrated to a small volume and transferred to an alumina column. Elution with petroleum ether afforded both a yellow-orange and a green band. The latter was collected and the solvent removed under reduced pressure. The compound is extremely reactive and decomposes rapidly and as a consequence the residue so isolated was identified by means of infrared only. Yield *ca.* 20%.

Reaction of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ *with* PR_3 ($R=C_2H_5$ *and* C_6H_5), $P(OR')_3$ ($R'=CH_3, C_2H_5, i\text{-}C_3H_7$ *and* C_6H_5) *and* $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ ($n=1$ *and* 2)

Apart from π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4[P(C_2H_5)_3]_2$, the tertiary and ditertiary phosphine and phosphite substituted derivatives isolated in this study were synthesised by one of two general methods, outlined below. The experimental details for the synthesis of each compound are summarised in Table 3. The most convenient synthesis is reported for those derivatives which may be obtained by more than one method.

Method A. A solution of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ and the appropriate ligand in benzene (*ca.* 80 ml) was irradiated with ultraviolet light until reaction was complete as determined by monitoring with infrared. The solution was filtered and the solvent removed under reduced pressure. The residue was crystallised from the solvent mixture listed in Table 3.

Method B. A solution of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ and the appropriate ligand in benzene (*ca.* 60 ml) was refluxed until reaction was complete as determined by infrared. The product was isolated as described under Method A and crystallised from the solvents recorded in Table 3. Separation of those mono- and bis-substituted derivatives isolated from the same reaction was achieved by means of fractional crystallisation.

Synthesis of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_4[P(C_2H_5)_3]_2$

A solution of π-$C_5H_5Fe_2P(C_6H_5)_2(CO)_5$ (0.50 g, 1.0 mmole) and $P(C_2H_5)_3$ (0.50 g, 4.2 mmole) in benzene (*ca.* 80 ml) was irradiated with ultraviolet light for 1 h. Extra $P(C_2H_5)_3$ (0.50 g, 4.2 mmole) was added and the resultant solution was refluxed for 3 h. Separation of the bis-substituted product from the mono-substituted derivative also present in the reaction mixture was achieved by means of fractional crystallisation. Recrystallisation of the product was effected from benzene/petroleum ether. Yield *ca.* 45%.

TABLE 3. PREPARATIVE DETAILS OF SUBSTITUTED DERIVATIVES

Reactants (quantities)[a]	Reaction temp.	Reaction[b] procedure	Reaction products	Crystallised from	(
$CpFe_2PPh_2(CO)_5$ (0.50 g, 1.0 mmole) PEt_3 (0.50 g, 4.2 mmole)	25	A (40 min)	$CpFe_2PPh_2(CO)_4PEt_3$ $CpFe_2PPh_2(CO)_5PEt_3$ $CpFe_2PPh_2(CO)_4(PEt_3)_2$	Not separated Not separated Not separated	*c* $<$ $<$
$CpFe_2PPh_2(CO)_5$ (0.50 g, 1.0 mmole) PEt_3 (0.50 g, 4.2 mmole)	80	B (1 h)	$CpFe_2PPh_2(CO)_5PEt_3$ $CpFe_2PPh_2(CO)_4(PEt_3)_2$	Benzene/pet. ether Not isolated	*ca* $<$
$CpFe_2PPh_2(CO)_5$ (0.50 g, 1.0 mmole) PPh_3 (0.29 g, 1.1 mmole)	80	B (1 h)	$CpFe_2PPh_2(CO)_4PPh_3$	Benzene/pet. ether	*ca*
$CpFe_2PPh_2(CO)_5$ (0.60 g, 1.2 mmole) $P(OMe)_3$ (0.15 g, 1.3 mmole)	80	B (1 h)	$CpFe_2PPh_2(CO)_4P(OMe)_3$	Benzene/pet. ether	*ca*
$CpFe_2PPh_2(CO)_5$ (0.50 g, 1.0 mmole) $P(OMe)_3$ (0.50 g, 4.0 mmole)	80	B (3.5 h)	$CpFe_2PPh_2(CO)_5P(OMe)_3$ $CpFe_2PPh_2(CO)_4[P(OMe)_3]_2$	Not isolated Benzene/methanol	*ca.* *ca.*
$CpFe_2PPh_2(CO)_5$ (0.50 g, 1.0 mmole) $P(OEt)_3$ (0.60 g, 3.6 mmole)	25	A (1.75 h)	$CpFe_2PPh_2(CO)_4P(OEt)_3$	Dichloromethane/ methanol	*ca.*
$CpFe_2PPh_2(CO)_5$ (0.50 g, 1.0 mmole) $P(O\text{-}i\text{-}Pr)_3$ (0.50 g, 2.4 mmole)	25	A (2.5 h)	$CpFe_2PPh_2(CO)_4P(O\text{-}i\text{-}Pr)_3$	Dichloromethane/ methanol	*ca.*
$CpFe_2PPh_2(CO)_5$ (0.50 g, 1.0 mmole) $P(O\text{-}i\text{-}Pr)_3$ (2.5 g, 12.0 mmole)	80	B (1 h)	$CpFe_2PPh_2(CO)_5P(O\text{-}i\text{-}Pr)_3$ $CpFe_2PPh_2(CO)_4[P(O\text{-}i\text{-}Pr)_3]_2$	Benzene/pet. ether Benzene/pet. ether	*ca.* *ca.*
$CpFe_2PPh_2(CO)_5$ (0.50 g, 1.0 mmole) $P(OPh)_3$ (0.34 g, 1.1 mmole)	80	B (30 min)	$CpFe_2PPh_2(CO)_4P(OPh)_3$	Not isolated pure	*ca.*
$CpFe_2PPh_2(CO)_5$ (0.50 g, 1.0 mmole) $P(OPh)_3$ (4.0 g, 12.9 mmole)	80	B (5.5 h)	$CpFe_2PPh_2(CO)_5P(OPh)_3$ $CpFe_2PPh_2(CO)_4[P(OPh)_3]_2$	Benzene/pet. ether Benzene/pet. ether	*ca.* *ca.*
$CpFe_2PPh_2(CO)_5$ (0.50 g, 1.0 mmole) $Ph_2PCH_2PPh_2$ (0.42 g, 1.1 mmole)	25	A (3.5 h)	$CpFe_2PPh_2(CO)_4Ph_2PCH_2PPh_2$[d]	Not isolated	
$CpFe_2PPh_2(CO)_5$ (0.50 g, 1.0 mmole) $Ph_2PCH_2PPh_2$ (0.42 g, 1.1 mmole)	80	B (1 h)	$[CpFe_2PPh_2(CO)_4]Ph_2PCH_2PPh_2$[e]	Dichloromethane/ pet. ether	*ca.* 6
$CpFe_2PPh_2(CO)_5$ (0.50 g, 1.0 mmole) $Ph_2PC_2H_4PPh_2$ (0.48 g, 1.2 mmole)	25	B (72 h)	$CpFe_2PPh_2(CO)_5Ph_2PC_2H_4PPh_2$ or $[CpFe_2PPh_2(CO)_5]_2Ph_2PC_2H_4PPh_2$	Benzene/pet. ether	*ca.* 6

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[a] Reaction solvent: benzene. [b] Reaction time in parentheses. [c] For those derivatives not isolated the yields are based infrared intensity data. [d] Mono-substituted derivative of $\pi\text{-}C_5H_5Fe_2P(C_6H_5)_2(CO)_5$. [e] Bis-substituted derivative of $C_5H_5Fe_2P(C_6H_5)_2(CO)_6$.

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