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

REACTIONS OF METAL CARBONYL DERIVATIVES
XI*. TERTIARY PHOSPHINE, PHOSPHITE AND STIBINE AND DITERTIARY PHOSPHINE AND ARSINE DERIVATIVES OF BIS(μ-PHENYLSULPHIDOTRICARBONYLIRON)**

J. A. DE BEER AND 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)

(Received September 8th, 1971)

SUMMARY

The ditertiary phosphines $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ ($n=1$ and 2), *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ and $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ and the ditertiary arsines $(C_6H_5)_2As(CH_2)_nAs(C_6H_5)_2$ ($n=1$ and 2) react with $[Fe(CO)_3SC_6H_5]_2$ to give a wide range of products, the nature of which depends on the reaction conditions and the ligand involved. Examples of the different types of compounds isolated include, (*i*) $Fe_2(CO)_5[(C_6H_5)_2PCH_2P(C_6H_5)_2](SC_6H_5)_2$, in which the ligand acts as a monodentate, (*ii*) $\{[Fe(CO)_2SC_6H_5]_2[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]\}_2$, in which two $[Fe(CO)_2SC_6H_5]_2$ moieties are bridged by two diphosphine ligands, (*iii*) $[Fe(CO)_2SC_6H_5]_2[(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]$, in which the ligand bridges the two iron atoms, and (*iv*) $Fe(CO)_3(SC_6H_5)_2Fe(CO)[(C_6H_5)_2PC_2H_2P(C_6H_5)_2]$, which contains the ligand chelated to a single iron atom. The tertiary phosphines PR_3 ($R=C_2H_5$ and C_6H_5), phosphites $P(OR')_3$ ($R'=CH_3$, C_2H_5, i-C_3H_7 and C_6H_5) and the stibine $Sb(C_6H_5)_3$ bring about mono-, bis- or tris-substitution in $[Fe(CO)_3SC_6H_5]_2$ depending on the reaction conditions and the ligand involved. Whereas in solution $[Fe(CO)_2L(SC_6H_5)]_2$ [$L=PR_3$ ($R=C_2H_5$ and C_6H_5), $P(OC_6H_5)_3$ and $Sb(C_6H_5)_3$] exist as a single isomer, $[Fe(CO)_2L'(SC_6H_5)]_2$ [$L'=P(OR')_3$ ($R'=CH_3$, C_2H_5 and i-C_3H_7)] occur as a mixture of isomers.

INTRODUCTION

It has been previously reported[3] that the reaction of $[Fe(CO)_3SR]_2$ ($R=C_2H_5$ or C_6H_5) with $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (Diphos) in benzene under reflux affords as sole product a compound characterised as $Fe(CO)_3(SR)_2Fe(CO)$Diphos and assigned a structure in which the ligand is chelated to a single iron atom. A recent more detailed study of the reaction of $[Fe(CO)_3SR]_2$ ($R=CH_3$ or C_2H_5) with

---

* For Part X see ref. 1.

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

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

this ligand revealed that a number of different products are formed however, depending on the reaction conditions[4]. This study confirmed that $Fe(CO)_3(SR)_2Fe(CO)$-Diphos ($R = CH_3$ or C_2H_5) is produced under certain experimental conditions but in low yield only. It was further shown that the reactions of $[Fe(CO)_3SR]_2$ ($R = CH_3$ and C_2H_5) with different ditertiary phosphine and arsine ligands under similar experimental conditions do not necessarily yield analogous products and that the type of product formed could be related to the donor and chelating properties of the ligand involved[4].

The reactions of $[Fe(CO)_3SC_6H_5]_2$ with various tertiary and ditertiary phosphines and arsines have now been studied in order to ascertain the influence of the group R on the reactivity of compounds of the type $[Fe(CO)_3SR]_2$ towards Group V donor ligands. The results of the study are reported here.

RESULTS

The reaction of $[Fe(CO)_3SC_6H_5]_2$ with an equimolar amount of the ditertiary phosphine $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (DPM) in benzene at room temperature afforded in high yield a compound characterised as $Fe_2(CO)_5DPM(SC_6H_5)_2$ (I) and containing the ligand bonded as a monodentate. An increase in the temperature of this reaction to that of benzene under reflux resulted in the formation of a bis-substituted derivative of formula $[Fe(CO)_2SC_6H_5]_2DPM$ (III) which was shown to contain the diphosphine ligand bridging the two iron atoms. This bis-substituted compound was also formed as the sole product in the reaction of $[Fe(CO)_3SC_6H_5]_2$ with excess $(C_6H_5)_2PCH_2P(C_6H_5)_2$(DPM) in refluxing xylene. Tris-substitution in $[Fe(CO)_3SC_6H_5]_2$ was effected on irradiation of a benzene solution of the iron dimer and excess of the above ligand with ultraviolet light. The product could not be isolated in crystalline form however and was identified by means of infrared spectroscopy.

The ditertiary phosphine $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (Diphos), similar to $(C_6H_5)_2PCH_2P(C_6H_5)_2$, effected mono-substitution in $[Fe(CO)_3SC_6H_5]_2$ on reaction in benzene at room temperature. Bis-substituted derivatives were also formed in low yield in this reaction. As a consequence the mono-substituted product could not be isolated pure and it was identified by means of infrared [ν(C–O) 2048 s, 1985 s, 1963 (sh) and 1936 m cm^{-1}, measured in cyclohexane]. The reaction of $[Fe(CO)_3SC_6H_5]_2$ with an equimolar amount of $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ in benzene under reflux was found to afford in low yield the tetranuclear compound $\{[Fe(CO)_2SC_2H_5]_2$-Diphos$\}_2$ as well as the asymmetrically bis-substituted derivative $Fe(CO)_3(SC_6H_5)_2$-Fe(CO)Diphos (IV) reported previously[3]. The two products could not be separated by means of fractional crystallisation or column chromatography. $Fe(CO)_3(SC_6H_5)_2Fe$-(CO)Diphos was thus isolated in impure form by rapid precipitation from the reaction solution. It was noted that $Fe(CO)_3(SC_6H_5)_2Fe(CO)$Diphos "rearranges" slowly to $\{[Fe(CO)_2SC_6H_5]_2$Diphos$\}_2$ in the solid state. The tetranuclear derivative $\{[Fe(CO)_2SC_6H_5]_2$Diphos$\}_2$ was obtained in high yield by addition of $[Fe(CO)_3SC_6H_5]_2$ in petroleum ether to an equimolar amount of $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$(Diphos) in petroleum ether (b.p. 80–100°) at 75°; the product separated from solution. The solubility of $Fe(CO)_3(SC_6H_5)_2Fe(CO)$Diphos in alcohol is low. $[Fe(CO)_3SC_6H_5]_2$ was thus reacted with an equimolar amount of $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ in this solvent under reflux in the hope that this bis-substituted derivative would separate from solution during reaction. However the product isolated by this procedure was shown to be the polymeric derivative $\{[Fe(CO)_2SC_6H_5]_2Diphos\}_n$. Significantly whereas the reaction of $[Mo(CO)_4P(CH_3)_2]_2$ with $(C_6H_5)_2PC_4H_8P(C_6H_5)_2$ in benzene on irradiation with ultraviolet light afforded the tetranuclear derivative $\{[Mo(CO)_3P(CH_3)_2]_2(C_6H_5)_2PC_4H_8P(C_6H_5)_2\}_2$, the corresponding reaction in alcohol gave the polymeric compound $\{[Mo(CO)_3P(CH_3)_2]_2(C_6H_5)_2PC_4H_8P(C_6H_5)_2\}_n$ $(n>2)^5$. The reaction of $[Fe(CO)_3SC_6H_5]_2$ with an equimolar amount of $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ in toluene under reflux afforded the symmetrically bis-substituted derivative $[Fe(CO)_2SC_6H_5]_2$Diphos (III) in good yield. However the products $Fe(CO)_2$Diphos$(SC_6H_5)_2$ (VI) and $Fe(CO)_3$Diphos which result from the asymmetric cleavage of the parent compound were also formed in this reaction when an excess of the ligand was employed. These mononuclear derivatives were found to be the major products in the reaction of $[Fe(CO)_3SC_6H_5]_2$ with excess $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ in xylene under reflux or in benzene under irradiation with ultraviolet light.

The asymmetrically bis-substituted derivative $Fe(CO)_3(SC_6H_5)_2Fe(CO)$-[*cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$] (IV) was formed as the sole product in the reaction of $[Fe(CO)_3SC_6H_5]_2$ with a slight excess of the ligand *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ in benzene under reflux. No mono-substituted intermediate although undoubtedly formed could be detected on monitoring the reaction with infrared. In contrast to the corresponding reaction involving $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ there was no evidence for the formation of the symmetrically bis-substituted derivative *viz.* $[Fe(CO)_2SC_6H_5]_2$-[*cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$] (III) in the reaction of $[Fe(CO)_3SC_6H_5]_2$ with an equimolar amount of *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ in toluene under reflux. Although extensive decomposition occurred in this reaction $Fe(CO)_2$[*cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$]$(SC_6H_5)_2$ (VI) and $[Fe(CO)_3$[*cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$] could be detected. These latter products were formed in fair yield in the reaction of $[Fe(CO)_3SC_6H_5]_2$ with excess of the ligand in toluene under reflux and in the photochemical reaction of $[Fe(CO)_3SC_6H_5]_2$ with excess *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ in benzene.

The ligand $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ was also found to afford an asymmetrically bis-substituted derivative *viz.* $Fe(CO)_3(SC_6H_5)_2Fe(CO)[(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]$ (IV) on reaction with an equimolar amount of $[Fe(CO)_3SC_6H_5]_2$ in benzene under reflux. The product could not be isolated directly from the reaction mixture however and further it decomposed on attempted purification by means of column chromatography. This compound could be isolated though from the reaction of $[Fe(CO)_3SC_6H_5]_2$ with an equimolar amount of the ligand in petroleum ether (60–80°) under reflux. $Fe(CO)_3(SC_6H_5)_2Fe(CO)[(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]$ is readily converted to $[Fe(CO)_2SC_6H_5]_2[(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]$ (III) at higher temperatures and thus the reaction of $[Fe(CO)_3SC_6H_5]_2$ with a slight excess of $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ in toluene under reflux afforded the symmetrically bis-substituted derivative in excellent yield. Extensive decomposition occurred on irradiation of a benzene solution of $[Fe(CO)_3SC_6H_5]_2$ and excess $(C_6H_5)_2PN(C_2H_5)$-$P(C_6H_5)_2$ with ultraviolet light but traces of $Fe(CO)_2[(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]$-$(SC_6H_5)_2$ (VI) and $Fe(CO)_3[(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]$ were detected in the reaction mixture.

The reactions of the ditertiary arsines $(C_6H_5)_2As(CH_2)_nAs(C_6H_5)_2$ $(n=1$ and $2)$ with $[Fe(CO)_3SC_6H_5]_2$ illustrate the considerably weaker donor properties of these ligands compared with their phosphine analogues. For instance even after 8

TABLE 1

MELTING POINTS AND CONDUCTIVITY, ANALYTICAL AND MOLECULAR WEIGHT DATA

Compound[a,b]	M.p.[c] (°C)	Conductivity[d] (Ohm^{-1}·cm^{2}·mol^{-1})	Analysis found (calcd.)(%)					Mol. wt. found (calc.)
			C	H	Fe	S	P	
$Fe_2(CO)_5PPh_3(SPh)_2$	144	0.1	57.1	3.4	15.3			720
			(57.4)	(3.4)	(15.3)			(732)
$[Fe(CO)_2PPh_3(SPh)]_2$	201	1.2	64.7	4.1	11.7			890
			(64.6)	(4.2)	(11.6)			(967)
$[Fe(CO)_2SbPh_3(SPh)]_2$	90 d.p.	0.1	54.2	3.5	9.6			1129
			(54.4)	(3.5)	(9.7)			(1148)
$[Fe(CO)_2P(OMe)_3(SPh)]_2$	97	0.1	38.4	3.9	16.2	9.2	8.7	699
			(38.3)	(4.1)	(16.2)	(9.3)	(9.0)	(690)
$[Fe(CO)_2P(OEt)_3(SPh)]_2$	oil	0.2	44.7	5.3	13.7			
			(45.1)	(5.1)	(14.0)			
$[Fe(CO)_2P(O\text{-}i\text{-}Pr)_3(SPh)]_2$	oil	0.1	48.8	6.2	12.4			
			(49.0)	(5.9)	(12.7)			
$Fe_2(CO)_5P(OPh)_3(SPh)_2$	105	0.1	53.6	3.3	14.0	8.2	3.9	756
			(53.9)	(3.2)	(14.3)	(8.2)	(4.0)	(780)
$[Fe(CO)_2P(OPh)_3(SPh)]_2$	113	0.1	58.7	3.9	10.5	6.1	5.8	1050
			(58.8)	(3.8)	(10.5)	(6.0)	(5.8)	(1063)
$Fe_2(CO)_3[P(OPh)_3]_3(SPh)_2$	68	0.1	61.7	4.1	8.4	4.9	7.1	1289
			(61.6)	(4.1)	(8.3)	(4.8)	(6.9)	(1345)
$Fe_2(CO)_5DPM(SPh)_2$	74 w.d.	0.5	59.5	4.0	12.7			894
			(59.0)	(3.8)	(13.1)			(854)
$[Fe(CO)_2SPh]_2DPM$	232 d.p.	0.5	59.2	3.7	13.6	7.7	7.3	783
			(59.4)	(3.9)	(13.5)	(7.7)	(7.5)	(829)
$Fe(CO)_3(SPh)_2Fe(CO)Diphos$		0.3	60.1	4.2	13.6			
			(60.0)	(4.1)	(13.3)			
$\{[Fe(CO)_2SPh]_2Diphos\}_2$	143 w.d.	0.2	60.1	4.4	13.0	7.7	7.3	*ca.* 1500[f]
			(60.0)	(4.1)	(13.3)	(7.6)	(7.4)	(1681)
$[Fe(CO)_2SPh]_2Diphos$	224	0.6	60.1	3.9	13.0	7.4	7.3	825
			(60.0)	(4.1)	(13.3)	(7.6)	(7.4)	(840)
$\{[Fe(CO)_2SPh]_2Diphos\}_n$	118 w.d.		59.8	4.1	12.9			
			(60.0)	(4.1)	(13.3)			
$[Fe(CO)_2Diphos(SPh)_2]\cdot 0.7$	127 d.p.	0.5	67.6	5.0	7.3	7.9	8.0	644
			(67.8)	(4.9)	(7.1)	(8.2)	(7.9)	(783)
$Fe(CO)_3(SPh)_2Fe(CO)L$	168	0.5	60.1	4.1	13.3	7.8	7.4	855
			(60.2)	(3.8)	(13.3)	(7.7)	(7.4)	(838)
$[Fe(CO)_2(L)(SPh)_2]\cdot 0.5\ C_6H_6$	99	0.3	67.3	4.6	7.5	8.1	7.8	634
			(67.5)	(4.6)	(7.3)	(8.4)	(8.1)	(766)
$Fe(CO)_3(SPh)_2Fe(CO)L'$	65 d.p.	0.4	58.8	3.8	12.8	1.8[e]		802
			(59.2)	(3.8)	(13.1)	(1.6[e])		(852)
$[Fe(CO)_2SPh]_2L'$	220 w.d.	0.1	59.3	3.9	13.0	(1.5[e])		885
			(59.2)	(3.8)	(13.1)	(1.6[e])		(852)
$[Fe(CO)_2SPh]_2DAM$	200 d.p.	0.2	54.3	3.6	12.0	6.9		894
			(53.9)	(3.5)	(12.2)	(7.0)		(914)
$[Fe(CO)_2SPh]_2Diars$	209	0.1	54.1	3.7	12.1	7.2		927
			(54.3)	(3.7)	(12.0)	(6.9)		(928)

[a] All compounds are diamagnetic; all are stable in air in the crystalline state apart from $Fe_2(CO)_5P(OPh)_3(SPh)_2$, $[Fe(CO)_2P(OR)_3SPh]_2$ (R=Et, i-Pr and Ph), $Fe(CO)_3(SPh)_2Fe(CO)L$ ($L=Ph_2PC_2H_4PPh_2$ and $Ph_2PNEtPPh_2$) and $Fe(CO)_2L'(SPh)_2$ ($L'=Ph_2PC_2H_4PPh_2$ and *cis*-$Ph_2PC_2H_2PPh_2$). [b] Abbreviations: Me, CH_3; Et, C_2H_5; i-Pr, iso-C_3H_7; Ph, C_6H_5; DPM $(C_6H_5)_2PCH_2P(C_6H_5)_2$; Diphos, $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$; L, *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$; L', $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$; DAM, $(C_6H_5)_2AsCH_2As(C_6H_5)_2$; Diars, $(C_6H_5)_2AsC_2H_4As(C_6H_5)_2$. [c] Abbreviations: d.p., decomposition point; w.d., with decomposition. [d] For *ca.* 10^{-3} *M* in acetone. [e] Nitrogen analysis. [f] See text for discussion.

h only a little of the mono-substituted derivative had formed in the reaction of $[Fe(CO)_3SC_6H_5]_2$ with an equimolar amount of $(C_6H_5)_2AsCH_2As(C_6H_5)_2$ (DAM) in refluxing benzene as determined by monitoring with infrared. The symmetrically bis-substituted derivative $[Fe(CO)_2SC_6H_5]_2$DAM (III) was formed simultaneously with the mono-substituted compound in the corresponding reaction in toluene and thus the latter could not be isolated. $[Fe(CO)_2SC_6H_5]_2$ DAM was obtained in excellent yield from the reaction of $[Fe(CO)_3SC_6H_5]_2$ with a slight excess of the ligand in xylene under reflux.

The ligand $(C_6H_5)_2AsC_2H_4As(C_6H_5)_2$ (Diars) behaved similarly to $(C_6H_5)_2AsCH_2As(C_6H_5)_2$ in its reactions with $[Fe(CO)_3SC_6H_5]_2$. A mono-substituted product was formed exceptionally slowly in the reaction of the ligand with the iron dimer in refluxing benzene while $[Fe(CO)_2SC_6H_5]_2$Diars (III) was readily produced in the corresponding reaction in refluxing xylene.

To assist in the identification of some of the products isolated from the reactions involving the bidentate ligands discussed above, the reactions of $[Fe(CO)_3SC_6H_5]_2$ with various monodentate ligands were also studied. Thus treatment of $[Fe(CO)_3SC_6H_5]_2$ with equimolar amounts of the ligands $L=P(C_2H_5)_3$ and $P(OR)_3$ ($R=CH_3$, C_2H_5 and $i\text{-}C_3H_7$) and excess of the ligands $L=P(C_6H_5)_3$ and $P(OC_6H_5)_3$ in benzene at room temperature yielded the mono-substituted derivatives $Fe_2(CO)_5L(SC_6H_5)_2$ (I) respectively. $Fe_2(CO)_5L(SC_6H_5)_2$ [$L=P(C_6H_5)_3$ and $P(OC_6H_5)_3$] were best obtained from the corresponding reactions employing reflux conditions however. In contrast the reactions of $[Fe(CO)_3SC_6H_5]_2$ with excess of the ligands $L=P(C_2H_5)_3$ and $P(OR)_3$ ($R=CH_3$, C_2H_5 and $i\text{-}C_3H_7$) in refluxing benzene afforded bis-substituted products formulated as $[Fe(CO)_2L(SC_6H_5)]_2$. Although $[Fe(CO)_2P(C_6H_5)_3(SC_6H_5)]_2$ (II) was shown to be formed in the reaction of $[Fe(CO)_3SC_6H_5]_2$ with excess $P(C_6H_5)_3$ in xylene under reflux, it was isolated in higher yield from the photochemical reaction of the iron dimer and excess $P(C_6H_5)_3$ in benzene. $[Fe(CO)_2Sb(C_6H_5)_3(SC_6H_5)]_2$ (II) was obtained similarly. Irradiation of a benzene solution of $[Fe(CO)_3SC_6H_5]_2$ and $P(OC_6H_5)_3$ resulted in the formation of either the bis-substituted compound $[Fe(CO)_2P(OC_6H_5)_3(SC_6H_5)]_2$ (II) or the tris-substituted derivative $Fe_2(CO)_3[P(OC_6H_5)_3]_3(SC_6H_5)_2$ (V) depending on the molar ratio employed and on the reaction period. However in the corresponding reactions of $[Fe(CO)_3SC_6H_5]_2$ with the ligands $L=P(C_2H_5)_3$ and $P(OCH_3)_3$, cleavage of the parent dimer to afford $Fe(CO)_3L_2$ was effected. A trace quantity of $Fe_2(CO)_3[P(OCH_3)_3]_3(SC_6H_5)_2$ (V) identified by means of infrared, was isolated as an oil from the reaction involving $P(OCH_3)_3$ however.

DISCUSSION

$Fe_2(CO)_5L(SC_6H_5)_2$

The crystalline compounds $Fe_2(CO)_5L(SC_6H_5)_2$ [$L=P(C_6H_5)_3$ and $P(OC_6H_5)_3$] and $Fe_2(CO)_5DPM(SC_6H_5)_2$ were characterised by elemental analysis and molecular weight measurements, as were all other compounds synthesised in this study unless otherwise stated. The derivatives $Fe_2(CO)_5L(SC_6H_5)_2$ [$L=P(C_2H_5)_3$ and $P(OR)_3$ ($R=CH_3$, C_2H_5 and $i\text{-}C_3H_7$)], which were isolated as oils were identified by means of their infrared spectra only.

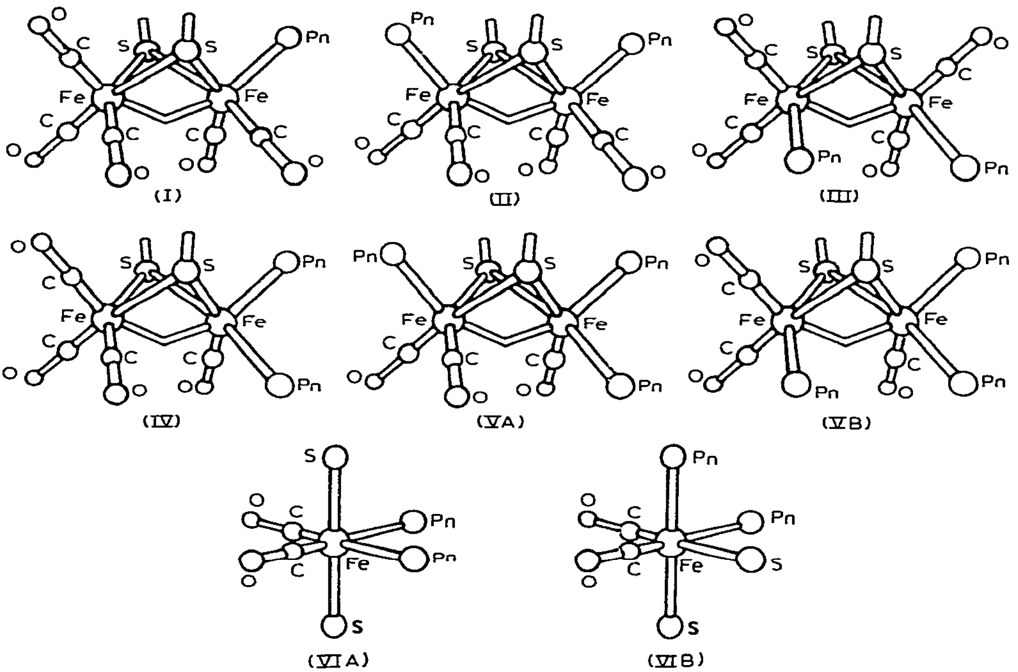
The infrared spectra of the above mono-substituted derivatives in the C–O

TABLE 2

INFRARED SPECTROSCOPIC DATA

Compound[a]	C–O stretching frequencies[b]	Compound[a]	C–O stretching frequencies[b]
$Fe_2(CO)_5PEt_3(SPh)_2$	2043 ms, 1986 s, 1970 s, 1928 m[c]	$Fe_2(CO)_5DPM(SPh)_2$	2049 s, 1987 s, 1969 (sh), 1937 m[c]
$[Fe(CO)_2PEt_3(SPh)]_2$	1985 m, 1950 s, 1920 ms, 1907 w[c]	$[Fe(CO)_2SPh]_2DPM$	1997 m, 1964 s, 1935 s, 1920 m[c]
$Fe_2(CO)_5PPh_3(SPh)_2$	2050 s, 1987 s, 1972 (sh), 1942 m[c]	$Fe_2(CO)_3(DPM)_2(SPh)_2$	1969 s, 1918 s, 1889 (sh)[c]
$[Fe(CO)_2PPh_3(SPh)]_2$	1992 s, 1947 m, 1928 s[d]	$Fe(CO)_3(SPh)_2Fe(CO)Diphos$	2028 s, 1964 ms, 1960 ms, 1914 w[c]
$[Fe(CO)_2SbPh_3(SPh)]_2$	2004 s, 1963 ms, 1949 s[c]	$\{[Fe(CO)_2SPh]_2Diphos\}_2$	1990 s, 1948 ms, 1928 ms[d]
$Fe_2(CO)_5P(OMe)_3(SPh)_2$	2052 s, 1997 s, 1986 m, 1976 s, 1940 w[c]	$[Fe(CO)_2SPh]_2Diphos$	1998 ms, 1962 s, 1932 ms, 1913 w[f]
$[Fe(CO)_2P(OMe)_3(SPh)]_2$	2017 ms, 1975 s, 1959 m, 1949 m, 1928 w[c]	$\{[Fe(CO)_2SPh]_2Diphos\}_n$	1986 s, 1940 ms, 1911 s[e]
	1999 ms, 1954 s, 1929 ms, 1913 m[e]	$Fe(CO)_2Diphos(SPh)_2$	2017 s, 1970 s[d]
$Fe_2(CO)_3[P(OMe)_3]_3(SPh)_2$	1985 s, 1938 s, 1920 (sh)[c]	$Fe(CO)_3Diphos$	1993 s, 1930 ms, 1909 s[c]
$Fe_2(CO)_5P(OEt)_3(SPh)_2$	2051 s, 1995 s, 1986 m, 1974 s, 1939 w[c]	$Fe(CO)_3(SPh)_2Fe(CO)L$	2029 s, 1967 ms, 1961 ms, 1923 w[c]
$[Fe(CO)_2P(OEt)_3(SPh)]_2$	2013 s, 1970 s, 1954 ms, 1944 (sh), 1923 m[c]	$Fe(CO)_2L(SPh)_2$	2025 s, 1981 s[f]
$Fe_2(CO)_5P(O\text{-}i\text{-}Pr)_3(SPh)_2$	2051 s, 1993 ms, 1985 ms, 1973 m, 1931 w[c]	$Fe(CO)_3L$	1998 s, 1933 ms, 1916 s[c]
$[Fe(CO)_2P(O\text{-}i\text{-}Pr)_3(SPh)]_2$	2014 s, 1968 ms, 1955 ms, 1940 (sh), 1917 w[c]	$Fe(CO)_3(SPh)_2Fe(CO)L'$	2028 s, 1968 ms, 1957 m, 1939 w[c]
$Fe_2(CO)_5P(OPh)_3(SPh)_2$	2055 s, 2005 s, 1988 ms, 1979 ms, 1952 w[c]	$[Fe(CO)_2SPh]_2L'$	2000 m, 1971 s, 1939 s, 1928 m[c]
$[Fe(CO)_2P(OPh)_3(SPh)]_2$	2026 s, 1984 ms, 1971 s[c]	$[Fe(CO)_2SPh]_2DPM$	1994 m, 1965 s, 1935 ms, 1920 w[c]
$Fe_2(CO)_3[P(OPh)_3]_3(SPh)_2$	2005 s, 1957 s(b)[c]	$[Fe(CO)_2SPh]_2Diars$	1996 ms, 1961 s, 1932 ms, 1917 w[f]

[a] Abbreviations: Me, CH_3; Et, C_2H_5; i-Pr, iso-C_3H_7; Ph, C_6H_5; DPM, $(C_6H_5)_2PCH_2P(C_6H_5)_2$; Diphos, $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$; L, *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$; L′, $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$; DAM, $(C_6H_5)_2AsCH_2As(C_6H_5)_2$; Diars, $(C_6H_5)_2AsC_2H_4As(C_6H_5)_2$. [b] Abbreviations: s, strong; ms, medium strong; m, medium; w, weak; sh, shoulder; b, broad. [c] Measured in C_6H_{12}. [d] Measured in CH_2Cl_2. [e] Measured as nujol mull. [f] Measured in CCl_4.



(I) (II) (III) (IV) (VA) (VB) (VIA) (VIB)

Fig. 1. Proposed structures of $Fe_2(CO)_5L(SC_6H_5)_2$ (I), $[Fe(CO)_2L(SC_6H_5)]_2$ (II), $[Fe(CO)_2SC_6H_5]_2L$ (III), $Fe(CO)_3(SC_6H_5)_2Fe(CO)L$ (IV), $Fe_2(CO)_3L_3(SC_6H_5)_2$ (VA or VB) and $Fe(CO)_2L(SC_6H_5)_2$ (VIA or VIB) showing the stereochemistry of the iron atoms only (Pn = P, As or Sb).

stretching region are summarised in Table 2. Although structural assignments cannot be made using this data, it is proposed, on the basis of the structures found for most compounds of the type $[Fe(CO)_2L(SR)]_2$ (R = alkyl or aryl; L = monodentate ligand) (*vide infra* and ref. 4), that a carbonyl group *trans* to the metal–metal bond in $[Fe(CO)_3SC_6H_5]_2$[6] is substituted [Fig. 1, structure (I)].

$[Fe(CO)_2L(SC_6H_5)]_2$

The derivatives $[Fe(CO)_2L(SC_6H_5)]_2$ [$L = P(C_6H_5)_3$, $Sb(C_6H_5)_3$ and $P(OR)_3$ ($R = CH_3$, C_2H_5, i-C_3H_7 and C_6H_5)] were characterised as described above whereas $[Fe(CO)_2P(C_2H_5)_3(SC_6H_5)]_2$, which was isolated as an oil and which decomposes in solution, was identified by means of infrared only.

TABLE 3

NMR SPECTROSCOPIC DATA

Compound[a]	CH_3 resonance[b,c]
$[Fe(CO)_2P(OMe)_3(SPh)]_2$	6.41 t[d]; 6.52 d (J_{PH} 11 Hz)[e]
$[Fe(CO)_2P(OEt)_3(SPh)]_2$	8.60 t (J_{HH} 7 Hz); 8.69 t (J_{HH} 7 Hz)[f]
$[Fe(CO)_2P(O\text{-}i\text{-}Pr)_3(SPh)]_2$	8.76 d (J_{HH} 6 Hz); 9.19 d (J_{HH} 6 Hz)[f]

[a] Abbreviations: Me, CH_3; Et, C_2H_5; Pr, C_3H_7; Ph, C_6H_5. [b] τ scale (TMS reference). [c] Abbreviations: d, doublet; t, triplet. [d] The band pattern of this triplet is characteristic of virtual coupling. The separation between the sharp outer peaks is 11 Hz. [e] Measured in C_6D_6 at 38°. [f] Measured in $CDCl_3$ at 38°.

The frequencies of the C–O stretching peaks observed in the infrared spectra of the above compounds are recorded in Table 2. The solution and solid state spectra of the compounds $[Fe(CO)_2L(SC_6H_5)]_2$ $[L=P(C_6H_5)_3, Sb(C_6H_5)_3$ and $P(OC_6H_5)_3]$ contain three bands in the C–O stretching region (see Fig. 2) consistent with a structure containing the two ligands bonded *trans* to the metal–metal bond and the phenyl groups *syn* disposed [structure(II)]. In contrast the infrared spectrum of $[Fe(CO)_2P(C_2H_5)_3(SC_6H_5)]_2$, measured in cyclohexane, contains four C–O stretching peaks with a band pattern very similar to those observed in the spectra of the derivatives of the type $[Fe(CO)_2SC_6H_5]_2L$ (L=ditertiary phosphine). Structure (III) is proposed for the latter compounds (*vide infra*) and by analogy a similar structure is proposed for $[Fe(CO)_2P(C_2H_5)_3(SC_6H_5)]_2$ in solution. The nujol mull spectrum of $[Fe(CO)_2P(OCH_3)_3(SC_6H_5)]_2$ also shows a band pattern in the C–O stretching region similar to those observed in the spectra of $[Fe(CO)_2SC_6H_5]_2L$ (L=ditertiary phosphine). It is thus suggested that $[Fe(CO)_2P(OCH_3)_3(SC_6H_5)]_2$ adopts structure (III) in the crystalline state. However the infrared spectrum of this compound measured in cyclohexane, as well as those of the oils $[Fe(CO)_2P(OR)_3(SC_6H_5)]_2$ $(R=C_2H_5$ and $i\text{-}C_3H_7)$ in the same solvent, contain five peaks in the C–O stretching region. Further the NMR spectra of $[Fe(CO)_2P(OR)_3(SC_6H_5)]_2$ $(R=CH_3, C_2H_5$ and $i\text{-}C_3H_7)$ contain two methyl resonances, the relative intensities of which vary with compound. It is thus apparent that these latter compounds occur as a mixture of isomers in solution and, on the basis of the proposed structures for $[Fe(CO)_2P(OCH_3)_3(SC_6H_5)]_2$ in the solid state and for $[Fe(CO)_2L(SC_6H_5)]_2$ $[L=P(C_6H_5)_3, Sb(C_6H_5)_3$ and $P(OC_6H_5)_3]$ in solution, it is suggested that these isomers have structures (II) and (III). Significantly the methyl resonance of higher intensity observed in the NMR spectrum of $[Fe(CO)_2P(OCH_3)_3(SC_6H_5)]_2$ occurs as a doublet whereas the weaker methyl resonance occurs as a triplet of separation 11 Hz. Triplets readily assigned to the methyl groups of $P(OCH_3)_3$ and of band patterns characteristic of virtual coupling are found in the NMR spectra of $[Fe(CO)_2P(OCH_3)_3(SR)]_2$ $(R=CH_3, i\text{-}C_3H_7$ and $t\text{-}C_4H_9)$. These compounds have been shown to adopt structure (II) both in solution

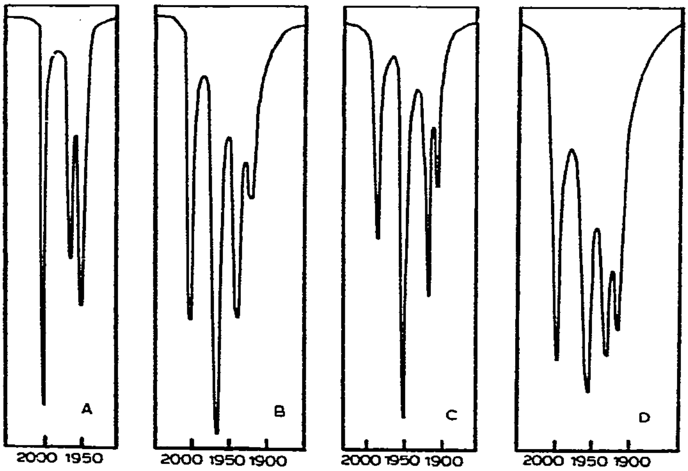


Fig. 2. Infrared spectra in the C–O stretching region of (A), $[Fe(CO)_2Sb(C_6H_5)_3(SC_6H_5)]_2$ measured in C_6H_{12}, (B), $[Fe(CO)_2SC_6H_5]_2(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ measured in CCl_4, (C), $[Fe(CO)_2P(C_2H_5)_3(SC_6H_5)]_2$ measured in C_6H_{12} and (D), $[Fe(CO)_2P(OCH_3)_3(SC_6H_5)]_2$ measured as a nujol mull.

and the solid state[7]. It is thus suggested that the structure of the major isomer of $[Fe(CO)_2P(OCH_3)_3(SC_6H_5)]_2$ in solution is that represented in Fig. 1 (III). The KBr spectrum of $[Fe(CO)_2P(OCH_3)_3(SC_6H_5)]_2$ is very similar to the solution spectrum indicating that this compound also occurs as a mixture of isomers in the "solid solution" phase. This spectrum slowly reverts to the nujol mull spectrum however, suggesting a slow crystallisation process. The Mössbauer spectrum of $[Fe(CO)_2P(OCH_3)_3(SC_6H_5)]_2$ contains a single quadrupole doublet consistent with symmetric substitution[4].

$[Fe(CO)_2SC_6H_5]_2L$

The infrared spectra of the compounds $[Fe(CO)_2SC_6H_5]_2L$ [L=DPM, Diphos, $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$, DAM and Diars] contain four peaks in the C–O stretching region (Table 2). The energy separation of *ca.* 80 cm^{-1} between the modes of highest and lowest frequency is consistent with a symmetric structure. Structure (III) which belongs to the point group C_s and for which four infrared-active C–O stretching modes are predicted, is thus proposed. Although the symmetry of compounds of the type $[Fe(CO)_2SC_6H_5]_2L$, in which the two donor atoms of the ligand L are bonded *trans* to the metal–metal bond and the phenyl groups are *anti* disposed, is lower than C_{2v}, three and not four infrared-active C–O stretching modes are expected in view of the close similarity of the infrared spectra in the C–O stretching region of *syn*- and *anti*-$[Fe(CO)_3SR]_2$ (R=CH_3, C_2H_5, t-C_4H_9 and $CH_2C_6H_5$)[8,9]. The latter and other possible structures for the above compounds are also readily eliminated based on stereochemical considerations.

The Mössbauer data for $[Fe(CO)_2SC_6H_5]_2DPM$ and $[Fe(CO)_2SC_6H_5]_2$-$[C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]$ are also consistent with symmetric substitution and structure (III)[4].

$Fe(CO)_3(SC_6H_5)_2Fe(CO)L$

The infrared spectra of the compounds $Fe(CO)_3(SC_6H_5)_2Fe(CO)L$ [L= Diphos, *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ and $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$] are summarised in Table 2. The energy separation of *ca.* 110 cm^{-1} between the C–O stretching modes of highest and lowest energy is consistent with an asymmetric structure for these derivatives while a frequency of *ca.* 2030 cm^{-1} for the highest energy mode suggests the presence of an $Fe(CO)_3$ moiety in the molecule. A structure containing the ligand chelated to a single iron atom is thus proposed [structure (IV)].

The presence of two non-coincident quadrupole doublets in the Mössbauer spectrum of $Fe(CO)_3(SC_6H_5)_2Fe(CO)[$*cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2]$ is also indicative of two nonequivalent iron environments[4].

$\{[Fe(CO)_2SC_6H_5]_2Diphos\}_2$

The chemical composition of $\{[Fe(CO)_2SC_6H_5]_2Diphos\}_2$ was established by elemental analysis. The compound, which is soluble in most common organic solvents apart from cyclohexane and petroleum ether, was shown from molecular weight measurements to "dissociate" in solution. By taking values at different time intervals and extrapolating to zero time, a molecular weight of *ca.* 1500 was obtained. This value demonstrates the "dimeric" nature of the initial species in solution. This "dissociation" in solution was monitored by means of infrared and it was observed that the intensity of the C–O stretching bands corresponding to $\{[Fe(CO)_2SC_6H_5]_2Diphos\}_2$ decreased with increase in intensity of C–O stretching modes corresponding to $Fe(CO)_3(SC_6H_5)_2Fe(CO)Diphos$ until an equilibrium between the two compounds was established. The existence of this equilibrium in solution readily explains the inability to synthesise $Fe(CO)_3(SC_6H_5)_2Fe(CO)Diphos$ free of $\{[Fe(CO)_2SC_6H_5]_2Diphos\}_2$ and further the inability to separate the two compounds by conventional methods.

The infrared spectrum of $\{[Fe(CO)_2SC_6H_5]_2Diphos\}_2$ measured in solution contains three peaks in the C–O stretching region. The frequencies of these modes are almost identical to the frequencies of the corresponding peaks observed in the infrared spectrum of $[Fe(CO)_2P(C_6H_5)_3(SC_6H_5)]_2$. Both compounds also exhibit very similar band patterns in this region. A structure in which two $[Fe(CO)_2(SC_6H_5)]_2$ groups are bridged by two $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ ligands bonded to the iron atoms in positions *trans* to the metal–metal bonds [*cf.* structure (II)], is proposed.

$\{[Fe(CO)_2SC_6H_5]_2Diphos\}_n$

The compound $\{[Fe(CO)_2SC_6H_5]_2Diphos\}_n$ is insoluble in all organic solvents and is thus considered to be polymeric in nature. Its infrared spectrum measured as a nujol mull contains three peaks in the carbonyl stretching region. The frequencies and relative intensities of these modes are very similar to those of the corresponding peaks observed in the solid-state infrared spectrum of $[Fe(CO)_2P(C_6H_5)_3(SC_6H_5)]_2$ and a structure in which $[Fe(CO)_2SC_6H_5]_2$ moieties are linked by $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ ligands bonded to the iron atoms in positions *trans* to the metal–metal bonds [*cf.* structure (II)], is thus proposed.

$Fe_2(CO)_3L_3(SC_6H_5)_2$ and $Fe_2(CO)_3(DPM)_2(SC_6H_5)_2$

The compound $Fe_2(CO)_3[P(OC_6H_5)_3]_3(SC_6H_5)_2$ was characterised as described above while the derivatives $Fe_2(CO)_3[P(OCH_3)_3]_3(SC_6H_5)_2$ and $Fe_2(CO)_3(DPM)_2(SC_6H_5)_2$ were identified by means of infrared spectroscopy only. The latter was formulated as a dinuclear and not a tetranuclear complex *viz.* $[Fe_2(CO)_3DPM(SC_6H_5)_2]_2DPM$ by analogy with the previously synthesised compounds $Fe_2(CO)_3(DPM)_2(SR)_2$ ($R=CH_3$ and C_2H_5)[4]. The infrared spectra of these derivatives contain three C–O stretching bands consistent with tris-substitution and structures (VA) and (VB). Although the infrared data cannot differentiate between the two possibilities, structure (VA) is favoured for $Fe_2(CO)_3[P(OC_6H_5)_3]_3(SC_6H_5)_2$ on the basis of the structure established for $[Fe(CO)_2P(OC_6H_5)_3(SC_6H_5)]_2$ and discussed above.

$Fe(CO)_2L(SC_6H_5)_2$

The compounds $Fe(CO)_2L(SC_6H_5)_2$ [L=Diphos and *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$] crystallised with solvent of crystallisation and in spite of prolonged drying under a high vacuum, the solvent could not be completely removed. The presence of the solvent in the crystal lattice was established by analysing the compound at various stages during the drying process. Two C–O stretching modes of approximately equal intensity are observed in the infrared spectra of these compounds. This observation is consistent with *cis*-disposition of the carbonyl groups and structures (VIA) and (VIB). These structures are analogous to the two alternatives proposed previously[10] for $Fe(CO)_2DiphosCl_2$.

$Fe(CO)_3L$

The compounds $Fe(CO)_3L$ [L = Diphos and *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$] were identified by comparison of their infrared spectra in the C–O stretching region with the previously reported[10,11] spectrum of $Fe(CO)_3$Diphos and the spectra of the compounds obtained by irradiating benzene solutions of $Fe(CO)_5$ and the ligands $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ and *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ with ultraviolet light.

The formation of products of the type $Fe(CO)_3(SC_6H_5)_2Fe(CO)L$ in the reactions of $[Fe(CO)_3SC_6H_5]_2$ with the ligands L = Diphos, *cis*-$(C_6H_5)_2PC_2H_2$-$P(C_6H_5)_2$ and $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ in benzene under reflux contrasts with the formation of $[Fe(CO)_2SC_6H_5]_2L$ in the corresponding reaction involving DPM and demonstrates the stronger chelating properties of the former ligands. Further the types of products formed in the various reactions of $[Fe(CO)_3SC_6H_5]_2$ with the ditertiary phosphines and arsines employed in this study are consistent with an increase in the tendency towards chelation along the series $(C_6H_5)_2PCH_2P(C_6H_5)_2 <$ $(C_6H_5)_2PC_2H_4P(C_6H_5)_2 \sim (C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2 <$ *cis*-$(C_6H_5)_2PC_2H_2P$-$(C_6H_5)_2$ and with the ditertiary arsines $(C_6H_5)_2As(CH_2)_nAs(C_6H_5)_2$ ($n = 1$ and 2) being weak chelating agents.

Compounds of structure (II) cannot be converted to those of structure (III) without rearrangement of the ligands around each iron atom and thus it is proposed that any isomerism of compounds of the type $[Fe(CO)_2L(SR)]_2$ (L = monodentate ligand) in solution between these structures must necessarily involve the monomers $Fe(CO)_2L(SR)$ as intermediates. In particular $Fe(CO)_2P(OCH_3)_3(SC_6H_5)$ is proposed as an intermediate in the isomerism of $[Fe(CO)_2P(OCH_3)_3(SC_6H_5)]_2$ on dissolution. It should be noted that the dimer $[Fe(CO)_3SC_6H_5]_2$ has been previously suggested to dissociate to the monomer $Fe(CO)_3(SC_6H_5)$ on dissolution[12,13].

The formation of the compounds $Fe(CO)_2L(SC_6H_5)_2$ and $Fe(CO)_3L$ in the reactions of $[Fe(CO)_3SC_6H_5]_2$ with excess of the ligands L = Diphos, *cis*-$(C_6H_5)_2$-$PC_2H_2P(C_6H_5)_2$ and $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ under the appropriate experimental conditions is also readily explained in terms of mononuclear species as intermediates. A mechanism which involves the asymmetric cleavage of the bis-substituted derivatives $Fe(CO)_3(SC_6H_5)_2Fe(CO)L$ is proposed. This scheme contrasts with the symmetric cleavage of $[Fe(CO)_2L(SC_6H_5)]_2$ to yield $Fe(CO)_2L(SC_6H_5)$ discussed above. Asymmetric cleavage of the type proposed has previously been established in the reactions of $[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$, $Fe_2(\pi\text{-}C_5H_5)_2(CO)_3L$ and $[Fe(\pi\text{-}C_5H_5)$-$(CO)]_2L'$ (L = tertiary phosphine, L′ = ditertiary phosphine) with halogens[14–18].

A comparison of the reactions reported in this study with those of $[Fe(CO)_3$-$SR]_2$ (R = CH_3 or C_2H_5) with various tertiary phosphites and tertiary and ditertiary phosphines and arsines[4] reveals that the former do not always parallel the latter under similar experimental conditions. For instance while the reaction of $[Fe(CO)_3$-$SC_6H_5]_2$ with excess DPM in benzene under reflux yields $[Fe(CO)_2SC_6H_5]_2$DPM, the corresponding reaction of $[Fe(CO)_3SR]_2$ (R = CH_3 or C_2H_5) with this ligand gives $[Fe(CO)_2DPM(SR)]_2$. Further, compounds of the type $Fe(CO)_2L'(SR)_2$ and $Fe(CO)_3L'$ (L′ = ditertiary phosphine) are not observed in any of the reactions involving $[Fe(CO)_3SR]_2$ (R = CH_3 or C_2H_5) while the derivatives $[Fe(CO)_2LSR]_2$ (L = tertiary phosphine or phosphite, R = CH_3 or C_2H_5) occur solely as an isomer of structure (II) in solution in contrast to the compounds $[Fe(CO)_2L(SC_6H_5)]_2$. The difference in reactivity of $[Fe(CO)_3SC_6H_5]_2$ and $[Fe(CO)_3SR]_2$ ($R=CH_3$ or C_2H_5) towards ditertiary phosphines and arsines L is readily explained in terms of the observation that compounds of the type $[Fe(CO)_2SR]_2L$ (III) are formed more readily for $R=C_6H_5$ than for $R=CH_3$ or C_2H_5. If it is assumed that the formation of the derivatives $[Fe(CO)_2SR]_2L$ (III) is via mono-substituted compounds, $Fe_2(CO)_5L(SR)_2$, which contain the ligand bonded *trans* to the metal–metal bond, then mononuclear species must necessarily be involved as intermediates. It is thus apparent that the overall difference in the reactivity of $[Fe(CO)_3SC_6H_5]_2$ and $[Fe(CO)_3SR]_2$ ($R=CH_3$ or C_2H_5) towards Group V donor ligands is related to the ease of cleavage (symmetric or asymmetric) of the bridging sulphido groups in derivatives of $[Fe(CO)_3SC_6H_5]_2$ compared with that in the methyl or ethyl analogues.

EXPERIMENTAL

The parent compound $[Fe(CO)_3SC_6H_5]_2$[19] and the ligands $(C_6H_5)_2P(CH_2)_n$-$P(C_6H_5)_2$ ($n=1$ and 2)[20], *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$[21] and $(C_6H_5)_2PN(C_2H_5)$-$P(C_6H_5)_2$[22] were synthesised according to literature methods and slight modifications of them while $(C_6H_5)_2As(CH_2)_nAs(C_6H_5)_2$ ($n=1$ and 2) were obtained commercially (Strem Chemicals). 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 621 grating spectrophotometer and on the Varian A 60A and HA 100 instruments respectively. Conductivities were determined with a Philips PW 9501 conductivity meter. The molecular weights were measured using a Mechrolab vapour pressure osmometer. The elemental analyses (C, H, S, P) were performed 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. Iron was determined by an atomic absorption spectroscopic method using a Techtron AA4 instrument.

Melting points, conductivity, analytical and molecular weight data are given in Table 1 (see p. 300).

The most convenient synthesis is reported for those derivatives which may be obtained by more than one method.

(i). $Fe_2(CO)_5P(C_6H_5)_3(SC_6H_5)_2$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $P(C_6H_5)_3$ (0.31 g, 1.2 mmole) in benzene (*ca.* 60 ml) was refluxed for 1 h. The solution was filtered and the solvent removed under reduced pressure. The residue was dissolved in a minimum of benzene and transferred to an alumina column. Elution with benzene/petroleum ether (1/3) afforded a red band which was collected. Removal of the solvent under reduced pressure afforded a red residue of the compound which was crystallised from petroleum ether (60–80°). Yield > 75%.

(ii). $[Fe(CO)_2P(C_6H_5)_3(SC_6H_5)]_2$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $P(C_6H_5)_3$ (0.66 g, 2.5 mmole) in benzene (*ca.* 100 ml) was irradiated with ultraviolet light for 1 h. The solution was filtered, concentrated to a small volume and transferred to an alumina column. The column was eluted with benzene/petroleum ether (1/3) to remove excess ligand and any mono-substituted product. Elution with benzene afforded a red band which was collected. The solvent was removed under reduced pressure to afford a red residue which was crystallised from dichloromethane/petroleum ether. Yield > 70%.

(iii). $[Fe(CO)_2Sb(C_6H_5)_3(SC_6H_5)]_2$

The compound was obtained by treating $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) with $Sb(C_6H_5)_3$ (0.88 g, 2.5 mmole), and isolated pure by the procedures described in *(ii)*. Yield >40%.

(iv). $[Fe(CO)_2P(OCH_3)_3(SC_6H_5)]_2$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $P(OCH_3)_3$ (0.5 g, 4.0 mmole) in benzene (*ca.* 60 ml) was refluxed for 2 h. The solution was filtered, concentrated to a small volume and transferred to an alumina column. The column was eluted in turn with 1/5 and 1/1 benzene/petroleum ether to afford a red band which was collected. The solvent was removed under reduced pressure to afford a red residue which was crystallised from benzene/petroleum ether. Yield > 70%.

(v). $[Fe(CO)_2P(OC_2H_5)_3(SC_6H_5)]_2$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $P(OC_2H_5)_3$ (0.66 g, 4.0 mmole) in benzene (*ca.* 60 ml) was refluxed for 2 h. The compound was isolated from the reaction mixture by the method described in *(iv)* and obtained as a red oil. Yield > 50%.

(vi). $[Fe(CO)_2P(O\text{-}i\text{-}C_3H_7)_3(SC_6H_5)]_2$

The compound was obtained by reacting $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) with $P(O\text{-}i\text{-}C_3H_7)_3$ (0.83 g, 4.0 mmole) in xylene (*ca.* 60 ml) under reflux for 2 h and isolated as a red oil by the procedure described in *(iv)*. Yield >40%.

(vii). $Fe_2(CO)_5P(OC_6H_5)_3(SC_6H_5)_2$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $P(OC_6H_5)_3$ (0.93 g, 3.0 mmole) in benzene (*ca.* 60 ml) was refluxed for 2 h. The solution was filtered and the solvent removed under reduced pressure. The residue was dissolved in petroleum ether and transferred to an alumina column. The column was eluted with petroleum ether to remove excess ligand. Elution with benzene/petroleum ether (1/3) afforded a red band which was collected. The solvent was removed under reduced pressure to afford a red oil which slowly crystallised. Yield > 60%.

(viii). $[Fe(CO)_2P(OC_6H_5)_3(SC_6H_5)]_2$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $P(OC_6H_5)_3$ (0.78 g, 2.5 mmole) in benzene (*ca.* 100 ml) was irradiated with ultraviolet light for 30 min. The bis-substituted product was separated from the excess ligand and any mono-substituted derivative by means of column chromatography, being finally eluted with benzene/petroleum ether (1/1), and was crystallised from benzene/petroleum ether. Yield >65%.

(*ix*). $Fe_2(CO)_3[P(OC_6H_5)_3]_3(SC_6H_5)_2$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $P(OC_6H_5)_3$ (1.86 g, 6.0 mmole) in benzene (*ca.* 100 ml) was irradiated with ultraviolet light for 8 h. The tris-substituted product was separated from the excess ligand and any bis-substituted derivative by means of column chromatography, being finally eluted with benzene/petroleum ether (1/1), and was crystallised from benzene/petroleum ether. Yield >45%.

(*x*). $Fe_2(CO)_5[(C_6H_5)_2PCH_2P(C_6H_5)_2](SC_6H_5)_2$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (0.41 g, 1.1 mmole) in petroleum ether (60–80°; *ca.* 60 ml) was refluxed for 5 min. The solution was filtered and cooled to −78°. The microcrystalline product which separated was isolated and dried thoroughly. Yield >70%.

(*xi*). $[Fe(CO)_2SC_6H_5]_2[(C_6H_5)_2PCH_2P(C_6H_5)_2]$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (0.41 g, 1.1 mmole) in toluene (*ca.* 100 ml) was refluxed for 1 h. The solution was filtered and the solvent removed under reduced pressure. The residue was crystallised from benzene/petroleum ether and the product so obtained recrystallised from dichloromethane/petroleum ether. Yield >70%.

(*xii*). $Fe(CO)_3(SC_6H_5)_2Fe(CO)[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (0.4 g, 1.0 mmole) in benzene (*ca.* 60 ml) was refluxed for 15 min. The solution was filtered and concentrated to a small volume. The compound was precipitated by the addition of petroleum ether. Yield >40%.

(*xiii*). $\{[Fe(CO)_2SC_6H_5]_2[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]\}_2$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) in petroleum ether (80–100°; *ca.* 25 ml) at *ca.* 70° was added to a solution of $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (0.4 g, 1.0 mmole) in petroleum ether (80–100°; *ca.* 60 ml) under reflux. The resultant solution was refluxed for 3 min. The crystalline compound which separated on cooling was isolated and dried thoroughly. Yield >75%.

(*xiv*). $[Fe(CO)_2C_6H_5]_2[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (0.4 g, 1.0 mmole) in toluene (*ca.* 60 ml) was refluxed for 2 h. The solution was filtered and the solvent removed under reduced pressure. The residue was dissolved in a minimum of benzene and transferred to an alumina column. The column was eluted in turn with benzene/petroleum ether (1/3) and benzene to afford a red band which was collected. The compound isolated from this solution was crystallised from benzene/petroleum ether. Yield >40%.

(*xv*). $\{[Fe(CO)_2SC_6H_5]_2[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]\}_n$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (0.4 g, 1.0 mmole) in ethanol (*ca.* 60 ml) was refluxed for 1 h. The compound which separated from solution was isolated and dried thoroughly. Yield >70%.

(*xvi*). $Fe(CO)_2[(C_6H_5)_2PC_2H_4P(C_6H_5)_2](SC_6H_5)_2$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ (1.0 g, 2.5 mmole) in xylene (*ca.* 60 ml) was refluxed for 1 h. The solution was filtered and the solvent removed under reduced pressure. The residue was dissolved in a minimum of benzene and transferred to an alumina column. The column was eluted with benzene/petroleum ether (3/1) to afford an orange band which was shown by means of infrared spectroscopy to be $Fe(CO)_3[(C_6H_5)_2PC_2H_4P(C_6H_5)_2]$. Elution of the column with dichloromethane/benzene (2/1) afforded a red band which was collected. The solvent was removed under reduced pressure and the residue crystallised from benzene/petroleum ether. Yield >40%.

(*xvii*). $Fe(CO)_3(SC_6H_5)_2Fe(CO)[(C_6H_5)_2PC_2H_2P(C_6H_5)_2]$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ (0.6 g, 1.5 mmole) in benzene (*ca.* 60 ml) was refluxed for 1 h. The solution was filtered and the solvent removed under reduced pressure. The residue was crystallised from benzene/petroleum ether and the product so obtained recrystallised from dichloromethane/petroleum ether. Yield >75%.

(*xviii*). $Fe(CO)_2[(C_6H_5)_2PC_2H_2P(C_6H_5)_2](SC_6H_5)_2$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ (1.0 g, 2.5 mmole) in benzene (*ca.* 100 ml) was irradiated with ultraviolet light for 5 h. The two products were separated by following the procedure described in (*xvi*). $Fe(CO)_3(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ was identified by means of infrared while $Fe(CO)_2[(C_6H_5)_2PC_2H_2P(C_6H_5)_2](SC_6H_5)_2$ was crystallised from benzene/petroleum ether. Yield of the latter compound >50%.

(*xix*). $Fe(CO)_3(SC_6H_5)_2Fe(CO)[(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]$

A solution of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ (0.41 g, 1.0 mmole) in petroleum ether (60–80°; *ca.* 80 ml) was refluxed for 3 h. The compound which separated from solution was isolated, washed with petroleum ether and dried thoroughly. Yield >35%.

(*xx*). $[Fe(CO)_2SC_6H_5]_2[(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2]$

The compound was obtained by heating a mixture of $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ (0.45 g, 1.1 mmole) in xylene (*ca.* 60 ml) under reflux for 1 h and was isolated in pure form by the procedure described in (*xi*). Yield >70%.

(*xxi*). $[Fe(CO)_2SC_6H_5]_2[(C_6H_5)_2AsCH_2As(C_6H_5)_2]$

The compound was obtained by heating $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $(C_6H_5)_2AsCH_2As(C_6H_5)_2$ (0.57 g, 1.2 mmole) in toluene (*ca.* 60 ml) under reflux for 6 h, and was isolated in pure form by the procedure described in (*xi*). Yield >60%.

(*xxii*). $[Fe(CO)_2SC_6H_5]_2[(C_6H_5)_2AsC_2H_4As(C_6H_5)_2]$

The compound was obtained by heating $[Fe(CO)_3SC_6H_5]_2$ (0.5 g, 1.0 mmole) and $(C_6H_5)_2AsC_2H_4As(C_6H_5)_2$ (0.58 g, 1.2 mmole) in xylene (*ca.* 60 ml) under reflux for 3 h, and was isolated in pure form by the procedure described in (*xi*). Yield >60%.

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.

REFERENCES

1 R. J. Haines and C. R. Nolte, *J. Organometal. Chem.*, 36 (1972) 163.
2 J. A. de Beer, R. J. Haines, R. Greatrex and N. N. Greenwood, *J. Organometal. Chem.*, 27 (1971) C33.
3 W. Hieber and A. Zeidler, *Z. Anorg. Allg. Chem.*, 329 (1964) 92.
4 J. A. de Beer, R. J. Haines, R. Greatrex and N. N. Greenwood, *J. Chem. Soc. A*, (1971) 3271.
5 R. H. B. Mais, P. G. Owston and D. T. Thompson, *J. Chem. Soc. A*, (1967) 1735.
6 L. F. Dahl and C. Wei, *Inorg. Chem.*, 2 (1963) 328.
7 J. A. de Beer, unpublished results.
8 R. B. King, *J. Amer. Chem. Soc.*, 84 (1962) 2460.
9 G. Bor, *J. Organometal. Chem.*, 11 (1968) 195.
10 T. A. Manuel, *Inorg. Chem.*, 2 (1963) 854.
11 J. Lewis, R. S. Nyholm, S. S. Sandhu and M. H. B. Stiddard, *J. Chem. Soc.*, (1964) 2825.
12 W. Hieber and P. Spacu, *Z. Anorg. Allg. Chem.*, 233 (1937) 353.
13 W. Hieber and W. Beck, *Z. Anorg. Allg. Chem.*, 305 (1960) 265.
14 R. J. Haines and A. L. du Preez, *J. Amer. Chem. Soc.*, 91 (1969) 769.
15 R. J. Haines and A. L. du Preez, *J. Chem. Soc. A*, (1970) 2341.
16 R. J. Haines and A. L. du Preez, *Chem. Commun.*, (1968) 1513.
17 R. J. Haines and A. L. du Preez, *Inorg. Chem.*, 8 (1969) 1459.
18 R. J. Haines, A. L. du Preez and G. T. W. Wittmann, *Chem. Commun.*, (1968) 611.
19 S. F. A. Kettle and L. E. Orgel, *J. Chem. Soc.*, (1960) 3890.
20 J. Chatt and F. A. Hart, *J. Chem. Soc.*, (1960) 1385.
21 A. M. Aguiar and D. Daigle, *J. Amer. Chem. Soc.*, 86 (1964) 2299.
22 G. Ewart, A. P. Lane, J. McKechnie and D. S. Payne, *J. Chem. Soc.*, (1964) 1543.