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REACTIONS OF METAL CARBONYL DERIVATIVES

XIII*. REACTION OF BIS[μ-(TERT-BUTYLSULPHIDO)TRICARBONYLIRON] WITH TERTIARY AND DITERTIARY PHOSPHINES AND PHOSPHITES

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)

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SUMMARY

The ligands L = $P(C_2H_5)_3$, $P(C_6H_5)_3$, $P(OCH_3)_3$ and $P(OC_6H_5)_3$ react with $[Fe(CO)_3(S\text{-}t\text{-}C_4H_9)]_2$ to give mono-substituted $Fe_2(CO)_5L(S\text{-}t\text{-}C_4H_9)_2$ or bis-substituted $[Fe(CO)_2L(S\text{-}t\text{-}C_4H_9)]_2$ depending on the reaction conditions. With the exception of $[Fe(CO)_2P(C_2H_5)_3(S\text{-}t\text{-}C_4H_9)]_2$, the latter derivatives occur both in solution and in the solid state as a single isomer in which the ligands L are bonded *trans* to the metal–metal bond. Whereas an asymmetrically bis-substituted product, $Fe(CO)_3(S\text{-}t\text{-}C_4H_9)_2Fe(CO)L'$ is formed in the reaction of $[Fe(CO)_3(S\text{-}t\text{-}C_4H_9)]_2$ with L' = *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$, symmetrically bis-substituted derivatives $[Fe(CO)_2(S\text{-}t\text{-}C_4H_9)]_2L'$, in which the ligand bridges the two iron atoms, are produced in the corresponding reactions involving L' = $(C_6H_5)_2P(CH_2)_nP(C_6H_5)_2$ ($n = 1$ and 2). The NMR spectrum of $[Fe(CO)_2P(OCH_3)_3(S\text{-}t\text{-}C_4H_9)]_2$, as well as those of the complexes $[Fe(CO)_2P(OCH_3)_3SR]_2$ (R = CH_3 and i-C_3H_7) which have also been synthesised in this study, is interpreted in terms of a virtual coupling effect.

INTRODUCTION

A previous study[2] revealed that bis-substituted derivatives of the type $[Fe(CO)_2L(SC_6H_5)]_2$ (L = tertiary phosphine or phosphite) occur as one of two isomeric forms or as a mixture of both in solution and the solid state. For instance while $[Fe(CO)_2P(C_6H_5)_3(SC_6H_5)]_2$ and $[Fe(CO)_2P(OC_6H_5)_3(SC_6H_5)]_2$ exist in solution and in the crystalline state as isomers with a structure in which the ligands are bonded *trans* to the metal–metal bond (*cf.* Fig. 1A), the compound $[Fe(CO)_2P(OCH_3)_3(SC_6H_5)]_2$ occurs in the solid phase as an isomer of structure analogous to that represented in Fig. 1B[2]. Furthermore, while the infrared data for $[Fe(CO)_2P(C_2H_5)_3$-

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* For Part XII see ref. 1.

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

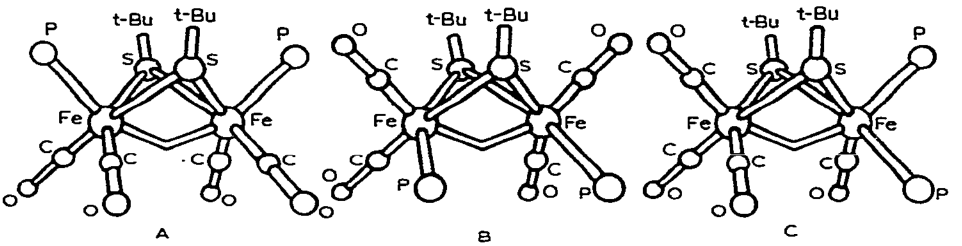

Fig. 1. Proposed structures of the derivatives of type A, *e.g.* $[Fe(CO)_2P(C_6H_5)_3(S\text{-}t\text{-}C_4H_9)]_2$, type B, *e.g.* $[Fe(CO)_2(S\text{-}t\text{-}C_4H_9)]_2[(C_6H_5)_2PCH_2P(C_6H_5)_2]$ and type C, *e.g.* $Fe(CO)_3(S\text{-}t\text{-}C_4H_9)_2Fe(CO)[(C_6H_5)_2PC_2H_2P(C_6H_5)_2]$, showing the stereochemistry of the iron atoms only.

TABLE 1

MELTING POINTS AND ANALYTICAL AND MOLECULAR WEIGHT DATA

Compound[a,b]	*M.p.*[c] (°*C*)	*Analyses found (calcd.) (%)* *C*	*H*	*S*	*P*	*Mol.wt.*[d] *Found* (*calcd.*)
$Fe_2(CO)_5PEt_3(S\text{-}t\text{-}Bu)_2$	Oil	41.6 (41.6)	5.7 (6.1)			
$Fe_2(CO)_5PPh_3(S\text{-}t\text{-}Bu)_2$	75	53.7 (53.8)	5.0 (4.8)	9.1 (9.3)	4.6 (4.5)	676 (692)
$Fe_2(CO)_5P(OMe)_3(S\text{-}t\text{-}Bu)_2$	91	34.6 (34.7)	4.6 (4.9)	11.6 (11.6)	5.8 (5.6)	552 (554)
$Fe_2(CO)_5P(OPh)_3(S\text{-}t\text{-}Bu)_2$	98	50.4 (50.3)	4.6 (4.5)	8.8 (8.7)	4.1 (4.2)	749 (740)
$[Fe(CO)_2PEt_3(S\text{-}t\text{-}Bu)]_2$	110	45.0 (45.2)	7.6 (7.6)			617 (638)
$[Fe(CO)_2PPh_3(S\text{-}t\text{-}Bu)]_2$	250 d.p.	62.4 (62.2)	5.3 (5.2)	6.9 (6.9)	6.6 (6.7)	880 (927)
$[Fe(CO)_2P(OMe)_3(S\text{-}t\text{-}Bu)]_2$	125	33.1 (33.3)	5.7 (5.6)	9.8 (9.9)	9.4 (9.5)	661 (650)
$[Fe(CO)_2P(OPh)_3(S\text{-}t\text{-}Bu)]_2$	158	56.3 (56.4)	4.6 (4.7)	6.1 (6.3)	6.1 (6.1)	994 (1023)
$[Fe(CO)_2(S\text{-}t\text{-}Bu)]_2[Ph_2PCH_2PPh_2]$[e]	181	56.2 (56.5)	5.0 (5.1)	8.1 (8.2)	7.7 (7.9)	786 (786)
$[Fe(CO)_2(S\text{-}t\text{-}Bu)]_2[Ph_2PC_2H_4PPh_2]$[f]	210	56.9 (57.0)	5.2 (5.3)	7.8 (8.0)	7.5 (7.7)	805 (800)
$Fe(CO)_3(S\text{-}t\text{-}Bu)_2Fe(CO)[Ph_2PC_2H_2PPh_2]$[g]	95	57.1 (57.2)	4.9 (5.0)	8.2 (8.0)	7.7 (7.8)	797 (798)
$[Fe(CO)_2P(OMe)_3(SMe)]_2$	Oil	25.6 (25.5)	4.4 (4.3)		10.8 (10.9)	
$[Fe(CO)_2P(OMe)_3(S\text{-}i\text{-}Pr)]_2$	102	30.7 (30.9)	5.2 (5.2)	10.4 (10.3)	9.8 (10.0)	610 (622)
$[Fe(CO)_2P(OMe)_3(SBz)]_2$	124	40.2 (40.1)	4.4 (4.5)			709 (718)

[a] Abbreviations: Me, CH_3; Et, C_2H_5; i-Pr, i-C_3H_7; t-Bu, t-C_4H_9; Ph, C_6H_5; Bz, $CH_2C_6H_5$. [b] All compounds are red, diamagnetic and non-electrolytes in acetone. [c] Abbreviation: d.p., decomposition point. [d] Measured in benzene. [e] Fe analysis: found, 14.5; calcd., 14.2. [f] Fe analysis: found 14.0; calcd. 14.0. [g] Colour: brown.

$(SC_6H_5)]_2$ are consistent with this compound occurring as a single isomer of structure of type B in solution, the spectra of $[Fe(CO)_2P(OR)_3(SC_6H_5)]_2$ ($R=CH_3$, C_2H_5 and $i\text{-}C_3H_7$) are best explained in terms of the presence of two isomers in solution[2]. In contrast, all bis-substituted derivatives of the type $[Fe(CO)_2L(SR)]_2$ ($R=CH_3$ or C_2H_5; L = tertiary phosphine, phosphite, arsine or stibine) thus far isolated have been shown to exist solely as the isomer of structure A in both solution and the solid state[3].

A study of the reactions of $[Fe(CO)_3(S\text{–}t\text{-}C_4H_9)]_2$ with various Group V donor ligands has now been made in order to determine whether the differences in isomerism behaviour of $[Fe(CO)_2L(SC_6H_5)]_2$ and $[Fe(CO)_2L(SR)]_2$ ($R=CH_3$ or C_2H_5) are of electronic or stereochemical origin. The results of this study are presented here.

RESULTS AND DISCUSSION

The tertiary phosphines $L=PR_3$ ($R=C_2H_5$ and C_6H_5) and phosphites $L=P(OR')_3$ ($R'=CH_3$ and C_6H_5) readily effected the replacement of a carbonyl group in $[Fe(CO)_3(S\text{–}t\text{-}C_4H_9)]_2$ on reaction in benzene at room temperature, giving monosubstituted derivatives characterised as $Fe_2(CO)_5L(S\text{–}t\text{-}C_4H_9)_2$. The molecular symmetry of these derivatives is low, and as a result the position of carbonyl substitution could not be established from the infrared data, summarised in Table 2. The NMR spectrum of $Fe_2(CO)_5P(C_6H_5)_3(S\text{–}t\text{-}C_4H_9)_2$ contains a single peak corresponding to the tertiary butyl protons whereas the spectra of $Fe_2(CO)_5P(OR)_3(S\text{–}t\text{-}C_4H_9)_2$ ($R=CH_3$ and C_6H_5) contain three peaks associated with these groups. It is thus apparent that the former compound occurs as the *syn*-isomer[4] in solution, whereas the latter are present as both the *anti*- and *syn*-isomers in this phase. The overlap of the $P(C_2H_5)_3$ and $S\text{–}t\text{-}C_4H_9$ resonances in the spectrum of $Fe_2(CO)_5P(C_2H_5)_3(S\text{–}t\text{-}C_4H_9)_2$ prevented the determination of the isomeric form of this derivative in solution.

Bis-substituted derivatives of the type $[Fe(CO)_2L(S\text{–}t\text{-}C_4H_9)]_2$ were formed on treating $[Fe(CO)_3(S\text{–}t\text{-}C_4H_9)]_2$ with the ligands $L=PR_3$ ($R=C_2H_5$ and C_6H_5) and $P(OR')_3$ ($R'=CH_3$ and C_6H_5) in toluene or xylene under reflux. Higher yields of these compounds were obtained by irradiating benzene solutions of $[Fe(CO)_3(S\text{–}t\text{-}C_4H_9)]_2$ and the above ligands with ultraviolet light however. The infrared spectra, both solution and solid state, of $[Fe(CO)_2L(S\text{–}t\text{-}C_4H_9)]_2$ [$L=P(C_6H_5)_3$, $P(OCH_3)_3$ and $P(OC_6H_5)_3$], as well as the solid state spectrum of $[Fe(CO)_2P(C_2H_5)_3(S\text{–}t\text{-}C_4H_9)]_2$, exhibit similar band patterns in the carbonyl stretching region, comprising three peaks of relative intensity strong, medium and strong. This number of infrared-active C–O stretching modes is consistent with the structure represented in Fig. 1A, belonging to the molecular point group C_{2v}*. Seven C–O stretching peaks are observed in the solution spectrum of $[Fe(CO)_2P(C_2H_5)_3(S\text{–}t\text{-}C_4H_9)]_2$ however. This is readily explaned in terms of the presence of more than one isomer in solution.

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* A more detailed discussion on the assignment of the structures of the related derivatives $[Fe(CO)_2L(SR)]_2$ (L = tertiary phosphine, phosphite, arsine or stibine; $R=CH_3$ or C_2H_5) has been presented previously[3].

TABLE 2

INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPIC DATA[a]

Compound	*C–O Stretching frequencies*[b] *(cm^{-1})*	*CH$_3$ resonance*[c,d]	*Assignment*
$Fe_2(CO)_5PEt_3(S\text{-}t\text{-}Bu)_2$	2035 ms, 1979 s, 1968 ms, 1959 ms, 1918 m[e].	See discussion	
$Fe_2(CO)_5PPh_3(S\text{-}t\text{-}Bu)_2$	2038 ms, 1981 s, 1963 ms, 1958 (sh), 1924 w[e].	8.91 s	S-t-Bu (*syn*-disposed)
$Fe_2(CO)_5P(OMe)_3(S\text{-}t\text{-}Bu)_2$	2040 s, 1985 s, 1977 (sh), 1961 s, 1933 w[e].	8.61 s, 8.65 s, 8.70 s 6.25 d (^3J(PH) 11.0 Hz)	S-t-Bu (*syn*- and *anti*-disposed) OMe
$Fe_2(CO)_5P(OPh)_3(S\text{-}t\text{-}Bu)_2$	2043 ms, 1994 s, 1981 (sh), 1966 ms, 1939 w[e].	8.68 s, 8.72 s, 8.81 s	S-t-Bu (*syn*- and *anti*-disposed)
$[Fe(CO)_2PEt_3S\text{-}t\text{-}Bu]_2$	1973 s, 1930 ms, 1903 s[f]; 1984 s, 1978 ms, 1946 s, 1939 ms, 1918 s, 1914 ms, 1894 w[e].	See discussion	
$[Fe(CO)_2PPh_3(S\text{-}t\text{-}Bu)]_2$	1973 s, 1931 ms, 1911 s[g]; 1987 s, 1944 ms, 1923 s[h].	9.36 s	S-t-Bu (*syn*-disposed)
$[Fe(CO)_2P(OMe)_3(S\text{-}t\text{-}Bu)]_2$	1985 s, 1941 ms, 1917 s[g]; 2001 s, 1959 ms, 1936 s[e].	8.63 s 6.21 t [$\lvert{}^3J(PH)+{}^6J(P'H)\rvert$ 11.2 Hz]	S-t-Bu (*syn*-disposed) OMe
$[Fe(CO)_2P(OPh)_3(S\text{-}t\text{-}Bu)]_2$	2006 s, 1960 s, 1945 s[g]; 2011 s, 1969 ms, 1953 s[e].	8.90 s	S-t-Bu (*syn*-disposed)
$[Fe(CO)_2(S\text{-}t\text{-}Bu)]_2(Ph_2PCH_2PPh_2)$	1984 ms, 1954 s, 1925 s, 1904 w[e].	8.61 s, 8.81 s	S-t-Bu
$[Fe(CO)_2(S\text{-}t\text{-}Bu)]_2(Ph_2PC_2H_4PPh_2)$	1985 ms, 1954 s, 1926 s, 1904 w[e].	8.61 s, 8.66 s	S-t-Bu
$[Fe(CO)_2(S\text{-}t\text{-}Bu)]_2(Ph_2PNEtPPh_2)$	1982 m, 1952 s, 1915 ms[f].	N.m.	

$Fe(CO)_3(S\text{-}t\text{-}Bu)_2Fe(CO)(Ph_2PC_2H_2PPh_2)$	2019 s, 1954 s, 1948 s, 1905 w^e.	8.90 s, 9.47 s	S-t-Bu
$[Fe(CO)_2P(OMe)_3(SMe)]_2$	2006 s, 1966 ms, 1943 s^e.	7.94 s, 8.60 s	S-t-Bu (isomer B)
		8.02 s	S-t-Bu (isomer A)
		6.25 d [^3J(PH) 11.2 Hz]	OMe (isomer B)
		6.27 t [$\|^3J(PH)+{}^6J(P'H)\|$ 11.5 Hz]	OMe (isomer A)
$[Fe(CO)_2P(OMe)_3(S\text{-}i\text{-}Pr)]_2$	1990 s, 1943 ms, 1919 s^g	8.66 d [^3J(HH) 6.5 Hz]	S-i-Pr (isomer B)
	2003 s, 1960 ms, 1938 s^e	8.82 d [^3J(HH) 6.5 Hz]	
		8.73 d [^3J(HH) 6.5 Hz]	S-i-Pr (isomer A)
		6.23 d [^3J(PH) 11 Hz]	OMe (isomer B)
		6.26 t [$\|^3J(PH)+{}^6J(P'H)\|$ 11.3 Hz]	OMe (isomer A)
$[Fe(CO)_2P(OMe)_3(SBz)]_2$	1996 ms, 1958 s, 1938 s, 1909 m^g; 2003 ms, 1967 s, 1928 ms, 1920 sh^e.	6.42 d [^3J(PH) 11.2 Hz]	OMe (isomer B)
		6.48 t [$\|^3J(PH)+{}^6J(P'H)\|$ 11.2 Hz]	OMe (isomer A)

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[a] Abbreviations: Me, CH_3; Et, C_2H_5; i-Pr, i-C_3H_7; t-Bu, t-C_4H_9; Ph, C_6H_5; Bz, $CH_2C_6H_5$.

[b] Abbreviations: s, strong; ms, medium strong; m, medium; w, weak; sh, shoulder.

[c] τ scale (TMS reference); measured in $CDCl_3$ at 38°.

[d] Abbreviations: s, singlet; d, doublet; t, triplet.

[e] Measured in cyclohexane.

[f] Measured in KBr disc.

[g] Measured as nujol mull.

[h] Measured in CCl_4.

[i] Measured in dichloromethane.

The NMR spectra of $[Fe(CO)_2L(S\text{-}t\text{-}C_4H_9)]_2$ $[L = P(C_6H_5)_3$, $P(OCH_3)_3$ and $P(OC_6H_5)_3]$ contain a single peak assigned to the protons of the tertiary butyl sulphido groups which is indicative of these compounds occurring as the *syn*-isomer in solution. The $P(C_2H_5)_3$ and $S\text{-}t\text{-}C_4H_9$ resonances in the spectrum of $[Fe(CO)_2P(C_2H_5)_3(S\text{-}t\text{-}C_4H_9)]_2$ overlap with the result that the latter cannot be unequivocally assigned. The methyl resonance corresponding to the ligand protons in the spectrum of $[Fe(CO)_2P(OCH_3)_3(S\text{-}t\text{-}C_4H_9)]_2$ consists of a triplet comprised of a broad central component and two sharp outer peaks of separation 11.2 Hz. This band pattern is characteristic of a virtual coupling effect resulting from the coupling between the phosphorus nuclei of the two $P(OCH_3)_3$ ligands being considerably greater than that between a phosphorus nucleus and the protons of the adjacent methoxy groups[5]. Methoxy resonances of similar band patterns are also observed in the spectra of $[Fe(CO)_2P(OCH_3)_3(SCH_3)]_2$ and $[Fe(CO)_2P(OCH_3)_3(S\text{-}i\text{-}C_3H_7)]_2$. Significantly these compounds also occur primarily or solely in solution as the isomer with structure A*. In contrast the methyl resonances associated with the methoxy groups in the NMR spectra of $[Fe(CO)_2P(OCH_3)_3(SC_6H_5)]_2$[2] and $[Fe(CO)_2P(OCH_3)_3(SCH_2C_6H_5)]_2$, which have been shown to be present primarily as isomer B in solution**, occur as doublets. Tertiary phosphine and phosphite transition metal derivatives displaying virtual coupling effects have received considerable attention of late but these effects have only been noted for mononuclear systems. The virtual coupling between trimethyl phosphite ligands bonded to different metal atoms in $[Fe(CO)_2P(OCH_3)_3(SR)]_2$ $(R = CH_3$, $i\text{-}C_3H_7$ and $t\text{-}C_4H_9)$ observed here is therefore of interest. It is suggested that it may be related to the ligands being disposed in positions *trans* to a metal–metal bond thereby facilitating transmission of the virtual coupling effect through this bond.

Irradiation of a benzene solution of $[Fe(CO)_3(S\text{-}t\text{-}C_4H_9)]_2$ and a large excess of $P(OCH_3)_3$ with ultraviolet light led to the formation of a compound which was presumed to be $Fe_2(CO)_3[P(OCH_3)_3]_3(S\text{-}t\text{-}C_4H_9)_2$ on the basis of its infrared spectrum [ν(C–O) 1965 s and 1910 s cm^{-1}, measured in dichloromethane; *cf.* $Fe_2(CO)_3[P(OCH_3)_3]_3(SCH_3)_2$: ν(C–O) 1968 s and 1915 s cm^{-1}, measured in dichloromethane[3]]. The rapid decomposition of this compound to $[Fe(CO)_2P(OCH_3)_3(S\text{-}t\text{-}C_4H_9)]_2$ on attempted column separation prevented its being isolated in a pure state however. Tris-substituted products were not detected in any of the reactions involving $P(C_2H_5)_3$, $P(C_6H_5)_3$ and $P(OC_6H_5)_3$.

The reactions of $[Fe(CO)_3(S\text{-}t\text{-}C_4H_9)]_2$ with different ditertiary phosphines were also studied and shown to give different products depending on the ligand involved and the reaction conditions. Thus treatment of $[Fe(CO)_3(S\text{-}t\text{-}C_4H_9)]_2$ with the "diphosphines" $(C_6H_5)_2PCH_2P(C_6H_5)_2$, $(C_6H_5)_2PC_2H_4P(C_6H_5)_2$ and $(C_6H_5)_2PN(C_2H_5)P(C_6H_5)_2$ in toluene or xylene under reflux readily afforded products characterised as $[Fe(CO)_2(S\text{-}t\text{-}C_4H_9)]_2$(Diphosphine) and shown to have

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* These derivatives were assigned structure A on the basis of the infrared evidence using the arguments employed in the elucidation of the structures of $[Fe(CO)_2L(S\text{-}t\text{-}C_4H_9)]_2$ $[L = P(C_6H_5)_3$ $P(OCH_3)_3$ and $P(OC_6H_5)_3]$ (*vide supra*).

** $[Fe(CO)_2P(OCH_3)_3(SCH_2C_6H_5)]_2$ was assigned structure B on the basis of the similarity of the band pattern in the C–O stretching region in its infrared spectrum with those observed in the spectra of compounds of the type $[Fe(CO)_2(SR)]_2$(Diphosphine) $(R = CH_3$, C_2H_5 or C_6H_5; Diphosphine = ditertiary phosphine) for which the structures have been previously established[2,3].

the structure illustrated in Fig. 1B*. In contrast the reaction of $[Fe(CO)_3(S\text{-}t\text{-}C_4H_9)]_2$ with *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ under similar conditions gave $Fe(CO)_3(S\text{-}t\text{-}C_4H_9)_2Fe(CO)[(C_6H_5)_2PC_2H_2P(C_6H_5)_2]$ shown to have the structure depicted in Fig. 1C*. This compound was obtained in higher yield by irradiating a benzene solution of $[Fe(CO)_3(S\text{-}t\text{-}C_4H_9)]_2$ and a slight excess of *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$ with ultraviolet light for a short period however. Mono-substituted derivatives were detected in the above reactions by monitoring them by means of infrared spectroscopy. No attempt was made to isolate these species.

The results of this study together with those relating to the reactions of $[Fe(CO)_3(SR)]_2$ ($R=CH_3$ and C_2H_5) and $[Fe(CO)_3(SC_6H_5)]_2$ with various tertiary phosphines and phosphites[2,3] serve to indicate that the structures of the derivatives of the type $[Fe(CO)_2L(SR)]_2$ in solution are not necessarily directly related to the stereochemistry of the group R and the ligand L but rather suggest that the isomerism behaviour of these derivatives is more of electronic origin.

EXPERIMENTAL

The compound $[Fe(CO)_3(S\text{-}t\text{-}C_4H_9)]_2$[6] and the ligands $(C_6H_5)_2P(CH_2)_n\text{-}P(C_6H_5)_2$ ($n=1$ and 2)[7], *cis*-$(C_6H_5)_2PC_2H_2P(C_6H_5)_2$[8] and $(C_6H_5)_2PN(C_2H_5)P\text{-}(C_6H_5)_2$[9] were synthesised according to literature methods and slight modifications of them. $[Fe(CO)_3(S\text{-}i\text{-}C_3H_7)]_2$ and $[Fe(CO)_3(SCH_2C_6H_5)]_2$ were obtained similarly to $[Fe(CO)_3(S\text{-}t\text{-}C_4H_9)]_2$. All experiments were performed under nitrogen. The photochemical reactions employed a Hanovia medium pressure arc photochemical reactor. Chromatographic separations were carried out 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 A60A and HA100 and Perkin–Elmer R20 instruments respectively. The elemental analyses were performed by the Alfred Bernhardt Microanalytical Laboratory, Elbach-über-Engelskirchen, West Germany. Molecular weights were determined by Mr. G. J. Roberts, National Chemical Research Laboratory, C.S.I.R., Pretoria.

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 (ca. 60 ml) of $[Fe(CO)_3(S\text{-}t\text{-}C_4H_9)]_2$ and the appropriate ligand was refluxed until reaction was complete as determined by monitoring with infrared. The solution was filtered and the solvent removed under reduced pressure. The product was separated from the residue, where necessary, by means of column chromatography and crystallised from the solvent mixture listed in Table 3.

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* See refs. 2 and 3 for more detailed discussions on the assignments of the structures of derivatives of this type.

TABLE 3

PREPARATIVE DETAILS[a]

Reaction product	*Reactants and quantities*	*Reaction procedure (time)*	*Reaction solvent*	*Reaction temp. (°C)*	*Crystallised from*	*Yield (%)*
$Fe_2(CO)_5PEt_3(S\text{-}t\text{-}Bu)_2$	$[Fe(CO)_3(S\text{-}t\text{-}Bu)]_2$ (0.46 g, 1.0 mmole) PEt_3 (0.24 g, 2.0 mmole)	A (1 h)	Benzene	25	Isolated as oil	N.m.
$Fe_2(CO)_5PPh_3(S\text{-}t\text{-}Bu)_2$	$[Fe(CO)_3(S\text{-}t\text{-}Bu)]_2$ (0.46 g, 1.0 mmole) PPh_3 (0.29 g, 1.1 mmole)	A (3 h)	Benzene	80	Dichloromethane/ methanol	80
$Fe_2(CO)_5P(OMe)_3(S\text{-}t\text{-}Bu)_2$	$[Fe(CO)_3(S\text{-}t\text{-}Bu)]_2$ (0.46 g, 1.0 mmole) $P(OMe)_3$ (0.15 g, 1.2 mmole)	A (30 min)	Benzene	80	Pet. ether	80
$Fe_2(CO)_5P(OPh)_3(S\text{-}t\text{-}Bu)_2$	$[Fe(CO)_3(S\text{-}t\text{-}Bu)]_2$ (0.46 g, 1.0 mmole) $P(OPh)_3$ (0.34 g, 1.1 mmole)	A (30 min)	Benzene	80	Methanol	80
$[Fe(CO)_2PEt_3(S\text{-}t\text{-}Bu)]_2$	$[Fe(CO)_3(S\text{-}t\text{-}Bu)]_2$ (0.46 g, 1.0 mmole) PEt_3 (0.30 g, 2.5 mmole)	B (2 h)	Benzene	25	Pet. ether	50
$[Fe(CO)_2PPh_3(S\text{-}t\text{-}Bu)]_2$	$[Fe(CO)_3(S\text{-}t\text{-}Bu)]_2$ (0.46 g, 1.0 mmole) PPh_3 (1.31 g, 5.0 mmole)	B (2 h)	Benzene	25	Benzene/pet. ether	40
$[Fe(CO)_2P(OMe)_3(S\text{-}t\text{-}Bu)]_2$	$[Fe(CO)_3(S\text{-}t\text{-}Bu)]_2$ (0.46 g, 1.0 mmole) $P(OMe)_3$ (0.37 g, 3.0 mmole)	A (3 h)	Toluene	110	Pet. ether/ methanol	60
$[Fe(CO)_2P(OPh)_3(S\text{-}t\text{-}Bu)]_2$	$[Fe(CO)_3(S\text{-}t\text{-}Bu)]_2$ (0.46 g, 1.0 mmole) $P(OPh)_3$ (0.93 g, 3.0 mmole)	B (4 h)	Benzene	25	Benzene/pet. ether	65
$Fe_2(CO)_3[P(OMe)_3]_3(S\text{-}t\text{-}Bu)_2$	$[Fe(CO)_3(S\text{-}t\text{-}Bu)]_2$ (0.46 g, 1.0 mmole) $P(OMe)_3$ (1.12 g, 9.0 mmole)	B (2 h)	Benzene	25	Not isolated	N.m.
$[Fe(CO)_2(S\text{-}t\text{-}Bu)]_2(Ph_2PCH_2PPh_2)$	$[Fe(CO)_3(S\text{-}t\text{-}Bu)]_2$ (0.46 g, 1.0 mmole) $Ph_2PCH_2PPh_2$ (0.46 g, 1.2 mmole)	A (30 min)	Xylene	140	Dichloromethane/ methanol	80
$[Fe(CO)_2(S\text{-}t\text{-}Bu)]_2(Ph_2PC_2H_4PPh_2)$	$[Fe(CO)_3(S\text{-}t\text{-}Bu)]_2$ (0.46 g, 1.0 mmole) $Ph_2PC_2H_4PPh_2$ (0.48 g, 1.2 mmole)	A (30 min)	Xylene	140	Dichloromethane/ methanol	60
$[Fe(CO)_2(S\text{-}t\text{-}Bu)]_2(Ph_2PNEtPPh_2)$	$[Fe(CO)_3(S\text{-}t\text{-}Bu)]_2$ (0.46 g, 1.0 mmole) $Ph_2PNEtPPh_2$ (0.50 g, 1.2 mmole)	A (2 h)	Toluene	110	Not isolated	N.m.
$Fe(CO)_3(S\text{-}t\text{-}Bu)_2Fe(CO)(Ph_2PC_2H_2PPh_2)$	$[Fe(CO)_3(S\text{-}t\text{-}Bu)]_2$ (0.46 g, 1.0 mmole) *cis*-$Ph_2PC_2H_2PPh_2$ (0.44 g, 1.1 mmole)	B (30 min)	Benzene	25	Dichloromethane/ methanol	55
$[Fe(CO)_2P(OMe)_3(SMe)]_2$	$[Fe(CO)_3(SMe)]_2$ (0.37 g, 1.0 mmole) $P(OMe)_3$ (0.37 g, 3.0 mmole)	A (2 h)	Benzene	80	Isolated as oil	80
$[Fe(CO)_2P(OMe)_3(S\text{-}i\text{-}Pr)]_2$	$[Fe(CO)_3(S\text{-}i\text{-}Pr)]_2$ (0.43 g, 1.0 mmole) $P(OMe)_3$ (0.37 g, 3.0 mmole)	A (12 h)	Toluene	110	Methanol	80
$[Fe(CO)_2P(OMe)_3(SBz)]_2$	$[Fe(CO)_3(SBz)]_2$ (0.53 g, 1.0 mmole) $P(OMe)_3$ (0.37 g, 3.0 mmole)	A (4 h)	Toluene	110	Pet. ether	90

[a] Abbreviations: Me, CH_3; Et, C_2H_5; i-Pr, i-C_3H_7; t-Bu, t-C_4H_9; Ph, C_6H_5; Bz, $CH_2C_6H_5$.

Method B

A solution of $[Fe(CO)_3(S-t-C_4H_9)]_2$ and the appropriate ligand in benzene (ca. 80 ml) was irradiated with ultraviolet light 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.

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