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Stereochemistry of the bis-substituted derivatives of bis-(μ-alkyl- and -phenylsulphidotricarbonyliron)

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The current interest in the synthesis and reactivity of bridged sulphido complexes of iron, particularly in view of their possible relevance to non-heme iron protein systems, and in the catalytic properties of compounds of the type $[Fe(CO)_2LPR_2]_2$ (L = phosphorus donor ligand, R = alkyl group)[1], prompts this report on a study of the reactions of $[Fe(CO)_3SR]_2$ ($R = CH_3, C_2H_5, t\text{-}C_4H_9$ and C_6H_5) with various donor ligands.

Treatment of $[Fe(CO)_3SR]_2$ ($R = CH_3$ or C_2H_5) with various tertiary phosphines or phosphites resulted in either mono-, bis- or tris-substitution in the parent dimer depending on the reaction conditions and the ligand employed. The infrared spectra of the bis-substituted derivatives $[Fe(CO)_2LSR]_2$ (L = tertiary phosphine or phosphite) show similar band patterns in the carbonyl stretching region, with three peaks of relative intensity strong, medium and strong (*e.g.* $[Fe(CO)_2P(C_6H_5)_3SCH_3]_2$ see Table 1). This number of infrared-active carbonyl stretching modes is consistent with a structure in which the carbonyl groups *trans* to the metal–metal bond in $[Fe(CO)_3SR]_2$ (ref. 2) have been replaced (isomer A). The appearance of a single quadrupole doublet in the Mössbauer spectrum of $[Fe(CO)_2P(C_6H_5)_3SCH_3]_2$ (see Table 1) is also consistent with symmetric substitution. It should be noted that a previous study reported the synthesis of $[Fe_2(CO)_5L(SR)_2]$, $[Fe(CO)_2LSR]_2$ and $[Fe(CO)_3(SR)_2Fe(CO)(C_6H_5)_2PC_2H_4P(C_6H_5)_2]$ [$R = C_2H_5$ or C_6H_5; $L = P(C_2H_5)_3, P(C_6H_{11})_3$ or $P(C_6H_5)_3$] but no spectroscopic data were recorded[3].

The reactions of $[Fe(CO)_3SR]_2$ ($R = CH_3$ or C_2H_5) with the ditertiary phosphines $(C_6H_5)_2PR'R(C_6H_5)_2$ [$R' = CH_2, C_2H_2, C_2H_4$ or $N(C_2H_5)$] afforded a large range of products. These included derivatives in which mono; bis- or tris-substitution had been effected, compounds in which the ligand acts as either a monodentate or a bidentate and derivatives in which the diphosphine behaves as either a chelating or a bridging ligand. $[Fe_2(CO)_4L'(SR)_2]$ (L' = ditertiary phosphine) was isolated in two isomeric forms. The infrared spectra of the derivatives occurring in one isomeric form contain four C–O stretching peaks with the frequencies of these peaks and the energy difference between those of highest and lowest frequency being

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TABLE 1

INFRARED AND MÖSSBAUER SPECTROSCOPIC DATA

Compound	C–O stretching frequencies[a] (cm^{-1})	Chemical isomer shift[b] δ/(mm · sec^{-1})	Quadrupole splitting Δ/(mm · sec^{-1})
$[Fe(CO)_2P(C_6H_5)_3SCH_3]_2$	1989(s), 1948(m), 1931(s)[c]	0.07 ± 0.01	0.74 ± 0.01
$[\{Fe(CO)_2SCH_3\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2]$	1988(m), 1965(s), 1927(s), 1916(sh)[c]	0.05 ± 0.01	1.08 ± 0.01
$[Fe^A(CO)_3(SCH_3)_2Fe^B(CO)(C_6H_5)_2PC_2H_2P(C_6H_5)_2]$	2023(s), 1958(s), 1951(s), 1913(w)[c]	A 0.04 ± 0.01	A 1.20 ± 0.01
		B 0.13 ± 0.01	B 0.63 ± 0.01
$[Fe(CO)_2P(OCH_3)_3SC_6H_5]_2$	1999(ms), 1954(s), 1929(ms), 1913(m)[d]	0.04 ± 0.01	1.00_5 ± 0.01
	2017(ms), 1975(s), 1959(m), 1949(m), 1928(w)[c]		

[a] Abbreviations: s, strong; ms, medium strong; m, medium; w, weak; sh, shoulder. [b] Data at 77K relative to iron. [c] Measured in cyclohexane. [d] Measured as nujol mull.

consistent with symmetric substitution (*e.g.* $[\{Fe(CO)_2SCH_3\}_2(C_6H_5)_2PCH_2P(C_6H_5)_2]$ see Table 1). The Mösbauer spectra of these compounds also suggest that the iron environments are equivalent, only a doublet being observed in each of the examples studied. A structure in which the ligand bridges two iron atoms as shown (isomer B) is proposed for these derivatives. The infrared, Mösbauer and mass spectral data for the derivatives occurring in the other isomeric form (*e.g.* $[Fe(CO)_3(SCH_3)_2Fe(CO)(C_6H_5)_2PC_2H_2P(C_6H_5)_2]$ see Table 1) are consistent with a structure in which the diphosphine ligand is chelated to a single iron atom (isomer C). For instance the separation between the peaks of highest and lowest frequency in the infrared spectra of these compounds is considerably larger than the corresponding separation for isomers A and B while the Mössbauer spectra contain two non-coincident quadrupole doublets. In addition the mass spectra contain a series of ions of the type $[Fe(CO)_nL']^+$ ($n = 0$–3). These ions are not observed in the mass spectra of isomers A and B. It is significant that in the reactions involving ditertiary phosphines there was no evidence for the formation of compounds of isomeric form A and in which the ligand acts as a bidentate. This is to be expected based on stereochemical considerations.

Products analogous to those formed in the reactions of $[Fe(CO)_3SR]_2$ ($R = CH_3$ or C_2H_5) with $(C_6H_5)_2PR'P(C_6H_5)_2$ [$R' = CH_2, C_2H_2, C_2H_4$ or $N(C_2H_5)$] were isolated from the reactions of $[Fe(CO)_3SC_6H_5]_2$ with these ligands. Further the bis-substituted derivative isolated from the reaction of $[Fe(CO)_3SC_6H_5]_2$ with $P(C_6H_5)_3$ was observed to occur as isomer A both in solution and in the solid state. However, based on infrared evidence, $[Fe(CO)_2P(C_2H_5)_3SC_6H_5]_2$ was shown to exist as isomer B in solution; this compound was isolated as an oil and thus its structure in the solid state could not be established. Furthermore $[Fe(CO)_2P(OCH_3)_3SC_6H_5]_2$ was found to exist solely as this isomer in the solid state while the infrared and NMR spectra of $[Fe(CO)_2P(OR)_3SC_6H_5]_2$ ($R = CH_3, C_2H_5$ and $i\text{-}C_3H_7$) in solution ($[Fe(CO)_2P(OC_2H_5)_3SC_6H_5]_2$ and $[Fe(CO)_2P(O\text{-}i\text{-}C_3H_7)_3SC_6H_5]_2$ were isolated as oils) can only be explained in terms of both isomers A and B occurring in solution (*e.g.* $[Fe(CO)_2P(OCH_3)_3SC_6H_5]_2$ see Table 1). It is proposed that the monomer $[Fe(CO)_2P(OCH_3)_3SC_6H_5]$ is an intermediate in the isomerism of $[Fe(CO)_2P(OCH_3)_3SC_6H_5]_2$ on dissolution. This monomer is analogous to $[Fe(CO)_3SC_6H_5]$ postulated to form in solution on dissolution of $[Fe(CO)_3SC_6H_5]_2$ (refs. 4 and 5).

The reactions of $[Fe(CO)_3S\text{-}t\text{-}C_4H_9]_2$ with various tertiary phosphines and phosphites were observed to parallel the corresponding reactions involving $[Fe(CO)_3SR]_2$ ($R = CH_3$ or C_2H_5). This is interpreted as demonstrating that the contrasting behaviour of $[Fe(CO)_3SR]_2$ ($R = CH_3$ or C_2H_5) and $[Fe(CO)_3SC_6H_5]_2$ towards certain tertiary phosphines and phosphites is of electronic rather than of stereochemical origin.

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