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Preliminary communication

Some novel dinuclear derivatives of iron containing both bridging carbonyls and bridging phosphido or sulphido groups

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Recent communications on the use of the transition metal derivatives π-$C_5H_5Ti\{N(CH_3)_2\}_3$ [1], $(\pi$-$C_5H_5)_2Ti(XR)_2$ ($R = CH_3, X = S$ [2]; $R = C_6H_5, X = S$ or Se [3]) and $(\pi$-$C_5H_5)_2Mo(SR)_2$ ($R = CH_3$ or n-C_4H_9) [4] as chelating donor ligands to prepare mixed metal complexes, *e.g.* π-$C_5H_5Ti\{N(CH_3)_2\}_3M(CO)_3$ (M = Cr, Mo or W), $\{(\pi$-$C_5H_5)_2Ti(SR)_2Mo(CO)_4$ ($R = CH_3$ or C_6H_5) and $[(\pi$-$C_5H_5)_2Mo(SCH_3)_2Rh(C_8H_{12})]PF_6$ and on the synthesis of some heteronuclear bridged phosphido derivatives through the interaction of ligands on different metal substrates, *e.g.*

$$Fe(CO)_4[P(C_6H_5)_2H] + \pi\text{-}C_3H_5Co(CO)_3 \rightarrow Fe(CO)_4P(C_6H_5)_2Co(CO)_3 + C_3H_6 \quad \text{(ref. 5)}$$

prompts this report on the synthesis and reactions of some novel dinuclear bridged phosphido and sulphido derivatives of iron in which the two iron atoms are in different oxidation states.

Treatment of the ligand $P(C_6H_5)_2Cl$ with the anion $[\pi$-$C_5H_5Fe(CO)_2]^-$ leads to the cleavage of the phosphorus–chlorine bond and the formation of π-$C_5H_5Fe(CO)_2P(C_6H_5)_2$. Significantly a similar cleavage is also effected when the ligand is bonded to a metal atom. Thus $[\pi$-$C_5H_5Fe(CO)_2]^-$ reacts with $Fe(CO)_4P(C_6H_5)_2Cl$ to afford a red crystalline compound characterised by elemental analysis, molecular weight determination and NMR spectroscopy as π-$C_5H_5Fe_2(CO)_6P(C_6H_5)_2$. This formulation was confirmed by the mass spectrum which shows the molecular ion (*m/e* 530 for ^{56}Fe isotope),

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and the stepwise loss of six carbonyl groups. The compound is also obtained by reacting the "tertiary phosphine" π-$C_5H_5Fe(CO)_2P(C_6H_5)_2$ with a suspension of $Fe_2(CO)_9$ in benzene at room temperature. The infrared spectrum of π-$C_5H_5Fe_2(CO)_6P(C_6H_5)_2$ contains C–O stretching peaks corresponding to terminal carbonyls only, and the ^{57}Fe Mössbauer spectrum (Fig.1a) comprises a pair of partially overlapping quadrupole split doublets arising from non-equivalent iron atoms. The assignment indicated in the figure is the only one acceptable on the basis of chemical isomer shifts for related compounds and yields the parameters listed in Table 1; those associated with the outer doublet (B) are diagnostic of five coordination in this type of molecule[6]. The structure shown in Fig.2a is thus proposed.

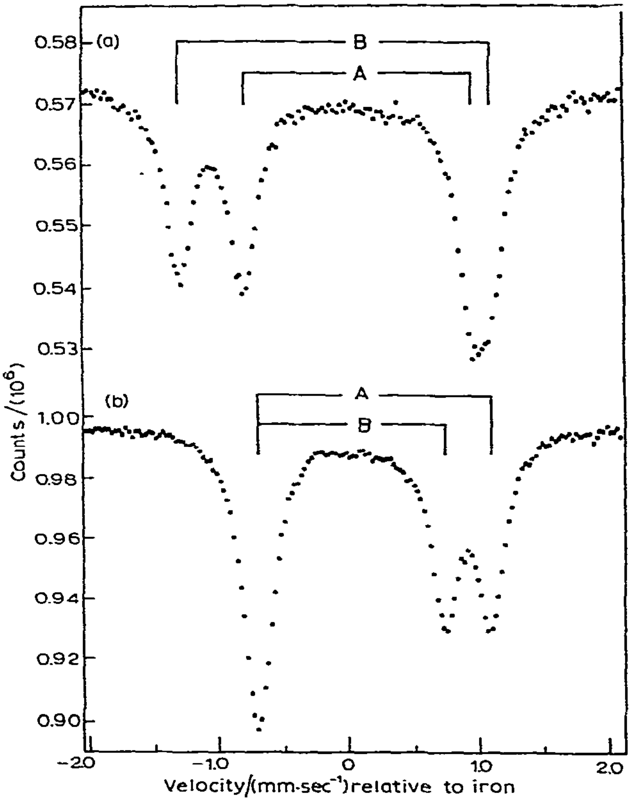

Fig.1. Mössbauer spectra of (a) π-$C_5H_5Fe_2(CO)_6P(C_6H_5)_2$ and (b) π-$C_5H_5Fe_2(CO)_5P(C_6H_5)_2$.

Attempts were made to obtain bridging sulphido derivatives analogous to π-$C_5H_5Fe_2(CO)_6P(C_6H_5)_2$ by reacting π-$C_5H_5Fe(CO)_2SR$ (R = CH_3, t-C_4H_9 or C_6H_5) with $Fe_2(CO)_9$. Spectroscopic evidence for the formation of π-$C_5H_5Fe_2(CO)_6SR$ was obtained but the products could not be isolated owing to their instability.

The general applicability of π-$C_5H_5Fe(CO)_2P(C_6H_5)_2$ as a donor ligand was demonstrated by its reactivity towards other transition metal derivatives. For example, it

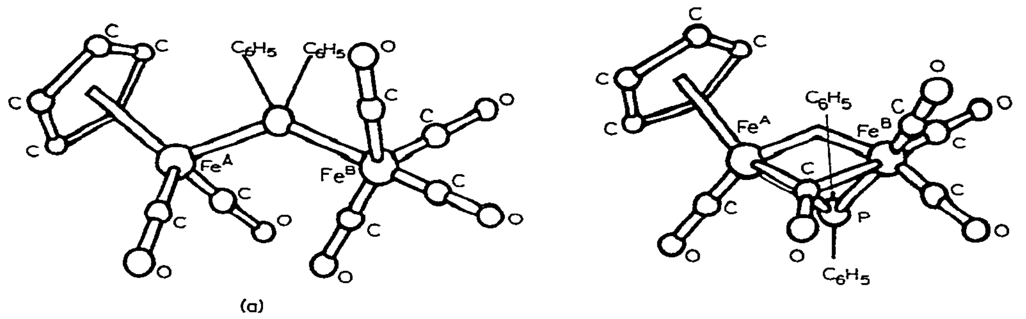

Fig.2. Proposed structures of (a) π-$C_5H_5Fe_2(CO)_6P(C_6H_5)_2$ (I) and (b) π-$C_5H_5Fe_2(CO)_5P(C_6H_5)_2$ (II) showing the stereochemistry of the iron atoms only.

displaces the chloride in π-$C_5H_5Fe(CO)_2Cl$ to afford $\{[\pi\text{-}C_5H_5Fe(CO)_2]_2P(C_6H_5)_2\}$ Cl and readily cleaves the halogen bridges in $[C_8H_{12}RhCl]_2$ and $[Rh(CO)_2Cl]_2$.

Irradiation of a benzene solution of π-$C_5H_5Fe_2(CO)_6P(C_6H_5)_2$ with ultraviolet light effects the replacement of a carbonyl by an "iron group" and the formation of a purple compound characterised as π-$C_5H_5Fe_2(CO)_5P(C_6H_5)_2$. The mass spectrum of this compound exhibits the molecular ion (*m/e* 502) and peaks corresponding to the successive loss of five carbonyl groups, otherwise it is identical to that of π-$C_5H_5Fe_2(CO)_6P(C_6H_5)_2$. A structure (Fig.2b) based on the known structures of $[\pi\text{-}C_5H_5Fe(CO)_2]_2$ [7,8] and $[Fe(CO)_3SC_2H_5]_2$ [9] and analogous to that recently established for π-$C_5H_5Fe_2(CO)_5C_2H_2COCH_3$ [10] is proposed for this derivative on the basis of its infrared and Mössbauer spectra. The former shows the presence of a bridging carbonyl group (ν(C–O) = 1747 cm^{-1}) and the latter (Fig.1b, Table 1) indicates non-equivalent iron atoms, neither of which are five coordinate. As for π-$C_5H_5Fe_2(CO)_6P(C_6H_5)_2$, the doublet with the larger chemical isomer shift is assigned to the cyclopentadienyl-bearing iron atom[11].

TABLE 1
MÖSSBAUER PARAMETERS AT 77 K

Compound [a]		Chemical isomer shift $\delta/(mm \cdot sec^{-1})$	Quadrupole splitting $\Delta/(mm \cdot sec^{-1})$
(I) π-$C_5H_5Fe_2(CO)_6P(C_6H_5)_2$	(A)	+0.09 ± 0.01	1.75 ± 0.01
	(B)	−0.09 ± 0.01	2.38 ± 0.01
(II) π-$C_5H_5Fe_2(CO)_5P(C_6H_5)_2$	(A)	+0.21 ± 0.01_5	1.77 ± 0.03
	(B)	+0.03 ± 0.01_5	1.42 ± 0.03

[a] (A) and (B) identify the individual iron environments and their associated resonances referred to in the Figures. In computing values for II the left hand peak has been treated as a singlet. It can, however, be fitted reasonably with two peaks separated by ~0.03 mm · sec^{-1} and this possibility has been taken into account in the errors quoted. Chemical isomer shifts relative to iron.

π-$C_5H_5Fe_2(CO)_6SR$ (R = CH_3, t-C_4H_9 or C_6H_5) were also shown to liberate carbon monoxide on irradiation with ultraviolet light but π-$C_5H_5Fe_2(CO)_5S$-t-C_4H_9 was the only product of type π-$C_5H_5Fe_2(CO)_5SR$ which could be isolated; $[\pi$-$C_5H_5Fe(CO)_2]_2$ and $[Fe(CO)_3SR]_2$ were the sole products in the other two reactions. π-$C_5H_5Fe_2(CO)_5S$-t-C_4H_9, separated from $[\pi$-$C_5H_5Fe(CO)_2]_2$ and $[Fe(CO)_3S$-t-$C_4H_9]_2$ by means of column chromatography and isolated as an impure green microcrystalline material is extremely reactive, however, and decomposes rapidly. The formation of π-$C_5H_5Fe_2(CO)_5P(C_6H_5)_2$ and related compounds by the method described above suggests that metal–metal interactions in π-$C_5H_5Fe_2(CO)_6P(C_6H_5)_2$ and analogous derivatives occurs.

The reactions of π-$C_5H_5Fe_2(CO)_5P(C_6H_5)_2$ with various tertiary phosphines and phosphites were shown to afford three types of products, depending on the reaction conditions. Thus ultraviolet irradiation of benzene solutions of this compound and the ligands L = PR_3 (R = C_2H_5 or C_6H_5) or $P(OR)_3$ (R = CH_3, C_2H_5, i-C_3H_7 or C_6H_5) affords solely or primarily green crystalline derivatives of composition π-$C_5H_5Fe_2(CO)_4LP(C_6H_5)_2$. These compounds contain a bridging carbonyl group and are thus structurally similar to π-$C_5H_5Fe_2(CO)_5P(C_6H_5)_2$. In contrast the reactions of this latter derivative with the ligands L = $P(C_2H_5)_3$ or $P(OR)_3$ (R = CH_3, C_2H_5, i-C_3H_7 or C_6H_5) in benzene under reflux afford π-$C_5H_5Fe_2(CO)_5LP(C_6H_5)_2$ and/or π-$C_5H_5Fe_2(CO)_4L_2P(C_6H_5)_2$ which were shown to contain terminal carbonyls only, and can therefore be considered as substituted derivatives of π-$C_5H_5Fe_2(CO)_6P(C_6H_5)_2$.

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REFERENCES

1 D.C. Bradley and A.S. Kasenally, *Chem. Commun.*, (1968) 1430.
2 K.K. Joshi, R. Wardle and V.A. Wilson, *Inorg. Nucl. Chem. Letters*, 6 (1970) 49.
3 H. Köpf and K.H. Däthlein, *Angew. Chem. Intern. Ed.*, 8 (1969) 980.
4 A.R. Dias and M.L.H. Green, *Chem. Commun.*, (1969) 962.
5 B.C. Benson, R. Jackson, K.K. Joshi and D.T. Thompson, *Chem. Commun.*, (1968) 1506.
6 R. Greatrex and N.N. Greenwood, *Discuss. Faraday Soc.*, 47 (1969) 126 and references therein.
7 O.S. Mills, *Acta Cryst.*, 11 (1958) 620.
8 R.F. Bryan, P.T. Greene, D.S. Field and M.J. Newlands, *Chem. Commun.*, (1969) 1477.
9 L.F. Dahl and C.H. Wei, *Inorg. Chem.*, 2 (1963) 328.
10 V.G. Andrianov and Yu.T. Struchkov, *Chem. Commun.*, (1968) 1590.
11 T.C. Gibb, R. Greatrex, N.N. Greenwood and D.T. Thompson, *J. Chem. Soc. A*, (1967) 1663.