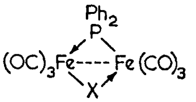
Binuclear Metal Carbonyls having both Phosphorus and Sulphur Bridges

By B. E. JOB, R. A. N. MCLEAN, and D. T. THOMPSON

(*Imperial Chemical Industries Limited, Petrochemical and Polymer Laboratory, The Heath, Runcorn, Cheshire*)

COMPOUNDS in which two transition-metal atoms are linked by two phosphorus or two sulphur bridges are well known.[1] We now describe the use of a new air-stable phosphine for the preparation of a binuclear iron compound having both a sulphur- and a phosphorus-bridge in the same molecule. The preparation of an analogue of this sulphur compound having two diphenylphosphido-bridging groups is also reported. Compound (Ia) is the first example of a binuclear metal carbonyl in which the metal atoms are linked by sulphur and phosphorus atoms having hydrocarbon substituents, although related binuclear manganese compounds having fluorocarbon substituents on the bridges are known.[1,2]



(Ia : X = SPh)
(Ib : X = PPh_2)

Phenylthiodiphenylphosphine (II) is obtained in 80—90% yields by treating sodium thiophenolate with a solution of diphenylchlorophosphine in ether under dry nitrogen.

$$\mathrm{Ph_2PCl + NaSPh \rightarrow \underset{(II)}{Ph_2PSPh} + NaCl}$$

The mass spectrum of (II) confirms its identity. In view of the marked sensitivity of tetraphenyldiphosphine to oxidation, especially in solution, TABLE

Physical data for the compounds (I) *and* (II)

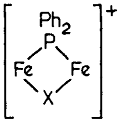
Compound	Description	M.p.	Dipole moment (D) (benzene)	Infrared spectra CO bands (cm.$^{-1}$) (hexane)
(Ia)	Orange prisms	163—165°	2·00	2060m, 2036*, 2020vs, 2018*, 1998ms, 1979ms, 1966vw
(Ib)	Yellow prisms	178—179°	3·52	2055m, 2052*, 2018vs, 1994m, 1990*, 1966s, 1957w
(II)	Colourless needles	50—52°		

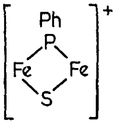
* Shoulder.

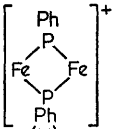
it is noteworthy that $PhSPPh_2$ is stable in air, even in hot chloroform solution, from which it can be conveniently recrystallised.

Phenylthiodiphenylphosphine with iron pentacarbonyl in benzene at 150° for 24 hr. affords μ-phenylthio-μ-diphenylphosphidobis(tricarbonyliron) (Ia) in 75% yield. Di-μ-diphenylphosphidobis(tricarbonyliron) (Ib) is obtained in 55% yield by heating iron pentacarbonyl with tetraphenyldiphosphine at 200—220° for 17 hr. Comparison of the infrared carbonyl frequencies and dipole moments obtained for the compounds (I) (see Table) with data[3–5] for di-μ-dimethylphosphido-bridged compounds previously described supports assignment of the structure depicted above to these two new bridged compounds. Electronic spectra and combustion analyses confirm these assignments.

The mass spectra of the compounds (I) include prominent peaks corresponding to the molecular ions and to fragments formed by successive loss of six carbonyl ligands. The resultant ions may be represented by structure (III). Further fragmentation occurs to a limited extent by loss of a single phenyl group but strong peaks consistent with (IV) or (V) indicate that elimination of two phenyl groups is favoured.


(III)


(IV)


(V)

Attempts to prepare a compound of formula $(OC)_4FePPh_2SPhFe(CO)_4$ have not been successful, although a preparation of $(OC)_4FePPh_2$-$PPh_2Fe(CO)_4$, m.p. 163°, is claimed.[6]

Dodecacarbonyltriruthenium reacts with $PhSPPh_2$ to afford the ruthenium analogue of (Ia), and the reactions of other metal carbonyls with Ph_2PSPh are being studied. The results of these investigations and a full account of the mass spectra will be reported later.

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