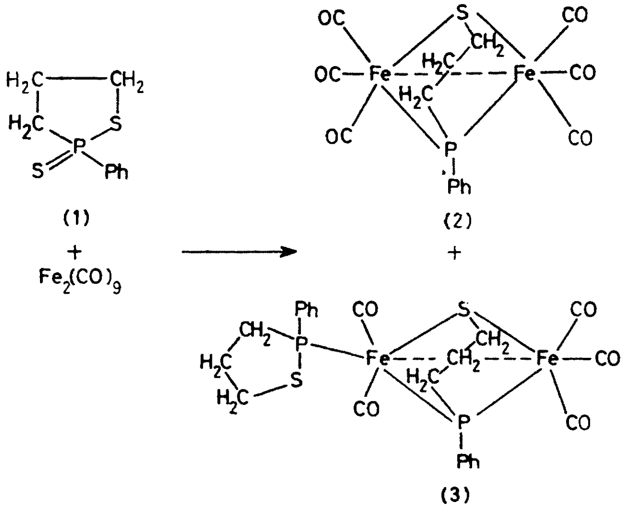
Reaction of $Fe_2(CO)_9$ with a Dithiophosphinate: *X*-Ray Crystal Structures of Two Complexes formed by Selective Cleavage of the Thiophosphoryl Bond

By FRANÇOIS MATHEY*
(*Equipe I.R.C.H.A.-C.N.R.S., Boite Postale* 28, 94320 *Thiais, France*)
and MARIE-BERNARD COMARMOND and DINO MORAS
(*Laboratoire de Cristallochimie et de Chimie Structurale, Institut Le Bel, Université Louis Pasteur, Strasbourg Cedex, France*)

Summary *X*-Ray crystal structure analysis of the two complexes formed shows that the reaction of $Fe_2(CO)_9$ with a cyclic dithiophosphinate occurs in two steps: firstly a complex with Fe–S–Fe and Fe–P–Fe bridges is formed which then reduces selectively the P–S thiophosphoryl bond of another dithiophosphinate molecule to give a thiophosphinite complex in which the original heterocycle is retained.

THE reduction–complexation of $P^V=S$ compounds by organometallic substrates leading to P^{III} complexes is now a well established procedure.[1,2] However, when P–S(C) bonds are present in the phosphorus compound the organometallic reagent cannot discriminate between the P···S single and double bonds and the reduction–complexation fails.[3] *A priori* it seems difficult to break the far stronger thiophosphoryl bond without affecting the weaker P–S(C) single bond. However, we have now achieved this and we describe here our preliminary results.



When the cyclic dithiophosphinate (**1**)[3] (1 g) was treated in boiling toluene with an excess of $Fe_2(CO)_9$ (6 g), two new complexes (**2**) and (**3**) were obtained. They were easily separated by chromatography on silica gel (hexane–benzene, 80:20). Complex (**2**) [m.p. 118 °C, *m/e* (70 eV) 462 (M^+, 41%) and 266 (100%); δ (^{31}P; $CDCl_3$; 85% H_3PO_4 as external standard, downfield shifts +ve) 133 p.p.m.; ν_{CO} (decalin) 2070m 2076vs, 1998s, 1975s, and 1964w cm^{-1}] was obtained as an orange solid after 5 h reaction; complex (**3**) [m.p. 182 °C, *m/e* 462 (M^+, 12%) and 476 (100%); δ (^{31}P, solvent, *etc.* as for **2**) 132·8 and 98·9 (J_{PP} 82 Hz); 132·5 and 99·3 (J_{PP} 73 Hz) p.p.m.; ν_{CO} (decalin) 2034m, 1982vs, 1970br,m, 1954s, and 1927w cm^{-1}] was obtained as a red solid after 18 h reaction. The splitting of the ^{31}P n.m.r. signals for (**3**) implies the presence of at least two isomers. It is not possible to determine whether these are P–P diastereoisomers or *cis–trans*-isomers. The crystal used for the *X*-ray analysis of (**3**) contains the *cis*-form with two enantiomorphs (space group $P2_1/c$). Suitable crystals for *X*-ray analysis of (**2**) and (**3**) were obtained by slow evaporation of CCl_4–MeOH solutions.

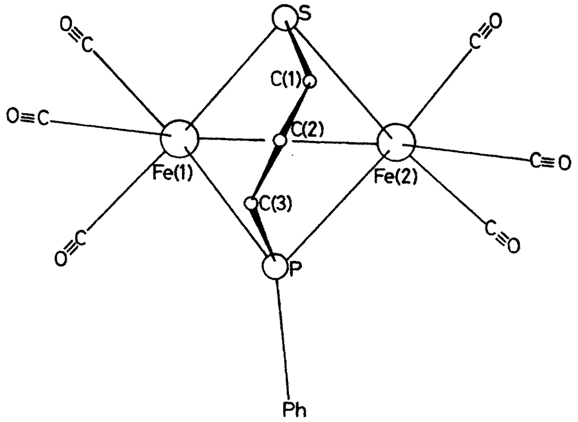


FIGURE 1. Molecular structure of complex (**2**). Hydrogen atoms have been omitted for clarity. Bond lengths: Fe(1)–Fe(2) 2·557(1), Fe(1)–S 2·261(1), Fe(2)–S 2·256(1), Fe(1)–P 2·201(1), and Fe(2)–P 2·208(1) Å.

Crystal data: Complex (**2**). $C_{15}H_{11}Fe_2O_6PS$; M = 461·99, monoclinic, space group $P2_1/c$, a = 10·562, b = 14·424, c = 12·797 Å, β = 105·842°, U = 1876 Å^3, Z = 4, D_m = 1·6, D_c = 1·64 g cm^{-3}. Anisotropic thermal parameters were used for all non-hydrogen atoms, and least-square refinement yielded a standard residual R^1 = 0·040 and a weighted residual R^2 = 0·051 [Philips PW1100 diffractometer, Mo-K_α radiation, 3216 reflections, $\sigma(I) < 0·3\,I$, $\theta < 30°$].

Complex (**3**): $C_{23}H_{22}Fe_2O_5P_2S_2$; M = 616·21, monoclinic, space group $P2_1/c$, a = 17·480, b = 8·733, c = 17·773 Å, β = 109·218°, U = 2562 Å^3, Z = 4, D_m = 1·6, D_c = 1·59 g cm^{-3}. Refinement has led to residuals R^1 = 0·047 and R^2 = 0·057 [Picker diffractometer, Mo-K_α radiation, 3480 reflections, $\sigma(I) < 0·3\,I$, θ_{max} = 30°].†

The molecular structures of complexes (**2**) and (**3**) are shown in Figures 1 and 2, respectively. In both compounds the two iron atoms, one sulphur, and one phosphorus atom form an 'open-book' structure, in which the Fe(1)–Fe(2) bond is the hinge. The angles between the Fe(1), Fe(2), S(1) and the Fe(1), Fe(2), P(1) planes are 103·07 in complex (**2**) and 102·73° in complex (**3**). The Fe–P (2·21) and Fe–S (2·26 Å) bond lengths are similar in the two compounds. The trimethylene bridges C(1)–C(2)–C(3) in (**2**) and C(21)–C(22)–C(23) in (**3**) link the sulphur atom to the phosphorus. The dihedral angles around the carbon–carbon bonds in the bridge (between 50 and 60°) show no constraints. In complex (**2**) for each iron atom, the co-ordination polyhedron (a distorted trigonal bipyramid) is completed by three carbonyl groups (average bond length C–O, 1·14; Fe–C, 1·78 Å). In complex (**3**) a five-membered heterocycle replaces one carbonyl group through an extra Fe(1)–P(2) bond [2.193(2) Å].

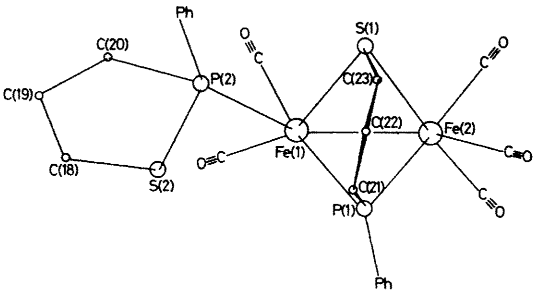


FIGURE 2. Molecular structure of complex (**3**). Bond lengths: Fe(1)–Fe(2) 2·579(1), Fe(1)–P(1) 2·205(2), Fe(2)–P(1) 2·221(2), Fe(1)–P(2) 2·193(2), Fe(1)–S(1) 2·275(2), Fe(2)–S(1) 2·271(2), and S(2)–P(2) 2·087(2) Å.

Thus, complex (**2**) results from the superposition of two known reactions: (i) the desulphuration of the P=S bond by $Fe_2(CO)_9$,[2] and (ii) the insertion of an $Fe_2(CO)_6$ species into the P–S(C) single bond.[4] In contrast (**3**) results from the hitherto unknown reduction–complexation of the P=S exocyclic bond of (**1**) by (**2**). It was checked separately that the reaction of equimolar quantities of (**1**) and (**2**) indeed afforded (**3**) in 58% yield (21 h in boiling toluene). The ability of (**2**) to discriminate between the P=S and CH_2–S–P sulphur atoms is perhaps partly related to its steric bulk.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The structure factor table is available as a supplementary publication No. SUP 22545 (22 pp.) from the British Library. For details of obtaining this material see Notice to Authors, No. 7, *J.C.S. Dalton* or *Perkin I* and *II*, Index Issues.

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