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STRUCTURAL STUDY OF IRON CARBONYL DERIVATIVES V *. SYNTHESIS AND CRYSTAL AND MOLECULAR STRUCTURE OF μ-(SC_6H_5)-μ-$(P(C_6H_5)_2)Fe_2(CO)_6$

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Summary

The title compound has been prepared by a new method and its crystal structure determined by a single-crystal X-ray study. The complex crystallizes in the orthorhombic space group $Pna2_1$, with a 16.544(1) Å, b 10.256(4) Å, c 28.76(1) Å and $Z = 8$. Full-matrix least-squares refinement of positional and anisotropic thermal parameters of the 68 non-hydrogen atoms (H atoms were included and held fixed) of the two independent molecules, with 2172 reflections, led to $R = 0.069$ and $R'' = 0.056$. The compound has the usual structure of iron carbonyl derivatives with an Fe_2XX' core. The Fe—Fe mean bond length is 2.610(2) Å. A comparison is made with similar derivatives having symmetric bridging systems Fe_2S_2 and Fe_2P_2.

Introduction

Binuclear complexes of iron carbonyl containing a metal—metal bond bridged through two ligands have been intensively studied recently, with emphasis on their structural features, their reactions and their possible applications in catalysis. We have been interested in determining crystal structures of such complexes with symmetric bridges Fe_2X_2, for example X = S, or with asymmetric ones Fe_2XX', where the two bridging ligands are different.

We report here the results of a single-crystal X-ray structural determination

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* For part IV see ref. 1.

of such a complex, with X = S and X′ = P, of formula μ-(SC_6H_5)-μ-($P(C_6H_5)_2$)-$Fe(CO)_6$, which we have prepared by a new method. Very recently, Mathey et al. [2] reported the structures of two similar complexes with an Fe_2SP core, and so we compare our results with those for these two complexes and also with those for derivatives having Fe_2S_2 and Fe_2P_2 cores.

Experimental

Synthesis of the complex

μ-(SC_6H_5)-μ-($P(C_6H_5)_2$)$Fe_2(CO)_6$, first described by Thompson et al. [3], has been synthesized by a different method, namely by ultraviolet irradiation with a high pressure mercury vapor lamp (Original Hanau TQ 150) of a mixture of two mol of $Fe(CO)_5$ with one mol of $P(C_6H_5)_2SC_6H_5$ in benzene. The complex is purified by crystallization in a CH_2Cl_2/pentane mixture at —20°C. The yield is about 35%. The compound has the same physical properties (melting point and ν(CO) frequencies) as that described by Thompson et al. [3].

X-ray crystallographic data

Crystals of $C_{24}H_{15}O_6PSFe_2$ (M = 574.1) are parallelepipeds of various sizes, red-brown and air-stable. They are found to be orthorhombic, with cell dimensions: a 16.544(1) Å, b 20.256(4) Å, c 28.76(1) Å, V = 4880 Å^3. The space group is $Pna2_1$, with Z = 8 and a calculated density of 1.56 g cm^{-3}. The unit-cell parameters, obtained from Weissenberg and precession photographs, have been refined using the θ angles of 25 reflections measured on a Nonius CAD-4 automatic diffractometer.

The intensities of 6630 independent reflections were collected at room temperature, for $2° < \theta < 30°$, on the automatic diffractometer, with a crystal of dimensions 0.10 × 0.12 × 0.13 mm. Owing to the size of the crystal and to the value of the absorption coefficient (μ 14.05 cm^{-1}) for the Mo-$K_{\bar{\alpha}}$ radiation used (λ 0.71069 Å), absorption corrections were deemed unnecessary.

The characteristics of diffractometer measurements were as follows: graphite monochromator, ω—2θ scan technique, scan angle: $S = 1.00 + 0.35 \text{ tg } \theta$ (in degrees), detector aperture: $D = 2.50 + 0.35 \text{ tg } \theta$ (in mm). Data processing was carried out using the program MAXE [4]. Corrections for Lorentz and polarization effects were applied, and reflections having $\sigma(I)/I > 1$ were considered to be unobserved. Finally, 2172 independent reflections were retained for the subsequent structure analysis.

Solution and refinement of the structure

The eight heavy atoms (4 Fe, 2 S and 2 P) of the asymmetric unit, constituted by two independent molecules, were located using the multisolution method with program MULTAN [5]. Many atoms of carbon and oxygen were also found by Fourier synthesis calculated with the normalized structure factors E of the set of phases having the best "figure of merit". Missing atoms were then located by Fourier-difference synthesis calculated on the basis of the heavy atoms parameters. Refinement of positional and thermal parameters, first isotropic, and then anisotropic, of the 68 non-hydrogen independent atoms (two molecules) led to a value of the factor $R = \Sigma(|F_0|—K|F_c|)/\Sigma|F_0|$ of 0.074.

The value of the weighted factor $R'' = [\Sigma\omega(|F_0|-K|F_c|)^2/\Sigma\omega|F_0|^2]^{1/2}$ is 0.063.

At this stage of the refinement, the positions of the 30 hydrogen atoms (all on phenyl rings) of the two independent molecules had been found on a Fourier-difference map. These atoms were included in calculated positions (C—H 1.0 Å, C—C—H 120°) and held fixed in further cycles of refinement, with isotropic thermal parameters equal to those of the carbon atoms to which they are bonded. The contribution of the hydrogen atoms is significant in lowering the R factor and giving a more homogeneous set of distances and angles for phenyl rings. After two last cycles of refinement of coordinates and anisotropic temperature factors for the 68 non-hydrogen atoms, final values of $R = 0.069$ and $R'' = 0.056$ were obtained.

Owing to the low data-to-parameter ratio, the change of isotropic to anisotropic temperature factors was performed in four cycles of refinement, only one half of molecule being treated in each cycle. During the last stages of the refinement, never more than 200 parameters were refined in one cycle.

No attempt was made to determine the absolute configuration of the molecule.

Full-matrix least-squares refinement were performed using SFLS-5 program [6]. The function minimized was $\Sigma\omega(|F_0|-K|F_c|)^2$. Atomic scattering factors, $\Delta f'$ and $\Delta f''$ coefficients of anomalous dispersion (here applied to Fe, S and P atoms) and weighting scheme are described in a previous publication [7].

Final atomic coordinates and anisotropic thermal parameters for the 60 non-hydrogen independent atoms, with estimated standard deviations in parentheses,

(continued on p. 206)

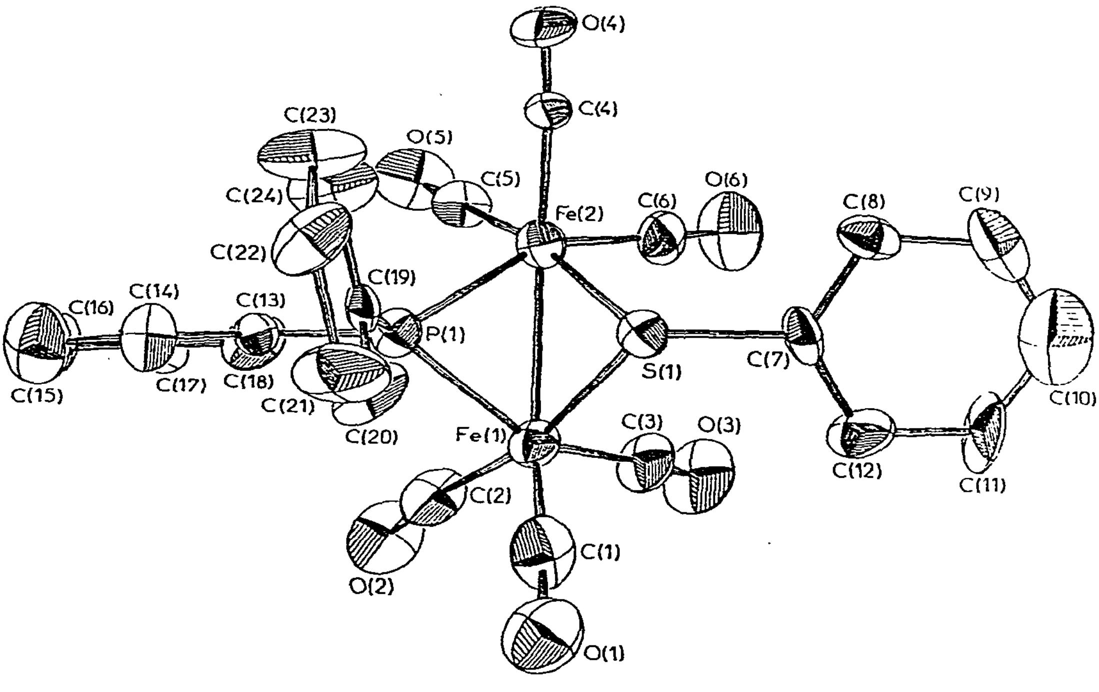

Fig. 1. ORTEP view of molecule I of $Fe_2(CO)_6$-μ-(SC_6H_5)-μ-$(P(C_6H_5)_2)$.

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS [a] FOR $Fe_2(CO)_6$-μ-(SC_6H_5)-μ-$(P(C_6H_5)_2)$

Coordinates				Anisotropic thermal parameters [b]					
	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Molecule I									
Fe(1)	2227(1)	1687(2)	5000	3.7(0.1)	2,9(0,1)	2,6(0.1)	0.1(0.1)	−0,2(0.1)	−0,5(0.1)
Fe(2)	3478(1)	2919(2)	5340(1)	2,7(0.1)	3.1(0,1)	2,9(0.1)	0,3(0,1)	0,4(0.1)	0(0.1)
S(1)	2830(3)	1228(4)	5694(2)	2,5(0.2)	2,8(0,2)	2,3(0.2)	0,2(0,2)	0,1(0.2)	−0,2(0.2)
P(1)	2198(3)	3624(5)	5358(2)	2,7(0,2)	2,7(0,2)	2,8(0,2)	0(0,2)	0,5(0,2)	−0,1(0.2)
O(1)	746(9)	339(9)	5252(5)	7,3(0,9)	5,6(0,8)	5,2(1.0)	−0,1(0,9)	0,1(0,5)	−0,9(0,7)
O(2)	1551(12)	2790(15)	4151(5)	15,4(1.2)	6,5(0,8)	3,5(0,6)	0,8(1.0)	−6,2(0,8)	0,7(0,7)
O(3)	3155(10)	−112(16)	4421(5)	10,3(1.1)	6,1(0,8)	4,6(1,0)	2,1(0,8)	1,0(0,8)	−3,2(0,7)
O(4)	4164(8)	3951(13)	6211(5)	7,1(0,9)	3,6(0,7)	3,9(0,7)	0,1(0,8)	−3,1(0,7)	−1,6(0,6)
O(5)	4072(8)	5039(14)	4772(5)	5,6(0,8)	7,5(0,9)	4,4(0,7)	−2,2(0,7)	1,0(0,5)	1,9(0,7)
O(6)	4817(8)	1249(14)	4979(6)	5,2(0,8)	7,1(0,8)	7,1(1,0)	2,6(0,7)	2,9(0,8)	−0,3(0,7)
C(1)	1364(13)	857(20)	5152(7)	4,9(1,2)	4,8(1,1)	5,0(1,3)	0,1(1,0)	1,5(0,9)	2,4(0,9)
C(2)	1816(13)	2466(20)	4492(8)	9,4(1,4)	4,1(1,0)	2,5(1,1)	−0,4(1,0)	−3,2(0,9)	0,3(0,7)
C(3)	2828(13)	535(19)	4664(7)	6,0(1,1)	3,8(1,0)	4,0(1,0)	0,9(0,9)	0,4(1,1)	−1,8(0,8)
C(4)	3950(10)	3536(16)	5879(7)	2,5(0,8)	1,9(0,8)	5,0(1,0)	−0,7(0,7)	−1,5(0,8)	0,2(0,6)
C(5)	3846(11)	4199(17)	4992(6)	4.1(0,9)	3,7(0,9)	1,5(1,1)	−1,3(0,8)	−0,1(0,8)	1,7(0,8)
C(6)	4283(11)	1855(19)	5119(8)	3.7(1,0)	2,8(0,9)	6,2(1,3)	−0,5(0,7)	−0,2(0,8)	1,4(0,8)
C(7)	3411(10)	−259(18)	5722(8)	1.6(0,8)	3,1(0,8)	4.1(1,0)	1,0(0,7)	0,5(0,9)	1,3(0,7)
C(8)	4104(11)	−285(19)	5996(6)	3.2(1.0)	4,3(1,0)	2,2(1,0)	−0,8(0.8)	−0,7(0,7)	0,6(0,7)
C(9)	4472(12)	−1533(24)	6068(8)	3,5(1,1)	6,8(1,4)	4,9(1,3)	1,0(1,2)	−0,2(1,0)	3,1(1,2)
C(10)	4210(16)	−2630(28)	5888(13)	8,1(1,0)	7,0(1,7)	8,6(2,0)	1,7(1,7)	1,7(1,5)	2,4(1,5)
C(11)	3549(15)	−2552(18)	5575(10)	9,2(1,6)	2,0(0,9)	8,2(1.7)	3,2(1.0)	−1,3(1,3)	−0,7(1,0)
C(12)	3147(12)	−1406(19)	5488(8)	3,4(1,0)	3,5(1,0)	7,7(1,3)	0,6(0,8)	−0,6(1,0)	−2,9(0,9)
C(13)	1886(10)	5103(17)	5068(7)	1.8(0,8)	2,9(0,8)	4.8(1,0)	0,5(0,6)	0(0,6)	−1,4(0,8)
C(14)	1296(11)	5897(17)	5265(5)	5,3(1,0)	3,9(0,9)	0,8(0,8)	1,3(0,7)	1,1(0,5)	0,3(0,6)
C(15)	1000(12)	7076(22)	5030(9)	5,2(1,2)	5,6(1,3)	8,2(1,3)	0,8(1,1)	3,1(1,1)	0,4(1,2)
C(16)	1309(15)	7350(19)	4604(9)	8,6(1,6)	2,5(1,0)	6,9(1,6)	1.4(1,1)	−1,5(1,3)	0,2(1,1)
C(17)	1886(13)	6572(21)	4410(8)	3.8(1.1)	5,0(1,1)	8,0(1.7)	−1.6(1,0)	−0,7(1,1)	3,2(1,2)
C(18)	2161(13)	5396(20)	4631(7)	6,4(1,2)	4,1(1.1)	1.8(1,1)	−0,2(0,9)	0,1(0,9)	−0,5(0,9)
C(19)	1748(9)	3732(15)	5924(6)	1.7(0,8)	1,9(0,7)	2,8(0,7)	0,9(0,6)	0,4(0,6)	−0,1(0,7)
C(20)	1090(12)	3018(18)	6070(7)	4,0(0,9)	3,5(0,9)	4,4(1,0)	−0,4(0,8)	2,8(0,7)	−2,9(0,8)
C(21)	745(12)	3093(23)	6526(8)	2,5(0,8)	6,5(1,3)	6,3(1,3)	−1,4(0,8)	1,0(0,8)	−1,6(1,0)
C(22)	1165(12)	3888(17)	6853(6)	4,9(1,0)	3,1(0.9)	2,7(1,0)	−0,5(0,8)	1,7(0,8)	−1,1(0,7)

C(23)	1815(12)	4538(18)	6720(6)	5.0(1.0)	5.6(1.2)	2.0(1.0)	−3.4(0.9)	0.2(0.8)	0.4(0.8)
C(24)	2122(11)	4562(20)	6277(7)	4.0(1.0)	5.1(1.0)	3.2(1.0)	−2.2(0.8)	1.6(1.0)	0.1(0.8)
Molecule II									
Fe(3)	4486(1)	1700(2)	3189(1)	3.8(0.1)	2.6(0.1)	2.7(0.1)	−0.1(0.1)	0.7(0.1)	0.3(0.1)
Fe(4)	5768(1)	2892(2)	2878(1)	2.5(0.1)	3.0(0.1)	2.9(0.1)	−0.3(0.1)	−0.3(0.1)	0.1(0.1)
S(2)	5111(3)	1234(4)	2515(2)	3.3(0.2)	1.9(0.2)	2.9(0.2)	−0.1(0.2)	−0.2(0.2)	−0.6(0.2)
P(2)	4503(3)	3625(5)	2840(2)	3.8(0.2)	2.3(0.2)	3.5(0.2)	−0.1(0.2)	0.2(0.2)	−0.4(0.2)
O(7)	2982(9)	435(13)	2981(6)	5.1(0.8)	5.2(0.8)	8.3(1.0)	0.2(0.5)	1.5(0.7)	1.0(0.7)
O(8)	5342(11)	−177(17)	3775(6)	12.1(1.3)	7.4(1.0)	6.1(1.0)	1.3(0.9)	−3.3(1.0)	2.3(0.8)
O(9)	3785(13)	2839(15)	3998(6)	18.0(1.7)	4.5(0.8)	6.3(1.0)	−0.2(0.8)	3.6(0.9)	2.0(0.7)
O(10)	6505(8)	3958(16)	2058(5)	4.0(0.7)	8.6(0.9)	4.2(0.6)	0.4(0.5)	1.2(0.5)	0.8(0.8)
O(11)	7070(9)	1182(14)	3208(5)	7.3(0.9)	6.0(0.8)	5.8(1.0)	2.3(0.7)	−0.8(0.8)	−1.4(0.7)
O(12)	6317(9)	4837(14)	3541(5)	6.6(0.8)	5.4(0.8)	6.7(1.0)	0.9(0.7)	−0.3(0.5)	−1.8(0.6)
C(25)	3541(10)	1001(22)	3090(9)	0.5(0.9)	7.9(1.5)	10.1(1.6)	−1.4(1.0)	1.3(0.7)	1.9(1.1)
C(26)	5037(14)	619(22)	3557(7)	6.6(1.2)	5.1(0.7)	3.6(1.0)	0.3(0.9)	0.2(0.5)	−0.9(0.9)
C(27)	4139(15)	2430(23)	3691(10)	9.8(1.6)	7.0(1.4)	4.5(1.0)	4.7(1.3)	1.9(1.3)	0(1.0)
C(28)	6200(11)	3578(19)	2392(6)	2.5(0.9)	4.4(1.0)	2.7(1.0)	−1.7(0.8)	−1.0(0.6)	0.3(0.8)
C(29)	6498(11)	1845(17)	3075(8)	3.8(0.9)	1.7(0.8)	6.3(1.4)	−0.5(0.7)	1.9(1.0)	−1.5(0.6)
C(30)	6069(13)	4078(18)	3289(7)	5.5(1.1)	3.4(1.0)	3.3(1.1)	−0.5(1.0)	1.4(1.0)	−1.4(1.0)
C(31)	5685(11)	−231(18)	2493(8)	4.5(1.1)	2.4(0.9)	4.4(1.0)	−0.1(0.6)	−1.3(1.1)	0.6(0.9)
C(32)	6363(12)	−213(23)	2193(8)	3.4(1.0)	6.9(1.3)	5.5(1.3)	2.3(1.0)	−1.0(0.9)	0(1.0)
C(33)	6783(12)	−1398(22)	2103(7)	4.9(1.1)	6.1(1.1)	3.1(0.9)	1.6(0.9)	−1.6(0.7)	−2.3(0.8)
C(34)	6516(13)	−2529(17)	2329(9)	7.0(1.3)	1.0(0.7)	5.9(1.4)	1.0(0.8)	−1.0(1.2)	2.0(0.8)
C(35)	5878(12)	−2551(20)	2606(9)	3.8(0.9)	3.7(1.0)	5.8(1.0)	−0.8(1.0)	−2.4(0.9)	−0.4(0.7)
C(36)	5441(11)	−1392(18)	2690(6)	3.2(0.9)	3.0(0.9)	3.1(1.0)	1.0(0.7)	−1.4(0.8)	0(0.7)
C(37)	4079(11)	3699(16)	2241(6)	4.0(1.0)	1.7(0.7)	3.9(1.0)	−0.4(0.6)	0(0.7)	−0.2(0.7)
C(38)	3343(10)	3066(20)	2140(7)	2.1(0.8)	4.8(1.0)	5.0(1.0)	−0.7(0.7)	−2.1(0.8)	1.6(0.7)
C(39)	3031(13)	3137(23)	1680(9)	4.8(1.3)	5.9(1.3)	7.2(1.3)	1.1(1.1)	−2.4(1.1)	−1.0(1.1)
C(40)	3441(12)	3848(20)	1350(6)	3.6(1.0)	5.7(1.0)	2.6(1.1)	−1.2(0.8)	−1.9(0.7)	1.9(0.7)
C(41)	4093(13)	4537(20)	1455(7)	4.7(1.3)	5.5(1.1)	3.9(1.0)	2.0(0.9)	−1.3(1.1)	2.3(0.7)
C(42)	4415(11)	4487(18)	1901(8)	3.5(0.9)	3.1(0.9)	4.8(1.0)	−1.1(0.7)	−0.9(0.7)	0.6(0.7)
C(43)	4107(11)	5132(17)	3105(6)	5.0(1.0)	1.9(0.8)	2.4(0.9)	−1.1(0.8)	1.3(0.7)	0.1(0.6)
C(44)	4409(11)	5497(22)	3558(7)	3.4(0.9)	5.5(1.0)	3.3(1.0)	−0.8(1.0)	0.2(0.7)	0.3(0.8)
C(45)	4160(14)	6668(18)	3765(7)	8.4(1.2)	2.6(0.9)	3.5(0.9)	1.4(1.0)	1.2(0.8)	−0.8(0.8)
C(46)	3647(14)	7424(17)	3516(7)	8.9(1.2)	2.3(0.8)	2.7(1.0)	1.2(0.8)	1.9(1.0)	1.0(0.8)
C(47)	3325(12)	7094(23)	3085(6)	6.1(1.1)	6.4(1.2)	2.8(0.9)	2.5(0.9)	−0.5(0.7)	−0.9(1.0)
C(48)	3582(11)	5986(19)	2873(7)	4.6(0.8)	4.0(0.9)	4.8(1.0)	2.1(0.7)	1.6(0.9)	−0.8(0.8)

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[a] The number in parentheses in this and subsequent tables is the standard deviation in the least significant digit. [b] The anisotropic temperature factors are in the form: $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

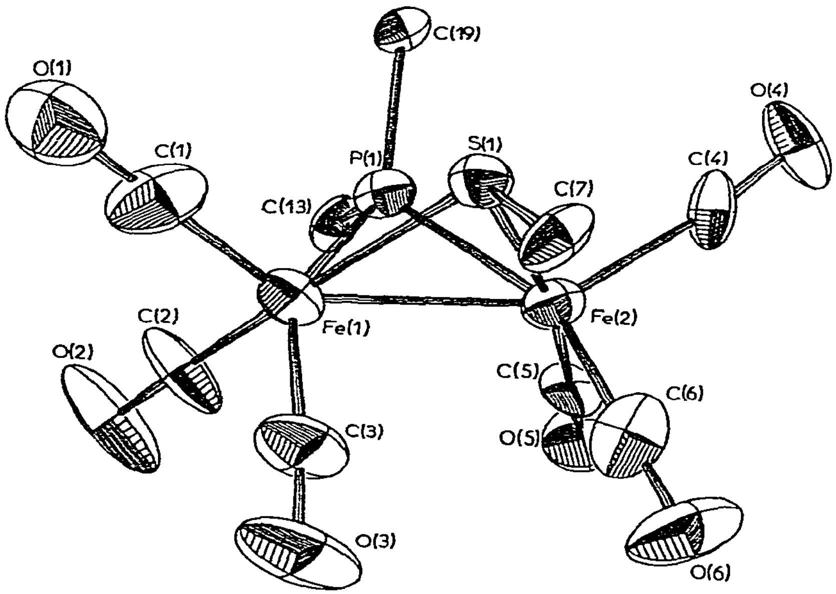

Fig. 2. Another ORTEP view of molecule I, with phenyl rings omitted for clarity.

are given in Table 1. The atomic numbering scheme used can be seen on Fig. 1 and 2, which give two views of one of the two independent molecules along two perpendicular directions, plotted with program ORTEP [8]. The most important interatomic distances and bond angles are given in Table 2.

Description and discussion of the structure

The molecular structure of μ-(SC_6H_5)-μ-$(P(C_6H_5)_2)Fe_2(CO)_6$ consists of two $Fe(CO)_3$ groups linked by one iron—iron bond bridged through two different ligands, one sulfur and one phosphorus atom. The two independent molecules are similar, but nevertheless there are some differences in mean bond distances and angles. These differences, however, are not significant at the 3σ level. Figures 1 and 2 show two views of molecule I along two perpendicular directions; on Fig. 2, phenyl rings have been omitted for clarity.

This structure can be related to that of iron carbonyl derivatives with an Fe_2X_2 or Fe_2XX' core showing a butterfly shape, which results from the junction of the basal planes of two distorted tetragonal pyramids along the edge XX′. These pyramids are formed by the five atoms coordinated to each iron atom, namely the three carbon atoms of carbonyl groups and the bridging S and P atoms. Iron atoms Fe(1) and Fe(2) of molecule I are displaced from their basal planes by 0.37 and 0.29 Å in the direction of the apical carbonyl groups, and iron atoms Fe(3) and Fe(4) of molecule II respectively by 0.43 and 0.35 Å. The dihedral angle between the planes Fe(1)—S(1)—P(1) and Fe(2)—S(1)—P(1) is 96.2°, and the one between the planes Fe(3)—S(2)—P(2) and Fe(4)—S(2)—P(2) is 96.6°. Iron—iron bonds Fe(1)—Fe(2) and Fe(3)—Fe(4) have respective lengths of 2.614(3) Å and 2.606(3) Å, with a mean value of 2.610 Å.

It is of particular interest to compare the present structure with that of analogous compounds with symmetric bridging systems Fe_2S_2 and Fe_2P_2. For the first type, many crystal structures have been determined [1,9—12], and their main structural characteristics are given in Table 3. For the second type, several structures have been reported by Clegg [13] and their characteristics are also given in Table 3. The values reported in this Table for the present complex are mean ones calculated for the two independent molecules.

Concerning Fe—S and Fe—P distances, the values found for the present complex with a mixed bridge are identical with those of the corresponding symmetric bridges. In contrast, for Fe—S—Fe and Fe—P—Fe angles, the values found for the mixed bridge are different from those of the symmetric bridges and are intermediate between values for Fe—S—Fe in Fe_2S_2 systems (67—68° C) and for Fe—P—Fe in Fe_2P_2 systems (72—74° C). Similarly, the value of the dihedral angle between (Fe^1—X—X') and (Fe^2—X—X') planes is also intermediate between the value of the two symmetric cores (near 90° for Fe_2S_2 and near 100° for Fe_2P_2).

Concerning the Fe—Fe bond length, the mean value found in the present derivative is not intermediate between those of symmetric bridges Fe_2S_2 and Fe_2P_2, but is clearly nearer to values for Fe_2P_2 systems. Here we must notice that in derivatives $Fe_2(CO)_6$-μ-$(PRR')_2$, the Fe—Fe bond length varies rather widely with the nature of the substituents R and R' in the phosphorine ligand, especially if we add to compounds given in Table 3 the one with $R = R' = CF_3$ [13], for which the Fe—Fe distance is 2.819 Å. For complexes with an Fe_2S_2 core, on the other hand, the Fe—Fe bond length always lies within the small range 2.50—2.54 Å.

Recently, Mathey and al. [2] determined the crystal structures of two derivatives possessing a mixed bridging system Fe_2SP, in which the dihedral angles (Fe^1—X—X')—(Fe^2—X—X'), the non-bonding distances S · · · P, and the other distances and angles for the central skeleton * are very similar to those found in the present complex. In those two derivatives, Fe—Fe bond lengths are respectively 2.557(1) and 2.579(1) Å.

In the light of the distances found for the iron—iron bond in the three known compounds having a mixed Fe_2SP core, we must conclude that, like the other characteristics of the central skeleton, the Fe—Fe distance for the mixed bridge, is intermediate between the values for the two corresponding symmetric bridges Fe_2S_2 and Fe_2P_2. That conclusion is different from that we reached for a derivative with a mixed bridging system Fe_2SN [7], in which the Fe—Fe distance was not intermediate between those found in corresponding symmetric bridges Fe_2S_2 and Fe_2N_2, but was strictly similar to values for Fe_2N_2 cores. However, the lack of structural data for other derivatives with a mixed Fe_2SN system does not allow to know if the only studied example is a special case or if the conclusion concerning the iron—iron bond could generally be the same as for Fe_2SP mixed systems.

The six phenyl rings of the two independent molecules are planar. The distances and angles of these rings have a quite great dispersion, but the mean

(Continued on p. 211)

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* Atomic coordinates for these two Fe_2SP complexes were kindly supplied to us by M.B. Comarmond and D. Moras.

TABLE 2

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (deg)

Molecule I		Molecule II		Molecule I		Molecule II	
Fe(1)—Fe(2)	2.614(3)	Fe(3)—Fe(4)	2.606(3)	S(1)—Fe(1)—P(1)	77.86(0.21)	S(2)—Fe(3)—P(2)	78.06(0.22)
Fe(1)—S(1)	2.280(5)	Fe(3)—S(2)	2.250(5)	S(1)—Fe(2)—P(1)	77.88(0.21)	S(2)—Fe(4)—P(2)	77.35(0.21)
Fe(2)—S(1)	2.279(5)	Fe(4)—S(2)	2.272(5)	Fe(1)—S(1)—Fe(2)	69.97(0.13)	Fe(3)—S(2)—Fe(4)	70.39(0.17)
Fe(1)—P(1)	2.238(5)	Fe(3)—P(3)	2.216(5)	Fe(1)—P(1)—Fe(2)	71.47(0.26)	Fe(3)—P(2)—Fe(4)	71.86(0.29)
Fe(2)—P(1)	2.237(5)	Fe(4)—P(2)	2.227(5)				
				Fe(1)—C(1)—O(1)	176.7(0.9)	Fe(3)—C(25)—O(7)	170.2(0.8)
Fe(1)—C(1)	1.719(20)	Fe(3)—C(25)	1.743(18)	Fe(1)—C(2)—O(2)	170.8(1.2)	Fe(3)—C(26)—O(8)	172.9(1.9)
Fe(1)—C(2)	1.798(23)	Fe(3)—C(26)	1.783(22)	Fe(1)—C(3)—O(3)	172.9(1.8)	Fe(3)—C(27)—O(9)	168.4(1.4)
Fe(1)—C(3)	1.822(20)	Fe(3)—C(27)	1.726(28)	Fe(2)—C(4)—O(4)	173.5(1.5)	Fe(4)—C(28)—O(10)	175.6(0.6)
Fe(2)—C(4)	1.848(18)	Fe(4)—C(28)	1.722(18)	Fe(2)—C(5)—O(5)	178.7(1.5)	Fe(4)—C(29)—O(11)	174.2(1.3)
Fe(2)—C(5)	1.759(17)	Fe(4)—C(29)	1.711(18)	Fe(2)—C(6)—O(6)	176.0(0.6)	Fe(4)—C(30)—O(12)	175.2(0.8)
Fe(2)—C(6)	1.835(19)	Fe(4)—C(30)	1.767(19)				
				Fe(1)—S(1)—C(7)	116.5(0.5)	Fe(3)—S(2)—C(31)	117.1(0.6)
C(1)—O(1)	1.187(25)	C(25)—O(7)	1.136(24)	Fe(2)—S(1)—C(7)	114.3(0.5)	Fe(4)—S(2)—C(31)	113.2(0.5)
C(2)—O(2)	1.124(28)	C(26)—O(8)	1.146(28)	Fe(1)—P(1)—C(13)	122.6(0.5)	Fe(3)—P(2)—C(37)	116.8(0.6)
C(3)—O(3)	1.105(25)	C(27)—O(9)	1.139(33)	Fe(1)—P(1)—C(19)	118.8(0.4)	Fe(3)—P(2)—C(43)	123.8(0.5)
C(4)—O(4)	1.104(23)	C(28)—O(10)	1.151(23)	Fe(2)—P(1)—C(13)	122.1(0.5)	Fe(4)—P(2)—C(37)	114.4(0.5)
C(5)—O(5)	1.133(22)	C(29)—O(11)	1.228(23)	Fe(2)—P(1)—C(19)	115.8(0.5)	Fe(4)—P(2)—C(43)	126.7(0.5)
C(6)—O(6)	1.153(23)	C(30)—O(12)	1.142(24)	C(13)—P(1)—C(19)	104.4(0.8)	C(37)—P(2)—C(43)	102.4(0.8)

S(1) ··· P(1)	2.839(6)	S(2) ··· P(2)	2.812(6)
S(1)—C(7)	1.805(18)	S(2)—C(31)	1.778(19)
P(1)—C(13)	1.806(18)	P(2)—C(37)	1.862(19)
P(1)—C(19)	1.792(16)	P(2)—C(43)	1.843(17)
C(7)—C(8)	1.393(25)	C(31)—C(32)	1.414(29)
C(8)—C(9)	1.432(30)	C(32)—C(33)	1.424(31)
C(9)—C(10)	1.313(38)	C(33)—C(34)	1.401(29)
C(10)—C(11)	1.416(40)	C(34)—C(35)	1.324(32)
C(11)—C(12)	1.373(28)	C(35)—C(36)	1.413(27)
C(12)—C(7)	1.424(27)	C(36)—C(31)	1.379(26)
C(13)—C(14)	1.393(24)	C(37)—C(38)	1.410(25)
C(14)—C(15)	1.469(29)	C(38)—C(39)	1.421(32)
C(15)—C(16)	1.357(36)	C(39)—C(40)	1.377(31)
C(16)—C(17)	1.363(32)	C(40)—C(41)	1.324(28)
C(17)—C(18)	1.436(30)	C(41—C(42)	1.392(29)
C(18)—C(13)	1.372(28)	C(42)—C(37)	1.384(26)
C(19)—C(20)	1.379(24)	C(43)—C(44)	1.444(27)
C(20)—C(21)	1.432(29)	C(44)—C(45)	1.402(28)
C(21)—C(22)	1.426(28)	C(45)—C(46)	1.355(29)
C(22)—C(23)	1.322(27)	C(46)—C(47)	1.390(27)
C(23)—C(24)	1.372	C(47)—C(48)	1.358(29)
C(24)	1.462(25)	C(48)—C(43)	1.401(26)

TABLE 3

COMPARISON OF THE MAIN STRUCTURAL PARAMETERS OF $Fe_2(CO)_6$-μ-(SC_6H_5)-μ-$(P(C_6H_5)_2)$ [a] THOSE OF IRON CARBONYL DERIVATIVES WITH Fe_2S_2 AND Fe_2P_2 CORES

Compound	$[C_2H_5SFe(CO)_3]_2$	$[C_6H_5CSFe(CO)_3]_2$	$[CH_3SFe_2CO)_6]_2S$
(a) Fe_2S_2 core			
References	9	10	11
Fe—Fe	2.537(10)	2.507(5)	2.540(5)
Fe—S	2.259(7)	2.259(3)	2.274(4) 2.248(4)
S ··· S	2.932(14)	2.876(7)	2.817(6)
Fe—S—Fe	68.3(3)	67.4(1)	68.3(1)
S—Fe—S	81.0(3)	78.7(1)	77.1(1)
Dihedral angle (Fe^1—X—X′)—(Fe^2—X—X′)	95.2(5)	91.8(5)	88.3(3)
R,R′	C_6H_5, C_6H_5	C_6H_5, CH_3	C_6H_5, H
(b) Fe_2P_2 core: molecules $Fe_2(CO)_6$-μ-$(PRR')_2$ [b]			
Fe—Fe	2.623(3)	2.619(1)	2.662(1)
Fe—P	2.233(3)	2.217(1)	2.212(1)
P ··· P	2.866(3)	2.864(2)	2.790(2)
Fe—P—Fe	72.0(1)	72.4(1)	74.0(1)
P—Fe—P	79.9(1)	80.5(1)	78.2(1)
Dihedral angle (Fe^1—X—X′)—(Fe^2—X—X′)	100.0	101.4	101.7
S ··· P			
S—Fe—P			

[a] Values given for the present compound are mean ones calculated for the two independent molecules. [b] J.I Huntsman and L.F. Dahl, unpublished work quoted in ref. 13. [c] This work.

TABLE 4

SHORTEST INTERMOLECULAR DISTANCES REFERRED TO MOLECULES I (x_1, y_1, z_1) OR II (x_2, y_2, z_2) [a]

$S(1)^I \cdots C(40)^X$	3.73 Å	$C(12)^I \cdots C(40)^X$	3.62 Å
$S(1)^I \cdots H(40)^X$	3.19	$C(12)^I \cdots H(40)^X$	2.77
$O(1)^I \cdots C(5)^{XII}$	3.27	$C(12)^I \cdots C(41)^X$	3.66
$O(2)^I \cdots O(11)^{XIV}$	3.03	$C(22)^I \cdots S(2)^{IX}$	3.72
$O(2)^I \cdots C(29)^{XIV}$	3.12	$C(22)^I \cdots C(31)^{IX}$	3.68
$O(2)^I \cdots C(30)^{XIV}$	3.23	$C(22)^I \cdots C(36)^{IX}$	3.60
$O(3)^I \cdots H(46)^{III}$	2.67	$C(23)^I \cdots C(39)^{IX}$	3.70
$O(4)^I \cdots H(21)^{XI}$	2.67	$S(2)^{II} \cdots H(22)^{VIII}$	3.07
$O(4)^I \cdots H(41)^{VII}$	2.56	$O(10)^{II} \cdots H(23)^V$	2.47
$C(5)^I \cdots O(9)^{II}$	3.18	$O(10)^{II} \cdots H(39)^{XIII}$	2.65
$C(5)^I \cdots H(11)^{XV}$	2.83	$C(34)^{II} \cdots H(47)^{XIII}$	2.88
$C(7)^I \cdots C(40)^X$	3.67	$C(36)^{II} \cdots H(22)^{VIII}$	2.72
$C(8)^I \cdots C(32)^{VI}$	3.56	$C(41)^{II} \cdots H(10)^{IV}$	2.85

[a] Numbering of molecules

I : x_1, y_1, z_1
II : x_2, y_2, z_2
III : $x_2, y_2 - 1, z_2$
IV : $\bar{x}_1 + 1, \bar{y}_1, z_1 - \frac{1}{2}$
V : $\bar{x}_1 + 1, \bar{y}_1 + 1, z_1 -$
VI : $\bar{x}_2 + 1, \bar{y}_2, z_2 + \frac{1}{2}$
VII : $\bar{x}_2 + 1, \bar{y}_2 + 1, z_2 + \frac{1}{2}$
VIII: $\bar{x}_1 + \frac{1}{2}, y_1 - \frac{1}{2}, z_1 - \frac{1}{2}$
IX : $\bar{x}_2 + \frac{1}{2}, y_2 + \frac{1}{2}, z_2 + \frac{1}{2}$
X : $\bar{x}_2 + \frac{1}{2}, y_2 - \frac{1}{2}, z_2 + \frac{1}{2}$
XI : $x_1 + \frac{1}{2}, \bar{y}_1 + \frac{1}{2}, z_1$
XII : $x_1 - \frac{1}{2}, \bar{y}_1 + \frac{1}{2}, z_1$
XIII: $x_2 + \frac{1}{2}, \bar{y}_2 + \frac{1}{2}, z_2$
XIV: $x_2 - \frac{1}{2}, \bar{y}_2 + \frac{1}{2}, z_2$
XV : $x_1, y_1 + 1, z_1$

)$Fe_2(CO)_6$-μ_4-S$Fe_2(CO)_6$S(py)	[μ-(SCH_3)$Fe(CO)_2P(CH_3)_3$]$_2$	$Fe_2(CO)_6$-μ-(SC_6H_5)$P(C_6H_5)_2$
	1	present work
2.532(1)	2.518(1)	2.610(2)
2.281(1)	2.273(1)	2.270(3)
2.255(1)		
2.804(2)	2.790(3)	
7.9(1)	67.3(1)	70.2(1)
6.4(1)	75.7(1)	
0.5(3)	90.9	96.4
$_3$, H	CH_3, CH_3	C
2.661(1)	2.665(2)	2.610(2)
2.203(1)	2.209(2)	2.229(3)
2.725(1)	2.925(4)	
4.3(1)	74.2(1)	71.7(2)
6.4(1)	82.9(1)	
0.5	107.3	96.4
		2.826(4)
		77.8(1)

values are normal, respectively 1.392(13), 1.398(12) and 1.399(11) Å for C—C distances of rings I (bonded to S), II and III (bonded to P) of the first molecule, and 1.393(12), 1.385(12) and 1.392(12) Å for the corresponding rings of the second molecule. The mean value of C—C—C angles is 119.9(7)° or 120.0(7)° for the different rings. The mean value of S—C distances for the two molecules is 1.792(8) Å, and the mean value of P—C distances is 1.826(7) Å, and these values are quite normal, Concerning angles Fe—S—C, Fe—P—C and C—P—C, the mean values well agree with those in the literature; in particular, for angles around phosphorus atoms, a small deviation from ideal tetrahedral symmetry is observed, as usual.

The $Fe(CO)_3$ groups all have the usual ternary symmetry. The mean Fe—C and C—O distances are respectively 1.797(8) and 1.134(10) Å for molecule I, and 1.742(9) and 1.157(11) Å for molecule II. The observed differences between the two molecules cannot be regarded as significant in the light of the spread of individual values. Mean Fe—C—O angles are 174.7(5)° and 172.8(5)° respectively, for molecules I and II. These values clearly deviate from 180° to a greater extent than usual. This is due to the relatively poor precision of the structural results, which arises from use of an insufficient number of reflections as compared with the great number of parameters to be refined, even with the refining process described.

The molecular packing arises from normal Van der Waals interactions. The shortest intermolecular distances, given in Table 4, correspond to oxygen—hydrogen and carbon—hydrogen contacts.

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