Dicarbonyltriphenylphosphine-(π-thioacrolein)iron(0)

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Abstract. Orthorhombic, *Pbca*, $a = 16 \cdot 401$ (8), $b = 16 \cdot 824$ (8), $c = 15 \cdot 012$ (8) Å, $25\,°C$, $Z = 8$, $(CO)_2[(C_6H_5)_3P]Fe(\pi\text{-}SC_3H_4)$, $D_x = 1 \cdot 431$ g cm^{-3}. The thioacrolein ligand, $CH_2{=}CH{-}CH_2{=}S$, is shown to π-bond to the iron atom in a manner similar to that previously found for butadiene-type complexes.

Introduction. The product of the reaction of thiete (thiacyclobutene) with nonacarbonyldiiron(0) was treated with triphenylphosphine to yield bright red-orange crystals whose analysis corresponded to the formula $(CO)_2[(C_6H_5)_3P]Fe(SC_3H_4)$ (Chang, 1970). Chemical and physical evidence indicated the possible presence of a π-bonded thiete ring. The structure was thus undertaken to determine the geometry of the thiete ring and its mode of bonding to the iron atom.

A crystal having the dimensions $0 \cdot 25 \times 0 \cdot 12 \times 0 \cdot 25$ mm was mounted with c^* coincident with the axis of rotation (φ). 1935 diffraction intensities (Mo $K\alpha$), of which 339 were considered to be unobserved, were gathered on a Canberra Industries automated G. E. XRD-6 diffractometer by using θ–2θ scans of $1°$ per min. 30-s background counts were taken at both ends of the scan range. The intensities were corrected for φ dependence (as determined from the 00*l* intensities at $\chi = 90°$) and Lorentz–polarization. No further absorption correction was deemed necessary ($\mu = 9 \cdot 36$ cm^{-1}). Two reference reflexions were monitored throughout the data collection and no significant intensity changes were noted.

The heavy-atom method was used to locate the positions of the iron, phosphorus, and sulfur atoms. A subsequent Fourier map revealed the positions of the other heavy atoms and clearly showed that the thiete ring had opened up to become a thioacrolein ligand. The structure was refined by a full-matrix least-squares program (*ORFLS*; Busing, Martin & Levy, 1962) with weights based on experimental counting statistics. The hydrogen atoms were located on a difference map calculated after the isotropic refinement of the heavy

Table 1. *Final structure parameters* (*with standard deviations in parentheses*)

The anisotropic thermal parameters are in the form $\exp\left[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\right]$.

(*a*) Heavy atoms (anisotropic thermal parameters $\times 10^4$)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0·08162 (5)	0·21134 (5)	0·08739 (6)	32 (0)	30 (0)	43 (1)	−1 (1)	−1 (1)	−4 (1)
P	−0·05348 (9)	0·19786 (9)	0·10196 (11)	32 (1)	21 (1)	29 (1)	−1 (1)	−1 (1)	−4 (1)
S	0·07950 (14)	0·28442 (12)	0·21791 (12)	67 (1)	38 (1)	60 (1)	7 (1)	−26 (1)	−16 (1)
O(1)	0·1022 (3)	0·3340 (3)	−0·0493 (3)	80 (4)	73 (4)	67 (5)	−20 (3)	−1 (3)	30 (3)
O(2)	0·0910 (3)	0·0716 (3)	−0·0254 (4)	67 (3)	51 (3)	103 (4)	9 (3)	−7 (3)	−45 (3)
C(1)	−0·1142 (3)	0·2892 (3)	0·1154 (3)	30 (3)	25 (3)	19 (4)	−1 (3)	−4 (3)	1 (3)
C(2)	−0·1964 (4)	0·2857 (4)	0·1378 (4)	39 (4)	33 (3)	43 (4)	2 (3)	−5 (3)	−1 (4)
C(3)	−0·2431 (4)	0·3532 (5)	0·1433 (4)	42 (4)	55 (4)	44 (5)	14 (4)	3 (4)	8 (4)
C(4)	−0·2071 (5)	0·4266 (4)	0·1283 (4)	62 (4)	45 (4)	33 (5)	33 (4)	−3 (4)	3 (4)
C(5)	−0·1278 (4)	0·4314 (4)	0·1083 (4)	62 (4)	28 (3)	40 (5)	10 (3)	−5 (4)	1 (4)
C(6)	−0·0794 (4)	0·3629 (3)	0·1015 (4)	44 (3)	29 (3)	33 (4)	4 (4)	0 (4)	4 (4)
C(7)	−0·0771 (4)	0·1353 (3)	0·1987 (4)	25 (3)	22 (3)	33 (4)	1 (3)	−2 (3)	3 (3)
C(8)	−0·0642 (4)	0·0543 (4)	0·1918 (4)	61 (4)	27 (4)	48 (5)	−2 (3)	−2 (4)	−3 (4)
C(9)	−0·0725 (5)	0·0065 (4)	0·2638 (5)	67 (4)	26 (4)	80 (5)	−5 (4)	−12 (5)	19 (4)
C(10)	−0·0926 (4)	0·0385 (4)	0·3458 (5)	54 (4)	53 (4)	54 (5)	5 (4)	2 (4)	32 (4)
C(11)	−0·1059 (4)	0·1167 (4)	0·3533 (4)	46 (4)	61 (4)	29 (5)	9 (4)	0 (4)	16 (4)
C(12)	−0·1004 (4)	0·1670 (4)	0·2796 (4)	30 (4)	33 (4)	44 (5)	4 (3)	5 (4)	2 (3)
C(13)	−0·1079 (3)	0·1495 (3)	0·0103 (4)	27 (3)	21 (3)	31 (4)	−1 (3)	−4 (3)	1 (3)
C(14)	−0·1788 (4)	0·1055 (4)	0·0256 (4)	39 (4)	38 (4)	47 (5)	−5 (4)	6 (4)	−1 (4)
C(15)	−0·2221 (4)	0·0703 (4)	−0·0451 (4)	44 (4)	44 (4)	42 (5)	−18 (3)	−12 (4)	0 (4)
C(16)	−0·1899 (4)	0·0766 (4)	−0·1279 (4)	57 (4)	31 (4)	44 (5)	−2 (4)	−19 (4)	−5 (4)
C(17)	−0·1227 (4)	0·1195 (4)	−0·1430 (4)	51 (4)	36 (4)	42 (5)	−2 (4)	8 (4)	−2 (4)
C(18)	−0·0795 (4)	0·1564 (3)	−0·0756 (4)	32 (3)	30 (3)	33 (4)	−5 (3)	−3 (3)	−1 (3)
C(19)	0·1151 (4)	0·1836 (4)	0·2158 (5)	49 (4)	52 (4)	54 (6)	15 (4)	−26 (4)	−2 (4)
C(20)	0·1773 (4)	0·1649 (4)	0·1631 (5)	39 (4)	41 (4)	67 (5)	4 (4)	2 (4)	−6 (4)
C(21)	0·2088 (4)	0·2258 (5)	0·1110 (5)	50 (5)	69 (5)	83 (6)	0 (4)	−20 (5)	2 (5)
C(22)	0·0942 (5)	0·2866 (5)	0·0019 (5)	64 (5)	57 (5)	53 (6)	−22 (5)	13 (5)	−3 (5)
C(23)	0·0876 (4)	0·1251 (4)	0·0178 (4)	28 (4)	40 (4)	65 (5)	−4 (4)	−1 (4)	−6 (4)

Table 1 *(cont.)*

(*b*) Hydrogen atoms (isotropic thermal parameters)
The hydrogen atoms are numbered in accordance with the carbon atoms to which they are bonded.

	x	y	z	B
H(2)	−0·227 (2)	0·241 (3)	0·139 (3)	3·81
H(3)	−0·296 (3)	0·357 (3)	0·153 (3)	4·66
H(4)	−0·246 (3)	0·473 (3)	0·130 (3)	4·36
H(5)	−0·101 (2)	0·477 (2)	0·100 (3)	3·92
H(6)	−0·020 (2)	0·368 (2)	0·093 (3)	3·72
H(8)	−0·047 (3)	0·036 (3)	0·137 (3)	4·38
H(9)	−0·056 (3)	−0·046 (3)	0·256 (3)	5·42
H(10)	−0·092 (3)	0·005 (2)	0·391 (3)	4·81
H(11)	−0·113 (3)	0·140 (3)	0·403 (3)	4·61
H(12)	−0·099 (3)	0·225 (2)	0·293 (3)	3·97
H(14)	−0·202 (3)	0·108 (3)	0·073 (3)	4·53
H(15)	−0·271 (3)	0·041 (3)	−0·028 (3)	4·41
H(16)	−0·215 (3)	0·054 (3)	−0·170 (3)	4·48
H(17)	−0·095 (3)	0·120 (3)	−0·195 (3)	4·32
H(18)	−0·017 (2)	0·179 (2)	−0·086 (3)	3·13
H(19)	0·078 (3)	0·133 (3)	0·241 (3)	5·28
H(20)	0·185 (3)	0·107 (3)	0·150 (3)	4·39
H(21*a*)	0·236 (3)	0·207 (3)	0·060 (3)	6·59
H(21*b*)	0·207 (3)	0·284 (3)	0·134 (3)	6·59

atoms ($R=0·136$). Each hydrogen atom was assigned the isotropic thermal parameter of the carbon atom to which it was attached. Continued refinement on the coordinates of all atoms and the anisotropic thermal parameters of the heavy atoms led to a conventional R of 0·076 for all reflections, 0·052 omitting the unobserved reflections, and a weighted R of 0·036. Atomic scattering factors, including $\Delta f'$ for Fe, were obtained from *International Tables for X-ray Crystallography* (1962) except for hydrogen, for which the scattering factor of Stewart, Davidson & Simpson (1965) was used. The final positional and thermal parameters are given in Table 1.†

Discussion. The bond distances and angles for dicarbonyltriphenylphosphine-(π-thioacrolein)iron(0) are given in Figs. 1 and 2 respectively, while the molecular geometry is illustrated in Fig. 3. No intermolecular contacts less than the sum of van der Waals radii are present.

The bond distances and angles for the carbonyl groups and the triphenylphosphine are generally those expected except for one C–C bond in each phenyl ring which is consistently shorter than the other C–C bonds. Each phenyl ring is planar within an average deviation of 0·011 Å. The perpendicular distances from each of the three planes to the phosphorus atom are as follows: plane C_{1-6}, 0·088 (2) Å; plane C_{7-12}, −0·229 (2) Å; plane C_{13-18}, 0·010 (2) Å.

The bond distances from the iron atom to the carbon atoms in the thioacrolein ligand are typical of those

found in butadiene-type π-bonded complexes (Johnson & Paul, 1970; Eiss, 1970). Other similarities are the planarity of the thioacrolein ligand, the four atoms showing an average deviation from the least-squares plane of only 0·006 Å, and the proximity of its bond angles to 120°. The perpendicular distance from the plane to the iron atom is 1·669 (1) Å.

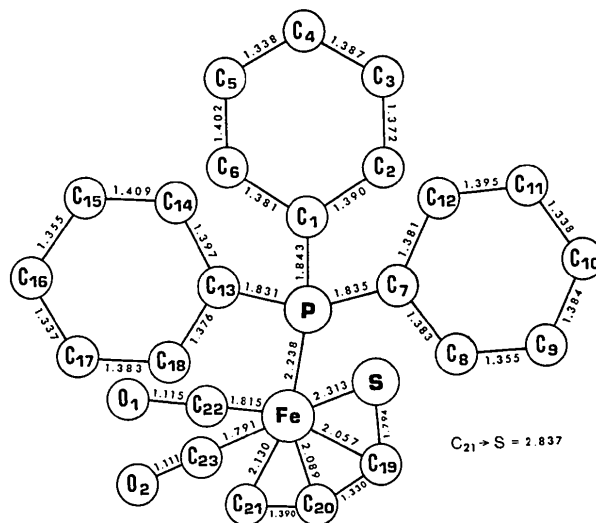It is interesting to note that the molecule thioacro-

Fig. 1. Bond distances for dicarbonyltriphenylphosphine(π-thioacrolein)iron(0). The e.s.d.'s for the bond distances are approximately as follows: for type H–H, 0·002 Å; for type H–L, 0·007 Å; for type L–L, 0·010 Å (H = Fe, P, S; L = C, O).
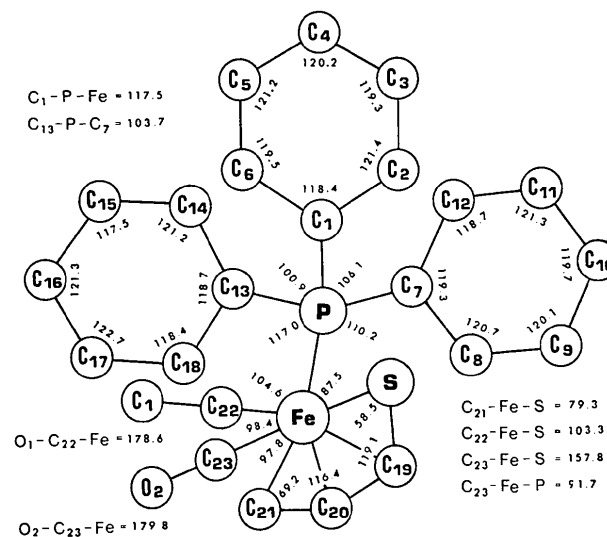

Fig. 2. Bond angles for dicarbonyltriphenylphosphine(π-thioacrolein)iron(0). The e.s.d.'s for the bond angles are approximately as follows: for P–Fe–S, 0·1°; for type H–H–L, 0·2°; for types H–L–L and L–L–L, 0·6° (H = Fe, P, S; L = C, O).
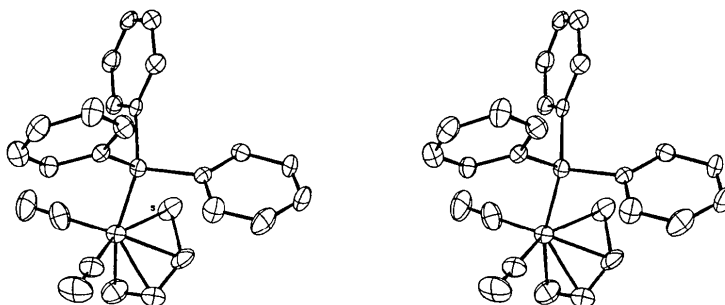
Fig. 3. A stereographic drawing of the molecule.

lein has not been isolated because of its extreme reactivity; however, as shown here, it can be stabilized by the formation of this π-bonded complex. The chemistry relating to this compound is to be published elsewhere (Takahashi, Chang, Tsai, Iwanami, Blidner & Dittmer, 1973).

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Phényl Méthylamino-2 Phényl-5 Thiazolinone-4

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Abstract. The compound $C_{10}H_{14}ON_2S$ crystallizes in the monoclinic space group $P2_1/c$ with cell parameters $a = 13 \cdot 196 \pm 0 \cdot 005$, $b = 9 \cdot 922 \pm 0 \cdot 005$, $c = 11 \cdot 656 \pm 0 \cdot 005$ Å, $\beta = 112° 20' \pm 30'$; $d_c = 1 \cdot 327 \pm 0 \cdot 002$, $d_m = 1 \cdot 32 \pm 0 \cdot 01$ g cm^{-3}, $Z = 4$, $|F_{000}| = 592$; $R = 0 \cdot 09$ for 2517 unweighted reflexions. The crystal stability is maintained only by van der Waals contacts.

Introduction. Cette molécule (Fig. 1) est tautomère de la phénylimino-2 méthyl-3 phényl-5 thiazolinone-4 (Bally & Mornon, 1973) et est le dernier terme de la série de 6 thiazolinones étudiées par notre équipe (Mornon & Raveau, 1971; Mornon & Bally, 1972; Bally & Mornon, 1972). La récapitulation des résultats fera l'objet d'une prochaine publication.

La structure a été résolue par application du programme *MULTAN* (Germain, Main & Woolfson,

1971) à partir des facteurs de structure normalisés déduits de la mesure par diffractomètre automatique Siemens des réflexions Cu $K\alpha$. La série de Fourier, tirée
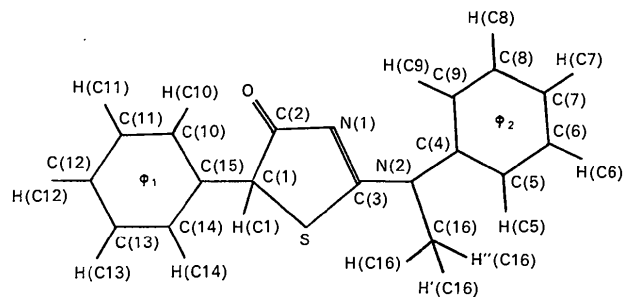

Fig. 1. Phényl méthylamino-2 phényl-5 thiazolinone-4.