Journal of Organometallic Chemistry, 315 (1986) 321–328
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PHENYLANTIMONY BIS(MONOTHIOACETATE); ITS PREPARATION, STRUCTURE AND STABILITY

M. HALL, D.B. SOWERBY* and C.P. FALSHAW
Department of Chemistry, University of Nottingham, Nottingham, NG7 2RD (Great Britain)

(Received May 30th, 1986)

Summary

Phenylantimony bis(monothioacetate) has been prepared and fully characterised by single crystal X-ray diffraction. The crystals are triclinic, $P\bar{1}$, with a 10.761(4), b 7.304(3), c 9.608(7) Å, α 112.84(5), β 102.57(5) and γ 100.17(5)°. The thioacetate groups bond primarily via sulphur (Sb–S 2.451, 2.471 Å) but substantial Sb · · · O interactions lead to a bis-chelate structure. Isolated $PhSb(SAc)_2$ molecules have distorted square-pyramidal geometry with an apical phenyl group but intermolecular Sb · · · S interactions (3.802 Å) *trans* to the phenyl group give weak dimers in the solid state. Attempts to prepare Ph_2SbSAc gave only mixtures of $PhSb(SAc)_2$ and Ph_3Sb; in the related acetate series, Ph_2SbOAc is well-known, but $PhSb(OAc)_2$ could not be prepared. Possible reasons for the instability of Ph_2SbSAc and $PhSb(OAc)_2$ are considered.

Introduction

We have previously prepared antimony tris(monothioacetate) and shown that in both this compound and the better known triacetate, $Sb(OAc)_3$, two of the ligands are chelating and one is simultaneously chelating and bridging [1]. In the diphenyl substituted acetate, Ph_2SbOAc, on the other hand, the ligand is strictly bridging leading to an infinite chain structure [2]. Our interest in the comparative ligand behaviour of the acetate and thioacetate groups led to attempts to prepare the monothioacetate, Ph_2SbSAc, from Ph_2SbCl and potassium thioacetate with ethanol, hexane, ether or dichloromethane as solvent. These reactions were unsuccessful and the only products isolated were the bis(monothioacetate), $PhSb(SAc)_2$, and triphenyl antimony. The bis(monothioacetate) can be more simply prepared as a low melting, white solid by a simple metathesis between $PhSbCl_2$ and potassium monothioacetate in ethanol.

In the corresponding acetate series, only Ph_2SbOAc has been reported; a previous attempt to produce $PhSb(OAc)_2$ was unsuccessful [3] and our attempts

0022-328X/86/$03.50

either by metathesis between $PhSbCl_2$ and sodium acetate in refluxing methanol or by treating PhSbO with acetic anhydride at 60°C for 24 h led to Ph_2SbOAc. In this connection, it is noteworthy that bis(dithiocarbamates), $PhSb(S_2CNR_2)_2$, are readily obtained, but the corresponding diphenyl compounds are unknown [4].

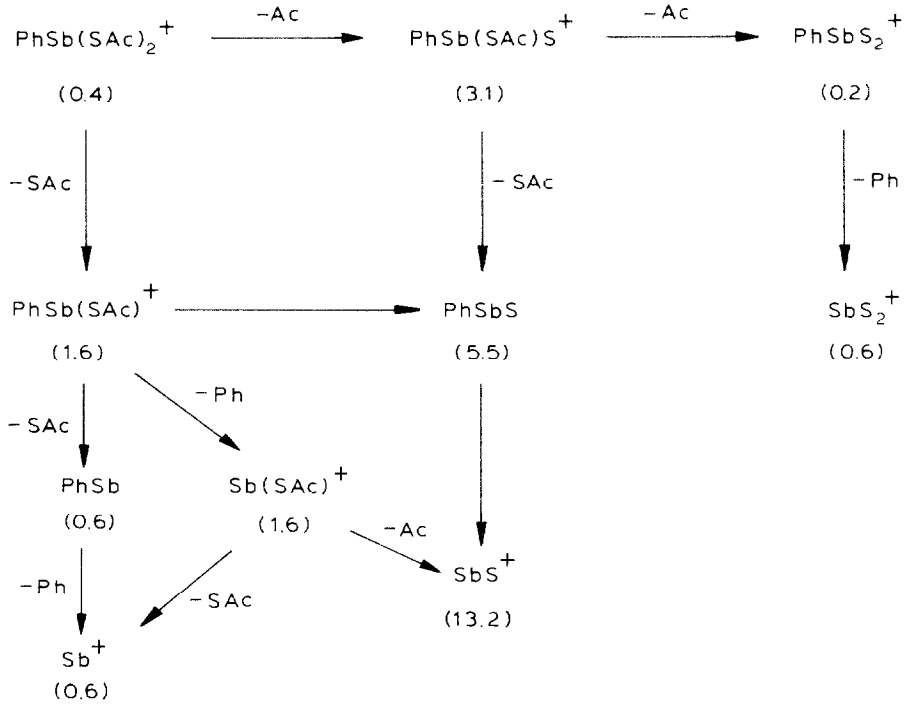
To investigate further the specific stability relationships in the series of phenyl substituted antimony(III) acetates and thioacetates, we have fully characterised the new compound, $PhSb(SAc)_2$.

Results and discussion

IR and mass spectra

The IR spectrum (see Experimental) includes, in addition to the expected phenyl and methyl group bands, a strong band at 1625 cm^{-1} assigned to $\nu(C{=}O)$ pointing to thioacetate bonding via the sulphur atom. The $Sb(SAc)_3$ spectrum also contains a band at this position and S-bonding there was confirmed by X-ray crystallography [1]. Strong bands at 385 and 640 cm^{-1} can then be assigned to $\nu(Sb{-}S)$ and $\nu(C{-}S)$, respectively.

Electron impact mass spectrometry, summarised for the Sb–S-containing fragments in Scheme 1, also provides evidence for Sb–S rather than Sb–O primary bonding. Fragmentation of the related $Sb(SAc)_3$ involved primarily loss of thioacetate groups [1], but here there is competition between thioacetate and acetyl group



SCHEME 1. Sb–S-containing fragments in the mass spectrum of $PhSb(SAc)_2$; figures in parentheses are % ion current carried.

loss. The major antimony-containing fragments are in fact $PhSb(SAc)S^+$, $PhSbS^+$ and SbS^+, but by far the greatest proportion of the ion current is carried by the $MeCO^+$ ion (33.3%). In comparison, the $MeCS^+$ ion carries 0.3%.

Structure of $PhSb(SAc)_2$

Confirmation of Sb–S bonding comes from a single crystal X-ray determination which also shows significant antimony–oxygen interaction. The molecular structure and the atom numbering scheme are shown in Fig. 1 and important bond distances and angles are summarised in Table 1.

The primary bonds from antimony to C(1), S(1) and S(2) form the usual pyramid but the angles vary from 84.8 to 97.2° and distances to the two independent sulphur atoms are unequal. The longer bond is to S(2) which, as discussed below, also forms a weak intermolecular Sb · · · S contact and probably accounts for bond lengthening. The two Sb–O secondary bonds are more nearly equal (mean 2.81 Å) and fall well within the sum of the Van der Waals radii (3.6 Å). The Sb–S distances are comparable with those in $Sb(SAc)_3$ but the Sb · · · O distances are longer than in the two chelating groups in $Sb(SAc)_3$ reflecting the lower Lewis acidity of antimony in the phenyl substituted compound. The third thioacetate group in $Sb(SAc)_3$ is a bridging-chelating group linking molecules into infinite chains; this type of intermolecular interaction is not found in the present compound.

The individual $SbSOC_2$ groups and the phenyl group are planar, as expected, but a plane (mean deviation 0.03 Å) can also be drawn through both thioacetate groups; the antimony lies 0.15 Å below this plane.

Coordination about antimony is thus distorted square pyramidal with the phenyl group in the apical position. Angles between C(1) and the basal sulphur and oxygens average 96.9 and 84.3°, respectively but those in the basal plane vary from a mean of 57.8° for the S–Sb–O chelate group through 84.8° (S(1)–Sb(1)–S(2)) to 158.3° (O(1)–Sb(1)–O(2)) showing the extent of distortion from square pyramidal

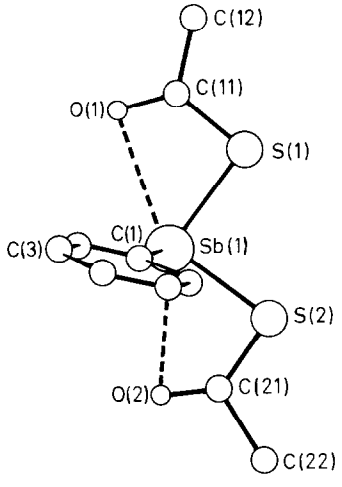


Fig. 1. Structure of $PhSb(SAc)_2$ showing the atom numbering scheme.

TABLE 1

BOND DISTANCES (Å) AND ANGLES (°) FOR $PhSb(SAc)_2$ (with estimated standard deviations in parentheses)

Sb(1)–C(1)	2.148(7)	C(1)–C(2)	1.35(1)
Sb(1)–S(1)	2.451(2)	C(2)–C(3)	1.39(1)
Sb(1)–S(2)	2.471(2)	C(3)–C(4)	1.36(1)
Sb(1)–O(1)	2.808(6)	C(4)–C(5)	1.38(1)
Sb(1)–O(2)	2.818(6)	C(5)–C(6)	1.38(1)
Sb(1)···S(2′) [a]	3.802(2)	C(6)–C(1)	1.41(1)
S(1)–C(11)	1.77(1)	S(2)–C(21)	1.76(1)
O(1)–C(11)	1.18(1)	O(2)–C(21)	1.19(1)
C(12)–C(11)	1.49(1)	C(22)–C(21)	1.50(1)
C(1)–Sb(1)–S(1)	97.2(2)	Sb(1)–C(1)–C(2)	116.8(5)
C(1)–Sb(1)–S(2)	96.6(3)	Sb(1)–C(1)–C(6)	123.2(5)
C(1)–Sb(1)–O(1)	83.6(2)	C(1)–C(2)–C(3)	120.2(7)
C(1)–Sb(1)–O(2)	85.1(2)	C(2)–C(3)–C(4)	120.3(8)
C(1)–Sb(1)–S(2′)	175.5(2)	C(3)–C(4)–C(5)	120.0(7)
S(1)–Sb(1)–S(2)	84.8(1)	C(4)–C(5)–C(6)	120.3(8)
S(1)–Sb(1)–O(1)	57.9(1)	C(5)–C(6)–C(1)	119.2(8)
S(1)–Sb(1)–O(2)	142.0(1)	C(6)–C(1)–C(2)	120.0(7)
S(1)–Sb(1)–S(2′)	78.3(1)		
S(2)–Sb(1)–O(1)	142.3(1)	Sb(1)–S(1)–C(11)	91.6(3)
S(2)–Sb(1)–O(2)	57.6(1)	Sb(1)–O(1)–C(11)	90.7(5)
S(2)–Sb(1)–S(2′)	83.1(1)	S(1)–C(11)–O(1)	119.8(6)
O(1)–Sb(1)–O(2)	158.3(2)	S(1)–C(11)–C(12)	115.9(6)
O(1)–Sb(1)–S(2′)	93.9(1)	O(1)–C(11)–C(12)	124.3(8)
O(2)–Sb(1)–S(2′)	98.4(1)	Sb(1)–S(2)–C(21)	91.5(3)
		Sb(1)–O(2)–C(21)	90.8(4)
		S(2)–C(21)–O(2)	120.0(6)
		S(2)–C(21)–C(22)	116.3(7)
		O(2)–C(21)–C(22)	123.7(8)

[a] Related by the symmetry operation $-x, 1-y, -z$.

geometry. This arrangement is also found in $MeSb(S_2COEt)_2$ [5], $MeBi(S_2CNEt_2)_2$ [6], and $PhBi(S_2COMe)_2$ [7].

The basic coordination about the central atom may be complicated by two factors, i.e. the stereochemical activity of the s^2 pair of electrons and the possibility of weak bonding between the central atom and a symmetry related sulphur atom. In the present case, the position *trans* to the phenyl group is occupied by a symmetry related sulphur atom at 3.802 Å (cf. ca. 4.0 Å for the Sb ··· S Van der Waals separation) giving weak dimerisation (see Fig. 2). It is thus unlikely that the lone pair of electrons is also located here. An alternative site for the electron pair would be in the SbS_2O_2 basal plane, bisecting the large O(1)–Sb(1)–O(2) angle and giving overall pseudo-pentagonal bipyramidal coordination. On simple electrostatic grounds this is unlikely, and as we have argued before [8] the lone pair is probably inactive. There is a significant non-bonded interaction between S(1) and S(2) at 3.32 Å, which is substantially shorter than the Van der Waals separation (ca. 3.8 Å) and this, together with the ligand bite could well account for the observed geometry.

The $PhSb(SAc)_2$ molecule has no molecular symmetry, the possible mirror plane through antimony perpendicular to the S_2O_2 basal plane is broken by the phenyl

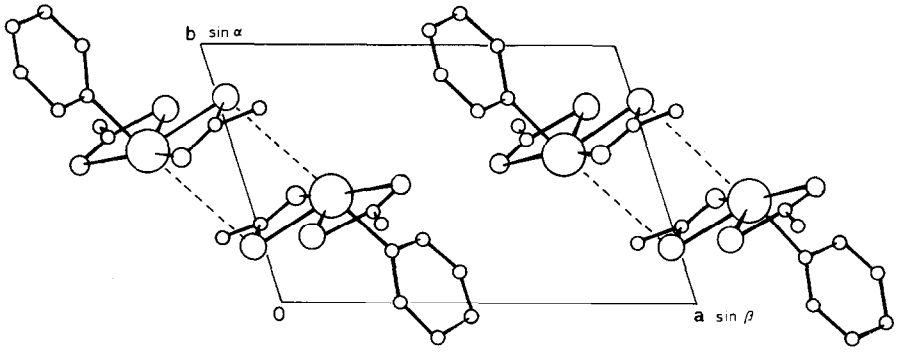


Fig. 2. Projection of the unit cell contents down the c axis.

group whose orientation is defined by S(1)–Sb(1)–C(1)–C(6) and S(2)–Sb(1)–C(1)–C(6) torsion angles of 15.2 and −70.3° respectively.

Instability of Ph_2SbSAc and $PhSb(OAc)_2$

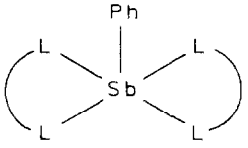
The isolation of $PhSb(SAc)_2$ and Ph_2SbOAc from reactions designed to produce Ph_2SbSAc and $PhSb(OAc)_2$ respectively, must imply that during the preparations there are phenyl group reorganisations. This is known to occur in mixtures of Ph_3Sb and SbX_3 (X = Cl or Br) when good yields of Ph_2SbX and $PhSbX_2$ can be obtained [9]. It is unlikely, however, that in the room temperature reactions between Ph_2SbCl and potassium thioacetate, there is an initial reorganisation of the monochloride to $PhSbCl_2$ and Ph_3Sb with the former reacting to give the observed product. The acetate reaction is less clear, as the reactions were carried out in refluxing methanol, and reorganisation as a preliminary step cannot be ruled out completely. A more attractive alternative is the initial formation of, respectively, Ph_2SbSAc and either $PhSbCl(OAc)$ or $PhSb(OAc)_2$, followed by reorganisation to the thermodynamically stable products.

Some insight into the different reorganisation paths can be gained from a comparison of the $Sb(OAc)_3$ and $Sb(SAc)_3$ structures and from the bonding pattern in substituted halogenoantimonate anions. Although the acetate and thioacetate structures are similar with strong, primary bonds to oxygens and sulphurs respectively and secondary interactions giving two asymmetrically chelating ligands and one which both chelates and bridges, bridging is far more important in the acetate (cf. Sb–O(6′) 2.600 and 3.043 Å respectively for the acetate and thioacetate [1]). Another important difference is in the angles at the primary bonded atoms, which range between 104.9 and 108.6° for the oxygens in $Sb(OAc)_3$ and between 89.7 and 93.3° at the sulphurs in $Sb(SAc)_3$.

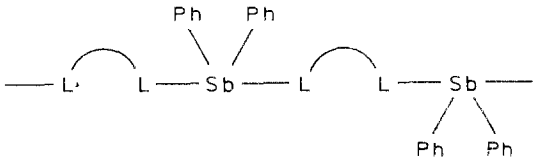
The similarities follow from the relatively high Lewis acidity of antimony in both compounds. Successive substitution by phenyl groups both lowers the antimony Lewis acidity and reduces the possibility of incorporating ligands in positions *trans* to phenyl substituents. These effects are shown most clearly in the extent to which members of the Ph_nSbCl_{3-n} series, where $n = 0$–3, will add further chloride ions from solution. The trichloride, for example, forms the $SbCl_4^-$, $SbCl_5^{2-}$ and $SbCl_6^{3-}$ series of anions, while the monophenyl derivative will add one or two

chloride ions. The diphenyl compound, on the other hand, gives $Ph_2SbCl_2^-$ only and anions based on Ph_3Sb cannot be obtained [10]. The structures of all these anions can be rationalised if chloride ions successively enter *trans* to chlorines in the starting compound. In this way, ionic charges can be delocalised by three centre-four electron bonding over linear Cl$^-$ ··· Sb–Cl systems. Such bonding is not possible if a chloride ion approaches *trans* to a phenyl group.

Constraints are imposed if a uninegative, potentially bidentate group (LL), such as acetate or thioacetate is considered in place of chlorine. A monomeric, bis-chelate structure (**1**), where the electronegative donor atoms occupy *trans* positions, can be predicted for $PhSb(LL)_2$ but the ligand in $Ph_2Sb(LL)$ would necessarily be bridging (**2**) if coordination sites *trans* to the phenyl groups were avoided. Structures **1** and **2**



(1)



(2)

are, in fact, observed for $PhSb(SAc)_2$ and Ph_2SbOAc, respectively. The absence of Ph_2SbSAc and $PhSb(OAc)_2$ must then be a function of differences in ligand behaviour of the two groups.

Both are classified as short bite ligands but the longer bite for thioacetate coupled with a preference for sulphur angles close to 90° will lead to chelation rather than bridging as the dominant bonding mode. The unknown Ph_2SbSAc would therefore not be stable and, because of the general lability of phenyl groups, reorganisation would occur giving the $PhSb(SAc)_2$ chelate and Ph_3Sb. The converse applies with the acetate group where the bite is shorter and the preferred angle at the bonded oxygen is much larger, i.e. close to 120° in Ph_2SbOAc. Formation of the unknown chelate $PhSb(OAc)_2$ would require the closing of the Sb–O–C angle but, because bridging is more stable, reorganisation takes place to give the diphenyl derivative Ph_2SbOAc and presumably $Sb(OAc)_3$ *.

The major influences in determining stability and structure in these systems are therefore (a) the absence of ligand atoms *trans* to a phenyl group, (b) the preservation of the preferred angles of ca. 90 and 120° at bonded sulphur and oxygen atoms, and (c) the maximising of secondary bonding via chelation for thioacetate and bridging for acetate.

Experimental

$PhSbCl_2$ and Ph_2SbCl were prepared by reorganisation of mixtures of Ph_3Sb and $SbCl_3$ in the appropriate ratio [9].

* A number of phenyl-substituted dicarboxylates are, in fact, known, e.g. $PhSb(O_2CR)_2$ where R = t-Bu, Ph or CF_3 (M. Wieber and I. Fetzer-Kremling, Z. Naturforsch. B, 39 (1984) 754) and $PhBi(O_2CR)_2$ where R = Me or CF_3 (G.B. Deacon, W.R. Jackson and J.M. Pfeiffer, Aust. J. Chem., 37 (1984) 527); bridging acetate groups are probably present in $PhBi(OAc)_2$ and the compound also redistributes to give Ph_2BiOAc.

Phenylantimony bis(monothioacetate)

Phenylantimony dichloride (4.1 g, 0.015 mol) and potassium thioacetate (3.4 g, 0.03 mol) were dissolved separately in the minimum volume of ethanol. On mixing, there was immediate precipitation of potassium chloride which was filtered off. The solvent was removed under vacuum from the mother liquor and the resulting oil was recrystallised from hexane. Yield 3.2 g, 61%, m.p. 55–57°C. (Found: C, 34.4; H, 2.9. $PhSb(SAc)_2$ calcd.: C, 34.4; H, 3.2%). Bands in the IR spectrum below 1700 cm^{-1} were at: 1625vs, 1475m, 1430s, 1360w, 1295w, 1260w, 1190m, 1160s, 1142s, 1118vs, 1095sh, 1060s, 1020m, 1000s, 956vs, 913w, 848m, 730vs, 690s, 640vs, 535m, 515s, 495s, 450s, and 385s cm^{-1}.

Attempted preparation of diphenylantimony monothioacetate

Solutions of diphenylantimony chloride (4.6 g, 0.015 mol) and potassium thioacetate (1.6 g, 0.016 mol) in ethanol were mixed as above to give an immediate precipitate of potassium chloride. After filtration and partial evaporation of the mother liquor, crystals of triphenylantimony, m.p. 50°C (lit. [11] 51–52°C) separated (Found: C, 61.4; H, 4.2. Ph_3Sb calcd.: C, 61.2; H, 4.3%). After filtration the mother liquor was evaporated to dryness and the residue recrystallised from hexane to give $PhSb(SAc)_2$. M.p. 54–57°C. (Found: C, 34.2; H, 3.0%). In reactions carried out in hexane, ether or dichloromethane, only triphenylantimony and/or phenylantimony bis(monothioacetate) were isolated.

Attempted preparation of phenylantimony diacetate

From $PhSbCl_2$. Phenylantimony dichloride and an excess of anhydrous sodium acetate were refluxed for 24 h in dry methanol. The solution was cooled and after filtration the volume was slowly reduced on a rotary evaporator until crystallisation. Cooling then gave crystals of diphenylantimony acetate, m.p. 130°C (lit. [12], 131–132°C). (Found: C, 50.3; H, 3.8. Ph_2SbOAc calcd.: C, 50.1; H, 4.0%.)

From $(PhSbO)_n$. Phenylantimony oxide, obtained by hydrolysis of $PhSbCl_2$, was dissolved in acetic anhydride by heating to ca. 60°C for 2 h. A small amount of undissolved solid was filtered off and the solution cooled to give crystals of Ph_2SbOAc. M.p. 132°C. (Found: C, 49.7; H, 3.7%.)

Crystal structure of $PhSb(SAc)_2$

Crystal data. $C_{10}H_{11}O_2S_2Sb$, $M = 349.1$, triclinic, a 10.761(4), b 7.304(3), c 9.608(7) Å, α 112.84(5), β 102.57(5), γ 100.17(5)°, U 649.7 $Å^3$, $Z = 2$, D_c 1.78 g cm^{-3}, $F(000) = 340$, space group $P\bar{1}$, Mo-K_α radiation, λ 0.7107 Å, μ 24.3 cm^{-1}, $R = 0.36$.

Structure determination. Crystals suitable for X-ray diffraction were obtained by slow crystallisation from hexane. Data were collected using a Hilger and Watts four circle diffractometer for 2121 observed reflections for which $I > 3\sigma(I)$, which were corrected for Lorentz and polarisation effects; an absorption correction was not necessary. Crystallographic calculations used the CRYSTALS programs [13]; scattering factors were for neutral atoms [14]. The antimony atom was located by Patterson methods and subsequent Fourier syntheses revealed the other non-hydrogen atoms. Full matrix least-squares refinement converged at $R = 0.088$ with isotropic and 0.052 with anisotropic thermal parameters, the hydrogen atoms placed at their calculated positions and application of a four coefficient Chebyshev

TABLE 2

ATOMIC COORDINATES ($\times 10^4$) FOR $PhSb(SAc)_2$ (with estimated standard deviations in parentheses)

Atom	x	y	z
Sb(1)	2044.5(4)	4162.5(6)	−40.8(5)
C(1)	3051(7)	1962(11)	−1099(7)
C(2)	3890(8)	2513(12)	−1823(9)
C(3)	4580(8)	1172(15)	−2534(11)
C(4)	4418(8)	−705(14)	−2503(11)
C(5)	3559(9)	−1288(13)	−1779(11)
C(6)	2859(8)	18(12)	−1081(9)
S(1)	1270(2)	2578(3)	1560(2)
C(11)	2860(8)	3635(12)	3005(9)
O(1)	3741(6)	4644(10)	2828(7)
C(12)	2990(9)	3135(16)	4380(10)
S(2)	−191(2)	2190(3)	−2001(2)
C(21)	199(8)	3110(13)	−3345(9)
O(2)	1287(6)	4162(10)	−3039(7)
C(22)	−894(11)	2426(16)	−4870(11)

weighting scheme. A final difference Fourier showed no peaks greater than 0.5 e $Å^{-3}$, except in the vicinity of the heavy atoms. Refined atomic coordinates are listed in Table 2.

References

1 M. Hall and D.B. Sowerby, J. Chem. Soc., Dalton Trans., (1980) 1292.
2 S.P. Bone and D.B. Sowerby, J. Organomet. Chem., 184 (1980) 181.
3 M and T Chemicals Inc., Neth. Appl. 6505219, Chem. Abstr., 64 (1966) 9766g.
4 E.J. Kupchik and C.T. Theisen, J. Organomet. Chem., 11 (1968) 627.
5 M. Wieber, D. Wirth and C. Burschka, Z. Anorg. Allg. Chem., 505 (1983) 141.
6 C. Burschka and M. Wieber, Z. Naturforsch. B, 34 (1979) 1037.
7 C. Burschka, Z. Anorg. Allg. Chem., 485 (1982) 217.
8 D.B. Sowerby, I. Haiduc, A. Barbul-Rusu and M. Salajan, Inorg. Chim. Acta, 68 (1983) 87; M.J. Begley, D.B. Sowerby and I. Haiduc, J. Chem. Soc., Dalton Trans., in press.
9 M. Nunn, D.B. Sowerby and D.M. Wesolek, J. Organomet. Chem., 251 (1983) C45.
10 M. Hall and D.B. Sowerby, unpublished work.
11 N.S. Vyazankin, G.A. Razuvaev, O.A. Kruglaya and G.S. Semchikova, J. Organomet. Chem., 6 (1966) 474.
12 J.R. Leebrick and N.L. Remes (M and T Chemicals Inc.), U.S. Patent 3 367 954; Chem. Abstr., 68 (1968) 105367.
13 J.R. Carruthers, CRYSTALS, The Oxford Crystallographic Programs, 1975.
14 International Tables for X-ray Crystallography, Kynoch Press, Birmingham, Vol. 4, 1974.