Synthesis of Diphenylantimony(III) Dialkyldithio- and Diaryldithio-phosphinates and -arsinates; Crystal Structures of $Ph_2SbS_2MPh_2$ (M = P or As)†

Christian Silvestru, Luminita Silaghi-Dumitrescu, and Ionel Haiduc *
Department of Chemistry, Babes-Bolyai University, Cluj-Napoca, Romania
Michael J. Begley, Michael Nunn, and D. Bryan Sowerby *
Department of Chemistry, University of Nottingham, Nottingham, NG7 2RD

Diphenylantimony(III) dithiophosphinates and dithioarsinates, $Ph_2SbS_2MR_2$ (M = P, R = Me, Et, Pr, or Ph; M = As, R = Me or Ph), have been synthesised and characterised by their i.r. and ^1H n.m.r. spectra. Structures have been determined for $Ph_2SbS_2MPh_2$ (M = P or As). The compounds crystallise in the triclinic space group $P\bar{1}$ ($Z = 2$), with $a = 9.099(3)$, $b = 11.397(3)$, $c = 12.382(4)$ Å, $\alpha = 114.54(2)$, $\beta = 106.93(2)$, and $\gamma = 75.41(2)°$ for M = P and $a = 9.155(3)$, $b = 11.518(3)$, $c = 12.390(4)$ Å, $\alpha = 115.07(2)$, $\beta = 106.39(2)$, and $\gamma = 75.48(2)°$ for M = As. In each compound there is one short Sb–S contact at 2.490(1) Å for M = P and 2.486(2) for M = As but there are two longer Sb · · · S contacts (3.440 and 3.474 Å for M = P and 3.590 and 3.369 Å for M = As). This leads to dimerisation and the formation of eight-membered $Sb_2S_4M_2$ rings with transannular Sb · · · S interactions. Antimony is thus in five-fold, distorted square-pyramidal co-ordination.

Ligands containing the $S_2P<$ grouping are known to exhibit a remarkable diversity of co-ordination patterns[1] and although their interactions with transition metals are well known,[2] it is only recently that main group and related organometallic derivatives have been investigated.[3] Antimony species are of interest not only because of their potential catalytic activity[4] but because structural investigations on $Sb[S_2P(OR)_2]_3$ (R = Me or Pr^i)[5] and $Sb(S_2PPh_2)_3$[6] have shown differing co-ordination properties leading to pentagonal pyramidal geometry about antimony in the latter. In view of this, it was of interest to investigate the structural changes resulting from the attachment of organic groups to antimony and we now report the preparation of a series of diphenylantimony dithiophosphinates and the crystal structure of $Ph_2SbS_2PPh_2$ (**1**).

In contrast to the large number of dithiophosphorus compounds, the related arsenic species are less well known, and are restricted to a number of transition metal[7] and Group 4 organometallic[8] derivatives. This paper also reports the synthesis of two substituted antimony dithioarsinates and the crystal structure of $Ph_2SbS_2AsPh_2$ (**2**).

Results and Discussion

In general the compounds have been prepared from diphenylantimony(III) acetate and either the free acid or the sodium salt of the appropriate dithiophosphinic or dithioarsinic acid, equations (1) and (2) (M = P, R = Me, Et, or Pr; M = As, R = Me or Ph). Details are summarised in Table 1. The products can be recrystallised without decomposition and although they are stable in air, they should be stored under nitrogen.

$$Ph_2SbO_2CMe + Ph_2P(S)SH \longrightarrow Ph_2SbS_2PPh_2 + HO_2CMe \quad (1)$$

$$Ph_2SbO_2CMe + R_2MS_2Na \longrightarrow Ph_2SbS_2MR_2 + NaO_2CMe \quad (2)$$

I.r. and N.M.R. Spectra.—I.r. bands in the 585—640 and 460—535 cm^{-1} regions can be assigned respectively to P=S and P–S stretching modes (see Table 2). Although in compounds of this type there is some mixing of the P–S and P–C stretching modes,[9] differences between either $\nu(P{=}S)$ and $\nu(P{-}S)$ or $\nu_{asym}(PS_2)$ and $\nu_{sym}(PS_2)$ can be used to determine the co-ordination behaviour of the ligand. Differences falling in the ranges 50—70 and 70—90 cm^{-1} are indicative of isobidentate and anisobidentate co-ordination respectively. Values in excess of 95 cm^{-1} imply unidentate co-ordination.[10] Separations between the main bands here are in the range 103—121 cm^{-1}, thus appearing to imply unidentate behaviour. The situation with the two arsenic derivatives is similar, with bands occurring at positions close to those in compounds known to have unidentate structures.[8,11]

As shown in Table 2, each of the main bands is split showing the in-phase and out-of-phase components expected from the solid-state dimeric structure (see below). The band splitting also occurs in solution spectra suggesting persistence of the dimer in $CHCl_3$ solution. The i.r. data, in particular the $\Delta\nu$ values, are thus rather misleading in predicting the co-ordination behaviour of these ligands.

Proton n.m.r. data summarised in Table 3 show the features expected for such organophosphorus[12] and organoarsenic[8,11] species. In all cases, the phenyl groups give complex multiplets with signals centred at 7.35 and 7.90 p.p.m. for the groups attached to phosphorus in $Ph_2SbS_2PPh_2$ compared with 7.21 and 7.43 p.p.m. for the analogous arsinate. Resonances of the Ph_2Sb protons also vary slightly with changes in substituent in the thiophosphinate moiety.

Structures of $Ph_2SbS_2PPh_2$ (**1**) *and* $Ph_2SbS_2AsPh_2$ (**2**).—*X*-Ray results show that the two compounds are isostructural and important bond distance and angle data are listed in Table 4. In agreement with the i.r. data, the dithio-phosphinate and -arsinate ligands are basically unidentate leading to pyramidal geometry about each antimony atom. Angles range between 92.6(1) and 94.2(1)° for (**1**) and 92.5(2) and 94.4(2)° for (**2**). Sb–C and Sb–S distances are as expected. The tetrahedral geometry about phosphorus and arsenic in the ligand is distorted with, in particular, the S(1)–M–S(2) angle increased to *ca.* 116°. The P–S bond distances in (**1**), 2.081(1) and 1.958(1) Å, are close to the single and double bond distances reported for $Me_2Sn[S(S)$-

---

† Diphenylantimony(III) diphenyldithio-phosphinate and -arsinate.

Supplementary data available (No. SUP 56470, 6 pp.): thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Preparation, properties, and elemental analysis of diphenylantimony dithio-derivatives

Complex	Dithio-derivative (g) Solvent (cm^3)	Ph_2SbO_2CMe (g) Solvent (cm^3)	M.p. (°C)	Yield (%)	Recrystallisation solvent	Found (calc.) (%)	
						C	H
$Ph_2SbS_2PMe_2$	$Me_2PS_2Na{\cdot}2H_2O$ (0.92)	1.674	104—105	63	MeCN	41.6	4.0
	$CHCl_3$ (20)	$CHCl_3$ (20)				(41.9)	(4.0)
$Ph_2SbS_2PEt_2$	$Et_2PS_2Na{\cdot}2H_2O$ (0.42)	0.67	71—73	76	$CHCl_3$	44.3	4.7
	Me_2CO (15)	Me_2CO (15)				(44.8)	(4.7)
$Ph_2SbS_2PPr_2$	Pr_2PS_2Na (0.68)	1.116	112—114	87	MeCN	46.9	5.5
	Me_2CO (20)	Me_2CO (20)				(47.3)	(5.3)
$Ph_2SbS_2PPh_2$	$Ph_2P(S)SH$ (0.50)	0.67	140—142	86	Me_2CO	54.9	3.8
	MeOH (15)	MeOH (15)				(54.9)	(3.8)
$Ph_2SbS_2AsMe_2$	$Me_2AsS_2Na{\cdot}2H_2O$ (0.45)	0.67	132	81	Me_2CO	37.2	3.3
	EtOH (20)	Me_2CO (15)				(37.8)	(3.6)
$Ph_2SbS_2AsPh_2$	Ph_2AsS_2Na (0.63)	0.67	126	86	Me_2CO	50.3	3.6
	Me_2CO (20)	Me_2CO (15)				(50.6)	(3.5)

Table 2. I.r. spectra of diphenylantimony dithio-derivatives (cm^{-1})

Compound	ν(M=S)	ν(M–S)	Δν(M–S)
$Ph_2SbS_2PMe_2$	597s	476s	121
	592 (sh)	465 (sh)	
$Ph_2SbS_2PEt_2$	588s	485s	103
	570 (sh)	460 (sh)	
$Ph_2SbS_2PPr_2$	605s	495s	110
	585m	512w	
$Ph_2SbS_2PPh_2$	640m	535s	105
	605s	495m	
$Ph_2SbS_2AsMe_2$	475m	414m	61
	470 (sh)	422 (sh)	
$Ph_2SbS_2AsPh_2$	485m	420m	65
	479 (sh)	426 (sh)	

Table 3. ^{1}H N.m.r. spectra of $Ph_2SbS_2MR_2$ (M = P or As)[a]

	$Ph_2SbS_2PR_2$[b]	
R	S_2PR_2	$(C_6H_5)_2Sb$[c]
Me	1.89	7.27, 7.46
	$^2J_{PH}$ = 12.2	
Et	1.15 (CH_3), 1.98 (CH_2)	7.29, 7.57
	$^2J_{PH}$ = 10.4, $^3J_{PH}$ = 21.04, $^3J_{HH}$ = 7.2	
Pr	0.91[d] (CH_3), 1.79[d] (CH_2)	7.22, 7.53
Ph	7.35,[c] 7.90[c]	7.35, 7.57

	$Ph_2SbS_2AsR_2$[e]	
R	S_2AsR_2	$(C_6H_5)_2Sb$[c]
Me	2.05	7.16, 7.39
Ph	7.21,[c] 7.43[c]	7.21, 7.43

[a] Chemical shifts (δ) are reported in p.p.m. relative to hexamethyldisiloxane; coupling constants are in Hz. [b] In $CDCl_3$. [c] Complex second-order multiplets. [d] Broad and poorly resolved. [e] In CCl_4.

Table 4. Interatomic distances (Å) and bond angles (°), with estimated standard deviations in parentheses, for $Ph_2SbS_2MPh_2$ *

	M = P	M = As
Sb(1)–S(1)	2.490(1)	2.486(2)
Sb(1)–S(2)	3.440(1)	3.590(2)
Sb(1)–S(2′)	3.474(1)	3.369(2)
Sb(1)–C(1)	2.151(4)	2.136(7)
Sb(1)–C(7)	2.155(4)	2.142(6)
M(1)–S(1)	2.081(1)	2.214(2)
M(1)–S(2)	1.958(1)	2.050(2)
M(1)–C(13)	1.811(4)	1.944(6)
M(1)–C(19)	1.817(4)	1.940(6)
Sb(1)–Sb(1′)	3.890(1)	3.912(2)
S(1)–Sb(1)–S(2)	68.3(1)	70.8(2)
S(1)–Sb(1)–S(2′)	175.9(1)	174.2(2)
S(1)–Sb(1)–C(1)	92.6(1)	93.1(2)
S(1)–Sb(1)–C(7)	92.9(1)	92.5(2)
S(2)–Sb(1)–S(2′)	111.5(1)	111.7(2)
S(2)–Sb(1)–C(1)	94.5(1)	95.2(2)
S(2)–Sb(1)–C(7)	159.7(1)	161.1(2)
S(2′)–Sb(1)–C(1)	91.5(1)	91.0(2)
S(2′)–Sb(1)–C(7)	86.6(1)	84.2(2)
C(1)–Sb(1)–C(7)	94.2(1)	94.4(2)
Sb(1)–S(1)–M(1)	97.1(1)	96.2(2)
Sb(1)–S(2)–M(1)	73.4(1)	70.9(2)
Sb(1)–S(2)–Sb(1′)	68.5(1)	68.3(2)
Sb(1′)–S(2)–M(1)	137.3(1)	134.2(2)
S(1)–M(1)–S(2)	115.7(1)	116.8(2)
S(1)–M(1)–C(13)	105.1(1)	104.2(2)
S(1)–M(1)–C(19)	105.0(1)	105.3(2)
S(2)–M(1)–C(13)	112.9(1)	113.8(2)
S(2)–M(1)–C(19)	111.6(1)	110.5(2)
C(13)–M(1)–C(19)	105.7(1)	105.3(3)

* Primed atoms are related to unprimed ones by the transformation *x*, *y*, *z* ⟶ −*x*, 1 − *y*, −*z*.

$PMe_2]_2$ (2.047 and 1.969 Å)[13] and $Ph_2P(S)SH$ (2.077 and 1.954 Å),[14] while the As–S distances in (**2**), 2.214(2) and 2.050(2) Å, can be compared with the single and double bond distances of 2.171 and 2.089 Å in $Me_2Sn[S(S)AsMe_2]_2$[8c] and 2.214 and 2.075 Å in $Me_2AsS(S)AsMe_2$.[11]

The antimony atoms in both (**1**) and (**2**), however, each form longer contacts, which are well within the sum of the van der Waals radii (*ca.* 4.0 Å), to two further sulphur atoms. The first is intermolecular, leading to dimerisation and the formation of eight-membered $Sb_2S_4M_2$ rings through Sb(1)···S(2′) interactions at 3.474 and 3.369 Å for (**1**) and (**2**) respectively. In passing, the longer Sb(1)···S(2′) distance for phosphorus is perhaps surprising but this is probably necessary here to maintain a suitable separation (*ca.* 3.9 Å) between the two antimony atoms. The second is an intramolecular interaction between Sb(1) and S(2) at 3.440 and 3.590 Å respectively for (**1**) and (**2**) which leads to two transannular contacts; the S(2) atoms then become effectively three-co-ordinate. The dimer structure, which is related to that in $Sn[S_2P(OPh)_2]_2$,[15] is shown in the Figure.

If these weaker bonds are considered, the co-ordination number of antimony is raised to five and the geometry about the heavy atom is distorted square pyramidal. *cis* Angles ranging

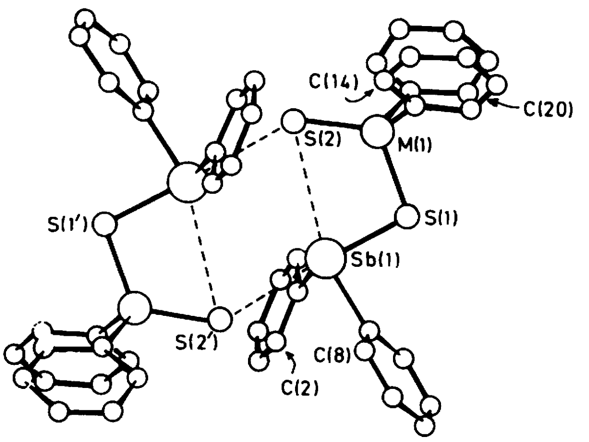

Figure. Molecular structure and atom-numbering scheme for the dimers formed by $Ph_2SbS_2MPh_2$ [M = P(**1**) or As(**2**)]

Table 5. Fractional atomic co-ordinates for $Ph_2SbS_2PPh_2$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	0.034 22(3)	0.596 20(2)	0.174 58(2)
S(1)	−0.068 0(2)	0.549 9(1)	0.316 48(9)
P(1)	−0.147 0(1)	0.376 43(9)	0.192 80(9)
S(2)	−0.199 3(1)	0.356 8(1)	0.021 74(9)
C(1)	−0.152 6(5)	0.753 2(4)	0.165 6(4)
C(2)	−0.304 2(5)	0.742 8(5)	0.157 0(4)
C(3)	−0.421 8(6)	0.845 0(6)	0.150 2(5)
C(4)	−0.390 3(7)	0.955 6(5)	0.148 5(5)
C(5)	−0.240 3(7)	0.965 5(5)	0.155 7(4)
C(6)	−0.121 4(5)	0.864 9(5)	0.164 1(4)
C(7)	0.187 7(5)	0.721 5(4)	0.320 4(4)
C(8)	0.342 0(5)	0.699 8(4)	0.311 6(5)
C(9)	0.445 2(6)	0.779 3(5)	0.401 9(5)
C(10)	0.396 4(6)	0.877 7(5)	0.500 5(5)
C(11)	0.245 2(7)	0.899 5(5)	0.511 1(5)
C(12)	0.139 7(5)	0.821 7(4)	0.420 5(4)
C(13)	0.002 5(4)	0.248 4(4)	0.223 3(4)
C(14)	0.062 3(5)	0.147 4(5)	0.130 2(4)
C(15)	0.171 0(6)	0.047 1(5)	0.152 7(5)
C(16)	0.218 4(5)	0.045 0(5)	0.267 6(5)
C(17)	0.163 2(6)	0.145 7(6)	0.360 8(5)
C(18)	0.057 3(6)	0.248 5(5)	0.340 6(5)
C(19)	−0.313 8(5)	0.370 0(4)	0.241 7(4)
C(20)	−0.306 0(6)	0.389 9(6)	0.361 5(5)
C(21)	−0.432 3(8)	0.371 3(7)	0.391 1(7)
C(22)	−0.564 1(7)	0.337 6(6)	0.304 6(7)
C(23)	−0.573 8(7)	0.322 6(6)	0.189 2(7)
C(24)	−0.448 3(6)	0.338 1(5)	0.156 0(5)

between 68.3(1) and 111.5(1)° for (**1**) and 70.8(2) and 111.7(2)° for (**2**) describe the extent of the distortion; in addition the angles between the apical atom, C(1), and the four basal atoms all exceed 90° [91.5(1)—94.5(1)° for (**1**) and 91.0(2)—95.2(2)° for (**2**)]. As a consequence the antimony atom is displaced by 0.18 and 0.15 Å for (**1**) and (**2**) respectively from the best plane through S(1), S(2), S(2'), and C(7) toward the apical atom. The maximum deviation of any basal atom from this best plane is 0.06 Å.

The antimony lone pair of electrons is sometimes considered to be sterically active and in the present case might occupy the space *trans* to C(1), giving pseudo-octahedral geometry about antimony. If this were the case, the antimony would lie below the S(1), S(2), S(2'), and C(7) plane with angles of less than 90° between the apical and basal atoms. The fact that this is not observed supports the absence of steric activity of the lone pair.

The four-membered Sb(1)S(2)Sb(1')S(2') ring is necessarily planar but distortion of the eight-membered ring from a chair to a twist-chair conformation is indicated by torsion angles in the $Sb_2S_4As_2$ ring of −103, −26, +46, −142, 103, 26, −46, and 142° for the bonds starting from Sb(1)–S(1).

Experimental

I.r. spectra were recorded on KBr discs and $CHCl_3$ solutions using a Spectrocord 75 spectrometer. ^1H N.m.r. spectra were recorded on $CDCl_3$ or CCl_4 solutions with hexamethyldisiloxane as standard using a Tesla B-487 spectrometer.

Preparation of Diphenylantimony Dithio-phosphinates and -arsinates.—The starting materials diphenylantimony acetate[16] and the sodium salts of the dithio-acids[7,17] were obtained by literature methods: diphenyldithiophosphinic acid was prepared by a modified method.[18] In general, the compounds were prepared by refluxing for *ca.* 2 h mixtures of stoicheiometric quantities of Ph_2SbO_2CMe and R_2MS_2Na in the appropriate solvent. After filtration of the sodium acetate, the solution was concentrated *in vacuo* to give the required product in high yield. Full details are included in Table 1.

Structure of $Ph_2SbS_2PPh_2$ (**1**).—*Crystal data.* $C_{24}H_{20}PS_2Sb$, $M = 524.8$, triclinic, $a = 9.099(3)$, $b = 11.397(3)$, $c = 12.382(4)$ Å, $\alpha = 114.54(2)$, $\beta = 106.93(2)$, $\gamma = 75.41(2)°$, $U = 1\,104.6$ Å^3, $Z = 2$, $D_c = 1.58$ g cm^{-3}, $F(000) = 524$, space group $P\bar{1}$, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 15.2$ cm^{-1}, crystal size 0.15 × 0.25 × 0.35 mm.

Structure determination. Data were measured for 4 026 reflections using a Hilger and Watts four-circle diffractometer of which 3 467 with $I > 3\sigma(I)$ were considered observed. The data were corrected for Lorentz and polarisation effects but an absorption correction was not applied. Data reduction and subsequent calculations used the CRYSTALS programs;[19] scattering factors were those for neutral atoms.[20] The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.041$ with anisotropic thermal parameters. The hydrogen atoms, which were placed at their calculated positions, were not refined in the final cycles. Application of a four-coefficient Chebyshev weighting scheme gave final convergence at $R = 0.031$. Refined atomic co-ordinates for the non-hydrogen atoms are collected in Table 5.

Structure of $Ph_2SbS_2AsPh_2$ (**2**).—*Crystal data.* $C_{24}H_{20}AsS_2Sb$, $M = 568.7$, triclinic, $a = 9.155(3)$, $b = 11.518(3)$, $c = 12.390(4)$ Å, $\alpha = 115.07(2)$, $\beta = 106.39(2)$, $\gamma = 75.48(2)°$, $U = 1\,122.4$ Å^3, $Z = 2$, $D_c = 1.68$ g cm^{-3}, $F(000) = 560$, space group $P\bar{1}$, Mo-K_α radiation, $\lambda = 0.7107$ Å, $\mu = 29.6$ cm^{-1}, crystal size 0.2 × 0.35 × 0.5 mm.

Structure determination. Data were collected and treated as in the foregoing determination for 4 105 reflections (3 452 observed). The measured intensities were standardised because of a substantial decrease in the intensity of standard reflections during data collection. This is probably as a consequence of crystal deterioration in the *X*-ray beam. The refinement converged at $R = 0.053$ with anisotropic thermal parameters and at $R = 0.043$ with the hydrogen atoms at their calculated (unrefined) positions and with a weighting scheme. Table 6 contains the refined atomic co-ordinates for the non-hydrogen atoms.

Table 6. Fractional atomic co-ordinates for $Ph_2SbS_2AsPh_2$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Sb(1)	0.033 93(5)	0.602 04(4)	0.175 11(4)
S(1)	−0.066 0(2)	0.560 3(2)	0.320 3(1)
As(1)	−0.149 88(7)	0.376 74(6)	0.188 38(6)
S(2)	−0.205 7(2)	0.352 1(2)	0.008 5(2)
C(1)	−0.148 8(7)	0.758 0(6)	0.167 6(6)
C(2)	−0.119 8(8)	0.869 6(7)	0.166 2(7)
C(3)	−0.237(1)	0.968 9(8)	0.158 4(7)
C(4)	−0.388(1)	0.957 3(8)	0.149 9(8)
C(5)	−0.418 2(9)	0.849 0(9)	0.150 0(8)
C(6)	−0.300 5(8)	0.748 2(7)	0.158 6(7)
C(7)	0.188 3(7)	0.724 7(6)	0.318 5(6)
C(8)	0.341 8(8)	0.700 4(7)	0.308 3(6)
C(9)	0.445 3(9)	0.777 5(9)	0.399 1(8)
C(10)	0.397(1)	0.877 3(9)	0.498 4(7)
C(11)	0.245(1)	0.901 5(8)	0.509 9(7)
C(12)	0.141 5(9)	0.826 3(7)	0.421 3(7)
C(13)	0.009 5(7)	0.242 4(6)	0.223 5(5)
C(14)	0.069 2(8)	0.142 2(7)	0.130 5(6)
C(15)	0.175 7(9)	0.042 7(8)	0.152 9(8)
C(16)	0.221 5(8)	0.043 2(8)	0.268 8(8)
C(17)	0.164 6(9)	0.146 2(9)	0.363 5(7)
C(18)	0.059 6(9)	0.245 8(8)	0.340 0(6)
C(19)	−0.328 3(8)	0.370 5(7)	0.240 7(7)
C(20)	−0.317(1)	0.384(1)	0.360 6(8)
C(21)	−0.443(1)	0.365(1)	0.389(1)
C(22)	−0.577(1)	0.337(1)	0.303(1)
C(23)	−0.585(1)	0.327(1)	0.191(1)
C(24)	−0.459 4(9)	0.344 4(8)	0.156 1(8)

Acknowledgements

We thank the British Council and the Ministry of Education (Bucharest) for supporting this co-operation.

References

1 I. Haiduc, *Rev. Inorg. Chem.*, 1981, **3**, 353.
2 J. R. Wasson, G. M. Woltermann, and A. J. Stoklosa, *Fortsch. Chem. Forsch.*, 1973, **35**, 65; W. Kuchen and H. Hertel, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 89.
3 K. C. Molloy, F. A. K. Nasser, C. L. Barnes, D. van der Helm, and J. J. Zuckerman, *Inorg. Chem.*, 1982, **21**, 960; R. C. Mehrotra, G. Srivastava, and B. P. S. Chauhan, *Coord. Chem. Rev.*, 1984, **55**, 207.
4 G. H. Dale and E. I. McKay, *Hydrocarbon Process.*, 1977, 97.
5 D. B. Sowerby, I. Haiduc, A. Barbul-Rusu, and M. Salajan, *Inorg. Chim. Acta*, 1983, **68**, 87.
6 M. J. Begley, D. B. Sowerby, and I. Haiduc, *J. Chem. Soc., Chem. Commun.*, 1980, 64.
7 M. Forster, H. Hertel, and W. Kuchen, *Angew. Chem., Int. Ed. Engl.*, 1970, **9**, 811; A. Müller and P. Werle, *Chem. Ber.*, 1971, **104**, 3872.
8 (*a*) L. Silaghi-Dumitrescu and I. Haiduc, *J. Organomet. Chem.*, 1982, **225**, 225; (*b*) I. Haiduc and L. Silaghi-Dumitrescu, *ibid.*, 1983, **259**, 65; (*c*) L. Silaghi-Dumitrescu, I. Haiduc, and J. Weiss, *ibid.*, 1984, **263**, 159.
9 I. Silaghi-Dimitrescu and I. Haiduc, *Rev. Roum. Chim.*, 1980, **25**, 814, 823.
10 I. Haiduc, I. Silaghi-Dumitrescu, R. Grecu, R. Constantinescu, and L. Silaghi-Dumitrescu, *J. Mol. Struct.*, 1984, **114**, 467.
11 R. A. Zingaro, K. J. Irgolic, H. D. O'Brien, and L. J. Edmondson, jun., *J. Am. Chem. Soc.*, 1971, **93**, 5677.
12 W. Kuchen, A. Mansch, D. Mootz, and M. Steffen, *Z. Anorg. Allg. Chem.*, 1981, **472**, 133; A. E. Storey, F. Zonnevijlle, and A. A. Pinkerton, *Inorg. Chim. Acta*, 1983, **75**, 103.
13 K. C. Molloy, M. B. Hossain, D. van der Helm, J. J. Zuckerman, and F. P. Mullins, *Inorg. Chem.*, 1981, **20**, 2172.
14 B. Krebs and G. Henkel, *Z. Anorg. Allg. Chem.*, 1981, **475**, 143.
15 J L. Lefferts, K. C. Molloy, M. B. Hossain, D. van der Helm, and J. J. Zuckerman, *Inorg. Chem.*, 1982, **21**, 1410.
16 C. Silvestru and I. Haiduc, *Inorg. Synth.*, 1985, **23**, 194; H. Schmidt, *Liebigs Ann. Chem.*, 1922, **429**, 123.
17 R. G. Cavell, W. Byers, and E. D. Day, *Inorg. Chem.*, 1971, **10**, 2710; W. Kuchen, H. Strolemberg, and J. Metten, *Chem. Ber.*, 1963, **96**, 1733.
18 W. A. Higgin, P. W. Vogel, and W. G. Craig, *J. Am. Chem. Soc.*, 1955, **77**, 1894.
19 J. R. Carruthers, CRYSTALS, the Oxford Crystallographic Programs.
20 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

Received 10*th July* 1985; *Paper* 5/1162