pentahydrate with N_2O_4 yields an adduct which decomposes to oxide nitrates on heating:

$$Bi(NO_3)_3.N_2O_4 \xrightarrow{200°} Bi_2O(NO_3)_4$$

$$\xrightarrow{415°} Bi_4O_5(NO_3)_2$$
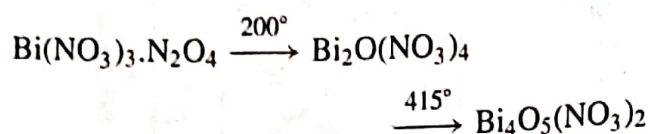
N_2O_5 also yields a 1:1 adduct and this has been formulated as $[NO_2]^+[Bi(NO_3)_4]^-$. Bi reacts with NO_2 in dimethyl sulfoxide to give the solvate $Bi(NO_3)_3.3Me_2SO$, whereas Sb gives the basic salt $SbO(NO_3).Me_2SO$. $Bi(ClO_4)_3.5H_2O$ dissolves in water to give complex polymeric oxocations such as $[Bi_6(OH)_{12}]^{6+}$ (p. 575).

The first stable arsazene [dark red ArN(H)-As=NAr, mp 173°C, Ar = $C_6H_2Bu^t_3$-2,4,6)] and its orange P analogue (mp 203°C) have been prepared by treating $AsCl_3$ (or PCl_3) with Li[NHAr]; an X-ray study found As–N 175 pm, As=N 171 pm and the angle NAsN 98.9° (compared with 163 pm, 157 pm and 103.8° for the N–P=N system.[130] The first 2-coordinate iminoarsine (containing an As=N double bond) was prepared by reacting AsH_3 with O-nitrosobis(trifluoromethyl)hydroxylamine at room temperature, and isolated as a volatile white solid at −86°:[131]

$$AsH_3 + (CF_3)_2NONO \longrightarrow$$

$$(CF_3)_2NON=AsH + H_2O$$
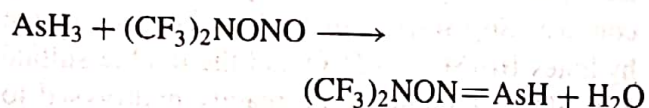
Numerous Sb–N and Bi–N containing species are also beginning to appear in the literature, for example:

(a) the Sb-subrogated *cyclo*-triphosphazene, $NPX_2NPX_2NSb(OOCMe)_2$, which was obtained as a white moisture-sensitive solid, the 4-coordinate Sb being pseudo trigonal bipyramidal with the lone pair of electrons in the N_2Sb: plane;[132]

(b) the azastibacubane cluster compound $(MeNSbCl_3)_4$, which was obtained in good yield as pale yellow crystals by the stoichiometric reaction of $SbCl_5$ with $MeNR_2$ (R = $SiMe_3$);[133]

(c) the homoleptic bismuth amide $Bi(NPh_2)_3$; an X-ray examination of the orange crystals found pyramidal Bi with Bi–N 220 pm (av) and angle NBiN 97° (av).[134]

13.3.8 Organometallic compounds[2,6,15,16,135–139]

All 3 elements form a wide range of organometallic compounds in both the +3 and the +5 state, those of As being generally more stable and those of Bi less stable than their Sb analogues. For example, the mean bond dissociation energies $\overline{D}(M-Me)/kJ\,mol^{-1}$ are 238 for $AsMe_3$, 224 for $SbMe_3$ and 140 for $BiMe_3$. For the corresponding MPh_3, the values are 280, 267, and 200 kJ mol^{-1} respectively, showing again that the M–C bond becomes progressively weaker in the sequence As>Sb>Bi. Comparison with organophosphorus compounds (p. 542) is also apposite. In most of the compounds the metals are 3, 4, 5 or 6 coordinate though a few multiply-bonded compounds are known in which they have a coordination number of 2. In view of the vast range of compounds which have been studied, only a representative selection of structure types will be given in this section.

[130] P. B. HITCHCOCK, M. F. LAPPERT, A. K. RAI and H. D. WILLIAMS, *J. Chem. Soc., Chem. Commun.*, 1633–4 (1986).

[131] H. G. ANG and F. K. LEE, *Polyhedron* **8**, 1461–2 (1989).

[132] S. K. PANDEY, R. HASSELBRING, A. STEINER, D. STALKE and H. W. ROESKY, *Polyhedron* **12**, 2941–5 (1993).

[133] W. NEUBERT, H. PRITZKOW and H. P. LATSCHA *Angew. Chem. Int. Edn. Engl.* **27**, 287–8 (1988).

[134] W. CLEGG, N. A. COMPTON R. J. ERRINGTON, N. C. NORMAN and N. WISHART, *Polyhedron* **8**, 1579–80 (1989).

[135] G. E. COATES and K. WADE, *Organometallic Compounds*, Vol. 1, *The Main Group Elements*, 3rd edn., pp. 510–44, Methuen, London, 1967.

[136] B. J. AYLETT, *Organometallic Compounds*, 4th edn., Vol. 1, *The Main Group Elements*, Part 2, pp. 387–521, Chapman & Hall, London, 1979.

[137] G. E. COATES, M. L. H. GREEN, P. POWELL and K. WADE, *Principles of Organometallic Chemistry*, pp. 143–9, Methuen, London, 1968.

[138] F. G. MANN, *The Heterocyclic Derivatives of P, As, Sb and Bi*, 2nd edn., Wiley, New York, 1970, 716 pp.

[139] S. PATAI (ed.) *The Chemistry of Organic As, Sb and Bi Compounds*, Wiley, Chichester, 1994, 962 pp.

Organoarsenic(III) compounds

The first 1-coordinate organoarsenic(III) compound, $RC\equiv As$, $(R = 2,4,6$-tri-t-butylphenyl) was isolated in 1986 as pale yellow crystals, mp. 114°C.[7]

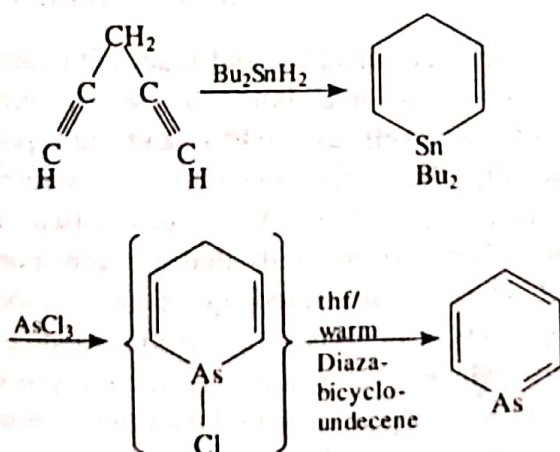Some examples of 2-coordinate organoarsenic(III) compounds are:


Arsabenzene   1-Arsanaphthalene
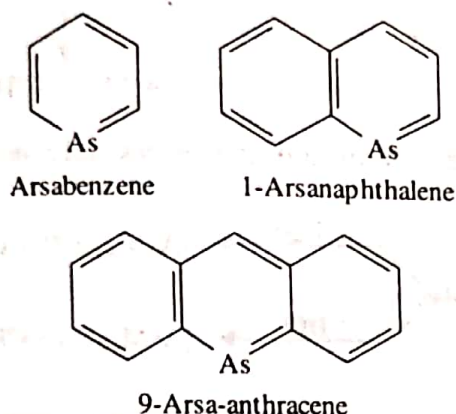
9-Arsa-anthracene

The first such compound to be prepared was the deep-yellow unstable compound 9-arsa-anthracene[140] but the thermally stable colourless arsabenzene (arsenin) can now conveniently be made by a general route from 1,4-pentadiyne:[141]

AsC_5H_5 is somewhat air sensitive but is distillable and stable to hydrolysis by mild acid or base. Using the same route, PBr_3 gave PC_5H_5 as a colourless volatile liquid (p. 544), $SbCl_3$ gave SbC_5H_5 as an isolable though rather labile substance which rapidly polymerized at room temperature, and $BiCl_3$ gave the even less-stable BiC_5H_5 which could only be detected spectroscopically by chemical trapping.[141,142] Arsanaphthalene is an air-sensitive yellow oil.[143] Complexes of some of these heterocycles are also known, e.g. $[Cr(\eta^6\text{-}C_5H_5As)_2]$,[144] $[Mo(\eta^6\text{-}C_5H_5As)(CO)_3]$,[145] and $[Fe(\eta^5\text{-}C_4H_4As)_2]$. i.e. diarsaferrocene.[146]

Most organoarsenic(III) compounds are readily prepared by standard methods (p. 497) such as the treatment of $AsCl_3$ with Grignard reagents, organolithium reagents, organoaluminium compounds, or by sodium-alkyl halide (Wurtz) reactions. As_2O_3 can also be used as starting material as indicated in the scheme on p. 595. AsR_3 and $AsAr_3$ are widely used as ligands in coordination chemistry.[6] Common examples are the 4 compounds $AsMe_{3-n}Ph_n (n = 0, 1, 2, 3)$. Multidentate ligands have also been extensively studied particularly the chelating ligand "o-phenylenebis(dimethylarsine)" i.e. 1,2-bis(dimethylarseno)benzene which can be prepared from cacodylic acid (dimethylarsinic acid) $Me_2AsO(OH)$ (itself prepared as indicated in the general scheme on p. 595):

$$Me_2AsO(OH) \xrightarrow{Zn/HCl} Me_2AsH \xrightarrow{Na/thf} NaAsMe_2$$
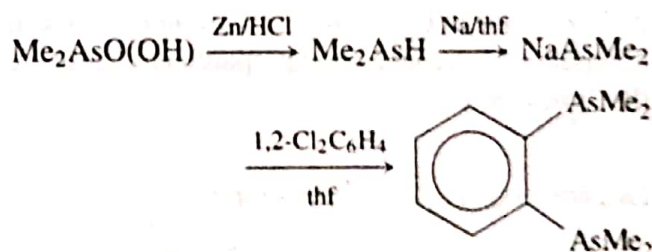
Arsine complexes are especially stable for b-class metals such as Rh, Pd and Pt, and such complexes have found considerable industrial use in hydrogenation or hydroformylation of alkenes,

[140] P. JUZI and K. DEUCHERT, *Angew. Chem. Int. Edn. Engl.* **8**, 991 (1969). H. VERMEER and F. BICKELHAUPT, ibid. 992.

[141] A. J. ASHE, *J. Am. Chem. Soc.* **93**, 3293–5 (1971).

[142] A. J. ASHE, *Acc. Chem. Res.* **11**, 153–7 (1978).

[143] A. J. ASHE, D. L. BELLVILLE and H. S. FRIEDMAN, *J. Chem. Soc., Chem. Commun.*, 880–1 (1979).

[144] C. ELSCHENBROICH, J. KROKER, W. MASSA, M. WÜNSCH and A. J. ASHE, *Angew. Chem. Int. Edn. Engl.* **25**, 571–2 (1986).

[145] A. J. ASHE and J. C. COLBURN, *J. Am. Chem. Soc.* **99**, 8099–100 (1977).

[146] A. J. ASHE, S. MAHMOUD, C. ELSCHENBROICH and M. WÜNSCH, *Angew. Chem. Int. Edn. Engl.* **26**, 229–30 (1987), and references cited therein.

oligomerization of isoprene, carbonylation of α-olefins, etc.

Halogenoarsines R_2AsX and dihalogenoarsines $RAsX_2$ are best prepared by reducing the corresponding arsinic acids $R_2AsO(OH)$ or arsonic acid $RAsO(OH)_2$ with SO_2 in the presence of HCl or HBr and a trace of KI. The actual reducing agent is I^- and the resulting I_2 is in turn reduced by the SO_2. Fluoro compounds are best prepared by metathesis of the chloro derivative with a metal fluoride, e.g. AgF. Interestingly, the compound Ph_3AsI_2 has been shown by X-ray analysis to contain 4-coordinate As and an almost linear As–I–I group with As–I 264 pm, I–I 300.5 pm and angle As–I–I 174.8°.[147]

Hydrolysis of R_2AsX yields arsinous acids R_2AsOH or their anhydrides $(R_2As)_2O$. An alternative route employs a Grignard reagent and As_2O_3, e.g. PhMgBr affords $(Ph_2As)_2O$. Hydrolysis of $RAsX_2$ yields either arsonous acids $RAs(OH)_2$ or their anhydrides $(RAsO)_n$. These latter are not arsenoso compounds $RAs{=}O$ analogous to nitroso compounds (p. 416) but are polymeric. Indeed, all these As^{III} compounds feature pyramidal 3-coordinate As as do the formally As^I compounds $(RAs)_n$ discussed on p. 584. A series of *planar* 3-coordinate arsenic(I) compounds have also been prepared and these are discussed on p. 597.

Organoarsenic(V) compounds

Among the compounds of As^V can be noted the complete series $R_{5-n}AsX_n$ ($n = 0-5$) where R can be alkyl or aryl. Thus $AsPh_5$ (mp 150°) can be prepared by direct reaction of LiPh on either $[AsPh_4]I$, Ph_3AsCl_2 or $Ph_3As{=}O$. Similarly, $AsMe_5$ has been prepared as a colourless, volatile, mobile liquid (mp $-6°$):[148]

$$Me_3AsCl_2 \xrightarrow[(-LiCl)]{LiMe} [AsMe_4]Cl \xrightarrow[(-LiCl)]{LiMe} AsMe_5$$

[147] C. A. MCAULIFFE, B. BEAGLEY, G. A. GOTT, A. G. MACKIE, P. M. MACRORY . and R. G. PRITCHARD, *Angew. Chem. Int. Edn. Engl.* **26**, 264–5 (1987).

[148] K.-H. MITSCHKE and H. SCHMIDBAUR, *Chem. Ber.* **106**, 3645–51 (1973).

The preparation is carried out in Me_2O at $-60°$ to avoid formation of the ylide $Me_3As{=}CH_2$ (mp 35°) by elimination of CH_4. $AsMe_5$ decomposes above 100° by one of two routes:
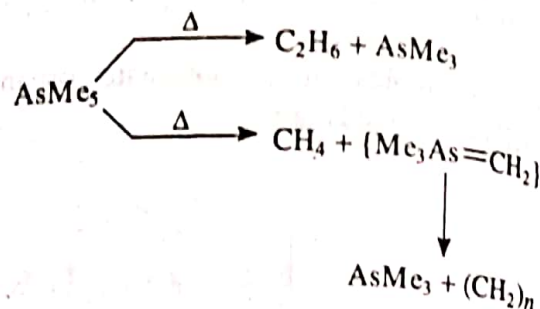
It is stable in air and hydrolyses only slowly:
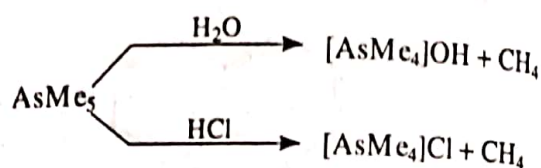
The aryl analogues are rather more stable.

Of the quaternary arsonium compounds, methyltriaryl derivatives are important as precursors of arsonium ylides, e.g.

$$[Ph_3AsMe]Br + NaNH_2 \xrightarrow{thf}$$

$$Ph_3As{=}CH_2 (mp\ 74°) + NaBr + NH_3$$
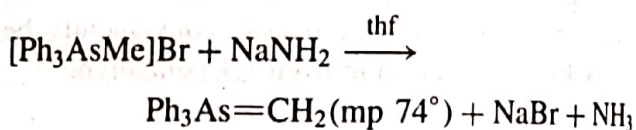
Such ylides are unstable and react with carbonyl compounds to give both the Wittig product (p. 545) as well as $AsPh_3$ and an epoxide. However, this very reactivity is sometimes an advantage since As ylides often react with carbonyl compounds that are unresponsive to P ylides. Substituted quaternary arsonium compounds are also a useful source of heterocyclic organoarsanes, e.g. thermolysis of 4-(1,7-dibromoheptyl)trimethylarsonium bromide to 1-arsabicyclo[3.3.0]octane:

As$_2$O$_3$ $\xrightarrow{\text{RX/NaOH (R = alkyl; Meyer)}}_{\text{RN}_2\text{Cl/NaOH (R = aryl; Bart)}}$ RAsO(ONa)$_2$

RAsO(ONa)$_2$ $\xrightarrow{\text{H}^+}$ RAsO(OH)$_2$

RAsH$_2$ $\xleftarrow{\text{Zn/HCl}}$ RAsO(OH)$_2$ $\xrightarrow[\text{or SnCl}_2/\text{HCl}]{\text{H}_3\text{PO}_2 \text{ or H}_3\text{PO}_3}$ (RAs)$_n$

(RAs)$_n$ $\xrightarrow{\text{Na}}$ RAsNa.RAsNa $\xrightarrow{\text{Na}}$ RAsNa$_2$

RAsH$_2$ $\xrightarrow{\text{Li, LiR or LiOR}}$ RAsHLi

RAsO(OH)$_2$ $\xrightarrow{\text{LiAlH}_4}$ RAsH$_2$

RAsO(OH)$_2$ $\xrightarrow{\text{SO}_2/\text{HCl/I}^-}$ RAsCl$_2$

RAsCl$_2$ $\xrightarrow{\text{LiNR}_2}$ RAs(NR$_2$)$_2$

RAsCl$_2$ $\xrightarrow{\text{OH}^-}$ (RAsO)$_n$ $\xrightarrow{\text{HX}}$ RAsX$_2$ $\rightarrow$ RAsX$_4$

RAsCl$_2$ $\xrightarrow{\text{Bart or Meyer}}$ R$_2$AsO.OH

$\xrightarrow{\text{4RMgX; [O]; hydrol}}$ R$_2$AsO.OH

R$_2$AsO.OH $\xrightarrow{\text{H}_3\text{PO}_2}$ R$_2$As.AsR$_2$

R$_2$AsO.OH $\xrightarrow{\text{Zn/HCl}}$ R$_2$AsH

R$_2$AsO.OH $\xrightarrow{\text{SO}_2/\text{HCl/I}^-}$ R$_2$AsCl

R$_2$AsCl $\xrightarrow{\text{LiAlH}_4}$ R$_2$AsH

R$_2$AsCl $\xrightarrow{\text{OH}^-}$ (R$_2$As)$_2$O

R$_2$As.AsR$_2$ $\xrightarrow{\text{Li}}$ R$_2$AsLi

R$_2$As.AsR$_2$ $\xrightarrow[\text{300° (Cadet)}]{\text{K(O}_2\text{CMe)}}$ (Hg, or Zn, or R$_2$AsH)

R$_2$AsCl $\xrightarrow{\text{Cl}_2}$ R$_2$AsCl$_3$

(R$_2$As)$_2$O $\xrightarrow{\text{RMgX}}$ R$_3$As

R$_2$AsCl $\xrightarrow{\text{RMgX}}$ R$_3$As

$\xrightarrow{\text{RMgX or RBr + Na}}$ R$_3$As

R$_3$As $\xrightarrow{\text{NaClNSO}_2\text{tolyl}}$ R$_3$As:NSO$_2$C$_6$H$_4$Me $\xrightarrow{\text{RLi}}$ R$_5$As

R$_3$As $\xrightarrow{\text{X}_2}$ R$_3$AsX$_2$ $\xrightarrow{\text{RLi}}$ R$_5$As

R$_3$As $\xrightarrow{\text{RX}}$ R$_4$As$^+$X$^-$

R$_3$As $\xrightarrow{\text{air}}$ R$_3$AsO

R$_3$AsX$_2$ $\xrightarrow{\text{OH}^-}$ R$_3$As(OH)X

R$_3$AsO $\xrightarrow{\text{HX}}$ R$_3$As(OH)X

As $\xrightarrow{\text{MeI}}$ R$_4$As$^+$X$^-$ $\xleftarrow{\text{RMgX}}$ R$_3$AsO

R$_4$As$^+$X$^-$ $\xrightarrow{\text{RLi}}$ R$_5$As

Some routes to organoarsenic compounds[137]

Arsonic acids $RAsO(OH)_2$ are amongst the most important organoarsonium compounds. Alkyl arsonic acids are generally prepared by the Meyer reaction in which an alkaline solution of As_2O_3 is heated with an alkyl halide:

$$As(ONa)_3 + RX \xrightarrow{heat} NaX + RAsO(ONa)_2$$

$$\xrightarrow{acidify} RAsO(OH)_2$$
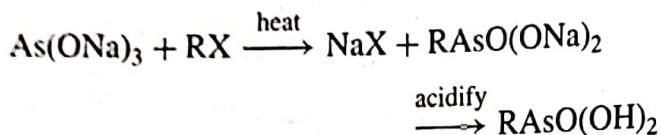
Aryl arsonic acids can be made from a diazonium salt by the Bart reaction:

$$As(ONa)_3 + ArN_2X \longrightarrow NaX + N_2$$

$$+ ArAsO(ONa)_2$$
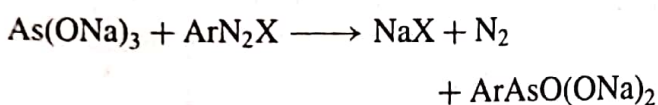
Similar reactions on alkyl or aryl arsonites yield the arsinic acids $R_2AsO(OH)$ and $Ar_2AsO(OH)$. Arsine oxides are made by alkaline hydrolysis of R_3AsX_2 (or Ar_3AsX_2) or by oxidation of a tertiary arsine with $KMnO_4$, H_2O_2 or I_2.

Physiological activity of arsenicals

In general As^{III} organic derivatives are more toxic than As^V derivatives. The use of organoarsenicals in medicine dates from the discovery in 1905 by H. W. Thomas that "atoxyl" (first made by A. Béchamp in 1863) cured experimental trypanosomiasis (e.g. sleeping sickness). In 1907 P. Erlich and A. Bertheim showed that "atoxyl" was sodium hydrogen 4-aminophenylarsonate
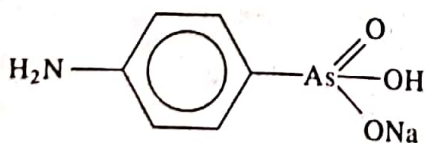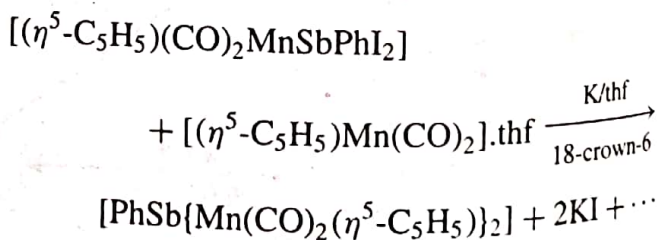

and the field was systematically developed especially when some arsenicals proved effective against syphilis. Today such treatment is obsolete but arsenicals are still used against amoebic dysentery and are indispensable for treatment of the late neurological stages of African trypanosomiasis.

Organoantimony and organobismuth compounds

Organoantimony and organobismuth compounds are closely related to organoarsenic compounds but have not been so extensively investigated. Similar preparative routes are available and it will suffice to single out a few individual compounds for comment or comparison. MR_3 (and MAr_3) are colourless, volatile liquids or solids having the expected pyramidal molecular structure. Some properties are in Table 13.13. As expected (p. 198) tertiary stibines are much weaker ligands than phosphines or arsines.[6] Tertiary bismuthines are weaker still: among the very few coordination complexes that have been reported are $[Ag(BiPh_3)]ClO_4$, $Ph_3BiNbCl_5$, and $Ph_3BiM(CO)_5$ (M = Cr, Mo, W).

An intriguing 3-coordinate organoantimony compound, which is the first example of trigonal-planar Sb^I, has been characterized.[149] The stibinidene complex $[PhSb\{Mn(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$ has been isolated as shiny golden metallic crystals (mp 128°) from the crown-ether catalysed reaction:

$$[(\eta^5\text{-}C_5H_5)(CO)_2MnSbPhI_2]$$

$$+ [(\eta^5\text{-}C_5H_5)Mn(CO)_2].thf \xrightarrow[\text{18-crown-6}]{K/thf}$$

$$[PhSb\{Mn(CO)_2(\eta^5\text{-}C_5H_5)\}_2] + 2KI + \cdots$$

149 J. VON SEYERL and G. HUTTNER, *Angew. Chem. Int. Edn. Engl.* **17**, 843–4 (1978).

Table 13.13 Some physical properties of MMe_3 and MPh_3

Property	AsMe₃	SbMe₃	BiMe₃	AsPh₃	SbPh₃	BiPh₃
MP/°C	−87	−62	−86	61	55	78
BP/°C	50	80	109	—	—	—
Bond angle at M	96°	—	97°	102°	—	94°
Mean M–C bond energy/kJ mol⁻¹	229	215	143	267	244	177
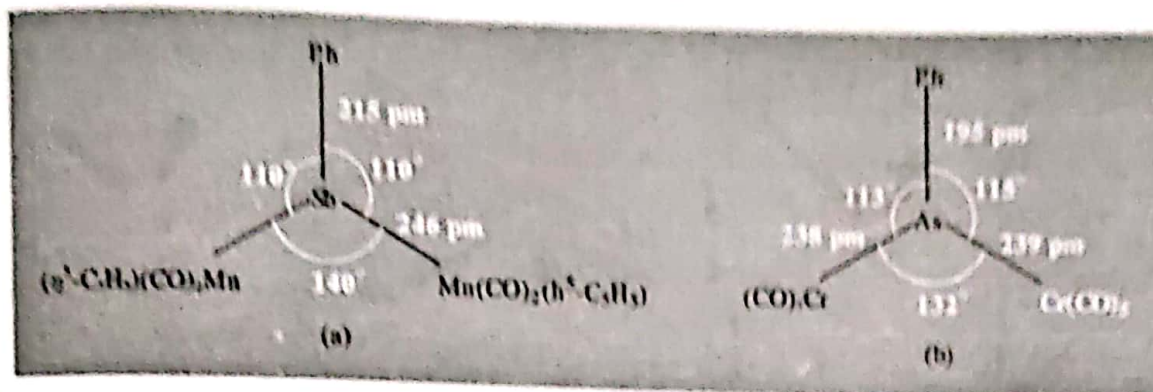
Figure 13.28 Planar structure of (a) [PhSb{Mn(CO)₂(η⁵-C₅H₅)}₂], and (b) [PhAs{Cr(CO)₅}₂]. Note the relatively short Sb–Mn and As–Cr bonds.

The structure is shown in Fig. 13.28a; the interatomic angles and distances suggest that the bridging {PhSbⁱ} group is stabilized by Sb–Mn π interactions. A similar route leads to 3-coordinate planar organoarsinidine complexes which can also be prepared by the following reaction sequence:
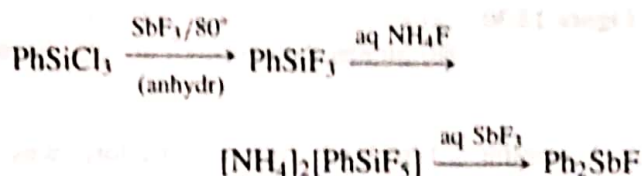
$$[Cr(CO)_6] \xrightarrow{PhAsH_2} [Cr(CO)_5(AsPhH_2)] \text{ yellow}$$

$$\xrightarrow{LiBu} [Cr(CO)_5(AsPhLi_2)] \text{ orange} \xrightarrow[\text{NCl}_2]{\text{cyclohexyl-}}$$

$$[\{Cr(CO)_5\}_2AsPh] \text{ dark violet (mp 104°)}$$
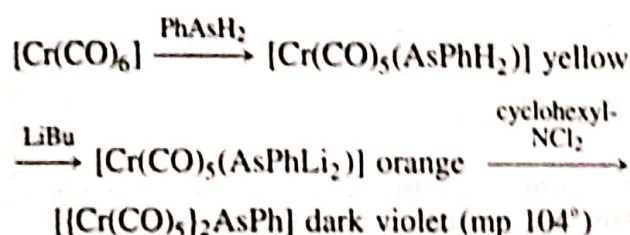
The chloro-derivative [ClAs{Mn(CO)₂-(η⁵-C₅H₅)}₂] (shiny black crystals, mp 124°) can now be much more readily obtained by direct reaction of AsCl₃ with [Mn(CO)₂-(η⁵-C₅H₅)].thf.[150]
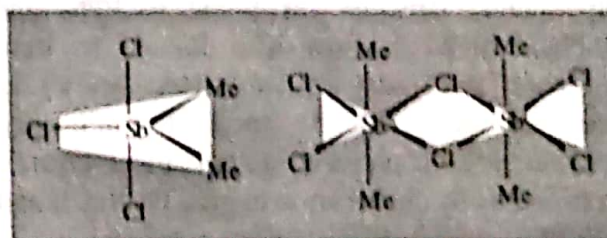
Halogenostibines R₂SbX and dihalogenostib-ines RSbX₂ (R = alkyl, aryl) can be prepared by standard methods. The former hydrolyse to the corresponding covalent molecular oxides (R₂Sb)₂O, whereas RSbX₂ yield highly poly-meric "stiboso" compounds (RSbO)ₙ. The sti-bonic acids, RSbO(OH)₂, and stibinic acids, R₂SbO(OH), differ in structure from phospho-nic and phosphinic acids (p. 512) or arsonic and arsinic acids (p. 594) in being high molecular weight materials of unknown structure. They are probably best considered as oxide hydroxides of organoantimony(V) cations. Indeed, through-out its organometallic chemistry Sb shows a propensity to increase its coordination num-ber by dimerization or polymerization. Thus Ph₂SbF consists of infinite chains of F-bridged pseudo trigonalbipyramidal units as shown in Fig. 13.29.[151] The compound could not be pre-pared by the normal methods of fluorinating Ph₂SbCl or phenylating SbF₃ but can be obtained as a white, air-stable, crystalline solid mp 154° by the following sequence of steps:

$$PhSiCl_3 \xrightarrow[\text{(anhydr)}]{SbF_3/80°} PhSiF_3 \xrightarrow{\text{aq NH}_4F}$$

$$[NH_4]_2[PhSiF_5] \xrightarrow{\text{aq SbF}_3} Ph_2SbF$$

Again, Me₂SbCl₃ is monomeric with equatorial methyl groups (C₂ᵥ) in solution (CH₂Cl₂, CHCl₃ or C₆H₆) but forms Cl-bridged dimers with *trans* methyl groups (D₂ₕ) in the solid:[152]

[150] J. VON SEYERL, U. MOERING, A. WAGNER, A. FRANK and G. HUTTNER, *Angew Chem. Int. Edn. Engl.* **17**, 844–5 (1978).

[151] S. P. BONE and D. B. SOWERBY, *J. Chem. Soc., Dalton Trans.*, 1430–3 (1979).

[152] N. BERTAZZI, T. C. GIBB and N. N. GREENWOOD, *J. Chem. Soc., Dalton Trans.*, 1153–7 (1976) K. DEHNICKE and H. G. NADLER, *Chem. Ber.* **109**, 3034–8 (1976).
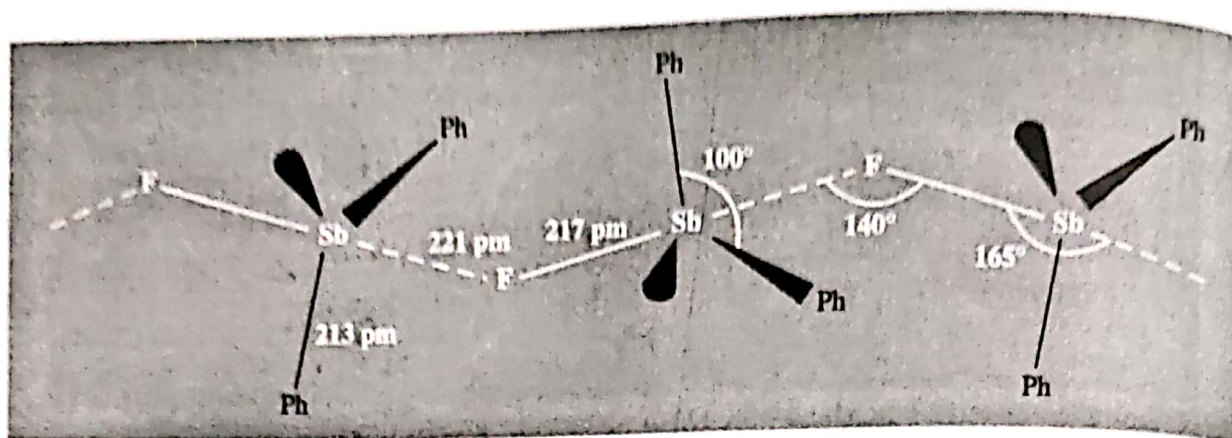
Figure 13.29 Structure of Ph_2SbF_2 showing polymeric chains of apex-shared pseudo trigonal bipyramidal units {$Ph_2FSb...F$}.
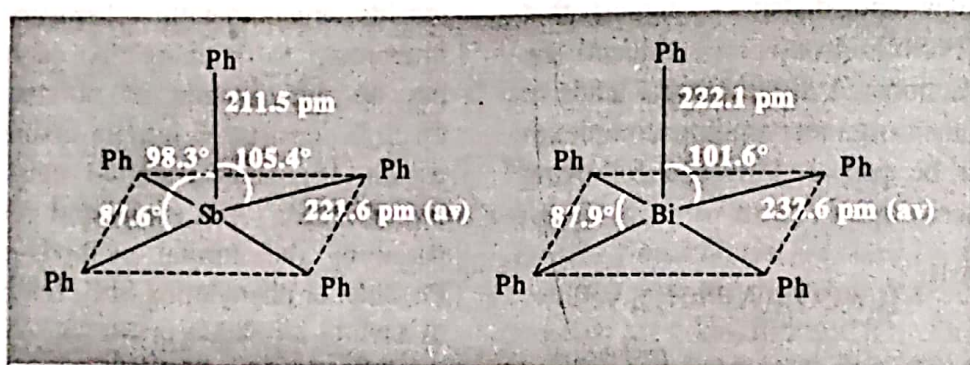

Figure 13.30 (a) Molecular geometry of $SbPh_5$ showing the slightly distorted square-pyramidal structure.[155]
(b) Similar data obtained at $-96°$ for the slightly more regular square-pyramidal $BiPh_5$.[159].

A similar Cl-bridged dimeric structure was established by X-ray analysis for Ph_2SbCl_3.[153]

Pentaphenylantimony, $SbPh_5$ (mp 171°), has attracted much attention as the first known example of a 10-valence-electron molecule of a main group element that has a square pyramidal structure[154,155] rather than the usual trigonal bipyramidal structure (as found in PPh_5 and $AsPh_5$). $BiPh_5$ is now also known to have a square pyramidal structure (see below) as does the *anion* $InCl_5^{2-}$ (p. 238). $SbPh_5$ can conveniently be prepared as colourless crystals from $SbPh_3$ by chlorination to give Ph_3SbCl_2 and

then reaction wtih LiPh:

$$Ph_3SbCl_2 + 3LiPh \longrightarrow 2LiCl + Li[SbPh_6]$$

$$\xrightarrow{H_2O} LiOH + C_6H_6 + SbPh_5$$
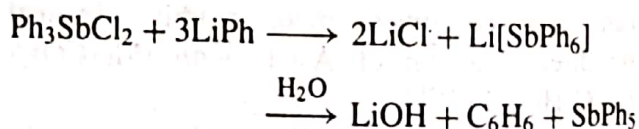
The structure, shown in Fig. 13.30(a), is based on a slightly distorted square–pyramidal coordination around the Sb atom (C_{2v} instead of C_{4v}), the $ipso-C_{ax}$–Sb–C_b angles being alternately 98.3° and 105.4°.[155] Vibrational spectroscopy suggests that the molecule retains its square-pyramidal structure even in solution, so the structure is not an artefact of crystal packing forces. The yellow cyclopropyl analogue, $Sb(C_3H_5)_5$, apparently has the same geomentry,[156] while the solvate $SbPh_5.\frac{1}{2}C_6H_{12}$

[153] J. BORDNER, G. O. DOAK and J. R. PETERS, *J. Am. Chem. Soc.* **96**, 6763–5 (1974).

[154] P. J. WHEATLEY, *J. Chem. Soc.* 3718–23 (1964).

[155] A. L. BEAUCHAMP, M. J. BENNETT and F. A. COTTON, *J. Am. Chem. Soc.* **90**, 6675–80 (1968).

[156] A. H. COWLEY, J. L. MILLS, T. M. LOEHR and T. V. LONG, *J. Am. Chem. Soc.* **93**, 2150–3 (1971).

and the *p*-tolyl derivative Sb(4-MeC$_6$H$_4$)$_5$ have almost undistorted trigonal bipyramidal structures.[157]

BiPh$_5$ is even more remarkable. Not only is it square pyramidal (Fig. 13.30b) but it is also highly coloured. It can be prepared as violet crystals by the direct reaction of Ph$_3$BiCl$_2$ with two moles of LiPh in ether at −75°.[158] The colour is retained in solution, and is due to a weak broad absorption in the green-yellow region (λ_{max} 532 nm, log ε 2.4).[159] Substitution on the phenyl rings modifies the colour and may also alter the structure, e.g.:[160] [BiPh$_3$(2-FC$_6$H$_4$)$_2$], which is square pyramidal with the *o*-fluorophenyl groups *trans*- basal, forms violet crystals but is reddish in solution, whereas [Bi(4-Me-C$_6$H$_4$)$_3$(2-F-C$_6$H$_4$)$_2$] is trigonal bipyramidal with axial fluorophenyl groups; it forms yellow crystals but again gives reddish solutions. The structures and colours have been interpreted in terms of relativistic effects which lower the energy of the a_1 LUMO in the C_{4v} structure.[161]

The pentamethyl compound, SbMe$_5$, is surprisingly stable in view of the difficulty of obtaining AsMe$_5$ and BiMe$_5$; it melts at −19°, boils at 127°, and does not inflame in air, though it oxidizes quickly and is hydrolysed by water. It resembles SbPh$_5$ in reacting with LiMe (LiPh) to give Li$^+$[SbR$_6$]$^-$ and in reacting with BPh$_3$ to give [SbR$_4$]$^+$[RBPh$_3$]$^-$.

Organobismuth(V) compounds are in general similar to their As and Sb analogues but are less stable and there are few examples known; e.g. [BiR$_4$]X and R$_3$BiX$_2$ are known but not R$_2$BiX$_3$ or RBiX$_4$, whereas all 4 classes of compound are known for P, As and Sb. Similarly, no pentaalkylbismuth compound is known, though as noted above BiPh$_5$ and its derivatives have been prepared. It decomposes spontaneously over a period of days at room temperature and reacts readily with HX, X$_2$ or even BPh$_3$ by cleaving 1 phenyl to form quaternary bismuth compounds [BiPh$_4$]X and [BiPh$_4$][BPh$_4$]; this latter compound (mp 228°) is the most stable bismuthonium salt yet known.

[157] C. BRABANT, J. HUBERT and A. L. BEAUCHAMP, *Can. J. Chem.* **51**, 2952–7 (1973).

[158] G. WITTIG and K. CLAUSS, *Liebig's Ann. Chem.* **578**, 136–46 (1952).

[159] A. SCHMUCK, J. BUSCHMANN, J. FUCHS and K. SEPPELT, *Angew. Chem. Int. Edn. Engl.* **26**, 1180–2 (1987).

[160] A. SCHMUCK, P. PYYKKÖ and K. SEPPELT, *Angew. Chem. Int. Edn. Engl.* **29**, 213–5 (1990).

[161] B. D. EL-ISSA, P. PYYKKÖ and H. M. ZANATI, *Inorg. Chem.* **30**, 2781–7 (1991).