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Recent developments in low coordination organo-antimony and bismuth chemistry

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Contents

Abstract

In this article a summary is given of recent developments in the chemistry of organo-antimony and organo-bismuth compounds that contain multiple bonds between the Group 15 element and a neighbouring atom. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Low coordination; Group 15; Antimony; Bismuth; Multiple bond; Heterocycle

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1. Introduction

Since the preparation of the first stable diphosphene, Mes*P=PMes*, Mes* = $C_6H_2^tBu_3$-2,4,6, [1] and phosphaalkyne, P≡C^{t}Bu [2] in 1981, the field of low coordination organophosphorus chemistry has rapidly expanded. Prior to that year it was widely believed that compounds containing localised multiple bonds between P and other elements would be incapable of existence at room temperature. This belief stemmed from the 'double bond rule' [3], which suggested that the extent of overlap between valence p-orbitals of elements of the second and subsequent rows with those of another element would be poor. In addition, as the principal quantum number of the valence electrons of an element increases, the ability of its valence p-electrons to participate in multiple bonding should decrease.

Low coordination P-chemistry is now a major area of study that has been the subject of numerous reviews [4] and several books [5]. Although low coordination arsenic compounds are generally less stable than their phosphorus counterparts, their chemistry has been similarly developed [6] and both compound classes are now widely used in organo-Group 15 chemistry and as ligands in organometallic synthesis. Until recently, this chemistry had not been extended to low coordination organo-antimony and bismuth compounds, mainly because of the increased instability of these compounds. Significant advances have however, been made in the field in the past five years and a summary of these will form the basis of this review.

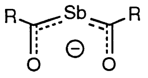
For the sake of this article low coordination antimony and bismuth compounds will be considered as compounds containing an λ^3,σ^2- or λ^3,σ^1-Sb or Bi centre that is bonded to at least one carbon atom and displays a degree of multiple bonding to at least one neighbouring atom. Compound classes that will not be treated here include stibinidines (RSb) and their metal complexes, and diatomic compounds (E≡E) and their metal complexes.

2. Acyclic systems

2.1. 2-Stiba-1,3-dionato complexes

There are only a handful of structurally authenticated acyclic compounds that contain either localised or delocalised Sb=C bonds and no examples of Bi=C bonds in acyclic systems. The only known acyclic system containing delocalised Sb=C bonds is the recently reported 2-stiba-1,3-dionato class of ligand, **1** [7]. The chemistries of the phosphorus and arsenic analogues of this ligand type are reasonably well established [8] and it has been found that the behaviour of **1** largely mirrors these. However, there are some differences that revolve around the relative weakness of the Sb–C bonds in **1**.

The lithium salts of **1**, viz. **2**, are readily prepared in moderate yield by treating the appropriate acyl chloride, RCOCl, with Li[Sb$(SiMe_3)_2$] [7]. In the cases where R = Mes ($C_6H_2Me_3$-2,4,6) or Mes* distibabutadienes are formed as by-products (see Section 2.2). Considering the presence of 2-coordinate Sb-centres in **2** the complexes display good thermal stability which is thought to arise from their bulky substituents and the delocalised nature of the stibadionato ligand.



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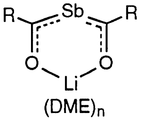
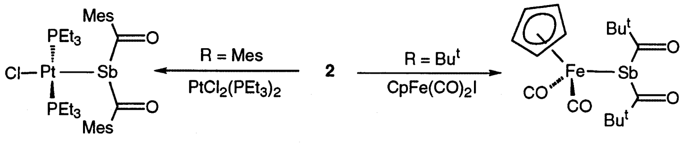


2 R = Mes*, n = 1
R = Mes, n = 0.5
R = Bu^t, n = 0.5

The X-ray crystal structure of **2**, R = ^{t}Bu, has been determined and this shows the compound to consist of dimeric units containing two Li–O intermolecular bridges. These units are linked in an infinite polymeric chain by bridging DME molecules. The Sb–C (2.15 Å average) and C–O bonds in this compound lie between the normal values for single and double interactions which confirms the delocalised nature of the heterodionate ligand.

A number of similarities between **2** and alkali metal-β-diketonate complexes have been identified and the use of such compounds as transfer reagents in the formation of transition metal complexes has begun to be explored. One difference **1** has to normal β-diketonate ligands is its potential ability to coordinate metal centres through either *O*,*O*-chelation or coordination to the pnicogen centre. This has been tested in two reactions (Scheme 1) both of which give rise to products containing η^1-Sb coordinated ligands, viz. **3** and **4** [9]. The X-ray crystal structure of **3** confirms this mode of ligation and shows the Sb-centre to have a pyramidal geometry. This combined with the fact that the Sb–C bond lengths are in the normal single bonded range lead to the conclusion that the ligand is now acting as a diacylantimonide as in closely related complexes that have been prepared by alternative synthetic routes [10]. A similar reaction between **2**, R = ^{t}Bu, and *cis*-[$PtCl_2(PEt_3)_2$] has been reported but this gives rise to Sb–C bond cleavage and the formation of a distibene complex (see Section 2.3).

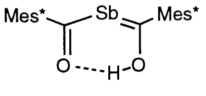
The further reactivity of the heavily substituted stibadionatolithium complex, **2**, R = Mes*, has been examined and it has been found that its treatment with a stoicheiometric amount of HCl affords the first stiba-enol, **5**, in high yield [11]. In solution, this compound is only briefly stable at room temperature but NMR studies suggest it is predominantly in its enol form and is fully delocalised. In the solid state it is more stable (dec. 103°C) and its crystal structure confirms that it exists in the enol form but with a rare example of a localised Sb–C double bond (see Section 2.2). The ability to metallate **5** has been demonstrated by its reaction



3 **4**

Scheme 1.

with $Na[N(SiMe_3)_2]$. This reaction yields the monomeric, 6-coordinate, thermally stable sodium complex, **6** [9]. The X-ray crystal structure of the compound reveals the heterodionate ligand to be delocalised and to coordinate the Na centre through *O*,*O*-chelation as in the corresponding lithium complexes. The fact that this complex is monomeric is thought to be a result of the bulky Mes* substituents preventing association. From the success of this reaction, it seems likely that similar metallation reactions could lead to a range of other metal-stibadionato complexes.



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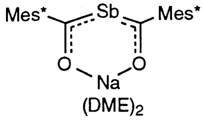

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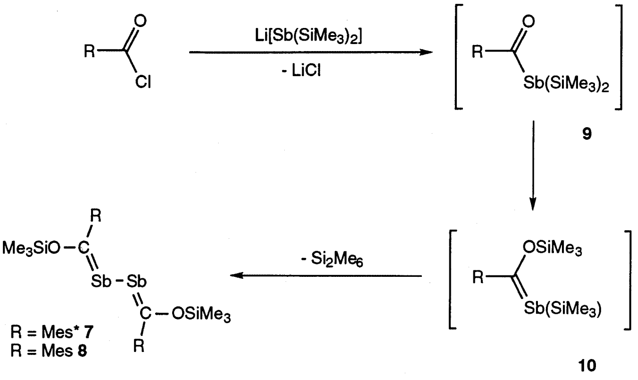
2.2. Compounds containing localised λ^3,σ^2-Sb=C and λ^3,σ^1-Sb≡C bonds

Molecular orbital calculations have been used to optimise the geometry of the model stibaalkene, $HSb{=}CH_2$, and these predicted an Sb–C bond length of 2.01 Å which compares reasonably well with the few experimentally observed Sb=C bonds (vide infra). Similar calculations were carried out on the stibaalkyne, Sb≡CH, which gave a theoretical Sb–C bond length of 1.88 Å [12]. In each case the HOMO was found to be the Sb–C π-bond and the LUMO the π* combination. The P and As analogues of these two compounds were similarly investigated and it was indicated that the HOMO–LUMO gaps for the Sb compounds were lower than for the lighter congeners and thus the Sb based compounds were predicted to have a greater reactivity. A more recent study [13] has examined the geometry, bond strengths and dipole moments of a series of stibaalkynes, Sb≡CR, R = H, Me, F and Ph, at a number of levels of theory. Using valence electron coupled electron pair calculations Sb–C bond lengths ranging from 1.857–1.872 Å were determined. A comparison was carried out between Sb≡CMe and Sb≡CPh which suggested that the Sb–C bond length in the latter is weaker and longer than in the former as a result of partial conjugation between the π-systems of the triple bond and the phenyl ring.

To date there have been no reports of any stibaalkyne or bismaalkyne. In addition systems containing localised Bi=C bonds have not been forthcoming. Indeed, there are only three examples of structurally characterised compounds containing Sb=C bonds. Two of these are the 2,3-distibabutadienes, **7** and **8**, depicted in Scheme 2 [11,14]. Both compounds are formed as low yield by-products in the synthesis of the stibadionato complexes, **2**, R = Mes* or Mes. It is not known what the mechanism of formation is but it has been suggested that it involves an initial salt elimination reaction to give **9**; a 1,3-silyl shift to give the unstable stibaalkene, **10**, which eliminates hexamethyldisilane in a coupling reaction to give the product. One interesting comparison that can be drawn between this reaction and that involving the treatment of Mes*COCl with $Li[As(SiMe_3)_2]$ is that in the



Scheme 2.

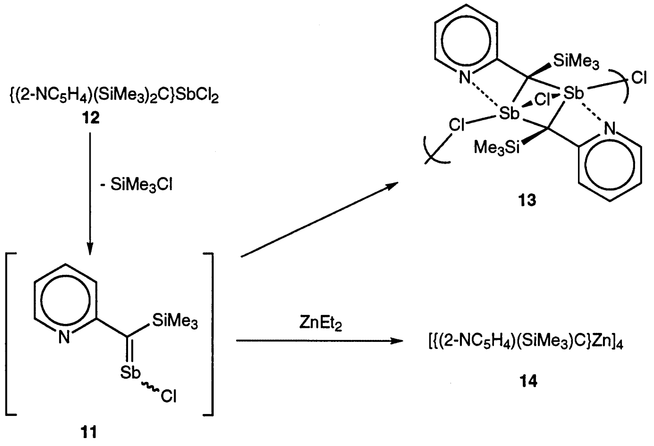
latter case the arsaalkyne, As≡CMes*, is formed and not the corresponding 2,3-diarsabutadiene [15]. The origin of this difference is not yet known.

Both **7** (dec. 213°C) and **8** (dec. 205°C) are remarkably thermally stable given they contain Sb=C bonds. This stability is believed to be derived from a combination of the bulky aryl substituents affording steric protection and the conjugated nature of the systems. Their X-ray crystal structures exhibit Sb–C bond lengths of 2.056(10) Å, **7**, and 2.065(5) Å, **8**, which are significantly shorter than normal Sb–C single bonds but longer than calculated for the stibaalkene, $HSb{=}CH_2$ (2.01 Å). In both compounds the SbSbC angles are acute, **7** 94.7(3)° and **8** 92.99(13)°, a situation that probably results from a significant degree of s-character to the Sb-lone pairs as has been suggested for the heavier dipnictenes (Section 2.3).

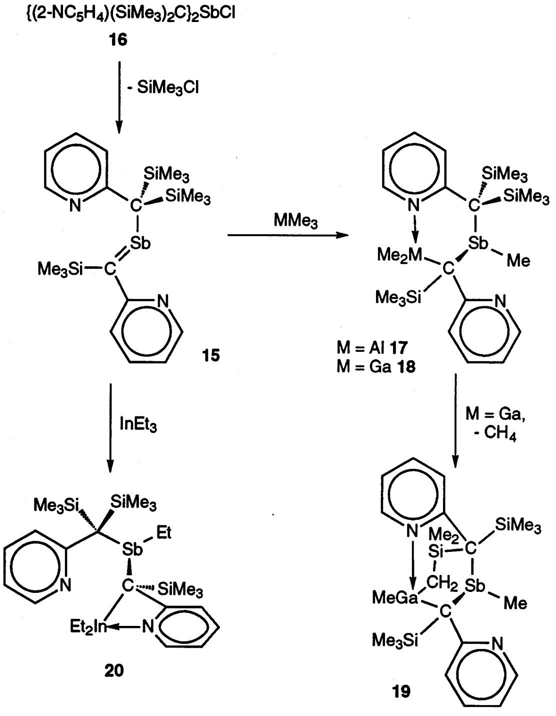
The only other example of a compound containing a localised Sb=C bond, at least in the solid state, is the aforementioned stiba-enol, **5** [11]. The two Sb–C bond lengths in this compound, 2.078(3) Å and 2.192(3) Å, suggest localisation of the system with the shorter bond length being close to those observed in **7** and **8**.

Although not structurally characterised, two other stibaalkenes have been implicated as transient intermediates in a series of novel reactions. The first of these, **11**, is prepared by mild thermolysis of **12** which leads to β-elimination of $SiMe_3Cl$ (Scheme 3). The unstable stibaalkene then undergoes a [2 + 2] cycloaddition reaction with itself to give the structurally characterised, polymeric C-centred geminal distibine, **13** [16]. It is thought that the concomitant stereochemical requirements of this reaction explain the *cis*-arrangement of the pyridyl ligands in **13**. The utility of **11** in organometallic synthesis has also been demonstrated by its reaction with $ZnEt_2$, which gives the structurally characterised geminal-organodizinc tetramer, **14** [17]. The mechanism of this reaction is thought to involve a metathetical exchange of two ethyl groups for the $(2\text{-pyridyl})(SiMe_3)C^{2-}$ fragment.

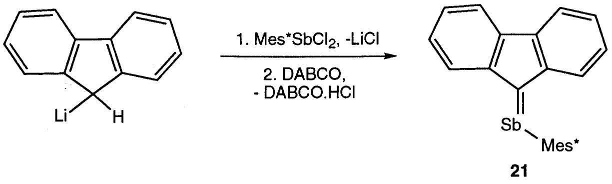
The other uncharacterised stibaalkene, **15**, is said to form by β-elimination of $SiMe_3Cl$ from **16** (Scheme 4). This reaction yields a red oil which contains a complex mixture of products including **15** which is thought to persist at room temperature [18]. Some direct evidence for the existence of **15** has come from the electrospray mass spectrum of this oil [19]. Indirect evidence arises from the reaction of the oil with $AlMe_3$ which yields the geminal-C-centered aluminium/antimony organometallic complex, **17**, via carboalumination of the Sb=C bond [20]. Not surprisingly the reaction of $GaMe_3$ with **15** affords the isostructural complex,



Scheme 3.



Scheme 4.



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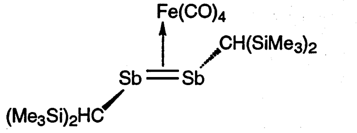
Scheme 5.

18. One difference between the two compounds is that upon mild thermolysis **18** undergoes methane elimination to give the unusual organometallic complex, **19**, which contains a strained bicyclo[2.2.2] type cage [21]. In a similar fashion the reaction of $InEt_3$ with **15** has been examined and shown to yield the first geminal-C-centred In/Sb organodimetallic species, **20**. The only real difference between **20** and its lighter Group 13 analogues is that in the former N → metal donation comes from the pyridyl group β-to the metal while in the latter two it comes from the other pyridyl functionality [19].

The only other mention of a stibaalkene in the literature is that of the fluorenylidene substituted species, **21**. This compound was too thermally unstable to isolate and was characterised only by mass spectroscopic evidence [22]. It was prepared by a two-stage process involving salt elimination and HCl elimination steps as outlined in Scheme 5.

2.3. *Dipnictenes, RE=E′R, E = Sb or Bi, E′ = Group 15 element*

The synthesis of the first diphosphene, Mes*P=PMes*, in 1981 was one of the major milestones in the history of low coordination chemistry. Since that time the chemistry of these compounds [4d] and, indeed, diarsenes, RAs=AsR [6], has been widely explored. Until recently corresponding distibenes and dibismuthenes have remained elusive though several early reports described the in-situ syntheses of complexes containing η^2- or η^2:η^1-coordinated distibene ligands, e.g. **22** and **23** [23,24]. The synthetic and structural aspects of these compounds have been summarised in a previous review [25].



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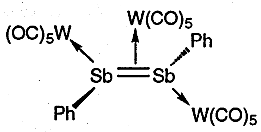

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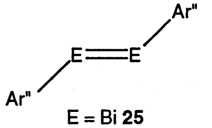
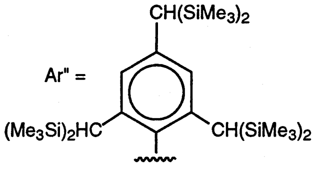
One subsequent report of an in-situ generated distibene complex has appeared [26]. This describes the reaction of a lithium stibadionate with a Pt(II) complex to give the formally Pt(0)-2,3-distibene-1,4-dione complex, **24** (Scheme 6). The functionalised distibene ligand is η^2-coordinated to the Pt centre through its π-system and exhibits a Sb–Sb bond length (2.7551(12) Å) almost midway between those normally seen for single and double bond distances. It was speculated that the mechanism of this intriguing reaction involves a short lived Pt(II) intermediate, $[Pt(PEt_3)_2[\eta^1\text{-}Sb\{C(O)^tBu\}_2]_2]$ which undergoes homolytic Sb–C bond cleavage to give **24** and the diketone, $\{^tBuC(O)\}_2$, which was spectroscopically detected as the major reaction by-product.

It was not until 1997 [27] and 1998 [28] that the first uncoordinated dibismuthene, **25**, and distibene, **26**, were prepared by deselenation of the triselenatripnictanes, $(Ar''ESe)_3$, E = Sb or Bi. Both compounds are very stable thermally and only moderately air sensitive in the solid state. This stability has been attributed to the extremely bulky aryl substituents, which also prevent oligomerisation of the dipnictenes. Interestingly, single crystals of **26** react with atmospheric oxygen to give the dioxadistibetane, $(Ar''Sb\text{-}\mu\text{-}O)_2$, with retention of crystallinity.

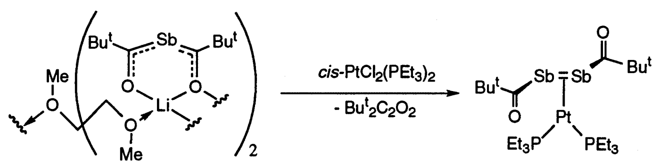


E = Bi **25**
E = Sb **26**



The X-ray crystal structures of **25** and **26** show them to exist as their *trans* isomers with E=E bonds 6 and 7% shorter than for corresponding E–E single bonds. This indicated a significant degree of double bond character to the E–E interactions in these compounds. Their UV–vis spectra exhibit absorptions corresponding to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. When these were compared to those for diphosphenes and diarsenes it was found that the positions of these transitions are red shifted on going from P → Bi. This phenomenon has been investigated by theoretical calculations [29]. Finally the FT-Raman spectra of **25** and **26** display E–E stretching frequencies of 103 and 207 cm^{-1}, values which are significantly higher in frequency than normal values for their single bonded counterparts.

The structural aspects of dipnictenes have been systematically explored by Power et al. [30] who have prepared the first homologous series of heavy element dipnictenes, **27**–**30** and **31**–**34**. These have been stabilised by substitution with the sterically encumbered *m*-terphenyl ligands, Ar^+ and Trip, and were prepared by reduction of the appropriate aryl pnicogen dihalides. One complete series, **27**–**30**, has been structurally characterised and in all cases the E=E bonds found to be significantly shorter than normal E–E bonds (Table 1). In addition, the EEC angles in these compounds steadily decrease with increasing Group 15 element atomic



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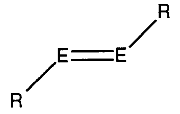
Scheme 6.

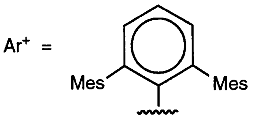
Table 1
Selected structural parameters for **27**–**30**

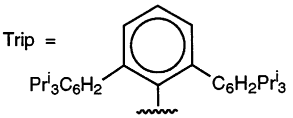
	E=E (Å)	EEC (°)
27	1.985(2)	103.7 (average)
28	2.276(3)	98.5(4)
29	2.6558(5)	94.1(1)
30	2.8327(14)	92.5(4)

weight. This led the authors to suggest that there is increasing s-orbital character to the lone pairs of the dipnictenes down the group and thus there is an increasing p-character to the σ- and π-bonds in these systems. A similar conclusion was drawn from a theoretical study that used DFT calculations to explore the bonding in the compounds PhE=EPh, E = P, As, Sb, Bi [31]. In a subsequent review concerning multiple bonding in main Group elements the structural aspects of these and related compounds were compared and it was concluded that the amount of shortening from a single to a double bond in dipnictenes falls by about 25% on going from phosphorus to bismuth [32]. Despite this, all evidence points toward a high degree of p-orbital overlap, even in dibismuthenes, which is contrary to the major premise of the 'double bond rule' which is that such overlap should greatly diminish as a group is descended. It is noteworthy that the structure and/or bonding of the heavier dipnictenes is briefly mentioned in two other recent review articles [33,34].

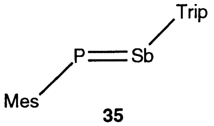


R = Ar$^+$	R = Trip
27 E = P	**31** E = P
28 E = As	**32** E = As
29 E = Sb	**33** E = Sb
30 E = Bi	**34** E = Bi





To date there are only three examples of unsymmetrical dipnictenes containing an Sb or Bi centre. The first of these, Mes*P=SbCH$(SiMe_3)_2$, was reported some time ago [35], is thermally unstable and was characterised by ^{31}P-NMR spectroscopy and mass spectrometry. The other two are more recent and have been structurally characterised. Compound **35** was prepared by a salt elimination reaction between Li_2PMes and $TripSbCl_2$ in very low yield (1%) [36]. Its crystal structure exhibits a P=Sb bond length of 2.335(2) Å, which lies between the normal E=E bond lengths of diphosphenes and distibenes. The thermally stable compound **36** was prepared in quantitative yield via a condensation reaction between (Bbt)SbH_2 and (Bbt)$BiBr_2$ [37]. Its FT-Raman spectrum displays a Sb–Bi stretch at 169 cm^{-1}, between the E–E stretches of the related compounds, **25** and **26**. All the solution spectroscopic data for **36** are consistent with it retaining its structure in solution at ambient temperature. However, when its solutions are heated at 80°C for 20 days or irradiated with UV light for 4 h a disproportionation reaction occurs leading to the formation of (Bbt)Sb=Sb(Bbt) and (Bbt)Bi=Bi(Bbt). There is evidence to suggest that the mechanism of these reactions involves a [2 + 2] cycloaddition of two molecules of **36** to give a saturated four-membered dimer, $Sb_2Bi_2(Bbt)_4$, which decomposes to give the homonuclear double bonded compounds.



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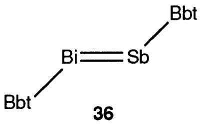

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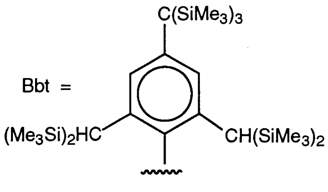
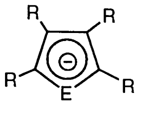


3. Five membered heterocyclic systems

3.1. *Stibolyl and bismolyl ring anions and their metal complexes*

The relative paucity of data available on low coordination antimony and bismuth compounds relative to their phosphorus and arsenic counterparts extends to five-membered heterocyclic systems. However, in this case the situation is not so clear cut thanks to the pioneering work of Ashe et al. on the chemistry of stibolyl and bismolyl ring anions, **37**. This field is now relatively well established and the literature covering the area up to 1995 has been reviewed [38]. The review article is extensive and describes the synthesis, structure, bonding, electrochemistry, spectroscopic data and further reactivity of coordination compounds derived from **37**. Complex types that are covered in the review display solely η^1-coordination as in **38** or η^5-coordination as in the heteroferrocenes, **39** and **40**, and heterocymantrenes, **41**.



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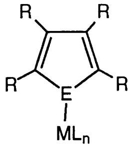

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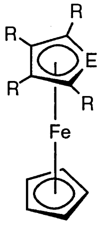

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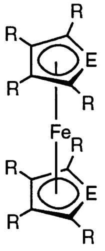

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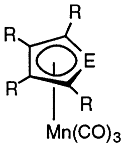

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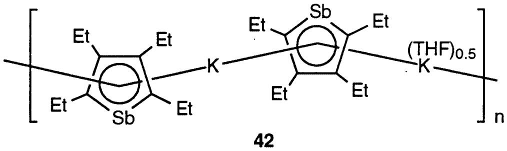
E = Sb or Bi
R = H, alkyl or aryl

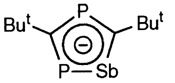
Little work in the area followed the publication of this review and thus the field of stibolyl and bismolyl coordination chemistry will not be covered here. One exception is the recent report on the preparation of the potassium stibolyl complex, **42**, the crystal structure of which shows it to be polymeric through η^5-coordination of each K centre to two partly delocalised stibolyl ring systems (Sb–C 2.096 Å average) [39].



42

3.2. The chemistry of the diphosphastibolyl ring anion, $[1,4,2\text{-}P_2SbC^t_2Bu_2]^-$

The only other 5-membered heterocyclic system containing a low coordinate antimony centre to be investigated is the diphosphastibolyl ring anion, $[1,4,2\text{-}P_2SbC^t_2Bu_2]^-$, **43**. The chemistry of this has been widely studied in the past 5 years. These endeavours have highlighted many parallels with the chemistry of the closely related triphospholyl ring anion, $[1,2,4\text{-}P_3C^t_2Bu_2]^-$, **44**, but also many differences. These differences arise from the relative weakness of the delocalised Sb–P double bond in **43** compared to the P–P bond in **44**.



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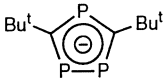
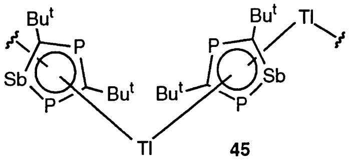


44

The ring anion, **43**, can be readily prepared, in high yield by the reaction of $Li[Sb(SiMe_3)_2]$ with either the phosphaalkyne, $P{\equiv}CBu^t$, or the phosphaalkene, $(Me_3Si)P{=}C(^tBu)(OSiMe_3)$ [40]. Unfortunately the preparation of **43** always involves contamination with ca. 20% of the triphospholyl anion, **44**. It is not known why this occurs but the products are difficult to separate, a fact, which complicates the coordination chemistry of **43**. Generally, metal complexes of **43** co-crystallise with the analogous complex containing **44** and so it is difficult to comment on the intramolecular geometrical parameters of these complexes. The corresponding diphosphabismolyl anion, $[1,4,2\text{-}BiP_2C^t_2Bu_2]^-$, can be prepared in an analogous fashion and is stable in solution at room temperature but decomposes when attempts are made to isolate it [9].

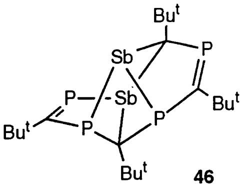
Two lithium salts of **43** have been structurally characterised, viz. $[Li(tmeda)_2]$ [**43**] [41] and $[Li(12\text{-}crown\text{-}4)_2]$ [**43**] [40]. In both structures the anion is planar and does not interact with the cation. In the former complex the ring co-crystallises with the triphospholyl anion, **44**. The latter complex, however, was obtained free of contamination with **44** by careful fractional crystallisation. The ring geometry in that case strongly suggests that the anion is fully delocalised though positional disorder between the adjacent Sb and P sites precludes comment on both the Sb–P and Sb–C bond lengths. A potassium salt of **43** has also be prepared by the reaction of K[Sb($SiMe_3$)$_2$] with excess (Me_3Si)P=C(^{t}Bu)($OSiMe_3$). In this case the X-ray crystal structure of the product showed it to exist as an infinite polymer in which each [K(DME)]$^+$ cation has an approximately η^5-interaction to 2 ring anions [9] in a similar fashion to **42**.

A number of main group complexes of **43** have been reported. In Group 13 the thallium complex, **45**, was prepared by the reaction of TlCl with **43** [42]. In solution, NMR studies imply that the complex is largely dissociated. In the solid state, however, the complex exists as a 'zig zag' polymer in which the heterocycles are delocalised (Sb–P 2.410 Å average, Sb–C 2.04 Å average). One interesting feature of the structure is that there are 'inter-strand' interactions between P-centres on one polymeric strand and alternating thallium centres on an opposite strand.



45

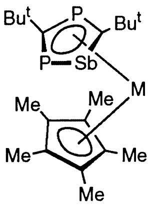
In Group 14, **43** does not react with $PbCl_2$ to give the expected hexahetero-plumbocene but instead the novel, highly strained organo-antimony cage compound, **46**, is formed in high yield (65%) [43]. The mechanism of this reaction is thought to involve an oxidative coupling of two equivalents of **43** followed by a [4 + 2] cycloaddition reaction to give the observed cage. High yields of **46** are also obtained when **43** is reacted with $InCl_3$ or $FeCl_3$. It is noteworthy that the use of this cage as a ligand in the formation of transition metal complexes has been investigated [44].



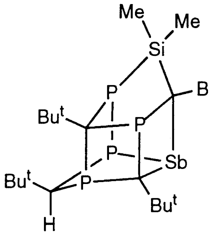
46

By contrast the expected heterostannocene and plumbocene complexes, **47**, are obtained when **43** is reacted with Cp*MCl, M = Sn or Pb [45]. As with the thallium complex, solution studies on these two compounds show that there is a significant degree of dissociation of the heterocycle from the metal centre. In the solid state, the X-ray crystal structure of **47**, M = Pb, supports the idea of a weak Pb–heterocycle interaction as it displays a very long metal–centroid distance of 2.761(4) Å. As is normally the case with plumbocenes, the complex is bent [cent.–Pb–cent. 144.2(8)°] with both rings η^5-coordinated to the metal centre.

When **43** is reacted with $SiMe_2Cl_2$ another unexpected reaction occurred to give a high yield of the novel cage compound, **48** [9]. The mechanism of this reaction probably involves $[SiMe_2(\eta^1\text{-}SbP_2C_2^tBu_2)_2]$ as an intermediate which undergoes a ring coupling reaction, with a concomitant elimination of antimony and proton abstraction from the solvent, in this case THF. The formation of **48** is, however, too rapid for any intermediates to be observed by NMR spectroscopy.

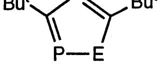


47 M = Sn or Pb



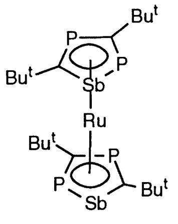
48

In Group 16 the reactions of **43** with $E(S_2CNEt_2)_2$, E = Se or Te, have been investigated [46]. The surprising result of these is the formation of the chalcogen substituted diphospholes, **49**, in high yield. These remarkable reactions seemingly involve a red–ox process as elemental antimony is deposited. The X-ray crystal structure of the $W(CO)_5$ complexes of both compounds, i.e. $[W(CO)_5(\eta^1\text{-}P_2EC_2^tBu_2)]$, have been reported and show the ring systems to be planar and partly delocalised [47].



49 E = Se or Te

A majority of the coordination chemistry that has been carried out with **43** involves the formation of transition metal complexes. Generally this ligand behaves similarly to the closely related triphospholyl anion, **44**, though a number of differences have been identified. A number of air stable Group 8 metallocenes, **50**–**53**, have been prepared by salt elimination reactions and can be purified by either chromatography or sublimation [48]. The reaction of **43** with $[RuCl_2(PPh_3)_3]$ yields a mixture of 3 compounds, namely the two distibatetraphospha-ruthenocene isomers, **50** and **51**, and the stibapentaphospha-ruthenocene, **52**. The presence of the latter arises from the unavoidable contamination of **43** with $[P_3C_2^tBu_2]^-$. From the variable temperature NMR spectra of the mixture, it has been suggested that the two heterocycles in **51** and **52** readily rotate with respect to each other but in **50** they do not. The X-ray crystal structure of **50** revealed that the two rings are eclipsed and there is likely a strong inter-ring Sb···Sb interaction which prevents the rotation of the heterocycles. This is analogous to behaviour observed by Ashe et al. for distibaferrocenes, **40** [38]. Interestingly, only one isomer of the polyheteroferrocene, **53**, is formed which appears to have a stronger Sb···Sb interaction than in **50**.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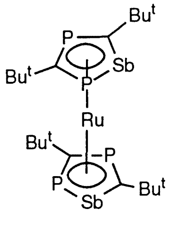
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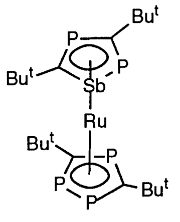
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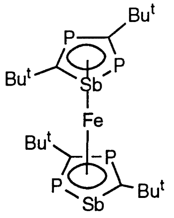
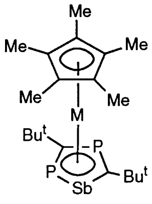

53

Two heteroleptic ferrocenes and ruthenocenes, **54**, have been synthesised by similar routes and both were crystallographically characterised [48,49]. Their crystal structures show that both rings are η^5-coordinated to the metal centre. Both compounds have also been utilised as P-donor ligands in their reaction with $[W(CO)_5(THF)]$ to give the η^5:η^1-heterobimetallic complexes, **55**, one of which was crystallographically characterised. Finally, the triple decker complex, **56**, can be prepared by the reaction of half an equivalent of **43** with $[Cp^*Ru(CH_3CN)_3][PF_6]$ [48].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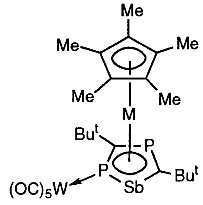
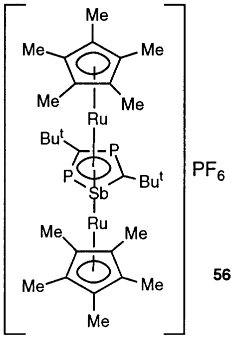
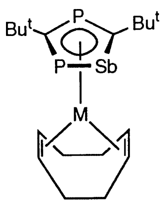

55

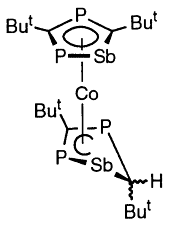
M = Fe or Ru


56

Several Group 9 complexes derived from **43**, have been reported [50]. Compounds **57** were prepared via the reaction of **43** with [MCl(COD)] and one, M = Rh, structurally characterised. In an attempt to form the polyheterocobaltocene, $[Co(\eta^5\text{-}P_2SbC_2^tBu_2)_2]$ **58**, by treating **43** with $CoCl_2$ the air stable, diamagnetic complex, **59**, was formed in moderate yield. It is believed that its mechanism of formation involves **58** as a reactive intermediate, which abstracts a proton from the reaction solvent. Variable temperature $^{31}P\{^1H\}$-NMR studies have been carried out on this compound with the conclusion that the two rings rotate with respect to each other, even at -60°C. In the solid state the structure of the closely related compound, **60** has been elucidated by X-ray crystallography which reveals that the protonated ligand, which contains the first example of a stibadiphosphabutadiene fragment, is largely delocalised.



57 M = Rh or Ir



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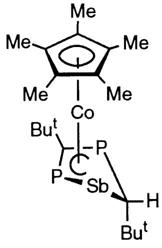
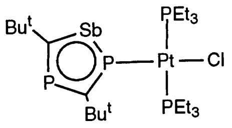


60

Coordination of **43** to Group 10 metal centres has also been examined [51] and again this has highlighted differences between its chemistry and that of **44**. Reaction of **43** with 1 equivalent of *cis*-$[\mathrm{PtCl_2(PEt_3)_2}]$ afforded **61**, the ring anion of which is solely η^1-coordinated to the metal centre. Its X-ray structure shows the heterocycle to ligate the Pt-centre through the P-centre adjacent to the Sb centre and it retains delocalisation upon coordination. More surprising was an attempt to form the bis-η^1-complex, $[\mathrm{PtCl_2(PEt_3)(\eta^1\text{-}P_2SbC_2^tBu_2)_2}]$, which instead led to the novel organometallic cage compound, **62**, in moderate yield. The mechanism of formation is unknown but it was suggested that it involves $[\mathrm{PtCl_2(PEt_3)_2(\eta^1\text{-}P_2SbC_2^tBu_2)_2}]$ as an unstable intermediate which undergoes a series of ring insertion and cycloaddition reactions.



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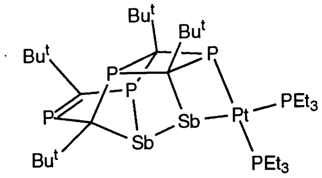
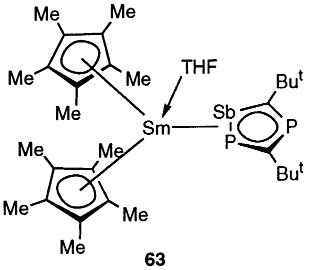


62

Finally two lanthanide complexes of **43** have been described, viz. **63** and **64** [41,52]. Both of these were formed by red–ox transmetallation reactions which in the case of **63** involved the reaction of Tl[**43**] with $[\mathrm{SmCp}^*_2]$ in THF. Compound **64** was similarly prepared by the treatment of Yb metal with a mixture of Tl[**43**] and Li[**43**]. In both cases X-ray crystallography has shown the compounds to contain η^2-ligated diphosphastibolyl ring anions, an unusual coordination mode that was compared to the common η^2-*N*,*N*-coordination of pyrazolate ring systems to lanthanides. Compound **64** also contains two η^5-coordinated heterocycles and in all cases, the rings appear to retain their delocalisation.



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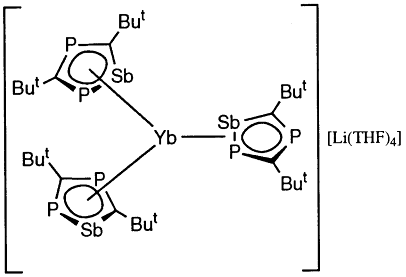
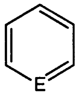


64

4. Six membered heterocyclic systems

The heavier Group 15 substituted benzenes, **65**, have all been synthesised along with a variety of substituted analogues. When E = P or As the heterocycles are reasonably stable and their coordination chemistry has been widely studied. However, when E = Sb or Bi the heterobenzenes are much less robust and little is known of their coordination chemistry. The majority of the work carried out on stiba- and bismabenzenes occurred in the late 1970's and early 1980's, mainly by A.J. Ashe and his co-workers. The field up to 1982 is summarised in two extensive reviews, which cover the synthesis, structure, spectral and physical properties, organic reactivity and coordination chemistry of substituted and unsubstituted stiba- and bismabenzenes [53,54]. There is little point resummarising that work here except to say that there is apparently only one known metal complex of a stibabenzene, $[Mo(CO)_3(\eta^6\text{-}SbC_5H_5)]$ [55], and no bismabenzene complexes. Not surprisingly this compound (m.p. 106–108°C) was found to be considerably more stable than free stibabenzene due to the interaction of the high energy π-electrons of the heterocycle with the metal centre.



65 E = P, As, Sb or Bi

Since 1982, surprisingly few accounts of stiba- and bismabenzene chemistry have appeared. The UV absorption and magnetic circular dichroism of stibabenzenes have, however, been assessed and compared to those of phospha- and arsabenzene [56]. The conclusion of the study was that against 'chemical intuition' the heterocentres in these three ring systems are more electronegative than carbon itself, at least in a π-electron sense. A number of other studies have used a variety of theoretical techniques to determine the degree of aromaticity and geometry of stiba- and bismabenzenes [57,58]. The conclusions drawn from these are in line with previous studies, which suggest the heterocycles are largely delocalised aromatic systems.

5. Conclusions

Compared to the now well established areas of low coordination phosphorus and arsenic chemistry, the low coordination chemistry of both antimony and bismuth is currently underdeveloped. The reason for this relative paucity of data lies largely with the decreasing strength of multiple bonds to the Group 15 element as the group is descended. Despite this, major advances in the area have been made in the last 5 years, which can be attributed to the development of new, sterically crowding ligand systems. This has allowed an entry to previously inaccessible compounds that contain Sb=C, Sb=Sb and Bi=Bi bonds. Comparisons of the properties of these compounds with their lighter 15 counterparts have shown that there are a number of similarities but also significant differences in their respective chemistries. The most significant of these differences is the increasing non-bonding character of the valence s-electrons and hence increasing p-orbital character to both the σ-, and π-bonds to the Group 15 element in such compounds.

There are several synthetic challenges in this area that are still open to the chemist. These include the synthesis of stable stiba- and bismaalkynes, $E\equiv CR$, $E = Sb$ or Bi, and the preparation of a compound containing a localised Bi=C double bond. Such compounds are of particular interest, as their preparation will allow structural and bonding comparisons to be drawn with their lighter Group 15 congeners. In addition, their likely high reactivity will see them as useful synthons in organo-Group 15 chemistry and as ligands in the formation of novel organometallic/coordination compounds. Given the knowledge gained in stabilising similar species, e.g. dibismuthenes and distibenes, it should not be long before these challenges are met.

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