

Annual review

Bismuth: annual survey covering the year 1993

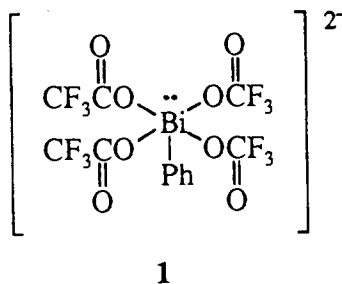
G. O. Doak^{*}, Leon D. Freedman

Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204, USA

Keywords: Bismuth

No review dealing solely with organobismuth compounds was published in 1993. Organobismuth compounds were briefly mentioned in *Ann. Rep. Prog. Chem., Sect. A* [1] and in *Organomet. Chem.*, also published annually [2]. A review on compounds of Group 15 which undergo inversion by the edge mechanism included organobismuth compounds [3].

Breeze and Wang [4] have prepared three interesting organobismuth(III) compounds in which the bismuth-containing anion possessed a 2⁻ charge. The first of these compounds, $[\text{Me}_2\text{NH}(\text{CH}_2)_3\text{NHMe}_2][\text{PhBi}(\text{O}_2\text{CCF}_3)_4]$, was obtained by treating triphenylbismuthine in THF with trifluoroacetic acid followed by the addition of *N,N,N',N'*-tetramethyl-1,3-propanediamine, in a 1:4:1 ratio. The resulting crystalline compound was characterized by elemental analysis (results not reported), ¹H NMR and X-ray diffraction. The geometry of the bismuth atom in the anion **1** was square-pyramidal.



The four oxygen atoms bonded to the bismuth were planar with the bismuth atom 0.27 Å above this plane. The four carbonyl oxygens all pointed upwards to form a cup-like structure. The cation was arranged above this cup, with the hydrogens forming weak hydrogen bonds

to the carbonyl oxygens of the anion (indicated by the N–O bond distances). The shapes and dimensions of the anion and cation readily allowed these hydrogen bonds to be formed and thus contributed to the unusual structure of the compound. When a similar reaction was carried out using *N,N,N',N'*-tetramethylethylenediamine, the structure of the resulting salt, $[\text{Me}_2\text{NH}(\text{CH}_2)_2\text{NHMe}_2][\text{PhBi}(\text{O}_2\text{CCF}_3)_4]$, was quite different. Only three of the trifluoroacetate groups pointed upward (with respect to the phenyl group). The fourth trifluoroacetate group was in the equatorial plane and both oxygen atoms were coordinated to the bismuth atom. The structure of the bismuth atom was thus pentagonal-pyramidal with all five coordinating oxygen atoms coplanar and with the bismuth atom 0.23 Å above this plane. Only two of the carbonyl oxygen atoms were hydrogen-bonded to the cation. The span between the ammonium groups was apparently too short to allow all four carbonyl groups to hydrogen-bond to the anion.

The third compound in this study was obtained by the reaction of triphenylbismuthine with trifluoroacetic acid and 1,3-bis(dimethylamino)-2-propanol to give $[\text{Me}_2\text{NHCH}_2\text{CH}(\text{OH})\text{CH}_2\text{NHMe}_2][\text{Bi}(\text{O}_2\text{CCF}_3)_4\text{Ph}]$. The structure of this compound was isomorphous with the first compound described above. The structure of the anion was similar to **1**, but the carbonyl oxygens were also hydrogen-bonded to the hydroxyl group (in addition to the dimethylamino groups). Unlike the first two compounds, which were stable in solution, the third compound decomposed rapidly in solution. The authors noted that the compound $\text{PhBi}(\text{O}_2\text{CCF}_3)_2$ was too unstable to be isolated. They attributed the stability of the anion $[\text{PhBi}(\text{O}_2\text{CCF}_3)_4]^{2-}$ to the stabilizing influence of the hydrogen bonds to the cation.

In a recent paper Clegg et al. [5] have reported the crystal and molecular structures of the bismuth compounds $\text{PhBiBr}_2 \cdot \text{THF}$ and $\text{PhBiI}_2 \cdot \text{THF}$ as well as the ionic complexes $[\text{NH}_4]_2[\text{Ph}_2\text{Bi}_2\text{I}_6] \cdot \text{Et}_2\text{O}$ and

^{*} Corresponding author.

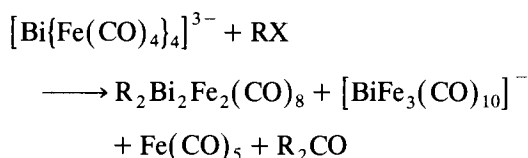
[PPh₄][Ph₂BiBr₂] and the solvated compound Ph₂BiBr · THF. They have now extended their investigation to the chloro compound PhBiCl₂ · THF (2) and to the two ionic compounds [Bu₄N]₂[Ph₂Bi₂Br₆] (3) and [Et₄N][Ph₂BiI₂] [6]. Compound 2 was isomorphous with the corresponding dibromo compound, with the geometry of the bismuth atom being square-pyramidal. The basal plane contained the oxygen of the THF atom, the two chlorine atoms, and a bridging chlorine atom from a neighboring PhBiCl₂ unit. The authors noted that the Bi–O distance in the dichloro compound was considerably shorter than the Bi–O distance in the dibromo compound (which, in turn, was shorter than the Bi–O distance in the diiodo compound). They suggested that the increasing electronegativity of the halogen atom, in the order I < Br < Cl, developed an increasing partial positive charge on the bismuth atom which bound the oxygen atom of the THF more strongly. The authors also commented in considerable detail on the nature of the bismuth–halogen bonds and suggested a weak interaction between the π-system of the phenyl ring and the bismuth atom.

The molecular structure of the anion [Ph₂Bi₂Br₆]²⁻ contained square-pyramidal bismuth atoms with two bridging bromine atoms. The Bi₂Br₆ unit was planar, with apical phenyl groups trans to each other with respect to this plane. Finally, the structure of the anionic complex [Ph₂BiI₂]⁻ was determined. This was a weakly bound dimer with Bi–I–Bi bridges. The geometry of the bismuth atom was disphenoidal or equatorially vacant trigonal-bipyramidal, with a I–Bi–I angle of 177.87°. Its structure was very similar to the anion in the compound [Ph₄P][Ph₂BiI₂], previously described [5].

Shieh et al. [7] have synthesized two organobismuth compounds with Bi–Fe bonds. The reaction of [Et₄N]₃[Bi{Fe(CO)₄]₄] with Me₂CHCH₂Br in MeCN gave, after work-up, [Et₄N]₂[Me₂CHCH₂Bi{Fe(CO)₄]₃] in 85% yield. The compound was characterized by elemental analysis, ¹H NMR, and infrared (IR) spectroscopy. When it was dissolved in acetic acid and stirred for 40 h, removal of the solvent and recrystallization of the residue from hexane gave two products, (Me₂CHCH₂)₂Bi₂Fe₂(CO)₈ and the known compound [Et₄N]₂[Bi₂Fe₄(CO)₁₃]. The first product was characterized by elemental analysis, IR, ¹H NMR and mass spectrometry. This compound could also be prepared from [Et₄N]₂[Me₂CHCH₂Bi{Fe(CO)₄]₃] by oxidation with MeI, but the isolation of the desired product was difficult because of the formation of Me₂Bi₂Fe₂(CO)₈ as a side-product. The crystal and molecular structures of the two new bismuth compounds were determined by X-ray diffraction. The geometry of the bismuth atom in the anion [(Me₂CHCH₂)Bi{Fe(CO)₄]₃]²⁻ was distorted tetrahedral with three Fe–Bi bonds. The second compound comprised a Bi₂Fe₂ parallelogram with each

bismuth atom bonded to two iron atoms and one isobutyl group in a pyramidal arrangement. In addition to the two new organobismuth–iron compounds described above, the authors mentioned that the reaction of [Et₄N]₃[Bi{Fe(CO)₄]₄] with MeI or EtI gave Me₂Bi₂Fe₂(CO)₈ and Et₂Bi₂Fe₂(CO)₈, respectively.

Shieh and coworkers have extended their investigation to the reaction of [Et₄N]₃[Bi{Fe(CO)₄]₄] with a number of alkyl halides and dihalides [8]. Besides the methyl and ethyl compounds, the benzyl compound (PhCH₂)₂Bi₂Fe₂(CO)₈ was obtained from benzyl chloride. In addition to the desired organobismuth–iron complexes, other products were produced:

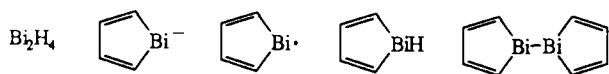


(R = Me, X = I; R = Et, X = I; R = PhCH₂, X = Br). When PhCH₂Br was used, the desired product could not be separated from (PhCH₂)₂CO and unreacted PhCH₂Br. Accordingly, the reaction was carried out with PhCH₂Cl, which yielded the complex [Et₄N]₂[(PhCH₂)Bi{Fe(CO)₄]₃]. Careful acidification of this product gave the desired (PhCH₂)₂Bi₂Fe₂(CO)₈. When *iso*-PrBr, BuBr or *iso*-BuBr was used, the reaction did not produce the R₂Bi₂Fe₂(CO)₈ complexes but the anionic complexes [Et₄N]₂[RBi{Fe(CO)₄]₃]. There was no reaction when *tert*-BuBr was used. The complexes R₂Bi₂Fe₂(CO)₈, where R was *iso*-Pr or Bu, were obtained by acidification of the [Et₄N]₂[RBi{Fe(CO)₄]₃] complexes with acetic acid.

In addition to the alkyl halides the reactions of [Et₄N]₃[Bi{Fe(CO)₄]₄] with several dihalides were investigated. The only product obtained from 1,2-dibromoethane was [Et₄N][BiFe₃(CO)₁₀], and no alkylated products were obtained from 1,2-dichloro- or 1,3-dichloropropane. However, 3-chloro-1-bromopropane gave [Et₄N]₂[Cl(CH₂)₃Bi{Fe(CO)₄]₃]. Acidification of this with acetic acid gave [Cl(CH₂)₃]₂Bi₂Fe₂(CO)₈. The complex [Et₄N]₂[Br(CH₂)₄Bi{Fe(CO)₄]₃] was not isolated when 1,4-dibromobutane was used, but careful acidification of the oily product obtained from the reaction gave the product [Br(CH₂)₄]₂Bi₂Fe₂(CO)₈. Except for the compound [Et₄N]₂[*iso*-PrBi{Fe(CO)₄]₃], which was characterized only by its IR spectrum, all of the new organobismuth–iron compounds described in this paper were characterized by elemental analysis, IR, ¹H NMR and mass spectrometry. The syntheses were carried out in a nitrogen atmosphere by means of Schlenk techniques.

Many distibines and dibismuthines show color changes when melted or dissolved in organic solvents. This effect, termed thermochromism, has been attributed to the molecular structure of such compounds

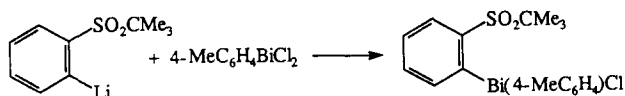
in that the molecules are aligned in chains with short intramolecular Sb–Sb or Bi–Bi bonds and with somewhat longer intermolecular contacts, which are about one Å shorter than the Van der Waals distance. Lohr and Ashe [9] have investigated the electronic structure of the following six bismuth compounds using both effective core potential (ECP) and relativistically parametrized semiempirical molecular orbital calculations:



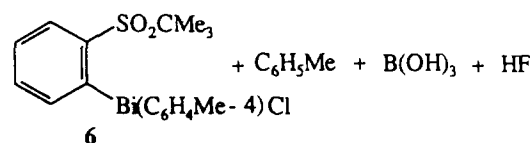
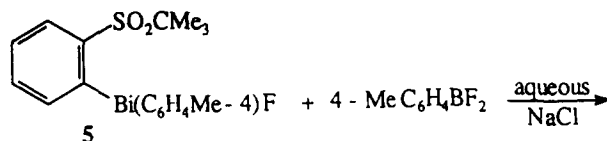
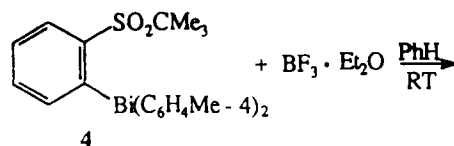
The calculation provided a good description of the geometries of the compounds, particularly with the relativistically parametrized semiempirical molecular orbital method.

A paper from Norman's laboratory has described the synthesis and the crystal and molecular structure of the bismuth(III) compound [Ph₂Bi(HMPA)₂][BF₄] (where HMPA was hexamethylphosphoramide) [10]. The synthesis involved the addition of HMPA to a solution of Ph₂BiBr in THF, followed by the addition of AgBF₄, also in THF. After removal of the AgBr and concentration of the filtrate, crystals of the desired product were obtained by diffusion into hexane layered over THF solution, which was allowed to stand at –20°C. The compound was characterized by ¹H, ¹³C, ¹¹B, ³¹P and ¹⁹F NMR and by elemental analysis. The crystal and molecular structure was determined by X-ray diffraction. The geometry of the Bi atom of the cation was essentially trigonal-bipyramidal, with two oxygens of the HMPA molecules in axial positions and the two phenyl groups (and presumably the Bi lone pair) in equatorial positions. The O–Bi–O angle was 167.5°, and the C–Bi–C angle (involving the phenyl groups) was 93.2°. The bond lengths (Bi–C and Bi–O) were within normal ranges. There were no close interionic contacts.

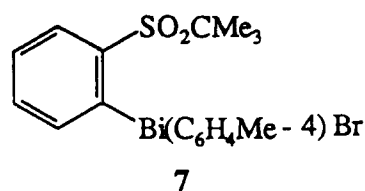
Suzuki and Murafuji [11] have recently described a general synthetic procedure for the preparation of chiral tertiary bismuthines. They found that when one of the ligands attached to the bismuth atom was the 2-(*tert*-butylsulfonyl)phenyl group, reactions such as iodination and dearylation could be carried out on compounds of the type 2-Me₃CSO₂C₆H₄BiAr₂ without formation of intractable mixtures. Suzuki et al. [12] have now extended this work to the preparation of chiral halobismuthines. They first attempted the preparation of such a compound by the following reaction:



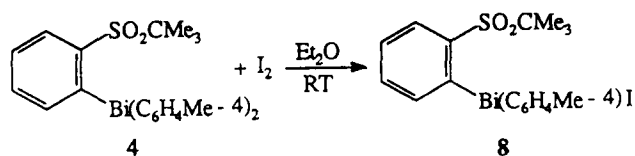
However, the principal product of the reaction was (2-C₆H₄SO₂CMe₃)₂BiC₆H₄Me-4. The successful synthesis of the desired chlorobismuthine was achieved in the following manner:



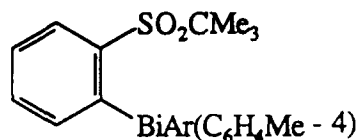
The intermediate fluoro compound **5** was unstable and could not be purified by recrystallization. Evidence that this compound was formed was shown by the presence of a sharp signal at 148 ppm (relative to CFCl₃) in the ¹⁹F NMR spectrum of the crude product. Treatment of the partially decomposed intermediate with aqueous sodium chloride gave (2-Me₃CSO₂C₆H₄)₂BiCl as one of the products of the reaction. If the intermediate **5** was treated with aqueous sodium bromide, the bromo compound **7** was formed in 90% yield after recrystallization.



The corresponding iodo compound **8** was prepared from **5** and aqueous sodium iodide. Compound **8** was also prepared in quantitative yield by iodination of compound **4**:

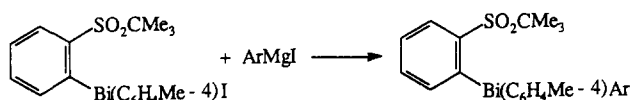


The starting tertiary bismuthine (**4**) in the above syntheses was obtained from 2-lithiophenyl *tert*-butyl sulfone and chlorodi-4-tolylbismuthine. Three other tertiary bismuthines, **9a**, **9b** and **9c**, and their reactions with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ were also investigated:

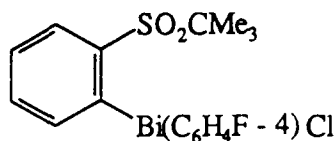


9a, b, c

(**9a**, Ar was 4-MeOC₆H₄; **9b**, Ar was 1-naphthyl; **9c**, Ar was 4-FC₆H₄). These compounds were prepared from the iodo compound **8** and the appropriate Grignard reagent:

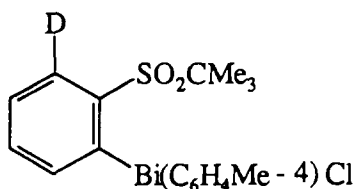


When **9a** or **9b** was treated with $\text{BF}_3 \cdot \text{Et}_2\text{O}$, the 4-MeOC₆H₄ or 1-naphthyl group was displaced to yield, after treatment with aqueous sodium chloride, compound **6**. With compound **9c**, however, the 4-tolyl group was displaced to yield compound **10**:



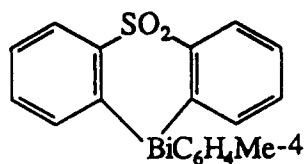
10

The ¹H NMR spectra of the halobismuthines **5**, **6**, **7** and **8** showed a large downfield shift for a signal associated with one aromatic proton in the molecule. This proton was identified as a proton ortho to the bismuth atom on the phenyl ring bearing the sulfonyl group in compound **6**, by comparing its ¹H NMR spectrum with that of the deuterated compound **11**.



11

The synthesis of **11** was described. In order to investigate further the surprising shifts of the aromatic proton in the ¹H NMR spectra of the monohalo bismuthines, the authors determined the crystal and molecular structures of compounds **4** and **6**. The molecular structure of **4** was similar to that of most other organobismuth(III) compounds, i.e. a pyramidal bismuth atom. The intramolecular SO-Bi distance was comparable to that in compound **12**, recently reported by Suzuki and coworkers:



12

By contrast, the geometry of the Bi atom in compound **6** was that of a pseudo-trigonal bipyramid with the chlorine and one sulfonyl oxygen atom in apical positions. The intramolecular Bi-O distance was considerably less than the sum of the Van der Waals radii, while the Bi-Cl distance was longer than that found in chlorobis[2,4,6-tris(trifluoromethyl)phenyl]bismuthine. The authors suggested that the structural results were in accord with the formation of a hypervalent three-center four-electron bond over the Bi, Cl, and O atoms which resulted in increasing the stability of the Bi-Cl bond. The distance between the Cl atom and the hydrogen atom ortho to the Bi atom was less than that of the Van der Waals radii, which suggested a weak Cl-H interaction. Anisotropic deshielding of this proton by the chlorine atom would explain the unique downfield shift of the proton in the ¹H NMR spectrum. Such a shift could not occur to the proton ortho to the Bi atom on the 4-tolyl group owing to free rotation of the tolyl group around the Bi-C bond. All of the new compounds in the present paper were characterized by elemental analyses, ¹H NMR, IR and mass spectrometry.

In another paper from Suzuki's laboratory, the oxidation of triphenyl- and tri-4-tolylbismuthines with several different oxidizing agents was reported [13]. The oxidation of triphenylbismuthine with hydrogen peroxide or *tert*-butyl hydroperoxide gave a complex mixture of decomposition products. Oxidation with ozone in dichloromethane at -78°C also gave a complex mixture which included triphenylbismuth dichloride as one of the products. However, the same oxidation with toluene as a solvent gave the hitherto unknown product, triphenylbismuth diformate, in 33% yield (accompanied by traces of the diacetate). Insoluble bismuth-containing

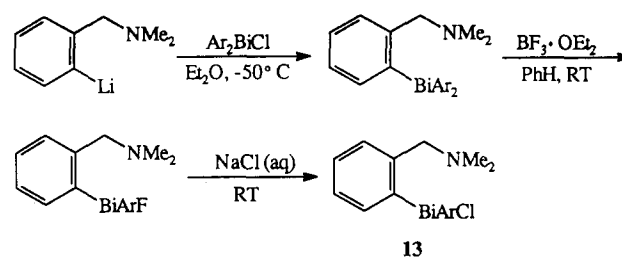
polymeric material was also formed. The yield of triphenylbismuth diformate could be increased to 57% by carrying out the oxidation in more dilute solution ($0.0125 \text{ mol dm}^{-3}$ vs. $0.0250 \text{ mol dm}^{-3}$). The largest yield of the diformate (96%) was obtained by adding a toluene solution of triphenylbismuthine to a saturated solution of ozone in toluene at -78°C . In this reaction, only traces of the diacetate and no polymeric material were formed. Under the same reaction conditions, tri-4-tolylbismuthine gave tri-4-tolylbismuth diformate in nearly quantitative yield. Tri-2-tolylbismuthine and trimesitylbismuthine, however, gave only insoluble polymeric material.

In order to study the mechanism of the reaction, the ozonolysis of triphenylbismuthine was carried out in a variety of solvents and under several different reaction conditions. Thus, in $[^2\text{H}_8]$ toluene, under optimum reaction conditions, the formate group was deuterated. In the presence of carbon dioxide, in addition to the diformate (25%) and starting material (35%), a 40% yield of triphenylbismuth carbonate was obtained. The use of ^{13}C -enriched carbon dioxide did not affect the ^{13}C content of the formate group (i.e. above the natural level). If triphenylbismuthine was added at RT to toluene previously ozonized at -78°C , the product consisted of starting material and the diformate in a 3:1 ratio. Under these same reaction conditions with ethyl acetate as the solvent, the triphenylbismuthine was recovered unchanged. However, oxidation of the same substrate in ethyl acetate at -78°C gave a small amount of the diformate (13%) as well as triphenylbismuth diacetate (39%). In ethyl propionate under the same conditions, some triphenylbismuth dipropionate (17%) was formed. When ethyl pivalate or ethyl trifluoroacetate was used as the solvent, the only identified products were triphenylbismuth dipivalate or difluoroacetate, respectively. These results suggested that the α -carbon of the ester solvent was the source of the carbon atom of the diformate group. Other solvents investigated in this study were acetone and ethyl methyl ketone. When a benzene solution of the diformate was shaken with an aqueous solution of sodium chloride, bromide, fluoride, or acetate, the formate group was displaced to give the corresponding dihalide or diacetate in almost theoretical yield.

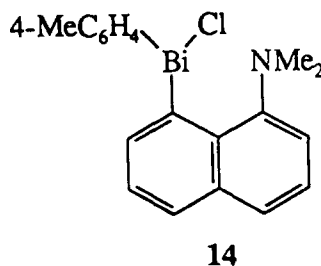
Triphenylbismuth and tri-4-tolylbismuth diformates were characterized by elemental analysis, ^1H and ^{13}C NMR, IR and mass spectrometry. In addition, the crystal and molecular structure of the triphenylbismuth diformate was determined by X-ray diffraction. The geometry of the bismuth atom was that of a distorted trigonal bipyramid. The Bi–O distance between the bismuth and the carbonyl oxygen atom was only 28% longer than the other Bi–O distance, i.e. the formate group was bidentate.

In continuation of their studies on chiral halobis-

muthines, Suzuki et al. [14] have reported the synthesis of chlorobismuthines, each containing a chiral bismuth atom. The following procedure was employed:



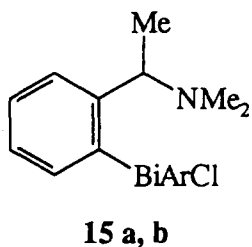
(Ar was 4-MeC₆H₄, 4-MeOC₆H₄, Ph, 4-ClC₆H₄ or 1-naphthyl). In all five compounds, the protons of the dimethyl groups and of the methylene group were diastereotopic as shown by ^1H NMR determinations in $[^2\text{H}_8]$ toluene. Except for the naphthalene compound, the methyl signals coalesced to a singlet at 70°C . The same signals of the naphthalene compound coalesced at 90°C . In $[^2\text{H}_6]$ DMSO the methyl signals of all five compounds coalesced at RT. The authors believed that the coalescence involved a reversible Bi–N bond dissociation followed by vertex inversion at the nitrogen atom and rotation of 180° at the CH₂–N bond. They preferred this mechanism to a process involving inversion of the chiral Bi atom without Bi–N dissociation. In addition to compound **13**, a similar compound in which Ar was Ph and the Cl was replaced by a Br atom was synthesized. The coalescence temperature of the NMe₂ signals of the latter compound was the same as that found for compound **13**. Another compound prepared was **14**, the synthesis of which involved a series of reactions similar to those used for preparing **13**.



The ^1H NMR signals of the NMe₂ group of **14** did not coalesce in $[^2\text{H}_8]$ toluene, even at 110°C .

The crystal and molecular structure of **13** (where Ar was 4-MeC₆H₄) was determined by X-ray diffraction. The geometry of the Bi atom was that of a distorted pseudo-trigonal bipyramid, with the Cl and the coordinating N atom in axial positions. The N–Bi–Cl angle was 162.9° and the Bi–N distance (2.525 \AA) was considerably shorter than the sum of the Van der Waals distances (3.66 \AA). The Cl atom was close to an ortho

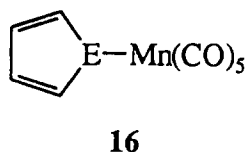
hydrogen (on the phenyl group containing the dimethylamino group) which accounted for the large downfield shift of one of the aromatic hydrogen atoms of **13**. The hydrogen atoms of the methylene group were staggered with one hydrogen above the tolyl group. The authors speculated that, if one of the methylene hydrogens was replaced by a bulky group, this group, for steric reasons, would be trans to the Ar group on the Bi atom. Accordingly they prepared compounds **15a** and **15b**:



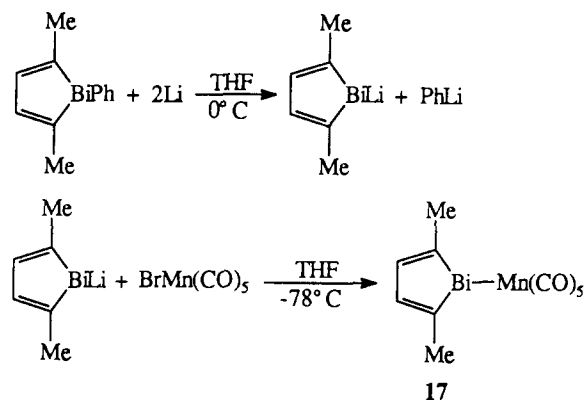
(**15a**, Ar was Ph; **15b**, Ar was 1-naphthyl). The synthesis of **15** involved the *ortho*-lithiation of (+)-*N,N*-dimethyl-1-phenylethylamine so that one of the ligands attached to bismuth was the 2-[(*R*)-1-(*N,N*-dimethylamino)ethyl]phenyl group. With both the methyne carbon atom and the Bi atom chiral, compound **15** existed as a diastereoisomeric pair. The ^1H NMR spectra of **15a** revealed the presence of two diastereoisomeric forms in a ratio of 77:23; similarly **15b** contained two diastereoisomers in a ratio of 78:22. The authors interpreted these results as indicating that the major isomers contained the Ar group and the dimethylamino group in trans position, with these two groups in cis position in the minor isomer. A study was carried out involving the ^1H NMR spectrum of **15a** at varying temperatures. In $[\text{}^2\text{H}_8]\text{toluene}$ the signals of the methyl hydrogens of the major isomer coalesced at 60°C , while the methyl hydrogen signals of the minor isomer were unaffected (i.e. they remained a doublet). However, in $[\text{}^2\text{H}_8]\text{DMSO}$ these same signals of both the major and the minor isomers coalesced at 30°C . Further studies were carried out in a solvent mixture of CDCl_3 and $[\text{}^2\text{H}_8]\text{DMSO}$. At -40°C the NMe_2 methyl signals of both major and minor isomers appeared as doublets (diastereotopically). On raising the temperature to -10°C , the signals of the minor isomer were unchanged, but the signals of the major isomer coalesced to a singlet. Further raising the temperature to 5°C caused the signals of both isomers to coalesce. Finally at 50°C two broad singlets were obtained. The authors thus concluded that two different mechanisms were involved, the reversible dissociation of the intramolecular Bi–N bond (below -10°C) and inversion around the

chiral Bi atom at higher temperatures. All of the new compounds were characterized by ^1H NMR, IR and mass spectrometry and by elemental analysis.

Compounds of the type **16** are known, and their spectral properties have been reported:

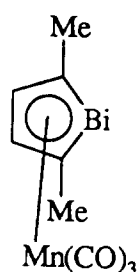


(where E was P, As or Sb). No compound where E was Bi, however, has been described. Ashe et al. have now prepared the bismolyl compound **17** by the following series of reactions [15]:



The phenyllithium was destroyed with gaseous ammonia, and the desired product was recrystallized from acetone. It was characterized by elemental analysis, ^1H and ^{13}C NMR, IR and mass spectroscopy. The crystal and molecular structure of **17** was also determined by means of X-ray diffraction. The dimethylbismolyl ring was nearly planar. The bond angles around the Bi atom were all substantially less than the tetrahedral angle, which suggested that the lone pair was essentially *s* in character. Bond distances and bond angles of **17** were compared with those of other known compounds containing Bi–Mn bonds. The preparation of **17** has now allowed a comparison of the IR spectra of the series of compounds **16**, where E was P, As, Sb and Bi. It was found that the $\nu(\text{CO})$ values decreased in the order $\text{P} > \text{As} > \text{Sb} > \text{Bi}$. This result was consistent with a decrease in the donor character of the pnicogen atom with increasing atomic number.

When **17** was heated to 125°C for 5 h, carbon monoxide was lost to yield the η^5 compound **18**:



18

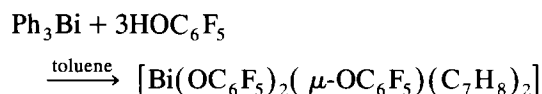
Crystals of **18** suitable for X-ray diffraction studies were not obtained, and the compound was characterized by ^1H and ^{13}C NMR and mass spectrometry.

A PM3 SCF study of the molecular and electronic structures of radical cations derived from methyl derivatives of elements of periodic Groups 13–16 has been carried out [16a]. The radical cations Me_3Bi^+ and $[\text{Me}_2\text{BiBiMe}_2]^+$ were among the species investigated. Further information on this subject has been given in the *Annual Survey of Antimony* for 1993, see Ref. [16b].

When sodium diethyl dithiocarbamate in aqueous solution was allowed to react with an alcoholic solution of bismuth trichloride, $\text{Bi}[\text{SC}(\text{S})\text{NEt}_2]_3$ was obtained in high yield [17]. When this compound reacted with bismuth trichloride in a 1:2 molar ratio, $\text{Cl}_2\text{BiSC}(\text{S})\text{NEt}_2$ was obtained. The reaction was carried out in acetonitrile–chloroform solution. Subsequent reaction of the dichloro compound with phenyllithium in THF solution in a molar ratio of 1:1 gave the compound $\text{PhBi}(\text{Cl})\text{SC}(\text{S})\text{NEt}_2$ in 52% yield. If the same reactants were used in a 1:2 molar ratio, $\text{Ph}_2\text{BiSC}(\text{S})\text{NEt}_2$ was obtained. The latter two compounds were characterized by elemental analysis, ^1H NMR and IR spectroscopy. Some IR spectral data were also reported for the compounds $\text{Cl}_2\text{BiSC}(\text{S})\text{NEt}_2$ and $\text{Bi}[\text{SC}(\text{S})\text{NEt}_2]_3$.

Previous papers from Whitmire's laboratory have reported the synthesis and properties of bismuth alkoxides, $\text{Bi}(\text{OR})_3$. It has been noted that, when R was a small group, such compounds existed as polymers; with bulky groups, monomers were obtained. Finally, medium-sized groups led to the formation of dimers. The present paper continues studies by Whitmire and coworkers on such bismuth compounds [18]. The dimeric compound $[\text{Bi}(\text{OCH}(\text{CF}_3)_2)_2(\mu\text{-OCH}(\text{CF}_3)_2(\text{THF}))_2]$ was prepared from BiCl_3 and $\text{NaOCH}(\text{CF}_3)_2$ in THF solution. When a similar reaction was carried out with bismuth trichloride and sodium pentafluorophenoxide, only complex (aryloxy) bismuth oxide clusters were obtained. The desired compound, however, was readily

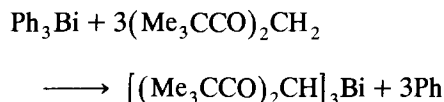
prepared by refluxing triphenylbismuthine and pentafluorophenol in toluene solution:



Ogawa and coworkers have pointed out that, although there are many mild methods for condensing carboxylic acids with amines or alcohols to form amides or esters, there are no reagents available which can differentiate between the reaction of carboxylic acids bearing α -hydrogen atoms and those without α -hydrogen atoms [19]. They have now found, however, that such a differentiation was possible if a tris(methoxyphenyl)bismuthine was used as a catalyst. Thus, phenoxyacetic acid (1.2 mmol) and 2-phenylethylamine (1.2 mmol) when refluxed in benzene solution for 12 h in the presence of tris(2-methoxyphenyl)bismuthine (0.4 mmol) gave *N*-(2-phenylethyl)phenoxyacetamide in 76% yield. Under the same reaction conditions, with the same amine and catalyst, benzoic, trimethylacetic, and 2,4,6-trimethylbenzoic acids did not give the corresponding amides, and the starting materials were recovered unchanged. The reaction described above (phenoxyacetic acid and 2-phenylethylamine with tris(2-methoxyphenyl)bismuthine) in benzene solution was studied further by varying the reaction conditions and by using various bismuthines as catalysts. With the same reactants in the absence of a solvent (at 90°C), the yield increased from 76 to 88%. The presence of an alkoxyphenyl group was essential for catalytic activity. No amide was produced with triphenylbismuthine as the catalyst. Several different methoxy-substituted phenylbismuthines were tried; all were effective catalysts. The largest yield (94%) occurred when tris(2,6-dimethoxyphenyl)bismuthine was used.

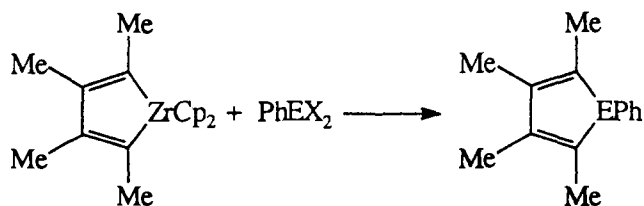
In addition to phenoxyacetic acid and 2-phenylethylamine, other acids containing an α -hydrogen atom (octanoic and epoxyoleic acids) and one other amine (aniline) gave satisfactory yields of the corresponding acetamides. In addition to amides, esters were readily formed from alcohols and acids containing α -hydrogen atoms. Phenoxyacetic acid and ethanol gave a 75% yield of (*N*-phenyl)phenoxyacetamide when tris(2-methoxyphenyl)bismuthine was used as the catalyst, but only a 37% yield with tris(2,6-dimethoxyphenyl)bismuthine. Benzyl alcohol gave the benzyl esters of phenoxyacetic and octanoic acids (with tris(2-methoxyphenyl)bismuthine as the catalyst) in 73 and 86% yields, respectively. Ethanolamine and *N*-ethylethanolamine gave the corresponding amides (but apparently no esters) with tris(2-methoxyphenyl)bismuthine as the catalyst in 65 and 43% yields, respectively. 1,2-Butanediol gave a mixture of products. All of the new compounds were characterized by elemental analysis, ^1H NMR and IR spectroscopy.

The crystal and molecular structure of $[(\text{Me}_3\text{CCO})_2\text{-CH}]_3\text{Bi}$ has been determined by X-ray diffraction [20]. The compound was prepared by the interaction of triphenylbismuthine and dipivaloylmethane with removal of the benzene formed in the reaction by distillation [21]:

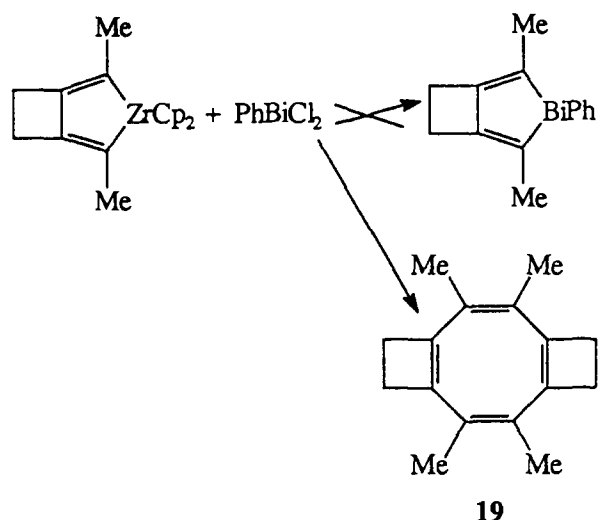


Although the cyclopentadienyl tricarbonyliron cation, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+$, is relatively unreactive to soft nucleophilic donors, Brown et al. [22] have suggested that the analogous indenyl compound, because of the formation of the ring-slipped intermediate (η^3) form, might have enhanced reactivity as compared with the cyclopentadienyl form. Accordingly, they prepared a large number of Group-15-substituted indenyl iron complexes from $[(\eta^5\text{-C}_9\text{H}_7)\text{Fe}(\text{CO})_3]\text{BF}_4$ by replacement of one carbonyl group by a variety of phosphines and phosphites, as well as by Ph_3As and Ph_3Sb . (Several ditertiary phosphines were also investigated.) The reactions were carried out in refluxing acetone. Although both Ph_3As and Ph_3Sb gave the desired products, Ph_3Bi failed to react, even after prolonged refluxing or irradiation with UV. However, the reaction of Ph_3Bi , the indenyl iron compound, and AgBF_4 in CH_2Cl_2 at RT apparently resulted in the formation of the desired bismuth compound as indicated by the appearance of two new peaks at 2068 and 2020 cm^{-1} in the IR spectrum (compared with peaks at 2118 and 2069 cm^{-1} in the starting indenyl iron compound). The bismuth compound could not be isolated successfully.

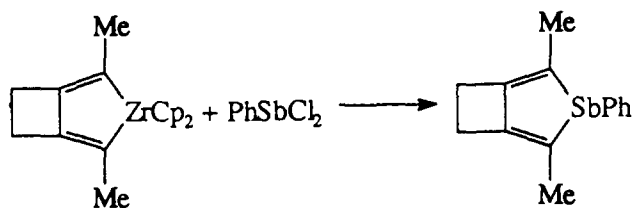
Zirconacyclopentadienes, which are easily prepared, have proved useful for preparing heterocyclic compounds of the main group elements. Thus, the following stiboles and bismoles have been prepared:



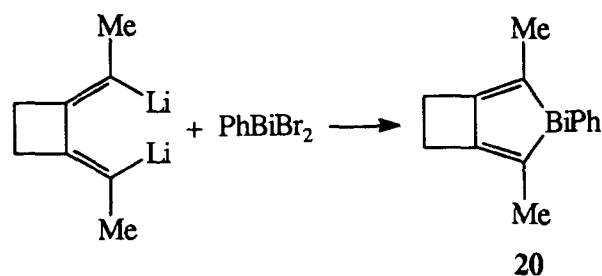
(where Cp was cyclopentadienyl, E was Sb or Bi, and X was Cl or Br). Spence et al. (in a paper from Buchwald's laboratory) [23] have now found that the following reaction gave an unexpected product:



Thus, addition of the zirconacyclopentadiene to the bismuthine gave the cyclooctatetraene **19** in 80% yield. It was characterized by elemental analysis, ¹H and ¹³C NMR and mass spectrometry. Only the expected phenylstibole was obtained by the interaction of the zirconium reagent with phenyldichlorostibine:

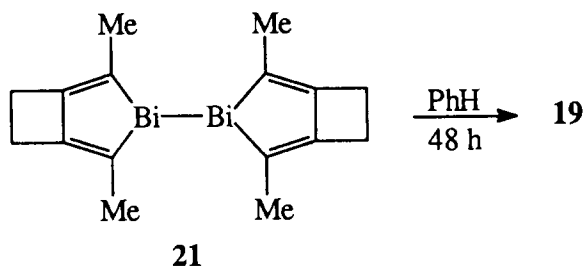


However, reaction of the zirconacyclopentadiene with BiBr_3 , SbCl_3 or GaCl_3 did lead to the formation of the cyclooctatetraene **19** as the principal organic product. The authors found that the desired bismole could be prepared from the dilithio compound, and was stable, both in solution and in the solid state:

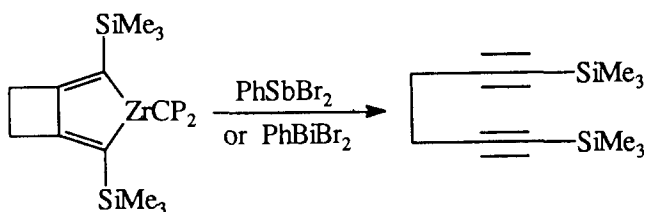


However, when **20** was treated with PhBiBr_2 it was converted into the cyclooctatetraene **19**. It was also found that slow addition of PhBiBr_2 to the zirconacyclopentadiene gave significant amounts of the bismole

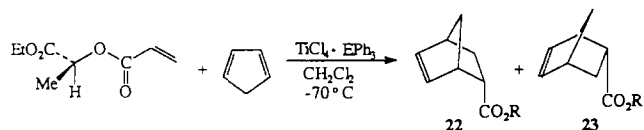
20, as well as the cyclooctatetraene **19**. Another example of the ease of formation of the cyclooctatetraene was found when the bibismole **21** was dissolved in benzene and kept for 48 h:



Finally, the authors found that the trimethylsilyl-substituted zirconacyclopentadiene, when treated with either PhSbBr₂ or PhBiBr₂, yielded a diyne:



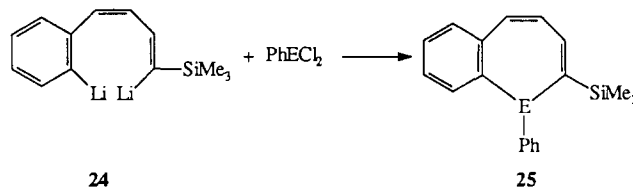
Lewis acids such as TiCl₄ have been used in organic synthesis to enhance the electrophilicity of substrates. Use of such Lewis acids, however, often leads to side-reactions such as polymerization or substrate decomposition. Thus, in the Diels–Alder reaction, the use of TiCl₄ often leads to considerable polymerization of the diene. Suzuki and Yamamoto [24] have found that the combination TiCl₄ · EPh₃ (E = As, Sb, Bi) modified the effect of TiCl₄ by preventing the polymerization of the diene without affecting its ability to accelerate the reactions. Thus, the Diels–Alder reaction of the acrylate of (*S*)-ethyl lactate with cyclopentadiene proceeded in the following manner



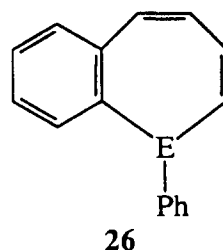
(where R was CH(Me)CO₂Et). When E was Bi, the ratio of **22** to **23** was 12:88. If TiCl₄ alone was used, polymerization of the diene occurred and the adducts were not obtained. The complexation of TiCl₄ with Ph₃Sb has been mentioned in Ref. [16b].

Heteropines (fully unsaturated seven-membered heterocyclic rings) containing Group-14 or Group-16 elements have been prepared, but only a few heteropines of Group-15 elements are known, and no heteropines

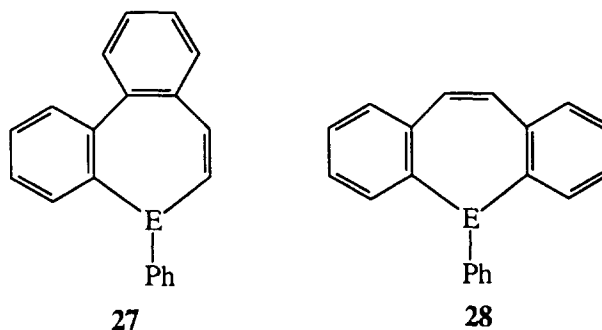
with arsenic or bismuth in the ring have been described. Yasuike et al. have now described, in a preliminary communication [25], the preparation of several heteropines containing the Group-15 elements P, As, Sb, and Bi. The 1-benzoheteropine **25** was prepared from the dilithio compound **24**



(where E was P, As, Sb, or Bi). By treatment of any of the above heteropines with tetrabutylammonium fluoride, the trimethylsilyl group was removed to give the 1-phenyl-1-benzoheteropines **26**:



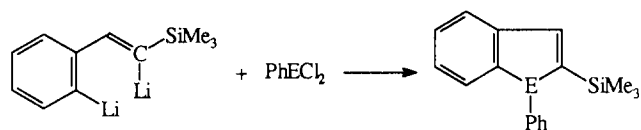
All of the heteropines **26** were thermolabile and decomposed to give naphthalene. The bismuth compound was the least stable. Thus, the half-life of the bismuth compound in toluene at 60 °C was 7 min. The trimethylsilyl-substituted heteropines **25** were considerably more stable than the compounds **26**. In addition to the monobenzo substituted heteropines, two different types of dibenzo substituted heteropines, **27** and **28**, were prepared



(where E was P, As, Sb or Bi). These dibenzo compounds were all considerably more stable than the corresponding monobenzo compounds. The new compounds were characterized by ¹H NMR determinations.

Although five-membered heterocyclic compounds in which the heteroelement is other than nitrogen, oxygen,

or sulfur are well known, such compounds are usually highly substituted, and the synthetic methods used for their preparation are generally not versatile. Kurita et al. [26] have now offered a versatile method for preparing a wide variety of C-unsubstituted 1-benzometalloles in which the heteroelement was a Group-14, -15 or -16 element. The preparation of the compounds containing the Group-15 element was carried out in the following manner:



(where E was P, As, Sb or Bi). The trimethylsilyl group was readily removed from these compounds by treatment with cesium fluoride or tetrabutylammonium fluoride to give the C-unsubstituted metalloles. They were characterized by elemental analysis and by ^1H NMR and mass spectrometry.

Trimethylbismuthine has been used as the source of bismuth for the preparation of a bismuth monofluoride visible-wavelength chemical laser [27].

In a paper devoted to the explosive decomposition of organometallic compounds of Groups 12–16, trimethyl- and triethyl-bismuthines were among the compounds discussed [28].

A paper by Ignatious et al. described the preparation and polymerization of arylbismuth, lead and tin derivatives of styrene and α -methylstyrene [29]. The bismuth compounds were styryl- and α -methylstyryldiphenylbismuthines. Homopolymers of the styryl compound and copolymers with methyl acrylate were prepared, but the α -methylstyryldiphenylbismuthine did not polymerize owing to side-reactions.

A US patent has been issued for the preparation of a radiopaque polymer by the copolymerization of diphenyl-4-styrylbismuthine and methyl methacrylate [30].

A Japanese patent for the preparation of antifouling coating materials incorporated $\text{PhBiCl}_2 \cdot (\text{pyridine})_2$ as one of the ingredients [31].

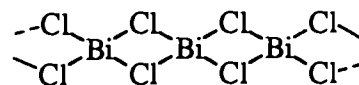
There has been an enormous amount of research in recent years on superconducting films, and such films containing bismuth oxide have been of considerable importance. The bismuth oxide has usually been obtained by chemical vapor deposition by the decomposition of organobismuth compounds (metal-organic chemical vapor deposition, MOCVD). Triphenylbismuthine has usually been the organobismuth compound of choice [32–36].

A Japanese patent covered the preparation of thin bismuth oxide films by chemical vapor deposition with

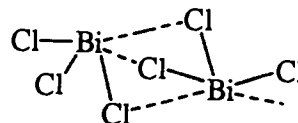
tri-4-tolylbismuthine or tris(4-ethylphenyl)bismuthine [37]. Thin films of bismuth titanate have also been prepared by chemical vapor deposition methods [38–40]. An indium arsenide bismuthide alloy has been prepared from triphenylbismuthine by organometallic vapor-phase epitaxy [41].

The Menshutkin complexes formed from antimony trichloride and benzene or other aromatic hydrocarbons are well known. No comparable complexes of bismuth trichloride are known, although a few complexes utilizing cyclopentadiene or its derivatives have been prepared. Frank et al. [42] have now prepared a 1:1 complex between bismuth trichloride and benzene and determined its crystal and molecular structure by X-ray diffraction. The compound contained the weakest bismuth π -system so far prepared. Thus, it readily lost benzene when dried in vacuo or when excess benzene was removed in a stream of argon at room temperature. The compound was a layered polymer with three short Bi–Cl and three long Bi–Cl contacts. The structure of the bismuth atom was a distorted pentagonal bipyramid with a chlorine and the benzene in axial positions. The Bi–C contacts were only slightly shorter than the sum of the Van der Waals radii. In the layered structure, two molecular fragments were linked to each other by weak chlorine bridges.

Müller-Becker, Frank and Schneider have prepared the 1:1 complexes $\text{C}_6\text{H}_4\text{Me}_2 \cdot \text{BiCl}_3$, where $\text{C}_6\text{H}_4\text{Me}_2$ was *o*-, *m*- or *p*-xylene [43]. The first two were prepared by warming BiCl_3 in the arene, while to prepare the third compound a mixture of *p*-xylene and toluene was used. The compounds were characterized by elemental analysis and X-ray diffraction. Bond lengths and bond angles for all three compounds were reported. The compounds obtained from *m*- and *p*-xylene contained four-membered BiClBiCl rings. Additional Bi–Cl contacts led to structures containing one-dimensional polymeric chains. With *m*-xylene the chains were of the following type:

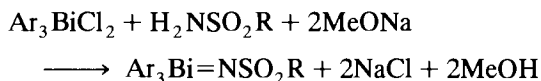


An arene moiety was η^6 -bonded to each bismuth atom. The compound with *p*-xylene was somewhat similar in structure. The compound from *o*-xylene was more complicated, with additional Bi–Cl contacts. Thus, two bismuth atoms were connected by three chlorine bridges of the following type:

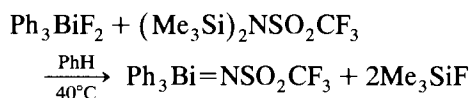


This resulted in a greatly strained trigonal-bipyramidal arrangement for the bismuth atom.

A number of triarylbismuth imines of the type $\text{Ar}_3\text{Bi}=\text{NSO}_2\text{R}$ have been synthesized [44]. Two different reactions were used for their preparation. The first reaction employed triarylbismuth dichlorides:

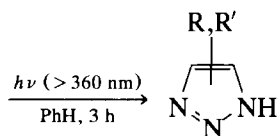
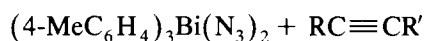


(where Ar was Ph or 4- FC_6H_4 and R was CF_3 , and where Ar was Ph and R was C_4F_9 or 4- MeC_6H_4). The reactions were carried out in acetonitrile or dichloromethane at RT. The products were stable for at least a week under dry nitrogen, but decomposed in solution. Hydrolysis gave the corresponding triarylbismuthine oxide. With $(4\text{-FC}_6\text{H}_4)_3\text{Bi}=\text{NSO}_2\text{CF}_3$, however, two broad peaks in the ^{19}F spectrum were assigned to the compounds $(4\text{-FC}_6\text{H}_4)_3\text{Bi}(\text{OH})\text{NHSO}_2\text{CF}_3$ and $[(4\text{-FC}_6\text{H}_4)_3\text{BiNHSO}_2\text{CF}_3]_2\text{O}$. A second method for preparing the imines utilized triphenylbismuth difluoride:



The yield by this method was nearly quantitative. The compounds were prepared in a nitrogen atmosphere using Schlenk techniques. They were characterized by elemental analysis and ^{19}F and ^1H NMR spectroscopy. The molecular weight of $\text{Ph}_3\text{Bi}=\text{NSO}_2\text{CF}_3$ (determined cryoscopically in dioxane) was normal.

A paper from Suzuki's laboratory concerned the photochemical decomposition of tri-4-tolylbismuth diazide in the presence of alkynes to form 1,2,3-triazoles [45]:



The irradiation was carried out in an argon atmosphere with a 125 W high-pressure mercury lamp placed 5 cm above a quartz flask containing the reactants. A copper sulfate filter was placed between the flask and the lamp. After 3 h a bismuth-containing residue was removed by filtration, and the filtrate was evaporated under reduced pressure to yield the crude product. This was purified by chromatography on silica gel. Five different monoalkynes were employed; phenylacetylene, diphenylacetylene, and three acetylenes of the type $\text{PhC}\equiv\text{CAr}$, where Ar was a substituted phenyl group. Two dialkynes, 4- $\text{MeC}_6\text{H}_4\text{C}\equiv\text{C}-\text{C}\equiv\text{CC}_6\text{H}_4\text{Me}$ -4 and 4- $\text{ClC}_6\text{H}_4\text{C}\equiv\text{C}-\text{C}\equiv\text{CC}_6\text{H}_4\text{Cl}$ -4, were also used. The yields, in all cases, were small (10%) to moderate

(54%). Although the products where R and R' were different were isolated as a single regioisomer, the exact isomer obtained was not determined.

The photolysis of tri-4-tolylbismuth diazide was also carried out in the absence of an alkyne to yield a complex mixture of products. The authors were unable to trap an azido radical with several different radical trapping agents. They believed the reaction probably occurred by a concerted 1,3-dipolar cycloaddition followed by loss of a bismuth moiety.

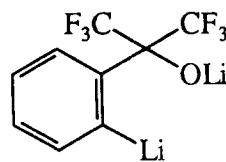
Ali and McWhinnie [46] have synthesized a number of organobismuth(III) and organobismuth(V) carboxylates of the type $\text{PhBi}(\text{O}_2\text{CR})_2$ and $\text{Ph}_3\text{Bi}(\text{O}_2\text{CR})_2$ and tested their use as paint driers. The bismuth(III) carboxylates included the acetato and monomaleato derivatives; the bismuth(V) carboxylates contained the acetato, propionato, benzoato and other groups. The shelf life of the bismuth driers was poor. One drier, a combination of $\text{Bi}(\text{O}_2\text{CC}_7\text{H}_{15})_3$ with tris(diethylthiocarbamate)bismuthine was superior to established driers.

Dodonov and Zinovyeva [47] have made use of peroxides and hydroperoxides for the oxidation of organoantimony(III) and organobismuth(III) compounds. Thus, the oxidation of triphenylbismuthine with three equivalents of $\text{Me}_3\text{CO}_2\text{H}$ gave $\text{Ph}_3\text{Bi}(\text{O}_2\text{CMe})_2$. Treatment of the latter compound with $(\text{MeCO})_2\text{O}$ gave $\text{Ph}_3\text{Bi}(\text{O}_2\text{CMe})_2$.

Another paper from Dodonov's laboratory has made use of the triphenylbismuthine/*tert*-butylhydroperoxide system for the oxidation of saturated normal hydrocarbons [48]. The ultimate products of this reaction were carboxylic acid anhydrides.

Two patents dealing with the use of triarylbismuth dicarboxylates as arylating agents in the preparation of immunosuppressant drugs have been applied for [49,50].

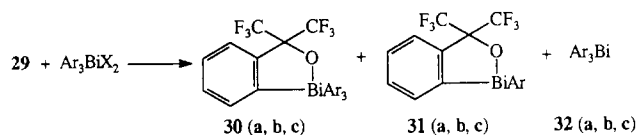
Akiba and coworkers have written a number of papers on heterocyclic organobismuth(V) compounds. In their work they have frequently made use of the dilithio compound **29** (which they termed the Martin ligand):



29

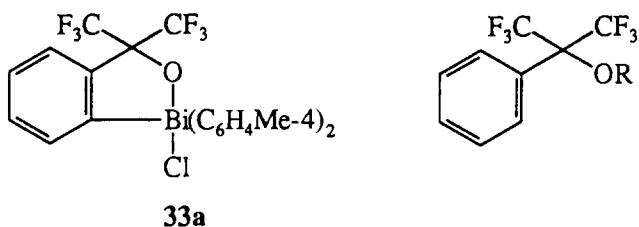
The most recent paper [51] from Akiba's laboratory has reported the preparation and the crystal and molecular structures of a number of new heterocyclic 10-Bi-5 organobismuth(V) compounds; compound **29** was used in their preparation. Thus, the reaction of **29** with triarylbismuth dihalides gave rise to the 10-Bi-5 com-

pounds **30a**, **30b** and **30c** as well as to the by-products **31a**, **31b** and **31c**, and **32a**, **32b** and **32c**:

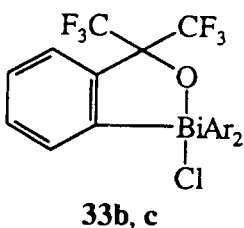


(**30a**, **31a**, **32a**, Ar was 4-MeC₆H₄; **30b**, **31b**, **32b**, Ar was 4-CF₃C₆H₄; **30c**, **31c**, **32c**, Ar was 4-FC₆H₄).

For the preparation of **30b**, **31b** and **32b**, and of **30c**, **31c** and **32c**, the dihalide used was the dichloride, but for **30a**, **31a** and **32a** both the dichloride and the dibromide were used. The above reactions were carried out in THF at -78 °C in a nitrogen atmosphere, and the products were separated by flash column chromatography followed by recrystallization from ether-hexane. When **30a** was treated with ethyl succinyl chloride, the chloro compound **33a**, together with **32a** and a bismuth-free ether, was formed:

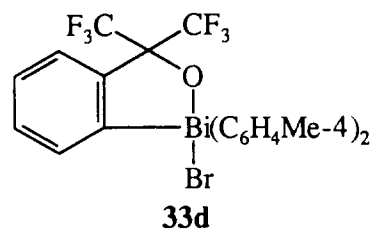


(where R was COCH₂CH₂CO₂Et). Compound **33a**, together with **32a** and a similar bismuth-free ether (except that R was 4-MeOC₆H₄CO), was obtained by treating **30a** with 4-methoxybenzoyl chloride. By either reaction, the yield of **33a** was small. It was obtained, however, in more than 95% yield, from **30a** and sulfonyl chloride. Accordingly, compounds **33b** and **33c** were prepared from **30b** and **30c**, respectively, and sulfonyl chloride:

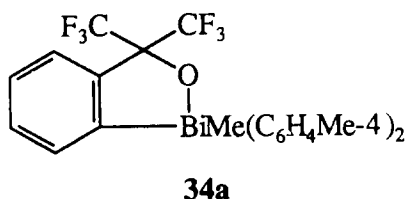


(**33b**, Ar was 4-CF₃C₆H₄; **33c**, Ar was 4-FC₆H₄).

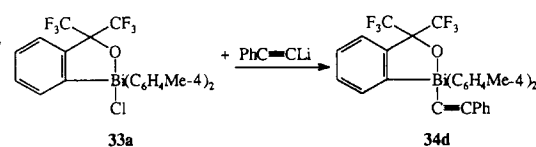
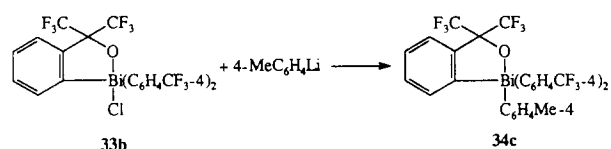
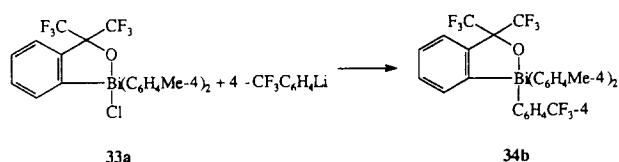
From **30a** and pyridinium bromide perbromide, **33d** was obtained:



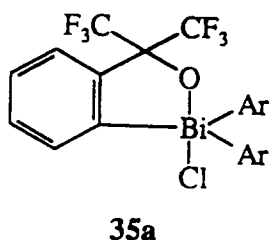
When compound **30a** was treated with methyl lithium at -78 °C and the reaction mixture quenched with water, **34a** was obtained in 86% yield:



Although this reaction was successful with methyl lithium, similar reactions with aryllithium reagents were not. The desired compounds could be prepared from monochloro compounds and aryllithium reagents:

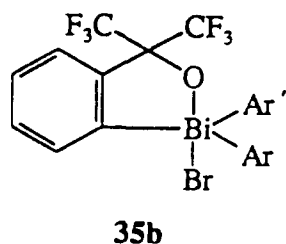


Treatment of **34b** with sulfonyl chloride gave a mixture of **35a** (81%) and **33a** (8%):

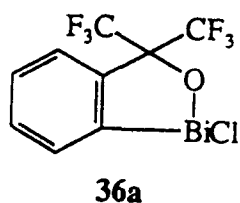


(where Ar was 4-MeC₆H₄ and Ar' was 4-CF₃C₆H₄).

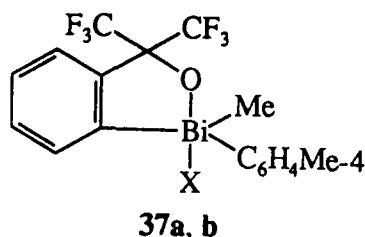
When a similar reaction was carried out using pyridinium bromide perbromide, **35b** (88%) (but no **33d**) was formed:



Treatment of **34a** with sulfuryl chloride gave **33a** (64%), together with a small amount of **36a**:



If pyridinium bromide perbromide was used, the monobromide **36b** (corresponding to **36a**) and **33d** (70%) were obtained. The authors suggested that **36a** and **36b** were formed via the intermediates **37a** and **37b**, but they were unable to isolate these products:

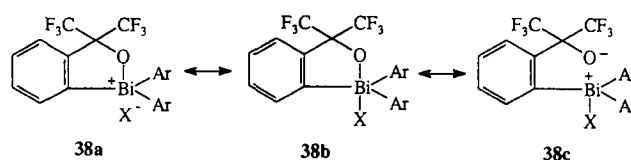


(**37a**, X was Cl; **37b**, X was Br). Treatment of **34c** with sulfuryl chloride gave **33b** (52%) with a small amount of **35a** (8%). Finally, compound **34d** was treated with sulfuryl chloride to give **33a** in 100% yield. Thus, the preferred order of cleavage of the Bi–C bond by halogenolysis was $\text{PhC}\equiv\text{C} > \text{Me} > 4\text{-MeC}_6\text{H}_4 > 4\text{-CF}_3\text{C}_6\text{H}_4$. The authors speculated as to the mechanism of the cleavage reaction and concluded that a direct electrophilic attack of the halogen at the aryl–bismuth bond without complexation was the most likely mechanism.

The new compounds described in the present paper were characterized by elemental analysis and by ^1H and

^{19}F NMR spectroscopy. In addition, the crystal and molecular structures of tri-4-tolylbismuth dichloride and of compounds **30a**, **33a**, **33b**, **33d**, **34a**, **34d** and **35a** were determined by X-ray diffraction. In all cases the geometry of the bismuth atom was that of a distorted trigonal bipyramid with the five-membered ring occupying equatorial-apical sites of the trigonal bipyramid.

The substituents attached to bismuth conformed to the apicophilicity rules. Thus, the oxygen and halogen atoms were in apical positions. In compound **34d**, the phenylethynyl group was in apical position, while the methyl group in compound **34a** was in an equatorial position. The Bi–halogen distances were slightly longer than the sum of the covalent radii, and there were no short intermolecular contacts involving bismuth and halogen. The length of the Bi–O bond was found to vary with the electronegativity of the other apical substituent. The authors suggested that this was due to the polarizable character of the three-center four-electron hypervalent bismuth bonds:

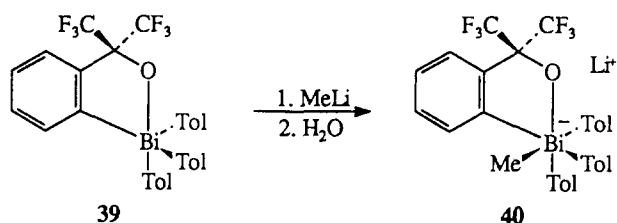


Thus, as the electronegativity of X increased, the contribution of the canonical form **38a** increased.

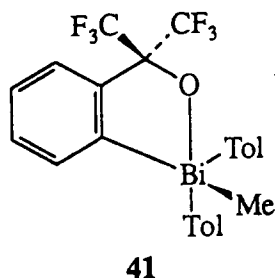
Compounds **35a** and **35b** contained five different groups attached to the bismuth atom. The ^{19}F NMR spectra of the two compounds gave a pair of quartets at room temperature (δ , -75.10 , -75.15 in 1,2-dichlorobenzene for **35a** and δ , -76.40 , -76.56 in toluene- d_6 for **35b**). Coalescence of these signals was observed at 150°C for **35a** and 170°C for **35b**, but there was no coalescence up to 170°C when the solutions were diluted 1:10. The authors therefore concluded that the coalescence at the higher concentration was due to intermolecular halogen exchange and that the barrier to intramolecular inversion was greater than 21 kcal mol^{-1} . They further suggested that the high energy barrier was due to the strain caused by placing the five-membered ring in two equatorial positions necessary for pseudorotation.

Another paper from Akiba's laboratory has described a number of 12-Bi-6 compounds in which the Bi atom was in a heterocyclic ring [52]. The first attempt to

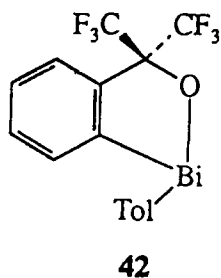
prepare such compounds employed the following reaction:



(where Tol1 was 4-MeC₆H₄). Only one of the possible isomeric forms of **40** has been shown above, i.e. the Me group could be trans to the O atom or trans to the phenyl group. Instead of **40**, compound **41** (70%) together with unreacted **39** (10%) were isolated.

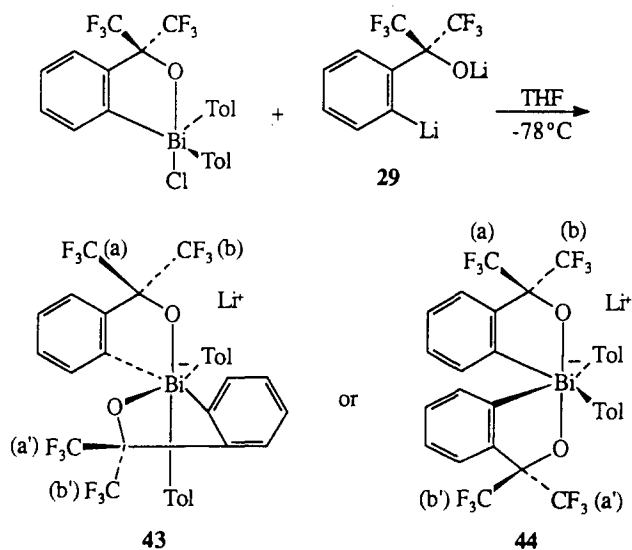


When the aqueous reaction mixture was stirred for 1 day, only 20% of **39** and no **41** was recovered. It would thus seem probable that **40** was formed and decomposed by an unknown mechanism to give **39** and **41**. In addition to the above reaction of **39** and MeLi, the reaction of **39** with EtLi or BuLi was attempted. In these reactions no Et or Bu compounds corresponding to **41** were isolated. Instead, the bismuth(III) compound **42** was obtained in 86.1% and 90.3% yields, respectively.

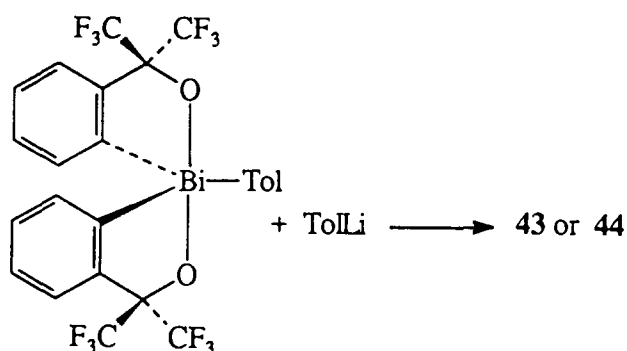


The authors suggested that compounds corresponding to **40** (with Et or Bu groups replacing the Me group) were formed but underwent reductive elimination to form, after hydrolysis, compound **42**.

In order to stabilize 12-Bi-6 ate complexes, the authors made use of the so-called Martin ligand **29**:

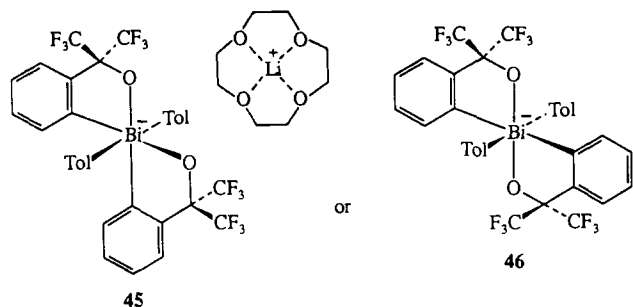


The ¹⁹F NMR spectrum of the resulting compound showed a pair of quartets at 0°C. These quartets coalesced at 70°C to a singlet that was stable to 150°C. When the solution was cooled back to 0°C, the same quartets were again formed. The same compound, as judged by the ¹⁹F NMR spectrum, was formed by the following reaction:



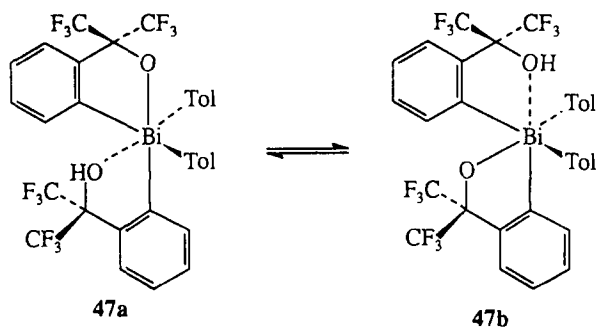
The ¹⁹F spectrum of the product was compatible with either formula **43** or **44** in which the fluorines (a = a' and b = b') would be magnetically equivalent. The authors suggested that the isomerization of **43** or **44** at 70°C occurred by intramolecular Bi-O cleavage, followed by pseudorotation of the resulting 10-Bi-5 compound and recyclization. In order to distinguish between **43** and **44**, 12-crown-4 was added to the ate complex solution in order to complex the lithium ion. The ¹⁹F NMR spectrum of the resulting solution gave a sharp singlet which was stable to 150°C. This result suggested that, in the compound without 12-crown-4, the lithium ion was complexed to two *cis*-oxygen atoms and that **43**, accordingly, was the preferred configuration. The

complex formed from 12-crown-4 could possess either of two configurations to explain the ^{19}F NMR spectral results:

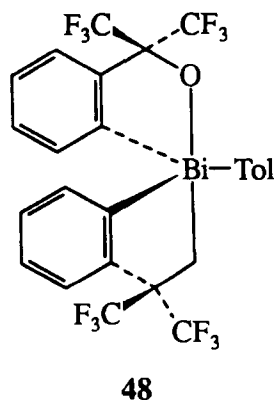


The authors were unable to determine experimentally whether **45** or **46** was preferred. However, ab initio calculations on some six coordinate Sb compounds and the known structures of some similar S and Te compounds strongly suggested that the anion with two *cis*-oxygen atoms should be the more stable.

The compound assigned structure **43** was remarkably stable. It did not react with (4-trifluoromethyl)benzoyl chloride (or with 4-chlorobenzoyl chloride in the presence of 12-crown-4) in refluxing THF. It did react with water to give the interesting alcohol **47a** \rightleftharpoons **47b**:

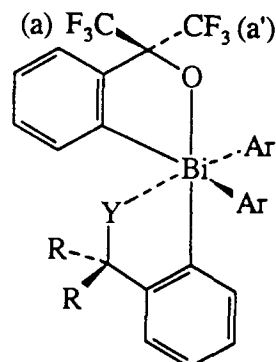


The alcohol was unstable at room temperature and lost toluene to give **48**:



The alcohol could be obtained nearly pure by flash column chromatography. At 0°C the ^{19}F NMR spectrum gave a singlet, which was explained by the rapid exchange of the OH proton between the two oxygen atoms. At -90°C , however, four pairs of quartets were obtained, which indicated that the prototropy was frozen out and that the hydroxyl oxygen coordinated to the Bi atom to form a six-coordinate structure.

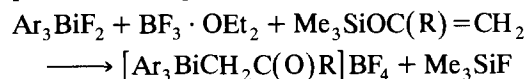
In order to further investigate 12-Bi-6 compounds similar to **47**, the authors synthesized compounds **49a**, **49b**, **49c** and **49d**:



49a, b, c, d

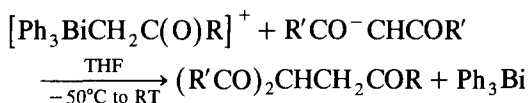
(**49a**, Ar = 4-MeC₆H₄, R = CF₃, Y = OMe; **49b**, Ar = 4-CF₃C₆H₄, R = CF₃, Y = OMe; **49c**, Ar = 4-MeC₆H₄, R = H, Y = NMe₂; **49d**, Ar = 4-CF₃C₆H₄, R = H, Y = NMe₂). The resulting compounds were stable to atmospheric moisture. The crystal and molecular structures of compounds **49b**, **49c** and **49d** were determined by X-ray diffraction. With **49b** the Bi–O distance, and with **49c** and **49d** the Bi–N distances, were all considerably shorter than the sum of the Van der Waals distances. The ^{19}F NMR spectra were also in accord with the structures determined by X-ray. Compounds **49a** and **49b** gave singlets at room temperature but four pairs of quartets at low temperatures. The coalescence temperatures and the free energies of activation of all four compounds were determined (in CD₂Cl₂ and toluene-*d*₈ for **49a** and **49b**, and in CD₂Cl₂ and acetone-*d*₆ for **49c** and **49d**).

The only known bismuthonium compounds containing an alkyl group are acetonyltriphenylbismuthonium perchlorate and tetrafluoroborate, [(MeCOCH₂)-Ph₃Bi]Y, where Y was ClO₄ or BF₄. A new paper from Suzuki's laboratory [53] has described the preparation of a series of monoalkyl bismuthonium tetrafluoroborates of the type [Ar₃BiCH₂C(O)R]BF₄, where Ar was Ph or 4-MeC₆H₄ and R was Me₃C, MeCHCH₂CH₃, Me₂CH, Ph or 4-BrC₆H₄. The compounds were prepared according to the following equation:

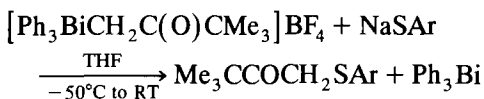


The bismuthonium compounds were obtained in yields of 87–99%. They were thermally stable and unaffected by air. They were characterized by elemental analysis and spectral data, which were not reported except for $[\text{Ph}_3\text{BiCH}_2\text{C}(\text{O})\text{CMe}_3]\text{BF}_4$. The crystal and molecular structure of this compound was determined by X-ray diffraction. The geometry of the bismuth atom was distorted tetragonal with C–Bi–C angles which varied from 102.1 to 118.4°. The Bi–O distance was considerably shorter than the sum of the Van der Waals radii, suggesting an interaction between the two atoms.

Several of the new bismuthonium salts were treated with sodium salts of β -diketones in THF solution to yield triketones in moderate yields:



(where R was Me_2CH , and R' was Ph, OMe, or OEt; where R was Ph, and R' was Ph; and where R was 4- BrC_6H_4 , and R' was Ph). In addition to their reactions with the anions of diketones, the bismuthonium salts reacted with aryl thiolates to yield ArS-substituted ketones:



(where Ar was Ph or 4- ClC_6H_4).

A number of papers have appeared from Seppelt's laboratory dealing with the chemistry and molecular structure of penta-arylbismuth compounds. A new paper from Seppelt's laboratory [54] deals with the preparation and structure of the hexaphenylbismuthate anion (a 12-Bi-6 structure). This anion had previously been prepared from pentaphenylbismuth and phenyllithium at low temperatures [55]. On warming it decomposed into its starting materials. The present authors repeated this preparation of $[\text{Ph}_6\text{Bi}]\text{Li}$. They found it necessary to use an excess of PhLi in order to drive the reaction to completion. The reactions were carried out in THF or diethyl ether, and the products contained molecules of solvent in the cation. From THF, yellow crystals of $[\text{Li}(\text{THF})_4][\text{Ph}_6\text{Bi}] \cdot 2\text{THF}$ were obtained. The crystal and molecular structure of this compound was determined by X-ray diffraction at -45°C . The compound contained four oxygen atoms from four THF molecules arranged tetrahedrally around each lithium atom, with two more uncoordinated THF atoms in the crystal lattice. The geometry of the bismuth atom was octahedral with T_h symmetry. The authors pointed out that this type of symmetry was extremely rare in chemistry. Deviations of bond angles from ideal octahedral values were equal to or less than 2.6°. All six Bi–C distances were nearly equal.

Cold dilute solutions of Ph_5Bi in THF gave crystals

of an adduct, but the crystal structure of this adduct could not be determined. However, concentrated solutions of Ph_5Bi in pyridine produced two different types of crystalline adducts. At -5°C , the complex $\text{Ph}_5\text{Bi} \cdot \text{C}_5\text{H}_5\text{N}$ was obtained; lower temperatures gave the adduct $\text{Ph}_5\text{Bi} \cdot 3\text{C}_5\text{H}_5\text{N}$. The crystal structure of the 1:1 adduct was determined by X-ray diffraction. The Bi–N bond was quite long (321 pm), so the contact was considered to be electrostatic. The orientation of the six rings surrounding the Bi atom was similar to that found in the $[\text{Ph}_6\text{Bi}]^-$ anion. In the adduct $\text{Ph}_5\text{Bi} \cdot 3\text{C}_5\text{H}_5\text{N}$, two of the pyridine molecules were noncoordinating. The remaining pyridine molecule was coordinated to the Bi atom by a bond somewhat shorter than in the first adduct. The $\text{Ph}_5\text{Bi} \cdot \text{C}_5\text{H}_5\text{N}$ adduct was disordered, with the molecule having six different orientations with respect to the Bi...N contact. The authors pointed out that the blue color of Ph_5Bi persisted in the solvated complexes $\text{Ph}_5\text{Bi}(\text{THF})$, $\text{Ph}_5\text{Bi} \cdot \text{C}_5\text{H}_5\text{N}$, and $\text{Ph}_5\text{Bi} \cdot 3\text{C}_5\text{H}_5\text{N}$, which indicated that the MO scheme, previously suggested to account for the color of the penta-arylbismuth compounds, remained qualitatively the same in the solvated complexes.

In a paper largely devoted to tetraalkyl- and tetra-arylantimony compounds, MO calculations on the unknown compound Me_5Bi suggested that the trigonal-bipyramidal structure of this compound would be more stable than the square-pyramidal structure [56].

References

- [1] D.A. Armitage, *Ann. Rep. Prog. Chem., Sect. A: Inorg. Chem.*, 88 (1993) 49; 89 (1993) 53.
- [2] J.L. Wardell, *Organomet. Chem.*, 22 (1993) 138; *Chem. Abstr.*, 120 (1994) 54568f.
- [3] Y. Yamamoto, *Kagaku (Kyoto)*, 48 (1993) 496; *Chem. Abstr.*, 119 (1993) 160335s.
- [4] S.R. Breeze and S. Wang, *Angew. Chem., Int. Ed. Engl.*, 32 (1993) 589.
- [5] W. Clegg, R.J. Errington, G.A. Fisher, D.C.R. Hockless, N.C. Norman, A.G. Orpen and S.E. Stratford, *J. Chem. Soc., Dalton Trans.* (1992) 1967.
- [6] W. Clegg, R.J. Errington, G.A. Fisher, R.J. Flynn and N.C. Norman, *J. Chem. Soc., Dalton Trans.* (1993) 637.
- [7] M. Shieh, Y. Liou, S.-M. Peng and G.-H. Lee, *Inorg. Chem.*, 32 (1993) 2212.
- [8] M. Shieh, Y. Liou, B.-W. Jeng, *Organometallics*, 12 (1993) 4926.
- [9] L.L. Lohr and A.J. Ashe III, *Organometallics*, 12 (1993) 343.
- [10] C.J. Carmalt, N.C. Norman, A.G. Orpen and S.E. Stratford, *J. Organomet. Chem.*, 460 (1993) C22.
- [11] H. Suzuki and T. Murafuji, *J. Chem. Soc., Chem. Commun.* (1992) 1143.
- [12] H. Suzuki, T. Murafuji and N. Azuma, *J. Chem. Soc., Perkin Trans. 1* (1993) 1169.
- [13] H. Suzuki, T. Ikegami, Y. Matano and N. Azuma, *J. Chem. Soc., Perkin Trans. 1* (1993) 2411.

- [14] H. Suzuki, T. Murafuji, Y. Matano and N. Azuma, *J. Chem. Soc., Perkin Trans. 1* (1993) 2969.
- [15] A.J. Ashe III, J.W. Kampf and D.B. Puranik, *J. Organomet. Chem.*, **447** (1993) 197.
- [16] (a) C. Glidewell, *J. Organomet. Chem.*, **461** (1993) 15; (b) G.O. Doak and L.D. Freedman, *J. Organomet. Chem.*, in press.
- [17] R. Shukla and P.K. Bharadwaj, *Polyhedron*, **12** (1993) 1079.
- [18] C.M. Jones, M.D. Burkart, R.E. Bachman, D.L. Serra, S.-J. Hwu and K.H. Whitmire, *Inorg. Chem.*, **32** (1993) 5136.
- [19] T. Ogawa, T. Hikasa, T. Ikegami, N. Ono and H. Suzuki, *Chem. Lett.* (1993) 815.
- [20] G.K. Fukin, A.P. Pisarevskii, A.I. Yanovskii and Yu. T. Struchkov, *Zh. Neorg. Khim.*, **38** (1993) 1205.
- [21] A.P. Pisarevskii, L.I. Martynenko and N.G. Dzyubenko, *Zh. Neorg. Khim.*, **37** (1992) 72.
- [22] D.A. Brown, N.J. Fitzpatrick, W.K. Glass, H.A. Ahmed, D. Cunningham and P. McArdle, *J. Organomet. Chem.*, **455** (1993) 157.
- [23] R.E.v.H. Spence, S.L. Buchwald and J.F. Richardson, *Acta Chem. Scand.*, **47** (1993) 326.
- [24] I. Suzuki and Y. Yamamoto, *J. Org. Chem.*, **58** (1993) 4783.
- [25] S. Yasuike, H. Ohta, S. Shiratori, J. Kurita and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.* (1993) 1817.
- [26] J. Kurita, M. Ishii, S. Yasuike and T. Tsuchiya, *J. Chem. Soc., Chem. Commun.* (1993) 1309.
- [27] D.J. Benard, *J. Appl. Phys.*, **74** (1993) 2900.
- [28] A.S. Nikishin, A.N. Moiseev and V.N. Votintsev, *Vysokochist. Veshchestva* (1992) 133; *Chem. Abstr.*, **119** (1993) 139400z.
- [29] F. Ignatious, Y. Delaviz, I. Cabasso and J. Smid, *Makromol. Chem., Macromol. Symp.*, **60** (1992) 247; *Chem. Abstr.*, **118** (1993) 125154q.
- [30] J. Smid, Y. Delaviz and I. Cabasso, US Patent 5 256 334; *Chem. Abstr.*, **120** (1994) 38216j.
- [31] S. Masuoka, M. Ito and Y. Pponda, Jpn. Kokai Tokkyo Koho JP 05 112,739 [93 112,739]; *Chem. Abstr.*, **119** (1993) 162559s.
- [32] T. Sato, Jpn. Kokai Tokkyo Koho JP 05 170, 597 [93 170, 597]; *Chem. Abstr.*, **119** (1993) 215706w.
- [33] H. Noshiro and N. Ootani, Jpn. Kokai Tokkyo Koho JP 04 285, 002 [92 285,002]; *Chem. Abstr.*, **118** (1993) 113816u.
- [34] S. Hasei, H. Kurosawa, T. Hirai and H. Yamane, Jpn. Kokai Tokkyo Koho JP 05 58,640 [93 58,640]; *Chem. Abstr.*, **119** (1993) 39021h.
- [35] S. Hayashida, T. Nakai, I. Kobayashi, Y. Sugimori, T. Tsuyama and S. Koshihara, *Adv. Supercond. III, Proc. 3rd Int. Symp. Supercond.* (1991) 1101; *Chem. Abstr.*, **118** (1993) 136509k.
- [36] J. Ishiai, S. Yamada and S. Yoshizawa, *4th Adv. Supercond. IV, Proc. Int. Symp. Supercond.* (1992) 829; *Chem. Abstr.*, **118** (1993) 224212p.
- [37] S. Akase, J. Tazaki, Y. Ino and R. Sakamoto, Jpn. Kokai Tokkyo Koho JP 05 271,940 [93 271,940]; *Chem. Abstr.*, **120** (1994) 149715r.
- [38] H. Wang, L.W. Fu and S.X. Shang, *J. Appl. Phys.*, **73** (1993) 7963.
- [39] H. Wang, L.W. Fu, S.X. Shang, S.Q. Yu, X.L. Wang, Z.K. Lu and M.H. Jiang, *Mater. Res. Soc. Symp. Proc.*, **243** (1992) 213; *Chem. Abstr.*, **119** (1993) 83833y.
- [40] J. Si and S.B. Desu, *J. Appl. Phys.*, **73** (1993) 7910.
- [41] K.T. Huang, C.T. Chiu, R.M. Cohen and G.B. Stringfellow, *J. Cryst. Growth*, **134** (1993) 29.
- [42] W. Frank, J. Schneider and S. Müller-Becker, *J. Chem. Soc., Chem. Commun.* (1993) 799.
- [43] S. Müller-Becker, W. Frank and J. Schneider, *Z. Anorg. Allg. Chem.*, **619** (1993) 1073.
- [44] S.V. Pasenok, N.V. Kirij, Y.L. Yagupolskii, D. Naumann and W. Tyrre, *J. Fluorine Chem.*, **63** (1993) 179.
- [45] H. Suzuki, C. Nakaya and Y. Matano, *Tetrahedron Lett.*, **34** (1993) 1055.
- [46] M. Ali and W.R. McWhinnie, *Appl. Organomet. Chem.*, **7** (1993) 137; *Chem. Abstr.*, **119** (1993) 74638m.
- [47] V.A. Dodonov and T.I. Zinovyeva, *Metaloorg. Khim.*, **5** (1992) 1265; *Chem. Abstr.*, **120** (1994) 30841p.
- [48] V.A. Dodonov and T.I. Zinovyeva, *Metaloorg. Khim.*, **6** (1993) 375; *Chem. Abstr.*, **120** (1994) 133804h.
- [49] P.J. Sinclair, M.J. Wyvratt, M. Goulet and H.M. Organ, PCT Int. Appl. WO 92 20,688; *Chem. Abstr.*, **119** (1993) 27929x.
- [50] M. Goulet, M.J. Wyvratt, P.J. Sinclair and F. Wong, Eur. Pat. Appl. EP 515 071; *Chem. Abstr.*, **118** (1993) 168893x.
- [51] X. Chen, K. Ohdoi, Y. Yamamoto and K. Akiba, *Organometallics*, **12** (1993) 1857.
- [52] Y. Yamamoto, K. Ohdoi, X. Chen, M. Kitano and K. Akiba, *Organometallics*, **12** (1993) 3297.
- [53] Y. Matano, N. Azuma and H. Suzuki, *Tetrahedron Lett.*, **34** (1993) 8457.
- [54] S. Wallenhauer, D. Leopold and K. Seppelt, *Inorg. Chem.*, **32** (1993) 3948.
- [55] D. Hellwinkel and G. Kiltbau, *Liebigs Ann. Chem.*, **705** (1967) 66.
- [56] A. Haaland, A. Hammel, K. Rypdal, O. Swang, J. Brunvoll, O. Gropen, M. Greune and J. Weidlein, *Acta Chem. Scand.*, **47** (1993) 368.