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Annual review

Bismuth
Annual review covering the year 1991

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Other than our annual survey covering the year 1989, no review dealing exclusively with bismuth was published in 1991. An excellent review of the preparation of tertiary phosphines, arsines, stibines, and bismuthines by the cleavage of compounds of the type R_3E or R_2ER' (where R and R′ were alkyl or aryl groups, and E = P, As, Sb, Bi) by an alkali metal in liquid ammonia, to give pnictides R_2EM or $RR'EM$ (where M = Li, Na, K), followed by reaction with an organic halide $R'X$ to give unsymmetrical tertiary phosphines, arsines, stibines, or bismuthines, was published [1]:

$$R_3E + 2M + NH_3 \longrightarrow R_2EM + MNH_2 + RH$$

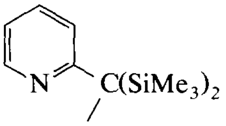
$$R_2EM + R'X \longrightarrow R_2ER' + MX$$

These reactions were termed the method of Müller, Hewertson, and Watson by the author of this review. Although all three carbon–bismuth bonds of triphenylbismuthine are cleaved by sodium metal in liquid ammonia, it is possible to prepare the bismuthide Ph_2BiNa under certain conditions. The dialkylbismuthides are readily prepared from tertiary bismuthines by alkali metal cleavage in liquid ammonia. From the bismuthides unsymmetrical tertiary bismuthines and/or dibismuthines were prepared:

$$2\ R_2BiM + XCH_2CH_2X \longrightarrow R_2BiBiR_2 + CH_2{=}CH_2 + 2\ MX$$

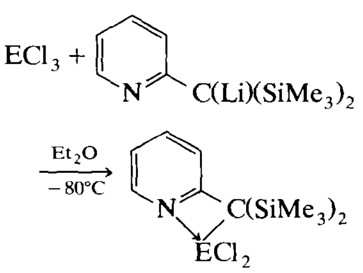
Organobismuth compounds were briefly mentioned in two volumes of the *Annual Reports on the Progress of Chemistry*, published by the Royal Society of Chemistry [2,3]. The use of tetraphenyldibismuthine for the preparation of compounds of the type Ph_2BiEPh (where E = Se, Te) was discussed in a volume devoted to mechanisms of inorganic and organometallic reactions [4]. A discussion of the preparation of organometallic compounds of the main group elements in a new text entitled *Organometallic Chemistry* included examples of the preparation of organobismuth compounds [5]. Wardell briefly reviewed organobismuth compounds described in the 1990 chemical literature [6]. The thermochemistry of several organic compounds of bismuth was briefly mentioned in two articles dealing with the energetics of organometallic species [7,8].

In continuation of studies of the main group chemistry of the highly hindered ligand **I**, Jones et al. [9] synthesized arsenic, antimony, and bismuth compounds containing this ligand.



I

Thus, the corresponding chlorides ECl_3 were treated with the lithium derivative of **I** to yield the compounds **II**:



II

(where E = As, Sb, Bi).

The bismuth compound was obtained as yellow prisms (after recrystallization from toluene) in 44% yield. It was characterized by ^{13}C and ^{1}H NMR and mass spectrometry, and by elemental analyses (results not reported). The molecular structure of the antimony

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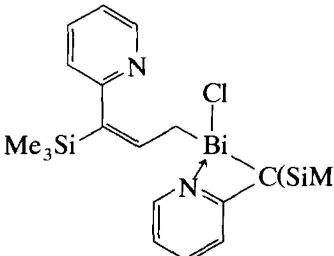
compound was reported to be distorted trigonal-bipyramidal with the carbon atom, one chlorine atom, and the antimony lone pair forming the equatorial plane. The bismuth compound was said to have a similar structure, but no structural data were reported.

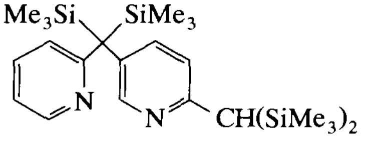
Although the reaction of 2 mol equiv. lithium derivative of I with $AsCl_3$ or $SbCl_3$ yielded intractable oils, a red crystalline solid was obtained from $BiCl_3$ at temperatures below 0°C. Above 0°C this solid decomposed to give orange crystals of compound III, which was shown by X-ray diffraction to have the following structure:



III

The two N-Bi distances in III were 2.95 and 2.485 Å. That one Bi-N bond was so much longer than the other Bi-N bond was unexpected, and was explained as a result of geometrical constraints of the pyridyl group and of the allyl plane of the potentially bidentate ligand.

When $BiCl_3$ was treated with 3 mol equiv. lithium derivative of I, a black solid of unknown composition and the bismuth-free compound IV were obtained.



IV

Compound IV was characterized by ^1H and ^{13}C NMR spectroscopy and by X-ray diffraction.

In a paper in a series devoted to the reactivity of molecules containing element–element bonds, Calderazzo et al. [10] studied exchange reactions of transition metal compounds containing element–element bonds such as Mn–Mn, Re–Re, Mo–Mo, and W–W. In such systems as $Mn_2(CO)_{10} + Re_2(CO)_{10} \rightleftharpoons 2MnRe(CO)_{10}$ and $Mo_2(C_5H_5)_2(CO)_6 + W_2(C_5H_5)_2(CO)_6 \rightleftharpoons 2\ MoW(C_5H_5)_2(CO)_6$ (where C_5H_5 was cyclopentadienyl), the reactions were found to reach an equilibrium value close to the statistical distribution. By contrast, when the same compounds were allowed to react with compounds containing element–element bonds of the main group elements As, Sb, or Bi, the exchange reactions went to completion. Thus, $(Ph_2Bi)_2$ reacted with $Cr_2(C_5H_5)_2(CO)_6$ in toluene solution at room temperature to give $Cr(C_5H_5)(BiPh_2)(CO)_3$ in 68% yield. The compound was characterized by elemental analysis and IR spectroscopy. The two compounds $M(C_5H_5)(BiPh_2)(CO)_3$ were prepared by two different methods:

$$K[M(C_5H_5)(CO)_3] + Ph_2BiCl \longrightarrow M(C_5H_5)(Ph_2Bi)(CO)_3 + KCl$$

$$M_2(C_5H_5)_2(CO)_6 + (Ph_2Bi)_2 \xrightarrow[\text{daylight}]{20^\circ C} 2\ M(C_5H_5)(Ph_2Bi)(CO)_3$$

(where M = Mo, W).

The second type of reaction did not take place in the dark. The compounds were characterized by elemental analyses, IR, and ^{13}C NMR spectroscopy. When the above molybdenum compound in toluene was treated with triphenylphosphine at room temperature for about 40 h with the rigid exclusion of light, the complex $Mo(C_5H_5)(Ph_2Bi)(CO)_2Ph_3P$ was obtained. The corresponding tungsten compound was prepared in a somewhat similar manner, but its preparation required irradiation with a mercury vapor lamp for 24 h. No exchange occurred between $Cr(C_5H_5)(Ph_2Bi)(CO)_3$ and triphenylphosphine, even when the mixture was irradiated with a mercury vapor lamp; only decomposition took place. The Bi–Cr or Bi–W bonds were cleaved by reaction of the chromium or tungsten complexes in toluene solution with iodine at room temperature:

$$M(C_5H_5)(Ph_2Bi)(CO)_3 + I_2 \xrightarrow{MePh} M(C_5H_5)I(CO)_3 + Ph_2BiI$$

Finally, the reaction between $Mn_2(CO)_{10}$ and $(Ph_2Bi)_2$ in toluene solution was investigated. No reaction occurred at room temperature. Irradiation with filtered visible light ($\lambda_{max} = 400$ nm) led to the formation of $Mn(CO)_5(Ph_2Bi)$ in 40% yield.

The authors discussed the reactions described in this paper in considerable detail and drew several conclusions. One major conclusion was that the ease of reaction was inversely proportional to the strengths of both the M–M (Cr, Mo, W, or Mn) and the E–E (Bi, Sb, or As) bonds. Thus, the Cr–Cr and Bi–Bi bonds were most easily cleaved. They mentioned that no oxidative addition across the Cr–Cr bond occurred with $(Ph_2P)_2$.

In a later paper dealing with the reactivity of compounds with element–element bonds, Calderazzo et al. [11] studied exchange reactions of organobismuth(III) and organoantimony(III) compounds, and the reduction of halobismuthines and halostibines by $Co(C_5H_5)_2$ or $Co(C_5Me_5)_2$. A solution of BiI_3 and Ph_3Bi (mol ratio 1 : 2) was sealed in an NMR tube under argon and the ^{13}C NMR spectrum was determined after several days. Resonances owing to Ph_3Bi, Ph_2BiI, and minor amounts of $PhBiI_2$ were found. In a second experiment

$(Ph_2Bi)_2$ and I_2 (mol ratio 1:1) were sealed together and kept at −30°C for 11 days. The ^{13}C NMR spectrum again showed a mixture of Ph_3Bi and Ph_2BiI, with minor amounts of $PhBiI_2$. A solution of Ph_3Bi and I_2 (mol ratio 1:1) sealed at room temperature for 4 days gave a very similar ^{13}C NMR spectrum. The solvent used in all of the above experiments was THF/1,4-dioxane-d_8.

The preparation of $(Ph_2Bi)_2$ was carried out by three different methods. A solution of Ph_3Bi (2 mol equiv.) in THF was added to a solution of BiI_3 (1 mol equiv.) and after 6 h at room temperature, the mixture was cooled to 0°C and a solution of $(C_5H_5)_2Co$ added dropwise. From this reaction $(Ph_2Bi)_2$ was obtained in 52% yield; a 96% yield of $(C_5H_5)_2CoI$ was also obtained. In a similar manner, the products from the reaction of Ph_3Bi and I_2 were reduced at −20°C with $(C_5H_5)_2Co$, to yield $(Ph_2Bi)_2$ in 43% yield. In a third experiment, Ph_2BiCl was reduced in THF by $(C_5Me_5)_2Co$ at −40°C to yield $(Ph_2Bi)_2$ in 76% yield. If, instead of $(C_5Me_5)_2Co$, $(C_5H_5)_2Co$ was used as the reducing agent, the principal product obtained was not $(Ph_2Bi)_2$ but $[Co(C_5H_5)_2][Ph_2BiCl_2]$:

$$(C_5H_5)_2Co + 2Ph_2BiCl \longrightarrow [(C_5H_5)_2Co][Ph_2BiCl_2] + \tfrac{1}{2}(Ph_2Bi)_2$$

The yield of the cobalt–bismuth complex was 77% according to the above stoichiometry. The compound was characterized by IR spectroscopy and elemental analyses. The two compounds $[(4\text{-}MeC_6H_4)_2Bi]_2$ and $(Me_2Bi)_2$ were obtained by the reduction of the corresponding bromobismuthines by $(C_5H_5)_2Co$. The tolyl compound, synthesized in 50% yield, was characterized by PMR and elemental analyses. The $(Me_2Bi)_2$ was obtained as an unstable yellow solid with a half-life at room temperature of about 20 min. It was characterized by its PMR spectrum. In addition to the bismuth compounds described above, a number of antimony compounds were prepared which are described in Ref. [12].

Cassidy and Whitmire [13] described the preparation of three new organobismuth compounds containing Bi–Fe bonds, and one new compound containing a Bi–Mn bond. The first compound $[Ph_2BiFe(CO)_4]PPN$ [where PPN was the bis(triphenylphosphine)nitrogen cation] was prepared according to the following equations:

$$Ph_2BiCl + Na_2Fe(CO)_4 \xrightarrow{THF} [Ph_2BiFe(CO)_4]Na + NaCl$$

$$[Ph_2BiFe(CO)_4]Na + [PPN]Cl \longrightarrow [Ph_2BiFe(CO)_4]PPN + NaCl$$

In the first reaction, 1 mol equiv. of each reactant was used. If, instead of adding [PPN]Cl 1 mol equiv. of Ph_2BiCl was added to the solution of $Na[Ph_2BiFe(CO)_4]$ and the mixture stirred for 15 minutes at 0°C, the product obtained in 29% yield was *cis*-$(Ph_2Bi)_2Fe(CO)_4$. The same product was obtained in larger yield (72%) when a mixture of Ph_2BiCl (1.15 mmol) and $Na_2Fe(CO)_4$ (0.584 mmol) in THF was stirred at 0°C for 40 min. This compound was unstable and was slowly converted in solution to $[PhBiFe(CO)_4]_2$. This latter compound was readily prepared from Ph_2BiCl and $Na_2Fe(CO)_4$ 3/2 dioxane in 50% yield when the reactants were stirred together in THF solution for several hours. In yet another synthetic procedure Ph_2BiNa (obtained from Ph_2BiCl and Na in liquid NH_3) was treated with excess $Fe(CO)_5$ to yield a mixture of *cis*-$(Ph_2Bi)_2Fe(CO)_4$ and $[PhBiFe(CO)_4]_2$. The products were readily separated by their differential solubility in CH_2Cl_2. Some $(Ph_2Bi)_2$ was also formed by this procedure. The manganese compound $Ph_2BiMn(CO)_5$ was prepared in 33% yield from $Na[Mn(CO)_5]$ (obtained by reduction of $Mn_2(CO)_{10}$ with sodium amalgam) and Ph_2BiI or Ph_2BiCl in THF. All of the new compounds were characterized by IR and PMR spectroscopy and (except for the manganese compound) by elemental analyses. The mass spectrum of the manganese compound was also reported.

The crystal and molecular structure of all four new compounds was determined by X-ray diffraction. The iron atom in the anion $[Ph_2BiFe(CO)_4]^-$ was trigonal–bipyramidal with the Ph_2Bi group in axial position. The bismuth atoms were pyramidal with the lone pair stereochemically active. The Fe–Bi–C angles were 104.0° and 101.6°. The iron atom in $(Ph_2Bi)_2Fe(CO)_4$ was pseudooctahedral with two Ph_2Bi groups in *cis*-positions. The compound $[PhBiFe(CO)_4]_2$ contained a planar Bi–Fe–Bi–Fe ring. The phenyl groups were *trans* to each other across the ring. The iron atom was pseudooctahedral with the PhBi group in *cis*-positions. The Mn atom in $Ph_2BiMn(CO)_5$ was octahedral, and the bismuth atom was pyramidal.

The preparation of tris[tris(2,4,6-trifluoromethyl)phenyl]bismuthine and chlorobis[tris(2,4,6-trifluoromethyl)phenyl]bismuthine has been described [14]. They were prepared from the corresponding lithium compound by two different methods which differed in the ratio of lithium compound to $BiCl_3$ (3:1 and 2:1) and in whether the $BiCl_3$ (in Et_2O solution) was added to the lithium compound, or the addition was in the reverse order. By either procedure the two compounds $[2,4,6\text{-}(CF_3)_3C_6H_2]_3Bi$ and $[2,4,6\text{-}(CF_3)_3C_6H_2]_2BiCl$ were obtained in about 30% and 10% yields, respectively. They were separated by means of their differential solubility in Et_2O. Both compounds were characterized by elemental analyses, ^1H and ^{19}F NMR, and mass spectrometry and, for the tertiary bismuthine, by its IR spectrum. The ^{19}F spectrum of the tertiary bismuthine gave two singlets in a ratio of 2:1 at RT but gave three singlets in a 1 : 1 : 1 ratio at −90°C. No further splitting of the inequivalent *ortho* groups was observed at the lowest temperature examined. The coalescence temperature was about −55°C which led to a calculated barrier to rotation around the Bi–C bond of 9.2 kcal mol^{-1}. The tertiary bismuthine was unstable in the air at RT. The ^{19}F spectrum, taken shortly after dissolving in benzene-d_6, showed significant amounts of 1,3,5-tris(trifluoromethyl)benzene. After standing for several days in a sealed vial, 2,4,6-tris(trifluoromethyl)phenol was detected and after several months crystals of bis[1,3,5-tris(trifluoromethyl)-phenyl] ether (identified by mass spectroscopy) were found. When the tertiary bismuthine (0.023 mmol) and $BiCl_3$ (0.634 mmol) were allowed to stand in THF solution in a sealed NMR tube at RT for 3 days, ^{19}F signals assignable to chlorobis[tris(2,4,6-trifluoromethyl)phenyl]bismuthine (in addition to those for the starting tertiary bismuthine) were found. An additional very small signal might have been a result of the presence of dichloro-2,4,6-tris(trifluoromethyl)phenylbismuthine. The crystal structures of the two bismuth compounds were determined by X-ray diffraction. Both compounds were pyramidal with no short intermolecular distances. The Bi–C bond distances in the tertiary bismuthine were slightly longer than those found in a number of other compounds containing this bond (e.g. $BiMe_3$, $BiPh_3$, and $Ph_2BiBiPh_2$). The sum of the angles around bismuth (317.9°) was also somewhat greater that those found for other bismuth compounds (e.g. 290.1° for $BiMe_3$ and 282° for $BiPh_3$). The sum of the angles in the chlorobismuthine were somewhat less (294.2°), and the B–C bond distances were shorter than in the tertiary bismuthine.

In a paper devoted largely to a study of the reactions of hypervalent iodine compounds with organometallic compounds containing CF_3 groups, the reactions of $(CF_3)_3Bi$ with ICl_3, $I(O_2CCF_3)_3$, and CF_3ICl_2 were reported [15]. Among the reaction products detected in the reaction of $(CF_3)_3Bi$ with ICl_3 (in pyridine or acetonitrile) were $(CF_3)_2BiCl$ and CF_3BiCl_2. Similarly, $(CF_3)_3Bi$ and $I(O_2CCF_3)_3$ gave $(CF_3)_2Bi(O_2CCF_3)$ and $CF_3Bi(O_2CCF_3)_2$. The principal iodine compound from ICl_3 was CF_3ICl_2, and from $I(O_2CCF_3)_3$ was CF_3-$I(O_2CCF_3)_2$. Bismuth-containing products from the reaction of $(CF_3)_3Bi$ with CF_3ICl_2 were $(CF_3)_2$ and CF_3BiCl_2, and the principal iodine-containing product was CF_3I.

A number of compounds of the type $[C_5H_5Fe(CO)_2$-$ER_3]BF_4$ (where E = P, As, Sb, Bi; and R = Me, Et, Me_2CH, Ph) were prepared and extensively studied by Schumann and Eguren [16]. One compound containing an amine ligand, $[C_5H_5Fe(CO)_2NMe_3]BF_4$, was also prepared. All attempts to prepare the compound $[C_5H_5Fe(CO)_2BiEt_3]BF_4$ were unsuccessful. However, the compounds containing the ligands Me_3Bi, $(Me_2CH)_3Bi$, or Ph_3Bi were all readily obtained. Two methods of synthesis were employed. One method involved the oxidative cleavage of the Fe–Fe bond in $[C_5H_5Fe(CO)_2]_2$ by the ferricinium ion in the presence of the Group 15 ligand:

$$[C_5H_5Fe(CO)_2]_2 + 2[(C_5H_5)_2Fe]BF_4 + R_3E \xrightarrow{CH_2Cl_2} [C_5H_5Fe(CO)_2ER_3]BF_4 + 2\,(C_5H_5)_2Fe$$

This method was only applicable to the preparation of compounds where ER_3 was PR_3, AsR_3, or $SbPh_3$. The other method involved the displacement of THF by the Group 15 donor ligand:

$$[C_5H_5Fe(CO)_2THF]BF_4 + R_3E \xrightarrow[RT]{CH_2Cl_2} [C_5H_5Fe(CO)_2ER_3]BF_4 + THF$$

All bismuth compounds and those where E = As, Sb and R = Me, Me_2CH were prepared by this method. All compounds, after recrystallization from CH_2Cl_2/Et_2O, were pale yellow crystals, and, except for the bismuth compounds, were air stable. The alkyl compounds, however, lost the R_3E ligand in donor solvents such as acetone or acetonitrile. All of the new compounds were characterized by ^1H and ^{13}C NMR and IR spectroscopy, and with those compounds where E was P, by ^{31}P NMR spectroscopy. The FAB(+) mass spectrum of the compound where ER_3 was $BiMe_3$ was also reported. The crystal structure of the cation $[C_5H_5Fe(CO)_2BiPh_3]^+$, determined by X-ray diffraction, was reported. Some bond angles and bond distances were listed. The Fe–Bi bond distance was only slightly longer than the sum of the covalent radii; this result would be expected for a bond involving principally σ-bonding. The structure of the compound consisted of discrete cations $[C_5H_5Fe(CO)_2BiPh_3]^+$ and anions BF_4^-, with no interaction between them. With the determination of the structure of this bismuth compound, it was possible to compare the bond distances and bond angles in all of the cations $[C_5H_5Fe$-$(CO)_2EPh_3]^+$, where E = P, As, Sb, Bi. The Fe–E bond lengths were found to increase from 2.204 Å (E = P) to 2.570 Å (E = Bi). This result was in accord with bonds involving principally σ-bonding.

The donor properties of the ligands ER_3 and the bond strengths of Fe–E bonds were investigated by several different methods. A comparison of the ν(CO) IR frequencies for the compounds reported herein showed no general trend. However, a comparison of the $^{13}C(CO)$ NMR shifts was more definitive. The authors listed in tabular form $\Delta\delta^{13}C(CO)$ values, where $\Delta\delta^{13}C(CO)$ was defined as $\delta^{13}C(CO)[C_5H_5Fe(CO)_2$-$ER_3]^+ - \delta^{13}C(CO)[C_5H_5Fe(CO)_3]^+$ (where E = N, P, As, Sb, Bi and R = Me, except for the case where E = N, Ph). On the basis of the results listed it was concluded that the donor properties of the coordinated

EPh_3 ligands decreased in the order P > As > Sb > Bi. The authors stated that this result could be explained by either a decreasing or increasing Fe–E bond strength.

A comparison of bond strengths was investigated by ligand substitution reactions. One mol equiv. PMe_3 displaced all other EMe_3 ligands from the cation $[C_5H_5Fe(CO)_2EMe_3]^+$; whereas $AsMe_3$ and $SbMe_3$ displaced only NMe_3 and $BiMe_3$. The addition of $AsMe_3$ to the $SbMe_3$ complex resulted in an equilibrium mixture of the two complexes with the $AsMe_3$ complex predominant. One mol equiv. PPh_3 also displaced all other EPh_3 ligands, but more slowly than the PMe_3 displacement reactions. However, under the conditions used (CD_2Cl_2, RT, 12–24 h), no other EPh_3 ligand displaced any other EPh_3 ligand. The results of these reactions were consistent with a fall in bond strength of the Fe–E bond in the order P > As > Sb > N > Bi.

Schumann et al. [17] prepared a number of molybdenum complexes of the type $[C_5H_5Mo(CO)_2L_2]BF_4$ (where L is a Group 15 donor ligand). In the majority of the compounds prepared L was a tertiary phosphine or $P(OMe)_3$, but in three of the compounds L was $AsPh_3$, $SbPh_3$, or $BiPh_3$. These last three compounds, as well as several of the phosphorus compounds, were prepared previously, but the method of synthesis reported in the present paper possessed major advantages over methods employed previously. The method consisted of the photochemically-initiated oxidative fission of the Mo–Mo bond in $[C_5H_5Mo(CO)_3]_2$ by $[(C_5H_5)_2Fe]BF_4$ in the presence of the ligand ER_3. The solvent employed was 1,2-dichloroethane and the yields were > 90%. ^{13}C NMR data for the carbonyl carbon atom, and IR data for the carbonyl group were reported for each compound. ^{95}Mo NMR data were also reported for all but the bismuth-containing compound which was stated to be too unstable and too insoluble to give satisfactory results. When attempts were made to crystallize $[C_5H_5Mo(CO)_2(PPh_3)_2]BF_4$ from CH_2Cl_2-acetone-ether, the resulting crystals were found to have the structure $[C_5H_5Mo(CO)_3PPh_3]BF_4$, as shown by X-ray diffraction. Most of the other compounds prepared in this study underwent a similar decomposition when stirred in acetone or acetonitrile.

The use of samarium compounds in inorganic and organic synthesis has recently been of considerable interest. Evans et al. [18] described the preparation of the compound $[(C_5Me_5)_2Sm]_2$ (μ-$\eta^2:\eta^2$-Bi_2) by the reaction of $(C_5Me_5)_2Sm$ with Ph_3Bi in benzene, toluene, or cyclohexane. The other products of the reaction were biphenyl and $(C_5Me_5)_2SmPh$ [or $(C_5Me_5)_2SmCH_2Ph$ when toluene was the solvent]. The bismuth-containing product was a red–brown crystalline solid, characterized by elemental analysis, PMR, and IR spectroscopy. The molecular and crystal structure was determined by X-ray diffraction. The compound contained a 4-membered ring with Bi–Sm–Bi bonds. The Sm–Bi–Sm angles were 129.6° and 127.6°. The Bi–Bi distance (2.851 Å) was shorter than Bi–Bi single bond distances and compared with compounds thought to contain some multiple bonding. The exact nature of the bonding in the compound was uncertain.

Huang and coworkers have written extensively on the use of elements of Groups 15 and 16 in organic synthesis. They recently showed [19] that triethyl- and tributylstibines were excellent reagents for promoting the reaction between aldehydes and allyl halides to form, after hydrolysis, homoallylic alcohols:

$$\mathrm{RCHO + CH_2{=}CHCH_2X + R'_3Sb} \longrightarrow \mathrm{RCH(OH)CH_2CH{=}CH_2 + \tfrac{1}{2}(R'_3SbX)_2O}$$

(where X = Br, I and R′ = Et, Bu)

Although the yields were excellent with aldehydes, the reaction failed completely with ketones. In a new paper from Huang's laboratory, it has been shown that the use of tributylbismuthine rather than tributylstibine allowed the condensation of both aldehydes and ketones in the above reaction [20]. In addition to the homoallylic alcohols, allylic ethers were also formed:

$$\mathrm{R^1R^2CO + CH_2{=}CHCH_2Br} \xrightarrow[\text{(2) } H_2O]{\text{(1) } Bu_3Bi} \mathrm{R^1R^2C(OH)CH_2CH{=}CH_2}$$
$$+\ \mathrm{R^1R^2C(OCH_2CH{=}CH_2)CH_2CH{=}CH_2}$$

In the above reaction where aldehydes were used, the ratio between the yields of the two products depended on the ratio between the starting aldehyde and allyl bromide. When this ratio was 1 : 1, the principal product was the alcohol, but when ⩾ 2 mol equiv. allyl bromide were used, the principal product was the ether. By contrast, when ketones were employed, the alcohol was always the principal product regardless of the ratio between the ketone and allyl bromide. The following aldehydes, RCHO (where R = Ph, 4-ClC_6H_4, 4-$O_2NC_6H_4$) furfural, nonanal, or cinnamaldehyde were used in the above reaction. The ketones used were 4-$O_2NC_6H_4COMe$, acetophenone, cyclopentanone, or cyclohexanone. The products were characterized by PMR, IR, and mass spectroscopy, and by elemental analyses. The reactions were carried out either without a solvent or in a solvent such as THF or hexane, and the total yields of products generally exceeded 90%. The two products formed in each reaction were readily separated by flash column chromatography.

Naumann and coworkers introduced the use of bis(perfluoroorgano)cadmium compounds for the preparation of a variety of perfluoroorgano organometallic compounds, including bismuth compounds of the type $(C_nF_{2n+1})_3Bi$ (where n = 1, 2, 3, 4, 6, 8). These bismuth compounds were found to be excellent perfluoroalkyl transfer reagents. They have now used the cadmium compound $Cd(CF_3)_2 \cdot 2MeCN$ to prepare two new bismuth compounds, $PhBi(CF_3)_2$ and Ph_2BiCF_3 [21]:

$$PhBiBr_2 + Cd(CF_3)_2 \cdot 2MeCN \xrightarrow[RT,\ 14\ d]{MeCN} PhBi(CF_3)_2 + CdBr_2 \cdot 2MeCN$$

$$2Ph_2BiCl + Cd(CF_3)_2 \cdot 2MeCN \xrightarrow[RT,\ 14\ d]{MeCN} 2Ph_2BiCF_3 + CdCl_2 \cdot 2MeCN$$

Both new compounds were oily liquids with penetrating odors which rapidly decomposed on exposure to the air. The compound Ph_2BiCF_3 was obtained in pure form in 58% yield, but $PhBi(CF_3)_2$ dismutated in MeCN during several days to give Ph_2BiCF_3, $Bi(CF_3)_3$, and Ph_3Bi, and the pure compound could not be isolated. The compound Ph_2BiCF_3 also dismutated but more slowly:

$$2Ph_2BiCF_3 \overset{MeCN}{\rightleftharpoons} PhBi(CF_3)_2 + Ph_3Bi$$

When Ph_2BiCF_3 was brominated at low temperature the principal products isolated were $CBrF_3$, PhBr, and $BiBr_3$. The ^{19}F NMR spectrum of the reaction mixture at −30°C gave a broad singlet at $\delta - 42.5$ ppm, which the authors said could be a result of the presence of $Ph_2Bi(CF_3)Br_2$. This signal disappeared when the temperature was raised. The new compounds were characterized by ^{19}F NMR and by mass spectra. It was found that Ph_2BiCF_3 reacted more rapidly than $Bi(CF_3)_3$ with ICl and with $AgNO_3$ to give CF_3I and $Ag[Ag(CF_3)_4]$, respectively.

In a paper devoted to cationic complexes of rhodium(I), the complex $[Rh(COT)(QNO)(Ph_3Bi)]ClO_4$ (where COT = 1,3,5,7-cyclooctatetraene and QNO = quinoline *N*-oxide) was prepared [22]. Triphenylbismuthine (0.1 mmol) was added to an acetone or dichloromethane solution of 0.1 mmol of $[Rh(COT)(QNO)_2]ClO_4$ to yield the triphenylbismuthine complex in 48% yield. It was characterized by elemental analysis and IR spectroscopy. It was stated that this is the first complex containing an Rh–Bi bond. The ν(N–O) bands in the complex occurred at 1231 and 1212 cm^{-1}, somewhat lower than the same bands in uncoordinated quinoline *N*-oxide (1240 and 1220 cm^{-1}). Bands at 625 and 1095 cm^{-1} were attributed to the uncoordinated ClO_4 anion.

Zinc telluride has proved to be a promising semiconductor for a variety of optoelectronic devices. Kuhn et al. [23] reported growing zinc telluride on GaAs, GaSb, and ZnTe substrates and doping the zinc telluride with As, Bi, Ga, In, or I derived from alkyl derivatives of these elements. For this purpose the ZnTe was grown on GaAs as the substrate at 350°C by means of atmospheric MOVPE. The samples were characterized by photoluminescence at 2 K and the Hall effect. The doping experiments were performed with diethylzinc as the zinc precursor and diisopropyltelluride as the tellurium precursor. Trimethylbismuthine was used as the source of bismuth. However, at low concentrations this had no influence on the photoluminescence spectrum, and at high concentrations precipitates appeared in the ZnTe layer. Tetraethyldiarsine and ethyl iodide were found to be promising precursors for doping ZnTe at low temperature.

The only previously known tertiary bismuthines containing acetylene groups are of the type $Ar_2BiC{\equiv}CPh$, prepared by Hartmann et al. in 1962 [24]. Rudolph and Wieber [25] prepared bismuthines of two different types, $Ar_2BiC{\equiv}CR$ (where Ar = Ph, $4\text{-}MeC_6H_4$ and R = Me, Me_3C) and $R_2BiC{\equiv}CR'$ (where R = Me and R′ = Ph, Me, Me_3C). The diaryl compounds were low-melting solids, stable in the absence of light and moisture. The dialkyl compounds were liquids, extremely sensitive to light and moisture and stable at RT for only a few hours. Both types of compounds were prepared from diaryl- or dialkylbromobismuthines and the appropriate sodium acetylide in liquid ammonia. All attempts to obtain pure tertiary bismuthines containing two acetylene groups from alkyl- or aryldibromobismuthines and sodium acetylides were unsuccessful. The ^1H and ^{13}C NMR spectra of the mixtures resulting from these reactions indicated that they contained both mono- and disubstitution products presumably produced by disproportionation:

$$2RBi(C{\equiv}CR')_2 \rightleftharpoons R_2Bi(C{\equiv}CR') + (R'C{\equiv}C)_3Bi$$

The new compounds were characterized by elemental analyses and by ^1H and ^{13}C NMR spectroscopy. The authors discussed the NMR results in some detail.

Naphthaleneytterbium was found to react with triphenylbismuthine (or diphenylmercury) in THF to yield $Ph_5Yb_2(THF)_4$ [26].

Benard and Winker [27] reported on a visible wave length chemical laser utilizing the intense blue BiF chemiluminescence. The transient BiF was thermally produced from a mixture of FN_3 and trimethylbismuthine, with SF_6 as a sensitizer using a pulsed CO_2 laser to initiate the pyrolysis of the FN_3. The FN_3 dissociated into FN and N_2, and the reaction of FN with Me_3Bi produced the BiF.

Masuda and coworkers have written a number of papers on the polymerization of substituted acetylenes. A recent paper from the same laboratory concerned the polymerization of pentafluorophenylacetylene and 4-butyl-2,3,5,6-tetrafluorophenylacetylene [28]. A number of catalysts were used for the polymerizations including WCl_6, $MoCl_5$, $NbCl_5$, and $TaCl_5$. Various cocatalysts were also used including triphenylbismuthine. The latter compound was less effective than several other organometallic compounds. The chemical and physical properties of the polymers were described.

Triphenylbismuthine and maleic anhydride in ratios of 1 : 1 to 1 : 1.15 were used as a cure catalyst system to improve the mechanical properties of hydroxy terminated binders for propellants [29].

Triphenylbismuthine (0.02% by weight) was an ingredient in a rocket propellant composition [30]. A Japanese patent described the preparation of metal oxide films from triphenylbismuthine when treated at high oxygen pressures with a glow discharge caused by a high frequency or microwave plasma [31].

Chain decomposition reactions of the two organometallic compounds, tetramethyltin and trimethylbismuthine, to produce fine metal particles with high efficiency were studied by Fujita and Shimo [32]. The decomposition was produced by a single laser irradiation using ArF (193 nm) or KrF (248 nm) excimer laser radiation. The explosive decomposition produced an excited bismuth atom and three methyl radicals. Two types of emission spectra were observed during the decomposition reaction, excited bismuth atomic lines and a broad structureless emission spectrum with a peak around 700 nm which was assigned to black body radiation from the fine metal particles formed during the decomposition.

Hashimoto et al. described the preparation and purification of compounds used for the preparation of Bi–Sr–Ca–Cu–O superconducting films [33]. Triphenylbismuthine was prepared by the Grignard reaction and purified by sublimation at 95°C and a pressure of 20 m Torr. Elemental analyses of the product before and after sublimation showed no change in composition. TG–DTA curves, IR and NMR spectra were also unchanged by sublimation. The UV-visible spectrum of the bismuthine between 200 and 350 nm at concentrations of 7×10^{-2} and 2×10^{-2} mol l^{-1}, showed that it did not obey the Lambert–Beer law, in that maximum absorption shifted to longer wave lengths at the higher concentration.

Among the various metal oxide superconductors that have been intensely investigated in recent years, thin films of Bi–Sr–Ca–Cu–O have been among the most important. The bismuth has usually been obtained by the decomposition of triphenylbismuthine by the MOCVD (metalorganic chemical vapor deposition) method [34–44]. Triethylbismuthine has also been used as a source of metallic bismuth by this procedure [41].

The bismuthine $4\text{-MeC}_6H_4SO_2N{=}BiPh_3$ was described as a moisture-sensitive solid, obtained by the reaction of triphenylbismuthine with chloramine-T in refluxing acetonitrile [45]. Suzuki et al. [46] were unable to obtain this compound as a crystalline solid under the previously described reaction conditions. Their product was either a pale yellow thick oil or a polymeric powder, insoluble in organic solvents. Three other bismuthimines $4\text{-MeC}_6H_4SO_2N{=}BiAr_3$ (where Ar = 4-MeC_6H_4, $2,4,6\text{-Me}_3C_6H_2$, 4-ClC_6H_4) were also prepared by the same procedure. The first two were pale yellow glassy solids, the third product was a yellow oil. All attempts to crystallize any of these compounds were unsuccessful. Only two of the products (where Ar = Ph, 4-MeC_6H_4) gave satisfactory elemental analytical results. The product where Ar = 4-ClC_6H_4 was extremely unstable, but the products where Ar = 4-MeC_6H_4, $2,4,6\text{-Me}_3C_6H_2$ changed from oil to glassy masses on storing in vacuo. Both PMR and IR spectral values were reported for all four bismuthimines.

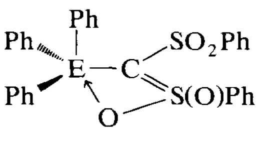
The bismuthimines, when heated with aldehydes in benzene (or in one case, acetonitrile), underwent reactions analogous to the Wittig reaction:

$$4\text{-MeC}_6H_4SO_2N{=}BiAr_3 + 4\text{-RC}_6H_4CHO \longrightarrow 4\text{-MeC}_6H_4SO_2N{=}CHC_6H_4R\text{-}4$$

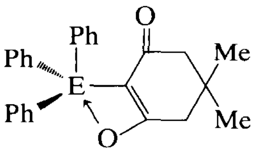
(where Ar = Ph, 4-MeC_6H_4, 4-ClC_6H_4).

The yields in the above reactions were generally small (16% where Ar = 4-ClC_6H_4 and R = H, but 80% where Ar = Ph and R = Me). The bismuthimine, where Ar = Ph, reacted with benzoyl chloride in hot benzene to yield Ph_3BiCl_2 (10%) and $4\text{-MeC}_6H_4SO_2NHCOPh$ (13%). The hydrogen bonded to the nitrogen was presumably supplied by atmospheric moisture. A significant amount of a bismuth-containing polymeric substance was also obtained. The same bismuthimine reacted rapidly at RT with phenylisocyanate to give, after aqueous work-up, two urea derivatives, $4\text{-MeC}_6H_4\text{-}SO_2NHCONHPh$ (45%) and PhNHCONHPh (38%). Copper powder or a copper salt promoted decomposition of the bismuthimines to yield $4\text{-MeC}_6H_4SO_2NH\text{-}Ar$ or $4\text{-MeC}_6H_4SO_2NAr_2$, Ar_3Bi, and 4-MeSO_2NH_2. The bismuthimine $4\text{-MeC}_6H_4SO_2N{=}BiPh_3$, when allowed to stand in the air, decomposed to yield Ph_3Bi, Ph_3BiO, $4\text{-MeC}_6H_4SO_2NH_2$, and a bismuth-containing polymeric powder. The authors suggested that the product first reported as $4\text{-MeC}_6H_4SO_2N{=}BiPh_3$ [45] was actually a mixture of these compounds.

In previous papers by Ferguson, Glidewell, and coworkers on the structures of ylides of Group 15 elements, it was shown that in ylides such as **V** or **VI**, there was considerable interaction between the hetero atom (As or Sb) and one of the sulfonyl or carbonyl oxygen atoms:



V



VI

(where E = As or Sb).

The geometry around the As or Sb atom was intermediate between tetrahedral and trigonal-bipyramidal. Although the bismuth compounds corresponding to **V** and **VI** are known, they are extremely insoluble in most solvents, and crystals suitable for X-ray diffraction studies have not been obtained. Accordingly, Ferguson, Glidewell, and coworkers [47] decided to prepare bis(trifluoroacetato)triphenylantimony and bis(trifluoroacetato)triphenylbismuth and compare their molecular structures. These compounds were obtained from the corresponding dibromides and silver trifluoroacetate and crystals suitable for X-ray examination were obtained by crystallization from petroleum ether. Both compounds consisted of isolated molecules. The geometry around the bismuth atom was that of a distorted trigonal bipyramid with three equatorial phenyl carbon atoms and the bismuth atom essentially planar and two oxygen atoms in axial positions with the O–Bi–O angle 175.1°. However, since one carbon (phenyl) atom, the bismuth atom, and all four oxygen atoms were also essentially planar, the geometry around the bismuth atom could have been considered pentagonal-bipyramidal with two phenyl groups in axial positions. The Bi–O (carbonyl) distances were only about 30% longer than the bonded Bi–O distances, with a ratio between bonded and non-bonded Bi–O distances in each case of 1.29. (If the carboxylate group was completely bidentate this ratio would be 1.0.) This result suggested considerable interaction between the carbonyl oxygen atoms and the bismuth atom.

The geometry around the antimony atom in bis(trifluoroacetato)triphenylantimony was also slightly distorted trigonal-bipyramidal, with the antimony atom and the three carbon (phenyl) atoms essentially planar (the C_3Sb plane). Two of the phenyl groups gave dihedral angles of 40.3° and 43.3° to the C_3Sb plane. (In the bismuth compound two of the phenyl groups were coplanar with the C_3Bi plane, the other phenyl group gave a dihedral angle of 98.5° with the C_3Bi plane.) The principal difference between the two compounds was the increased Sb–O (carbonyl) distances in the antimony compound. These distances were 3.209 and 3.231 Å, considerably longer than the corresponding Bi–O distances, and the ratios Sb–O (carbonyl) to Sb–O (bonded oxygen) were 1.52 and 1.50. These results suggested a very asymmetric bonding of the trifluoroacetato groups with essentially no interaction between the antimony atom and the carbonyl oxygen atoms.

Sharutin and Bychkov [48] showed that vanadocene and cobaltocene reduced dichlorotriphenylbismuth to triphenylbismuthine. The reactions were carried out in sealed ampoules in toluene solution. At RT, vanadocene was oxidized to chlorodicyclopentadienylvanadium, but at 100°C dichlorodicyclopentadienylvanadium was formed. With cobaltocene at 100°C, in addition to triphenylbismuthine, small amounts of metallic bismuth were found.

Triphenylbismuth oxide was one of several organometallic oxide catalysts used for the preparation of cross-linked polymers from monomers such as vinyl chloride [49].

Unlike its arsenic and antimony congeners, Ph_5Bi possesses an intense violet color. Seppelt and coworkers have published a series of papers on the synthesis and molecular structure of pentaarylbismuth compounds. These were found to possess either C_{4v} or D_{3h} symmetry; only those with C_{4v} symmetry possessed the violet color. In one recent paper [50], extended Hückel calculations of BiH_5 were carried out, both with and without relativistic corrections. While the calculations without relativistic corrections gave qualitatively similar diagrams (but with smaller HOMO–LUMO splitting for the C_{4v} model) the HOMO–LUMO splitting changed by about 27% on applying the relativistic correction for the C_{4v} model, but only about 14% for the D_{3h} model. The color then would be the consequence of relativistic effects on an empty molecular orbital. While these results are plausible, Pyykkö and coworkers [50] suggested that they should be verified by more fundamental methods, applied on more realistic model systems. Accordingly, they carried out quasirelativistic multiple-scattering X_α(MS X_α) and pseudopotential Hartree–Fock calculations on EX_5 model systems (where E = Bi, Sb and X = H, C≡CH) for C_{4v} and D_{3h} symmetries. It was concluded that the intense purple color of Ph_5Bi was related to the relativistic stabilization of the a_1 LUMO, as previously concluded by Seppelt and coworkers.

A paper from Schmidbaur's laboratory described the three compounds obtained from the reaction of [2.2.2] paracyclophane with arsenic, antimony, or bismuth trichloride [51]. The bismuth compound contained 3 $BiCl_3$ molecules, each of which was engaged in an η^6-π complexation with a phenyl group of the paracyclophane. The units were then cross-linked by chlorine bridges. One mol of benzene of crystallization was present in each molecule of the complex. This benzene did not participate in coordinating with the bismuth. The compounds were characterized by PMR and IR spectroscopy and by elemental analyses. The molecular and crystal structure of each compound was determined by X-ray diffraction. Selected bond distances and bond angles were reported. The average of the Bi–phenyl ring distances was shorter than the Sb–phenyl ring distances. This result indicated stronger π-bonding in the bismuth compound.

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