BISMUTH *

ANNUAL SURVEY COVERING THE YEAR 1977

G. O. DOAK AND LEON D. FREEDMAN

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27650 (U.S.A.)

A monograph on the organometallic chemistry of antimony and bismuth was published in the Soviet Union in the Russian language in 1976 [1]. Several recent review articles have briefly mentioned organobismuth compounds. A short review article on organoarsenic, antimony, and bismuth compounds mentioned a few new organobismuth compounds [2], while heterocyclic compounds were given in a survey devoted to heterocyclic compounds of phosphorus, arsenic, antimony, and bismuth [3]. A review article devoted to the structural chemistry of these same elements has been published in Russian [4], and in a review article on organotin compounds a few compounds containing tin-bismuth bonds were mentioned [5]. An article on the biological effects of organometallic compounds included references to organobismuth compounds [6]. Organobismuth compounds subjected to X-ray diffraction in 1975 or 1976 were listed in Vol. 8 of *Molecular Structures and Dimensions* [7]. Brief mention of organobismuth compounds has been made in two books devoted to vibrational spectra of organometallic compounds [8] and homoatomic rings, chains, and macromolecules of main-group elements [9].

An interesting series of reactions between Me_2BiBr and the transition metal complexes $[\eta^5-C_5H_5(CO)_3M]Na$, where M = Cr, Mo, and W, has been reported by Panster and Malisch [10]. The transition metal complexes first reacted with Me_2BiBr to form the expected $Cp(CO)_3M-BiMe_2$ (where $Cp = \eta^5-C_5H_5$). These underwent further reactions to form $[Cp(CO)_3M]_2BiMe$ and $[Cp(CO)_3M]_2BiBr$. These last two compounds could be separated by extraction of the methyl compound with hot hexane. In this manner the three complexes $[Cp(CO)_3M]_2BiMe$ and the Mo and Cr complexes $[Cp(CO)_3M]_2BiBr$ were prepared and characterized by ^1H NMR and IR spectra as well as by elementary analyses. Although the dimethyl complexes $Cp(CO)_3MBiMe_2$ were not isolated, they were formed by the reaction:

$$Cp(CO)_3MH + BiMe_3 \longrightarrow Cp(CO)_3MBiMe_2 + MeH$$

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* Bismuth; Annual Survey covering the year 1976 see J. Organometal. Chem., Vol. 147 (1978) 233-237.

The tungsten compound $Cp(CO)_3WBiMe_2$ reacted with $THF{\cdot}Cr(CO)_5$ in the following manner:

$$Cp(CO)_3WBiMe_2 + THF{\cdot}Cr(CO)_5 \xrightarrow{THF} THF + Cp(CO)_3WBi(Me)_2Cr(CO)_5$$

Wieber and Baudis [11] have prepared a number of interesting organobismuth compounds of the type Ph_2BiSR and $Ph_2BiSRSBiPh_2$, where SR was a group such as SEt, $SCMe_3$, SC(O)Me, SCH_2Ph, or SC_6H_4Cl-*p* and SRS was the group SCH_2CH_2S or $SCH_2CH_2CH_2S$. The compounds were characterized by elemental analyses, mass spectra, and ^1H NMR spectra.

Stelzer and Unger [12] have reported on the molybdenum complex *cis*-$Mo(CO)_4(Me_2PLi)_2$ which was formed by the action of butyllithium on the phosphine *cis*-$Mo(CO)_4(Me_2PH)_2$. The lithium compound reacted with compounds of P, Sb, Bi, Si, Zr and Ti to form complexes containing these elements. Thus, *cis*-$Mo(CO)_4(MePLi)_2$ and Me_2BiCl formed the complex $(CO)_4Mo(PMe_2{-}BiMe{-}BiMe{-}PMe_2)$. The ^1H NMR spectrum of this bismuth compound was reported.

Levason and co-workers [13] have prepared two interesting organobismuth compounds as potentially quadridentate ligands. The compounds were tris(*o*-dimethylarsinophenyl)bismuthine and tris(3-dimethylarsinopropyl)bismuthine. Both compounds were obtained as oils and the synthesis of the second compound proved to be difficult and required the slow addition of the appropriate Grignard reagent to $BiCl_3$ at -30^o. The two ligands formed coordination compounds with Ni(II) salts. Thus NiX_2 (X = Cl, Br, or I) formed the complexes $[NiL^1X][BPh_4]$, where L^1 was tris(*o*-dimethylarsinophenyl)bismuthine. The ^1H NMR spectra of these compounds suggested that the geometry of the nickel was square pyramidal with the three arsenic atoms and the bismuth atom coordinated to the nickel. In a similar manner the cobalt complex $[CoL^1Br][BPh_4]$ was prepared. Its spectra suggested a similar structure to the nickel compounds. The complex $[Ni_2L^1{}_3][ClO_4]_4$ obtained from nickel(II) perchlorate hexahydrate did not contain a Bi-Ni bond. The only complexes of tris(3-dimethylarsinopropyl)bismuthine (L^2) were $[NiL^2(OH_2)_2][ClO_4]_2$ and $[NiL^2(OH_2)_2][BF_4]_2$, in which the nickel exhibited trigonal-bipyramidal geometry. Attempts to obtain other complexes with L^2 were unsuccessful. The paper discussed the theroretical aspects of the bismuth-metal bonded complexes in some detail. A bismuthine (and a stibine) containing manganese has been prepared in 81% yield by means of the following reaction [14]:

$$3\ LiC_5H_4Mn(CO)_3 + BiCl_3 \longrightarrow [(CO)_3MnC_5H_4]_3Bi + 3\ LiCl$$

(where C_5H_4 was a disubstituted cyclopentadiene)

When the bismuth compound was heated to 300°, metallic Bi and $[(CO)_3MnC_5H_4]_2$ were obtained.

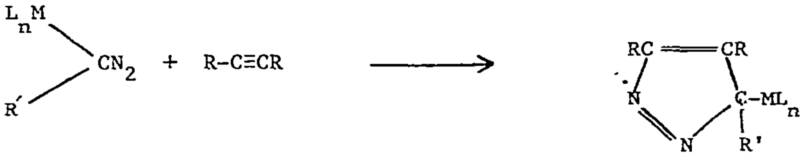
Since the pyridine homologs containing P, As, Sb, or Bi as the heteroatom are now all known, Ashe and Colburn [15] attempted the preparation of molybdenum-carbonyl complexes of these homologs. Although the authors were successful in obtaining complexes with the P, As, and Sb compounds, the extreme instability of bismabenzene (bismin) frustrated all efforts to produce a bismin complex.

Although $(CF_3)_3E$ (where E = N, P, As, and Sb) are well known, the corresponding bismuth compound has not been adequately characterized. Morrison and Lagow [16] have now reported a successful synthesis of $(CF_3)_3Bi$ from BiI_3 and C_2F_6 in an apparatus that produced CF_3 radicals by means of a glow discharge generated by a radio frequency generator at 8.6 MHz. The reaction was carried out at about 1 torr. A description of the apparatus used to generate the CF_3 radicals was given. The $(CF_3)_3Bi$ was purified by distillation at -55°. It was a colorless liquid which fumed when exposed to the air and was hydrolyzed by base to yield fluoroform. It decomposed at 100° in a sealed tube to yield metallic bismuth. The ^{19}F NMR spectrum of the compound gave a single fluorine peak at -45.9 ppm referred to CF_3CO_2H, and the mass spectrum gave a molecular ion which was 6.8% of the base peak.

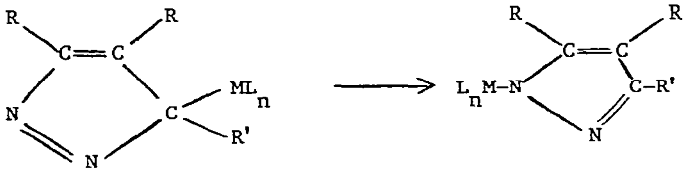
A study of the reaction of a number of organometallic-substituted diazoalkanes with the strongly basic phosphine $P(NMe_2)_3$ has been carried out by Krommes and Lorberth [17]. The products were phosphazines of the type $L_nM(R)C{=}N{-}N{=}P(NMe_2)_3$ (where M was a group IV or group V element, MeHg, etc.). The arsenic compounds reacted spontaneously, the antimony compound reacted slowly in refluxing pentane, and the bismuth compound $Me_2BiC(N_2)CO_2Et$ did not react. The ^{13}C NMR spectra for a series of known organometallic diazoalkanes have been reported by Grüning and co-workers [18]. Direct metal-carbon coupling constants $J(M{-}^{13}C)$ and chemical shifts were determined. It was concluded that electron release by the methyl-metal substituents led to strong shielding of the α-carbon atoms in heterodiazoalkanes. The bismuth compound studied was $Me_2BiC(N_2)CO_2Et$ and the following chemical shifts (δ in ppm) were reported: $Bi{-}^{13}CH_3$, 11.9; $Bi{-}^{13}C(N_2)$, 26.3; $O{-}^{13}CH_2$, 61.5; $OCH_2{}^{13}CH_3$, 15.5; and $^{13}C = O$, 166.0.

A study of the 1,3-dipolar cycloaddition reactions of a series of organometallic compounds of the type $L_nMC(N_2)R$ (where L_nM = Me_3Sn, Me_3Pb, Me_2Sb, Me_2As, Me_2Bi, MeHg and other organomercury compounds, and

R = L_nM, CO_2Et, C(O)Me, and C(O)Ph) with the acetylene carboxylic ester $MeO_2CC{\equiv}CCO_2Me$ has been reported [19]. In the majority of reactions, pyrazoles were formed according to the following equation:



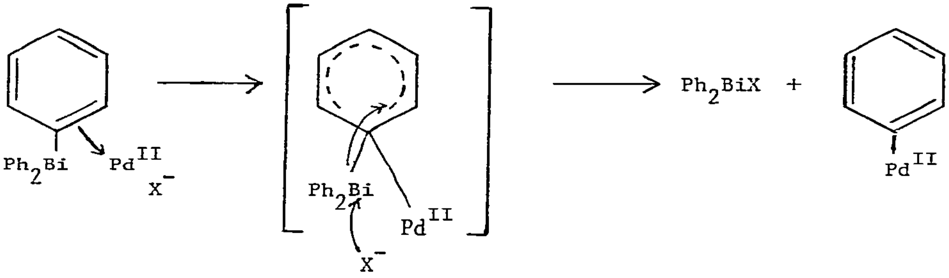
These pyrazoles may undergo rearrangement to the isopyrazoles:



The pyrazoles obtained were characterized by elemental analysis, IR, Raman, ^1H NMR and mass spectra. In the case of bismuth the two diazo compounds $(Me_2Bi)_2CN_2$ and $Me_2BiC(N_2)CO_2Et$ were used but only in the case of the second compound was a reaction product crystallized and characterized.

The diazoalkane-arsenic compound $Me_2AsC(N_2)H$ was found to react with a variety of amides of Groups IV and Groups V elements to give arsenodiazoalkanes of the type $(Me_2As)(L_nM)CN_2$ [20]. The one bismuth compound employed was $Me_2BiN(Me)(SiMe_3)$ which yielded the diazoalkane $(Me_2Bi)(AsMe_2)CN_2$. This compound was unstable and decomposed between -20 and -10° so that neither an IR spectrum nor elementary analyses could be otained. The ^1H NMR (but not the ^{13}C NMR) spectrum was reported Apparently the compound was two unstable to allow the ^{13}C NMR spectrum to be obtained.

Kawamura and co-workers [21] have studied the migration of phenyl groups from phenyl derivatives of some Group V and Group VI compounds to palladium in the compound $Pd(OAc)_2$. The phenyl palladium compounds were not isolated; instead the reaction was run in the presence of an olefin (1-octene or ethyl acrylate) which in turn was phenylated by the phenylpalladium compound. The reaction was carried out in a reaction cell at constant temperature. The phenyl compound of Group V or VI was mixed with the $Pd(OAc)_2$ in MeCN, stirred for 5 minutes, and then the olefin was added. The course of the reaction was then followed by analyzing the phenylated olefins and the biphenyl produced in the reaction. The bismuth compounds studied were Ph_3Bi and Ph_3BiCl_2. It was found that phenyl groups attached to bismuth (as well as antimony) were rapidly transferred to palladium as compared with phenyl groups attached to arsenic where the transfer was slow. Similarly all three phenyl groups were transferred from Ph_3Bi and Ph_3BiCl_2, whereas with arsenic only two phenyl groups were transferred. These results were explained in terms of the weaker Bi-C bond and the decreasing electronegativities in the order $Bi<Sb<P<As$. The following mechanism was suggested for the reaction of Ph_3Bi with the palladium compound:



In a study of liquid hydrogen bromide as a solvent, Peach [22] reported on the reaction of the Ph_3E compounds (E = N, P, As, Sb, and Bi) as well as Ph_3CCl and PCl_3 in liquid hydrogen bromide. With Ph_3Bi the following reaction occurred:

$$Ph_3Bi + 3\ HBr \rightarrow BiBr_3 + 3\ PhH$$

No further studies on Ph_3Bi were carried out.

In a study of the reactions of compounds of the type Ar_3E (where E = N, P, As, Sb, and Bi) with selenium dioxide, El Sheikh and co-workers [23] have shown that with triarylbismuth compounds the Bi-C bonds were cleaved according to the following equation:

$$2\ Ar_3Bi + 9\ SeO_2 + 3\ H_2O \rightarrow 6\ ArSeO_2H + Bi_2(SeO_3)_3$$

The bismuth compounds used in this study were Ph_3Bi, *o*-, *m*-, and $(p\text{-}MeC_6H_4)_3Bi$, and $(p\text{-}ClC_6H_4)_3Bi$.

It is known that olefin metathesis is catalysed by binary systems such as WCl_6, $MoCl_5$, or $ReCl_5$ used in conjunction with such organometallic compounds as R_4Sn, RMgI, RLi or $R_{3-n}AlCl_n$, where R is alkyl or aryl. The metathesis is of the following type:

$$2\ R_1CH{=}CHR_2 \rightleftarrows R_1CH{=}CHR_1 + R_2CH{=}CHR_2$$

The present paper [24] deals with the catalysts WCl_6-Ph_3Bi, WCl_6-Ph_4Pb, and WCl_6-Ph_4Sn. The binary systems WCl_6-Ph_3As and WCl_6-Ph_3Sb were ineffective as catalysts. Good metathesis with WCl_6-Ph_3Bi was obtained in an extremely narrow Bi/W ratio range. The olefin used was 2-heptene. The mechanism of catalyst formation in these systems was investigated by gas chromatography product analysis of the reactions of Ph_3Bi, Ph_4Sn, and Ph_4Pb with WCl_6. The products of these reactions were PhH, PhCl, and PhPh. The catalytic activity of the binary system appeared to be dependent on the amount of these reaction products formed. The authors concluded that for successful catalysis the central atom of the cocatalyst must be one that could donate a carbanion to the tungsten.

Taniewski and Tomczyk [25] have reported that replacing Ph_3P with either Ph_3As or Ph_3Bi has a profound effect on the isomerization activity of the catalytic complex π-C_3H_5NiCl-Et_nAlCl_{3-n}-Ph_3E (where E = P, As, or Bi) when used for propylene dimerization. The use of Ph_3As gave the highest isomerization activity and the highest selectivity for 2-methyl-2-pentene.

Rogozhin and co-workers [26] have studied the effect of temperature on the electronic spectra of a number of phenyl derivatives of Group III, IV, and V elements. Whereas there was little effect on either the intensity or the position of the long-wave band maxima in the compounds Ph_4Si, Ph_3Ga, and $[1,3,5\text{-}(CH_3)_3C_6H_2]_3B$ when the temperature was lowered from 295 to 77°K, there was a marked effect on the compounds Ph_3E, where E = N, P, As, Sb, and Bi. In all of these compounds there was an increase in the extinction coefficient and a bathochromic shift of the long-wave band. On the basis of these results the authors concluded that the effectiveness of $p\pi$ coupling between the unshared electrons of the heteroatom and the ring increased as the temperature was lowered. The spectra of the P, As, Sb, and Bi compounds at 295°K showed not only strong principal bands at 260, 250, 255, and 257 nm, respectively, but weaker bands at 270, 260, 265, and 280 nm, respectively. In the case of Ph_3P and Ph_3Bi these bands have previously been assigned to $n \longrightarrow \pi^*$ transitions.

These assignments were disputed by the present authors, who, on the basis of the observed temperature effects, believed that these bands should be assigned to $\pi\ell, \pi^*$ type transitions for two different conformations of the Ph$_3$E molecules, one conformation predominating at 295°K, the other more nearly planar conformation predominating at 77°K.

In addition to the Ph$_3$E compounds, the authors studied the four mesityl compounds, [1,3,5-(CH$_3$)$_3$C$_6$H$_2$]E, where E was P, As, Sb, or Bi. With these compounds lowering the temperature from 295 to 77°K not only produced the increase in intensity and the bathochromic shift as seen with the phenyl compounds but resulted in the appearance of a new sharp band for each compound in the 250-270 nm region. A steric effect was proposed to explain this phenomenon.

In an interesting paper Pombrik and co-workers [27] have reported on the transmission of electronic effects, as measured by the ^{19}F chemical shift, in a series of compounds of the type Ar$_2$MC$_6$H$_4$F-p, where M = Sb, Bi, CH, and N. The study necessitated the synthesis of a number of new compounds. The bismuth compounds prepared were of the type p-FC$_6$H$_4$BiAr$_2$, where Ar was p-Me$_2$NC$_6$H$_4$, p-MeOC$_6$H$_4$, p-MeC$_6$H$_4$, Ph, p-ClC$_6$H$_4$, m-ClC$_6$H$_4$, or p-FC$_6$H$_4$. The authors were unable to prepare in a pure state the compounds where Ar = 3,4-Cl$_2$C$_6$H$_3$ and 3,4,5-Cl$_3$C$_6$H$_2$. The bismuth compounds were obtained by the reaction of p-FC$_6$H$_4$BiBr$_2$ and the appropriate Grignard reagent and were characterized by elemental analyses. It was concluded that the electronic effects were transmitted in the case of Bi-C$_{ar}$, Sb-C$_{ar}$, and C-C$_{ar}$ compounds predominantly by an inductive mechanism whereas the electronic effect with N-C$_{ar}$ compounds involved a classical resonance effect to a significant extent.

The ^{13}C NMR spectra of the triphenyl compounds Ph$_3$E, where E = P, As, Sb, and Bi, as well as the ^{13}C spectra for a number of coordination compounds of the P, As, and Sb compounds have been recorded [28]. The substituent effects of electron-donor and electron-acceptor substituents were then compared with the Hammett-Taft constants (σ_R^o). Since Ph$_3$Bi was the only bismuth compound considered, relatively little information on organobismuth compounds was obtained. The ^{13}C chemical shifts for Ph$_3$Bi were -138.33, -131.26, and -128.52 (all in ppm relative to TMS) for the o-, m-, and p- positions, and σ_R^o was -0.123. The authors concluded that these results were suggestive of a strong delocalization of the lone pair to the π framework of the rings. In accordance with this conclusion the low donor capacity of trivalent bismuth compounds is readily understood.

The mass spectra of the triphenyl compounds Ph$_3$E and of the o-, m- and p-tolyl compounds (MeC$_6$H$_4$)$_3$E, where E = P, As, Sb, and Bi have been studied by Spalding [29]. In general the spectra of the *m*- and *p*-derivatives were similar but differed significantly from those of the *o*-compounds. In the case of the tolyl bismuth compounds the base peak was the ion $[C_7H_7Bi]^+$. Similarly, the base peak of the phenyl compound was $[C_6H_5Bi]^+$. In the case of $(o\text{-}MeC_6H_4)_3Bi$ the molecular ion comprised 6.3% of the total ion current, whereas with the other compounds the molecular ion comprised only a trace of the total ion current. With the bismuth compounds relatively few ions were found.

Dipole moments for a number of *para* and *meta* substituted triaryl compounds of the Group V elements P, As, Sb, and Bi, have been determined by Claeys and co-workers [30]. The *para* substituents for all of the compounds were 4-F, 4-Cl, and 4-Me, the *meta* substituents were 3-F and 3-Cl. Dipole moments for the unsubstituted triaryl compounds were also reported. The experimental value found for Ph_3Bi was 0.47 D and for $(p\text{-}CH_3C_6H_4)_3Bi$ was 0.66 D. The moments for the 4-F, 4-Cl, 3-F, and 3-Cl bismuth compounds were 2.37 D, 2.59 D, 2.53 D, and 2.61 D, respectively. The reasons for these dipole moments were discussed in some detail. Conformational parameters, corresponding to the molecular geometry as derived from the experimental dipole moments of the *m*-substituted compounds, were listed for all of the compounds.

Ahrland and co-workers [31] have studied the thermodynamics of complex formation between silver(I) perchlorate and the triphenyl compounds Ph_3E (where E = N, P, As, Sb, and Bi) in DMSO solution. Stability constants were determined by potentiometric measurements using silver electrodes. With the P, As, and Sb compounds, coordination up to three ligands was found in solution and compounds of the type $[Ag(Ph_3M)_4]ClO_4$ precipitated from solution at high ligand concentrations. By contrast, with Ph_3N and Ph_3Bi only mono-ligand complexes could detected in solution. The affinity sequences were in the order $N << P > As > Sb > Bi$.

The thermodynamic functions, entropy, heat capacity, free energy function, and enthalpy of Me_3Bi have been evaluated in 100^o steps from 289.15 to 1000^oK by the use of the rigid rotator-harmonic oscillator approximation [32].

In a theoretical paper by Beagley and Medwid [33] the vibrational force fields, amplitudes, and zero-point average structures of the molecules Me_3E, where E was N, P, As, Sb, and Bi, were considered. The data for the computations were taken from the literature. This paper is discussed in more detail in the Antimony section.

An error in our annual surveys of organoantimony [34] and organobismuth [35] chemistry for 1975 has been kindly called to our attention by Professor M. Wieber of the University of Würzburg. In discussing a paper by Ouchi, Honda, and Kitazima [36], we erroneously stated that they had described compounds of the type $Ph_3Sb(SSCR)_2$ and $Ph_3Bi(SSCR)_2$. Actually these authors had prepared triphenylantimony dicarboxylates and triphenylbismuth dicarboxylates by the following type of reaction:

$$Ph_3EBr_2 + 2\ RSCH_2CO_2H + 2\ Et_3N \longrightarrow Ph_3E(O_2CCH_2SR)_2 + 2\ Et_3NH^+\ Br^-$$

(where E was Sb or Bi and R was Me, Et, Pr, Me_2CH, Bu, Ph, or $PhCH_2$)

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