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THE SYNTHESIS AND PROPERTIES OF SUBSTITUTED TERTIARY BISMUTHINE LIGANDS

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The synthesis of functionally substituted (OMe, -NMe₂, -SMe) organobismuthine ligands - specifically (*o*-MeOC₆H₄)₃Bi, (*o*-MeSC₆H₄)₃Bi, (*o*-Me₂NC₆H₄)₃Bi, (*o*-MeOC₆H₄)Ph₂Bi, (*o*-MeSC₆H₄)Ph₂Bi and (*o*-Me₂NC₆H₄)Ph₂Bi is described. (*o*-Chlorophenyl)diphenylbismuthine reacts with sodium diphenylstibide (NaSbPh₂) to give (*o*-diphenylstibinophenyl)diphenylbismuthine *o*-C₆H₄(SbPh₂)(BiPh₂). The ¹H nmr and mass spectra of these ligands, and of (*o*-MeC₆H₄)₃Bi and (*p*-MeC₆H₄)₃Bi are reported and discussed.

INTRODUCTION

The chemistry of organobismuth compounds is not extensive¹ due both to the weak C-Bi bond, and to limited efforts in the area. The coordination chemistry of bismuth ligands is very limited indeed,^{2,3} and largely confined to substituted carbonyl complexes. One way in which the weak donor power of bismuthines may be overcome, and new examples of M-Bi linkages produced is the incorporation of other donor groups into the bismuthine. Examples of this approach are the arsenic-bismuth and phosphorus-bismuth ligands Bi(*o*-C₆H₄AsMe₂)₃, Bi(CH₂CH₂CH₂AsMe₂)₃,⁴ *o*-C₆H₄(PPh₂)(BiPh₂) and *o*-C₆H₄(AsPh₂)(BiPh₂),⁵ and the present work describes oxygen (-OMe), sulphur (-SMe) and nitrogen (-NMe₂) analogues. (*o*- and *p*-MeOC₆H₄)₃Bi and (*p*-Me₂NC₆H₄)₃Bi have been described,^{6,7} and we^{8,9} have recently discussed some antimony analogues.

RESULTS AND DISCUSSION

Tris (*o*-methoxyphenyl)bismuthine (*o*-MeOC₆H₄)₃Bi, was prepared in moderate yield (20%) from *o*-MeOC₆H₄MgBr and BiCl₃ in tetrahydrofuran. The ligand was recrystallised from acetone, and retains some solvent, melting at 151-152°C. Supniewski⁷ prepared the compound in diethyl ether and reported an MP of 169°C. Our product once melted and cooled remelts at 167°C and is clearly the same compound. Tris(*o*-methylthiophenyl)bismuthine (*o*-MeSC₆H₄)₃Bi was readily prepared from *o*-C₆H₄(SMe)Br,⁸ *n*-BuLi and BiCl₃ in THF. Both ligands are white crystalline solids which are indefinitely stable.

In contrast tris(*o*-dimethylaminophenyl)bismuthine (*o*-Me₂NC₆H₄)₃Bi proved to be difficult to obtain in the pure state. The reaction of *o*-C₆H₄Br(NMe₂),⁹ *n*-BuLi and BiCl₃ in THF gave a clear oil, which was dissolved in ethanol and allowed to crystallise slowly in the refrigerator. The yield of yellowish crystals (11%) was poor. These crystals appear to be indefinitely stable in the dark, but on exposure to light for several hours they become

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discoloured and turn pale green. The material also appears to be light sensitive in solution, since solutions in acetone, CH_2Cl_2 or ethanol left on the bench to crystallise, often deposited greenish materials which did not completely redissolve in the same solvent. Gilman and Yablunsky⁶ appear to have had similar problems with $(p\text{-Me}_2\text{NC}_6\text{H}_4)_3\text{Bi}$, although they did not discuss it in detail.

The unsymmetrical ligands $\text{Ph}_2\text{Bi}(o\text{-C}_6\text{H}_4\text{Y})$ ($\text{Y} = \text{OMe}, \text{SMe}, \text{NMe}_2$) were prepared from $o\text{-C}_6\text{H}_4\text{BrY}$, $n\text{-BuLi}$ and Ph_2BiCl , all of the reactions being conducted at 0°C , followed by warming to room temperature, since refluxing of the reaction mixtures seems to produce considerable decomposition. (*o*-Methoxyphenyl)diphenylbismuthine is a white crystalline solid, but the (*o*-methylthiophenyl)diphenylbismuthine was obtained as a colourless oil. The oil became very viscous on cooling, but all attempts to crystallise it even at -20°C failed. The amine-bismuthine $o\text{-Me}_2\text{NC}_6\text{H}_4\text{-BiPh}_2$ appears to be somewhat sensitive to light, but the decomposition seems to be less readily produced than with $(\text{Me}_2\text{NC}_6\text{H}_4)_3\text{Bi}$. The proton nmr spectra of these ligands are listed in Table I.

The monogrynard reagent derived¹⁰ from *o*-bromochlorobenzene ($o\text{-ClC}_6\text{H}_4\text{MgBr}$) reacted with Ph_2BiCl at 0°C to give a poor yield of *o*-chlorophenyldiphenylbismuthine, a yellowish waxy solid MP 68°C . Gilman⁶ briefly mentions the tris(*o*-chlorophenyl)bismuthine analogue. It seemed that $o\text{-ClC}_6\text{H}_4\text{BiPh}_2$ could be a useful intermediate, providing the chlorine can be substituted without breaking the Bi-C bonds. Carbon-bismuth bonds are readily cleaved by RLi ,¹¹ so that reaction with group VB nucleophiles seemed a better approach to new ligands rather than the $n\text{-BuLi}/\text{R}_2\text{ECl}$ route. A similar approach ($\text{NaSbPh}_2 + o\text{-C}_6\text{H}_4\text{Br}(\text{SbPh}_2)$) was successful in the preparation of $o\text{-C}_6\text{H}_4(\text{SbPh}_2)_2$.¹² We find that LiSbPh_2 in THF reacts with $o\text{-ClC}_6\text{H}_4\text{BiPh}_2$ to give the new ligand $o\text{-C}_6\text{H}_4(\text{SbPh}_2)(\text{BiPh}_2)$ as white needles. The preparation of this stibine-bismuthine means that of the series $o\text{-C}_6\text{H}_4(\text{EPh}_2)(\text{E}'\text{Ph}_2)$ ($\text{E}, \text{E}' = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) all the possible combinations are known⁵ except for $o\text{-C}_6\text{H}_4(\text{BiPh}_2)_2$.

The mass spectra of the bismuthines were recorded (Experimental section) since they provide the clearest evidence for the constitution of the products obtained. There are contradictory reports in the literature of the mass spectra of BiPh_3 both Bi^+ ^{13,14} and PhBi^+ ^{15,16} being reported as base peaks, although all agree that the parent ion is either of very low intensity or not detected. Spalding¹⁵ reports that $(p\text{-tolyl})_3\text{Bi}$ is similar, but that $(o\text{-tolyl})_3\text{Bi}$ differs in giving a parent ion ($\text{I} = 6.3\%$ of the ion current). We generally confirm these observations although in our spectra Bi^+ was the base peak for both the tolylbismuthines, whilst Spalding¹⁵ reports BiC_7H_7^+ as base.

The effect of *o*-substituents is clear in the spectra of $(o\text{-MeOC}_6\text{H}_4)_3\text{Bi}$ and $o\text{-MeOC}_6\text{H}_4\text{BiPh}_2$. The latter shows Bi^+ as base peak and an intense PhBi^+ , but only weak $[\text{P-Ph}]^+$ and $[\text{P-C}_7\text{H}_7\text{O}]^+$, and we did not detect a parent ion. In contrast the former shows a parent ion, an intense $[\text{P-C}_7\text{H}_7\text{O}]^+$ ion and $[\text{BiC}_7\text{H}_7\text{O}]^+$ is the base peak. Similar effects are

TABLE I
¹H NMR Data on the bismuthines^a

$\text{Bi}(o\text{-C}_6\text{H}_4\text{CH}_3)_3$	2.3–2.9(m) C_6H_4	7.55(s) CH_3
$\text{Bi}(p\text{-C}_6\text{H}_4\text{CH}_3)_3$	2.4(d) 2.85(d) C_6H_4	7.7(s) CH_3
$\text{Bi}(o\text{-C}_6\text{H}_4\text{OCH}_3)_3$	2.5–3.1(m) C_6H_4	6.3(s) OCH_3
$\text{Bi}(o\text{-C}_6\text{H}_4\text{OCH}_3)(\text{C}_6\text{H}_5)_2$	2.2–3.0(m) $\text{C}_6\text{H}_4 + \text{C}_6\text{H}_5$	6.3(s) OCH_3
$\text{Bi}(o\text{-C}_6\text{H}_4\text{SCH}_3)_3$	2.3–2.9(m) C_6H_4	7.6(s) SCH_3
$\text{Bi}(o\text{-C}_6\text{H}_4\text{SCH}_3)(\text{C}_6\text{H}_5)_2$	2.2–2.8(m) $\text{C}_6\text{H}_4 + \text{C}_6\text{H}_5$	7.8(s) SCH_3
$\text{Bi}[o\text{-C}_6\text{H}_4\text{N}(\text{CH}_3)_2]_3$	2.4–2.8(m) C_6H_4	7.3(s) NCH_3
$\text{Bi}[o\text{-C}_6\text{H}_4\text{N}(\text{CH}_3)_2](\text{C}_6\text{H}_5)_2$	2.2–2.8(m) $\text{C}_6\text{H}_4 + \text{C}_6\text{H}_5$	7.4(s) NCH_3

^aIn CDCl_3 τ scale relative TMS. Intensities are as expected.

seen in the spectra of both (*o*-MeSC₆H₄)₃Bi and *o*-MeSC₆H₄BiPh₂, and in the amine-bismuthines.

The spectrum of *o*-ClC₆H₄BiPh₂ is reminiscent of BiPh₃, only Bi⁺ and BiPh⁺ are prominent bismuth-containing fragments. The spectrum of *o*-C₆H₄(BiPh₂)(SbPh₂) is consistent with those reported for the lighter analogues.^{5,11,17}

EXPERIMENTAL

Physical measurements were made as described previously.⁸ Diphenylchlorobismuth, Ph₂BiCl was obtained from BiCl₃ and Ph₃Bi.⁵ All reactions were conducted under a dry dinitrogen atmosphere.

Tris(o-methoxyphenyl)bismuthine

The grignard reagent prepared from *o*-bromoanisole (30 g, 0.16 mol) and magnesium (3.8 g, 0.16 mol) in dry tetrahydrofuran (100 cm³) was treated dropwise with a solution of bismuth trichloride (16.8 g, 0.05 mol) in THF (50 cm³). The mixture was stirred at room temperature for 1 hour, and then hydrolysed with aqueous ammonium chloride solution. The organic layer was separated, dried (Na₂SO₄), and evaporated, and the oil crystallised from ethanol. Recrystallisation from acetone gave a white crystalline solid 7.5 g, 20%. MP 150–152° (on remelting 167°C see text) fd C = 47.5%, H = 3.6%. C₂₁H₂₁O₃Bi req C = 47.8%, H = 3.7%. Mass spectrum† m/e = 530(1.5) C₂₁H₂₁O₃Bi; 423(21.5) C₁₄H₁₄O₂Bi; 316(100) C₇H₇OBi; 214(8.5) C₁₄H₁₄O₂; 209(63) Bi; 107(16) C₇H₇O.

(o-Methoxyphenyl)diphenylbismuthine

o-Bromoanisole (15 g, 0.08 mol) was added dropwise to a stirred solution of *n*-butyllithium (40 cm³ 2 M) in THF (100 cm³) at 0°C, and after 1 hour, chlorodiphenylbismuth (32 g, 0.08 mol) in THF (100 cm³) was added. The greyish mixture was stirred for a further 1 hour, allowed to warm to room temperature and worked up as above. The product was recrystallised from ethanol 31 g, 82%. MP 74°C. fd C = 48.5%, H = 3.6%. C₁₉H₁₇OBi req C = 48.1%, H = 3.6%. Mass spectrum: 393(1) C₁₃H₁₂OBi; 363(3.5) C₁₂H₁₀Bi; 316(7) C₇H₇OBi; 286(75) C₆H₅Bi; 209(100) Bi; 154(11) C₁₂H₁₀.

Tris(o-methylthiophenyl)bismuthine

Was prepared in a similar manner to the methoxy analogue from *o*-bromophenylmethylsulphide (20 g, 0.09 mol), *n*-BuLi (45 cm³, 1.6 M), and bismuth trichloride (10.4 g, 0.03 mol) in THF, and recrystallised from ethanol. 7.5 g, 40%. MP 117–118°C. fd C = 43.2%, H = 3.4%. C₂₁H₂₁S₃Bi req C = 43.6%, H = 3.6%. Mass spectrum: 578(30) C₂₁H₂₁S₃Bi; 563(25) C₂₀H₁₈S₃Bi; 455(57) C₁₄H₁₄S₂Bi; 332(32) C₇H₇SBi; 317(28) C₆H₄SBi; 231(10.5) C₁₃H₁₁S₂; 216(20.5) C₁₂H₈S₂; 209(100) Bi; 199(33) C₁₃H₁₁S; 184(59) C₁₂H₈S; 123(30) C₇H₇S; 108(41) C₆H₄S.

(o-Methylthiophenyl)diphenylbismuthine

Was obtained similarly from *o*-C₆H₄Br(SMe) (9.7 g, 0.05 mol), *n*-BuLi (36 cm³, 1 M) and Ph₂BiCl (19.0 g, 0.05 M) in diethyl ether/THF. The product was an oil which did not solidify

†M/e (% internal base) ion.

after 10 weeks at -10°C , or crystallise from ethanol, acetone, CH_2Cl_2 or *i*-propanol. It was purified by pumping at 10^{-1} torr for 3 days at room temperature. 14 g, 61%. fd C = 47.6%, H = 4.1%. $\text{C}_{19}\text{H}_{17}\text{SbBi}$ req C = 47.8%, H = 3.6%. Mass spectrum: 486(7) $\text{C}_{19}\text{H}_{17}\text{SbBi}$; 409(21) $\text{C}_{13}\text{H}_{12}\text{SbBi}$; 363(5) $\text{C}_{12}\text{H}_{10}\text{Bi}$; 332(11) $\text{C}_7\text{H}_7\text{SbBi}$; 317(7) $\text{C}_6\text{H}_4\text{SbBi}$; 286(85.5) $\text{C}_6\text{H}_5\text{Bi}$; 209(100)Bi; 184(11) $\text{C}_{12}\text{H}_8\text{S}$; 154(12) $\text{C}_{12}\text{H}_{10}$.

Tris(o-dimethylaminophenyl)bismuthine

Was prepared similarly to the methoxy compound from *o*- $\text{C}_6\text{H}_4\text{Br}(\text{NMe}_2)$ (20 g, 0.1 mol) *n*-BuLi (50 cm³, 1 M) and BiCl_3 (10.5 g, 0.03 mol) in diethyl ether/THF. The oil obtained was dissolved in ethanol, and crystallised slowly in the dark. 2 g, 11%. MP $127\text{--}130^{\circ}\text{C}$. The yellowish crystals were stirred in the dark, fd C = 50.3%, H = 5.1%, N = 7.2%. $\text{C}_{24}\text{H}_{30}\text{N}_3\text{Bi}$ req C = 50.6%, H = 5.3%, N = 7.4%. Mass spectrum: 569(1.5) $\text{C}_{24}\text{H}_{30}\text{N}_3\text{Bi}$; 449(32.5) $\text{C}_{16}\text{H}_{20}\text{N}_2\text{Bi}$; 329(5) $\text{C}_8\text{H}_{10}\text{NBi}$; 240(5) $\text{C}_{16}\text{H}_{20}\text{N}_2$; 209(13) Bi; 121(100) $\text{C}_8\text{H}_{10}\text{N}$; 105(14) $\text{C}_7\text{H}_7\text{N}$.

(o-Dimethylaminophenyl)diphenylbismuthine

Was prepared from *o*- $\text{C}_6\text{H}_4\text{Br}(\text{NMe}_2)$ (10.0 g, 0.05 mol), *n*-BuLi (27 cm³, 1 M), Ph_2BiCl (20.2 g, 0.05 mol) in diethyl ether/THF at 0°C . The oil was crystallised from a 1 : 1 ethanol/acetone mixture at 0°C . 3.5 g, 15%. MP $72\text{--}73^{\circ}\text{C}$. fd C = 49.3%, H = 4.4%, N = 3.0%. $\text{C}_{20}\text{H}_{20}\text{NBi}$ req C = 49.6%, H = 4.1%, N = 2.9%. Mass spectrum: 483(2) $\text{C}_{20}\text{H}_{20}\text{NBi}$; 406(3) $\text{C}_{13}\text{H}_{15}\text{NBi}$; 363(5) $\text{C}_{12}\text{H}_{10}\text{Bi}$; 329(1) $\text{C}_8\text{H}_{10}\text{NBi}$; 286(80) $\text{C}_6\text{H}_5\text{Bi}$; 209(100) Bi; 197(8) $\text{C}_{14}\text{H}_{15}\text{N}$; 154(17) $\text{C}_{12}\text{H}_{10}$; 121(17.5) $\text{C}_8\text{H}_{10}\text{N}$.

(o-Chlorophenyl)diphenylbismuthine

The grignard reagent prepared from *o*-bromochlorobenzene (20 g, 0.1 mol) in diethyl ether (200 cm³) and magnesium (3 g, 0.15 mol) was transferred into a dropping funnel, and added slowly to a stirred solution of Ph_2BiCl (40 g, 0.1 mol) in THF (200 cm³) at 0°C , and the mixture allowed to stand for 1 hour. It was hydrolysed, the organic layer separated, dried (Na_2SO_4) and evaporated. The oil remaining was crystallised from ethanol. 11 g, 22%. MP 68°C . fd C = 44.6%, H = 3.0%. $\text{C}_{18}\text{H}_{14}\text{ClBi}$ req C = 44.6%, H = 2.95%. Mass spectrum†: 398(1.5) $\text{C}_{12}\text{H}_9\text{ClBi}$; 363(2) $\text{C}_{12}\text{H}_{10}\text{Bi}$; 320(15) $\text{C}_6\text{H}_4\text{ClBi}$; 286(65) $\text{C}_6\text{H}_5\text{Bi}$; 209(100) Bi; 154(10) $\text{C}_{12}\text{H}_{10}$.

(o-Diphenylstibinophenyl)diphenylbismuthine

Lithium diphenylstibide solution⁹ prepared from lithium (1.5 g, 0.2 mol), triphenylantimony (7.0 g, 0.02 mol) and THF (100 cm³), was filtered to remove the excess lithium, BuCl (1.3 g, 0.15 mol) added, and the resulting solution added dropwise to a solution of *o*-chlorophenyldiphenylbismuthine (10 g 0.02 mol) in THF (100 cm³) at 0°C . The red stibide colour was discharged, and the mixture developed a green colour. Hydrolysis and work up in the usual way gave a white solid. This was recrystallised from *i*-propanol. 8.5 g, 57%. MP $59\text{--}61^{\circ}\text{C}$. fd C = 50.9%, H = 3.4%. $\text{C}_{24}\text{H}_{30}\text{SbBi}$ req C = 50.4%, H = 3.35%. Mass spectrum†: 714(2) $\text{C}_{30}\text{H}_{24}\text{SbBi}$; 637(1) $\text{C}_{24}\text{H}_{19}\text{SbBi}$; 560(4) $\text{C}_{18}\text{H}_{14}\text{SbBi}$; 351(6.5) $\text{C}_{18}\text{H}_{14}\text{Sb}$; 286(87) $\text{C}_6\text{H}_5\text{Bi}$; 275(40) $\text{C}_{12}\text{H}_{10}\text{Sb}$; 273(30) $\text{C}_{12}\text{H}_8\text{Sb}$; 209(100) Bi; 198(52) $\text{C}_6\text{H}_5\text{Sb}$; 154(38) $\text{C}_{12}\text{H}_{10}$.

†¹²¹Sb and ³⁵Cl only. Relative intensities uncorrected.

Tris(o-tolyl)bismuthine and Tris(p-tolyl)bismuthine

These were prepared from the *o*-bromotoluene or *p*-bromotoluene, Mg and BiCl₃ as described in the literature.^{7,18}

Tris(o-tolyl)bismuthine (51%. MP 130°C (Lit 128).⁷ fd C = 52.3%, H = 4.2%. C₂₁H₂₁Bi req C = 52.3%, H = 4.35%. Mass spectrum: 482(12) C₂₁H₂₁Bi; 391(27) C₁₄H₁₄Bi; 300(52) C₇H₇Bi; 209(100) Bi; 182(19) C₁₄H₁₄; 91(10) C₇H₇.

Tris(p-tolyl)bismuthine (40%). MP 114–115°C (Lit 117°C).¹⁸ fd C = 52.5%, H = 4.1%. C₂₁H₂₁Bi req C = 52.3%, H = 4.35%. Mass spectrum: 391(21) C₁₄H₁₄Bi; 300(82.5) C₇H₇Bi; 209(100) Bi; 182(18) C₁₄H₁₄; 91(55) C₇H₇.

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