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THE SYNTHESIS OF SOME BIDENTATE BISMUTH-CONTAINING LIGANDS

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Summary

The synthesis and properties including mass spectra of (*o*-diphenylphosphinophenyl)diphenylbismuthine, *o*-$C_6H_4(PPh_2)(BiPh_2)$ and (*o*-diphenylarsinophenyl)diphenylbismuthine, *o*-$C_6H_4(AsPh_2)(BiPh_2)$ are described. The failure of attempts to prepare α,ω-bis(diphenylbismuthino)alkanes is discussed.

Introduction

Compared with the quite vast organic chemistry of arsenic and antimony relatively few organobismuth compounds have been prepared [1], and many of the reported compounds are in need of re-examination by modern physical techniques. The use of organobismuthines in coordination chemistry has attracted little attention [1,2], due both to the very poor donor properties of bismuth and the weakness of the carbon—bismuth bond which makes decomposition of the ligand not uncommon. We recently prepared two bismuth—triarsine ligands [3,4] and examined their coordinating ability towards nickel(II), cobalt(II) [3,4] and palladium(II) [5] salts. Here we report attempts to prepare some bidentate ligands containing bismuth donors.

Experimental

Physical measurements were made as described previously [6]. Triphenylbismuth (Fluka Co.) was recrystallised from methanol m.p. 77—78°C (literature 78°C [7]). All preparations were conducted under a dinitrogen atmosphere.

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Chlorodiphenylbismuth *

Triphenylbismuth (87.8 g, 0.2 mol) and anhydrous bismuth trichloride (30.9 g, 0.1 mol) were dissolved separately in dry tetrahydrofuran (THF), the solutions decanted from any insoluble material and mixed. The THF was distilled off and the cream solid pumped dry. The solid appears to be indefinitely stable under dry dinitrogen but darkens in air, probably due to hydrolysis. M.p. 183—185°C (literature 183°C [8]). Analyses: Found C, 36.2; H, 3.1; Cl, 9.05. $C_{12}H_{10}$-BiCl calcd.: C, 36.3; H, 2.5; Cl, 8.95%. Mass spectrum: *m/e* 363, *I* 2% ($BiPh_2^+$), *m/e* 321, *I* 1% ($PhBi\overset{+}{C}l$), *m/e* 286, *I* 36.5% ($PhBi^+$), *m/e* 244, *I* 3% (BiCl), *m/e* 209, *I* 98% (Bi), *m/e* 54, *I* 100% (Ph—Ph).

(o-Diphenylarsinophenyl)diphenylbismuthine, o-$C_6H_4(AsPh_2)(BiPh_2)$

o-Bromophenyldiphenylarsine (20 g, 0.052 mol) was converted to the *o*-lithio derivative by reaction with n-butyllithium as described previously [9] and a slurry of chlorodiphenylbismuth (20.6 g, 0.052 mol) in dry THF (100 ml) was added dropwise with vigorous stirring. The light brown solution was stirred for 2 h and then hydrolysed by addition of aqueous ammonium chloride (100 ml). The organic layer was separated, the aqueous layer extracted with dichloromethane (100 ml), and the combined organic solutions dried over anhydrous sodium sulphate. The solution was filtered, rotatory evaporated to leave a brown oil, which was dissolved in dichloromethane (100 ml) and added to cold methanol (100 ml). On standing at 0°C for several days a white product separated. This was recrystallised from n-butanol. Yield 12 g, 35%. Analyses: Found, C, 54.0; H, 3.4. $C_{30}H_{24}AsBi$ calcd.: C, 54.1; H, 3.6%. M.p. 155—157°C. IR (cm^{-1}): 3030m, 1570w, 1560w, 1460m, 1420s, 1290w, 1170w, 1060m, 1045m, 1010m, 1000w, 985m, 745m, 725s, 715s, 680s, 480w, 460s, 435m, 415m, 330m, 310s, 220s$^+$, 215s$^+$.

(o-Diphenylphosphinophenyl)diphenylbismuthine, o-$C_6H_4(PPh_2)(BiPh_2)$

This was prepared in an essentially similar manner from *o*-bromophenyldiphenylphosphine (17.0 g, 0.05 mol), n-BuLi (0.05 mol) and Ph_2BiCl (20.6 g, 0.05 mol). Yield 9.5 g, 30%. Analyses: Found C, 58.0; H, 3.7. $C_{30}H_{34}PBi$ calcd.: C, 57.8; H, 3.9%. M.p. 168—170°C. IR (cm^{-1}): 3030m, 1575w, 1560w, 1470m, 1425s, 1300w, 1300w, 1170w, 1150w, 1080m, 1050m, 1020m, 1010w, 990s, 750w, 740s, 720s, 688s, 510s, 495s, 480s, 445s, 435s, 220s$^+$, 210s$^+$.

Attempted preparation of 1,3-bis(diphenylbismuthino)propane, $Ph_2Bi(CH_2)_3BiPh_2$

Chlorodiphenylbismuth (15.0 g, 0.038 mol) was suspended in liquid ammonia (200 ml) at —78°C and sodium (1.6 g, 0.07 g at.) was added rapidly with vigorous stirring to produce a green, and then a red solution. After stirring at —33°C for 1 h, 1,3-dibromopropane (3.1 g, 0.15 mol) was added, the ammonia was boiled off, and the residue was treated successively with diethyl ether (100 ml) and deoxygenated ammonium chloride solution (100 ml). The organic layer was separated, dried over anhydrous sodium sulphate, and the solvent removed in vacuo to yield a white oil, which was crystallised from methanol. Yield ~5 g. Analy-

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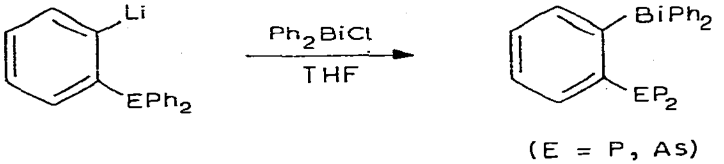
* Care, Ph_2BiCl is said to be a powerful sternutator. When handled in an adequate fume hood with due care, no irritant effects were noted.

ses: Found, C, 48.4; H, 3.4%; m.p. 74°C. Triphenylbismuth, Ph_3Bi, calcd.: C, 49.1; H, 3.4%; m.p. 78°C.

If the red solution was stirred for 4 h before addition of $Br(CH_2)_3Br$ work up yielded much black solid (Bi?) and an air-sensitive ether extract which yielded a small quantity of white powder on evaporation under nitrogen. Analyses: Found, C, 9.9; H, 1.5%. Decomposes >160°C.

Results and discussion

The reaction of chlorodiphenylbismuth with the appropriate *o*-lithiophenyl compound, *o*-$C_6H_4(EPh_2)Li$ (E = P, As) resulted in the formation of the bismuthine—phosphine and bismuthine—arsine compounds in low yield:



analogous to the preparations of other members of this series [10]. The alternative preparative route from *o*-$C_6H_4(EPh_2)Br$ and $NaBiPh_2$ is unattractive due to the instability of the latter. Since it appears that *o*-bromophenyldiphenylstibine cannot be successfully lithiated [11] we have been unable to devise a synthesis for the bismuthine—stibine, *o*-$C_6H_4(BiPh_2)(SbPh_2)$.

Ditertiary bismuthines are known only with acetylenic, $R_2BiC{\equiv}CBiR_2$ [12], or *p*-phenylene, *p*-$C_6H_4(BiPh_2)_2$ [7] backbones. Significantly, the latter was obtained from *p*-$C_6H_4Li_2$ and Ph_2BiCl, but not from $NaBiPh_2$ and *p*-$C_6H_4I_2$ [7]. In view of this, and of our previous failure to obtain *o*-phenylenebis(diphenylstibine) from $NaSbPh_2$ and *o*-$C_6H_4X_2$, it is most unlikely that *o*-phenylenebis(diphenylbismuthine) could be obtained from $NaBiPh_2$ and *o*-$C_6H_4X_2$ (X = halogen). Diarsines and distibines containing trimethylene backbones are not prone to elimination, unlike the dimethylene analogues which decompose by elimination of ethylene [1] and hence we felt that 1,3-bis(diphenylbismuthino)propane offered the best chance of obtaining a potentially chelating ditertiary bismuthine. Sodium diphenylbismuthide, $NaBiPh_2$, was prepared in liquid ammonia by the method of Gilman [13] and immediate treatment with 1,3-dibromopropane discharged the red colour of the anion, and a white solid was obtained on workup. However, analytical data, infrared and mass spectral examination of this revealed only the presence of triphenylbismuth. If the solution of $NaBiPh_2$ was allowed to stand for some time before treatment with the dihalide the products of the reaction consisted of much black solid (probably metallic bismuth) and an air-sensitive ether extract which yielded an unidentifiable white powder of low carbon content (<10%) on evaporation.

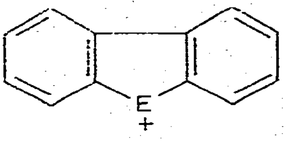
The failure to prepare $Ph_2Bi(CH_2)_3BiPh_2$ is in keeping with the lack of existing tertiary bismuthines with both alkyl and aryl substituents on the same bismuth atom, despite numerous attempts to prepare them [1]. In passing it may be noted that the instability of sodium diphenylbismuthide even at low temperatures in liquid ammonia makes it an unattractive synthetic reagent.

TABLE 1

MASS SPECTRA OF THE LIGANDS

o-$C_6H_4(PPh_2)(BiPh_2)$			o-$C_6H_4(AsPh_2)(BiPh_2)$		
Mass	Relative intensity	Fragment	Mass	Relative intensity	Fragment
624	21	$C_{30}H_{24}PBi$	668	28	$C_{30}H_{24}AsBi$
547	34	$C_{24}H_{19}PBi$	591	48	$C_{24}H_{19}AsBi$
470	3.5	$C_{18}H_{14}PBi$	514	4.5	$C_{18}H_{14}AsBi$
338	15	$C_{24}H_{19}P$	306	8.5	$C_{18}H_{15}As$
337	54	$C_{24}H_{18}P$	304	4	$C_{18}H_{13}As$
286	14.5	C_6H_5Bi	286	34	C_6H_5Bi
262	10	$C_{18}H_{15}P$	229	14	$C_{12}H_{10}As$
261	7.5	$C_{18}H_{14}P$	227	100	$C_{12}H_8As$
260	9	$C_{18}H_{13}P$	209	75	Bi
209	55	Bi	154	22.5	$C_{12}H_{10}$
185	3	$C_{12}H_{10}P$	152	67.5	$C_{12}H_8$, C_6H_5As
183	100	$C_{12}H_8P$	151	19	C_6H_4
154	12	$C_{12}H_{10}$	78	32	C_6H_6
152	10.5	$C_{12}H_8$	77	20	C_6H_5
108	6	C_6H_5P	75	3	As
107	9.5	C_6H_4P			
78	28	C_6H_6			
77	24	C_6H_5			

The infrared spectra of o-$C_6H_4(PPh_2)(BiPh_2)$ and o-$C_6H_4(AsPh_2)(BiPh_2)$ are generally similar to those of the other ligands in this series [14], and the absorptions marked ($^+$) are probably associated with the Bi—Ph system [15]. The mass spectral fragmentation patterns (Table 1) are also characteristic of ligands of this type [16]. As previously noted [16] the base peak is the heterocyclic ion, I, containing the lighter Group VB element. There are weak peaks due to Ph_3E^+ (E = P, As), but no evidence for $Ph_2EBiPh_2^+$. In view of the weakness of C—Bi bonds, in the mass spectrum [17] of Ph_3Bi the major peaks are PhBi (91%) and Bi (100%), whilst Ph_3Bi is only 0.1%, the relatively intense parent and P — Ph ions exhibited by these two ligands are unexpected. Other bismuth-containing ions correspond to P — $2Ph^+$, $PhBi^+$ and Bi^+. There is no evidence for Ph_2Bi^+ or the bismuth analogue of I.



(I)

(E = P, As)

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