

## Synthesis of New Bismuth Organometallic Compounds. Part II

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In a previous paper the authors reported the synthesis of new organometallic compounds of bismuth III, by direct reaction of  $\text{BiCl}_3$  with aliphatic amines namely: diethyl, butyl- and t-butylamine [1].

This paper is an extension of the previous work and reports the synthesis of a new aromatic amine bismuth III complex.

Diphenylamine reacts with bismuth trichloride in a more difficult way than the aliphatic amines, to produce a substitution product. There is no evidence in the literature about such a reaction. The only work found was the ionization of aromatic amines in the vacuum adsorption on active clays [2]. Within the study of coloured adsorption complexes of diphenylamine vapor on active clays, the  $\text{Ph}_2\text{NH}$  vapor adsorbed on  $\text{BiCl}_3$  was recorded and studied at  $-180^\circ\text{C}$ , where a purple colour was produced which vanished reversibly on heating to room temperature [2]. A blue colour is produced on the surface of the betonite powder fired at  $800^\circ\text{C}$  and outgassed, when diphenylamine vapor is passed over *in vacuo* at about  $150^\circ\text{C}$ . This colour does not disappear on heating, but is destroyed immediately by passing dry  $\text{NH}_3$  under 10 mm Hg [3]. In an attempt to understand the nature of these absorption spectrum shifts in the adsorption of aromatic amines on active clays, the previous authors explained that the yellow colour observed in adsorption on  $\text{BiCl}_3$  may be due to  $\text{BiCl}_2$ , known to form yellow or brown molecular compounds with aromatic molecules.

Furthermore, the yellow film of  $\text{Ph}_2\text{NH}$  on  $\text{BiCl}_2$  has an adsorption maximum at 420–430  $m\mu$ , which they have attributed to energy resonance between  $\text{Ph}_2\text{NH}^+$  and  $\text{BiCl}_2$  on account of the closeness of their absorption spectra and the resulting shift to longer wavelength. A similar resonance effect underlies the yellow coloring of solutions of  $\text{Ph}_2\text{NH}$  in liquid  $\text{SO}_2$  and on films of gaseous  $\text{SO}_2$  adsorbed on solid  $\text{Ph}_2\text{NH}$  at  $-80^\circ\text{C}$  [3].

These are the only examples found in the literature on the direct reaction of aromatic amines with  $\text{BiCl}_3$  in the vapor state. Therefore, this present work

is considered to be the first direct reaction of an aromatic amine in solution with bismuth trichloride, which exhibits many difficulties.

## Experimental

### Materials and Methods

Diphenylamine was technically pure; bismuth trichloride 99% pure was anhydrous, product of Merck. All solvents were purified and dried following the standard methods. The reactions were carried out in a standard apparatus consisting of 3-necked round bottom flasks equipped with a magnetic stirrer, condenser and  $\text{N}_2$  inlet under  $\text{N}_2$  atmosphere.

Infrared spectra were recorded on a Perkin-Elmer M 508 spectrophotometer,  $^1\text{H}$  NMR spectra on a Varian T-60, mass spectra at 70 eV on an AEIMS-25 double beam mass spectrometer and the microanalyses were carried out by Mikroanalytisches Labor, Pascher, Bonn, where  $\text{V}_2\text{O}_5$  was added for all C, H, N and Cl combustion.

### Procedure

Either 1.58 g or 3.16 g (0.005 or 0.01 M) of pure anhydrous  $\text{BiCl}_3$  was suspended in 25 ml dry absolute benzene in a three-necked flask equipped with a condenser,  $\text{N}_2$  inlet and a pressure equalizing funnel. To the above suspension, a solution of either 0.85 g or 1.70 g of diphenylamine (0.005 or 0.01 M) in absolute benzene was added dropwise for 1–2 h. During the reaction HCl was evolved. The reaction proceeds until no HCl is detected. After cooling, the white precipitate was filtered off, washed three times with  $\text{OCl}_4$ , three times with ether, successively, and dried. Melting point (m.p.) =  $153^\circ\text{C}$  (from  $\text{CHCl}_3$ ). Yield = 75%.

### The Blue Colour Phenomenon

Whenever the greyish product is exposed to light and air, a bluish green coloured layer is formed on the surface. This phenomenon, however, is especially noticeable if the reaction is carried out in the normal atmosphere, *i.e.* not under nitrogen. The green-bluish colour was also noticed on dissolving the product in methanol (m.p.  $142^\circ\text{C}$ ).

## Results and Discussion

The difficulties observed in the reaction of diphenylamine with  $\text{BiCl}_3$  compared to aliphatic amines, together with the blue colour phenomenon and the lack of literature on the above reaction is a challenging problem.

However the experimental elemental microanalysis (*Anal.* Found: C, 23.51; H, 2.20; N, 2.70; Bi, 44.3;

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Cl, 25.43% compared to Calc.: C, 23.27; H, 1.96; N, 3.00; Bi, 45.0; Cl, 26.73%) suggests the possible ionic structure:  $[(C_6H_5)_2NHBiCl_2]^+[C_6H_5NHBiCl_4]^- \cdot HCl$  or the formula  $C_{18}H_{18}N_2Bi_2Cl_7$ .

This ionic structure may also explain the bluish colour phenomenon, which was attributed to the ion  $(C_6H_5)_2NH^+$  which has an adsorption maxima at 420–430  $m\mu$  [3]. In our case, if the product is exposed to the atmosphere, two types of colour were noticed; a blue colour on the middle surface of the compound and a greenish colour on the edges of the compound.

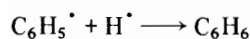
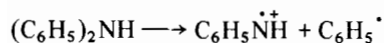
On the other hand, the yellowish green coloured crystals produced on dissolving the product in methanol may be attributed to a  $BiCl_2$  molecular product with an aromatic amine which is known to form such yellow colours with aromatic molecules [3].

The  $^1H$  NMR spectrum of the product in acetone  $d_6$  with TMS as an internal standard shows the  $C_6H_5$  protons at  $\delta = 7.3$  ppm and the singlet signal of NH proton at  $\delta = 6.2$  ppm in the expected ratio 5:1. The same trend appears in  $^1H$  NMR recorded in  $C_6D_6$  ( $C_6H_5$  protons at 7.15 ppm and NH proton at 6.7 ppm).

A third  $^1H$  NMR spectrum of the product recorded in  $CD_3CD$  gave a similar ratio of protons but different chemical shifts of signals ( $C_6H_5$  at 7.5 and NH at 5.8 ppm).

The IR spectrum shows the most characteristic bands at  $3560\text{ cm}^{-1}$  (NH stretching vibration),  $3390\text{ cm}^{-1}$  (complex vibration) and  $3040\text{ cm}^{-1}$  (C–H aromatic stretching vibration). The medium bands at 2600 and 2400, the weak bands at 2535 and 2460 and the shoulder at  $2285\text{ cm}^{-1}$  are attributed to complexation. The strong sharp bands at 1495 and  $1600\text{ cm}^{-1}$  are considered as skeletal C–C stretching vibrations as well as secondary aromatic amine vibrations. The band at  $1325\text{ cm}^{-1}$  is the C–N secondary aromatic amine. The bands at  $480\text{ cm}^{-1}$  and  $420\text{ cm}^{-1}$  and the shoulder at  $380\text{ cm}^{-1}$  could be attributed to Bi–N coordination bonding and that at  $315\text{ cm}^{-1}$  may be due to Bi–Cl bonding. Those strong bands at 690 and  $760\text{ cm}^{-1}$ , characteristic out of plane C–H ring bending vibrations [4], are shifted to 695 and  $780\text{ cm}^{-1}$  in the complex.

The mass spectrum (Table I) shows the important fragments. From the spectroscopic evidence and the microanalysis besides the expected explanation of the blue colour, one can suggest the following mechanism for the reaction:



or

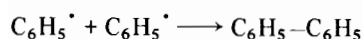
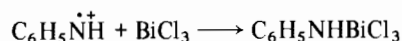
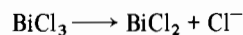
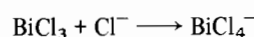


TABLE I. Mass Spectrum

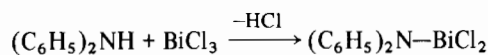
$m/e$	%	Assignment
36	47	HCl
51	25	$NH_2Cl$
77	18	$C_6H_5$
84	25	$NCl_2$
167	32	$C_6H_5-N-C_6H_4$
168	45	$C_6H_5-N-C_6H_5$
169	100	$C_6H_5-NH-C_6H_5$



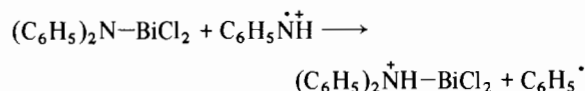
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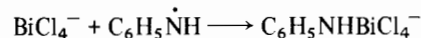
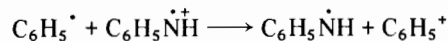
The substitution product from the following reaction



may react with the ion  $C_6H_5\dot{N}H$  as



and the radical could react as follows:



Therefore, this mechanism gives good support to the explanation of the colour and good proof for the suggested structural formula.

### Acknowledgements

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### References

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3. A. I. Sidrova and A. N. Terenin, *Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk*, 152 (1950).
4. C. J. Pouchert, 'The Aldrich Library of Infrared Spectra', 2nd edn., Aldrich Chemical Co. Inc., Milwaukee, U.S.A., 1978, p. 630F.