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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 $BiCl_3$ with aliphatic amines namely: diethyl, butyl- and t-butylamine [1].

This paper is an extention 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 Ph_2NH vapor adsorbed on $BiCl_3$ was recorded and studied at –180 °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 °C and outgassed, when diphenylamine vapor is passed over *in vacuo* at about 150 °C. This colour does not disappear on heating, but is destroyed immediately by passing dry 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 $BiCl_3$ may be due to $BiCl_2$, known to form yellow or brown molecular compounds with aromatic molecules.

Furthermore, the yellow film of Ph_2NH on $BiCl_2$ has an adsorption maximum at 420–430 mμ, which they have attributed to energy resonance between Ph_2NH^+ and $BiCl_2$ 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 Ph_2NH in liquid SO_2 and on films of gaseous SO_2 adsorbed on solid Ph_2NH at –80 °C [3].

These are the only examples found in the literature on the direct reaction of aromatic amines with $BiCl_3$ 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 N_2 inlet under N_2 atmosphere.

Infrared spectra were recorded on a Perkin-Elmer M 508 spectrophotometer, ^1H 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 V_2O_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 $BiCl_3$ was suspended in 25 ml dry absolute benzene in a three-necked flask equipped with a condenser, 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 OCl_4, three times with ether, successively, and dried. Melting point (m.p.) = 153 °C (from $CHCl_3$). 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 °C).

Results and Discussion

The difficulties observed in the reaction of diphenylamine with $BiCl_3$ 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 mμ [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 cm^{-1} (NH stretching vibration), 3390 cm^{-1} (complex vibration) and 3040 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 cm^{-1} are attributed to complexation. The strong sharp bands at 1495 and 1600 cm^{-1} are considered as skeletal C–C stretching vibrations as well as secondary aromatic amine vibrations. The band at 1325 cm^{-1} is the C–N secondary aromatic amine. The bands at 480 cm^{-1} and 420 cm^{-1} and the shoulder at 380 cm^{-1} could be attributed to Bi–N coordination bonding and that at 315 cm^{-1} may be due to Bi–Cl bonding. Those strong bands at 690 and 760 cm^{-1}, characteristic out of plane C–H ring bending vibrations [4], are shifted to 695 and 780 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:

$$(C_6H_5)_2NH \longrightarrow C_6H_5\overset{\bullet+}{N}H + C_6H_5^{\bullet}$$

$$C_6H_5^{\bullet} + H^{\bullet} \longrightarrow C_6H_6$$

or

$$C_6H_5^{\bullet} + C_6H_5^{\bullet} \longrightarrow C_6H_5{-}C_6H_5$$

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	$C_6H_5{-}NH{-}C_6H_5$

$$BiCl_3 \longrightarrow BiCl_2 + Cl^-$$

$$C_6H_5\overset{\bullet+}{N}H + BiCl_3 \longrightarrow C_6H_5NHBiCl_3$$

or

$$BiCl_3 + Cl^- \longrightarrow BiCl_4^-$$

The substitution product from the following reaction

$$(C_6H_5)_2NH + BiCl_3 \xrightarrow{-HCl} (C_6H_5)_2N{-}BiCl_2$$

may react with the ion $C_6H_5\overset{\bullet+}{N}H$ as

$$(C_6H_5)_2N{-}BiCl_2 + C_6H_5\overset{\bullet+}{N}H \longrightarrow (C_6H_5)_2\overset{+}{N}H{-}BiCl_2 + C_6H_5^{\bullet}$$

and the radical could react as follows:

$$C_6H_5^{\bullet} + C_6H_5\overset{\bullet+}{N}H \longrightarrow C_6H_5\overset{\bullet}{N}H + C_6H_5^{+}$$

$$BiCl_4^- + C_6H_5\overset{\bullet}{N}H \longrightarrow C_6H_5NHBiCl_4^-$$

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

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