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# Sterically crowded aryl bismuth compounds: synthesis and characterization of bis{2,4,6-tris(trifluoromethyl)phenyl}bismuth chloride and tris{2,4,6-tris(trifluoromethyl)phenyl}bismuth

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## Abstract

The reactions of $BiCl_3$ with 2,4,6-tris(trifluoromethyl)phenyl lithium ($LiR_f$) in ether solution in 1:2 and 1:3 ratios have led to the isolation of $Bi(R_f)_2Cl$ (**I**) and $Bi(R_f)_3$ (**II**). The hexane-soluble compounds have been spectroscopically and structurally characterized. **I**: monoclinic space group $P2_1/c$, $a = 8.816(2)$, $b = 30.459(6)$, $c = 8.817(2)$ Å, $\beta = 109.58(2)°$, $Z = 4$, $V = 2230.7(8)$ Å$^3$; **II**: monoclinic space group $P2_1/c$, $a = 11.769(2)$, $b = 17.029(3)$, $c = 16.213(3)$ Å, $\beta = 102.74(3)°$, $Z = 4$, $V = 3169.3(10)$ Å$^3$. Both compounds are monomeric in the solid state. Compound **II** is unstable in solution even under inert atmosphere producing $R_fH$. In the solid state the compound is stable in inert atmosphere but decomposes slowly upon exposure to air producing $R_fOH$ and $(R_f)_2O$. In the presence of $BiCl_3$, **II** undergoes exchange to produce **I** and another complex which is probably $Bi(R_f)Cl_2$.

## Introduction

The organic chemistry of bismuth has been examined for pharmaceutical applications and also for the utility of high oxidation state bismuth complexes in organic synthesis [1]. Aryl bismuth compounds are well known in the literature and have generally been prepared from Grignard or organolithium reagents [1]. In contrast to the lighter Group V elements where bulky substituents have been used to stabilize main group-main group multiple bonding [2], very little of this chemistry has been examined for bismuth. Of the triaryl bismuth complexes, only triphenylbismuth [3] and tris(mesityl)bismuth [4] ($Bi(Mes)_3$) have been structurally characterized. No structural data have been reported for diarylbismuth halide complexes. $BiPh_3$ and $Bi(Mes)_3$ are pyramidal as expected for the presence of the lone pair of electrons on bismuth. The lone pair, however, is diffuse, and in the related sterically crowded $Bi(NPh_2)_3$ [5] the bismuth atom is essentially planar.

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We have recently discovered an improved synthesis of 1,3,5-tris-(trifluoromethyl)benzene ($R_fH$) [6] which affords both a bulky and electron deficient ligand. Lithiation of $R_fH$ with n-butyl lithium produces the dimeric compound $[LiR_f(OEt_2)]_2$ [7] which we have structurally characterized [8] ($[LiR_f(OEt_2)]_2$ will hereafter be referred to simply as $LiR_f$). We wish to report here the reaction of this lithium compound with $BiCl_3$ which has been shown to produce $Bi(R_f)_2Cl$ (**I**) and $Bi(R_f)_3$ (**II**).

## Experimental

### General

All manipulations were performed under an inert atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. Diethyl ether was distilled from sodium/benzophenone and then $LiAlH_4$ prior to use. n-Hexane was distilled from sodium/benzophenone. Commercial n-butyl lithium (1.54 *M*) was used as received. Elemental analyses were obtained from Beller Mikroanalytisches Laboratorium, Göttingen.

Commercial $BiCl_3$ was refluxed with $SOCl_2$ for several hours. The $SOCl_2$ was then removed by distillation and the solid $BiCl_3$ dried under vacuum in a hot water bath. The solid was then dissolved in diethyl ether, filtered and the ether removed under vacuum in a hot water bath.

### Synthesis of I and II

The lithiation of $R_fH$ was carried out in approximately 100 mL of $Et_2O$ as previously described [7]. The amount of $R_fH$ used was calculated to be approximately 5–10% in excess of that required for reaction in a 2 : 1 or 3 : 1 stoichiometry with approximately 5 g of $BiCl_3$ in ca. 100 mL of $Et_2O$. In the case of the 3 : 1 reaction, the $BiCl_3$ was added dropwise to the $LiR_f$ solution while, for the 2 : 1 reaction, the $LiR_f$ solution was added to the $BiCl_3$ dissolved in $Et_2O$. After the addition, the mixtures were stirred overnight. In both cases mixtures of **I** and **II** were obtained. The solutions were filtered through Celite and cooled in a freezer to yield first a white precipitate of **I**. Removal of this precipitate followed by concentration and further cooling produced well-shaped yellow crystals of **II**. Yields were typically less than 10% for **I** and approximately 30% for **II**.

*Characterization data for I.* $^{19}F$ NMR($C_6D_6$): $-56.0$ (*ortho*) singlet, $-63.3$ (*para*) singlet, area ratio 2 : 1. $^1H$ NMR($C_6D_6$): 7.6 ppm, singlet. Mass spectrum: The parent ion was not observed but a peak corresponding to parent − F at 787 *m/z* was seen as was a mass of 771 *m/z* for parent − Cl. Other strong peaks observed were 209 *m/z* (Bi), 490 *m/z* ($BiR_f$) and 525 ($Bi(R_f)Cl$). M.p. 142–143°C. Analyses (%): Found: C, 26.7; H, 0.6. Calcd. for $BiC_{18}H_4F_{18}Cl$: C, 26.8; H, 0.5.

*Characterization data for II.* $^{19}F$ NMR ($C_6D_5CD_3$, ppm): room temp. $-56.7$ (*ortho*) singlet, $-63.3$ (*para*) singlet, area ratio 2:1; $-90$ °C, $-54.4$, $-59.2$, $-62.9$ , ratio 1 : 1 : 1. Coalescence temperature ca. $-55$°C. A signal of variable intensity was also present corresponding to $R_f-H$. $^1H$ NMR($C_6D_6$): 7.5 ppm, singlet. Mass spectrum: The parent ion was not observed but a peak corresponding to parent − F at 1033 *m/e* was seen as was a peak at mass 771 *m/z* for $Bi(R_f)_2$. Other strong peaks observed were 209 *m/z* (Bi) and 490 *m/z* ($BiR_f$). M.p. 132–134°C. Single crystals suitable for X-ray analysis were obtained by slow cooling of an n-hexane solution. Analyses (%) Found: C, 31.0; H, 0.7. Calcd. for $BiC_{27}H_6F_{27}$: C, 30.8; H, 0.6. IR spectrum (nujol mull, $cm^{-1}$) : 1621(s), 1580(w), 1297(s), 1290(s), 1196(s), 1152(s), 1135(s), 1118(s), 1080(s), 1000(m), 915(s), 851(m), 738(m), 604(s).

Crystals of **II** which were loaded into a small screw-cap vial in air were allowed to stand capped for several months on the laboratory shelf. After a couple of weeks, the crystals began to develop a glassy appearance and to smell of $R_fOH$ which has a characteristic pungent odor. Signals for $R_fOH$ were also detected in unsealed NMR samples which had been allowed to stand for several days. After a couple of months small clear, colorless needle- and plate-like crystals developed on the surface of the yellow bismuth residue. Attempted X-ray analysis of these crystals failed as all examined apparently were multiple. The mass spectrum, however, very clearly indicated this new compound to be $(R_f)_2O$ with the parent ion observed at 578 $m/z$ (m.p. 118–120°C). $^{19}F$: $\delta = -62.1$ (*para*), $-59.1$ (*ortho*) ppm; $^1H$ $\delta = 8.35$ ppm.

*Exchange reactions of II*

**II** (25 mg, 0.023 mmol) was placed in an NMR tube with a small amount of benzene-$d_6$ for use as lock. To this was added 1 mL of a solution of $BiCl_3$ (200 mg, 0.634 mmol) dissolved in tetrahydrofuran (25 mL, 0.025 m$M$) and the NMR tube was sealed. After three days the $^{19}F$ NMR spectrum showed peaks assignable to the $R_fH$ ($\delta = -64.0$ ppm), $Bi(R_f)_3$ ($\delta = -57.4$, $-64.4$ ppm; 2 : 1) and $Bi(R_f)_2Cl$ ($\delta = -56.7$, $-64.3$ ppm; 2 : 1). A very small signal ($\delta = -56.2$ ppm) in the same

Table 1

Crystallographic data collection parameters for **I** and **II**

| | | |
|---|---|---|
| Empirical Form. | $C_{18}H_4F_{18}ClBi$ | $C_{27}H_6F_{27}Bi$ |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ |
| Unit cell $a$ (Å) | 8.816(2) | 11.769(2) |
| $b$ (Å) | 30.459(6) | 17.029(3) |
| $c$ (Å) | 8.817(2) | 16.213(3) |
| $\beta$ (°) | 109.58(2) | 102.74(3) |
| $V$ (Å$^3$) | 2230.7(8) | 3169.3(10) |
| Z | 4 | 4 |
| Formula wt. (g/mol) | 806.6 | 1052.3 |
| Density (calc., g/cm$^3$) | 2.402 | 2.205 |
| Absorption coef. ($mm^{-1}$) | 8.152 | 5.720 |
| $F(000)$ | 1496 | 1976 |
| Color | pale yellow | yellow |
| Size (mm) | 0.4×0.4×0.3 | 0.4×0.3×0.3 |
| Diffractometer | Siemens-Stoe AED4 | Siemens–Stoe AED4 |
| Radiation | Mo-$K_\alpha$ | Mo-$K_\alpha$ |
| $2\theta$ range | 7.0–45° | 7.0–45° |
| Temp (K) | 294 | 294 |
| Reflections collected | 6050 | 5909 |
| Independent reflections | 2904($R_{int}$ = 6.95%) | 4091($R_{int}$ = 2.37%) |
| Observed reflections | 2652 | 3278 |
| $R$; $R_w$ (%, obs. data) | 4.6; 4.5 | 5.7; 5.5 |
| Data to parameters ratio | 7.7 : 1 | 5.9 : 1 |
| GOF | 1.57 | 1.91 |

region as the signals for the *ortho*-$CF_3$ groups was also seen, which is probably due to the presence of $Bi(R_f)Cl_2$ which has not yet been isolated. No signal ascribable to the *para*-$CF_3$ group was observed which is probably due to the small amount present or by accidental overlap with the signals from I and II.

### *X-ray diffraction analyses*

Crystals of I and II suitable for X-ray analysis were grown by cooling concentrated hexane solutions. X-ray intensity data were obtained on a Siemens-Stoe four-circle diffractometer over the range of $7 \leqslant 2\theta \leqslant 45°$ for both I and II using $2\theta$-$\omega$ scans. Data collection parameters are provided in Table 1. Data were

Table 2

Atomic coordinates $(\times 10^4)$ and equivalent isotropic displacement coefficients $(Å^2 \times 10^3)$ for I

| | *x* | *y* | *z* | *U*(eq) [a] |
|---|---|---|---|---|
| Bi(1) | 3552(1) | 8549(1) | 7923(1) | 44(1) |
| Cl(1) | 1913(3) | 8150(1) | 9251(3) | 80(1) |
| C(11) | 1542(9) | 8400(2) | 5467(10) | 39(3) |
| C(12) | 2015(9) | 8159(2) | 4393(10) | 39(3) |
| C(13) | 959(9) | 7990(3) | 2966(11) | 47(3) |
| C(14) | −681(10) | 8082(3) | 2626(11) | 50(3) |
| C(15) | −1199(10) | 8318(3) | 3645(12) | 55(4) |
| C(16) | −120(9) | 8479(2) | 5067(12) | 45(3) |
| C(12a) | 3762(10) | 8037(3) | 4732(12) | 54(4) |
| F(12a) | 4306(6) | 7781(2) | 6045(7) | 73(2) |
| F(12b) | 4063(7) | 7833(2) | 3571(8) | 87(3) |
| F(12c) | 4720(5) | 8399(2) | 5089(8) | 74(2) |
| C(14a) | −1826(13) | 7888(4) | 1057(14) | 74(5) |
| F(14a) | −2053(15) | 8144(5) | −101(12) | 211(7) |
| F(14b) | −1589(15) | 7540(3) | 745(15) | 296(9) |
| F(14c) | −3335(10) | 7920(4) | 984(14) | 184(6) |
| C(16a) | −879(9) | 8742(3) | 5993(13) | 62(4) |
| F(16a) | −1921(8) | 9044(2) | 5109(9) | 119(4) |
| F(16b) | −1821(8) | 8500(2) | 6623(10) | 98(4) |
| F(16c) | 92(5) | 8960(2) | 7274(7) | 73(2) |
| C(21) | 3127(8) | 9273(3) | 8634(11) | 44(3) |
| C(22) | 3272(9) | 9389(3) | 10187(10) | 44(3) |
| C(23) | 2892(9) | 9805(3) | 10570(12) | 50(3) |
| C(24) | 2427(9) | 10125(3) | 9389(14) | 55(4) |
| C(25) | 2394(9) | 10029(3) | 7852(12) | 53(4) |
| C(26) | 2755(10) | 9613(3) | 7476(11) | 48(3) |
| C(22a) | 3851(10) | 9075(3) | 11567(12) | 59(4) |
| F(22a) | 2645(6) | 8906(2) | 11993(7) | 76(3) |
| F(22b) | 4807(7) | 9284(2) | 12910(7) | 77(2) |
| F(22c) | 4707(6) | 8741(2) | 11330(6) | 66(2) |
| C(24a) | 1955(12) | 10563(3) | 9834(18) | 70(5) |
| F(24a) | 2057(23) | 10861(3) | 8873(19) | 232(12) |
| F(24b) | 617(10) | 10589(3) | 9872(19) | 204(9) |
| F(24c) | 2937(10) | 10727(3) | 11088(15) | 169(6) |
| C(26a) | 2765(13) | 9555(3) | 5801(12) | 64(4) |
| F(26a) | 3711(8) | 9226(2) | 5693(8) | 83(3) |
| F(26c) | 3250(10) | 9910(2) | 5218(9) | 111(4) |
| F(26b) | 1351(9) | 9450(2) | 4760(7) | 104(3) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$) for **II**

| | $x$ | $y$ | $z$ | $U$(eq) [a] |
|---|---|---|---|---|
| Bi | 6060(1) | 5598(1) | 2533(1) | 48(1) |
| C(11) | 7232(11) | 4539(7) | 3197(9) | 57(5) |
| C(12) | 7465(10) | 3986(7) | 2617(9) | 51(5) |
| C(13) | 8238(10) | 3358(7) | 2863(9) | 55(5) |
| C(14) | 8828(11) | 3303(8) | 3681(10) | 59(5) |
| C(15) | 8663(11) | 3851(8) | 4265(9) | 60(5) |
| C(16) | 7863(10) | 4459(7) | 4030(8) | 50(5) |
| C(12′) | 6883(13) | 4012(8) | 1670(10) | 66(6) |
| F(12a) | 5749(7) | 4148(5) | 1525(5) | 82(4) |
| F(12b) | 7332(8) | 4586(5) | 1303(5) | 85(4) |
| F(12c) | 7024(9) | 3360(5) | 1279(6) | 100(4) |
| C(14′) | 9731(11) | 2675(8) | 3919(8) | 87(8) |
| F(14a) | 9700(9) | 2364(7) | 4654(7) | 135(6) |
| F(14b) | 9610(8) | 2094(5) | 3387(7) | 105(4) |
| F(14c) | 10788(8) | 2944(5) | 3994(9) | 135(6) |
| C(16′) | 7792(13) | 5019(10) | 4744(11) | 71(6) |
| F(16a) | 8100(10) | 4690(7) | 5492(6) | 124(5) |
| F(16b) | 8461(9) | 5641(6) | 4720(7) | 108(5) |
| F(16c) | 6748(8) | 5337(5) | 4683(6) | 85(4) |
| C(21) | 4103(10) | 5192(6) | 2387(8) | 44(4) |
| C(22) | 3307(10) | 5651(7) | 1783(8) | 52(5) |
| C(23) | 2122(11) | 5495(8) | 1594(10) | 66(6) |
| C(24) | 1710(11) | 4874(8) | 2006(10) | 64(6) |
| C(25) | 2451(12) | 4404(8) | 2540(10) | 66(6) |
| C(26) | 3624(10) | 4572(8) | 2730(8) | 52(5) |
| C(22′) | 3690(14) | 6328(9) | 1285(12) | 74(7) |
| F(22a) | 2823(9) | 6743(6) | 881(8) | 133(6) |
| F(22b) | 4268(9) | 6064(6) | 733(6) | 97(4) |
| F(22c) | 4412(8) | 6820(5) | 1780(6) | 86(4) |
| C(24′) | 418(14) | 4713(7) | 1768(10) | 105(10) |
| F(24a) | −45(16) | 4909(21) | 2399(17) | 178(14) |
| F(24b) | −192(14) | 5090(20) | 1125(21) | 193(15) |
| F(24c) | 155(12) | 3971(8) | 1643(22) | 125(9) |
| F(24d) | 82(36) | 4387(47) | 1031(26) | 178(14) |
| F(24e) | 110(37) | 4247(43) | 2312(36) | 193(15) |
| F(24f) | −180(37) | 5353(16) | 1754(53) | 125(9) |
| C(26′) | 4329(14) | 3995(9) | 3297(11) | 70(6) |
| F(26a) | 3748(7) | 3559(6) | 3742(7) | 117(5) |
| F(26b) | 4897(9) | 3484(5) | 2901(7) | 105(4) |
| F(26c) | 5183(8) | 4304(5) | 3885(6) | 87(4) |
| C(31) | 6321(10) | 6633(7) | 3521(8) | 49(5) |
| C(32) | 5577(9) | 6940(7) | 4007(8) | 44(4) |
| C(33) | 5824(11) | 7610(8) | 4467(8) | 56(5) |
| C(34) | 6828(11) | 8037(7) | 4509(7) | 52(5) |
| C(35) | 7586(11) | 7743(7) | 4044(8) | 51(5) |
| C(36) | 7361(11) | 7066(8) | 3564(8) | 58(5) |
| C(32′) | 4422(13) | 6556(8) | 4018(10) | 63(6) |
| F(32a) | 3970(7) | 6830(5) | 4662(5) | 79(3) |
| F(32b) | 4510(7) | 5769(4) | 4127(6) | 75(3) |
| F(32c) | 3626(7) | 6690(5) | 3320(6) | 75(3) |
| C(34′) | 7098(10) | 8736(7) | 5016(8) | 75(7) |
| F(34a) | 8186(12) | 8957(16) | 5157(26) | 143(11) |
| F(34b) | 6855(36) | 8685(13) | 5760(12) | 121(9) |

Table 3 (continued)

| | $x$ | $y$ | $z$ | $U(\mathrm{eq})$ [a] |
|---|---|---|---|---|
| F(34c) | 6509(28) | 9343(8) | 4668(17) | 125(9) |
| F(34d) | 6186(22) | 9126(38) | 5123(51) | 143(11) |
| F(34e) | 7708(71) | 9240(31) | 4690(33) | 121(9) |
| F(34f) | 7689(70) | 8620(22) | 5788(20) | 125(9) |
| C(36′) | 8253(13) | 6863(11) | 3062(12) | 77(7) |
| F(36a) | 7969(13) | 7134(7) | 2297(9) | 147(7) |
| F(36b) | 9286(8) | 7164(7) | 3375(9) | 152(7) |
| F(36c) | 8438(7) | 6108(5) | 2987(7) | 102(5) |

[a] Equivalent isotropic $U$ defined as one-third of the trace of the orthogonalized $U_{ij}$ tensor.

corrected for Lorentz/polarization effects and for absorption (empirical psi scans). The structures were solved using the direct methods routine of SHELXS86 [9]. Full matrix least-squares refinements minimized the function $\Sigma w(F_o - F_c)$ [10]. Hydrogen atoms were included in calculated positions using a riding model with fixed isotropic $U$ value. Both compounds showed disorder in the *para*-$CF_3$ groups. For **II**, the C–F and F–F distances were restrained to be equal for all of the *para*-$CF_3$ groups. After applying these restraints, difference maps showed peaks corresponding to two disordered F positions. This disorder did not prove resolvable for any of the $CF_3$ groups of **I**, but it was possible to include a second set of F positions for two of the *para*-$CF_3$ groups in **II**. The populations of these sets were refined, and the major components for groups centered about C(24) and C(34) were found to be 64 and 57%, respectively. The disordered component about C(14) was located but had only a small population (5%) and was not included in the final refinements. The thermal parameters of the fluorine atoms of the minor components were also restrained to be equal to those of the corresponding, opposing fluorine atoms of the

Table 4

Bond distances (Å) for **I**

| | | | |
|---|---|---|---|
| Bi(1)–Cl(1) | 2.463(3) | Bi(1)–C(11) | 2.338(7) |
| Bi(1)–C(21) | 2.356(8) | C(11)–C(12) | 1.368(12) |
| C(11)–C(16) | 1.408(10) | C(12)–C(13) | 1.390(10) |
| C(12)–C(12a) | 1.514(11) | C(13)–C(14) | 1.403(12) |
| C(14)–C(15) | 1.345(15) | C(14)–C(14a) | 1.531(13) |
| C(15)–C(16) | 1.385(12) | C(16)–C(16a) | 1.456(15) |
| C(12a)–F(12a) | 1.345(11) | C(12a)–F(12b) | 1.298(13) |
| C(12a)–F(12c) | 1.361(10) | C(14a)–F(14a) | 1.246(17) |
| C(14a)–F(14b) | 1.132(16) | C(14a)–F(14c) | 1.314(15) |
| C(16a)–F(16a) | 1.349(11) | C(16a)–F(16b) | 1.359(14) |
| C(16a)–F(16c) | 1.343(11) | C(21)–C(22) | 1.378(13) |
| C(21)–C(26) | 1.413(12) | C(22)–C(23) | 1.382(12) |
| C(22)–C(22a) | 1.497(12) | C(23)–C(24) | 1.384(13) |
| C(24)–C(25) | 1.378(16) | C(24)–C(24a) | 1.488(14) |
| C(25)–C(26) | 1.374(12) | C(26)–C(26a) | 1.491(15) |
| C(22a)–F(22a) | 1.343(12) | C(22a)–F(22b) | 1.360(10) |
| C(22a)–F(22c) | 1.323(11) | C(24a)–F(24a) | 1.266(19) |
| C(24a)–F(24b) | 1.194(16) | C(24a)–F(24c) | 1.257(15) |
| C(26a)–F(26a) | 1.328(13) | C(26a)–F(26c) | 1.326(13) |
| C(26a)–F(26b) | 1.316(11) | | |

Table 5

Bond angles ( ° ) for **I**

| | | | |
|---|---|---|---|
| Cl(1)-Bi(1)-C(11) | 87.8(2) | Cl(1)-Bi(1)-C(21) | 99.5(2) |
| C(11)-Bi(1)-C(21) | 106.9(3) | Bi(1)-C(11)-C(12) | 115.7(5) |
| Bi(1)-C(11)-C(16) | 126.9(7) | C(12)-C(11)-C(16) | 116.8(7) |
| C(11)-C(12)-C(13) | 123.9(7) | C(11)-C(12)-C(12a) | 121.4(7) |
| C(13)-C(12)-C(12a) | 114.6(8) | C(12)-C(13)-C(14) | 116.7(8) |
| C(13)-C(14)-C(15) | 121.4(7) | C(13)-C(14)-C(14a) | 115.8(9) |
| C(15)-C(14)-C(14a) | 122.8(8) | C(14)-C(15)-C(16) | 120.7(8) |
| C(11)-C(16)-C(15) | 120.5(9) | C(11)-C(16)-C(16a) | 126.1(7) |
| C(15)-C(16)-C(16a) | 113.4(7) | C(12)-C(12a)-F(12a) | 111.0(8) |
| C(12)-C(12a)-F(12b) | 115.2(7) | F(12a)-C(12a)-F(12b) | 107.0(7) |
| C(12)-C(12a)-F(12c) | 111.0(7) | F(12a)-C(12a)-F(12c) | 104.9(6) |
| F(12b)-C(12a)-F(12c) | 107.2(9) | C(14)-C(14a)-F(14a) | 112.0(11) |
| C(14)-C(14a)-F(14b) | 117.5(10) | F(14a)-C(14a)-F(14b) | 112.2(14) |
| C(14)-C(14a)-F(14c) | 111.5(11) | F(14a)-C(14a)-F(14c) | 91.8(11) |
| F(14b)-C(14a)-F(14c) | 108.9(12) | C(16)-C(16a)-F(16a) | 113.8(9) |
| C(16)-C(16a)-F(16b) | 113.0(8) | F(16a)-C(16a)-F(16b) | 102.4(7) |
| C(16)-C(16a)-F(16c) | 117.4(7) | F(16a)-C(16a)-F(16c) | 105.5(8) |
| F(16b)-C(16a)-F(16c) | 103.1(9) | Bi(1)-C(21)-C(22) | 122.3(6) |
| Bi(1)-C(21)-C(26) | 120.8(7) | C(22)-C(21)-C(26) | 116.9(7) |
| C(21)-C(22)-C(23) | 121.9(8) | C(21)-C(22)-C(22a) | 122.4(8) |
| C(23)-C(22)-C(22a) | 115.7(8) | C(22)-C(23)-C(24) | 119.8(9) |
| C(23)-C(24)-C(25) | 119.6(8) | C(23)-C(24)-C(24a) | 118.1(11) |
| C(25)-C(24)-C(24a) | 122.3(10) | C(24)-C(25)-C(26) | 120.2(8) |
| C(21)-C(26)-C(25) | 121.2(9) | C(21)-C(26)-C(26a) | 123.5(8) |
| C(25)-C(26)-C(26a) | 115.3(8) | C(22)-C(22a)-F(22a) | 112.7(7) |
| C(22)-C(22a)-F(22b) | 110.5(7) | F(22a)-C(22a)-F(22b) | 104.7(8) |
| C(22)-C(22a)-F(22c) | 114.8(9) | F(22a)-C(22a)-F(22c) | 107.3(7) |
| F(22b)-C(22a)-F(22c) | 106.1(6) | C(24)-C(24a)-F(24a) | 112.2(14) |
| C(24)-C(24a)-F(24b) | 115.6(9) | F(24a)-C(24a)-F(24b) | 105.3(13) |
| C(24)-C(24a)-F(24c) | 114.7(9) | F(24a)-C(24a)-F(24c) | 96.9(10) |
| F(24b)-C(24a)-F(24c) | 110.2(15) | C(26)-C(26a)-F(26a) | 111.9(7) |
| C(26)-C(26a)-F(26c) | 113.4(8) | F(26a)-C(26a)-F(26c) | 107.2(10) |
| C(26)-C(26a)-F(26b) | 113.6(10) | F(26a)-C(26a)-F(26b) | 103.8(8) |
| F(26c)-C(26a)-F(26b) | 106.3(8) | | |

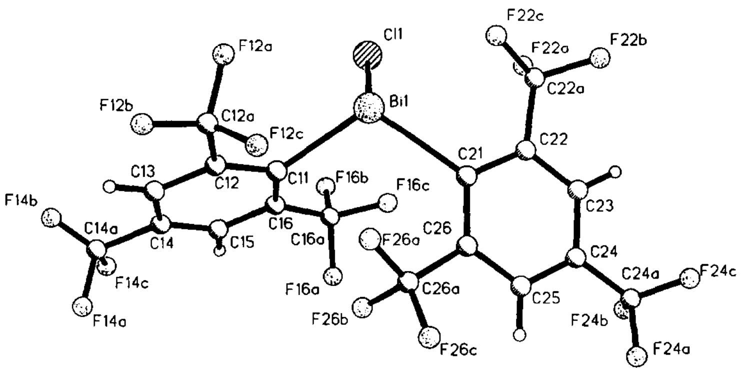

Fig. 1. Molecular structure and atom numbering scheme for I.

Table 6

Bond distances ( ° ) for **II**

| | | | |
|---|---|---|---|
| Bi–C(11) | 2.379(13) | Bi–C(21) | 2.367(12) |
| Bi–C(31) | 2.356(13) | C(11)–C(12) | 1.401(20) |
| C(11)–C(16) | 1.398(18) | C(12)–C(13) | 1.403(17) |
| C(12)–C(12′) | 1.538(20) | C(13)–C(14) | 1.357(19) |
| C(14)–C(15) | 1.373(21) | C(14)–C(14′) | 1.497(18) |
| C(15)–C(16) | 1.396(18) | C(16)–C(16′) | 1.516(22) |
| C(12′)–F(12a) | 1.324(17) | C(12′)–F(12b) | 1.314.(18) |
| C(12′)–F(12c) | 1.307(17) | C(14′)–F(14a) | 1.311(18) |
| C(14′)–F(14b) | 1.301(16) | C(14′)–F(14c) | 1.306(16) |
| C(16′)–F(16a) | 1.311(19) | C(16′)–F(16b) | 1.327(19) |
| C(16′)–F(16c) | 1.327(18) | C(21)–C(22) | 1.429(16) |
| C(21)–C(26) | 1.370(18) | C(22)–C(23) | 1.386(17) |
| C(22)–C(22′) | 1.533(22) | C(23)–C(24) | 1.394(21) |
| C(24)–C(25) | 1.348(19) | C(24)–C(24′) | 1.509(20) |
| C(25)–C(26) | 1.377(18) | C(26)–C(26′) | 1.471(19) |
| C(22′)–F(22a) | 1.294(18) | C(22′)–F(22b) | 1.316(22) |
| C(22′)–F(22c) | 1.329(18) | C(24′)–F(24a) | 1.304(33) |
| C(24′)–F(24b) | 1.300(33) | C(24′)–F(24c) | 1.306(19) |
| C(24′)–F(24d) | 1.298(54) | C(24′)–F(24e) | 1.296(67) |
| C(24′)–F(24f) | 1.296(37) | C(26′)–F(26a) | 1.325(21) |
| C(26′)–F(26b) | 1.344(20) | C(26′)–F(26c) | 1.331(17) |
| C(31)–C(32) | 1.401(19) | C(31)–C(36) | 1.419(18) |
| C(32)–C(33) | 1.360(17) | C(32)–C(32′) | 1.513(19) |
| C(33)–C(34) | 1.376(18) | C(34)–C(35) | 1.382(20) |
| C(34)–C(34′) | 1.442(17) | C(35)–C(36) | 1.383(18) |
| C(36)–C(36′) | 1.503(24) | C(32′)–F(32a) | 1.355(20) |
| C(32′)–F(32b) | 1.353(15) | C(32′)–F(32c) | 1.320(16) |
| C(34′)–F(34a) | 1.305(19) | C(34′)–F(34b) | 1.302(30) |
| C(34′)–F(34c) | 1.302(24) | C(34′)–F(34d) | 1.305(47) |
| C(34′)–F(34e) | 1.303(70) | C(34′)–F(34f) | 1.306(39) |
| C(36′)–F(36a) | 1.296(23) | C(36′)–F(36b) | 1.315(18) |
| C(36′)–F(36c) | 1.314(21) | | |

major component. The C–F and F–F distances after final refinement were 1.308(6) and 2.081(10) Å, respectively. For **II**, only the major sets of F atoms of the disordered $CF_3$ groups are shown. Atomic positions, bond distance and angle data are given in Tables 2–7. Diagrams of **I** and **II** are found in Figs. 1 and 2, respectively.

## Results and discussion

The reaction of $LiR_f$ with $BiCl_3$ produces compounds **I** and **II** as a mixture which may be separated with difficulty by fractional crystallization from ether or n-hexane. Compound **I** is generally less soluble than compound **II** in these solvents. The separation is complicated by the instability of **II**. The lithium aryl reagent has been shown to react with a number of post-transition metal halides to produce $M(R_f)_2$ species [7] but this is the first report where three of these bulky ligands have been attached to a single atom.

Unlike most tri-aryl bismuth compounds, **II** decomposes slowly in solution and upon exposure to air. $^{19}F$ spectra of **II**, taken shortly after dissolving in benzene-$d_6$

Table 7

Bond angles (°) for **II**

| | | | |
|---|---|---|---|
| C(11)-Bi-C(21) | 106.1(4) | C(11)-Bi-C(31) | 106.5(4) |
| C(21)-Bi-C(31) | 105.3(4) | Bi-C(11)-C(12) | 112.7(9) |
| Bi-C(11)-C(16) | 130.0(10) | C(12)-C(11)-C(16) | 116.2(11) |
| C(11)-C(12)-C(13) | 122.2(12) | C(11)-C(12)-C(12′) | 122.7(11) |
| C(13)-C(12)-C(12′) | 115.1(12) | C(12)-C(13)-C(14) | 119.3(13) |
| C(13)-C(14)-C(15) | 120.5(12) | C(13)-C(14)-C(14′) | 118.9(13) |
| C(15)-C(14)-C(14′) | 120.5(12) | C(14)-C(15)-C(16) | 120.4(12) |
| C(11)-C(16)-C(15) | 121.2(12) | C(11)-C(16)-C(16′) | 124.8(11) |
| C(15)-C(16)-C(16′) | 114.0(11) | C(12)-C(12′)-F(12a) | 113.1(13) |
| C(12)-C(12′)-F(12b) | 109.8(11) | F(12a)-C(12′)-F(12b) | 106.2(11) |
| C(12)-C(12′)-F(12c) | 112.6(11) | F(12a)-C(12′)-F(12c) | 107.0(11) |
| F(12b)-C(12′)-F(12c) | 107.7(14) | C(14)-C(14′)-F(14a) | 111.3(13) |
| C(14)-C(14′)-F(14b) | 113.8(10) | F(14a)-C(14′)-F(14b) | 105.9(12) |
| C(14)-C(14′)-F(14c) | 112.4(11) | F(14a)-C(14′)-F(14c) | 105.9(11) |
| F(14b)-C(14′)-F(14c) | 106.9(12) | C(16)-C(16′)-F(16a) | 112.7(13) |
| C(16)-C(16′)-F(16b) | 110.3(14) | F(16a)-C(16′)-F(16b) | 108.9(12) |
| C(16)-C(16′)-F(16c) | 113.9(11) | F(16a)-C(16′)-F(16c) | 107.8(14) |
| F(16b)-C(16′)-F(16c) | 102.6(12) | Bi-C(21)-C(22) | 112.6(8) |
| Bi-C(21)-C(26) | 131.5(8) | C(22)-C(21)-C(26) | 115.7(10) |
| C(21)-C(22)-C(23) | 121.5(12) | C(21)-C(22)-C(22′) | 123.3(11) |
| C(23)-C(22)-C(22′) | 115.2(11) | C(22)-C(23)-C(24) | 118.6(12) |
| C(23)-C(24)-C(25) | 121.0(12) | C(23)-C(24)-C(24′) | 116.9(12) |
| C(25)-C(24)-C(24′) | 121.9(13) | C(24)-C(25)-C(26) | 119.6(13) |
| C(21)-C(26)-C(25) | 123.5(11) | C(21)-C(26)-C(26′) | 122.8(11) |
| C(25)-C(26)-C(26′) | 113.6(12) | C(22)-C(22′)-F(22a) | 112.7(13) |
| C(22)-C(22′)-F(22b) | 110.9(12) | F(22a)-C(22′)-F(22b) | 108.1(15) |
| C(22)-C(22′)-F(22c) | 112.3(14) | F(22a)-C(22′)-F(22c) | 106.9(12) |
| F(22b)-C(22′)-F(22c) | 105.6(13) | C(24)-C(24′)-F(24a) | 108.9(15) |
| C(24)-C(24′)-F(24b) | 117.6(17) | F(24a)-C(24′)-F(24b) | 104.5(21) |
| C(24)-C(24′)-F(24c) | 114.0(13) | F(24a)-C(24′)-F(24c) | 104.2(23) |
| F(24b)-C(24′)-F(24c) | 106.4(21) | C(24)-C(24′)-F(24d) | 113.5(24) |
| C(24)-C(24′)-F(24e) | 110.8(21) | F(24d)-C(24′)-F(24e) | 106.9(41) |
| C(24)-C(24′)-F(24f) | 111.3(20) | F(24d)-C(24′)-F(24f) | 106.8(45) |
| F(24e)-C(24′)-F(24f) | 107.2(44) | C(26)-C(26′)-F(26a) | 115.3(13) |
| C(26)-C(26′)-F(26b) | 113.9(14) | F(26a)-C(26′)-F(26b) | 105.5(12) |
| C(26)-C(26′)-F(26c) | 114.6(12) | F(26a)-C(26′)-F(26c) | 103.3(13) |
| F(26b)-C(26′)-F(26c) | 102.8(12) | Bi-C(31)-C(32) | 131.1(8) |
| Bi-C(31)-C(36) | 113.8(9) | C(32)-C(31)-C(36) | 114.7(11) |
| C(31)-C(32)-C(33) | 122.5(11) | C(31)-C(32)-C(32′) | 121.3(11) |
| C(33)-C(32)-C(32′) | 116.1(12) | C(32)-C(33)-C(34) | 123.2(13) |
| C(33)-C(34)-C(35) | 115.6(11) | C(33)-C(34)-C(34′) | 122.9(13) |
| C(35)-C(34)-C(34′) | 121.5(12) | C(34)-C(35)-C(36) | 122.9(12) |
| C(31)-C(36)-C(35) | 121.1(13) | C(31)-C(36)-C(36′) | 123.5(12) |
| C(35)-C(36)-C(36′) | 115.3(13) | C(32)-C(32′)-F(32a) | 111.5(11) |
| C(32)-C(32′)-F(32b) | 112.7(11) | F(32a)-C(32′)-F(32b) | 105.8(12) |
| C(32)-C(32′)-F(32c) | 112.6(12) | F(32a)-C(32′)-F(32c) | 106.1(12) |
| F(32b)-C(32′)-F(32c) | 107.6(11) | C(34)-C(34′)-F(34a) | 114.9(18) |
| C(34)-C(34′)-F(34b) | 114.0(15) | F(34a)-C(34′)-F(34b) | 105.4(26) |
| C(34)-C(34′)-F(34c) | 112.3(13) | F(34a)-C(34′)-F(34c) | 104.8(20) |
| F(34b)-C(34′)-F(34c) | 104.5(21) | C(34)-C(34′)-F(34d) | 114.2(28) |
| F(34a)-C(34′)-F(34d) | 129.4(29) | C(34)-C(34′)-F(34e) | 112.6(26) |
| F(34d)-C(34′)-F(34e) | 105.2(45) | C(34)-C(34′)-F(34f) | 115.1(19) |
| F(34d)-C(34′)-F(34f) | 103.3(48) | F(34e)-C(34′)-F(34f) | 105.3(40) |
| C(36)-C(36′)-F(36a) | 111.9(14) | C(36)-C(36′)-F(36b) | 113.5(15) |
| F(36a)-C(36′)-F(36b) | 104.6(16) | C(36)-C(36′)-F(36c) | 115.2(15) |
| F(36a)-C(36′)-F(36c) | 105.8(15) | F(36b)-C(36′)-F(36c) | 105.0(13) |

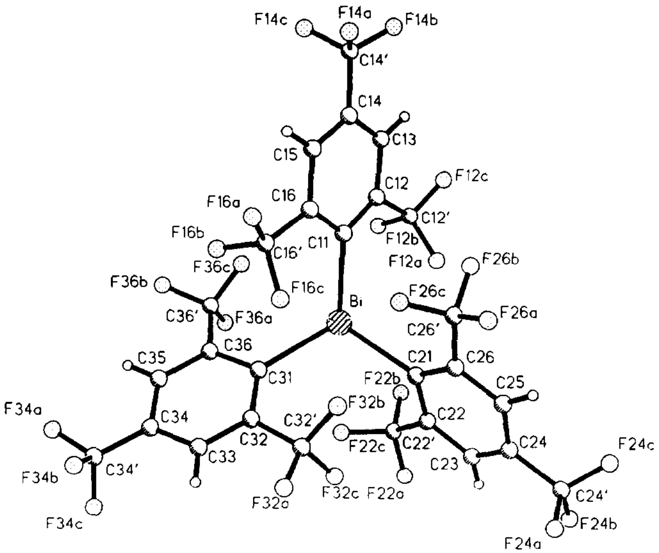

Fig. 2. Molecular structure and atom numbering scheme for **II**. Only the major components of the disordered *para*-$CF_3$ groups are shown.

show significant amounts of $R_fH$. Upon standing in air, solid **II** produces $R_fOH$ [10] and $(R_f)_2O$ which probably arise via an oxidation or oxidation/hydrolysis of the bismuth compound. As with most other main group alkyls, simple hydrolysis of organobismuth compounds would be expected to proceed according to eq. (1) rather than producing oxygen-containing organic compounds. Oxidation of $BiEt_3$ has been examined and among the products of that reaction were found $Et_2O$ and $Et_2O_2$ [12]. One supposes as an intermediate a mixed bismuth aryloxy/aryl compound which reductively eliminates the ether. Such an intermediate has not yet been observed.

$$BiR_3 + 3H_2O \rightarrow Bi(OH)_3 + 3RH \qquad (1)$$

The single-crystal X-ray structures of **I** and **II** have been studied. Both molecules may be described as pyramidal and no short intermolecular contacts are observed. The Bi–C bond distances are 2.338(7) to 2.356(8) Å for **I** and range from 2.356(13) to 2.379(13) Å for **II**. These distances are slightly longer than those found for $BiMe_3$ (2.264(4) Å, electron diffraction) [13], $BiPh_3$ (2.24 Å) [3], $Bi_2Ph_4$ (2.28(2); 2.28(6) Å) [14], $[Fe(CO)_4BiMe]_2$ (2.28(1) Å) [15], $[Fe(CO)_4BiPh]_2$ (2.27(2) Å) [16], $Fe(CO)_4\{BiPh_2\}_2$ (2.24(2) Å) [16], $Co(CO)_3(PPh_3)\{BiPh_2\}$ (2.25(2), 2.28(2) Å) [17] and $Bi(Mes)_3$ (2.24(2) to 2.32(1) Å) [4], reflecting the steric demands of the $R_f$ ligand. This is also seen in the sums of the angles about Bi which are 317.9° for **II** but only 290.1° for $BiMe_3$, 282° for $BiPh_3$, 308.1° for $Bi(Mes)_3$. The presence of the less-sterically demanding Cl in **I** allows these angles to relax to a more common total of 294.2°. The Bi–Cl distance of 2.463(3) Å is comparable to 2.48(2) Å found in $BiCl_3$ [18] and in the $BiCl_3$/arene $\pi$-complexes recently examined by Schmidbaur et al. (arene = mesitylene, 2.465(5) to 2.489(4) Å; hexamethylbenzene, 2.404(8) to 2.438(8) Å) [19].

In the $^{19}F$ NMR spectrum at room temperature only one signal is seen for all of the fluorine atoms of the inequivalent *ortho* groups. Upon cooling to −90°C two separate *ortho*-$CF_3$ signals are observed so that rotation around the Bi–C bonds must be frozen out by this temperature. Using the peak separation and the approximate coalescence temperature of −55°C, a barrier to rotation of 9.2 kcal/mol can be calculated from the equation

$$\Delta G_c^{\ddagger} = 2.3RT_c(10.32 + \log(T_c/k_c))$$

where $k_c = \pi\Delta\nu/2^{1/2}$, $T_c$ is the coalescence temperature, and $\Delta\nu$ is the separation in hertz of the two exchanging peaks at the slow exchange limit. No indication of further splitting of the *ortho* peaks was observed to the lowest temperature examined even though the F atoms are not equivalent. This is not surprising considering the known propensity for $CF_3$ groups to rotate.

Bismuth aryl compounds are known to undergo facile exchange with bismuth trihalides to yield mixed halo-aryl complexes [1]. It was, therefore, of interest to investigate if the bulkiness of the $R_f$ ligand would deter the exchange process. When bismuth trichloride and **II** were mixed in an NMR tube in THF (with a small amount of deuterated benzene to serve as lock) and allowed to stand for a couple of days, signals appeared in the $^{19}F$ NMR spectrum which were attributable to **I** and **II**. Another very weak signal appeared at lower field in the region expected for the *ortho*-$CF_3$ groups, which is almost certainly due to the presence of a small amount of $Bi(R_f)Cl_2$. The $^{19}F$ signals for the *ortho*-$CF_3$ groups shift consistently with substitution being −57.36 ppm for **II**, −56.78 ppm for **I** and −56.20 ppm for the supposed $Bi(R_f)Cl_2$.

## Summary

Bismuth chloride reacts with the bulky aryl lithium reagent, $[LiR_f \cdot OEt_2]_2$, to produce the corresponding diarylchloro and triaryl bismuth complexes. The latter compound is the first example known where three of the bulky $R_f$ ligands are bonded to the same metal atom. The triaryl complex is unstable in solution and in the solid state when exposed to air, probably owing to the steric crowding around the main group atom. Furthermore, the bulkiness of the ligand does not inhibit exchange reactions between the aryl bismuth complexes and $BiCl_3$.

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## Supplementary material

Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, W-7514 Eggenstein-Leopoldshafen 2 (Germany) on quoting the depository number 54683, the names of the authors and the journal citation.

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