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Preliminary communication

Diphenyl(trifluoromethyl)bismuth and phenylbis(trifluoromethyl)bismuth—new organoperfluoroalkyl derivatives of trivalent bismuth

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Abstract

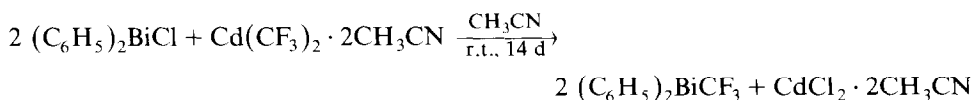
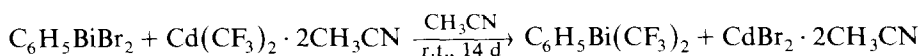
Diphenyl(trifluoromethyl)bismuth and phenylbis(trifluoromethyl)bismuth have been synthesized from $\text{Cd}(\text{CF}_3)_2 \cdot 2\text{CH}_3\text{CN}$ and the corresponding phenylbismuth halides. The reactions of the new compounds are similar to those of tris(perfluoroorgano)bismuth compounds and mixed phenyl-alkyl bismuth derivatives.

Tris(perfluoroorgano)bismuth derivatives are available in good yields from the reactions of BiCl_3 or BiBr_3 with bis(perfluoroorgano)cadmium complexes [1].



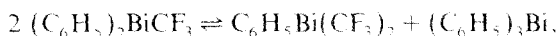
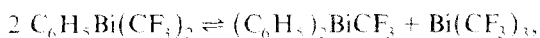
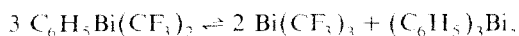
(X: Cl, Br; R_f : $\text{C}_n\text{F}_{2n+1}$ ($n = 1, 2, 3, 4, 6, 8$), C_6F_5 ; D: unidentate ligand).

These derivatives, especially tris(trifluoromethyl)bismuth, are excellent perfluoroalkyl-group transfer reagents, comparable in properties to those of the cadmium compounds and, in addition, more selective. This was shown by the reactions with AgNO_3 to give $\text{Ag}[\text{Ag}(\text{CF}_3)_4]$, with $\text{C}_6\text{H}_5\text{COCl}$ to give $\text{C}_6\text{H}_5\text{COCF}_3$, and with halogens or interhalogen compounds to give the corresponding trifluorohalomethane [2]. In order to develop new polar trifluoromethyl group transfer reagents we decided to make the previously unknown $\text{C}_6\text{H}_5\text{Bi}(\text{CF}_3)_2$ and $(\text{C}_6\text{H}_5)_2\text{BiCF}_3$. The compounds were prepared as shown in the following equations:



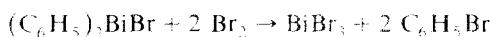
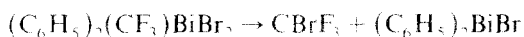
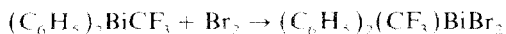
At 40°C the reactions take on 3 days. During the reactions traces of α,α,α -trifluorotoluene are always formed. Both bismuth compounds are oily liquids of penetrating odour, which like $\text{Bi}(\text{CF}_3)_3$ [1] and alkyl-diphenylbismuth [3], rapidly decompose on exposure to air.

In acetonitrile solution the compounds dismutate, like $(\text{CH}_3)_2\text{BiAr}$ [4], as follows:



However, the inverse reaction of $\text{Bi}(\text{CF}_3)_3$ with $(\text{C}_6\text{H}_5)_3\text{Bi}$ gave no evidence for mixed derivatives.

A low temperature bromination of $(\text{C}_6\text{H}_5)_2\text{BiCF}_3$ yielded primarily CBrF_3 , $\text{C}_6\text{H}_5\text{Br}$, and BiBr_3 . The ^{19}F NMR spectra recorded at -30°C showed a broad singlet at $\delta -42.5$ ppm that may arise from $(\text{C}_6\text{H}_5)_2(\text{CF}_3)\text{BiBr}_2$. This singlet disappeared when the temperature was raised. The intensity of the CBrF_3 -resonance in the ^{19}F NMR spectrum increased as that of the $(\text{C}_6\text{H}_5)_2(\text{CF}_3)\text{BiBr}_2$ resonance decreased.



These results are consistent with those for $\text{Bi}(\text{R}_f)_3$ (R_f : CF_3 , C_6F_5) [2] and $(\text{C}_6\text{H}_5)_2\text{BiR}$ (R : $n\text{-C}_5\text{H}_{11}$, $n\text{-C}_6\text{H}_{13}$, $c\text{-C}_5\text{H}_9$) [3] with elemental bromine.

The reactions of $(\text{C}_6\text{H}_5)_2\text{BiCF}_3$ with ICl and AgNO_3 to yield CF_3I and $\text{Ag}[\text{Ag}(\text{CF}_3)_4]$, respectively, are much faster than the corresponding reactions of $\text{Bi}(\text{CF}_3)_3$.

The possible use of the reactions of these and related compounds in organometallic and organic synthesis is in progress.

Experimental

Preparation of $(\text{C}_6\text{H}_5)_2\text{BiCF}_3$ and $\text{C}_6\text{H}_5\text{Bi}(\text{CF}_3)_2$. To a solution of 0.39 g (1.0 mmol) $(\text{C}_6\text{H}_5)_2\text{BiCl}$ in 10 ml CH_3CN were added 0.66 g (2.0 mmol) $\text{Cd}(\text{CF}_3)_2 \cdot 2\text{CH}_3\text{CN}$. The mixture was stirred for 14 days at ambient temperature then 0.2 g of RbBr and 1 ml CH_3OH were added to destroy the excess of $\text{Cd}(\text{CF}_3)_2 \cdot 2\text{CH}_3\text{CN}$ and $\text{Cd}(\text{CF}_3)\text{Cl} \cdot 2\text{CH}_3\text{CN}$ formed during the reaction. The precipitate was filtered off and washed with 5 ml of CH_3CN and the washings added to the main filtrate. After removal the solvent in high vacuum a colourless viscous liquid (0.31 g) was obtained with properties consistent with its being a mixture of $(\text{C}_6\text{H}_5)_2\text{BiCF}_3$ and $\text{C}_6\text{H}_5\text{Bi}(\text{CF}_3)_2$ in a ratio of 4:1. Repeated high vacuum distillation gave pure $(\text{C}_6\text{H}_5)_2\text{BiCF}_3$ in 58% yield. $\text{C}_6\text{H}_5\text{Bi}(\text{CF}_3)_2$ was obtained by a similar procedure from the reaction of 0.45 g (1.0 mmol) $\text{C}_6\text{H}_5\text{BiBr}_2$ with 0.99 g (3.0 mmol) $\text{Cd}(\text{CF}_3)_2 \cdot 2\text{CH}_3\text{CN}$. Storage of a solution of $\text{C}_6\text{H}_5\text{Bi}(\text{CF}_3)_2$ in acetonitrile for several days led to a dismutation into $(\text{C}_6\text{H}_5)_2\text{BiCF}_3$, $\text{Bi}(\text{CF}_3)_3$ and $(\text{C}_6\text{H}_5)_3\text{Bi}$, and so the pure compound could not be isolated.

Spectral data of $(C_6H_5)_2BiCF_3$ and $C_6H_5Bi(CF_3)_2$. ^{19}F NMR spectra (Bruker AC 200, ^{19}F : 188.3 MHz, CCl_3F ext., CH_3CN) $(C_6H_5)_2BiCF_3$: δ -38.6 ppm, $^1J(^{19}F-^{13}C) = 390.8$ Hz, $^1\Delta(^{19}F-^{12/13}C) 0.127$ ppm, $C_6H_5Bi(CF_3)_2$: δ -36.2 ppm, $^1J(^{19}F-^{13}C) = 389.1$ Hz, $^1\Delta(^{19}F-^{12/13}C) 0.127$ ppm, splitting of the ^{13}C satellites into quartets, $^4J(^{19}F-^{19}F) = 4.8$ Hz. $(Bi(CF_3)_3)$: δ -33.9 ppm, $^1J(^{19}F-^{13}C) = 390.5$ Hz, $^1\Delta(^{19}F-^{12/13}C) 0.139$ ppm, splitting of the ^{13}C satellites into septets, $^4J(^{19}F-^{19}F) = 4.7$ Hz [1].

Mass spectrum (Varian CH5 (modified), EI, 13 eV, 75°C). $(C_6H_5)_2BiCF_3$: 432 ($(C_6H_5)_2BiCF_3^+$, 9.7%), 413 ($(C_6H_5)_2BiCF_2^+$, 1.0%), 363 ($(C_6H_5)_2Bi^+$, 100%), 355 ($(C_6H_5)BiCF_3^+$, 21.2%), 336 ($(C_6H_5)BiCF_2^+$, 13.7%), 286 ($(C_6H_5)Bi^+$, 78.4%), 209 (Bi^+ , 28.4%), 154 ($(C_6H_5)_2^+$, 18.0%).

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