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Syntheses and Chemistry of Methylantimony and Methylbismuth Dihalides: An Extended Two-Dimensional Framework in the Crystal Structure of CH_3BiCl_2 and Molecular Units in the Structures of $[CH_3ECl_2(2,2'\text{-bipyridine})]$ (E = Sb, Bi)

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Summary: CH_3SbPh_2 reacts with HCl to give CH_3SbCl_2. CH_3BiCl_2 and CH_3BiBr_2 are formed by reaction of CH_3BiPh_2 with HCl or HBr. The adducts $[CH_3ECl_2(bipy)]$ (E = Sb, Bi, bipy = 2,2′-bipyridine) are obtained by combining the components in diethyl ether or tetrahydrofuran. The crystal structures of CH_3BiCl_2 and $[CH_3ECl_2(bipy)]$ (E = Sb, Bi) have been determined by single-crystal X-ray diffraction.

Introduction

Alkylantimony and alkylbismuth dihalides REX_2 (R = alkyl, E = Sb, Bi; X = Cl, Br, I) are amphoteric molecules with Lewis acidic sites at the metal atoms trans to the metal−halogen bond and Lewis basic functions mainly through the lone pairs of electrons of the halogen atoms. In the absence of external donors they coordinate with each other, forming dimers when the alkyl groups are bulky or polymers when the alkyl substituents are slim. Particularily strong extended interactions exist in crystalline phases of the methyl derivatives CH_3SbCl_2,[1] CH_3SbBr_2,[1] CH_3SbI_2,[2] and CH_3BiI_2,[3] which consist of infinite chains, $[(CH_3)E(\mu\text{-}X)_2]_x$ (E = pnicogen; X = halogen).

In the course of investigations of the structures and the chemistry of alkylantimony(III) and alkylbismuth(III) halides[4] we report here on new synthetic pathways leading to CH_3SbCl_2, CH_3BiCl_2, or CH_3BiBr_2, on the exceptional crystal structure of CH_3BiCl_2, and on the syntheses and structures of 1:1 complexes of CH_3SbCl_2 and CH_3BiCl_2 with 2,2′-bipyridine (bipy). Methylantimony dichloride was synthesized before by thermal elimination of CH_3Cl from $(CH_3)_2SbCl_3$[5] or by reactions of $Sn(CH_3)_4$,[6] $Pb(CH_3)_4$,[5] or $(CH_3)_2SbCl$[7]with $SbCl_3$. The first methods for the syntheses of CH_3BiX_2 (X = Cl, Br), i.e., the reaction of $(CH_3)_3Bi$ with BiX_3 in a 1:2 molar ratio, were reported by Marquardt already in 1887.[8] The 2,2′-bipyridine ligand has been widely used before for the complexation of inorganic and organometallic compounds, including antimony(III) and bismuth(III) halides. However, $[PhSbCl_2(bipy)]$[9] is the only bipyridine complex of an organoantimony dihalide that was characterized by X-ray crystallography. Crystal structures of adducts of bipyridine with organobismuth halides have not been reported before.

Results and Discussion

Pure samples of CH_3SbCl_2, CH_3BiCl_2, and CH_3BiBr_2 are obtained in a sequence of reactions (eq 1), starting with the syntheses of diphenylantimony or diphenylbismuth chloride, followed by alkylation with CH_3MgI.

$$Ph_3E \xrightarrow{ECl_3} Ph_2ECl \xrightarrow{CH_3MgI} Ph_2ECH_3 \xrightarrow{HX} CH_3EX_2 \quad (1)$$

$$E = Sb,\ X = Cl;\ E = Bi,\ X = Cl, Br$$

Action of gaseous HCl or HBr on CH_3SbPh_2 or CH_3BiPh_2 in $CHCl_3$ or CH_2Cl_2 results in the substitution of the phenyl groups by halogen atoms. Methylantimony dichloride is obtained as a colorless liquid after removal of the solvent. Methylbismuth dichloride and methylbismuth dibromide precipitate as white and yellow solids, respectively, from the reaction mixture.

The yields of the last step of the reactions (1) are close to 90% for the antimony compound and almost quantitative for the bismuth derivatives. The overall yields lie between 50 and 70%. Both bismuth halides are insoluble in aromatic or aliphatic hydrocarbons. They are only slightly soluble in dichloromethane, chloroform, and diethyl ether and readily soluble in ethanol, tetrahydrofuran, or dimethyl sulfoxide. Methylbismuth dichloride is air-stable both in solution and in the solid state. Single crystals were obtained by evaporation of a solution in ethanol in the air at ambient temperature. Methylbismuth dibromide decomposes in solution but is air-stable as a solid.

The crystal structure of CH_3BiCl_2 consists of puckered two-dimensional nets of methylbismuth units and chlorine atoms. The methyl groups are directed to one side

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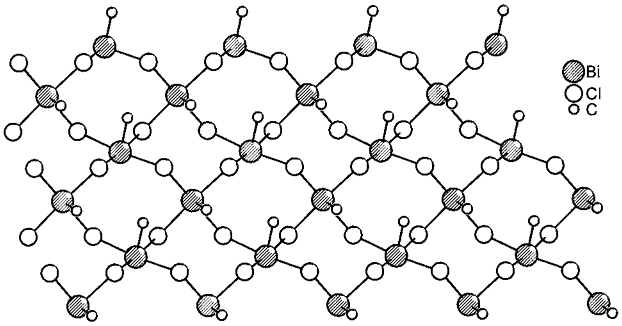

Figure 1. View of a single layer in the crystal structure of CH_3BiCl_2. Bi−Cl−Bi = 122.60(10)°.

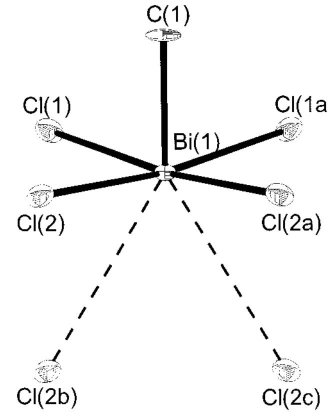

Figure 2. Coordination around the bismuth atom in the crystal structure of CH_3BiCl_2. Important bond lengths (Å) and angles (deg): Bi(1)−C(1) = 2.225(12), Bi(1)−Cl(1) = 2.7411(15), Bi(1)−Cl(2) = 2.7553(13), Bi(1)···Cl(2b,c) = 3.648(2); C(1)−Bi(1)−Cl(1) = 85.4(2), C(1)−Bi(1)−Cl(2) = 87.8(2), Cl(1)−Bi(1)−Cl(2) = 91.40(4), Cl(1)−Bi(1)−Cl(1a) = 88.49(6), Cl(2)−Bi(1)−Cl(2a) = 87.91(5).

of the array of the inorganic atoms. The chlorine atoms occupy bridging positions between two bismuth atoms, which have a square-pyramidal environment with apical methyl groups and basal chlorine atoms. A view of the puckered CH_3BiCl_2 net is given in Figure 1. The meshes of the net consist of eight-membered $[(CH_3)Bi]_4Cl_4$ heterocycles, where four bismuth atoms and four chlorine atoms form regular Bi_4 or Cl_4 squares with dihedral angles of 37.4° between the Bi_4 planes and the Cl_4 planes. The conformation of the heterocycles combines aspects of saddle and crown conformations.

The coordination sphere of the bismuth atoms is shown in Figure 2. The bond lengths around the bismuth atom are Bi−C = 2.225(12) Å and Bi−Cl = 2.7411(15), 2.7553(13) Å. Similar values have been reported[4] for $(Me_3Si)_2CHBiCl_2\cdot 0.5Et_2O$ (Bi−C = 2.237(14) Å, Bi−Cl (bridging) 2.704(5), 2.824(4) Å), another polymeric alkylbismuth dichloride.

The bismuth center in CH_3BiCl_2 lies 0.168 Å beneath the basal square. It is directed toward two chlorine atoms of an adjacent net. The inter-net Bi···Cl contact distances of 3.648(2) Å are shorter than the sum of the corresponding van der Waals radii ($\Sigma(\mathrm{rvdW})_{\mathrm{Bi,Cl}} = 4.2$ Å). Such close interactions between two nets lead to an inorganic layer of bismuth and chlorine atoms which is confined by the organic layer of the methyl groups. A section of the layers is presented in Figure 3. Inorganic and organic layers can also be distinguished in the chain structures of CH_3BiI_2[3] and CH_3SbX_2 (X = Cl, Br, I).[1,2]

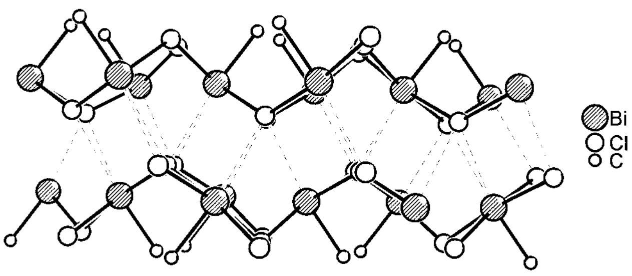

Figure 3. View of a section of the double layers in the crystal structure of CH_3BiCl_2.

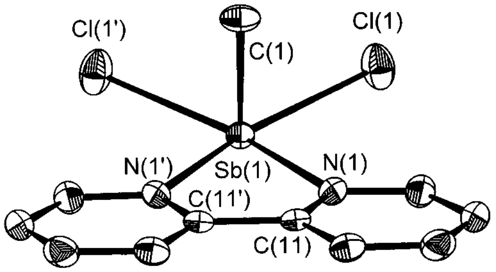

Figure 4. Representation of the molecular geometry and the atom-numbering scheme for $[CH_3SbCl_2(bipy)]$. Important bond lengths (Å) and angles (deg): Sb(1)−C(1) = 2.130(4), Sb(1)−N(1) = 2.379(3), Sb(1)−Cl(1) = 2.6341(10), N(1)−C(11) = 1.347(4), N(1)−C(15) = 1.338(4), C(11)−C(11′) = 1.477(6); C(1)−Sb(1)−N(1) = 85.49(13), C(1)−Sb(1)−Cl(1) = 84.48(8), N(1)−Sb(1)−Cl(1) = 90.15(7), N(1)−Sb(1)−Cl(1′) = 157.29(7), N(1)−Sb(1)−N(1′) = 68.77(13), Cl(1′)−Sb(1)−Cl(1) = 109.05(4).

Addition of 2,2′-bipyridine to a solution of CH_3SbCl_2 in diethyl ether (1:1 molar ratio) results in the precipitation of a solid containing the complex and diethyl ether. Purification by sublimation at reduced pressure gives yellow, air-stable crystals of $[CH_3SbCl_2(bipy)]$ in 73% yield. The reaction of CH_3BiCl_2 with 2,2′-bipyridine (1:1 molar ratio) is performed in tetrahydrofuran. The complex $[CH_3BiCl_2(bipy)]$ precipitates as a white air-stable solid in 89% yield after the addition of the ligand. Both bipyridine complexes are soluble in coordinating solvents such as dimethyl sulfoxide (DMSO) or acetonitrile but insoluble in hydrocarbons. NMR spectroscopic investigations indicate that the complexes are labile in solution. Spectra obtained from crystals of the complexes in $(CD_3)_2SO$ show the signals of the free bipyridine ligands. The coordination of the ligand is, however, preserved under the conditions of mass spectrometry. Electron impact mass spectra show signals of fragment ions $[CH_3ECl_2(bipy) - CH_3]^+$ (E = Sb, Bi) at highest mass.

Single crystals of $[CH_3SbCl_2(bipy)]$ were obtained by gas-phase diffusion of diethyl ether into a solution of the complex in acetonitrile. Single crystals of $[CH_3BiCl_2(bipy)]$ grew in a solution in dichloromethane that was exposed to the ambient atmosphere. The crystal structures of both complexes are depicted in Figures 4 and 5.

The structures feature molecular units, $[CH_3ECl_2(bipy)]$ (E = Sb, Bi), with tetragonal-pyramidal coordination of the antimony or bismuth atom. The methyl groups occupy the apical positions. The nitrogen atoms of the bipyridyl ligands and the chlorine atoms are in basal sites. The Sb−N and Sb−Cl bond lengths of $[CH_3SbCl_2(bipy)]$ compare well with the analogous phenylantimony compound: ($[CH_3SbCl_2(bipy)]$, Sb−N = 2.379-

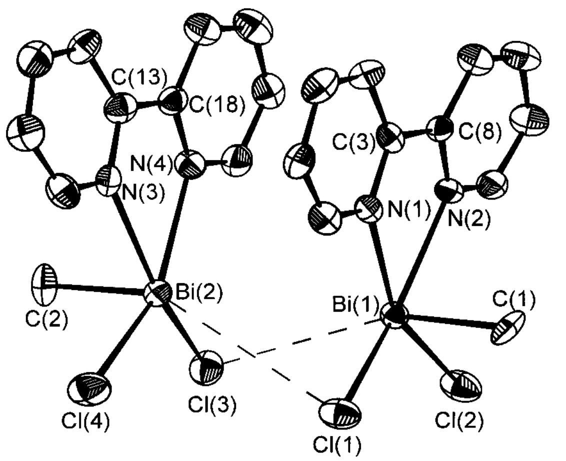

Figure 5. Representation of the molecular geometry and the atom-numbering scheme for $[CH_3BiCl_2(bipy)]$. Important bond lengths (Å) and angles (deg): Bi(1)−C(1) = 2.230(11), Bi(1)−N(1) = 2.483(9), Bi(1)−N(2) = 2.486(8), Bi(1)−Cl(1) = 2.709(3), Bi(1)−Cl(2) = 2.678(3); C(1)−Bi(1)−N(1) = 86.6(3), C(1)−Bi(1)−N(2) = 83.3(4), C(1)−Bi(1)−Cl(1) = 85.7(4), C(1)−Bi(1)−Cl(2) = 86.2(3), N(1)−Bi(1)−N(2) = 65.6(3), N(1)−Bi(1)−Cl(2) = 156.6(2), N(2)−Bi(1)−Cl(2) = 91.4(2), N(1)−Bi(1)−Cl(1) = 88.9(2), N(2)−Bi(1)−Cl(1) = 152.8(2), Cl(2)−Bi(1)−Cl(1) = 112.65(9); Bi(2)−C(2) = 2.233(10), Bi(2)−N(3) = 2.521(9), Bi(2)−N(4) = 2.548(9), Bi(2)−Cl(3) = 2.675(3), Bi(2)−Cl(4) = 2.649(3); C(2)−Bi(2)−N(3) = 83.5(4), C(2)−Bi(2)−N(4) = 87.4(4), C(2)−Bi(2)−Cl(3) = 86.3(3), C(2)−Bi(2)−Cl(4) = 86.5(3), N(3)−Bi(2)−N(4) = 64.8(3), N(3)−Bi(2)−Cl(4) = 91.9(2), N(4)−Bi(2)−Cl(4) = 156.3(2), N(3)−Bi(2)−Cl(3) = 155.8(2), N(4)−Bi(2)−Cl(3) = 93.0(2), Cl(4)−Bi(2)−Cl(3) = 109.40(10).

(3) Å, Sb−Cl = 2.6341(10) Å; $[PhSbCl_2(bipy)]$,[9] Sb−N = 2.43(1) Å, Sb−Cl = 2.556(5) Å). The antimony centers of both complexes lie below the plane of the basal ligands ($[CH_3SbCl_2(bipy)]$, 0.225 Å; $[PhSbCl_2(bipy)]$, 0.16 Å[9]). The Bi−Cl bonds in $[CH_3BiCl_2(bipy)]$ (Bi−Cl = 2.709(3), 2.678(3) Å) are only slightly shorter than in CH_3BiCl_2. The Bi−N bond lengths in $[CH_3BiCl_2(bipy)]$ (Bi−N = 2.521(9), 2.548(9) Å) are in the range of the corresponding distances in $[(BiCl_3)_2(bipy)_3]$ (Bi−N = 2.51(3)−2.71(3) Å).[10] Crystals of $[CH_3BiCl_2(bipy)]$ consist of molecular dimers. The $[CH_3BiCl_2(bipy)]$ molecules are associated on the basal plane through intermolecular Bi···Cl (3.639(33), 3.945(52) Å) and Bi···Bi (4.203(6) Å) contacts, which are shorter than the sum of the respective van der Waals radii $\Sigma(\mathrm{rvdW})_{\mathrm{Bi,Cl}} = 4.2$; $\Sigma(\mathrm{rvdW})_{\mathrm{Bi,Bi}} = 4.8$ Å). The bismuth atoms lie 0.203 Å (Bi(1)) or 0.182 Å (Bi(2)) below the basal plane.

A comparison of the novel structures presented here with related compounds of antimony or bismuth reveals some interesting aspects. The two-dimensional net structure of CH_3BiCl_2 is unusual, because the four other known crystal structures of methylantimony and methylbismuth dihalides consist of one-dimensional chains. A common feature of all the dihalides is the (distorted) square-planar environment of the heavy pnicogen centers. It is well-known that as a consequence of the larger atomic radius and the more metallic character of bismuth compared with antimony, the Lewis acidity of Sb(III) compounds is lower than that of related Bi(III) compounds. This trend is reflected in the predominantly molecular character of CH_3SbCl_2,[1] where the crystal structure consists of chains of associated molecules with short Sb−Cl bonds and longer Sb···Cl contacts. In contrast, the Bi−Cl bond lengths in CH_3BiCl_2 are almost equal and the molecular character is completely lost. Both compounds exist, however, as molecules in solutions with donor solvents or in complexes with the bipy ligand. Another consequence of the relatively high Lewis acidity of the bismuth centers in both the structures of CH_3BiCl_2 and $[CH_3BiCl_2(bipy)]$ is the tendency to increase the coordination beyond the coordination number 5 through Bi···Cl contacts to neighboring chains or molecules.

The square-pyramidal geometry and the position of the central pnicogen atom below the basal plane in particular observed in the structures of CH_3BiCl_2 and $[CH_3ECl_2(bipy)]$ (E = Sb, Bi) are not uncommon in the structural chemistry of the organo dihalides of Sb or Bi and their derivatives. Often these features are discussed in terms of the VSEPR model, and in fact it is tempting to envisage a stereochemical activity of the lone pair of electrons at the antimony or bismuth atoms trans to the organic groups. However, the assumption of an s character of the orbital with the lone pair of electrons at Sb or Bi would also account for the general square-pyramidal geometry, and the observed distortions may rather result from the intermolecular contacts or from the small bite angle of the bipyridine ligands than from the lone pair activity.

Experimental Section

The reactions and manipulations were performed under an atmosphere of dry argon. Chemical shifts are reported in δ units (ppm) referenced to $CHCl_3$ (7.25 ppm, ^1H), C_6D_5H (7.15 ppm, ^1H), C_6D_6 (128.0 ppm, ^{13}C), $(CD_3)_2SO$ (39.43 ppm, ^{13}C), and $(CD_3)(CD_2H)SO$ (2.50 ppm, ^1H).

Preparation of CH_3SbCl_2. A gentle flow of dry HCl is introduced into a solution of 36.19 g (124.4 mmol) of CH_3SbPh_2[11] in 150 mL of $CHCl_3$ for 80 min followed by a flow of argon (20 min). The resulting mixture is stirred for 12 h at room temperature, and the solvent is removed at 40 mbar. Distillation of the slight yellow residue at 25 mbar (bp 95−105 °C) gives 22.97 g (88.9%) of CH_3SbCl_2. ^1H NMR (C_6D_6, 200 MHz, 23 °C): 1.06 (s, 3 H, CH_3) (lit.[7] 1.1). ^{13}C NMR (C_6D_6, 50 MHz, 23 °C): 27.33 (CH_3).

Preparation of $[CH_3SbCl_2(bipy)]$. Dropwise addition of a solution of 1.05 g (6.72 mmol) of 2,2′-bipyridine in 30 mL of diethyl ether at 25 °C to a stirred solution of 1.24 g (5.96 mmol) of CH_3SbCl_2 in 10 mL of diethyl ether gives a yellow solid. The mixture is stirred for 12 h to complete the reaction and the solution removed with a syringe. The solid is washed two times with 20 mL of diethyl ether, dried at reduced pressure, and sublimed at 120 °C and 10^{-3} mbar to give 1.72 g (73.0%) of $[CH_3SbCl_2(bipy)]$ (mp 202−205 °C). Anal. Calcd for $C_{11}H_{11}Cl_2N_2Sb$ (363.88): C, 36.31; H, 3.05. Found: C, 35.93; H, 2.90. MS (EI, 70 eV): 347 (15) $[M^+ - CH_3]$, 206 (3) $[CH_3SbCl_2^+]$, 191 (24) $[SbCl_2^+]$, 171 (12) $[CH_3SbCl^+]$, 156 (100) $[C_{10}H_8N_2^+]$, 78 (25) $[C_5H_4N^+]$.

Preparation of CH_3BiPh_2. A solution of 18.90 g (47.41 mmol) of Ph_2BiCl[12] in 250 mL of THF is added dropwise at room temperature with stirring to a Grignard solution prepared from 7.413 g (52.223 mmol) of CH_3I and 1.475 g (60.675mmol) of magnesium filings in 80 mL of diethyl ether. The suspension is stirred overnight at room temperature. The

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Table 1. Crystal Data, Data Collection, and Structure Refinement Parameters for CH_3BiCl_2, [CH_3SbCl_2(bipy)], and [CH_3BiCl_2(bipy)]

	CH_3BiCl_2	[CH_3SbCl_2(bipy)]	[CH_3BiCl_2(bipy)]
formula	CH_3BiCl_2	$C_{11}H_{11}Cl_2N_2Sb$	$C_{11}H_{11}BiCl_2N_2$
fw	294.91	363.87	451.10
color	yellow	yellow	colorless
temp, K	173(2)	173(2)	173(2)
cryst size, mm	0.7 × 0.4 × 0.3	0.5 × 0.3 × 0.15	0.6 × 0.4 × 0.1
cryst syst	orthorhombic	monoclinic	triclinic
space group	*Pbcm*	$P2_1/m$	$P\bar{1}$
a, Å	10.211(3)	5.5520(10)	9.340(2)
b, Å	6.255(2)	16.092(4)	11.052(5)
c, Å	7.650(3)	7.0970(10)	13.420(2)
α, deg	90	90	91.74(2)
β, deg	90	92.775(13)	91.15(2)
γ, deg	90	90	107.89(2)
V, Å^3	488.6(3)	633.3(2)	1317.1(7)
Z	4	2	4
d_{calcd}, g cm^{-3}	4.009	1.908	2.275
μ(Mo Kα), mm^{-1}	36.978	2.573	13.766
scan method	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
F(000)	504	352	832
scan range, deg	$3.82 \leq \theta \leq 27.54$	$2.53 \leq \theta \leq 27.49$	$2.50 \leq \theta \leq 27.49$
no. of measd data	3942	2110	6904
no. of unique data	608 ($R_{int} = 0.0879$)	1497 ($R_{int} = 0.0395$)	5866 ($R_{int} = 0.0318$)
no. of params	26	80	294
no. of data with $I > 2\sigma(I)$	608	1497	5866
abs cor	DIFABS[17]	DIFABS[17]	DIFABS[17]
wR2(all data)[a]	0.0979	0.0691	0.1516
R1(all data)[a]	0.0417	0.0318	0.0697
wR2($I > 2\sigma(I)$)[a]	0.0954	0.0652	0.1398
R1($I > 2\sigma(I)$)[a]	0.0384	0.0262	0.0536
GOF on F^2	1.078	1.050	1.027
residual density, e Å^{-3}	+2.966; −3.448	+0.670; −0.893	+3.200; −2.733

[a] Definition of the R values: $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

solvent is removed at reduced pressure, and the residue is extracted with petroleum ether. Removal of the solvent gives 11.88 g (66.3%) of colorless, liquid CH_3BiPh_2. ^{1}H NMR ($CDCl_3$, 200 MHz): 1.50 (s, 3 H, CH_3), 7.28−7.54 (m, 6 H, m- + p-C_6H_5), 7.73−7.95 (m, 4 H, o-C_6H_5). MS (EI, 70 eV): 378 (0.8) [M$^+$], 363 (38) [M$^+$ − CH_3], 301 (4) [M$^+$ − C_6H_5], 286 (10) [M$^+$ − CH_3 − C_6H_5], 224 (6) [M$^+$ − 2 C_6H_5], 209 (100) [Bi$^+$], 154 (3) [$(C_6H_5)_2^+$], 77 (2) [$C_6H_5^+$].

Preparation of CH_3BiCl_2. A gentle flow of dry HCl is introduced at 0 °C into a solution of 10.0 g (26.44 mmol) of CH_3BiPh_2 in 120 mL of $CHCl_3$ for 2 h followed by a flow of argon for 20 min. The solvent is removed from the white suspension, and 7.58 g (97.4%) of white solid CH_3BiCl_2 remains (mp 246−249 °C dec; lit.[8] mp 242 °C). Anal. Calcd for CH_3BiCl_2 (294.92): C, 4.07; H, 1.03. Found: C, 4.13; H, 1.12. ^{1}H NMR (d_6-DMSO, 200 MHz, 23 °C): 1.56 (s, 3 H, CH_3). ^{13}C NMR (d_6-DMSO, 50 MHz, 23 °C): 74.28 (CH_3). MS (EI, 70 eV): 294 (25) [M$^+$], 279 (79) [M$^+$ − CH_3], 259 (48) [M$^+$ − Cl], 244 (46) [M$^+$ − CH_3 − Cl], 224 (6) [M$^+$ − 2 Cl], 209 (100) [Bi$^+$].

Preparation of CH_3BiBr_2. A gentle flow of dry HBr is introduced into a solution of 3.375 g (8.923 mmol) of CH_3BiPh_2 in 40 mL of CH_2Cl_2 for 1 h at 25 °C followed by a flow of argon for 20 min. The solvent is removed from the yellow precipitate by a syringe, and the residue is washed with 20 mL of CH_2Cl_2 and dried under vacuum. A 3.35 g (97.8%) amount of CH_3BiBr_2 remains as a yellow solid (mp 195−197 °C dec; lit.[8] mp 214 °C). Anal. Calcd for CH_3BiBr_2 (383.82): C, 3.13; H, 0.79. Found: C, 3.35; H, 0.81. ^{1}H NMR (d_6-DMSO, 200 MHz, 23 °C): 1.77 (s, 3 H, CH_3). ^{13}C NMR (d_6-DMSO, 50 MHz, 23 °C): 69.29 (CH_3). MS (EI, 70 eV): 382 (32) [M$^+$], 369 (100) [M$^+$ − CH_3], 303 (13) [M$^+$ − Br], 288 (44) [M$^+$ − CH_3 − Br], 224 (7) [M$^+$ − 2 Br], 209 (85) [Bi$^+$].

Preparation of [CH_3BiCl_2(bipy)]. A solution of 0.58 g (3.69 mmol) of 2,2′-bipyridine in 20 mL of tetrahydrofuran (thf) is added dropwise with stirring at 25 °C to a solution of 1.06 g (3.59 mmol) of CH_3BiCl_2 in 10 mL of thf. A white solid precipitates, and the suspension is stirred for 12 h to complete the reaction. The solvent is removed with a syringe and the residue washed two times with 10 mL of thf. Removal of the solvent at reduced pressure gives 1.45 g (89.2%) of [CH_3BiCl_2(bipy)] (mp 208−210 °C). Anal. Calcd for $C_{11}H_{11}Cl_2N_2Bi_1$ (451.10): C, 29.29; H, 2.46. Found: C, 29.41; H, 2.42. MS (EI, 70 eV): 435 (0.9) [M$^+$ − CH_3], 415 (0.1) [M$^+$ − Cl], 400 (0.5) [M$^+$ − Cl − CH_3], 365 (0.3) [M$^+$ − CH_3 − 2 Cl], 294 (11) [$CH_3BiCl_2^+$], 279 (42) [$BiCl_2^+$], 259 (19) [CH_3BiCl^+], 244 (14) [BiCl$^+$], 224 (3) [CH_3Bi^+], 209 (21) [Bi$^+$], 156 (100) [$C_{10}H_8N_2^+$], 78 (8) [$C_5H_4N^+$].

X-ray Crystallography. The details of the crystal structure determination and refinement are given in Table 1. Data were collected on a Siemens P4 four-circle diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). For this purpose the crystals were attached with Kel-F oil to a glass fiber and cooled under a nitrogen stream to 173 K.

The structures were solved, after Lp correction, by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.[13] The drawings were created by the Diamond program by Crystal Impact GbR.[14]

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Supporting Information Available: Tables of crystal data and structure refinement details, atom coordinates and U values, bond distances and angles, anisotropic thermal parameters, and dihedral angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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