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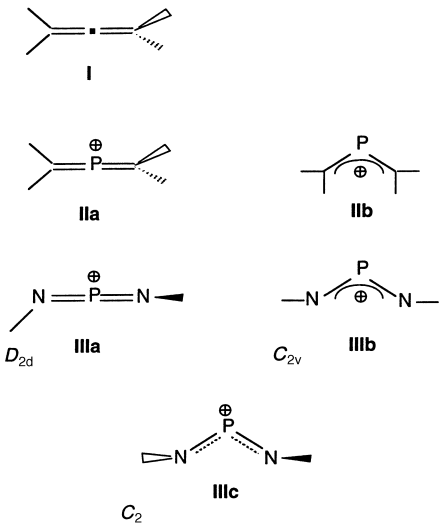
Synthesis of the Adduct DMAP · BrP(=N-Mes*)$_2$ and of the Salt [(DMAP)$_2$P(=NMes*)$_2$]$^+$Br**

Markus Blättner, Martin Nieger, Alexander Ruban, Wolfgang W. Schoeller, and Edgar Niecke*

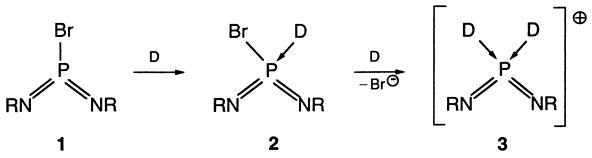
Dedicated to Professor Reinhard Schmutzler on the occasion of his 65th birthday

Allenes **I** are fundamental compounds with a linear structure (D_{2d} symmetry). This implies sp hybridization at the central carbon atom.[1] The hypothetical 2-phosphonio-allenic cation **IIa** is isovalent to **I**, but its central phosphorus atom is not sp hybridized.[2] The s orbital at the phosphorus atom becomes stereochemically active under formation of a "bent" 2-phosphaallyl cation **IIb**.[3] According to ab initio calculations[5] this geometry is favored over that of **IIa**.



Quantum-chemical calculations predict a linear arangement of atoms (D_h) for the cations PO_2^+ and PS_2^+.[6] For these cations a bis-donor adduct has been obtained recently.[7] Here we report on the first synthesis and crystal structure analysis of a bis-donor adduct of the imine analogue of **II** as well as on ab initio calculations on model compounds that support the findings.

Treatment of the bromobis(arylimino)phosphorane **1** (R = Mes* = 2,4,6-tBu$_3$C$_6$H$_2$)[8] with one equivalent of *p*-dimethylaminopyridine (DMAP = D) in CH_2Cl_2 furnished the donor/acceptor adduct **2** in good yield (75 %) in the form of air- and moisture-sensitive light yellow crystals. Subsequent reaction of **2** with a second equivalent of DMAP proceeded by halogen/nucleophile exchange to give the cation **3**, whose bromide was isolated at low temperature as yellow crystals from a little CH_2Cl_2.



Initial information concerning the constitution of **2** and **3** · Br$^-$ was obtained from multinuclear NMR investigations. The ^1H and ^{13}C NMR data clearly indicated the presence of Mes* substituents at the nitrogen atoms as well as the attachment of one (**2**) or two donor molecules (DMAP) (**3**) to the phosphorus atom. As expected the ^{31}P NMR signals appeared at higher fields ($\delta = -93.2$ (**2**), -57.2 (**3**)) than those of bis(imino)phosphoranes,[9] indicating an increase of coordination number at the phosphorus atom.

Crystal structure analyses of **2** and **3** · Br$^-$ gave evidence for the formation as a monoadduct of the bromobis(imino)phosphorane and as a bisadduct of the bis(imino)phosphonium cation (Figures 1 and 2).[10] In both compounds the phosphorus atoms adopt a strongly distorted tetrahedral geometry. The N-P-N bond angle at the phosphorus atom (N1-P1-N2

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[**] This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (SFB 334). Part of this work was reported at the International Conference on Phosphorus Chemistry, Cincinnati, USA, **1998**. DMAP = *p*-dimethylaminopyridine; Mes* = 2,4,6-tBu$_3$C$_6$H$_2$.

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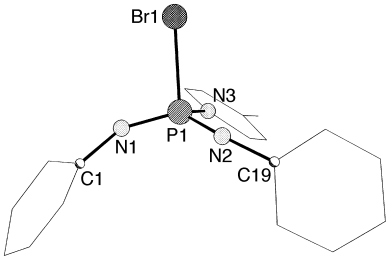


Figure 1. Molecular structure of **2** (solvent, hydrogen atoms, and peripheral groups omitted for clarity). Selected distances [pm] and angles [°]: P1-Br1 231.9(2), P1-N1 152.8(5), P1-N2 148.6(5), P1-N3 181.5(5); N2-P1-N1 130.6(3), N2-P1-N3 107.8(2), N1-P1-N3 103.6(2), N2-P1-Br1 113.2(2), N1-P1-Br1 102.5(2), N3-P1-Br1 92.2(2).

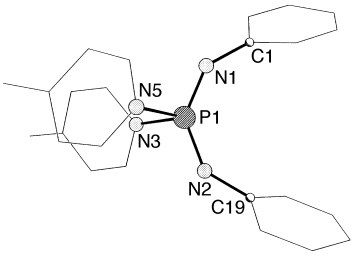
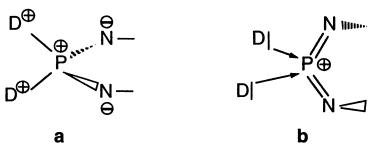


Figure 2. Molecular structure of **3** (solvent, anion, hydrogen atoms, and peripheral groups omitted for clarity). Selected bond lengths [pm] and angles [°]: P1-N1 152.8(4), P1-N2 152.6(4), P1-N3 183.0(4), P1-N5 181.2(4); N1-P1-N2 135.9(2), N1-P1-N3 110.3(2), N1-P1-N5 100.6(2), N2-P1-N3 100.9(2), N2-P1-N5 110.7(2), N3-P1-N5 88.7(2).

130.6(3)° (**2**), 135.9(3)° (**3**)) is widened with respect to that in the bis(imino)phosphorane IP(=NMes)$_2$ (121.9(2)°[8]), while the angle Br1-P1-N3 (92.2(2)°) in **2** and N1-P1-N5 (88.7(2)°) in **3** are more compressed. The sterically demanding aryl substituents at N1 and N2 are arranged differently to each other (**2**: *exo/endo*, **3**: *endo/endo*). The different conformations may be attributed to a delicate balance of steric hindrance between the crowded donor ligands (DMAP) and the bulky substituents at the nitrogen substituents (Mes*). Remarkably, in comparison with **3** the bis-donor adduct $Py_2[PS_2]^+$ is less tetrahedrally distorted (S-P-S 124°, N-P-N 94°[7b]). The dihedral angle between the planes of both aryl rings and the N1-P-N2 unit is 16°. The P–N(aryl) distances (148.6(5), 152.8(5) pm (**2**); 152.6(4), 152.8(4) pm (**3**)) correspond to those in bis(imino)phosphoranes,[9] and indicate the high degree of P–N double-bond character in **2** and **3**. On the contrary the P–N(DMAP) bond lengths (181.5(5) pm (**2**); 181.2(4), 183.0(4) pm (**3**)) are longer than the P–N single bond in the amionobis(imino)phosphorane $(Me_3Si)_2NP(=NSiMe_3)_2$ (164.6 pm[14]). The P – Br distance in **2** (231.9(2) pm) corresponds to those of a typical single bond between these atoms. The shortest contact between the anion and the electrophilic phosphorus center in the bis-donor adduct **3** is 719 pm and indicates the formation of a salt.

The structure of **3** can be described by the two limiting structures **a** and **b**. The limiting structure **a** with a strong charge separation corresponds to a classical multipolar phosphonium structure with tetrahedral coordination at the phosphorus atom. The limiting structure **b** describes the cation as a donor–acceptor complex between a heteroallenic cation and two Lewis donors. Each of the two nitrogen donor ligands transfers electron density into the two approximately orthogonal π-orbitals of the 2-phospha-heteroallene. This results in a geometry which strongly deviates from an ideal tetrahedral environment.



a **b**

According to quantum-chemical calculations (MP2(fc)/6-31g*),[15] the parent cation $[P(=NMe)_2]^+$ displays the structure **III c** with C_2 symmetry and the following parameters: P–N 153.6 pm, N-P-N 137.5°, H-N-P 142.4°). This structure is slightly lower in energy than linear structure (D_{3d} symmetry (**III c**), $\Delta E = 7.2$ kcal mol^{-1}[16]). In other words the "donor-free" cation is a highly flexible structure. The addition of two nitrogen donor ligands to the cation $[P(=NMe)_2]^+$ is strongly exothermic (e.g., $\Delta E = -64.3$ kcal mol^{-1} for the addition of two molecules of NH_3). The bond lengths and angles show a significant dependence on the basicity of the donor ligands, whereas with increasing strength of the P–N(donor) bond in the series $NH_3 < Py < DMAP$ (N–P: 195.9, 191.3, 187.9 pm, respectively) the distortion of the tetrahedral geometry dimishes (N(donor)-P-N(donor) 90.0, 89.4, 91.2, respectively, N(Me)-P-N(Me) 146.2, 142.6, 140.4°, respectively).

The peculiar bonding situation is reflected in the Laplacian distribution of the electron density of the MP2 wavefunction.[17] Figure 3 shows the electron density distribution for

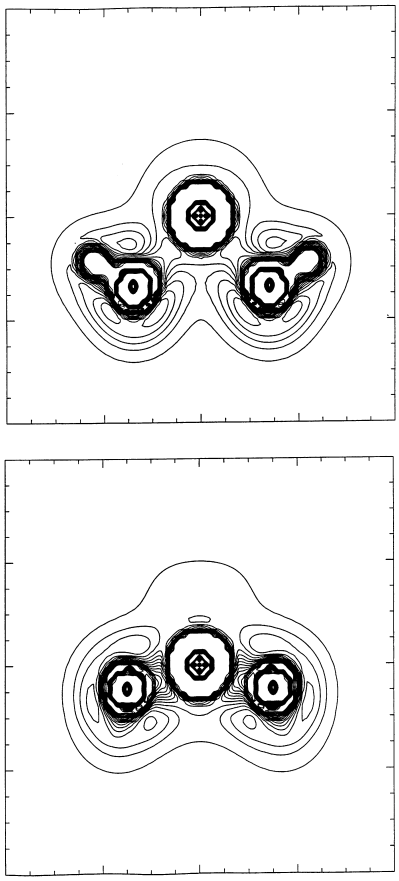


Figure 3. Laplacian of the electron density distribution in the cation $[(H_3N)_2P(=NMe)_2]^+$ in the N-P-N planes $(H_3)N$-P-$N(H_3)$ (top: P–N(imine) bonds) and (Me)N-P-N(Me) (bottom: donor–acceptor bonds). A large scale unit corresponds to 3.75 Bohr.

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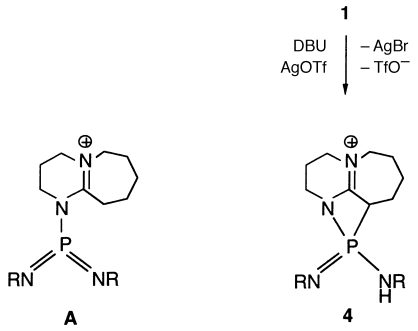
the cation $[(NH_3)_2P(=NMe)_2]^+$ in the N-P-N planes (H_3)N-P-N(H_3) (top) and (Me)N-P-N(Me) (bottom). In the former case electron density is predominantly localized at the nitrogen atoms of the donor ligands (NH_3) which point towards the phosphorus atom. For the latter the electron density is distributed equally between the central phosphorus atom and the two nitrogen atoms. The two donor ligands interact only weakly with the cationic heteroallene. The bonding features of the "free cation" $[P(=NMe)_2]^+$, namely the large N-P-N angle and the P–N double-bond character, are preserved.

It should be mentioned that the product of the reaction of **1** with 1.8-diazabicyclo[5.4.0]undec-7-ene (DBU) in the presence of AgOTf ($Tf = F_3CSO_2$) was described as the onio-substituted bis(imino)phosphorane **A**.[18] However, as we have proven by NMR spectroscopy as well as by a single-crystal X-ray diffraction study,[10] the reported cation is not the donor adduct **A**, but the onio-substituted iminophosphorane **4**.[19]



Experimental Section

2: A solution of **1** (1.0 g, 1.58 mmol) in toluene (25 mL) was treated with DMAP (0.19 g, 1.58 mmol) dissolved in toluene (10 mL). After the mixture had been stirred at room temperature for 30 min, the solvent was removed under reduced pressure and the remaining solid residue was recrystallized from CH_2Cl_2 at $-24\,^\circ$C. Yield: 78.4%; m.p. 112–114 °C (decomp); ^{31}P NMR (ext.; C_6D_6): $\delta = -93.2$; ^{1}H NMR ($CDCl_3$): $\delta = 1.23$ (s, 18H; *p*-tBu), 1.25 (s, 18H; *o*-*t* Bu), 1.52 (s, 18H; *o*-tBu), 3.31 (s, 6H; NMe_2), 6.71 (br., 2H; *m*-C_2H_4N), 7.06 (s, 2H; C_6H_2), 8.53 (br., 2H; *o*-C_2H_4N); ^{13}C NMR ($CDCl_3$): $\delta = 31.9$ (s; *p*-CCH_3), 32.2 (s; *o*-CCH_3), 34.8 (s; *p*-CCH_3), 36.9 (s; *o*-CCH_3), 41.2 (s; NCH_3), 107.2 (s; *m*-Py), 122.8 (s; *m*-Ar), 138.1 (d, ^2J(P,C) = 28.1 Hz; *ipso*-Ar), 139.9 (d, ^3J(P,C) = 12.8 Hz; *o*-Ar), 140.8 (s; *o*-Py), 143.4 (s; *p*-Ar), 156.8 (s; *p*-Py).

3: A solution of **1** (0.19 g, (1.58 mmol) in CH_2Cl_2 (15 mL) was treated with DMAP (0.38 g, 3.17 mmol) dissolved in CH_2Cl_2 (5 mL). After the the mixture had been stirred at room temperature for 30 min, the solvent was removed under reduced pressure and the remaining solid residue was recrystallized from CH_2Cl_2 at $-24\,^\circ$C. Yield: 84.5%, m.p. 124–125 °C (decomp); ^{31}P NMR (ext.; CH_2Cl_2): $\delta = -57.2$; ^{1}H NMR ($CDCl_3$): $\delta = 1.07$ (s, 36H; *o*-*t*Bu), 1.20 (s, 18H; *p*-*t*Bu), 3.29 (s, 12H; NMe_2), 6.71 (br., 4H; *m*-C_2H_4N), 7.03 (d, *J*(P,H) = 7.6 Hz, 2H; C_6H_2), 8.53 (br., 4H; *o*-C_2H_4N); ^{13}C NMR ($CDCl_3$): $\delta = 31.9$ (s; *p*-CCH_3), 32.9 (s; *o*-CCH_3), 34.7 (s; *p*-CCH_3), 36.9 (d, *J*(P,C) = 0.8 Hz; *o*-CCH_3), 107.2 (s; *m*-Py), 122.8 (s; *m*-Ar), 139.9 (d, ^1J(P,C) = 30.2 Hz; *ipso*-Ar), 140.0 (d, ^2J(P,C) = 8.0 Hz; *o*-Ar), 141.7 (d, *J*(P,C) = 7.9 Hz; *o*-Py), 143.4 (s; *p*-Ar), 156.8 (s; *p*-Py).

4: A solution of **1** (1.0 g, 1.58 mmol) in toluene (40 mL) was treated with DBU (0.24 g, 1.58 mmol) dissolved in toluene (5 mL). After the mixture had been stirred at room temperature for 30 min, it was treated with $AgOSO_2CF_3$ (0.40 g, 1.58 mmol) and then stirred for a further 30 min at room temperature. After separation of the AgBr, the filtrate was concentrated and the product crystallized at $-30\,^\circ$C. Yield: 67.6%, m.p. 138–140 (decomp); ^{31}P NMR (ext.; C_6D_6) $\delta = -11.7$; ^{1}H NMR (C_6D_6): $\delta =$ 1.20 (s, 9H; *p*-tBu), 1.22 (s, 9H; *p*-*t*Bu), 1.25 (s, 18H; *o*-*t*Bu), 1.27 (s, 9H; *o*-*t*Bu), 1.49 (s, 9H; *o*-tBu), 4.12 (s, 1H; NH), 7.05 (d, *J*(P,H) = 5.1 Hz, 2H; C_6H_2), 7.16 (s, 2H; C_6H_2), [DBU signals: 1.15–1.30 (m), 1.50–1.54 (m), 2.36–2.79 (m), 3.32–3.36 (m)].

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[10] X-ray structure analysis of **2** ($C_{43}H_{68}BrN_4P \cdot 0.5$ toluene): yellow crystals, crystal dimensions $0.20 \times 0.40 \times 0.53$ mm^3; $M_r = 797.96$; monoclinic, space group $P2_1/c$ (no. 14), $a = 11.041(1)$, $b = 20.605(4)$, $c = 19.996(5)$ Å, $\beta = 94.68(1)^\circ$, $V = 4.534(2)$ nm^3, $Z = 4$, $\mu(Cu_{K\alpha}) = 1.817$ mm^{-1}, $T = 208(2)$ K, $F(000) = 1716$. A total of 6951 reflections up to $2\theta_{max.} = 120^\circ$ were measured on an Enraf-Nonius CAD4 diffractometer with $Cu_{K\alpha}$ radiation, 6731 of which were independent and used for all calculations. The structure was solved by direct methods (SHELXS-86[11]) and refined to F^2 anisotropically, the H atoms were refined with a riding model (SHELXL-93[12]). The final quality coefficient $wR2(F^2)$ was 0.2508, with a conventional $R(F) = 0.0808$ for 456 parameters and 22 restraints. An empirical absorption correction on the basis of ψ scans was applied (min/max transmission 0.410/0.842). One of the *p*-*t*Bu groups and the toluene molecule are disordered. X-ray structure analysis of $\mathbf{3} \cdot Br^-$ ($C_{50}H_{78}BrN_6P \cdot 3CH_2Cl_2$): yellow crystals, crystal dimensions $0.10 \times 0.28 \times 0.43$ mm^3; $M_r = 1128.84$; monoclinic, space group $P2_1/n$ (no. 14), $a = 10.542(2)$, $b = 11.213(2)$, $c = 51.27(2)$ Å, $\beta = 91.96(2)^\circ$, $V = 6.057(3)$ nm^3, $Z = 4$, $\mu(Cu_{K\alpha}) = 3.895$ mm^{-1}, $T = 200(2)$ K, $F(000) = 2384$. A total of 9715 reflections up to $2\theta_{max} = 120^\circ$ were measured on an Enraf-Nonius CAD4 diffractometer with $Cu_{K\alpha}$ radiation, 8998 of which were independent and used for all calculations. The structure was solved by direct methods (SHELXS-86[11]) and refined to F^2 anisotropically, the H atoms were refined with a riding model (SHELXL-93[12]). The final quality coefficient $wR2(F^2)$ was 0.2397, with a conventional $R(F) = 0.0744$ for 603 parameters and 141 restraints. An empirical absorption correction was applied[13]. One *p*-*t*Bu group is disordered. X-ray structure analysis of $\mathbf{4} \cdot TfO^-$ ($[C_{45}H_{74}N_4P][SO_3CF_3] \cdot$ toluene): colorless crystals, crystal dimensions $0.13 \times 0.20 \times 0.20$ mm^3; $M_r = 943.26$; triclinic, space group $P\bar{1}$ (no. 2), $a = 10.075(2)$, $b = 15.041(4)$, $c = 19.398(4)$ Å, $\alpha = 104.98(2)^\circ$, $\beta = 98.79(2)^\circ$, $\gamma = 100.13(2)^\circ$, $V = 2.734(1)$ nm^3, $Z = 2$, $\mu(Cu_{K\alpha}) = 1.227$ mm^{-1}, $T = 200(2)$ K, $F(000) = 1020$. A total of 7346 reflections up to $2\theta_{max} = 110^\circ$ were measured

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on an Enraf-Nonius CAD4 diffractometer with $Cu_{K\alpha}$ radiation, 6856 of which were independent and used for all calculations. The structure was solved by direct methods (SHELXS-86[11]) and refined to F^2 anisotropically, the H atoms were refined with a riding model (SHELXL-93[12]). The final quality coefficient $wR2(F^2)$ was 0.2540, with a conventional $R(F) = 0.0780$ for 545 parameters and 91 restraints. One *p*-*t*Bu group and the triflate are disordered. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132812 (**2**), CCDC-132813 (**3**·Br^-), and CCDC-132814 (**4**·TfO^-). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[18] V.Romanenko, M. Sanchez, *Coord. Chem. Rev.* **1997**, *158*, 275–324.

[19] Representative structural data for **4**·TfO^- $[CF_3SO_3]^-$: P–N(Mes*) 153.5(5), P–N(H,Mes*) 162.7(5), P–N(heterocycle) 174.4(5), P–C 188.3(6) pm.

$(2,6\text{-}Mes_2H_3C_6)_2BiH$, a Stable, Molecular Hydride of a Main Group Element of the Sixth Period, and Its Conversion to the Dibismuthene $(2,6\text{-}Mes_2H_3C_6)BiBi(2,6\text{-}Mes_2C_6H_3)$**

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Element derivatives of hydrogen are an important and fundamental compound class.[1] This is especially true for main group element hydrides, which are widely used as reducing agents. However, many such hydrides are currently unknown as stable species. For example, there are no stable hydride derivatives of members of the sixth period of the p-block (e.g., Tl, Pb, or Bi[2]). It is doubtful that their lack of stability is due to inherent weakness in the element–hydrogen bonds since these are comparable in strength to element–carbon bonds[3] and alkyl and aryl derivatives of these elements are already well-known. It is more probable that coordinative unsaturation in the hydrides provides a relatively low-energy decomposition pathway unavailable in the alkyl or aryl derivatives. If this hypothesis is correct it should be possible to synthesize stable hydrides of these metals by using sterically encumbering groups to hinder decomposition. It is now shown that the use of the sterically encumbering properties of terphenyl substituents enables the first stable hydride of bismuth to be prepared and characterized.

Treatment of the very crowded diarylbismuth halide $(2,6\text{-}Mes_2H_3C_6)_2BiCl$ (**1**) with $LiAlH_4$ in Et_2O/PhMe solution affords the hydride derivative $(2,6\text{-}Mes_2H_3C_6)_2BiH$ (**2**) in about 30% yield. The corresponding reaction using $LiAlD_4$ gave the deuteride $(2,6\text{-}Mes_2H_3C_6)_2BiD$ (**3**). The compounds **1**–**3** were characterized by C,H elemental analysis, ^1H NMR, ^2H NMR (**3** only), ^{13}C NMR, and IR spectroscopy and by X-ray crystallography in the case of **1** and **2**.[4] The structure of **1** (Figure 1) provides evidence of high steric congestion at the bismuth center. Although the bismuth center remains pyramidally coordinated (sum of angles at Bi 309.26°), there are very large distortions in the geometry at the C(*ipso*) carbon atoms bound to bismuth. Thus, the Bi-C(*ipso*)-C(*ortho*) angles in the C(1) and C(25) terphenyl groups differ by 28.6 and 34.8°, respectively. In addition, the C(1) and C(25) aromatic ring planes deviate by 27 and 10° from the extended line of the Bi(1)–C(1) and Bi(1)–C(25) bonds. The Bi–C bond lengths of 2.337(7) and 2.418(8) Å are also quite long (cf. ca. 2.28, 2.328(13), and 2.357(14) Å in the crowded molecules $BiMes_3$[5], $Bi[CH(SiMe_3)_2]_3$[6] and $Bi[2,4,6\text{-}Ph_3C_6H_2]_3$[7]) and the C(1)-Bi-C(25) angle (123.9(3)°) is very wide in comparison to the usual angles seen in trivalent bismuth com-

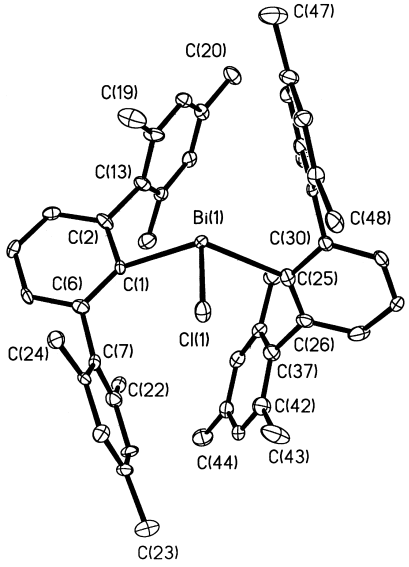

Figure 1. Structure of **1** (H atoms not shown). Selected bond lengths [Å] and angles [°]: Bi(1)-C(1) 2.337(7), Bi(1)-C(25) 2.418(8), Bi(1)-Cl(1) 2.483(3); C(1)-Bi(1)-C(25) 123.9(3), C(1)-Bi(1)-Cl(1) 98.43(19), C(25)-Bi(1)-Cl(1) 86.93(17).

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