

Synthesis and crystal structure of [C₆H₅Hg(H₂NSiMe₃)] [H₂N{B(C₆F₅)₃}₂], a phenyl–mercury(II) cation stabilised by a non-coordinating counter-anion

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Abstract

The new heteroleptic mercury(II) complex PhHgN(SiMe₃)₂ (**1**) reacts with the strong Brønsted acid [H(OEt)₂][H₂N{B(C₆F₅)₃}₂] with cleavage of a N–Si bond to give [C₆H₅Hg(H₂NSiMe₃)] [H₂N{B(C₆F₅)₃}₂] (**2**), a phenyl–mercury(II) cation stabilised by a primary amine and a non-coordinating counter-anion. Attempts to generate donor-free aryl mercury cations were not successful. The crystal structure of **2** · CH₂Cl₂ shows short π-bonding interactions between the metal and the phenyl ring of a neighbouring cation; the geometry about the mercury(II) atom is nearly linear. The X-ray structures of the new salts [H₂N(SiMe₃)₂ · H₃NSiMe₃][B(C₆F₅)₄]₂ and [Et₃O][H₂N{B(C₆F₅)₃}₂] · CH₂Cl₂ are also presented.

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1. Introduction

In the past few years, we have been interested in the isolation of electron deficient complexes of Zn, Cd and Mg and their use as initiators for ring-opening polymerisation of polar monomers [1–5]. With this aim, strong Brønsted acids such as [H(OEt)₂][B(C₆F₅)₄] [6] or [H(OEt)₂][H₂N{B(C₆F₅)₃}₂] [7] have been employed as a convenient way to generate cationic metal species by protolysis of a metal alkyl, amido or alkoxide bonds. We have recently isolated a stable *sec*-alkyl carbocation that was generated by the attack of an in situ generated Me₃Sn⁺ cation on a suitably substituted propene (Scheme 1). The resulting carbocation is stabilised by the parallel orientation of the empty p-orbital of C⁺ and the β-C–Sn bond [8,9]. This has prompted us to investigate the chemistry of other heavy metal cations with the aim of probing the general role of heavy metal

substituents in the stabilisation of carbocations, and we have more recently focused on cationic derivatives of tin [10] and thallium [11].

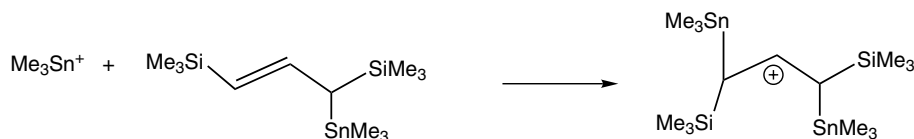
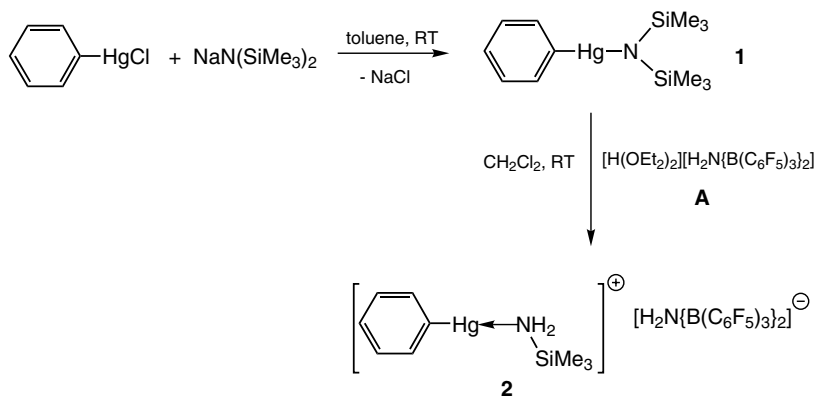
Here we report attempts to generate cationic mercury complexes with organometallic ligands, including the synthesis of the new heteroleptic mercury complex PhHgN(SiMe₃)₂, and the preparation of [C₆H₅Hg(H₂NSiMe₃)] [H₂N{B(C₆F₅)₃}₂], a rare example of a structurally characterised phenyl–mercury(II) cation stabilised by a perfluorinated non-coordinating counter-anion. The crystal structures of the unexpected reaction products [H₂N(SiMe₃)₂ · H₃NSiMe₃]²⁺[B(C₆F₅)₄]₂[−] and [Et₃O]⁺[H₂N{B(C₆F₅)₃}₂][−] · CH₂Cl₂ are also described.

2. Results and discussion

The new heteroleptic mercury(II) complex PhHgN(SiMe₃)₂ (**1**) was prepared by treatment of PhHgCl with freshly prepared NaN(SiMe₃)₂ in toluene at room temperature (Scheme 2) and isolated as a colourless solid in high yield. Compound **1** is highly soluble in chlorinated solvents

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Scheme 1. Involvement of Me_3Sn^+ in the formation of a tin-stabilised carbocation.

Scheme 2.

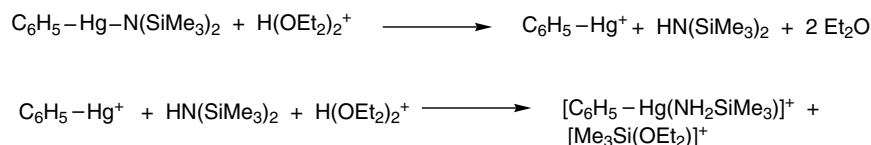
but only dissolves sparingly in aromatic and aliphatic hydrocarbons.

The reaction of **1** with an equimolar amount of $[\text{H}(\text{OEt})_2][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ (**A**) in dichloromethane yielded a white powder (**Scheme 2**). The ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{11}B and ^{19}F NMR spectra were consistent with the formulation $[\text{PhHg}(\text{H}_2\text{NSiMe}_3)][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ (**2**), and this was corroborated by elemental analysis. The presence of the primary amine H_2NSiMe_3 in the coordination sphere was unexpected; evidently it resulted from cleavage of a N–Si bond of $\text{HN}(\text{SiMe}_3)_2$ formed after protolysis of the Hg–N bond in **1**. A possible mechanism is outlined in **Scheme 3**. The ^{11}B NMR spectrum consists of a single peak at $\delta -5.3$ characteristic of the amidodiborate anion [7]. In the ^{19}F NMR spectrum, the typical resonances of the counter-anion are located at $\delta -133.4$, -160.5 and -166.0 , and there is no sign of significant $\text{Hg}\cdots\text{F}$ contact in the solution-state. Compound **2** is very soluble in dichloromethane, slightly less so in chloroform and is insoluble in toluene and light petroleum. Crystals of $\mathbf{2} \cdot \text{CH}_2\text{Cl}_2$ suitable for crystallographic studies were isolated as colourless blocks from a dichloromethane/light petroleum mixture (6:1) kept at -28°C .

The solid-state structure of $\mathbf{2} \cdot \text{CH}_2\text{Cl}_2$ was determined by X-ray diffraction. The asymmetric unit of $\mathbf{2} \cdot \text{CH}_2\text{Cl}_2$

consists of an ion pair and a disordered molecule of CH_2Cl_2 ; there is no interaction between the solvent molecule and the cationic fragment. A view of the ion pair is illustrated in **Fig. 1**. The Hg(1)–C(4) bond length of $2.044(2) \text{ \AA}$ is slightly shorter than that found in Ph_2Hg [$2.088(3) \text{ \AA}$] [12] or in the five-coordinate cation of $[(\text{tren-Me}_6)\text{HgPh}][\text{CF}_3\text{SO}_3]$ [Hg–C 2.086 \AA ; tren = tris(2-dimethylaminoethyl)amine] [13]. The Hg(1)–N(1) interatomic distance of $2.1185(19) \text{ \AA}$ to the primary amine in $\mathbf{2} \cdot \text{CH}_2\text{Cl}_2$ is much shorter than the Hg–N distances in $[(\text{tren-Me}_6)\text{HgPh}][\text{CF}_3\text{SO}_3]$ (2.266 \AA to the central N atom; 2.682 – 2.733 \AA to the three side-arm N atoms) [13] and in $[\text{Hg}(\text{TLA-H})(\text{CH}_2)\text{COCH}_3][\text{ClO}_4]_2$ [$2.615(4) \text{ \AA}$; TLA = tris{(2-[6-methylpyridyl]methyl)amine}] [14], evidently as a consequence of the increased steric hindrance of the ligand in the latter case. The geometry around the mercury(II) atom in $\mathbf{2} \cdot \text{CH}_2\text{Cl}_2$ is almost linear, as indicated by the C(4)–Hg(1)–N(1) angle of $176.80(7)^\circ$. The nitrogen atom N(1) is tetrahedral, and the Si(1)–N(1)–Hg(1) angle of $111.60(9)^\circ$ lies within the range (109.5 – 123.4) expected for related compounds [15]. The positions of the two hydrogen atoms H(101) and H(102) were refined freely.

Within the unit cell, two $[\text{PhHg}(\text{H}_2\text{NSiMe}_3)]^+$ cations were found to be related via a crystallographic inversion centre. The phenyl ring in one asymmetric unit lies above



Scheme 3.

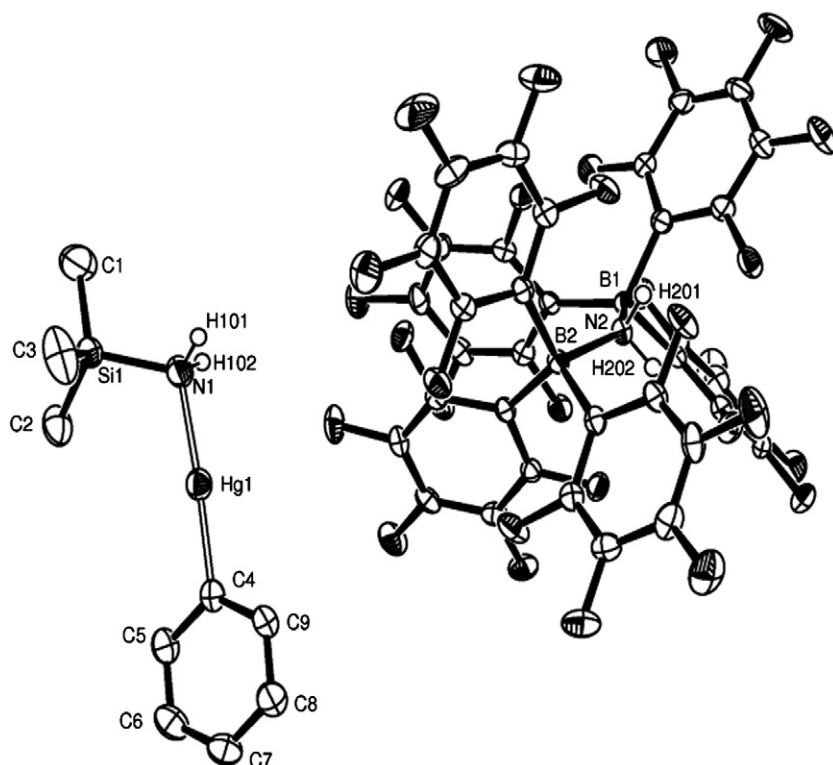


Fig. 1. View of the ion pair $[\text{PhHg}(\text{H}_2\text{NSiMe}_3)]^+[\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]^- \cdot \text{CH}_2\text{Cl}_2$ ($2 \cdot \text{CH}_2\text{Cl}_2$). Solvent molecule and hydrogen atoms (except those on nitrogen atoms) are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles ($^\circ$): Hg(1)–C(4) 2.044(2), Hg(1)–N(1) 2.1185(19), N(1)–Si(1) 1.8351(19), N(1)–H(101) 0.935(17), N(1)–H(102) 0.943(17), N(2)–B(1) 1.647(2), N(2)–B(2) 1.638(2), N(2)–H(201) 0.864(15), N(2)–H(202) 0.873(15); C(4)–Hg(1)–N(1) 176.80(7), Si(1)–N(1)–Hg(1) 111.60(9), B(1)–N(2)–B(2) 132.85(14).

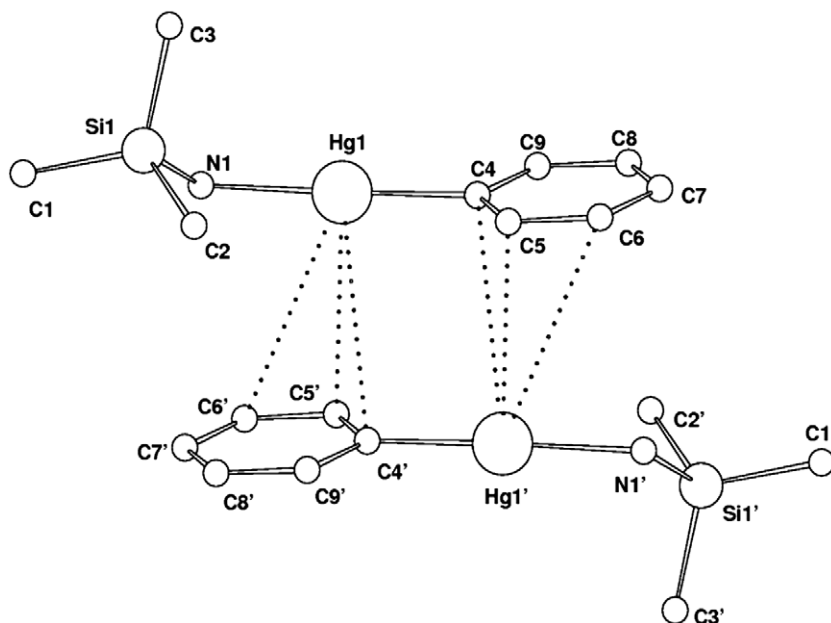


Fig. 2. View of the two $[\text{PhHg}(\text{H}_2\text{NSiMe}_3)]^+$ cations in $2 \cdot \text{CH}_2\text{Cl}_2$ showing the significant Hg–C_{arene} interactions. Selected distances (Å): Hg(1)–C(4') 3.580(2), Hg(1)–C(5) 3.276(2), Hg(1)–C(6) 3.710(2), Hg(1)–C(7) 4.324(2), Hg(1)–C(8) 4.543(2), Hg(1)–C(9) 4.214(2), Hg(1)–Hg(1) 4.3688(10).

the mercury(II) atom of the second cation (Fig. 2); thus each Hg(II) atom is involved in intermolecular π -bonding with a neighbouring aromatic ring. The arene exhibits a propensity towards η^3 -coordination to the heavy metal. The distances

Hg(1)–C(5) and Hg(1)–C(4) of 3.276(2) and 3.580(2) Å, respectively, are remarkably short, while the slightly longer Hg(1)–C(6) interatomic distance of 3.710(2) Å suggests a weaker interaction. The other distances to C(7), C(8) and

C(9) are unexceptional. Whereas Hg–C_{arene} distances shorter than 3.00 Å were found in [(C₆Me₆)Hg(O₂CCF₃)₂] [16] or the mercury(I) compound [(C₆Me₆)HgHg][AlCl₄]₂ [17], the Hg(1)–C(5) and Hg(1)–C(4) distances in **2** · CH₂Cl₂ compare well with the Hg–C_{arene} distances in, for example, [Hg{PhN₃C₆H₄N₃(H)Ph}]NO₃ [3.40(1), 3.41(1) Å] [18], {Hg[CH₃C(O)–C₆H₄N₃C₆H₄–C(O)CH₃]C₅H₅N}_n [3.487(6), 3.574(7) Å] [19], and {Hg[NNN(PhBr)₂]₂}_n [3.297(6), 3.429(6) Å] [20]. However, NMR spectroscopy does not provide evidence that the dimeric motif is preserved in solution.

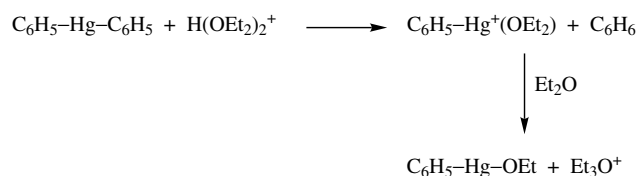
The closest Hg(1)···Hg(1) interatomic distance of 4.3688(10) Å rules out the existence of a metallophilic interaction, since it is clearly outside the upper limit of distances regarded as indicative of mercuriphilic bonds (3.7–4.0 Å) [21].

Compound **2** · CH₂Cl₂ does not display any Hg···F contacts to the amidodiborate anion in the solid-state; the shortest Hg–F distance to F(12) of 2.9688(11) Å is longer than the sum of the van der Waals radii for mercury (1.55 Å) and fluorine (1.35 Å) [22,23]. The geometry around the nitrogen atom N(2) in the [H₂N{B(C₆F₅)₃]₂][–] counter-anion in **2** · CH₂Cl₂ resembles closely that reported for [Na(OEt₂)₄][H₂N{B(C₆F₅)₃]₂] [7], with a B(1)–N(2)–B(2) angle of 132.85(14)° and N(2)–B(1) and N(2)–B(2) bond lengths of 1.647(2) and 1.638(2) Å, respectively. The anion is stabilised by five intramolecular N–H···F hydrogen bonds in the range 1.988(16)–2.40(2) Å; the shortest

of these hydrogen bonds is only a little longer than that identified in [Na(OEt₂)₄][H₂N{B(C₆F₅)₃]₂] (1.90 Å).

To probe the robustness of the N–Si bond in hexamethyldisilazane (HMDS) towards Brønsted acids where the counter-anion is weakly or non-coordinating, [Ph₂MeNH][B(C₆F₅)₄] (**B**) was reacted with a large excess of HMDS in dichloromethane. A white solid was obtained, and NMR spectroscopic characterisation and micro-analysis were consistent with the formulation [H₂N(SiMe₃)₂ · H₃NSiMe₃][B(C₆F₅)₄]₂ (**3**). The excellent isolated yield (90% relative to **B**) identifies **3** as the main product of the reaction. Clearly, ammonium salts such as **B** are sufficiently acidic to cleave one of the N–Si bonds in HMDS. Compound **3** is soluble in dichloromethane and chloroform but insoluble in hydrocarbons.

Colourless plates of **3** were obtained by recrystallisation from a dichloromethane/light petroleum mixture, and its solid-state structure was determined by X-ray diffraction crystallography (Fig. 3). The asymmetric unit consists of



Scheme 4.

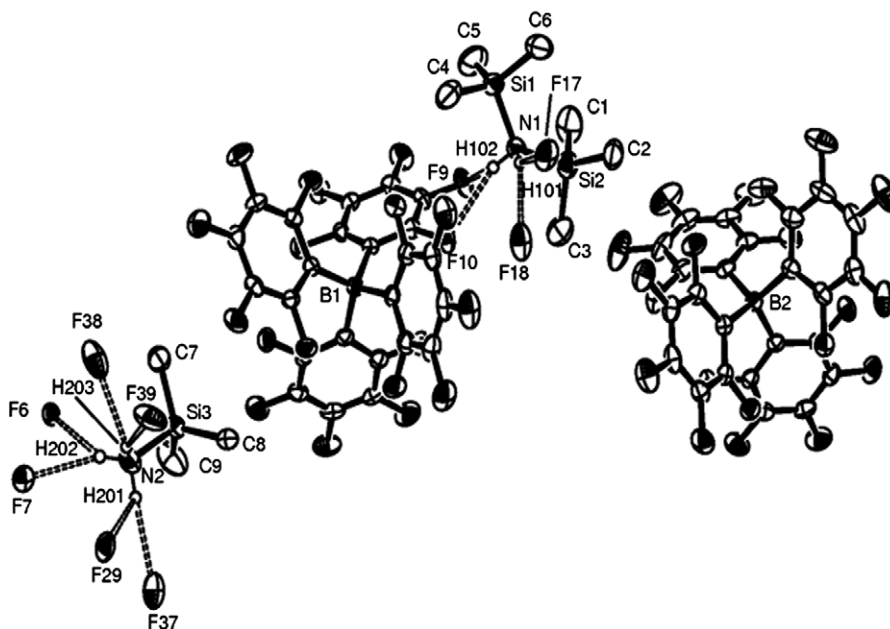


Fig. 3. View of the two ion pairs [H₂N(SiMe₃)₂][B(C₆F₅)₄] and [H₃NSiMe₃][B(C₆F₅)₄] in **3**. All hydrogen atoms except those on nitrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): N(1)–Si(1) 1.8643(19), N(1)–Si(2) 1.8673(19), N(1)–H(101) 0.971(10), N(1)–H(102) 0.966(9), N(2)–Si(3) 1.877(2), N(2)–H(201) 0.965(10), N(2)–H(202) 0.965(10), N(2)–H(203) 0.973(10), N(1)–H(101)···F(17) 2.444(14), N(1)–H(101)···F(18) 2.302(17), N(1)–H(102)···F(9) 2.188(16), N(1)–H(102)···F(10) 2.391(16), N(2)–H(201)···F(29) 2.43(2), N(2)–H(201)···F(37) 2.476(12), N(2)–H(202)···F(6) 2.438(18), N(2)–H(202)···F(7) 2.30(2), N(2)–H(203)···F(38) 2.46(2), N(2)–H(203)···F(39) 2.383(14); Si(1)–N(1)–Si(2) 127.68(10), Si(1)–N(1)–H(102) 106.4(13), H(101)–N(1)–H(102) 106.9(19), Si(3)–N(2)–H(202) 113.1(18), N(1)–H(101)–F(17) 150.2(19), N(1)–H(101)–F(18) 139.3(18), N(1)–H(102)–F(9) 143.9(19), N(1)–H(102)–F(10) 144.5(19), N(2)–H(201)–F(29) 122(2), N(2)–H(201)–F(37) 165(2), N(2)–H(202)–F(6) 149(2), N(2)–H(202)–F(7) 143(2), N(2)–H(203)–F(38) 125(2), N(2)–H(203)–F(39) 158(2).

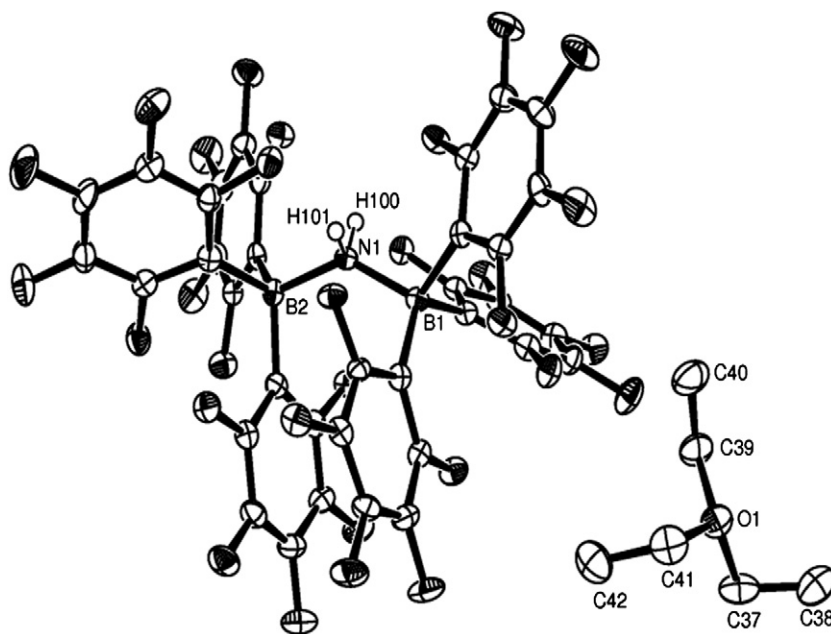


Fig. 4. View of the ion pair $[\text{Et}_3\text{O}][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2] \cdot \text{CH}_2\text{Cl}_2$ ($\mathbf{4} \cdot \text{CH}_2\text{Cl}_2$). The solvent molecule and hydrogen atoms on the oxonium are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles ($^\circ$): O(1)–C(37) 1.521(5), O(1)–C(39) 1.487(4), O(1)–C(41) 1.486(5), C(37)–C(38) 1.479(6), C(39)–C(40) 1.493(6), C(41)–C(42) 1.499(7), N(1)–B(1) 1.629(5), N(1)–B(2) 1.637(5), N(1)–H(100) 0.854(18), N(1)–H(101) 0.862(19); C(39)–O(1)–C(41) 116.9(3), C(37)–O(1)–C(41) 115.2(3), C(37)–O(1)–C(39) 112.4(3), B(1)–N(1)–B(2) 132.5(3).

the ion pairs $[\text{H}_2\text{N}(\text{SiMe}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{H}_3\text{NSiMe}_3][\text{B}(\text{C}_6\text{F}_5)_4]$. The positions of the five protons on nitrogen atoms were refined freely. In the $[\text{H}_2\text{N}(\text{SiMe}_3)_2]^+$ cation, the nitrogen atom N(1) lies in a distorted tetrahedral arrangement. The Si(1)–N(1)–Si(2) angle of $127.68(10)^\circ$ is quite obtuse in comparison of the H(101)–N(1)–H(102) angle [$106.9(19)^\circ$], while the Si(*i*)–N(1)–H(*j*) angles are in the range $103.4(14)$ – $106.4(13)^\circ$. There are four N(1)–H···F hydrogen bonds with neighbouring anions, ranging between 2.188(16) and 2.444(14) Å. In the $[\text{H}_3\text{NSiMe}_3]^+$ cation, the Si(3)–N(2)–H(*i*) angles are in the range $112.8(17)$ – $113.3(17)^\circ$, while the H(*i*)–N(2)–H(*j*) are between $104(2)^\circ$ and $108(2)^\circ$. Six N(2)–H···F hydrogen bonds with fluorine atoms from surrounding counter-anions have been found in the range 2.30(2)–2.476(12) Å.

Attempts to generate a phenylmercury(II) cationic species displaying inter- and/or intramolecular Hg–arene π -bonding interactions by protolysis of Ph_2Hg with an equimolar amount of $[\text{H}(\text{OEt}_2)_2][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ in diethyl ether yielded an intractable oily material which could not be satisfactorily characterised by NMR spectroscopy. However, a few crystals suitable for X-ray diffraction were isolated on attempted recrystallisation from a dichloromethane/light petroleum mixture at -28°C and identified as the oxonium salt $[\text{Et}_3\text{O}][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2] \cdot \text{CH}_2\text{Cl}_2$ ($\mathbf{4} \cdot \text{CH}_2\text{Cl}_2$). A possible mechanism for the formation of the oxonium cation by-product involves electrophilic ether cleavage of a $[\text{PhHg}(\text{OEt}_2)]^+$ intermediate, as illustrated in Scheme 4, though no evidence for the formation of PhHgOEt could be detected.

The crystal structure of $\mathbf{4} \cdot \text{CH}_2\text{Cl}_2$ was determined by X-ray diffraction (Fig. 4). There is disorder in the lattice CH_2Cl_2 molecule, and no contact with the cation. The arrangement around O(1) in the Et_3O^+ cation is close to trigonal planar. The C(39)–O(1)–C(41), C(37)–O(1)–C(41) and C(37)–O(1)–C(39) angles are $116.9(3)^\circ$, $115.2(3)^\circ$ and $112.4(3)^\circ$, respectively, and the oxygen atom lies 0.346(4) above the plane formed by C(37), C(39) and C(41). Overall, the structure of the oxonium cation is very similar to that in $[\text{Et}_3\text{O}][\text{BPh}_4]$ [24]. The structure of the counter-anion is almost identical to that found in $\mathbf{2} \cdot \text{CH}_2\text{Cl}_2$; the expected intramolecular N–H···F stabilising hydrogen bonds are found in the range 2.01(3)–2.32(4) Å, and the B(1)–N(1)–B(2) angle is $132.5(3)^\circ$.

3. Conclusion

The reaction of the heteroleptic mercury amide $\text{PhHgN}(\text{SiMe}_3)_2$ with $[\text{H}(\text{OEt}_2)_2][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ leads to the formation of the primary amine complex $[\text{PhHg}(\text{H}_2\text{NSiMe}_3)][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ as the result of facile N–Si bond protolysis, even under mild conditions. The $[\text{PhHg}(\text{H}_2\text{NSiMe}_3)]^+$ cation is stabilised by intermolecular π -interactions with its symmetry-related neighbour in the unit cell, which results in asymmetric η^3 -phenyl coordination. The Hg···C distances range from ca. 3.27 to 3.58 Å. The “naked” or ether-stabilised $[\text{PhHg}]^+$ cation could not be isolated; attempts to generate such a species by reacting Ph_2Hg with an equimolar amount of $[\text{H}(\text{OEt}_2)_2][\text{H}_2\text{N}$

$\{\text{B}(\text{C}_6\text{F}_5)_3\}_2$] in diethyl ether yielded the oxonium salt $[\text{Et}_3\text{O}][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ as the only isolable product, presumably the result of ether cleavage by a $[\text{C}_6\text{H}_5\text{Hg}(\text{OEt}_2)]^+$ intermediate.

4. Experimental

4.1. General procedures

All manipulations were performed under argon using standard Schlenk techniques. Solvents were pre-dried, and distilled under inert atmosphere over sodium (low-sulphur toluene), sodium–benzophenone (diethyl ether, THF), sodium–potassium alloy (light petroleum, b.p. 40–60 °C) or calcium hydride (dichloromethane). NMR solvents were dried over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. NMR spectra were recorded using a Bruker Avance DPX-300 spectrometer. Chemical shifts are reported in ppm. ^1H NMR spectra (300.13 MHz) are referenced to the residual protons of the deuterated solvent used. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (75.47 MHz) were referenced internally to the *D*-coupled ^{13}C resonances of the NMR solvent. ^{11}B (96.29 MHz) and ^{19}F (282.38 MHz) NMR spectra were referenced externally to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and CFCl_3 , respectively. $\text{HN}(\text{SiMe}_3)_2$ (97%) was purchased from Aldrich and distilled under reduced pressure prior to use. Diphenylmercury (97%) (Aldrich) was heated to 140 °C under vacuum for several hours before use. The compounds PhHgCl [25], $\text{B}(\text{C}_6\text{F}_5)_3$ [26,27], $[\text{H}(\text{OEt}_2)_2][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ (**A**) [7], and $[\text{Ph}_2\text{MeNH}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**B**) [28] were prepared following literature methods.

4.2. Synthesis of $\text{PhHgN}(\text{SiMe}_3)_2$ (**I**)

Freshly prepared $\text{NaN}(\text{SiMe}_3)_2$ (3.30 g, 18.0 mmol) was added with a side-arm to a suspension of PhHgCl (5.81 g, 18.5 mmol) in toluene (200 ml). The reaction mixture was stirred overnight at room temperature, and the volatiles were removed under vacuum. Extraction with light petroleum (3 × 100 ml) and filtration through Celite yielded a colourless solution from which a fine white powder was obtained after removal of the solvent in vacuo, yield 6.40 g (14.6 mmol, 81%). ^1H NMR (CD_2Cl_2 , 25 °C, 300.13 MHz): δ 7.46–7.24 (m, 5H, C_6H_5), 0.19 (s, 18H, SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C, 75.47 MHz): δ 136.7, 128.9, 128.6 (all aryl- C_6H_5), 5.0 (s, SiCH_3). Anal. found (calc.) for $\text{C}_{12}\text{H}_{23}\text{HgNSi}_2$: C 32.10 (32.90); H 5.49 (5.29); N 3.56 (3.20)%.

4.3. Synthesis of $[\text{PhHg}(\text{H}_2\text{NSiMe}_3)][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ (**2**)

To a solution of $[\text{H}(\text{OEt}_2)_2][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ (**A**) (0.74 g, 0.62 mmol) in dichloromethane (20 ml) was added **1** (0.28 g, 0.64 mmol). The resulting colourless solution was stirred overnight at room temperature. Light petro-

leum was added until a slightly brown solid precipitated which was isolated by filtration and washed thoroughly with light petroleum to afford a fine white powder in a yield of 0.37 g (0.26 mmol, 42%). Single-crystals of $2 \cdot \text{CH}_2\text{Cl}_2$ suitable for X-ray crystallography were obtained by recrystallisation from a dichloromethane/light petroleum mixture (4:3) stored at –28 °C. ^1H NMR (CD_2Cl_2 , 25 °C, 300.13 MHz): δ 7.55–7.25 (m, 5H, C_6H_5), 5.70 (m, 2H, $\text{B}-\text{NH}_2-\text{B}$), 3.10 (br, 2H, $\text{Hg}-\text{NH}_2-\text{Si}$), 0.63 (s, 9H, SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C, 75.47 MHz): δ 150.2, 146.5, 140.0, 138.1, 136.9, 135.1 (all aryl- C_6F_5), 135.7, 131.6, 130.5 (all aryl- C_6H_5), 1.0 (s, SiCH_3). ^{11}B NMR (CD_2Cl_2 , 25 °C, 96.29 MHz): δ –5.3. ^{19}F NMR (CD_2Cl_2 , 25 °C, 282.38 MHz): δ –133.4 [d, $J(\text{F},\text{F}) = 19.8$ Hz, 12F, *o*-F], –160.5 [t, $J(\text{F},\text{F}) = 19.8$ Hz, 6F, *p*-F], –166.0 [t, $J(\text{F},\text{F}) = 19.8$ Hz, 12F, *m*-F]. Anal. found (calc.) for $\text{C}_{45}\text{H}_{18}\text{B}_2\text{F}_{30}\text{HgN}_2\text{Si}$ (1406.89): C 38.53 (38.42); H 1.21 (1.29); N 1.87 (1.99)%.

4.4. Synthesis of $[\text{H}_2\text{N}(\text{SiMe}_3)_2 \cdot \text{H}_3\text{NSiMe}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ (**3**)

$\text{HN}(\text{SiMe}_3)_2$ (5.00 ml, 3.97 g, 24.6 mmol) was rapidly added to solution of $[\text{Ph}_2\text{MeNH}][\text{B}(\text{C}_6\text{F}_5)_4]$ (**B**) (1.29 g, 1.49 mmol) in dichloromethane (30 ml). The resulting green solution was stirred overnight at room temperature, and the volatiles were pumped off to afford a pale-green oily material. Upon repeated washings with light petroleum (3 × 40 ml) followed by re-precipitation in dichloromethane/light petroleum, a white solid was obtained and dried to constant weight. Colourless crystals were recovered by recrystallisation from a dichloromethane/light petroleum mixture (6:1) stored at –28 °C, yield of 1.08 g (0.67 mmol, 90% relative to **B**). ^1H NMR (CD_2Cl_2 , 25 °C, 300.13 MHz): δ 4.50 (br, 5H, $\text{NH}_2 + \text{NH}_3$), 0.60 (br s, 27H, SiCH_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 25 °C, 75.47 MHz): δ 150.0, 146.8, 140.2, 138.3, 136.9, 135.0 (all aryl- C_6F_5), 0.2 (br, SiCH_3), –1.1 (br, SiCH_3). ^{11}B NMR (CD_2Cl_2 , 25 °C, 96.29 MHz): δ 11.7. ^{19}F NMR (CD_2Cl_2 , 25 °C, 282.38 MHz): δ –131.6 [d, $J(\text{F},\text{F}) = 19.8$ Hz, 8F, *o*-F], –161.7 [t, $J(\text{F},\text{F}) = 19.8$ Hz, 4F, *p*-F], –165.6 [t, $J(\text{F},\text{F}) = 19.8$ Hz, 8F, *m*-F]. Anal. found (calc.) for $\text{C}_{57}\text{H}_{32}\text{B}_2\text{F}_{40}\text{N}_2\text{Si}_3$ (1610.70): C 42.23 (calc. 42.50); H 1.79 (2.00); N 1.63 (1.74) %.

4.5. Reaction of Ph_2Hg with **A**

The addition of Ph_2Hg (0.60 g, 1.7 mmol) to a solution of **A** (2.01 g, 1.7 mmol) in Et_2O (40 ml) followed by stirring at room temperature for 3 h and removal of the volatile fraction under vacuum yielded an intractable pale brown oil which could not be characterised successfully by spectroscopic methods. Upon attempted recrystallisation from a dichloromethane/light petroleum mixture stored at –28 °C, crystals of $[\text{Et}_3\text{O}][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2] \cdot \text{CH}_2\text{Cl}_2$ ($4 \cdot \text{CH}_2\text{Cl}_2$) were obtained as colourless blocks, and their structure was determined by X-ray diffraction.

4.6. X-ray crystallographic studies of $2 \cdot \text{CH}_2\text{Cl}_2$, **3** and $4 \cdot \text{CH}_2\text{Cl}_2$

Crystals were suspended in perfluorinated polyether oil, mounted on a glass fibre and transferred directly to the cold N_2 stream of either to an Oxford Diffraction Xcalibur S diffractometer ($2 \cdot \text{CH}_2\text{Cl}_2$ and **3**) or to a Bruker-Nonius KappaCCD diffractometer ($4 \cdot \text{CH}_2\text{Cl}_2$). The structure was solved by direct methods using SIR92 [29] ($2 \cdot \text{CH}_2\text{Cl}_2$ and **3**) or SHELXS-97 [28] ($4 \cdot \text{CH}_2\text{Cl}_2$). Refinement was carried out against F^2 using SHELXL-97 [30] within the WINGX program suite [31].

Crystal data for $2 \cdot \text{CH}_2\text{Cl}_2$: $[\text{C}_9\text{H}_{16}\text{HgNSi}][\text{C}_{36}\text{H}_2\text{B}_2\text{F}_{30}\text{N}] \cdot \text{CH}_2\text{Cl}_2$, colourless block $0.20 \times 0.20 \times 0.20$ mm; triclinic spacegroup $P\bar{1}$ (No. 2); lattice constants $a = 11.58699(11)$ Å, $b = 13.3787(18)$ Å, $c = 16.366(5)$ Å, $\alpha = 99.177(17)^\circ$, $\beta = 101.021(15)^\circ$, $\gamma = 96.255(9)^\circ$, $V = 2432.8(9)$ Å³, $Z = 2$; $\mu(\text{Mo K}\alpha) = 3.453$ mm⁻¹; $2\theta_{\text{max}} = 68.16^\circ$; 17980 independent reflections measured ($R_{\text{int}} = 0.0315$), of which 10974 were considered observed with $I > 2\sigma(I)$; max. residual electron density 1.611 and -0.911 e Å⁻³; 776 parameters (all non-hydrogen atoms were refined anisotropically, the positions of H(101) and H(102) were located experimentally, all others were calculated from idealised positions); $R_1 = 0.0278$ ($I > 2\sigma(I)$), $wR_2 = 0.0521$ (all data).

*Crystal data for **3**:* $[\text{C}_6\text{H}_{20}\text{NSi}_2][\text{C}_3\text{N}_{12}\text{NSi}][\text{C}_{24}\text{BF}_{20}]_2$, colourless plate $0.04 \times 0.40 \times 0.40$ mm; triclinic spacegroup $P\bar{1}$ (No. 2); lattice constants $a = 9.0223(7)$ Å, $b = 17.0579(15)$ Å, $c = 20.7275(16)$ Å, $\alpha = 83.567(7)^\circ$, $\beta = 87.638(6)^\circ$, $\gamma = 81.456(7)^\circ$, $V = 3133.7(4)$ Å³, $Z = 2$; $\mu(\text{Mo K}\alpha) = 0.237$ mm⁻¹; $2\theta_{\text{max}} = 55.026^\circ$; 14212 independent reflections measured ($R_{\text{int}} = 0.0469$), of which 7305 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.232 and -0.282 e Å⁻³; 966 parameters (all non-hydrogen atoms were refined anisotropically, the positions hydrogens bound to nitrogen were located experimentally, all others were calculated from idealised positions); $R_1 = 0.0362$ ($I > 2\sigma(I)$), $wR_2 = 0.0705$ (all data).

Crystal data for $4 \cdot \text{CH}_2\text{Cl}_2$: $[\text{C}_6\text{H}_{15}\text{O}][\text{C}_{36}\text{H}_2\text{B}_2\text{F}_{30}\text{N}] \cdot \text{CH}_2\text{Cl}_2$, colourless block $0.20 \times 0.50 \times 0.50$ mm; monoclinic spacegroup $P2_1/c$ (No. 14); lattice constants $a = 16.0249(4)$ Å, $b = 14.0892(4)$ Å, $c = 19.9188(4)$ Å, $\beta = 92.7229(14)^\circ$, $V = 4492.15(19)$ Å³, $Z = 4$; $\mu(\text{Mo K}\alpha) = 0.309$ mm⁻¹; $2\theta_{\text{max}} = 55.16^\circ$; 10294 independent reflections measured ($R_{\text{int}} = 0.1102$), of which 5943 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.826 and -0.595 e Å⁻³; 742 parameters (all non-hydrogen atoms were refined anisotropically, the positions of H(100) and H(101) were located experimentally, all others were calculated from idealised positions); $R_1 = 0.0630$ ($I > 2\sigma(I)$), $wR_2 = 0.2036$ (all data).

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Appendix A. Supplementary material

Full tables of bond lengths and angles, tables of non-hydrogen and hydrogen atomic coordinates and anisotropic thermal parameters for non-hydrogen atoms are available from the Cambridge Crystallographic Data Centre. CCDC 608249, 608250 and 608251 contain the supplementary crystallographic data for ($2 \cdot \text{CH}_2\text{Cl}_2$), **3** and ($4 \cdot \text{CH}_2\text{Cl}_2$). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.09.021.

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