of $NaBa_2O$ could not be prepared; an excess of Na and Ba in the reaction mixture is necessary to stabilize the compound, and this in turn results in the contamination of the product by NaBa and Na_2Ba upon cooling. In a temperature-dependent Guinier measurement[17] pure $NaBa_2O$, obtained from ground single crystals and mixed with powdered glass to reduce absorption effects, begins to decompose to BaO at around 435 K with full decomposition at 490 K. On the other hand, when a sample containing excess Na and Ba is heated, the diffraction lines of $NaBa_2O$ can be observed up to 525 K. However, reaction of the samples with glass could not be excluded under these conditions.

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[18] Details of the crystal-structure solution and refinement based on single-crystal data: CAD-4 diffractometer, crystal size $0.2 \times 0.15 \times 0.1$ mm, orthorhombic, space group *Cmma* (no. 67), $a = 6.5907(3)$, $b = 15.327(1)$, $c = 6.9385(5)$ Å, Ba in $8m$ $(0,y,z)$ with $y = 0.08701(2)$ and $z = 0.19869(5)$, Na in $4g$ $(0,¼,z)$ with $z = 0.6889(7)$, O in $4a$ $(¼,0,0)$, $V = 700.90(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.973$ g cm^{-3}, $2\theta_{max} = 49.94°$, $Ag_{K\alpha}$ radiation, $\lambda = 0.56086$ Å, ω-θ scan, measured at 293 K, 2618 collected and 703 unique reflections ($R_{int} = 0.0216$), absorption correction: ψ-scan, $\mu = 5.877$ mm^{-1}, crystal structure solved using direct methods (SHELXS 97[19]), full-matrix least-squares refinement (anisotropic for all atoms) on F^2 (SHELXL 97[19]), 15 parameters refined, $R1(I > 2\sigma(I)) = 0.0297$, $wR2(I > 2\sigma(I)) = 0.0768$, $R1$(all data) $= 0.0309$, $wR2$(all data) $= 0.0777$, GOF $= 1.183$. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-411905.

[19] SHELXTL Version 5.1, Bruker AXS, **1998**.

[20] Powder X-ray diffraction data, collected on samples of ground single crystals sealed in capillaries,[16] was used for full-profile Rietveld refinement; the CSD Package[21] was employed. The atomic positions obtained were consistent with those from the refinement of the single-crystal data, though less accurate. The thermal displacement parameters had to be fixed; the unit cell parameters were refined to $a = 6.5916(3)$ Å, $b = 15.3282(8)$ Å, and $c = 6.9628(4)$ Å with $R_{int} = 0.082$ and $R_{profile} = 0.252$.

[21] "CSD—Universal program package for single crystal and/or powder structure data treatment": L. G. Akselrud, Yu. N. Grin, P. Yu. Zavalij, V. K. Pecharsky, V. S. Fundamenskii, *12th European Crystallographic Meeting*, Moscow, **1989**, *3*, 155 (http://imr.chem.binghamton.edu/zavalij/CSD.html).

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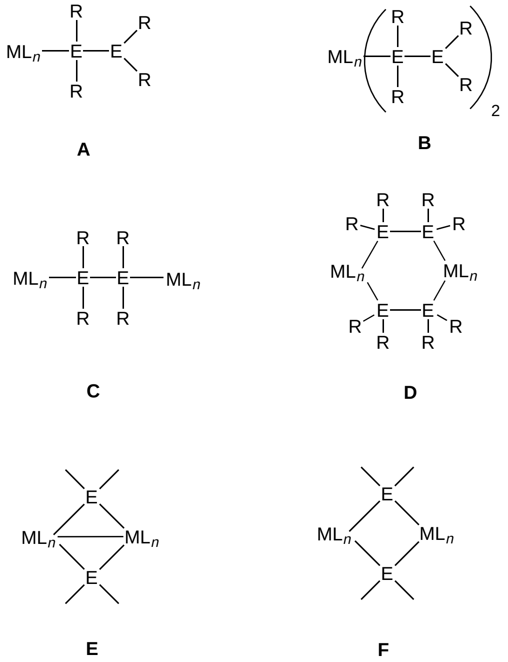
Reactions of Et_4Bi_2 with tBu_3M (M = Al, Ga)—Synthesis of Complexes with a Bidentate Dibismuthane Ligand**

Andreas Kuczkowski, Stephan Schulz,* and Martin Nieger

Dedicated to Professor Oskar M. Glemser on the occasion of his 90th birthday

Since Cadet's discovery of the "fuming liquid" in 1757, numerous tetraorganodipnicogens of the type R_4E_2 (E = P, As, Sb) containing a central E–E bond have been synthesized.[1] Detailed investigations on their reactions with transition metal complexes showed their ability to form monodentate (Scheme 1, type A and B) and bidentate complexes (type C and D) under preservation of the central E–E bond. In addition, heterocycles (type E and F) were formed under E–E bond cleavage.[1, 2]



Scheme 1. Coordination modes for transition metal complexes with dipnicogen ligands R_4E_2.

In contrast, reactions with main group metal complexes such as Group 13 trialkyl compounds have been investigated to a far lesser extent. $[Me_4P_2][BH_3]_2$ (type C) was synthesized almost 50 years ago by Nöth and Burg;[3] however, the only structurally characterized compounds known were $Me_4P_2(BH_3)_2$[4] and $Me_4P_2(BH_2Br)_2$[5] prior to our recent

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syntheses and X-ray crystal structure determinations of four distibane bisadducts $[Sb_2R_4][MR'_3]_2$ (M = Al, Ga; type C).[6] Distibane bisadducts are stable in the pure form, but readily undergo consecutive reactions in solution under Sb–Sb bond cleavage to give four- and six-membered heterocycles of type F.[6] An analogous reaction pathway was observed by Breunig et al. in the synthesis of the six-membered stibinoindane $[\{(Me_3SiCH_2)_2InSbMe_2\}_3]$ from Me_4Sb_2 and $(Me_3SiCH_2)_3In$.[7]

The low stability of the distibane bisadducts $[Sb_2R_4][MR'_3]_2$ is not surprising, since the stability of the E–E bond in tetraorganodipnicogens R_4E_2 generally decreases with increasing atomic number of the central pnicogen E. Consequently, distibanes and dibismuthanes exhibit the strongest tendency toward disproportionation into the elemental pnicogens E and triorganopnicogens R_3E. As a result only a few stable dibismuthanes have been synthesized and structurally characterized,[8] and, to the best of our knowledge, dibismuthanes have not been reported to serve as a mono- or bidentate ligand. Evidently, both the very weak Bi–Bi bond and the high s character of the lone pairs of electrons limit their potential for further complexation reactions.[9]

In an attempt to gain insight into the reactivity of dibismuthanes toward Group 13 trialkyl compounds, we treated tetraethyldibismuthane Et_4Bi_2 with tri(*tert*)butylalane and -gallane, respectively, in a 2:1 molar ratio [Eq. (1); M = Al (**1**), Ga (**2**)].

$$2\,t\text{Bu}_3\text{M} + \text{Bi}_2\text{Et}_4 \longrightarrow [\text{Et}_4\text{Bi}_2][\text{M}t\text{Bu}_3]_2 \qquad (1)$$

Since Et_4Bi_2 is only stable below 0 °C,[8a] the reagents were precooled to −20 °C and combined in a flask in the glovebox. The reaction with $t\text{Bu}_3\text{Ga}$ immediately yielded an orange solid, which was recrystallized from *n*-pentane at −30 °C to give orange crystals, while the analogous reaction with $t\text{Bu}_3\text{Al}$ resulted in the formation of a dark brown, partially insoluble (metallic) solid. However, if the latter reaction was carried out in *n*-pentane at −78 °C, it yielded a light red solution, which on storage at −60 °C gave yellow crystals after 48 h. Both crystalline products were shown by NMR spectroscopy and single-crystal X-ray diffraction to be the desired dibismuthane bisadducts $[\text{Bi}_2\text{Et}_4][\text{M}t\text{Bu}_3]_2$ (M = Al (**1**), Ga (**2**); type C).

The stability of **1** and **2** both in the pure form and in solution differ significantly. While **2** can be stored at −30 °C in the dark under an inert gas atmosphere without decomposition for weeks, **1** decomposes slowly to give a brown solid. The same tendency was observed in solution. Compound **2** can be dissolved at −30 °C without decomposition, while **1** undergoes consecutive reactions, as was shown by ^{1}H NMR experiments. The signals observed for **2** in [D$_8$]toluene at −30 °C revealed the presence of the organic substituents Et and *t*Bu in a relative intensity ratio of 2:3, clearly indicating the presence of the bisadduct. The resonance signals are shifted to lower field (*t*Bu–M) and higher field (Et–Bi), respectively, as was observed for the corresponding distibane bisadducts $[Sb_2R_4][MR'_3]_2$[6] and the simple Lewis acid–base adducts $R'_3M{-}BiR_3$ (M = Al, Ga).[10] In contrast, the ^{1}H NMR spectrum of **1** recorded at −30 °C shows resonance signals due to the Et and *t*Bu groups in an intensity ratio of 1:1, which is not consistent with the formation of a bisadduct. A spectrum of **1** with the correct signal intensity was finally obtained from a freshly prepared sample, which was dissolved in [D$_8$]toluene and measured at −60 °C.[11]

The stability of **1** and **2** in the gas phase seems to be limited. The mass spectrum of **2** only shows signals for the fragmentation products (Et_4Bi_2 and $t\text{Bu}_3\text{Ga}$) of the bisadduct.[12]

Single crystals of **1** and **2** suitable for an X-ray structure determination were obtained from solutions in *n*-pentane at −60 °C.[13] As was observed for the corresponding distibane bisadducts, the substituents bound to bismuth in **1** and **2** adopt staggered conformations. The $\text{M}t\text{Bu}_3$ fragments are arranged *trans*, presumably for steric reasons (Figure 1 and 2). How-

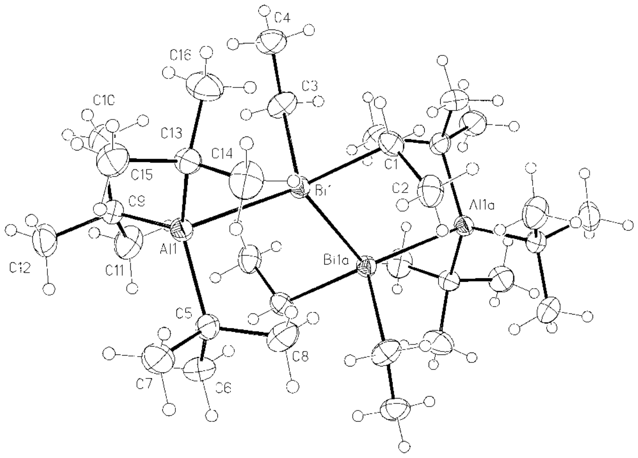

Figure 1. Molecular structure of $[\text{Et}_4\text{Bi}_2][\text{Al}t\text{Bu}_3]_2$ (**1**). Selected bond lengths [Å] and angles [°]: Bi1-Al1 3.084(1), Bi1-Bi1a 2.983(1), Bi1-C1 2.258(3), Bi1-C3 2.275(4), Al1-C5 2.003(4), Al1-C9 2.018(4), Al1-C13 2.026(3); Al1-Bi1-Bi1a 126.7(1), C1-Bi1-C3 94.5(1), C1-Bi1-Bi1a 95.4(1), C3-Bi1-Bi1a 97.8(1), C5-Al1-C9 118.4(2), C5-Al1-C13 116.9(2), C9-Al1-C13 117.5(2).

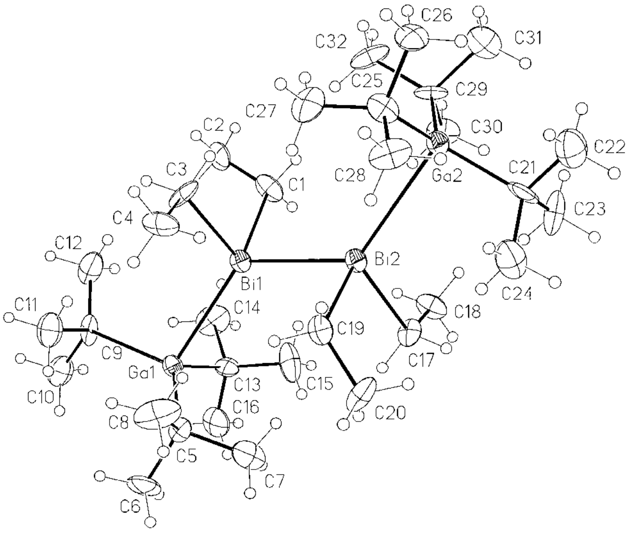

Figure 2. Molecular structure of $[\text{Et}_4\text{Bi}_2][\text{Ga}t\text{Bu}_3]_2$ (**2**). Selected bond lengths [Å] and angles [°]: Bi1-Ga1 3.099(2), Bi2-Ga2 3.114(2), Bi1-Bi2 2.984(1), Bi1-C1 2.274(15), Bi1-C3 2.284(14), Bi2-C17 2.286(14), Bi2-C19 2.286(15), Ga1-C5 2.006(15), Ga1-C9 2.056(17), Ga1-C13 2.045(18), Ga2-C21 2.030(20), Ga2-C25 2.065(17), Ga2-C29 2.029(15); Ga1-Bi1-Bi2 130.2(1), Ga2-Bi1-Bi2 129.7(1), C1-Bi1-C3 93.7(6), C1-Bi1-Bi2 97.5(5), C3-Bi1-Bi2 94.7(5), C17-Bi2-C19 96.6(6), C17-Bi2-Bi1 98.3(4), C19-Bi2-Bi1 96.7(4), C5-Ga1-C9 115.5(6), C5-Ga1-C13 120.1(6), C9-Ga1-C13 118.7(7), C21-Ga2-C25 119.0(8), C21-Ga2-C29 117.5(8), C25-Ga2-C29 116.9(7).

ever, only **1** possesses crystallographic C_i symmetry with the center of symmetry in the Bi–Bi bond. The Bi–Bi bond lengths (2.983(1) (**1**), 2.984(1) Å (**2**)) are almost identical to those of uncomplexed dibismuthanes (Ph_4Bi_2: 2.990, $(Me_3Si)_4Bi_2$: 3.035, $(HC{\equiv}CMe)_2BiBi(MeC{\equiv}CH)_2$: 2.990 Å),[14] despite the increased steric pressure within the adducts. The solid-state structures show no evidence for a Bi–Bi bond weakening.[15] The same tendency was established for the corresponding distibane bisadducts $[Sb_2Et_4][MtBu_3]_2$ (M = Al, Ga).[6] The Al–Bi (3.084(1) Å (**1**)) and Ga–Bi bond lengths (3.099(2) (Ga1–Bi1), 3.114(2) Å (Ga2–Bi2) (**2**)) are comparable to those found in $i\mathrm{Pr}_3BiMt\mathrm{Bu}_3$ (3.088(1) (M = Al),[10b] 3.135(1) Å (M = Ga) [10a]), but more than 30 pm longer than the sum of the covalent radii,[16] indicating only weak acid–base interactions. The M–Bi, M–C (average values: 2.016 (**1**), 2.036 (Ga1), 2.041 Å (Ga2) (**2**)), and Bi–C distances (average values: 2.267 (**1**), 2.279 (Bi1), 2.286 Å (Bi2) (**2**)) as well as the sum of the C-Bi-C and C-Bi-Bi bond angles (287.7° (**1**), 285.9° (Bi1), 291.6 (Bi2) (**2**)) in **1** and **2** are almost identical. Compared to the sum of the C-Sb-C and C-Sb-Sb bond angles observed in the distibane bisadducts $[Sb_2Et_4][MtBu_3]_2$ (292.9° (M = Al), 291.1° (M = Ga)), they are slightly decreased. This points to a higher s character of the dative Bi–M bonding electron pairs, as was observed for the simple Lewis acid–base adducts $R'_3M{-}BiR_3$ (M = Al, Ga), and to a higher p character of the Bi–C and Bi–Bi bonding electron pairs compared to those of the stibane bisadducts. Consequently, the sum of the C-M-C bond angles in $[Bi_2Et_4][MtBu_3]_2$ (352.8° (**1**); 354.3°, 353.4° (**2**)) is slightly larger than those found in $[Sb_2Et_4][MtBu_3]_2$ (350.2° (M = Al), 351.1°(M = Ga), indicating Et_4Bi_2 to be a weaker Lewis base than Et_4Sb_2.[17] Currently, we are investigating the nature of the reaction product(s) of **1** and **2** in solution.

Experimental Section

$[Et_4Bi_2][Al\mathit{t}Bu_3]_2$, **1** ($M = 930.83\ \mathrm{g\,mol^{-1}}$): $t\mathrm{Bu}_3Al$ (2 mmol, 0.40 g) was added at −78 °C to a solution of Et_4Bi_2 (1 mmol, 0.53 g) in *n*-pentane (5 mL). The resulting red solution was stored at −60 °C. After 48 h, yellow crystals of **1** were obtained. Yield: 0.43 g, 0.47 mmol, 47 %. M.p. < −15 °C. NMR data:[18] ^1H NMR (300 MHz, $[D_8]$toluene, −60 °C): $\delta = 1.43$ (s, 27 H; *t*Bu), 1.95 (t, $^3J_{H,H} = 7.8$ Hz, 6 H; *Me*CH_2), 2.34–2.55 (m, 4 H; Me*CH₂*); $^{13}C\{^1H\}$ NMR (80 MHz, $[D_8]$toluene, −60 °C): $\delta = 0.7$ ($Me\mathit{CH_2}$), 15.4 ($\mathit{Me}CH_2$), 31.1 ($\mathit{Me_3}CAl$).

$[Et_4Bi_2][Ga\mathit{t}Bu_3]_2$, **2** ($M = 1016.31\ \mathrm{g\,mol^{-1}}$): Precooled (−20 °C) Et_4Bi_2 (1 mmol, 0.53 g) and $t\mathrm{Bu}_3Ga$ (2 mmol, 0.48 g) were combined in a flask in glovebox. The resulting orange solid was dissolved in cold (−30 °C) *n*-pentane (5 mL) and stored at −30 °C. After 10 h, orange crystals of **2** had formed. Yield: 0.86 g, 0.85 mmol, 85 %. M.p. below −10 °C. NMR data:[18] ^1H NMR (300 MHz, $[D_8]$toluene, −30 °C): $\delta = 1.35$ (s, 27 H; *t*Bu), 2.06 (t, $^3J_{H,H} = 7.8$ Hz, 12 H; $\mathit{CH_3}CH_2$), 2.42–2.62 (m, 8 H; $CH_3\mathit{CH_2}$); $^{13}C\{^1H\}$ NMR (80 MHz, $[D_8]$toluene, −30 °C): $\delta = 1.4$ ($CH_3\mathit{CH_2}$), 17.2 ($\mathit{CH_3}CH_2$), 32.0 ($\mathit{CH_3}C$); MS (EI, 12 eV): *m/z* (%): 57 (100) $[t\mathrm{Bu}]^+$, 241 (10) $[t\mathrm{Bu}_3Ga]^+$, 267 (20) $[BiEt_2]^+$.

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[11] The proton resonances observed in the NMR spectra of **1** and **2** correspond to an ABX_3 spin system as was shown by simulation. The chemical shifts and coupling constants were determined as follows: **1**: $\delta = 1.95$ (3 H), 2.39 (1 H), 2.50 (1 H); $^3J_{H,H} = 7.1$, 8.6 Hz, $^2J_{H,H} = 18.7$ Hz; **2**: $\delta = 1.06$ (3 H), 2.47 (1 H), 2.56 (1 H); $^3J_{H,H} = 7.2$, 8.5 Hz, $^2J_{H,H} = 17.0$ Hz.

[12] A mass spectrum of **1** could not be obtained due to the thermal instability of **1** at ambient temperature. The same reason accounts for the unsuccessful attempts to obtain reliable elemental analyses of both **1** and **2**. It was not possible to prepare the samples under cold (−20 °C) conditions, which is necessary to avoid significant decomposition of the compounds, in particular of the alane bisadduct **1**.

[13] $[Bi_2Et_4][Al\mathit{t}Bu_3]_2$ ($C_{32}H_{74}Al_2Bi_2$) **1**, light yellow crystals, crystal dimensions 0.35 × 0.20 × 0.10 mm; $M_r = 930.8$; monoclinic, space group $P2(1)/c$ (no. 14), $a = 8.5064(1)$, $b = 16.1566(3)$, $c = 15.0684(3)$ Å, $\beta = 104.804(1)°$, $V = 2002.2(1)$ Å³, $Z = 2$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 8.838\ \mathrm{mm^{-1}}$, $\rho_{calcd} = 1.544\ \mathrm{g\,cm^{-3}}$, $T = 123(2)$ K, $F(000) = 916$. By using a Nonius Kappa CCD diffractometer, 39642 reflections ($2\theta_{max} = 50°$) were collected (3513 unique, $R_{int} = 0.0839$). The structure was solved by Patterson methods (SHELXS 97)[19] and refined by full-matrix least-squares on F^2 (SHELXL 97).[20] All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model. $R_1 = 0.020$ ($I > 2\sigma(I)$), $wR_2 = 0.034$, 163 parameters, largest max./min. in the final difference Fourier synthesis: 1.017/−0.703 e Å⁻³. An empirical absorption correction was applied (max./min. transmission 0.4940/0.2109). $[Bi_2Et_4][Ga\mathit{t}Bu_3]_2$ ($C_{32}H_{74}Ga_2Bi_2$) **2**, light orange crystals, crystal dimensions 0.30 × 0.15 × 0.10 mm; $M_r = 1016.3$; monoclinic, space group $P2(1)/n$ (no. 14), $a = 8.5385(7)$, $b = 16.1156(11)$, $c = 29.010(2)$ Å, $\beta = 91.445(2)°$, $V = 3990.6(5)$ Å³, $Z = 4$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu = 10.145\ \mathrm{mm^{-1}}$, $\rho_{calcd} = 1.692\ \mathrm{g\,cm^{-3}}$, $T = 123(2)$ K, $F(000) = 1976$. By using a Nonius Kappa CCD diffractometer, 9111 reflections ($2\theta_{max} = 50°$) were collected (5222 unique, $R_{int} = 0.0731$). The structure was solved by Patterson methods (SHELXS 97)[19] and refined by full-matrix least-squares on F^2 (SHELXL 97).[20] All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model. $R_1 = 0.062$ ($I > 2\sigma(I)$), $wR_2 = 0.191$, 325 parameters,

largest max./min. in the final difference Fourier synthesis: 2.275/ − 2.815 e Å^{-3}. An empirical absorption correction was applied (max./ min. transmission 0.3854/0.1220). 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-164447 (**1**) and CCDC-164446 (**2**). 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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[15] Unfortunately the X-ray crystal structure of Et_4Bi_2 is unknown to date, allowing no comparison of the Bi–Bi bond length between the uncomplexed and complexed form.

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The $XeCl^+$ Ion: $[XeCl]^+[Sb_2F_{11}]^-$**

Stefan Seidel and Konrad Seppelt*

XeF_2, XeF_4, and XeF_6 are the only binary noble gas compounds that are thermodynamically stable against decomposition into the elements. $XeCl_2$, however, has only been detected in matrix,[1] not counting the single unreproduced report, in which it was claimed $XeCl_2$ could be prepared by high frequency discharge of Xe, F_2, and $SiCl_4$ or CCl_4 and that it is stable up to 80 °C.[2]

Cocrystallisates of RbCl or CsCl and, XeO_3 are known, however, which have Xe–Cl contact distances of 275(5) to 297(1) pm.[3] Quite recently $(C_6F_5Xe)_2Cl^+$ was prepared from $C_6F_5Xe^+$ and $(CH_3)_3SiCl$. In the solid state it shows contact distances between Xe and Cl of 284.7(1) and 278.4(2) pm and a Xe-Cl-Xe bond angle of 116.96(8)°. Also $C_6F_5Xe{-}Cl$ has been isolated under very careful conditions starting with $C_6F_5Xe^+$ and the HCl–pyridine adduct $4\text{-}ClC_5H_4N \cdot HCl$. Because of its instability in solution no further detailed structure information is available, but it can be assumed that it contains a real Xe–Cl bond.[4] Since the bond strength is stronger in XeF^+ than in XeF_2, salts with the $XeCl^+$ ion could be the most stable species with a Xe–Cl bond.

We reacted $[XeF]^+[SbF_6]^-$ in HF/SbF_5 solution with small amounts of $SbCl_5$. Besides the nucleophilic Cl/F exchange [Eq. (1)], oxidation of Cl^- also takes place: An intermediate blue solution is observed, which is stable at room temperature for some time. This blue solution probably contains Cl_4^+, the first oxidation product of chlorine in the liquid phase, which has recently been identified in the form of the blue salt $[Cl_4]^+[IrF_6]^-$.[5] We did not succeed in crystallizing this blue product. After the decomposition into Cl_3^+,[5] the color of the solution changes to green and finally to orange, from which orange crystals were isolated. These melt at about −20 °C under partial decomposition.

$$XeF^+ \text{ (yellow)} + Cl^- \longrightarrow XeCl^+ \text{ (orange)} + F^- \qquad (1)$$

The unit cell contains two crystallographically different, but otherwise essentially similar $[XeCl]^+[Sb_2F_{11}]^-$ units (Figure 1, only Molecule I is shown).[6] The Xe–Cl distance is much shorter (230.9(2) pm; Molecule II: 230.4(2) pm) than any Xe–Cl distances measured to date in Xe–Cl compounds and corresponds to a Xe–Cl single bond, as is also predicted by ab initio calculations (230.07 pm, see Table 1). For comparison, isoelectronic ICl has a I–Cl bond length of 230.3 pm in the gaseous state and of 235.1–244.0 pm in the solid.[7] Similarly to the XeF^+ and KrF^+ ion,[8, 9] a contact is observed between the $XeCl^+$ ion and an F atom of the $Sb_2F_{11}^-$ ion, which leads to

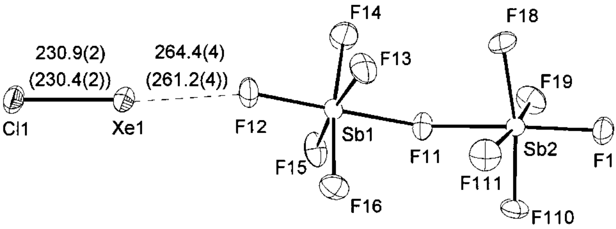

Figure 1. Ion pair $[XeCl]^+[Sb_2F_{11}]^-$ in the crystal (ORTEP representation, 50% probability ellipsoids). Ion pair I is depicted (distances in pm; numbers in parentheses: distances for ion pair II).

Table 1. Calculated bond lengths *r* [pm] for the singlet state and singlet–triplet energy separation Δ*E* [kJ mol^{-1}] for diatomic noble gas halogen cations; CCSD approximation (numbers in parentheses: MP2 approximation).

Cation	*r* [pm]	Δ*E* [kJ mol^{-1}]
ArF^+[a]	168.2 (165.2)	55.8 (76.7)
$ArCl^+$	210.6 (208.1)	−32.6 (−30.9)
$ArBr^+$	238.5 (236.4)	−101.4 (−112.9)
ArI^+	269.4 (263.4)	−115.7 (−128.1)
KrF^+[b]	174.9 (173.5)	99.3 (134.9)
$KrCl^+$	217.7 (215.4)	29.4 (39.4)
$KrBr^+$	238.7 (237.9)	−27.3 (−35.8)
KrI^+	261.6 (260.2)	−57.9 (−66.5)
XeF^+[c]	189.9 (189.4)	117.9 (154.5)
$XeCl^+$	232.9 (230.7)	74.8 (86.1)
$XeBr^+$	254.4 (253.2)	21.8 (16.4)
XeI^+[d]	276.6 (275.3)	−13.9 (−21.7)

[a] See also ref. [12]. [b] 176.5(3) pm in $[KrF]^+[SbF_6]^-$.[9] [c] 188.8(2) pm in $[XeF]^+[SbF_6]^-$.[18] [d] See also ref. [11]. Especially in this combination of two heavy atoms the spin-orbit coupling can strongly influence the values. This is not taken into account.

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