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First successful reaction of a silyl anion with hafnium tetrachloride

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Hafnium tetrachloride reacts with the tris(trimethylsilyl)silyl potassium tmen adduct (1) to form a [tris(trimethylsilyl)silyl]trichlorohafnium tmen complex (2); reaction of 2 with 2,6-dimethylphenylisonitrile leads to insertion into the silicon hafnium bond (4).

The chemistry of group 4 silyl compounds is a rapidly developing area,[1] which contributes important aspects to the research on catalysis[2,3] and new materials.[4] However, most of this chemistry studied so far involves compounds with cyclopentadienyl (Cp) or related ligands.[1] Although there are a few examples of Cp-free silyl Zr[5,6] and Hf[6] complexes, the seemingly most straightforward way to access this class of compounds, namely the reaction of a silyl anion with a group 4 tetrahalide has not been reported so far. A likely reason for this is that this reaction under the conditions usually employed suffers from severe side reactions. The strongly Lewis acidic character of the metal halides activates ethereal solvents present from the generation of the silyl reagents and makes them susceptible for nucleophilic attack by the silyl anion.

In the course of our studies of oligosilyl anions[7] we have investigated alternative donor molecules for oligosilyl potassium compounds. For example we have prepared the tris(trimethylsilyl)silyl potassium tmen adduct (**1**) which is obtained in the reaction of tetrakis(trimethylsilyl)silane and potassium *tert*-butoxide in toluene in the presence of three equivalents of tetramethylethylenediamine (tmen).†

The reaction of two equivalents of **1** with hafnium tetrachloride in toluene gave, in a clean reaction, a hafnium trichloride tris(trimethylsilyl)silyl tmen complex (**2**) besides one equivalent of tris(trimethylsilyl)silane. Reaction of only one equivalent of **1** leads to incomplete formation of **2** accompanied by the hafnium tetrachloride tmen complex (**3**). This seems to indicate the formation of the latter compound as the first step in the course of reaction. Interestingly, no crystal structure analysis of a hafnium tmen complex has been reported so far, so that the compounds in this report constitute the first examples of this class of compounds.

Crystal structure analysis of **3**‡ reveals a distorted octahedron (Fig. 1). The bite angle of the tmen ligand [76.9(4)°] and the angle of the chloro ligands in *trans*-position to the nitrogen atoms [102.98(18)°] are the only *cis*-dihedral angles differing significantly from the ideal 90°. All other angles range between 86.8(3) and 91.9(3)°. The slightly elongated bond length between hafnium and Cl(2) [2.382(3) Å] and Cl(4) [2.385(4) Å] compared to those between hafnium and Cl(1) [2.362(3) Å] and Cl(3) [2.368(4) Å] suggest that the chloro ligand exhibits a stronger *trans* effect than tmen. This is consistent to what has been found for a related zirconium compound.[8] The crystal structure of **2**‡ shows again distorted octahedral geometry with the silyl ligand in the *trans*-position to a nitrogen atom (Fig. 2). The silyl hafnium bond length [2.802(6) Å] lies within the range of the values found so far.[6a,9] The bond distance between the nitrogen in *trans*-position to the silyl ligand and hafnium [2.473(14) Å] is substantially elongated compared to the one with the one *trans* to the chloro ligand [2.378(14) Å].

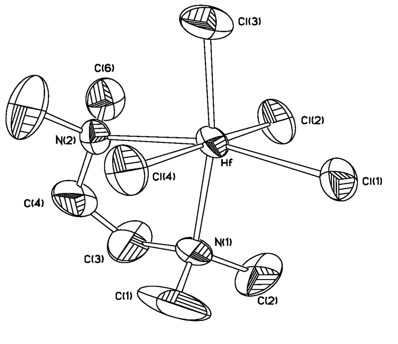

Fig. 1 Molecular structure of **3** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (°): Hf–N(1) 2.372(11), Hf–N(2) 2.369(9), Hf–Cl(1) 2.362(3), Hf–Cl(2) 2.382(3), Hf–Cl(3) 2.368(4), Hf–Cl(4) 2.385(4); N(1)–Hf–N(2) 76.9(4), Cl(1)–Hf–Cl(3) 102.98(18), Cl(2)–Hf–Cl(4) 175.33(14).

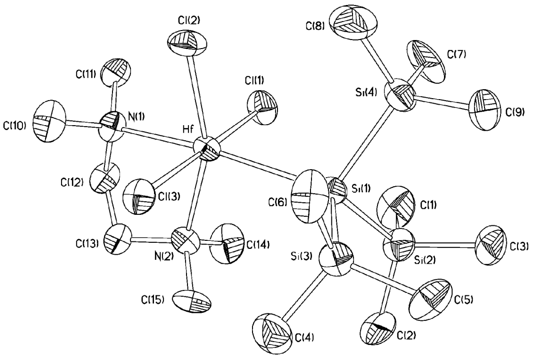

Fig. 2 Molecular structure of **2** with thermal ellipsoids at the 30 % probability level. Selected bond distances (Å) and angles (°): Hf–Si(1) 2.802(6), Hf–N(1) 2.473(14), Hf–N(2) 2.378(14), Hf–Cl(1) 2.367(5), Hf–Cl(2) 2.361(5), Hf–Cl(3) 2.392(5); N(1)–Hf–N(2) 74.8(6), Cl(1)–Hf–Cl(3) 177.52(19), Si(1)–Hf–N(1) 167.3(4), Si(4)–Si(1)–Si(3) 104.2(3), Si(4)–Si(1)–Si(2) 101.8(3), Si(3)–Si(1)–Si(2) 105.3(3).

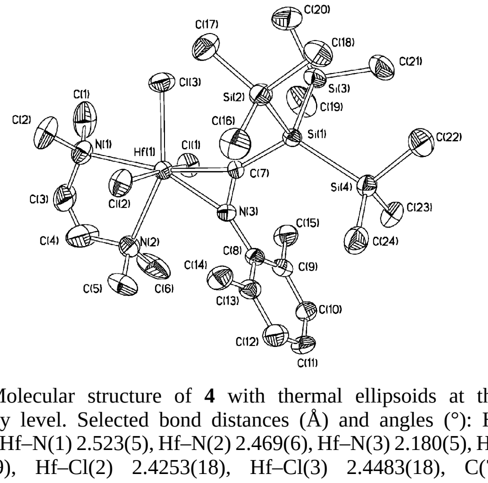

Fig. 3 Molecular structure of **4** with thermal ellipsoids at the 30% probability level. Selected bond distances (Å) and angles (°): Hf–C(7) 2.212(6), Hf–N(1) 2.523(5), Hf–N(2) 2.469(6), Hf–N(3) 2.180(5), Hf–Cl(1) 2.4338(19), Hf–Cl(2) 2.4253(18), Hf–Cl(3) 2.4483(18), C(7)–N(3) 1.273(7); N(1)–Hf–N(2) 74.0(2), Cl(1)–Hf–Cl(2) 169.25(7), Si(4)–Si(1)–Si(3) 107.83(10), Si(4)–Si(1)–Si(2) 108.48(10), Si(3)–Si(1)–Si(2) 109.12(10).

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The Si–Hf bond in **2** can be cleaved by reaction with water or hydrogen to form tris(trimethylsilyl)silane. Insertion into the silyl–metal bond can be accomplished with 2,6-dimethylphenylisonitrile[5*b*,10] to give compound **4**.† Structure analysis‡ of this compound exhibits a distorted octahedron with the tmen ligand almost coplanar with the metallazirine ring (Fig. 3). Both bonds of chloro [2.4253(18), 2.4338(19), 2.4443(18) Å] and nitrogen [2.469(6), 2.523(5) Å] atoms to hafnium are significantly elongated compared to the structures of **2** and **3**. Due to the more electron donating properties of the imine ligand the hafnium nitrogen bond length increases from 2.369(9) Å in **3** to 2.523(5) Å.

Experiments to test for the catalytic activity of **2** with respect to dehydropolymerisation of phenylsilane[2] and 1,2-dimethyldisilane[11] proved to be not successful.

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Notes and references

† *Preparation* of **1**: all experimental manipulations were performed under rigorously anaerobic conditions using standard Schlenk techniques or a nitrogen filled glovebox. Tetrakis(trimethylsilyl)silane (1.50 g, 4.68 mmol) and potassium *tert*-butanolate (0.55 g, 4.90 mmol) were suspended in 20 mL of toluene. Tetramethylethylenediamine (tmen) (1.63 g, 14.0 mmol) was added at 0 °C and then the solution was stirred at r.t. for 2 h. The resultant green solution was concentrated, redissolved in pentane, filtered and cooled to −36 °C to obtain colorless crystals of **1** which were isolated by filtration (yield: 1.95 g, 80%). ^{1}H NMR (500 MHz, C_6D_6): δ 1.94 (s, 8H), 1.89 (s, 24H), 0.64 (s, 27H). ^{13}C NMR (125.7 MHz, C_6D_6): δ 57.3, 45.6, 7.52. ^{29}Si NMR (59.3 MHz, C_6D_6): δ −5.1, −189.7. Anal. Calc. for $C_{21}H_{59}KN_4Si_4$: C, 48.58; H, 11.45. Found: C, 48.09; H: 11.33%.

Preparation of **2**: $HfCl_4$ (0.50 g, 1.56 mmol) and **1** (1.62 g, 3.12 mmol) were dissolved in 6 mL cold toluene (-36°C). The orange solution was allowed to warm slowly to r.t., then treated with 3 mL pentane and the obtained precipitate was removed by filtration. The solution was reduced in volume and thin plate orange crystals could be isolated by filtration (yield: 0.63 g, 62%). ^{1}H NMR (300 MHz, C_6D_6): δ 2.23 (s, 12H), 1.61 (s, 4H), 0.65 (s, 27H). ^{13}C NMR (75.4 MHz, C_6D_6): δ 57.9, 51.6, 5.4. ^{29}Si NMR (59.3 MHz, C_6D_6): δ −2.6, −56.3. Anal. Calc. for $C_{15}H_{43}Cl_3HfN_2Si_4$: C, 27.77; H, 6.68. Found: C, 28.27; H: 6.68%.

Preparation of **4**: in an NMR-tube, **2** (50 mg, 0.077 mmol) was dissolved in C_6D_6 and treated with 2,6-dimethylphenylisocyanide (11 mg, 0.085 mmol) leading to an immediate change from bright orange to pale yellow, and after filtration crystalline **4** was obtained. ^{1}H NMR (300 MHz, C_6D_6): δ 6.97 (s, 1H), 6.90 (s, 2H), 2.67 (s, 3H), 2.48 (s, 2H), 2.36 (s, 3H), 2.22 (s, 3H), 2.10 (s, 3H), 2.05 (s, 2H), 0.43 (s, 6H), 0.29 (s, 27 H). ^{13}C NMR (75.4 MHz, C_6D_6): δ 246.9, 153.2, 128.2, 128.0, 127.8, 127.7, 127.6, 59.0, 57.3, 51.3, 19.9, 18.5, 2.8, 2.7, 2.6. ^{29}Si NMR (59.3 MHz, C_6D_6): δ −11.2, −80.8. Anal. Calc. for $C_{24}H_{52}Cl_3HfN_3Si_4$: C, 36.96.77; H, 6.72. Found: C, 36.67; H: 6.88%.

‡ *Crystal data* for $HfC_{15}H_{43}N_2Cl_3Si_4$ **2**: orthorhombic, space group *Pbca* (no. 61), $a = 14.212(3)$, $b = 13.760(3)$, $c = 30.415(6)$ Å, $V = 5948(2)$ Å^3, $Z = 8$, $D_c = 1.449$ g cm^{-3}, $\mu = 3.94$ mm^{-1} (Mo-Kα, $\lambda = 0.71073$ Å), $T = 223$ K; the structure was solved by direct methods and refined by full matrix least squares procedures: $R_1 = 0.0814$ and 0.1409 ($wR_2 = 0.1693$ and 0.1721) for 4345 unique measured reflections. CCDC reference number 177994.

For $HfC_6H_{16}N_2Cl_4$ **3**: orthorhombic, space group $Pna2_1$ (no. 33), $a = 14.797(5)$, $b = 7.552(3)$, $c = 12.000(4)$ Å, $V = 1341.0(8)$ Å^3, $Z = 4$, $D_c = 2.162$ g cm^{-3}, $\mu = 8.54$ mm^{-1} (Mo-Kα, $\lambda = 0.71073$ Å), $T = 273$ K; the structure was solved by direct methods and refined by full matrix least squares procedures: $R_1 = 0.0329$ and 0.0450 ($wR_2 = 0.0574$ and 0.0598) for 1907 unique measured reflections. CCDC reference number 177992.

For $HfC_{30}H_{58}N_3Cl_3Si_4$ **4**: orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 11.625(2)$, $b = 12.164(2)$, $c = 29.975(6)$ Å, $V = 4238.8(15)$ Å^3, $Z = 4$, $D_c = 1.344$ g cm^{-3}, $\mu = 2.79$ mm^{-1} (Mo-Kα, $\lambda = 0.71073$ Å), $T = 223$ K; the structure was solved by direct methods and refined by full matrix least squares procedures: $R_1 = 0.0305$ and 0.0331, ($wR_2 = 0.0786$ and 0.0797) for 6073 unique measured reflections. CCDC reference number 177993.

See http://www.rsc.org/suppdata/cc/b2/b201508k/ for crystallographic data in CIF or other electronic format.

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