degree of filling in which two of the five π^* states remain unoccupied, which effectively results in two, relatively strongly delocalized double bonds in the bicyclic system. A completely singly bonded Si polymer of this type would require four additional valence electrons so that the π^* levels would also be filled. The bond distances suggest that the (-Si4-Si3-Si8-Si7-)$_2$ and (-Si16-Si14-Si13-Si18-)$_2$ ring fragments carry the majority of the double-bond character (Figure 2c). We will report elsewhere on an explanation of why highly charged Zintl anions of Si are so frequently planar.[8]

The Si_{10}^{10-} units in the polyanion structure are ecliptically stacked (Figure 2a). Despite the relatively large distance of $c/2 = 4.91$ pm between neighboring rings, one-dimensional conductivity along the stacking direction could arise through $\pi^* - \pi^*$ interactions. Such interactions were recently suggested for a related Group 14 compound in which bond lengths of 430 to 500 pm were observed between ecliptically stacked planar Zintl anions.[3, 4, 8] One-dimensional conductivity originates from interactions between ecliptically stacked ring systems, whereas semiconducting properties are observed in the perpendicular direction. Such semiconductors are at the border between intermetallic phases and common Zintl compounds, which strongly adhere to the valence rules. As their structural details can nevertheless be understood with electron-counting rules and a semiconducting character predominates, we call such compounds "extended Zintl phases". This description is supported by practically all of the band-structure calculations we have carried out to date on such silicides; all of the occupied electronic states are Si-centered (similar to the MO scheme in Figure 2b). In this respect, these species may be differentiated from intermetallic phases.

From a small number of examples, it can already be seen that topochemical reactions can be carried out on two-dimensional polyanions of silicon and germanium—such as those in $CaSi_2$,[10] Li_3NaSi_6,[11] and Li_7Ge_{12}[12, 13]—to afford new element modifications[11, 13] and siloxanes[14, 15]; this fosters a continued excitement in this area of research. In this respect, the Si polymer anions we recently discovered in $Ba_2Eu_3Si_7$,[15] Ca_3Si_4, $Ca_{14}Si_{19}$,[4, 2[and the title compound $Sr_{13}Mg_2Si_{20}$[4] could be of interest.

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[6] Differential thermal analysis (DTA) investigations on probes of Sr/Mg/Si compositions 33.3/11.7/55 and 40/10/50 demonstrate that $Sr_{13}Mg_2Si_{20}$ decomposes peritectically above 1253 K. As established by a powder diagram, pure $Sr_{13}Mg_2Si_{20}$ may be obtained by tempering a sample of the former composition at 1223 K ($t_1 = 99$ h). The crystal investigated was isolated from a synthesis at 1243 K ($t_1 = 8$ d). At this temperature, $Sr_{13}Mg_2Si_{20}$ is the main product and Sr_4Si_7 and $SrSi_2$ are side products. In the products of syntheses at 1234 K ($t_1 = 10$ h) and 1243 K ($t_1 = 99$ h) for the latter composition, one finds predominantly $Si_{13}Mg_2Si_{20}$ with SrSi as a minor component. If either composition is subsequently tempered at about 1363 K ($t_1 = 30$ and 10 h, respectively) SrSi is obtained as the main component with minor Sr_4Si_7 and $Sr_2Mg_{2-x}Si_3$ impurities.

[7] Crystal structure: *Pbam* (no. 55), $a = 15.200(3)$, $b = 23.201(6)$, $c = 9.832(2)$ Å, $Z = 4$, $V = 3464.1$ Å^3, $\rho_{calcd} = 3.354$ g cm^{-3}, 2907 independent reflections ($R_{int,F^2} = 0.176$), 2109 reflections with $F^2 > 2\sigma(F^2)$, $R(F^2) = 0.085$, $R_w(F^2) = 0.164$. Further details of the crystal structure determination may be obtained from the Fachinformationszentrum, Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666 (Frau S. Höhler-Schlimm); e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-408183.

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Formation of Adamantane-Like Structures by Reaction of Titanocene Fluorides with an Iminoalane**

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Herbert W. Roesky,* Peihua Yu, and Isabel Usón

*Dedicated to Professor Sir John Meurig Thomas
on the occasion of his 65th birthday*

Imido transition metal complexes play an important role both in biological processes such as nitrogen fixation as well as in a series of industrial processes.[1] Cycloadditions, C–H activations, and ring-opening polymerizations can all be catalyzed by imido complexes.[1, 2] Numerous imidotitanium

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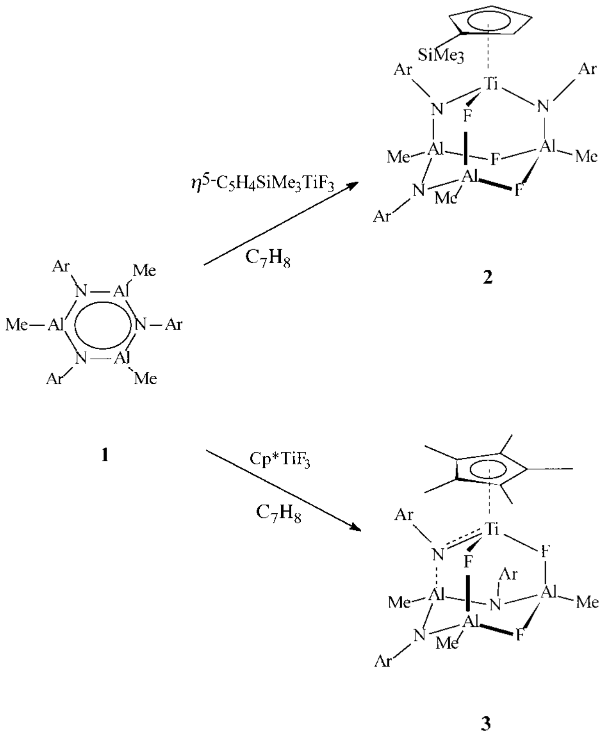
chlorides as well as the corresponding oxygen-containing complexes have recently been reported;[3] however, syntheses of fluorine-containing imido compounds have thus far remained elusive.

Herein, we report on the reaction of titanocene fluorides with the trimeric iminoalane **1**,[4] which exhibits quasiaromatic properties and contains Lewis acidic, three-coordinate aluminum centers. The reactions of **1** with η^5-$C_5H_4SiMe_3TiF_3$ and Cp^*TiF_3 ($Cp^* = \eta^5$-C_5Me_5) in toluene lead under fluorine–nitrogen metathesis to the adamantane-like cage compounds **2** and **3**, respectively (Scheme 1). These novel titanocene compounds were characterized by IR and NMR spectroscopy, mass spectrometry, and elemental analysis. Compound **2**[5] crystallizes in the triclinic space group $P\bar{1}$ and contains an $[(Al_3NF_2)(TiN_2F)]$ adamantane core (Figure 1). The structure of **2** consists of a six-membered Al_3NF_2 ring with μ_2-bridging fluorine and nitrogen atoms (av Al–F distance: 180.3 pm, av Al–N distance: 180.7 pm). The Al_3 plane resides in a chair conformation with an average Al-F-Al angle of 131.8° and an Al-N-Al angle of 116.4°. The Al_3 plane is capped by a μ_3-$F(NAr)_2TiC_5H_4SiMe_3$ ligand. The average Ti–N distance is 188.9 pm and the Ti–F distance 202.0 pm; the average Ti-N-Al angle is 116.5° and the Ti-F-Al angle 131.1°. The environment of the titanium atom is pseudotetrahedral. The $C_5H_4SiMe_3$ ligand completes this coordination sphere.



Scheme 1. Reactions of **1** with titanocene fluorides. Ar = 2,6-$i$$Pr_2C_6H_3$.

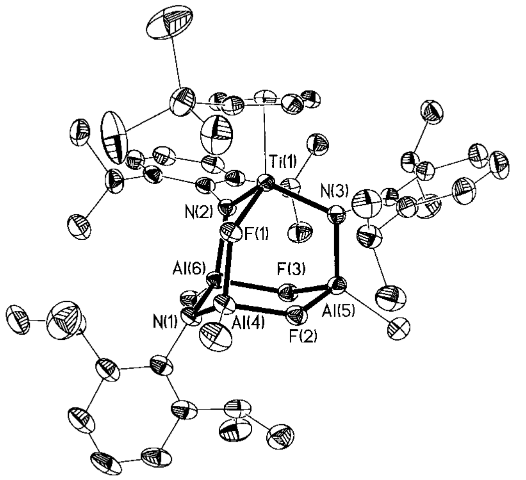
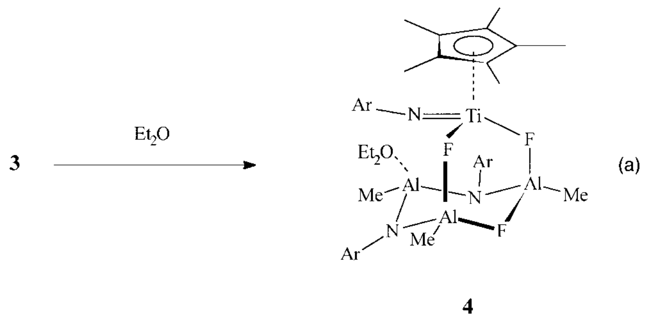


Figure 1. Molecular structure of **2** in the crystal. Selected distances [pm] and angles [°]: Al(4)–F(1) 176(1), Al(4)–N(1) 178(2), Al(4)–F(2) 181(1), Al(5)–F(3) 175(1), Al(5)–N(3) 183(2), Al(6)–F(3) 187(1), Al(6)–N(2) 193(2), Ti(1)–F(1) 202(1), Ti(1)–N(3) 191(2); Al(5)-F(2)-Al(4) 132.6(8), Al(4)-F(1)-Ti(1) 131.1(7), Al(4)-N(1)-Al(6) 116.4(9), Ti(1)-N(2)-Al(6) 117.8(9), N(1)-Al(6)-F(3) 102.6(8).

Treatment of **3** with the donor solvent diethyl ether leads to **4** through cleavage of an aluminum–nitrogen bond. This is the first compound, containing a titanium–nitrogen double bond obtained by a metathesis; hereby an intramolecular stabilization of such a double bond by fluorine was established for the first time.[8]



The ^{19}F NMR spectra of **2**–**4** contain signals for the Al–Ti-bridging fluorine atoms (**2**: $\delta = -151.9$; **3**: $\delta = -168.2, -158.4$; **4**: $\delta = -168.1, -158.4$), which are strongly shifted to higher field with respect to those of the starting materials ($\delta = 164.5$ and 124.0). This was also established for other compounds with Ti-F-Al substructures.[9] The signals at $\delta \approx -135$ are assigned to the Al-bridging fluorine atoms. These findings indicate that the structures of the compounds are similar in the solid state and in solution[9, 10] and confirm the structure formulated for **3**.

Compound **4** crystallizes in the monoclinic space group $P2_1/c$ (Figure 2). The structure of **4** consists of a six-membered Al_3N_2F ring with μ_2-bridging fluorine and nitrogen atoms (av Al–F distance: 181.4 pm, av Al–N distance: 182.4 pm). The Al_3 plane resides in a chair conformation with an Al-F-Al angle of 129.6° and an Al-N-Al angle of 125.6°. The atoms Al(1) and Al(2) are bridged by a μ_2-$F_2TiCp^*(NAr)$ ligand, the average Ti-F-Al angle is 142.4°. One diethyl ether molecule is coordinated at Al(3). The environment of the titanium atom is pseudotetrahedral, the coordination sphere is completed by the Cp* ligand. The average Ti–F distance is 204.4 pm. The Ti(1)–N(2) bond length of 173.0 pm[7] is considerably shorter than that in **2**, and is in accord with the lengths of Ti–N double bonds in other compounds.[8]

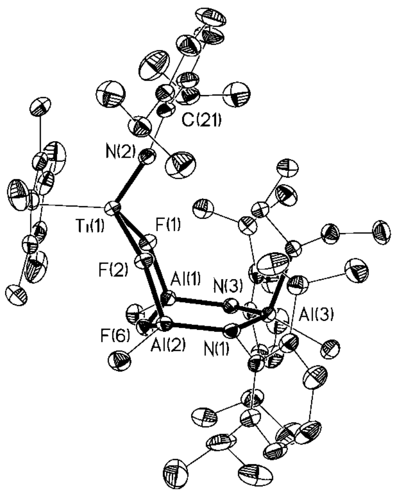


Figure 2. Molecular structure of **4** in the crystal. Selected distances [pm] and angles [°]: Ti(1) – N(2) 173(2), Ti(1) – F(2) 204(2), N(1) – Al(2) 180(2), F(1) – Al(1) 178(2), F(2) – Al(2) 178(2), F(6) – Al(1) 181(2); C(21)-N(2)-Ti(1) 167.9(2), N(1)-Al(3)-N(3) 113.2(11), Al(1)-F(6)-Al(2) 129.6(9), Al(1)-F(1)-Ti(1) 142.3(9).

Experimental Section

2: **1** (1.3 g, 2.0 mmol) in toluene (40 mL) was added dropwise to a solution of $C_5H_4SiMe_3TiF_3$ (0.48 g, 2.0 mmol) in toluene (40 mL) at 0 °C and stirred. The mixture was allowed to warm to room temperature and stirred for a further 12 h. After removal of the volatile components in vacuo the residue was washed with *n*-hexane (30 mL). Compound **2** (1.16 g, 65 %) was obtained as a red microcrystalline solid. Single crystals were obtained from toluene at − 22 °C over four weeks. M.p.: 190 °C; ^{1}H NMR (250 MHz, C_7D_8, TMS): $\delta = -1.12$ (d, 3 H; $AlCH_3$), − 0.68 (t, 3 H; $AlCH_3$), − 0.53 (dd, 3 H; $AlCH_3$), 0.21 (s, 9 H; $Si(CH_3)_3$), 1.09 – 1.65 (m, 36 H; $CH(CH_3)_2$), 3.02 (sept., 1 H; $CH(CH_3)_2$), 3.31 (sept., 1 H; $CH(CH_3)_2$), 3.49 (sept., 1 H; $CH(CH_3)_2$), 3.89 (m, 3 H; $CH(CH_3)_2$), 5.53, 6.04, 6.11, 6.79 (4 m, each 1 H; $C_5H_4Si(CH_3)_3$), 6.90 – 7.15 (m, 9 H; arom. H); ^{19}F NMR (235 MHz, C_7D_8, $CFCl_3$): $\delta = -151.9$ (d, 1 F), − 133.4 (m, 1 F), − 132.4 (m, 1 F); IR (KBr, Nujol): $\tilde{\nu} = 1588$, 1422, 1308, 1250, 1179, 1108, 1045, 891, 776, 637, 563, 432 cm^{-1}; EI-MS: m/z (%): 891 (20, M^+), 162 (100, $C_{12}H_{18}$); elemental analysis: calcd for $C_{47}H_{73}Al_3F_3N_3SiTi$: C 63.1, H 8.2, F 6.4, N 4.7; found: C 62.7, H 8.2, F 6.3, N 4.7.

3: **1** (0.99 g, 1.5 mmol) in toluene (30 mL) was added dropwise to a solution of Cp^*TiF_3 (0.36 g, 1.5 mmol) in toluene (40 mL) at 0 °C and stirred. The mixture was allowed to warm to room temperature and stirred for a further 12 h. After removal of the volatile components in vacuo the residue was washed with *n*-hexane (30 mL). Compound **3** (0.81 g, 60 %) was obtained as a dark red solid. M.p.: 105 °C (decomp); ^{1}H NMR (200 MHz, C_6D_6, TMS): $\delta = -0.80$ (s, 3 H; $AlCH_3$), − 0.60 (m, 3 H; $AlCH_3$), − 0.15 (m, 3 H; $AlCH_3$), 1.10 – 1.41 (m, 36 H; $CH(CH_3)_2$), 1.98 (s, 15 H; $C_5(CH_3)_5$), 2.60 (sept., 2 H; $CH(CH_3)_2$), 3.05 (sept., 1 H; $CH(CH_3)_2$), 3.25 (m, 2 H; $CH(CH_3)_2$), 3.80 (sept., 1 H; $CH(CH_3)_2$), 6.88 – 7.15 (m, 9 H; arom. H); ^{19}F NMR (188 MHz, C_6D_6, $CFCl_3$): $\delta = -168.2$ (d, 1 F), − 158.4 (t, 1 F), − 135.9 (s, 1 F); IR (KBr, Nujol): $\tilde{\nu} = 1455$, 1422, 1383, 1268, 1178, 1040, 901, 793, 670, 571 cm^{-1}; EI-MS: m/z (%): 593 (5, $M^+ - Cp^* - 4\ CH(CH_3)_2$), 162 (100, $C_{12}H_{18}$); elemental analysis: calcd for $C_{49}H_{79}Al_3F_3N_3Ti$: C 65.7, H 8.8, F 6.3, N 4.7; found: C 65.3, H 8.9, F 5.6, N 4.6.

4: **3** (0.90 g, 1.0 mmol) was dissolved in diethyl ether (40 mL) at room temperature and then stirred for a further 2 h. Compound **4** crystallized at − 22 °C within 12 h. Compound **4** (0.75 g, 77 %) was obtained as a dark red crystalline solid. M.p.: 120 °C (decomp), ^{1}H NMR (200 MHz, C_6D_6, TMS): $\delta = -0.75$ (s, 3 H; $AlCH_3$), − 0.60 (m, 3 H; $AlCH_3$), − 0.15 (m, 3 H; $AlCH_3$), 0.85 (t, 6 H; CH_2CH_3), 1.10 – 1.41 (m, 36 H; $CH(CH_3)_2$), 1.98 (s, 15 H; $C_5(CH_3)_5$), 2.55 – 3.70 (several sept., 6 H; $CH(CH_3)_2$), 3.25 (q, 4 H; CH_2CH_3), 6.88 – 7.15 (m, 9 H; arom. H); ^{19}F NMR (188 MHz, C_6D_6, $CFCl_3$): $\delta = -168.1$ (m, 1 F), − 158.4 (m, 1 F), − 139.4 (m, 1 F); IR (KBr, Nujol): $\tilde{\nu} = 1590$, 1430, 1380, 1260, 1187, 1101, 1040, 891, 796, 671, 566, 438 cm^{-1}; EI-MS: m/z (%): 162 (100, $C_{12}H_{18}$); elemental analysis: calcd for $C_{53}H_{85}Al_3F_3N_3OTi$: C 65.6, H 8.7, Al 8.4, F 5.8, N 4.3; found C 65.0, H 8.6, Al 8.5, F 5.3, N 4.5.

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[5] Crystal structure analyses:[11] **2**: $C_{47}H_{73}Al_3F_3N_3SiTi$, $M_r = 894.01$, triclinic, space group $P\bar{1}$, $a = 1312.9(3)$, $b = 1316.7(3)$, $c = 1662.6(3)$ pm, $\alpha = 74.62(3)$, $\beta = 81.93(3)$, $\gamma = 61.99(3)°$, $V = 2.446(1)$ nm^3, $Z = 2$, $\rho_{calcd} = 1.214$ mg m^{-3}, $F(000) = 956$, $\lambda = 71.073$ pm, $T = 133$ K, $\mu(Mo_{K\alpha}) = 0.299$ mm^{-1}. Crystal dimensions: $0.3 \times 0.3 \times 0.2$ mm^3, $4° \leq 2\Theta \leq 52°$; of the 51 623 reflections collected, 9959 were independent and were used in the structure refinement of 541 parameters. The R values are $R1 = \Sigma \mid F_o - F_c \mid / \mid \Sigma F_o = 0.0424$ ($I > 2\sigma(I)$) and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w F_o^4]^{0.5} = 0.1152$ (all data); min./max. residual electron density $= -412/365$ e nm^{-3}. **4** · 2 $C_4H_{10}O$: $C_{61}H_{105}Al_3F_3N_3O_3Ti$, $M_r = 1114.32$, monoclinic, space group $P2_1/c$, $a = 1622.2(6)$, $b = 2698(2)$, $c = 3047(2)$ pm, $\beta = 97.98(2)°$, $V = 13.20(1)$ nm^3, $Z = 8$, $\rho_{calcd} = 1.122$ mg m^3, $F(000) = 4832$, $\lambda = 71.073$ pm, $T = 133$ K, $\mu(Mo_{K\alpha}) = 0.155$ mm^{-1}. Crystal dimensions: $0.2 \times 0.3 \times 0.2$ mm^3, $4° \leq 2\Theta < 52°$; of the 226 699 reflections collected, 23 381 were independent and were used in the structure refinement of 1479 parameters with 481 restraints. The R values are $R1 = 0.0559$ ($I > 2\sigma(I)$) and $wR2 = 0.1225$ (all data); min./max. residual electron density: $-547/792$ e nm^{-3}.

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[10] In the ^{19}F NMR spectra recorded at room temperature and at 70 °C the F atoms are inequivalent, which is attributed to the steric effects of the ligands.

[11] The data were collected on a Stoe-Siemens-Huber four-circle diffractometer with a Siemens-CCD area detector. The intensities were recorded with φ and ω scans. The data were integrated with the program SAINT. The structures were solved with direct methods (SHELXS-90/96)[6] and refined according to least-squares methods against F^2.[7] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the refinement in geometrically ideal positions. All disorders were resolved with distance and ADP restraints and refined anisotropically. 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-100 627. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).