

Well-defined imidotitanium alkyl cations: α -C-H or β -Si-C agostic interactions, migratory insertion *vs* [2+2] cycloaddition, and the first structurally authenticated AlMe₃ adduct of any transition metal alkyl cation

Supporting information

Characterising data for [Ti(N^tBu)(Me₃[9]aneN₃)Me][BAR^F₄] (3-BAR^F₄) (NMR only)

¹H NMR (C₆D₅Br, 299.9 MHz, 293 K): 2.34 (6H, br. m, CH₂), 2.20 (9H, s, NMe), 2.15 (6H, br. m, CH₂), 0.93 (9H, s, NCM₃), 0.69 (3H, s, TiMe). ¹³C{¹H} NMR (C₆D₅Br, 75.4 MHz, 293 K): 148.8 (br. d, ¹J_{C-F} 239 Hz, 2-C₆F₅), 138.6 (br. d, ¹J_{C-F} 251 Hz, 4-C₆F₅), 136.7 (br. d, ¹J_{C-F} 246 Hz, 3-C₆F₅), 69.9 (NCMe₃), 55.0 (CH₂), 50.5 (NMe), 40.3 (¹J_{CH} 116 Hz, TiMe), 31.4 (NCMe₃). ¹⁹F NMR (C₆D₅Br, 282.1 MHz, 293 K): -131.8 (d, ³J 10.6 Hz, 2-C₆F₅), -161.8 (t, ³J 21.2 Hz, 4-C₆F₅), -165.8 (app.t, app. ³J 18.1 Hz, 3-C₆F₅).

Characterising data for [Ti(N^tBu)(Me₃[9]aneN₃)(CH₂SiMe₃)]BAR^F₄] (4-BAR^F₄) (NMR only)

¹H NMR (CD₂Cl₂, 500.0 MHz, 213 K): 3.63 (2H, m, NCH₂), 3.06 (2H, m, NCH₂), 2.95 (6H, s, NMe *cis*), 2.90-2.50 (8H, overlapping m, NCH₂), 2.40 (3H, s, NMe *trans*), 2.02 (2H, s, CH₂SiMe₃), 1.11 (9H, s, NCM₃), 0.17 (9H, s, CH₂SiMe₃). ¹³C{¹H} NMR (CD₂Cl₂, 125.7 MHz, 213 K): 147.6 (br. d, ¹J_{C-F} 247 Hz, 2-C₆F₅), 137.8 (br. d, ¹J_{C-F} 225 Hz, 4-C₆F₅), 135.9 (br. d, ¹J_{C-F} 247 Hz, 3-C₆F₅), 69.8 (NCMe₃), 55.9-54.9 (series of overlapping singlets, NCH₂ and CH₂SiMe₃), 51.5 (NMe *cis*), 48.7 (NMe *trans*), 30.7 (NCMe₃), 1.3 (SiMe₃). ¹⁹F NMR (CD₂Cl₂, 282.1 MHz, 293 K): -133.5 (d, ³J 10.6 Hz, 2-C₆F₅), -164.0 (t, ³J 20.4 Hz, 4-C₆F₅), -167.9 (app. t, app. ³J 18.1 Hz, 3-C₆F₅). ²⁹Si NMR (HMQC ¹H-observed, CD₂Cl₂, 299.9 MHz, 293 K): -15.9 (CH₂SiMe₃). ²⁹Si NMR (HMQC ¹H-observed, C₅D₅Br, 299.9 MHz, 293 K): -17.5 (CH₂SiMe₃).

Characterising data for [Ti(N^tBu)(Me₃[9]aneN₃)(CH₂SiMe₃)(Ph₃PO)]BAR^F₄] (5-BAR^F₄)

¹H NMR (CD₂Cl₂, 499.9 MHz, 293 K): 7.83 (6H, m, 2-PPh₃), 7.76 (3H, m, 4-PPh₃), 7.62 (6H, m, 3-PPh₃), 3.45 (1H, m, NCH₂), 3.34 (1H, m, NCH₂), 3.15 (3H, s, NMe *cis*), 2.95 – 2.75 (2H, overlapping m, NCH₂), 2.82 (3H, s, NMe *cis*), 2.63 (2H, overlapping m, NCH₂), 2.53 (2H, overlapping m, NCH₂), 2.50 – 2.32 (4H, overlapping m, NCH₂), 2.07 (3H, s, NMe *trans*), 1.12 (9H, s, NCM₃), 0.95 (1H, d, ²J 10.2 Hz, CH_aH_bSiMe₃), 0.10 (1H, d, ²J 10.2 Hz, CH_aH_bSiMe₃), 0.04 (9H, s, CH₂SiMe₃). ¹³C{¹H} NMR (CD₂Cl₂, 125.7 MHz, 293 K): 148.5 (br. d, ¹J_{C-F} 244 Hz, 2-C₆F₅), 138.6 (br. d, ¹J_{C-F} 246 Hz, 4-C₆F₅), 136.8 (br. d, ¹J_{C-F} 246 Hz, 3-C₆F₅), 134.5 (d, ⁴J_{C-P} 2.7 Hz, 4-C₆H₅), 133.6 (d, ²J_{C-P} 11.4 Hz, 2-C₆H₅), 129.7 (d, ³J_{C-P} 6.1

Hz, 3-C₆H₅), 69.4 (NCMe₃), 57.7 (CH₂), 56.9 (CH₂), 56.2 (CH₂), 56.0 (CH₂), 55.1 (CH₂), 54.0 (CH₂), 53.7 (NMe *cis*), 52.2 (NMe *cis*), 50.0 (CH₂SiMe₃), 48.9 (NMe *trans*), 33.1 (NCMe₃), 4.1 (SiMe₃). ¹⁹F NMR (CD₂Cl₂, 282.1 MHz, 293 K): -133.5 (d, ³J 10.6 Hz, 2-C₆F₅), -164.0 (t, ³J 20.4 Hz, 4-C₆F₅), -167.9 (app. t, app. ³J 18.1 Hz, 3-C₆F₅). ³¹P {¹H} NMR (CD₂Cl₂, 121.5 MHz, 293 K): 43.4 (PPh₃). ²⁹Si NMR (HMQC ¹H-observed, CD₂Cl₂, 299.9 MHz, 293 K): -0.7 (CH₂SiMe₃). IR (NaCl plates, Nujol mull, cm⁻¹): 2921 (s, br.), 2853 (s), 1643 (m), 1592 (w), 1513 (s), 1412 (w), 1354 (w), 1299 (w), 1275 (m), 1231 (m), 1205 (w), 1141 (s), 1121 (s), 1086 (s), 1007 (m), 980 (s), 907 (m), 849 (m), 820 (m), 775 (m), 755 (m), 726 (s), 695 (m), 684 (m), 662 (m). Anal. Found (calcd. for C₅₉H₅₆BF₂₀N₄OPSiTi.0.33C₆H₁₄): C 53.9 (53.7), H 4.6 (4.5), N 4.1 (4.1).

Characterising data for [Ti(N^tBu)(Me₃[9]aneN₃){Me₃SiCH₂C(NⁱPr)₂}[BAR^F₄] (6-BAR^F₄)

¹H NMR (CD₂Cl₂, 499.9 MHz, 293 K): 3.96 (2H, app. sept., app. ³J 6.6 Hz, CHMe₂), 3.86 (2H, m, NCH₂), 3.26 (6H, s, NMe *cis*), 3.18 (2H, m, NCH₂), 2.98 (2H, m, NCH₂), 2.86 (2H, m, NCH₂), 2.65 - 2.50 (4H, overlapping m, NCH₂), 2.25 (2H, s, CH₂SiMe₃), 2.12 (3H, s, NMe *trans*), 1.41 (6H, d, ³J 6.6 Hz, CHMe₂), 1.21 (6H, d, ³J 6.6 Hz, CHMe₂), 1.01 (9H, s, NCMe₃), 0.16 (9H, s, SiMe₃). ¹³C {¹H} NMR (CD₂Cl₂, 75.4 MHz, 293 K): 168.5 (CCH₂SiMe₃), 148.5 (br. d, ¹J_{C-F} 238 Hz, 2-C₆F₅), 138.6 (br. d, ¹J_{C-F} 247 Hz, 4-C₆F₅), 136.7 (br. d, ¹J_{C-F} 250 Hz, 3-C₆F₅), 70.8 (NCMe₃), 57.5 (NCH₂), 56.6 (NCH₂), 54.2 (NCH₂), 52.4 (NMe *cis*), 50.4 (CHMe₂), 47.2 (NMe *trans*), 32.7 (NCMe₃), 26.4 (CHMe₂), 25.1 (CHMe₂), 17.1 (CH₂SiMe₃), -0.1 (SiMe₃). ¹⁹F NMR (CD₂Cl₂, 282.1 MHz, 293 K): -133.5 (d, ³J 10.6 Hz, 2-C₆F₅), -164.0 (t, ³J 20.4 Hz, 4-C₆F₅), -167.9 (app. t, app. ³J 18.1 Hz, 3-C₆F₅). ²⁹Si NMR (HMQC ¹H-observed, CD₂Cl₂, 299.9 MHz, 293 K): 2.1 (CH₂SiMe₃). IR (NaCl plates, Nujol mull, cm⁻¹): 2920 (s), 2853 (s), 1642 (m), 1513 (s), 1204 (w), 979 (s), 775 (w), 757 (w), 683 (w), 663 (m). ES⁺MS (MeCN): *m/z* 503.6 (12%) [M]⁺, 215.2 (100%) [ⁱPrNHC(CH₂SiMe₃)NHⁱPr]⁺, 172.2 (13%) [Me₃[9]aneN₃H]⁺. Anal. Found (calcd. for C₄₈H₅₅BF₂₀N₆SiTi): C 48.9 (48.8), H 4.8 (4.7), N 7.2 (7.1).

Characterising data for [Ti(N^tBu)(Me₃[9]aneN₃)(*m*-Me)₂AlMe₂][BAR^F₄] (7-BAR^F₄)

¹H NMR (CD₂Cl₂, 500.3 MHz, 293 K): 3.76 (2H, m, CH₂), 3.19 (2H, m, CH₂), 3.18 (6H, s, NMe *cis*), 2.96 (2H, m, CH₂), 2.84 (2H, m, CH₂), 2.75 (2H, m, CH₂), 2.64 (2H, m, CH₂), 2.34 (3H, s, NMe *trans*), 1.14 (9H, s, NCMe₃), 0.86 (6H, s, μ -AlMe₂), -0.48 (3H, s, AlMe “down”), -0.87 (3H, s, AlMe “up”). ¹³C {¹H} NMR (CD₂Cl₂, 125.8 MHz, 293 K): 148.1 (br. d, ¹J_{C-F} 243 Hz, 2-C₆F₅), 138.2 (br. d, ¹J_{C-F} 243 Hz, 4-C₆F₅), 136.2 (br. d, ¹J_{C-F} 243 Hz, 3-C₆F₅), 73.2 (NCMe₃), 57.1 (CH₂), 56.6 (CH₂), 55.7 (CH₂), 54.5 (NMe *cis*), 49.9 (NMe *trans*), 30.2 (NCMe₃), 23.3 (μ -AlMe₂), -4.9 (br., AlMe “down”), -7.6 (br., AlMe “up”). ¹⁹F NMR (CD₂Cl₂, 282.1 MHz, 293 K): -133.5 (d, ³J 10.6 Hz, 2-C₆F₅), -164.0 (t, ³J 20.4 Hz, 4-C₆F₅), -167.9 (app. t, app. ³J 18.1 Hz, 3-C₆F₅). Selected ¹H NMR shifts and ¹J_{C-H} coupling constants in C₆D₅Br (299.9 MHz, 293 K): 0.38 (6H, s, ¹J_{C-H} 110 Hz, μ -AlMe₂), -0.45 (3H, s, ¹J_{C-H} 113 Hz, AlMe “down”), -0.87 (3H, s,

$^1J_{\text{C-H}}$ 113 Hz, AlMe “up”). IR (NaCl plates, Nujol mull, cm^{-1}): 2922 (s, br.), 2860 (s), 1644 (s), 1515 (s), 1299 (w), 1271 (s), 1233 (s), 1199 (w), 1086 (s), 998 (m), 979 (s), 889 (w), 784 (m), 775 (m), 756 (m), 736 (m), 725 (m), 684 (m), 661 (m). Anal. Found (calcd. for $\text{C}_{41}\text{H}_{42}\text{AlBF}_{20}\text{N}_4\text{Ti}$): C 46.5 (46.6), H 3.9 (4.0), N 5.3 (5.3). “Up” and “down” refer to the orientation with respect to the triazacyclononane ring.

Computational Details

Calculations were carried out with the hybrid B3PW91 density functional,^{1,2} as implemented in the Gaussian03 package³ on the model systems $[\text{Ti}(\text{NMe})(\text{H}_3[9]\text{aneN}_3)\text{R}_2]$ (R = Me (**1a**) or R = CH_2SiMe_3 (**2a**)), $[\text{Ti}(\text{NMe})(\text{H}_3[9]\text{aneN}_3)\text{R}]^+$ (R = Me (**3a**) or CH_2SiMe_3 (**4a**)) and $[\text{Ti}(\text{NMe})(\text{H}_3[9]\text{aneN}_3)(\mu\text{-Me})_2\text{AlMe}_2]^+$. The Ti and Si atoms were represented with the quasi relativistic effective core pseudo-potentials (RECP) of the Stuttgart group and the associated basis sets augmented with a polarization function ($\alpha = 0.500$, Ti; $\alpha = 0.284$, Si).^{4,5} The remaining atoms (C, H, Al and N) were represented with 6-31G(d,p) basis sets.⁶ This ensemble of RECP and basis sets is called BI. The B3PW91 geometry optimizations were performed without any symmetry constraints and the nature of the extrema (local minima or transition states) was checked by analytical frequency calculations. The NMR calculations were performed at the B3PW91 level on the B3PW91/BI geometries with a basis set consisting of the all-electron Wachters basis set for Ti⁷ supplemented by a f polarization function,⁸ and IGLOO-II type basis set for C, H, N, and Si.⁹ The chemical shifts and J(C-H) coupling constants were computed in the GIAO approximation as implemented in Gaussian03.¹⁰ The GIAO magnetic shielding tensor of the Si, C, and H atoms were evaluated at the B3PW91/IGLOO-II level for the SiMe_4 molecule optimized with the same method and basis set to serve as a reference for the calculation of the chemical shifts.

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