Electronic Supplementary Material (ESI) for Dalton Transactions

Site selectivity and reversibility in the reactions of titanium hydrazides with Si–H, Si–X, C–X and H^+ reagents: Ti=N_α 1,2-silane addition, N_β alkylation, N_α protonation and σ-bond metathesis

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SUPPORTING INFORMATION

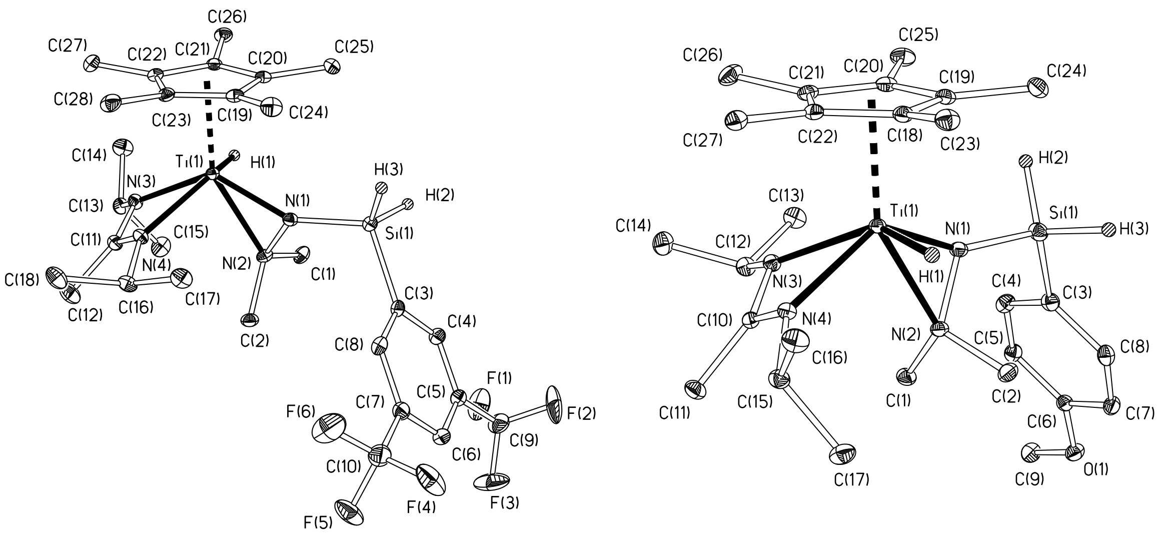

Fig. S1. Displacement ellipsoid plot (20% probability) of Cp*Ti{MeC(N^{i}Pr)$_2$}(H){N(NMe$_2$)SiH$_2$Ar^F} (**5**, left) and Cp*Ti{MeC(N^{i}Pr)$_2$}(H)-{N(NMe$_2$)SiH$_2$Ar^{OMe}} (**6**, right). C-bound H atoms omitted for clarity, and other H atoms are drawn as spheres of an arbitrary radius.

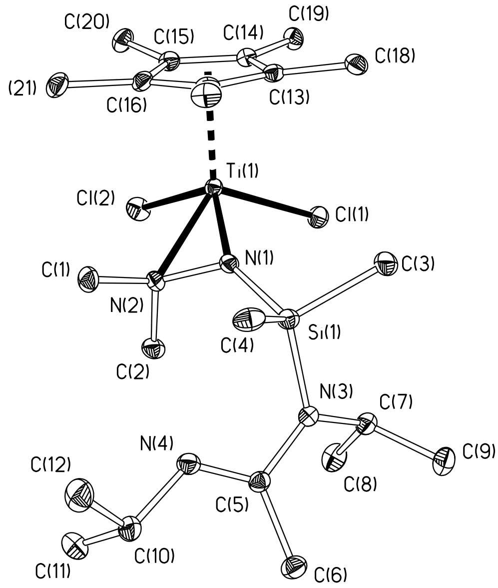

Fig. S2. Displacement ellipsoid plot (20% probability) of Cp*Ti{N(NMe_2)-$SiMe_2$N(^{i}Pr)CMeN^{i}Pr}Cl_2 (**12**). H atoms omitted for clarity.

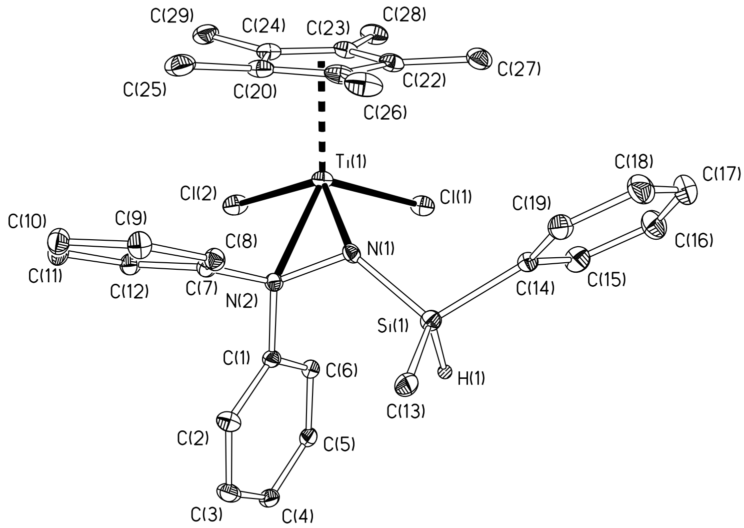

Fig. S3. Displacement ellipsoid plot (20% probability) of Cp*Ti{N(NPh_2)SiH(Me)Ph}Cl_2 (**15**). C-bound H atoms omitted for clarity, and H(1) drawn as a sphere of an arbitrary radius.

Table S1. Selected bond lengths (Å) and angles (°) for Cp*Ti{N(NPh$_2$)SiH(Me)Ph}Cl$_2$ (**15**). Cp$_{cent}$ refers to the C$_5$Me$_5$ ring carbon centroid.

Ti(1)–Cp$_{cent}$	2.079	Ti(1)–N(1)	1.932(2)
Ti(1)–N(2)	2.197(2)	Ti(1)–Cl(1)	2.3103(10)
Ti(1)–Cl(2)	2.3265(9)	N(1)–N(2)	1.438(3)
N(1)–Si(1)	1.775(2)		
Cp$_{cent}$–Ti(1)–N(1)	116.8	Cp$_{cent}$–Ti(1)–N(2)	130.5
Cp$_{cent}$–Ti(1)–Cl(1)	109.9	Cp$_{cent}$–Ti(1)–Cl(2)	110.6
N(1)–Ti(1)–N(2)	40.13(9)	Ti(1)–N(1)–Si(1)	142.81(15)
N(1)–Si(1)–C(13)	111.07(14)	N(1)–Si(1)–C(14)	109.51(12)

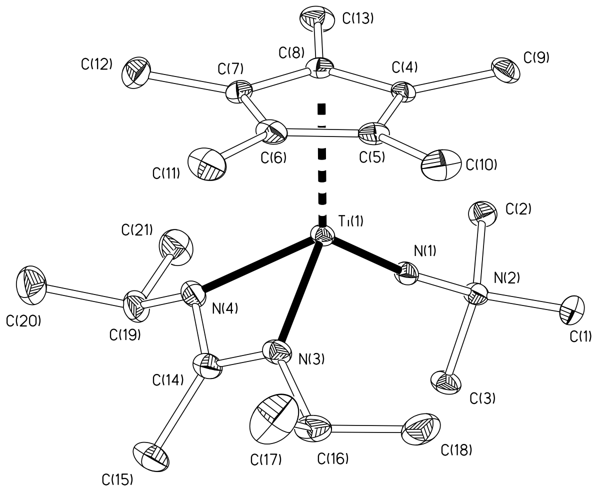

Fig. S4. Displacement ellipsoid plot (20% probability) of [Cp*Ti{MeC(N^{i}Pr)$_2$}(NNMe$_3$)]$^+$ (**20$^+$**). H atoms and iodide counter-ion omitted for clarity.

Experimental and Computational Details

General methods and instrumentation. All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent.[1] Deuterated solvents were refluxed over the appropriate drying agent, distilled and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ^{1}H, $^{13}C-\{^{1}H\}$, ^{11}B, ^{19}F, ^{29}Si and ^{2}H NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers. ^{1}H and ^{13}C spectra are referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). ^{2}H NMR spectra were referenced to the natural abundance deuterium resonance of the protio solvent. ^{19}F, ^{29}Si and ^{11}B spectra were referenced externally to $CFCl_3$, $SiMe_4$ and $Et_2O{\cdot}BF_3$, respectively. Assignments were confirmed as necessary with the use of DEPT-135, DEPT-90, and two dimensional ^{1}H-^{1}H and ^{13}C-^{1}H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were recorded on a Nicolet Magna 560 E.S.P. FTIR spectrometer. Samples were prepared in a dry-box as Nujol mulls between NaCl plates, and the data are quoted in wavenumbers (cm^{-1}). Mass spectra were recorded by the mass spectrometry service of Oxford University's Department of Chemistry. Elemental analyses were carried out by Elemental Microanalysis Ltd or by the Elemental Analysis Service at the London Metropolitan University.

Starting materials. $Cp^*Ti\{MeC(N^iPr)_2\}(NNR_2)$ (R = Me (**1**) or Ph (**2**)),[2] $Cp^*Ti\{MeC(N^iPr)_2\}(NTol)$ (**3**),[3] $PhSiD_3$,[4] Ar^FSiH_3 (Ar^F = 3,5-$C_6H_3(CF_3)_2$),[5] $Ar^{OMe}SiH_3$ (Ar^{OMe} = 4-C_6H_4OMe),[6] $PhSiH_2Br$,[7] and $[Et_3NH][BBh_4]$[8] were prepared according to the literature methods. $B(C_6F_5)_3$ and the amine-boranes were kindly donated by DSM Elastomers BV and Professor S. Aldridge, respectively. Other reagents were obtained commercially and used as received.

$Cp^*Ti\{MeC(N^iPr)_2\}(H)\{N(NMe_2)SiH_2Ph\}$ (4). To a stirred solution of $Cp^*Ti\{MeC(N^iPr)_2\}(NNMe_2)$ (**1**, 0.300 g, 0.780 mmol) in pentane (10 mL) was added $PhSiH_3$ (0.194 mL, 0.780 mmol) all at room temperature. An immediate colour change from dark green to yellow was observed. Yellow crystals were obtained from a concentrated solution of pentane at -30 °C after 2 d. The solution was then filtered, and the product (**4**) washed with pentane and dried *in vacuo*. Yield: 0.223 g (58%). Diffraction-quality crystals were grown from a concentrated pentane solution at -30 °C. ^{1}H NMR (C_6D_6, 499.9 MHz, 293 K): δ 7.71 (2 H, d, ^{3}J = 7.5 Hz, *o*-C_6H_5), 7.20 (3 H, m, overlapping *m*- and *p*-C_6H_5), 5.41 (1 H, d, ^{2}J = 8.0 Hz, Si$\underline{H}_a$H), 5.37 (1 H, d, ^{2}J = 8.0 Hz, SiH$\underline{H}_b$), 5.16 (1 H, s, Ti-H), 3.49 (1 H, app. sept., app. ^{3}J = 6.5 Hz, NC$\underline{H}_a$MeMe), 3.04 (1 H, app. sept., app. ^{3}J = 6.5 Hz, NC$\underline{H}_b$MeMe), 2.83 (3 H, s, NN$\underline{Me}$Me), 2.48 (3 H, s, NNMe$\underline{Me}$), 2.17 (15 H, s, C_5Me_5), 1.61 (3 H, s, $MeCN_2$), 1.20 (3 H, d, ^3J = 6.5 Hz, NCH_a<u>Me</u>Me), 1.09 (6 H, overlapping 2 × d, 2 × ^3J = 6.5 Hz, overlapping NCH_aMe<u>Me</u> and NCH_b<u>Me</u>Me), 1.00 (3 H, d, ^3J = 6.5 Hz, NCH_bMe<u>Me</u>). ^{13}C-{^{1}H} NMR (C_6D_6, 125.7 MHz, 293 K): δ 171.6 (Me<u>C</u>N_2), 137.3 (*i*-C_6H_5), 136.1 (*o*-C_6H_5), 130.0 (*p*-C_6H_5), 129.9 (*m*-C_6H_5), 118.8 (<u>C</u>$_5Me_5$), 60.3 (NN<u>Me</u>Me), 50.8 (NNMe<u>Me</u>), 48.3 (N<u>C</u>H_aMeMe), 47.2 (N<u>C</u>H_bMeMe), 27.0 (NCH_b<u>Me</u>Me), 26.5 (NCH_aMe<u>Me</u>), 25.6 (NCH_a<u>Me</u>Me), 24.6 (NCH_bMe<u>Me</u>), 13.9 (C_5<u>Me</u>$_5$), 12.4 (<u>Me</u>CN_2). ^{29}Si NMR (HMQC ^{1}H-observed, C_6D_6, 299.9 MHz, 293 K): δ -42.3 (SiH_2Ph). IR (NaCl plates, Nujol mull, cm^{-1}): 2180 (s), 2125 (s), 1558 (s), 1506 (m), 1457 (s), 1428 (s), 1387 (m), 1367 (m), 1339 (m), 1327(m), 1310 (w), 1244 (w), 1220 (w), 1199 (s), 1174 (w), 1140 (w), 1121 (m), 1112 (m), 1065 (w), 1049 (w), 1018 (s), 939 (s), 919 (w), 875 (s), 742 (s), 719 (m), 701 (s), 621 (w), 614 (s). EI-MS: *m/z* = 490 $[M]^+$ (100 %). Anal. Found (calcd for $C_{26}H_{46}N_4SiTi$): C, 62.91 (63.65); H, 9.68 (9.45); N, 10.48 (11.42) %. The poor agreement between the found and calculated values is attributed to the lability of the compound (which has been crystallographically characterised) *in vacuo*. Note that the corresponding compound **8** prepared from **1** and $PhSiH_2Cl$ was not labile and gave a CHN combustion analysis within the accepted ranges.

Cp*Ti{MeC(N^{i}Pr)$_2$}(D){N(NMe$_2$)SiD$_2$Ph} (4-*d*$_3$). To a stirred solution of Cp*Ti{MeC(N^{i}Pr)$_2$}(NNMe$_2$) (**1**, 50.0 mg, 0.13 mmol) in benzene (5 mL) was added $PhSiD_3$ (15.0 mg, 0.13 mmol) all at room temperature. An immediate colour change from dark green to yellow was observed. After 1 h, volatiles were removed under reduced pressure to afford **4-*d*$_3$** as a yellow solid in quantitative yield. ^{2}H NMR (C_6H_6, 76.7 MHz, 293 K): δ 5.39 (br. s, SiD_2), 5.14 (br s, Ti-D). IR (NaCl plates, Nujol mull, cm^{-1}): 1586 (w), 1576 (w), 1559 (w), 1544 (w), 1507 (m), 1457 (s), 1339 (m), 1327 (m), 1219 (w), 1199 (m), 1174 (w), 1122 (m), 1112 (m), 1018 (s), 890 (m), 757 (s), 742 (w), 701 (s), 681 (m), 640 (s).

Cp*Ti{MeC(N^{i}Pr)$_2$}(H){N(NMe$_2$)SiH$_2$Ar^F} (5). To a stirred solution of Cp*Ti{MeC(N^{i}Pr)$_2$}(NNMe$_2$) (**1**, 0.100 g, 0.26 mmol) in pentane (2 mL) was added Ar^FSiH_3 (Ar^F = 3,5-$C_6H_3(CF_3)_2$) (0.064 g, 0.26 mmol) all at room temperature. An immediate colour change from dark green to yellow was observed. The concentrated solution afforded yellow crystals at -30 °C after 2 d. The solution was then filtered, and the yellow crystals (**5**) were dried *in vacuo*. Yield: 0.125 g (76%). Diffraction-quality crystals were grown from a saturated pentane solution at -30 °C. ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 8.09 (2 H, s, *o*-$C_6H_3(CF_3)_2$), 7.80 (1 H, s, *p*-$C_6H_3(CF_3)_2$), 5.19 (1 H, s, Ti-H), 5.18 (1 H, d, ^2J = 8.1 Hz, Si<u>H</u>$_a$H), 5.12 (1 H, d, ^2J = 8.1 Hz, SiH<u>H</u>$_b$), 3.45 (1 H, app. sept, app. ^3J = 6.3 Hz, NC<u>H</u>$_a$MeMe), 3.01 (1 H, app. sept, app. ^3J = 6.3 Hz, NC<u>H</u>$_b$MeMe), 2.65 (3 H, s, NN<u>Me</u>Me), 2.33 (3 H, s, NNMe<u>Me</u>), 2.07 (15 H, s, C_5Me_5), 1.56 (3 H, s, $MeCN_2$), 1.15 (3 H, d, ^3J = 6.3 Hz, NCH_a<u>Me</u>Me), 1.03 (3 H, d, ^3J = 6.3 Hz, NCH_aMe<u>Me</u>), 1.02 (3H, d, ^3J = 6.3 Hz, NCH_b<u>Me</u>Me), 0.90 (3 H, d, ^3J = 6.3 Hz, NCH_bMe<u>Me</u>). ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ

171.9 ($Me\underline{C}N_2$), 141.5 (m-$\underline{C}_6H_3(CF_3)_2$), 135.2 ($o$-$\underline{C}_6H_3(CF_3)_2$), 131.1 ($CF_3$), 125.9 ($i$-$\underline{C}_6H_3(CF_3)_2$), 123.4 ($p$-$\underline{C}_6H_3(CF_3)_2$), 119.2 ($\underline{C}_5Me_5$), 60.6 (NN$\underline{Me}$Me), 50.9 (NNMe$\underline{Me}$), 48.3 ($N\underline{C}H_aMeMe$), 47.1 ($N\underline{C}H_bMeMe$), 26.9 ($NCH_b\underline{Me}Me$), 26.3 ($NCH_aMe\underline{Me}$), 25.5 ($NCH_a\underline{Me}Me$), 24.4 ($NCH_bMe\underline{Me}$), 13.8 ($C_5\underline{Me}_5$), 12.5 ($\underline{Me}CN_2$). ^{19}F NMR ($C_6D_6$, 282.1 MHz, 293 K): δ -62.7 (6 F, s, CF_3). ^{29}Si NMR (HMQC ^{1}H-observed, C_6D_6, 299.9 MHz, 293 K): δ -44.3 (SiH_2Ar^F). IR (NaCl plates, Nujol mull, cm^{-1}): 2195 (w), 2137 (w), 1565 (w), 1506 (w), 1365 (m), 1358 (m), 1340 (w), 1279 (s), 1203 (w), 1178 (m), 1141 (s), 1104 (m), 1024 (m), 940 (w), 902 (m), 878 (s), 843 (w), 799 (w), 727 (m), 707 (m), 682 (m), 500 (s). EI-MS: m/z = 626 $[M]^+$ (90%), 579 $[M - NMe_2 - H_3]^+$ (100 %), 412 $[M - Ar^F - H]^+$ (40 %). Anal. Found (calcd for $C_{28}H_{44}F_6N_4SiTi$): C, 53.85 (53.67); H, 6.89 (7.08); N, 8.81 (8.94) %.

Cp*Ti{MeC(N^{i}Pr)$_2$}(H){N(NMe$_2$)SiH$_2$Ar^{OMe}} (6). To a stirred solution of Cp*Ti{MeC(N^{i}Pr)$_2$}($NNMe_2$) (**1**, **0.**110 g, 0.29 mmol) in pentane (2 mL) was added $Ar^{OMe}SiH_3$ (0.040 g, 0.29 mmol) all at room temperature. An immediate colour change from dark green to yellow was observed. The concentrated solution afforded yellow crystals at -30 °C after 2 d. The solution was then filtered, and the product (**6**) dried *in vacuo*. Yield: 0.114 g (76%). Diffraction-quality crystals were grown from a saturated pentane solution at -30 °C. ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.65 (2 H, d, ^3J = 8.7 Hz, o-C_6H_4OMe), 6.84 (2 H, d, ^3J = 8.7 Hz, m-C_6H_4OMe), 5.46 (1 H, d, ^2J = 8.1 Hz, $Si\underline{H}_aH$), 5.41 (1 H, d, ^2J = 8.1 Hz, $SiH\underline{H}_b$), 5.16 (1 H, s, Ti-H), 3.51 (1 H, app. sept, app. ^3J = 6.6 Hz, $NC\underline{H}_aMeMe$), 3.28 (3 H, s, OMe), 3.07 (1 H, app. sept, app. ^3J = 6.6 Hz, $NC\underline{H}_bMeMe$), 2.88 (3 H, s, NN$\underline{Me}$Me), 2.52 (3 H, s, NNMe$\underline{Me}$), 2.19 (15 H, s, C_5Me_5), 1.62 (3 H, s, $MeCN_2$), 1.21 (3 H, d, ^3J = 6.6 Hz, $NCH_a\underline{Me}Me$), 1.10 (6 H, overlapping 2 × d, 2 × ^3J = 6.6 Hz, overlapping $NCH_aMe\underline{Me}$ and $NCH_b\underline{Me}Me$), 1.03 (3 H, d, ^3J = 6.6 Hz, $NCH_bMe\underline{Me}$). ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 171.6 ($Me\underline{C}N_2$), 161.6 (p-C_6H_4OMe), 137.6 (i-C_6H_4OMe), 137.3 (o-C_6H_4OMe), 118.8 ($\underline{C}_5Me_5$), 114.1 (m-C_6H_4OMe), 61.0 (NN$\underline{Me}$Me), 54.5 (OMe), 50.8 (NNMe$\underline{Me}$), 48.3 ($N\underline{C}H_aMeMe$), 47.2 ($N\underline{C}H_bMeMe$), 27.0 ($NCH_bMe\underline{Me}$), 26.5 ($NCH_a\underline{Me}Me$), 25.6 ($NCH_aMe\underline{Me}$), 24.6 ($NCH_b\underline{Me}Me$), 14.0 ($C_5\underline{Me}_5$), 12.4 ($\underline{Me}CN_2$). ^{29}Si NMR (HMQC ^{1}H-observed, C_6D_6, 299.9 MHz, 293 K): δ -42.1 (SiH_2Ar^{OMe}). IR (NaCl plates, Nujol mull, cm^{-1}): 2188 (m), 2094 (m), 1594 (m), 1558 (m), 1501 (s), 1399 (w), 1336 (w), 1328 (w), 1280 (m), 1248 (m), 1224 (w), 1200 (m), 1180 (m), 1113 (s), 1024 (s), 939 (s), 880 (s), 826 (m), 812 (m), 730 (m), 639 (w), 608 (m), 497 (s). Anal. Found (calcd for $C_{27}H_{48}N_4OSiTi$): C, 62.63 (62.29); H, 9.46 (9.29); N, 10.32 (10.76) %

Cp*Ti{MeC(N^{i}Pr)$_2$}(H){N(NMe$_2$)SiH$_2$Bu} (7). To a solution of Cp*Ti{MeC(N^{i}Pr)$_2$}($NNMe_2$) (**1**, 0.200 g, 0.52 mmol) in diethyl ether (3 mL) was added $BuSiH_3$ (67.9 µL, 0.52 mmol) all at room temperature. An immediate colour change from dark green to yellow was observed. After 1 h, volatiles were removed under reduced pressure to afford **7** as a yellow waxy solid which was washed with pentane and dried carefully *in vacuo*. Compound **7** rapidly lost $BuSiH_3$ *in vacuo* and a satisfactory elemental analysis could not be obtained. Yield: 0.053 g (22%). ^{1}H NMR (C_6D_6, 499.9 MHz, 293 K): δ 5.05 (1 H, s, Ti-H), 4.84 (2 H, m, SiH_2), 3.53 (1 H, app. sept., app. ^3J = 6.5 Hz, $NC\underline{H}_aMeMe$), 3.08 (1 H, app. sept., app. ^3J = 6.5 Hz, $NC\underline{H}_bMeMe$), 2.84 (3 H, s, $NN\underline{Me}Me$), 2.56 (3 H, s, $NNMe\underline{Me}$), 2.17 (15 H, s, C_5Me_5), 1.64 (3 H, s, $MeCN_2$), 1.38 (4 H, m, overlapping $SiCH_2C\underline{H}_2CH_2CH_3$ and $SiCH_2CH_2C\underline{H}_2CH_3$), 1.23 (3 H, d, ^3J = 6.5 Hz, $NCH_a\underline{Me}Me$), 1.13 (3 H, d, ^3J = 6.5 Hz, $NCH_aMe\underline{Me}$), 1.09 (3 H, d, ^3J = 6.5 Hz, $NCH_b\underline{Me}Me$), 0.98 (3 H, d, ^3J = 6.5 Hz, $NCH_bMe\underline{Me}$), 0.91 (3 H, t, ^3J = 7.0 Hz, $SiCH_2CH_2CH_2C\underline{H}_3$), 0.81 (2 H, m, $SiC\underline{H}_2CH_2CH_2CH_3$). ^{13}C-{^{1}H} NMR ($C_6D_6$, 125.7 MHz, 293 K): δ 171.5 ($Me\underline{C}N_2$), 118.5 ($\underline{C}_5Me_5$), 60.8 ($NN\underline{Me}Me$), 50.4 ($NNMe\underline{Me}$), 48.3 ($N\underline{C}H_aMeMe$), 47.2 ($N\underline{C}H_bMeMe$), 27.1 ($NCH_b\underline{Me}Me$), 26.7 ($SiCH_2\underline{C}H_2CH_2CH_3$), 26.5 ($NCH_aMe\underline{Me}$), 26.2 ($SiCH_2CH_2\underline{C}H_2CH_3$), 25.6 ($NCH_a\underline{Me}Me$), 24.5 ($NCH_bMe\underline{Me}$), 16.3 ($Si\underline{C}H_2CH_2CH_2CH_3$), 14.0 ($SiCH_2CH_2CH_2\underline{C}H_3$), 13.8 ($C_5\underline{Me}_5$), 12.4 ($\underline{Me}CN_2$). ^{29}Si NMR (HMQC ^{1}H-observed, C_6D_6, 299.9 MHz, 293 K): δ -36.6 (SiH_2Bu). IR (NaCl plates, Nujol mull, cm^{-1}): 2165 (w), 2106 (m), 1559 (m), 1506 (m), 1457 (s), 1339 (m), 1201 (s), 1174 (m), 1122 (w), 1079 (w), 1021 (s), 944 (m), 891 (s), 667 (m). EI-MS: *m/z* = 427 $[M - CH_2CH_2CH_3]^+$ (100 %).

NMR tube scale reaction of Cp*Ti{MeC(N^iPr)$_2$}(D){N(NMe_2)SiD_2Ph} (4-*d*$_3$) with H_2. A solution of Cp*Ti{MeC(N^iPr)$_2$}(D){N(NMe_2)SiD_2Ph} (**4-*d*$_3$**, 14.2 mg, 0.029 mmol) in C_6D_6 (0.6 mL) in an NMR tube equipped with a J. Young Teflon valve was freeze-pump-thawed three times. The solution was then exposed to H_2 at a pressure of *ca.* 4 bar at room temperature and was monitored using ^{1}H NMR spectroscopy for 4 d. A separate, parallel reaction was carried out in C_6H_6 and monitored using ^{2}H NMR spectroscopy.

NMR tube scale reaction of Cp*Ti{MeC(N^iPr)$_2$}(D){N(NMe_2)SiD_2Ph} (4-*d*$_3$) with $BuSiH_3$. To a solution of Cp*Ti{MeC(N^iPr)$_2$}(D){N(NMe_2)SiD_2Ph} (**4-*d*$_3$**, 13.5 mg, 0.027 mmol) in C_6D_6 (0.6 mL) in an NMR tube equipped with a J. Young Teflon valve was added $BuSiH_3$ (3.55 μL, 0.52 mmol) all at room temperature. The solution was then monitored using ^{1}H NMR spectroscopy for 2 d. A separate, parallel reaction was carried out in C_6H_6 and monitored using ^{2}H NMR spectroscopy.

Cp*Ti{MeC(N^iPr)$_2$}(Cl){N(NMe_2)SiH_2Ph} (8). To a solution of Cp*Ti{MeC(N^iPr)$_2$}($NNMe_2$) (**1**, **0.**100 g, 0.260 mmol) in pentane (5 mL) was added $PhSiH_2Cl$ (35.0 μL, 0.260 mmol) all at room temperature. The volatiles were removed under reduced pressure following colour change and precipitation after 10 min to afford **8** as an orange solid which was washed with pentane and dried *in vacuo*. Yield: 0.063 mg (46%). Diffraction-quality crystals were grown from a saturated toluene solution at -30 °C. ^{1}H NMR (toluene-*d*$_8$, 499.9 MHz, 253 K): δ 7.61 (2 H, d, ^3J = 7.5 Hz, *o*-C_6H_5), 7.17 (2 H, t, ^3J = 7.5 Hz, *m*-C_6H_5), 7.13 (1 H, t, ^3J = 7.5 Hz, *p*-C_6H_5), 5.30 (1 H, d, ^2J = 6.5 Hz, Si$\underline{H}_a$H), 5.25 (1 H, d, ^2J = 6.5 Hz, SiH$\underline{H}_b$), 4.34 (1 H, app. sept., app. ^3J = 7.0 Hz, NC$\underline{H}_a$MeMe), 3.00 (1 H, app. sept., app. ^3J = 7.0 Hz, NC$\underline{H}_b$MeMe), 2.98 (3 H, s, NN$\underline{Me}$Me), 2.47 (3 H, s, NNMe$\underline{Me}$), 2.12 (15 H, s, C_5Me_5), 1.55 (3 H, s, $MeCN_2$), 1.32 (6 H, overlapping 2 × d, 2 × ^3J = 7.0 Hz, overlapping NCH$_a\underline{MeMe}$), 1.07 (6 H, overlapping 2 × d, 2 × ^3J = 7.0 Hz, overlapping NCH$_b\underline{MeMe}$). ^{13}C-{^{1}H} NMR (toluene-d_8, 125.7 MHz, 253 K): δ 170.3 (Me$\underline{C}N_2$), 136.0 (*i*-C_6H_5), 134.7 (*o*-C_6H_5), 130.0 (*p*-C_6H_5), 128.2 (*m*-C_6H_5), 125.1 ($\underline{C}_5Me_5$), 54.8 (NN$\underline{Me}$Me), 49.7 (N$\underline{C}H_a$MeMe), 48.5 (N$\underline{C}H_b$MeMe), 48.3 (NNMe$\underline{Me}$), 27.1 (NCH$_b$Me$\underline{Me}$), 23.9 (NCH$_a$Me$\underline{Me}$), 22.9 (NCH$_b\underline{Me}$Me), 22.8 (NCH$_a\underline{Me}$Me), 15.3 ($\underline{Me}CN_2$), 13.9 ($C_5\underline{Me}_5$). ^{29}Si NMR (HMQC ^{1}H-observed, C_6D_6, 299.9 MHz, 293 K): δ -45.6 (SiH_2Ph). IR (NaCl plates, Nujol mull, cm^{-1}): 2155 (s), 2127 (s), 1519 (s), 1457 (s), 1429 (s), 1391 (m), 1356 (m), 1340 (m), 1198 (s), 1168(m), 1110 (m), 1084 (w), 1067 (w), 1015 (s), 989 (m), 948 (s), 923 (w), 902 (m), 868 (s), 810 (s), 786 (w), 756 (w), 719 (s), 700 (m), 690 (w), 680 (w), 622 (w), 613 (m), 580 (m). EI-MS: *m/z* = 165 [*M* – Cp*Ti{MeC(N^{i}Pr)$_2$}Cl]$^+$ (25 %), 213 [Ti{N(NMe_2)Si(H_2)Ph}]$^+$ (30 %), 276 [Cp*Ti($NNMe_2$)Cl]$^+$ (15 %), 359 [Cp*Ti{MeC(N^{i}Pr)$_2$}Cl]$^+$ (100 %). Anal. Found (calcd for $C_{26}H_{45}ClN_4SiTi$): C, 59.28 (59.47); H, 8.37 (8.64); N, 10.38 (10.67) %.

NMR tube scale synthesis of Cp*Ti{MeC(N^{i}Pr)$_2$}(Cl){N(NMe_2)SiH(Me)Ph} (9). To a solution of Cp*Ti{MeC(N^{i}Pr)$_2$}($NNMe_2$) (**1**, 20.0 mg, 0.052 mmol) in C_6D_6 (0.6 mL) in an NMR tube equipped with a J. Young Teflon valve was added Ph(Me)SiHCl solution (7.90 µL, 0.052 mmol) all at room temperature. An immediate colour change from dark green to orange was observed and the ^{1}H NMR spectrum recorded immediately showed complete conversion to **9**. The volatiles were removed under reduced pressure and the product **9** characterised by ^{1}H NMR spectroscopy. Major isomer: ^{1}H NMR (toluene-d_8, 299.9 MHz, 253 K): δ 7.61 (2 H, d, ^3J = 7.5 Hz, *o*-C_6H_5), 7.25 (2 H, app. t, app. ^3J = 7.5 Hz, *m*-C_6H_5), 7.18 (1 H, app. t, app. ^3J = 7.5 Hz, *p*-C_6H_5), 5.52 (1 H, q, ^3J = 3.6 Hz, SiH), 4.40 (1 H, app. sept, app. ^3J = 6.9 Hz, NC$\underline{H}_a$MeMe), 3.00 (3 H, s, NN$\underline{Me}$Me), 2.97 (1 H, app. sept, app. ^3J = 6.9 Hz, NC$\underline{H}_b$MeMe), 2.48 (3 H, s, NNMe$\underline{Me}$), 2.14 (15 H, s, C_5Me_5), 1.59 (3 H, s, $MeCN_2$), 1.33 (6 H, m, overlapping NCH$_a\underline{MeMe}$), 1.09 (6 H, m, overlapping NCH$_b\underline{MeMe}$), 0.47 (3 H, d, ^3J = 3.6 Hz, SiMe). ^{13}C-{^{1}H} NMR (toluene-d_8, 75.4 MHz, 253 K): δ 169.8 (Me$\underline{C}N_2$), 139.6 (*i*-C_6H_5), 135.4 (*o*-C_6H_5), 129.6 (*p*-C_6H_5), 127.9 (*m*-C_6H_5), 125.0 ($\underline{C}_5Me_5$), 54.7 (NN$\underline{Me}$Me), 51.0 (NNMe$\underline{Me}$), 49.4 (N$\underline{C}H_a$MeMe), 48.3 (N$\underline{C}H_b$MeMe), 27.1 (overlapping NCH$_b\underline{MeMe}$), 22.7 (overlapping NCH$_a\underline{MeMe}$), 15.6 ($\underline{Me}CN_2$), 13.9 ($C_5\underline{Me}_5$), -0.7 (SiMe). ^{29}Si NMR (toluene-d_8, 299.9 MHz, 253 K): δ -21.9 (SiH(Me)Ph). Minor isomer: ^{1}H NMR (toluene-d_8, 299.9 MHz, 253 K): δ 7.61 (2 H, d, ^3J = 7.5 Hz, *o*-C_6H_5), 7.25 (2 H, app. t, app. ^3J = 7.5 Hz, *m*-C_6H_5), 7.18 (1 H, app. t, app. ^3J = 7.5 Hz, *p*-C_6H_5), 5.47 (1 H, q, ^3J = 3.6 Hz, SiH), 4.24 (1 H, app. sept, app. ^3J = 6.9 Hz, NC$\underline{H}_a$MeMe), 3.14 (3

H, s, NNMeMe), 2.84 (1 H, app. sept, app. ^3J = 6.9 Hz, NCH_bMeMe), 2.19 (3 H, s, NNMeMe), 2.15 (15 H, s, C_5Me_5), 1.51 (3 H, s, $MeCN_2$), 1.31 (6 H, m, overlapping NCH_aMeMe), 1.06 (6 H, m, overlapping NCH_bMeMe), 0.58 (3 H, d, ^3J = 3.6 Hz, SiMe). ^{13}C-{^1H} NMR (toluene-d_8, 75.4 MHz, 253 K): δ 169.6 ($MeCN_2$), 137.9 (*i*-C_6H_5), 134.5 (*o*-C_6H_5), 129.8 (*p*-C_6H_5), 128.0 (*m*-C_6H_5), 124.9 (C_5Me_5), 54.6 (NNMeMe), 50.6 (NNMeMe), 49.5 (NCH_aMeMe), 48.1 (NCH_bMeMe), 23.8 (overlapping NCH_aMeMe), 22.8 (overlapping NCH_bMeMe), 15.1 ($MeCN_2$), 14.2 (C_5Me_5), 0.1 (SiMe). ^{29}Si NMR (toluene-d_8, 299.9 MHz, 253 K): δ -22.6 (SiH(Me)Ph).

NMR tube scale synthesis of Cp*Ti{MeC(N^iPr)$_2$}(Cl){N(NMe_2)$SiHMe_2$} (10). To a solution of Cp*Ti{MeC(N^iPr)$_2$}($NNMe_2$) (**1**, 17.9 mg, 0.047 mmol) in toluene-d_8 (0.6 mL) in an NMR tube equipped with a J. Young Teflon valve was added Me_2SiHCl (5.20 µL, 0.047 mmol) all at room temperature. An immediate colour change from dark green to orange was observed and the ^1H NMR spectrum recorded immediately showed complete conversion to **10** which was characterised by NMR spectroscopy. ^1H NMR (toluene-d_8, 499.9 MHz, 243 K): δ 5.09 (1 H, app. sept, app. ^3J = 3.5 Hz, SiH), 4.30 (1 H, app. sept, app. ^3J = 6.5 Hz, NCH_aMeMe), 2.95 (3 H, s, NNMeMe), 2.94 (1 H, app. sept, app. ^3J = 6.5 Hz, NCH_bMeMe), 2.46 (3 H, s, NNMeMe), 2.15 (15 H, s, C_5Me_5), 1.56 (3 H, s, $MeCN_2$), 1.35 (3 H, d, ^3J = 6.5 Hz, NCH_aMeMe), 1.33 (3 H, d, ^3J = 6.5 Hz, NCH_aMeMe), 1.06 (3 H, d, ^3J = 6.5 Hz, NCH_bMeMe), 0.98 (3 H, d, ^3J = 6.5 Hz, NCH_bMeMe), 0.23 (3 H, d, ^3J = 3.5 Hz, SiHMeMe), 0.19 (3 H, d, ^3J = 3.5 Hz, SiHMeMe). ^{13}C-{^1H} NMR (toluene-d_8, 125.7 MHz, 243 K): δ 169.9 ($MeCN_2$), 124.5 (C_5Me_5), 55.4 (NNMeMe), 50.3 (NNMeMe), 49.4 (NCH_aMeMe), 48.3 (NCH_bMeMe), 27.1 (NCH_bMeMe), 24.1 (NCH_aMeMe), 23.0 (NCH_bMeMe), 22.9 (NCH_aMeMe), 15.4 ($MeCN_2$), 14.1 (C_5Me_5), 2.9 (SiHMeMe), 1.1 (SiHMeMe). ^{29}Si NMR (HMQC ^1H-observed, toluene-d_8, 299.9 MHz, 243 K): δ -14.1 ($SiHMe_2$).

Cp*Ti{N(NMe_2)SiH(Ph)N(^iPr)CMeN^iPr}Cl_2 (11). To a stirred solution of Cp*Ti{MeC(N^iPr)$_2$}($NNMe_2$) (**1**, 0.305 g, 0.798 mmol) in benzene (20 mL) was added $PhSiHCl_2$ (117.0 µL, 0.798 mmol) all at room temperature. An immediate colour change from dark green to orange was observed. After 16 h, the volatiles were removed under reduced pressure to give an oily crude, which was then washed with cold pentane and dried *in vacuo* to afford **11** as an orange solid. Yield: 0.258 g (58%). Diffraction-quality crystals were grown from a saturated diethyl ether solution at -30 °C. ^1H NMR (C_6D_6, 499.9 MHz, 293 K): δ 7.60 (2 H, d, ^3J = 7.5 Hz, *o*-C_6H_5), 7.18 (3 H, m, overlapping *m*- and *p*-C_6H_5), 5.82 (1H, s, SiH), 3.33 (2 H, app. sept, app. ^3J = 6.5 Hz, NCHMeMe), 3.24 (3 H, s, NNMeMe), 2.86 (3 H, s, NNMeMe), 2.06 (15 H, s, C_5Me_5), 1.31 (3 H, s, $MeCN_2$), 0.94 (6 H, overlapping 2 × d, 2 × ^3J = 6.5 Hz, overlapping NCHMeMe), 0.88 (6 H, overlapping 2 × d, 2 × ^3J = 6.5 Hz, overlapping NCHMeMe). Cooling an NMR sample in toluene-d_8 to 203 K gave broadening of the resonances but decoalescence was not achieved. ^{13}C-{^1H} NMR (C_6D_6, 125.7

MHz, 293 K): δ 159.7 (Me$\underline{C}N_2$), 140.6 (*i*-C_6H_5), 133.6 (*o*-C_6H_5), 128.7 (*p*-C_6H_5), 127.9 ($\underline{C_5}Me_5$), 127.8 (*m*-C_6H_5), 54.0 (NNMe$\underline{Me}$), 50.0 (NN$\underline{Me}$Me), 47.4 (N$\underline{C}$HMeMe), 24.4 (NCH$\underline{Me}$Me), 24.1 (NCHMe$\underline{Me}$), 13.5 ($C_5\underline{Me_5}$), 13.1 ($\underline{Me}CN_2$). ^{29}Si NMR (HMQC ^{1}H-observed, C_6D_6, 299.9 MHz, 293 K): δ -45.5 (SiH). IR (NaCl plates, Nujol mull, cm^{-1}): 2183 (w), 1617 (m), 1603 (m), 1427 (m), 1414 (w), 1365 (m), 1320 (m), 1307 (s), 1189 (w), 1174 (w), 1159 (w), 1127 (w), 1108 (m), 1070 (s), 1015 (w), 918 (w), 861 (s), 806 (w), 742 (s), 715 (m), 704 (m), 695 (m), 582 (s). EI-MS: *m/z* = 218 $[Cp^*TiCl]^+$ (50 %), 276 $[Cp^*Ti(NNMe_2)Cl]^+$ (35 %), 417 $[M – \{MeC(N^iPr)_2\}]^+$ (55 %). Anal. Found (calcd for $C_{26}H_{44}Cl_2N_4SiTi$): C, 55.90 (55.81); H, 7.83 (7.93); N, 9.73 (10.01) %.

$Cp^*Ti\{N(NMe_2)SiMe_2N(^iPr)CMeN^iPr\}Cl_2$ (12). To a stirred solution of $Cp^*Ti\{MeC(N^iPr)_2\}(NNMe_2)$ (**1**, 0.305 g, 0.80 mmol) in benzene (20 mL) was added Me_2SiCl_2 (96.5 μL, 0.80 mmol) all at room temperature. An immediate colour change from dark green to orange was observed. The volatiles were removed under reduced pressure after 3 h to afford **12** as an orange solid. Yield: 0.169 g (41%). Diffraction-quality crystals were grown from a saturated diethyl ether solution. ^{1}H NMR (toluene-d_8, 499.9 MHz, 223 K): δ 3.87 (1 H, app. sept, app. ^3J = 6.5 Hz, NC$\underline{H}_a$MeMe), 3.35 (1 H, app. sept, app. ^3J = 6.5 Hz, NC$\underline{H}_b$MeMe), 3.04 (6 H, s, NN$\underline{MeMe}$), 2.00 (15 H, s, C_5Me_5), 1. 47 (3 H, s, $MeCN_2$), 1.11 (6 H, overlapping 2 × d, 2 × ^3J = 6.5 Hz, overlapping NCH$_b\underline{Me}$Me and NCH$_b$Me$\underline{Me}$), 1.03 (6 H, overlapping 2 × d, 2 × ^3J = 6.5 Hz, overlapping NCH$_a\underline{Me}$Me and NCH$_a$Me$\underline{Me}$), 0.51 (6 H, s, Si$\underline{Me_2}$). ^{13}C-{^{1}H} NMR (toluene-d_8, 125.7 MHz, 223 K): δ 158.6 (Me$\underline{C}N_2$), 127.3 ($\underline{C_5}Me_5$), 53.5 (NN$\underline{Me_2}$), 49.2 (N$\underline{C}H_b$MeMe), 45.6 (N$\underline{C}H_a$MeMe), 24.6 (overlapping NCH$_b\underline{Me}$Me and NCH$_b$Me$\underline{Me}$), 23.3 (overlapping NCH$_a\underline{Me}$Me and NCH$_a$Me$\underline{Me}$), 16.7 ($\underline{Me}CN_2$) 13.5 ($C_5\underline{Me_5}$), 3.9 (Si$\underline{Me_2}$). ^{29}Si NMR (toluene-d_8, 299.9 MHz, 223 K): δ -12.9 ($SiMe_2$). IR (NaCl plates, Nujol mull, cm^{-1}): 1667 (s), 1457 (s), 1341 (m), 1314 (m), 1204 (m), 1174 (w), 1126 (m), 1092 (m), 1015 (m), 973 (w), 888 (m), 789 (m), 721 (m). EI-MS: *m/z* = 199 $[M – Cp^*TiCl_2NNMe_2]^+$ (90 %), 276 $[Cp^*TiClNNMe_2]^+$ (50 %), 369 $[M – \{MeC(N^iPr)_2\}]^+$ (100 %). Anal. Found (calcd for $C_{22}H_{44}Cl_2N_4SiTi$): C, 51.56 (51.66); H, 8.26 (8.67); N, 10.82 (10.95) %.

NMR tube scale synthesis of $Cp^*Ti\{MeC(N^iPr)_2\}(Br)\{N(NMe_2)SiH_2Ph\}$ (13). To a solution of $Cp^*Ti\{MeC(N^iPr)_2\}(NNMe_2)$ (**1**, 25.0 mg, 0.065 mmol) in toluene-d_8 (0.6 mL) in an NMR tube equipped with a J. Young Teflon valve was added $PhSiH_2Br$ (12.3 mg, 0.065 mmol) all at room temperature. An immediate colour change from dark green to brown was observed and the ^{1}H NMR spectrum recorded immediately showed complete conversion to **13** which was characterised by NMR spectroscopy. ^{1}H NMR (toluene-d_8, 299.9 MHz, 193 K): δ 7.62 (2 H, d, ^3J = 6.6 Hz, *o*-C_6H_5), 7.13 (3 H, m, overlapping *m*- and *p*-C_6H_5), 5.30 (1 H, d, ^2J = 5.7 Hz, Si$\underline{H}_a$H), 5.23 (1 H, d, ^2J = 5.7 Hz, SiH$\underline{H}_b$), 4.72 (1 H, br. s, NC$\underline{H}_a$MeMe), 3.07 (3 H, s, NN$\underline{Me}$Me), 2.71 (1 H, br. s, NC$\underline{H}_b$MeMe), 2.32 (3 H, s, NNMe$\underline{Me}$), 2.13 (15 H, s, C_5Me_5), 1.39 (3 H, s, $MeCN_2$), 1.31 (6 H, m, overlapping

NCH$_a$<u>MeMe</u>), 0.92 (6 H, m, overlapping NCH$_a$<u>MeMe</u>). ^{13}C-{^{1}H} NMR (toluene-d_8, 75.4 MHz, 193 K): δ 170.0 (Me<u>C</u>N$_2$), 137.1 (*i*-C_6H_5), 134.3 (*o*-C_6H_5), 129.1 (*p*-C_6H_5), 128.5 (<u>C</u>$_5$Me$_5$), 128.2 (*m*-C_6H_5), 57.8 (NN<u>Me</u>Me), 50.7 (N<u>C</u>H$_a$MeMe), 48.4 (N<u>C</u>H$_b$MeMe), 47.0 (NNMe<u>Me</u>), 26.7 (NCH$_b$<u>Me</u>Me), 23.8 (NCH$_a$Me<u>Me</u>), 22.5 (NCH$_a$<u>Me</u>Me), 22.1 (NCH$_b$Me<u>Me</u>), 15.9 (<u>Me</u>CN$_2$), 14.3 (C$_5$<u>Me</u>$_5$) ^{29}Si NMR (HMQC ^{1}H-observed, toluene-d_8, 299.9 MHz, 193 K): δ -41.7 (SiH$_2$Ph). ES$^+$-MS (sample prepare *in situ* in THF): *m/z* = 489 [*M* – Br]$^+$ (100 %).

Cp*Ti{N(NPh$_2$)SiH$_2$Ph}Cl$_2$ (14). To a solution of Cp*Ti{MeC(N^{i}Pr)$_2$}(NNPh$_2$) (**2**, 0.200 g, 0.395 mmol) in benzene (5 mL) was added PhSiH$_2$Cl (105.3 μL, 0.790 mmol) in benzene (5 mL) all at room temperature. A colour change from dark green to brown was observed. After 20 h, the volatiles were reduced under reduced pressure to give a brown oil which contained **14** and the side-product ^{i}PrNC(Me)N(^{i}Pr)SiH$_2$Ph (**16**) which could not be separated. Combined yield: 0.213 g (83 %).

Data for **14**: ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.64 (4 H, d, ^3J = 7.5 Hz, *o*-C_6H_5), 7.44 (2 H, d, ^3J = 7.5 Hz, *o*-C_6H_5Si), 7.10 (2 H, t, ^3J = 7.5 Hz, *m*-C_6H_5Si), 7.05 (1 H, t, ^3J = 7.5 Hz, *p*-C_6H_5Si), 6.87 (4 H, t, ^3J = 7.5 Hz, *m*-C_6H_5), 6.75 (2 H, t, ^3J = 7.5 Hz, *p*-C_6H_5), 5.15 (2 H, s, SiH$_2$), 1.87 (15 H, s, C$_5$Me$_5$). ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 149.9 (*i*-C_6H_5), 136.2 (*o*-C_6H_5Si), 133.7 (*i*-C_6H_5Si), 130.5 (*p*-C_6H_5Si), 130.0 (<u>C</u>$_5$Me$_5$), 128.6 (*m*-C_6H_5), 128.1 (*m*-C_6H_5Si), 126.8 (*p*-C_6H_5), 126.0 (*o*-C_6H_5), 13.2 (C$_5$<u>Me</u>$_5$). ^{29}Si NMR (HMQC ^{1}H-observed, C_6D_6, 299.9 MHz, 293 K): δ -30.6 (SiH$_2$). IR (NaCl plates, Nujol mull, cm^{-1}): 2152 (s), 1590 (s), 1488 (s), 1452 (s), 1277 (m), 1158 (s), 1058 (s), 1023 (s), 1003 (w), 970 (m), 862 (s), 833 (s), 762 (s), 633 (m), 616 (m), 607 (m). EI-MS: *m/z* = 542 [*M*]$^+$ (50 %), 472 [*M* – Cl$_2$]$^+$ (50 %), 253 [Cp*TiCl$_2$]$^+$ (70 %). An elemental analysis could not be obtained due to contamination witn **16**.

Data for **16**: ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.92 (2 H, d, ^3J = 7.5 Hz, *o*-C_6H_5), 7.23 (3 H, app. t, app. ^3J = 7.5 Hz, overlapping *m*- and *p*-C_6H_5), 5.33 (2 H, s, SiH$_2$), 3.38 (2 H, sept, ^3J = 6.6 Hz, NC<u>H</u>Me$_2$), 1.36 (3 H, s, MeCN$_2$), 1.09 (12 H, d, ^3J = 6.6 Hz, NCH<u>Me</u>$_2$). ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 159.9 (Me<u>C</u>N$_2$), 137.9 (*i*-C_6H_5), 135.2 (*o*-C_6H_5), 129.0 (*m*-C_6H_5), 127.4 (*p*-C_6H_5), 47.3 (N<u>C</u>HMeMe), 24.7 (NCH<u>Me</u>$_2$), 10.7 (<u>Me</u>CN$_2$). ^{29}Si NMR (HMQC ^{1}H-observed, C_6D_6, 299.9 MHz, 293 K): δ -58.1 (SiH$_2$). IR (NaCl plates, Nujol mull, cm^{-1}): 2966 (s), 2931 (s), 2868 (m), 2151 (m), 2107 (m), 1629 (s), 1457 (m), 1428 (s), 1393 (s), 1364 (s), 1323 (s), 1261 (w), 1218 (m), 1176 (w), 1163 (w), 1140 (w), 1129 (w), 1116 (s), 1067 (w), 1019 (m), 975 (s), 900 (s), 874 (s), 808 (m), 737 (m), 699 (s), 656 (w), 638 (m). EI-HRMS: *m/z* found (calcd. for $C_{14}H_{24}N_2Si$, [*M*]$^+$) 248.1707 (248.1709).

Cp*Ti{N(NPh$_2$)SiH(Me)Ph}Cl$_2$ (15). To a solution of Cp*Ti{MeC(N^{i}Pr)$_2$}(NNPh$_2$) (**2**, 0.203 g, 0.40 mmol) in benzene (5 mL) was added Ph(Me)SiHCl (120.2 μL, 0.80 mmol) in benzene (5 mL) all at room temperature. After 2d, the volatiles were removed under reduced pressure to yield a brown oil. Diffraction-quality crystals of **15** were grown from benzene/hexane layering at 4 °C. Yield of **15**: 90 mg (40%) The side product ^{i}PrNC(Me)N(^{i}Pr)SiH(Me)Ph (**17**) could not be isolated in a pure form free from **15** and was characterised by spectroscopic methods.

Data for **15**: ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.74 (2 H, d, ^{3}J = 7.5 Hz, o_a-C_6H_5), 7.59 (2 H, d, ^{3}J = 7.5 Hz, o_b-C_6H_5), 7.53 (2 H, d, ^{3}J = 7.5 Hz, *o*-C_6H_5Si), 7.20 (3 H, m, overlapping m_b- and p_b-C_6H_5), 6.89 (2 H, t, ^{3}J = 7.5 Hz, m_a-C_6H_5), 6.82 (3 H, m, overlapping *m*-C_6H_5Si and p_a-C_6H_5), 6.70 (1 H, app. t, app. ^{3}J = 7.5 Hz, *p*-C_6H_5Si), 5.43 (1 H, q, ^{3}J = 3.6 Hz, SiH), 1.86 (15 H, s, C_5Me_5), 0.07 (3 H, d, ^{3}J = 3.6 Hz, SiMe). ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 150.6 (i_a-C_6H_5), 150.5 (*i*-C_6H_5Si), 136.5 (i_b-C_6H_5), 135.8 (o_b-C_6H_5), 130.3 (p_b-C_6H_5), 130.0 ($\underline{C}_5Me_5$), 128.7 (*m*-C_6H_5Si), 128.4 (m_a-C_6H_5), 128.2 (m_b-C_6H_5), 127.4 (o_a-C_6H_5), 127.2 (p_a-C_6H_5), 126.4 (*p*-C_6H_5Si), 124.9 (*o*-C_6H_5Si), 13.2 ($C_5\underline{Me}_5$), -4.6 (SiMe). ^{29}Si NMR (HMQC ^{1}H-observed, C_6D_6, 299.9 MHz, 293 K): δ -12.3 (SiH(Me)). IR (NaCl plates, Nujol mull, cm^{-1}): 2154 (s), 1954 (w), 1891 (w), 1586 (s), 1427 (s), 1309 (m), 1257 (s), 1211 (m), 1192 (w), 1167 (w), 1150 (s), 1118 (s), 1086 (w), 1079 (w), 1069 (w), 1041 (s), 1031 (s), 1021 (s), 1001 (m), 985 (w), 970 (w), 914 (w), 878 (s), 861 (s), 812 (s), 760 (s), 741 (s), 731 (s), 701 (s), 690 (s), 628 (w), 617 (w), 606 (w), 590 (m). EI-MS: *m/z* = 421 $[M – Cp^*]^+$ (100 %). Anal. Found (calcd for $C_{29}H_{34}Cl_2N_2SiTi$): C, 62.61 (62.48); H, 6.00 (6.15); N, 4.93 (5.03) %.

Data for **17**: ^{1}H NMR (C_6D_6, 299.9 MHz, 293 K): δ 7.84 (2 H, d, ^{3}J = 7.5 Hz, *o*-C_6H_5), 7.27 (2 H, t, ^{3}J = 7.5 Hz, *m*-C_6H_5), 7.07 (1 H, t, ^{3}J = 7.5 Hz, *p*-C_6H_5), 5.16 (1 H, q, ^{3}J = 3.6 Hz, SiH), 3.38 (2 H, app. sept, app. ^{3}J = 6.6 Hz, NC$\underline{H}$MeMe), 1.36 (3 H, s, $MeCN_2$), 1.16 (6 H, d, ^{3}J = 6.6 Hz, NCH$\underline{Me}$Me), 0.97 (6 H, d, ^{3}J = 6.6 Hz, NCHMe$\underline{Me}$), 0.78 (3 H, d, ^{3}J = 3.6 Hz, SiMe). ^{13}C-{^{1}H} NMR (C_6D_6, 75.4 MHz, 293 K): δ 158.7 (Me$\underline{C}N_2$), 140.2 (*i*-C_6H_5), 134.6 (*o*-C_6H_5), 129.5 (*p*-C_6H_5), 127.5 (*m*-C_6H_5), 47.3 (N$\underline{C}$HMeMe), 24.6 (NCH$\underline{Me}$Me), 24.4 (NCHMe$\underline{Me}$), 10.9 ($\underline{Me}CN_2$), -0.5 (SiMe). ^{29}Si NMR (HMQC ^{1}H-observed, C_6D_6, 299.9 MHz, 293 K): δ -35.4 (SiH(Me)). EI-HRMS: *m/z* found (calcd. for $C_{15}H_{26}N_2Si$, $[M]^+$) 262.1870 (262.1865).

NMR tube scale synthesis of Cp*Ti{MeC(N^{i}Pr)$_2$}(Cl){N(Tol)SiH$_2$Ph} (18). To a solution of Cp*Ti{MeC(N^{i}Pr)$_2$}(NTol) (**3**, 15.0 mg, 0.035 mmol) in toluene-d_8 (0.6 mL) in an NMR tube equipped with a J. Young Teflon valve was added $PhSiH_2Cl$ (4.70 μL, 0.035 mmol) all at room temperature. An immediate colour change from dark green to brown was observed. The product **18** formed quantitatively and was characterised by NMR spectroscopy. ^{1}H NMR data (toluene-d_8, 299.9 MHz, 253 K): δ 7.74 (2 H, d, ^{3}J = 7.3 Hz, *o*-C_6H_5), 7.06 (3 H, m, overlapping *m*- and *p*-C_6H_5), 6.94 (2 H, d, ^{3}J = 8.0 Hz, *o*-$C_6\underline{H}_4$Me), 6.78 (2 H, d, ^{3}J = 8.0 Hz, *m*-$C_6\underline{H}_4$Me), 5.43 (1 H, d, ^{2}J = 8.7 Hz, Si$\underline{H}_a$H), 5.08 (1 H, d, ^{2}J = 8.7 Hz, SiH$\underline{H}_b$), 4.50 (1 H, app. sept., app. ^{3}J = 7.2 Hz, NC$\underline{H}_a$MeMe), 3.70 (1 H, app. sept., app. ^{3}J = 7.2 Hz, NC$\underline{H}_b$MeMe), 2.09 (3 H, s, $C_6H_4\underline{Me}$), 1.81 (15 H, s, C_5Me_5), 1.75 (3 H, s, $MeCN_2$), 1.49 (3 H, d, ^{3}J = 7.2 Hz, NCH$_a\underline{Me}$Me), 1.45 (3 H, d, ^{3}J = 7.2 Hz, NCH$_b\underline{Me}$Me), 1.24 (3 H, d, 2 × ^3J = 7.2 Hz, NCH$_a$Me$\underline{Me}$), 1.21 (3 H, d, 2 × ^3J = 7.2 Hz, NCH$_b$Me$\underline{Me}$). ^{13}C-{^{1}H} NMR (toluene-d_8, 75.4 MHz, 253 K): δ 170.3 (Me$\underline{C}$N$_2$), 155.1 (overlapping *i*-C$_6$H$_5$ and *i*-$\underline{C}_6$H$_4$Me), 137.1 (*o*-C$_6$H$_5$), 134.0 (*p*-$\underline{C}_6$H$_4$Me), 132.1(*m*-$\underline{C}_6$H$_4$Me), 129.6 (*p*-C$_6$H$_5$), 128.4 (*o*-$\underline{C}_6$H$_4$Me), 127.4 ($\underline{C}_5$Me$_5$), 127.3 (*m*-C$_6$H$_5$), 51.1 (N$\underline{C}$H$_a$MeMe), 49.1 (N$\underline{C}$H$_b$MeMe), 26.3 (NCH$_b$Me$\underline{Me}$), 24.3 (NCH$_b$$\underline{Me}$Me), 23.5 (NCH$_aMe\underline{Me}$), 23.0 (NCH$_a$$\underline{Me}$Me), 20.9 (C$_6H_4$$\underline{Me}$), 16.8 ($\underline{Me}CN_2$), 13.0 (C$_5$$\underline{Me}_5$). ^{29}Si NMR (HMQC ^{1}H-observed, C$_6$D$_6$, 299.9 MHz, 293 K): δ -35.7 (SiH$_2$).

NMR tube scale synthesis of Cp*Ti{MeC(N^{i}Pr)$_2$}(Br){N(Tol)SiH$_2$Ph} (19). To a solution of Cp*Ti{MeC(N^{i}Pr)$_2$}(NTol) (**3**, 20.0 mg, 0.047 mmol) in toluene-d_8 (0.6 mL) in an NMR tube equipped with a J. Young Teflon valve was added PhSiH$_2$Br (8.70 mg, 0.047 mmol) all at room temperature. An immediate colour change from dark green to brown was observed. The product **19** was formed quantitatively and characterised by NMR spectroscopy. ^{1}H NMR data (toluene-d_8, 299.9 MHz, 253 K): δ 7.68 (2 H, d, ^3J = 6.9 Hz, *o*-C$_6$H$_5$), 7.04 (3 H, m, overlapping *m*- and *p*-C$_6$H$_5$), 6.90 (2 H, d, ^3J = 8.4 Hz, *o*-C$_6$$\underline{H}_4$Me), 6.69 (2 H, d, ^3J = 8.4 Hz, *m*-C$_6$$\underline{H}_4$Me), 5.43 (1 H, d, ^2J = 8.7 Hz, Si$\underline{H}_a$H), 5.04 (1 H, d, ^2J = 8.7 Hz, SiH$\underline{H}_b$), 4.66 (1 H, app. sept, app. ^3J = 6.9 Hz, NC$\underline{H}_a$MeMe), 3.66 (1 H, app. sept, app. ^3J = 6.9 Hz, NC$\underline{H}_b$MeMe), 2.10 (3 H, s, C$_6$H$_4$$\underline{Me}$), 1.84 (15 H, s, C$_5Me_5$), 1.75 (3 H, s, MeCN$_2$), 1.51 (3 H, d, ^3J = 6.9 Hz, NCH$_a$$\underline{Me}$Me), 1.42 (3 H, d, ^3J = 6.9 Hz, NCH$_b$$\underline{Me}$Me), 1.24 (3 H, d, ^3J = 6.9 Hz, NCH$_a$Me$\underline{Me}$), 1.17 (3 H, d, ^3J = 6.9 Hz, NCH$_b$Me$\underline{Me}$). ^{13}C-{^{1}H} NMR (toluene-d_8, 75.4 MHz, 253 K): δ 170.3 (Me$\underline{C}$N$_2$), 163.2 (*i*-C$_6$H$_5$), 158.6 (*i*-$\underline{C}_6$H$_4$Me), 137.2 (*o*-C$_6$H$_5$), 133.5 (*p*-$\underline{C}_6$H$_4$Me), 132.4 (*m*-$\underline{C}_6$H$_4$Me), 129.7 (*p*-C$_6$H$_5$), 128.5 (*o*-$\underline{C}_6$H$_4$Me), 127.7 ($\underline{C}_5$Me$_5$), 127.3 (*m*-C$_6$H$_5$), 52.3 (N$\underline{C}$H$_a$MeMe), 49.1 (N$\underline{C}$H$_b$MeMe), 26.7 (NCH$_b$Me$\underline{Me}$), 24.3 (NCH$_b$$\underline{Me}$Me), 23.4 (NCH$_aMe\underline{Me}$), 23.3 (NCH$_a$$\underline{Me}$Me), 20.9 (C$_6H_4$$\underline{Me}$), 16.8 ($\underline{Me}CN_2$), 13.4 (C$_5$$\underline{Me}_5$). ^{29}Si NMR (C$_6D_6$, 299.9 MHz, 293 K): δ -35.5 (SiH$_2$Ph).

[Cp*Ti{MeC(N^{i}Pr)$_2$}(NNMe$_3$)]I (20-I). To a solution of Cp*Ti{MeC(N^{i}Pr)$_2$}(NNMe$_2$) (**1**, 0.308 g, 0.80 mmol) in pentane (10 mL) was added MeI (50.0 μL, 0.80 mmol). After 2 h an orange powder had precipitated. The solution was filtered and the powder washed with pentane (3 x 5 mL) and dried *in vacuo* to give **20-I** as a pale orange powder. Yield: 0.330 g (78%). Diffraction-quality crystals were grown from slow cooling of a saturated benzene solution. ^{1}H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): δ 3.81 (2 H, br, app. sept., app. ^3J = 5.8 Hz, NC$\underline{H}$MeMe), 3.54 (9 H, s, NNMe$_3$) 2.16 (3 H, s, MeCN$_2$), 1.83 (15 H, s, C$_5$Me$_5$), 0.93 (6 H, d, ^3J = 5.8 Hz, NCH$\underline{Me}$Me), 0.82 (6 H, d, ^3J = 5.8 Hz, NCHMe$\underline{Me}$). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 75.4 MHz, 293 K): δ 165.0 (CN$_2$), 123.9 ($\underline{C}_5$Me$_5$), 61.5 (NNMe$_3$), 49.8 (N$\underline{C}$HMeMe), 26.5 (NCH$\underline{Me}$Me), 25.8 (NCHMe$\underline{Me}$), 14.2 ($\underline{Me}$CN$_2$), 13.2 (C$_5$$\underline{Me}_5$). IR (NaCl plates, Nujol mull, cm^{-1}): 1540 (w), 1458 (s), 1345 (m), 1328 (m), 1253 (m), 1208 (m), 1160 (w), 1122 (w), 1021 (w), 815 (w), 668 (w). ES$^+$-MS (THF): *m/z* = 397 [**20**]$^+$ (100 %). Anal. found (calcd. for C$_{21}$H$_{41}$IN$_4$Ti): C, 47.90 (48.10); H, 7.98 (7.88); N, 10.52 (10.69) %.

[Cp*Ti{MeC(N^{i}Pr)$_2$}(NNMe$_2$Et)]Br (21-Br). To a stirred solution of Cp*Ti{MeC(N^{i}Pr)$_2$}(NNMe$_2$) (**1**, 0.300 g, 0.780 mmol) in benzene (10 mL) was added EtBr (58.6 μL, 0.780 mmol) in benzene (10 mL) all at room temperature. After 2 d, the solution was filtered, and the volatiles were removed under reduced pressure to afford a yellow-brown solid. The crude material was then washed with cold pentane, filtered, and dried *in vacuo* to give **21-Br** as a red-brown solid. Yield: 0.164 g (43%). Diffraction-quality crystals were grown by THF/pentane layering at 4 °C. ^{1}H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): δ 3.83 (2 H, q, ^3J = 7.2 Hz, C<u>H</u>$_2$CH$_3$), 3.75 (2 H, sept, ^3J = 6.6 Hz, NC<u>H</u>MeMe), 3.41 (6 H, s, NNMe$_2$), 1.98 (15 H, s, C$_5$Me$_5$), 1. 93 (3 H, s, MeCN$_2$), 1.05 (9 H, m, overlapping CH$_2$C<u>H</u>$_3$ and NCH<u>Me</u>Me), 0.98 (6 H, d, ^3J = 6.6 Hz, NCHMe<u>Me</u>). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 75.4 MHz, 293 K): δ 165.6 (Me<u>C</u>N$_2$), 122.1 (<u>C</u>$_5$Me$_5$), 65.6 (<u>C</u>H$_2$CH$_3$), 57.9 (NNMe$_2$), 49.3 (N<u>C</u>HMeMe), 25.6 (NCH<u>Me</u>Me), 25.1 (NCHMe<u>Me</u>), 14.2 (<u>Me</u>CN$_2$) 13.0 (C$_5$<u>Me</u>$_5$), 9.2 (CH$_2$<u>C</u>H$_3$). IR (NaCl plates, Nujol mull, cm^{-1}): 1457 (s), 1331 (m), 1226 (w), 1206 (m), 1173 (w), 1155 (m), 1119 (w), 1021 (m), 799 (w), 770 (w). ES$^+$-MS (THF): *m/z* = 411 [**21**]$^+$ (100 %). A satisfactory elemental analysis could not be obtained.

[Cp*Ti{MeC(N^{i}Pr)$_2$}(NNMe$_2$CH$_2$Ph)]Br (22-Br). To a stirred solution of Cp*Ti{MeC(N^{i}Pr)$_2$}(NNMe$_2$) (**1**, 0.218 g, 0.570 mmol) in benzene (10 mL) was added PhCH$_2$Br (67.7 μL, 0.570 mmol) in benzene (10 mL) all at room temperature. After 16 h, the resultant brown solution was filtered, and the volatiles were removed under reduced pressure to give a waxy red brown solid. It was then washed with cold pentane and dried *in vacuo* to afford **22-Br** as a red-brown solid. Yield: 0.134 g (43%). ^{1}H NMR (C$_6$D$_6$, 499.9 MHz, 293 K): δ 7.33 (2 H, d, ^3J = 7.5 Hz, *o*-C$_6$H$_5$), 7.20 (2 H, t, ^3J = 7.5 Hz, *m*-C$_6$H$_5$), 7.06 (1 H, t, ^3J = 7.5 Hz, *p*-C$_6$H$_5$), 4.74 (2H, s, C<u>H</u>$_2$Ph), 3.78 (2 H, app. sept, app. ^3J = 6.5 Hz, NC<u>H</u>MeMe), 2.52 (6 H, s, NNMe$_2$), 2.07 (15 H, s, C$_5$Me$_5$), 1.61 (3 H, s, MeCN$_2$), 1.18 (6 H, d, ^3J = 6.5 Hz, NCH<u>Me</u>Me), 1.07 (6 H, d, ^3J = 6.5 Hz, NCHMe<u>Me</u>). ^{13}C-{^{1}H} NMR (C$_6$D$_6$, 125.7 MHz, 293 K): δ 169.0 (Me<u>C</u>N$_2$), 141.9 (*i*-C$_6$H$_5$), 128.5 (overlapping *m*- and *o*-C$_6$H$_5$), 127.2 (*p*-C$_6$H$_5$), 125.0 (<u>C</u>$_5$Me$_5$), 56.6 (<u>C</u>H$_2$Ph), 49.6 (N<u>C</u>HMeMe), 49.0 (NN<u>Me</u>$_2$), 25.5 (NCH<u>Me</u>Me), 24.0 (NCHMe<u>Me</u>), 15.6 (<u>Me</u>CN$_2$), 13.9 (C$_5$<u>Me</u>$_5$). IR (NaCl plates, Nujol mull, cm^{-1}): 1653 (w), 1602 (w), 1457 (s), 1353 (m), 1332 (m), 1200 (m), 1172 (w), 1130 (m), 1076 (w), 1016 (m), 814 (w), 792 (w), 752 (m), 739 (w), 723 (w), 710 (m), 491 (s). ES$^+$-MS (THF): *m/z* = 473 [**22**]$^+$ (100 %). Anal. found (calcd. for C$_{27}$H$_{45}$BrN$_4$Ti): C, 58.70 (58.59); H, 8.30 (8.20); N, 10.20 (10.12) %.

[Cp*Ti{MeC(N^{i}Pr)$_2$}{N(NMe$_2$)H}][BPh$_4$] (23-BPh$_4$). To a stirred solution of Cp*Ti{MeC(N^{i}Pr)$_2$}(NNMe$_2$) (**1**, 0.300 g, 0.78 mmol) in THF (10 mL) was added a solution of [Et$_3$NH][BPh$_4$] (0.331 g, 0.78 mmol) in THF (10 mL) all at room temperature. The resulting red solution was stirred for 1 h. Volatiles were removed under reduced pressure to afford **23-BPh$_4$** as a red solid which was washed with cold pentane, filtered, and dried *in vacuo*. Yield: 0.382 g (61%). Diffraction-quality crystals were grown by THF/pentane layering. ^{1}H NMR (C_6D_5Br, 299.9 MHz, 293 K): δ 7.74 (8 H, br. m, *o*-C_6H_5), 7.11 (8 H, t, ^{3}J = 6.9 Hz, *m*-C_6H_5), 6.96 (4 H, t, ^{3}J = 6.9 Hz, *p*-C_6H_5), 2.94 (2 H, app. sept, app. ^{3}J = 6.6 Hz, NCHMeMe), 1.59 (15 H, s, C_5Me_5), 1.53 (6 H, s, $NNMe_2$), 1.43 (3 H, s, $MeCN_2$), 0.76 (6 H, d, ^{3}J = 6.6 Hz, NCHMeMe), 0.43 (6 H, d, ^{3}J = 6.6 Hz, NCHMeMe). NH resonance not observed in C_6D_5Br but found at 8.94 ppm in THF-d_8. ^{13}C-{^{1}H} NMR (C_6D_5Br, 75.4 MHz, 293 K): δ 164.5 (*i*-C_6H_5), 162.5 ($MeCN_2$), 136.9 (*o*-C_6H_5), 128.3 (C_5Me_5), 126.2 (*m*-C_6H_5), 122.4 (*p*-C_6H_5), 50.1 (NCHMeMe), 50.0 ($NNMe_2$), 25.8 (NCHMeMe), 24.2 (NCHMeMe), 13.1 (C_5Me_5), 12.7 ($MeCN_2$). ^{11}B-{^{1}H} NMR (C_6D_5Br, 96.2 MHz, 293 K): δ -5.9 (BPh_4). IR (NaCl plates, Nujol mull, cm^{-1}): 3266 (w), 1636 (w), 1580 (m), 1341 (w), 1205 (m), 1172 (w), 1123 (w), 1065 (w), 1032 (m), 1011 (m), 844 (w), 815 (w), 795 (w), 732 (m), 704 (m), 625 (m), 611 (m). ES^{+}-MS (THF): *m/z* = 383 [**23**]$^{+}$ (100 %). ES^{-}-MS (THF): *m/z* = 319 [BPh_4]$^{-}$ (100 %). Anal. found (calcd. for $C_{48}H_{67B}N_4OTi$ (**23-BPh$_4$**·THF)): C, 74.52 (74.41); H, 8.50 (8.72); N, 7.58 (7.23) %.

NMR tube scale synthesis of [Cp*Ti{MeC(N^{i}Pr)$_2$}{N(NPh$_2$)H}][BPh$_4$] (24-BPh$_4$). To a solution of Cp*Ti{MeC(N^{i}Pr)$_2$}(NNPh$_2$) (**2**, 10.3 mg, 0.020 mmol) in THF-d_8 (0.3 mL) in an NMR tube equipped with a J. Young Teflon valve was added a solution of an excess of [Et_3NH][BPh_4] (17.1 mg, 0.041 mmol) in THF-d_8 (0.3 mL) all at room temperature. A slow colour change from dark yellow to dark green was observed. The reaction was monitored by ^{1}H NMR spectroscopy. After 16 h, **24-BPh$_4$** had been formed quantitatively (along with Et_3N) and was characterised by NMR spectroscopy. ^{1}H NMR (THF-d_8, 299.9 MHz, 293 K): δ 7.29 (8 H, br. m, *o*-C_6H_5), 6.87 (8 H, t, ^{3}J = 7.5 Hz, *m*-C_6H_5), 6.72 (4 H, t, ^{3}J = 7.5 Hz, *p*-C_6H_5), 3.61 (2 H, app. sept, app. ^{3}J = 6.6 Hz, NCHMeMe), 1.97 (15 H, s, C_5Me_5), 1.76 (3 H, s, $MeCN_2$), 1.13 (12 H, d, ^{3}J = 6.6 Hz, overlapping NCHMeMe). NH not observed and $NNPh_2$ resonances obscured by [BPh_4]$^{-}$. ^{13}C-{^{1}H} NMR (THF-d_8, 75.4 MHz, 293 K): δ 165.1 (*i*-C_6H_5), 163.0 ($MeCN_2$), 137.4 (*o*-C_6H_5), 126.1 (*m*-C_6H_5), 124.1 (C_5Me_5), 122.2 (*p*-C_6H_5), 48.5 (NCH_aMeMe), 45.2 (NCH_bMeMe), 22.9 (NCHMeMe), 21.8 (NCHMeMe), 17.9 ($MeCN_2$), 11.9 (C_5Me_5). $NNPh_2$ resonances obscured by [BPh_4]$^{-}$. ^{11}B-{^{1}H} NMR (THF-d_8, 96.2 MHz, 293 K): δ -6.6 (BPh_4).

NMR tube scale synthesis of [Cp*Ti{MeC(N^{i}Pr)$_2$}{N(H)Tol}][BPh$_4$] (25-BPh$_4$). To a solution of Cp*Ti{MeC(N^{i}Pr)$_2$}(NTol) (**3**, 10.0 mg, 0.023 mmol) in THF-d_8 (0.3 mL) in an NMR tube equipped with a J. Young Teflon valve was added a solution of an excess of [Et_3NH][BPh_4] (19.6 mg, 0.047 mmol) in THF-d_4 (0.3 mL) all at room temperature. An immediate colour change from dark green to brown was observed. The reaction was monitored by ^{1}H NMR spectroscopy. After 20 min, **25-BPh$_4$** had been formed quantitatively (along with Et_3N) and was characterised by NMR spectroscopy. ^{1}H

NMR (THF-d_8, 299.9 MHz, 293 K): δ 7.29 (8 H, br. m, *o*-C_6H_5), 6.87 (10 H, m, overlapping *m*-C_6H_5 and *o*-C_6H_4Me), 6.73 (4 H, t, ^3J = 7.2 Hz, *p*-C_6H_5), 6.50 (2 H, d, ^3J = 8.1 Hz, *m*-C_6H_4Me), 3.60 (2 H, app. sept, app. ^3J = 6.3 Hz, NC$\underline{H}$MeMe), 2.21 (3 H, s, 4-$C_6H_4\underline{Me}$), 2.04 (15 H, s, C_5Me_5), 1.75 (3 H, s, $MeCN_2$), 1.13 (12 H, d, ^3J = 6.3 Hz, overlapping NCH$\underline{MeMe}$). N$\underline{H}$ not observed. ^{13}C-{^{1}H} NMR (THF-d_8, 75.4 MHz, 293 K): δ 165.1 (*i*-C_6H_5), 163.0 (Me$\underline{C}N_2$), 137.4 (overlapping *o*-C_6H_5 and *i*-C_6H_4Me), 129.9 (overlapping *o*-C_6H_4Me and *p*-C_6H_4Me) 126.0 (*m*-C_6H_5), 124.2 ($\underline{C_5}Me_5$), 122.2 (overlapping *p*-C_6H_5 and *m*-C_6H_4Me), 48.5 (N$\underline{C}H_a$MeMe), 45.2 (N$\underline{C}H_b$MeMe), 22.9 (NCH$\underline{Me}$Me), 21.8 (NCHMe$\underline{Me}$), 21.3 (4-$C_6H_4\underline{Me}$), 17.9 ($\underline{Me}CN_2$), 11.7 ($C_5\underline{Me_5}$). ^{11}B-{^{1}H} NMR (THF-d_8, 96.2 MHz, 293 K): δ -6.6 (BPh_4).

Crystal structure determinations. Crystal data collection and processing parameters are given in Table S2. Crystals were mounted on glass fibers using perfluoropolyether oil and cooled rapidly in a stream of cold N_2 using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.[9] The structures were solved by direct methods (SIR92[10]) and further refinements and all other crystallographic calculations were performed using the CRYSTALS program suite.[11] Other details of the structure solution and refinements are given in the Supporting Information (CIF data).

Computational details. All the calculations have been performed with the Gaussian09 package[12] at the M06 level.[13] The titanium atom was represented by the relativistic effective core potential (RECP) from the Stuttgart group (12 valence electrons) and its associated basis set,[14] augmented by an f polarisation function (α = 0.869).[15] The atoms (C, H, N) were represented by a 6-31G(d,p) basis set and Cl by a 6-31+G(d,p) basis set.[16] The Si and Br atoms were represented by RECP from the Stuttgart group and the associated basis set,[17] augmented by a *d* polarisation function.[18] Full optimisation of geometry was performed without any symmetry constraint, followed by analytical computation of the Hessian matrix to identify the nature of the located extrema as minima or TSs. Connection between reactant and product through a given TS was checked by optimisation of slightly altered geometries of the TS along the two directions of the TS vector associated to the imaginary frequency. All energies given in the text are Gibbs free energies in solution (toluene) calculated by using the approximation reported by Maseras *et al*. ($\Delta G_{sol} = \Delta E_{sol} + (\Delta G - \Delta E)$).[19] ΔE_{sol} was obtained by single point calculations using a 6-311++G(d,p) basis set for C, H, N, Cl, Br and including solvent with the SMD approach.[20] NBO calculations were performed using the NBO 5.9 program interfaced with Gaussian.[21]

Table S2. Data collection and processing parameters for Cp*Ti{MeC(N^{i}Pr)$_2$}(H){N(NMe$_2$)SiH$_2$R} (R = Ph (**4**), Ar^F (**5**) or Ar^{OMe} (**6**), Cp*Ti{MeC(N^{i}Pr)$_2$}(Cl){N(NMe$_2$)SiH$_2$Ph} (**8**), Cp*Ti{N(NMe$_2$)SiH(Ph)N(^{i}Pr)CMeN^{i}Pr}Cl$_2$ (**11**), Cp*Ti{N(NMe$_2$)SiMe$_2$N(^{i}Pr)CMeN^{i}Pr}Cl$_2$ (**12**), Cp*Ti{N(NPh$_2$)SiH(Me)Ph}Cl$_2$ (**15**), [Cp*Ti{MeC(N^{i}Pr)$_2$}(NNMe$_3$)]I (**20-I**), [Cp*Ti{MeC(N^{i}Pr)$_2$}(NNMe$_2$Et)]Br (**21-Br**) and [Cp*Ti{MeC(N^{i}Pr)$_2$}{N(NMe$_2$)H}][BPh$_4$] (**23-BPh$_4$**).

		4·0.25(C$_5$H$_{12}$)	**5**	**6**	**8**
empirical formula		$C_{26}H_{46}N_4SiTi \cdot 0.25(C_5H_{12})$	$C_{28}H_{44}F_6N_4SiTi$	$C_{27}H_{48}N_4OSiTi$	$C_{26}H_{45}ClN_4SiTi$
fw		508.70	626.66	520.69	525.11
temp / K		150	150	150	150
wavelength / Å		0.71073	0.71073	0.71073	0.71073
space group		$P\,2_1/c$	$P2_1/n$	$P\,\bar{1}$	$P\,\bar{1}$
a / Å		8.5949(2)	8.65520(10)	8.57190(10)	9.8784(2)
b / Å		11.3073(3)	24.6871(3)	9.90560(10)	10.3809(3)
c / Å		31.4337(9)	15.1275(2)	18.2095(2)	15.6151(4)
α / deg		90	90	80.3853(4)	94.6300(11)
β / deg		92.4007(12)	100.2706(5)	87.2553(4)	99.7244(13)
γ / deg		90	90	71.1128(5)	114.5284(13)
V / Å^3		3052.21(14)	3180.53(7)	1442.34(3)	1415.38(6)
Z		4	4	2	2
d (calcd) / Mg·m^{-3}		1.107	1.309	1.199	1.232
abs coeff / mm^{-1}		0.340	0.366	0.363	0.460
R indices:^{a}	R_1 =	0.0637	0.0528	0.0353	0.0481
	R_w =	0.0686	0.0618	0.0378	0.0548

^{a} $R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$; $R_w = \sqrt{\{\Sigma w(|F_o|-|F_c|)^2 / \Sigma w|F_o|^2\}}$ for data with I > 3σ(I).

Table S2. (Contd.)

	11	**12**	**15**	**20-I**
empirical formula	$C_{26}H_{44}Cl_2N_4SiTi$	$C_{22}H_{44}Cl_2N_4SiTi$	$C_{29}H_{34}Cl_2N_2SiTi$	$C_{21}H_{41}IN_4Ti$
fw	559.55	511.51	557.49	524.39
temp / K	150	150	150	150
wavelength / Å	0.71073	0.71073	0.71073	0.71073
space group	$P\,2_1/c$	$P\,2_1/c$	$P\,\bar{1}$	$P\,\bar{1}$
a / Å	11.5517(2)	11.5599(3)	8.4930(2)	10.0805(3)
b / Å	14.3261(2)	16.9818(4)	11.6230(3)	16.6347(4)
c / Å	18.0286(3)	13.9465(3)	14.6209(3)	17.7081(5)
α / deg	90	90	95.5060(10)	116.9766(13)
β / deg	97.201(1)	91.892(1)	96.0935(9)	94.7391(11)
γ / deg	90	90	98.8666(12)	91.8067(14)
V / $Å^3$	2960.0(1)	2736.32(11)	1408.69(6)	2629.29(13)
Z	4	4	2	4
d (calcd) / $Mg \cdot m^{-3}$	1.256	1.242	1.314	1.325
abs coeff / mm^{-1}	0.531	0.568	0.557	1.512
R indices:[a] R_1 =	0.0557	0.0482	0.0525	0.0390
R_w =	0.0598	0.0511	0.0562	0.0385

[a] $R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$; $R_w = \sqrt{\{\Sigma w(|F_o|-|F_c|)^2 / \Sigma w|F_o|^2\}}$ for data with $I > 3\sigma(I)$.

Table S2. (Contd.)

	21-Br·0.5(THF)	**23-BPh$_4$**
empirical formula	$C_{22}H_{43}BrN_4Ti{\cdot}0.5(C_4H_8O)$	$C_{44}H_{59}BN_4Ti$
fw	527.47	702.69
temp / K	150	150
wavelength / Å	0.71073	0.71073
space group	$P\ \bar{1}$	$P\ n\ a\ 2_1$
a / Å	10.2911(5)	28.0165(4)
b / Å	16.2599(6)	15.8661(2)
c / Å	18.4540(9)	8.97260(10)
α / deg	69.245(2)	90
β / deg	78.120(2)	90
γ / deg	86.849(2)	90
V / Å^3	2825.2(2)	3988.43(9)
Z	4	4
d (calcd) / Mg·m^{-3}	1.240	1.170
abs coeff / mm^{-1}	1.736	0.250
R indices:[a] R_1 =	0.0780	0.0519
R_w =	0.0737	0.0576

[a] $R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$; $R_w = \sqrt{\{\Sigma w(|F_o|-|F_c|)^2 / \Sigma w|F_o|^2\}}$ for data with I > 3σ(I).

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Coordinates and energies

MeSiH3
E: -45.550505
G: -45.514317
Esol: -45.5642005261

Si	1.651590	0.039079	-4.083587
H	1.817940	1.230768	-3.203286
H	2.177687	-1.155920	-3.364050
H	2.465348	0.244971	-5.315629
C	-0.166105	-0.204959	-4.526030
H	-0.559964	0.668567	-5.054464
H	-0.296655	-1.078723	-5.171728
H	-0.769550	-0.356079	-3.625803

m1
E: -708.110324
G: -707.857777
Esol:-708.277734837

Ti	0.041775	0.416197	0.089700
N	1.349770	-0.677961	0.122297
N	2.613209	-1.185657	0.102427
C	3.216630	-1.042883	-1.212914
C	2.631644	-2.566938	0.559098
C	1.498842	2.240106	0.215480
C	0.488523	2.476084	1.174801
C	-0.738720	2.669094	0.490505
C	-0.495797	2.528898	-0.888122
C	0.886665	2.251346	-1.062600
N	-1.425321	-0.595028	-0.993383
N	-1.611004	-0.224584	1.194212
C	-2.046780	-0.912745	0.144136
C	-3.071253	-2.003636	0.228045
C	-1.410448	-1.507735	-2.107923

C	-2.167973	-0.340818	2.513944
H	-3.786422	-1.934366	-0.597765
H	-2.575062	-2.979658	0.150754
H	-3.619623	-1.975140	1.172441
H	-0.780792	-2.391607	-1.905053
H	-1.955956	-1.311330	2.989367
H	2.540559	2.024621	0.423859
H	1.388100	2.068054	-2.007241
H	-1.241728	2.565398	-1.673301
H	-1.706173	2.821129	0.955038
H	0.626136	2.484279	2.251339
H	-3.258318	-0.191314	2.527511
H	-1.732914	0.436538	3.152622
H	-0.987481	-1.003098	-2.982183
H	-2.414553	-1.859063	-2.389886
H	4.240594	-1.433343	-1.194938
H	2.633987	-1.587142	-1.983129
H	3.248360	0.016516	-1.485747
H	3.666933	-2.922890	0.613148
H	2.184248	-2.620698	1.555043
H	2.058345	-3.226628	-0.121581

m2

E: -753.699321
G: -753.382763
Esol: -753.87813432

Ti	0.556033	0.323504	1.413739
N	0.692052	0.796817	-0.432411
N	-0.484456	1.488321	-0.086216
N	-0.971579	0.834178	2.857464
N	-1.219103	-0.867023	1.522467
Si	1.316933	0.591166	-2.061628
C	-0.386465	2.947552	-0.123263
C	-1.703806	1.034906	-0.750834
C	-1.698565	-0.227702	2.590474
C	-2.878717	-0.725967	3.370913
C	-1.155990	1.755048	3.936132
C	-1.701350	-2.152044	1.109839
C	2.062775	-1.449548	1.067263
C	2.817881	-0.265598	1.246990
C	2.609973	0.196312	2.564372
C	1.717710	-0.702096	3.200163
C	1.395424	-1.723289	2.281295
H	1.039548	1.866676	2.003846
H	1.155236	1.856189	-2.844368
H	2.764492	0.275157	-1.904027
H	-1.219295	3.369083	0.452530
H	0.553472	3.250413	0.338397
H	-0.440242	3.319788	-1.159889
H	-2.574579	1.371289	-0.174921
H	-1.711098	-0.055594	-0.799344
H	-1.772101	1.457592	-1.768882

H	-3.710817	-0.965530	2.699466
H	-2.612730	-1.651701	3.896728
H	-3.224064	-0.002673	4.113146
H	-0.471914	1.543969	4.774202
H	-2.739903	-2.121947	0.736634
H	-1.668274	-2.920855	1.903458
H	-1.080233	-2.520065	0.281631
H	-0.921892	2.770848	3.592060
H	-2.180209	1.764653	4.338642
H	3.042019	1.083617	3.005506
H	1.323026	-0.599964	4.204814
H	3.404965	0.233967	0.485025
H	1.988465	-2.026583	0.150985
H	0.712281	-2.545040	2.460619
C	0.472012	-0.827637	-2.974311
H	0.978330	-1.052994	-3.919447
H	0.497417	-1.728447	-2.349393
H	-0.575662	-0.598743	-3.195869

m2’

E = -753.681063
G = -753.363893
Esol = -753.86003811

Ti	0.149383	-0.310329	-0.293957
N	0.765586	0.713586	-1.756804
N	0.169705	1.808921	-1.121667
N	-0.961708	0.279651	1.503671
N	-1.974871	-0.115322	-0.392315
C	1.091162	2.881670	-0.757816
C	-0.975823	2.362303	-1.842986
C	-2.125862	0.200820	0.888886
C	-3.453716	0.421474	1.555518
C	-0.850420	0.684640	2.879894
C	-3.060978	-0.510976	-1.241891
C	0.124920	-2.230579	-1.623586
C	1.468921	-1.978409	-1.261548
C	1.583977	-2.130877	0.138717
C	0.304235	-2.483779	0.640927
C	-0.584855	-2.561849	-0.446122
H	0.603967	3.564537	-0.052434
H	1.982428	2.471126	-0.281699
H	1.391257	3.451762	-1.655056
H	-1.557176	3.005380	-1.171496
H	-1.611062	1.550467	-2.195445
H	-0.636668	2.964150	-2.704535
H	-4.274762	0.404231	0.834653
H	-3.642321	-0.354047	2.307739
H	-3.468763	1.385665	2.075572
H	-1.689165	0.328776	3.497559
H	-3.780795	0.302866	-1.434492
H	-3.637663	-1.368582	-0.852931
H	-2.658189	-0.812452	-2.217909

H	0.065824	0.270505	3.316267
H	-0.792519	1.779146	2.995817
H	2.497436	-2.086801	0.718728
H	0.054803	-2.612686	1.688151
H	2.264635	-1.670494	-1.930528
H	-0.293544	-2.143643	-2.619720
H	-1.645836	-2.770220	-0.381894
H	1.271055	0.920706	-2.618132
Si	2.094161	0.425073	1.348223
H	2.212741	-0.464791	2.567927
H	1.893712	1.805110	1.939668
C	3.850987	0.463884	0.567566
H	3.860711	1.099672	-0.326674
H	4.606606	0.845848	1.262770
H	4.167093	-0.537453	0.249914

m5

E: -708.111826

G: -707.855428

Esol: -708.27876765

Ti	0.053101	0.167149	0.303244
N	-0.863180	0.509214	1.775313
N	-0.892309	-0.902681	1.825628
C	-2.241009	-1.456333	1.668874
C	-0.261250	-1.454174	3.028148
C	2.199668	0.302541	1.234778
C	2.181621	1.193211	0.136487
C	2.110558	0.425637	-1.053757
C	2.039775	-0.931388	-0.694357
C	2.079184	-1.009874	0.720797
N	-1.092815	-0.859951	-1.150566
N	-0.749247	1.310687	-1.280412
C	-1.139746	0.217231	-1.924770
C	-1.486415	0.194532	-3.381646
C	-1.305580	-2.191548	-1.644792
C	-0.533799	2.560904	-1.957257
H	-0.564123	0.125356	-3.975630
H	-2.113018	-0.664484	-3.636188
H	-2.002204	1.110966	-3.683071
H	-2.343280	-2.365541	-1.972223
H	-1.468437	2.996476	-2.342500
H	2.252014	0.585266	2.279253
H	2.035157	-1.923090	1.304302
H	1.928146	-1.769713	-1.373587
H	2.046259	0.823008	-2.061603
H	2.224149	2.276262	0.195084
H	0.170401	2.484753	-2.804226
H	-0.117529	3.286431	-1.250583
H	-1.102210	-2.902882	-0.835176
H	-0.642422	-2.457229	-2.485551
H	-2.187361	-2.551572	1.624946

H	-2.865646	-1.155907	2.522951
H	-2.677305	-1.071906	0.744806
H	-0.149330	-2.541021	2.925847
H	0.720549	-0.999411	3.170355
H	-0.880365	-1.232917	3.910079

m6

E: -753.693478589

G: -753.379238

Esol: -753.87171434

Ti	0.125297	0.112930	0.297062
N	-1.637899	0.024915	-0.435520
N	-1.272837	-1.318452	-0.660269
C	-1.134192	-1.634741	-2.081231
C	-2.085613	-2.321896	0.021365
C	-0.520070	-0.496387	2.457882
C	0.198268	0.714022	2.579384
C	1.539727	0.458237	2.203698
C	1.649805	-0.905812	1.866070
C	0.376718	-1.498019	2.005648
N	1.575922	-0.717663	-1.082784
N	1.422998	1.431901	-0.738725
C	2.230008	0.435613	-1.076294
C	3.707764	0.570994	-1.282572
C	2.245709	-1.982857	-1.206634
C	1.889853	2.778686	-0.556772
H	4.219189	0.455386	-0.315491
H	4.094007	-0.198339	-1.957444
H	3.971006	1.556127	-1.677464
H	2.534768	-2.199330	-2.247569
H	2.334276	3.191586	-1.475909
H	-1.580592	-0.614525	2.652455
H	0.133880	-2.533041	1.791712
H	2.545170	-1.403738	1.510447
H	2.333660	1.195885	2.150046
H	-0.200230	1.661730	2.912887
H	2.641250	2.880290	0.246690
H	1.034918	3.406329	-0.287301
H	1.555985	-2.779197	-0.894625
H	3.154941	-2.082602	-0.587649
H	-0.708447	-2.639588	-2.193056
H	-2.116654	-1.601218	-2.578780
H	-0.458085	-0.910195	-2.539899
H	-1.577667	-3.293676	-0.017632
H	-2.234634	-2.038437	1.065508
H	-3.072133	-2.425282	-0.461342
Si	-3.274292	0.665582	-0.401916
H	-3.973668	0.290285	0.872888
H	-0.459863	1.681773	0.598446
H	-4.073277	0.068790	-1.522557
C	-3.149095	2.527534	-0.558018
H	-2.617330	2.786227	-1.479215

H	-4.135990	3.001125	-0.570546
H	-2.571507	2.923870	0.282787

m4

E: -753.675110
G: -753.361848
Esol: -753.853952013

Ti	0.266401	0.254232	-0.287177
N	-1.565600	-0.294440	-0.302526
N	-2.324216	-1.048312	0.660845
C	-2.695734	-0.212123	1.783205
C	-1.667892	-2.278793	1.068406
C	-0.384805	2.430673	-0.931440
C	0.565514	1.987703	-1.871139
C	1.813644	1.854052	-1.200168
C	1.622508	2.209798	0.143037
C	0.251732	2.525940	0.327511
N	0.886415	-0.235189	1.667938
N	1.590879	-1.374209	-0.068511
C	1.899148	-0.927729	1.138107
C	3.251647	-1.054886	1.769263
C	1.047104	0.470543	2.914391
C	2.565389	-2.004353	-0.922750
H	3.190162	-1.066640	2.860851
H	3.761509	-1.960628	1.430343
H	3.873515	-0.196304	1.478807
H	1.143767	-0.222950	3.763279
H	2.983236	-2.915633	-0.468987
H	-1.438897	2.598514	-1.119307
H	-0.219992	2.812820	1.260874
H	2.374622	2.175643	0.924494
H	2.733344	1.490367	-1.645769
H	0.384677	1.782837	-2.918251
H	3.407825	-1.340094	-1.180336
H	2.073717	-2.287278	-1.857368
H	0.155858	1.078655	3.103153
H	1.917359	1.148775	2.939624
H	-3.355671	-0.777418	2.452697
H	-1.816556	0.131004	2.361308
H	-3.238732	0.665774	1.414979
H	-2.376519	-2.869450	1.662633
H	-1.395486	-2.849966	0.175055
H	-0.756047	-2.100762	1.664004
Si	-2.634809	-0.256147	-1.719014
H	-2.036397	0.645958	-2.751392
H	0.512975	-0.398163	-1.845470
H	-3.957231	0.313289	-1.308316
C	-2.844818	-1.984014	-2.430890
H	-3.301202	-2.648294	-1.690144
H	-3.475002	-1.979505	-3.326571
H	-1.859341	-2.382301	-2.699277

m3

E: -753.677024
G: -753.36143
Esol: -753.855833442

Ti	0.283305	0.617356	-0.195413
N	-1.060968	-0.211160	0.492709
N	-2.220131	-0.657953	1.034749
C	-3.082858	0.424322	1.477806
C	-1.986238	-1.637400	2.085386
C	-0.825196	2.604062	-0.746247
C	0.302093	2.548833	-1.601544
C	1.464261	2.634773	-0.805126
C	1.055571	2.762599	0.541130
C	-0.354330	2.748165	0.584240
N	1.669207	0.025448	1.297246
N	1.880691	-0.695398	-0.776626
C	2.113502	-0.943089	0.509371
C	2.681944	-2.230738	1.022987
C	1.483373	-0.179726	2.708758
C	2.244846	-1.638672	-1.800251
H	3.169916	-2.097535	1.992403
H	1.861254	-2.950496	1.159932
H	3.397038	-2.670063	0.322004
H	0.833888	-1.042473	2.938798
H	1.868954	-2.661877	-1.624254
H	-1.863411	2.541948	-1.053017
H	-0.967451	2.810887	1.475390
H	1.716688	2.791624	1.398782
H	2.486538	2.548903	-1.153403
H	0.276790	2.420265	-2.678238
H	3.336117	-1.710318	-1.930098
H	1.834173	-1.305259	-2.760937
H	1.000031	0.709065	3.132985
H	2.435891	-0.318003	3.244069
H	-4.034887	0.015873	1.835499
H	-2.610954	1.005534	2.294005
H	-3.277945	1.097148	0.636468
H	-2.937728	-2.087150	2.392768
H	-1.323942	-2.421835	1.702149
H	-1.504927	-1.176658	2.969928
Si	-1.405708	-0.822864	-2.273674
H	-1.318730	-0.924920	-3.768789
H	-0.140806	-0.000860	-2.039066
H	-2.624800	-0.036996	-1.955296
C	-1.372718	-2.551998	-1.533579
H	-2.002613	-2.559425	-0.640035
H	-1.740252	-3.296243	-2.246636
H	-0.352481	-2.819700	-1.237332

tsm1-5

E: -708.092565
G: -707.838224

Esol: -708.260405679

Ti	-0.326695	-0.125838	0.230002
N	0.855426	-1.186272	0.898870
N	1.852114	-0.618334	1.688317
C	3.156045	-0.742676	1.052222
C	1.859597	-1.175861	3.033387
C	-1.667417	-0.128236	2.168737
C	-2.537327	-0.360325	1.072224
C	-2.593324	0.824207	0.297396
C	-1.717885	1.762340	0.873243
C	-1.143327	1.172420	2.032053
N	0.574712	1.014998	-1.265157
N	-0.734927	-0.716957	-1.712716
C	0.161038	0.144179	-2.184591
C	0.715927	0.095456	-3.574987
C	1.632004	1.957300	-1.514900
C	-1.223830	-1.844775	-2.458111
H	0.939623	1.099811	-3.946524
H	1.653518	-0.475847	-3.577223
H	0.026672	-0.392201	-4.268822
H	2.541270	1.494428	-1.932265
H	-0.439797	-2.587561	-2.672842
H	-1.406989	-0.847211	2.935868
H	-0.399267	1.628337	2.677722
H	-1.487998	2.745901	0.480091
H	-3.134320	0.944961	-0.633879
H	-3.076690	-1.280568	0.872599
H	-1.685299	-1.552833	-3.413964
H	-1.997115	-2.348507	-1.868266
H	1.915503	2.431527	-0.568674
H	1.325406	2.761904	-2.201676
H	3.908728	-0.218294	1.652795
H	3.453521	-1.802047	0.945161
H	3.114248	-0.291705	0.056352
H	2.624340	-0.672735	3.636653
H	0.881776	-1.013777	3.497095
H	2.065268	-2.261282	3.016427

tsm5-6

E: -753.659056

G: -753.342858

Esol: -753.838186999

Ti	-0.061679	0.023435	-0.043425
N	0.285207	-1.336039	1.160833
N	1.584401	-0.842726	0.980251
C	2.463562	-1.831617	0.349490
C	2.205346	-0.324780	2.201934
C	-0.097888	1.986498	1.232998
C	-1.258666	2.069089	0.421934
C	-0.849473	2.203435	-0.917507
C	0.564491	2.212704	-0.944048
C	1.030589	2.085641	0.380073

N	0.831816	-0.558946	-1.899598
N	-1.320416	-0.742187	-1.564924
C	-0.357734	-0.695801	-2.471997
C	-0.589925	-0.681325	-3.950380
C	2.021363	-0.272187	-2.653621
C	-2.718402	-0.727344	-1.892361
H	-0.773313	0.352747	-4.276946
H	0.277670	-1.057399	-4.499600
H	-1.468505	-1.272721	-4.223222
H	2.407787	-1.156719	-3.184934
H	-3.000304	-1.539065	-2.579907
H	-0.090299	1.903235	2.314578
H	2.070281	2.051086	0.685340
H	1.185040	2.275618	-1.830739
H	-1.503682	2.236689	-1.782718
H	-2.281303	1.999530	0.776641
H	-3.047069	0.223572	-2.348487
H	-3.299467	-0.866265	-0.973309
H	2.809311	0.055954	-1.963700
H	1.893458	0.530622	-3.400490
H	3.418636	-1.359322	0.087621
H	2.644805	-2.662602	1.047045
H	1.979287	-2.209348	-0.552702
H	3.160409	0.154353	1.955002
H	1.544573	0.400944	2.679147
H	2.384172	-1.148491	2.908633
Si	-1.465452	-0.972926	2.260708
H	-2.789919	-0.307574	2.668662
H	-1.693385	-0.333010	0.816073
H	-0.619030	-0.489979	3.401507
C	-1.885889	-2.808183	2.175189
H	-1.045121	-3.417156	2.515727
H	-2.780273	-3.044127	2.760285
H	-2.073111	-3.065776	1.125598

tsm3-4
E: -753.663624905
G: -753.348028
Esol: -753.842873098

Ti	-0.639263	-0.149885	-0.200873
N	0.998039	-0.794551	0.153848
N	1.978298	-1.500321	0.774940
C	1.481565	-2.431715	1.764636
C	3.073024	-0.663773	1.225799
C	-1.606596	-2.242718	-0.572435
C	-2.227259	-1.345644	-1.472051
C	-2.966969	-0.404150	-0.713153
C	-2.796424	-0.716211	0.647955
C	-1.947142	-1.845030	0.743352
N	-0.703317	1.107521	1.519834
N	-0.669052	1.941649	-0.507658
C	-0.330124	2.130599	0.763383

C	0.502479	3.274422	1.252667
C	-0.223861	0.942266	2.864675
C	-0.338536	2.889827	-1.539747
H	0.293213	3.507105	2.300543
H	1.563777	2.993890	1.179905
H	0.353772	4.175698	0.652237
H	0.875865	0.859371	2.935506
H	0.742115	3.090501	-1.627742
H	-0.952568	-3.063513	-0.847371
H	-1.611590	-2.311610	1.662542
H	-3.176248	-0.140079	1.482509
H	-3.503638	0.450057	-1.108089
H	-2.125688	-1.360413	-2.550990
H	-0.848840	3.853499	-1.388716
H	-0.674065	2.492773	-2.503534
H	-0.647570	0.020650	3.282725
H	-0.539782	1.766235	3.523309
H	2.320595	-3.004731	2.174317
H	0.958742	-1.921699	2.596890
H	0.785788	-3.130519	1.289748
H	3.861690	-1.292762	1.653046
H	3.490697	-0.119824	0.371834
H	2.750629	0.072604	1.987880
Si	1.360334	-0.796701	-1.933891
H	0.699585	-1.480330	-3.109206
H	-0.162133	0.085202	-1.883993
H	2.417614	-1.806720	-1.581513
C	2.290367	0.771545	-2.455474
H	2.484970	1.389771	-1.568714
H	3.255472	0.516445	-2.906867
H	1.715810	1.373073	-3.166957

m7

E: -805.142722

G: -804.883844

Esol: -805.336507378

Ti	0.243944	0.067985	-0.715309
N	-0.543716	0.034830	0.805904
C	2.284549	0.629923	0.276590
C	2.289033	1.210834	-1.014395
C	2.279045	0.167820	-1.970576
C	2.252847	-1.058467	-1.270913
C	2.257240	-0.776815	0.117638
N	-0.875558	-1.034912	-2.064678
N	-0.846574	1.196711	-2.075283
C	-1.495147	0.087802	-2.431672
C	-2.840690	0.108606	-3.086662
C	-1.530410	-2.317805	-2.096042
C	-1.441638	2.501491	-2.211263
H	-3.030811	-0.809968	-3.646970
H	-3.616419	0.199592	-2.314906
H	-2.941437	0.963665	-3.760512

H	-2.395374	-2.370065	-1.415909
H	-2.376762	2.608769	-1.639215
H	2.249743	1.156638	1.223929
H	2.206546	-1.500019	0.924248
H	2.182598	-2.042974	-1.721195
H	2.214132	0.290192	-3.045293
H	2.260123	2.273047	-1.235017
H	-1.655863	2.754934	-3.260451
H	-0.738900	3.253235	-1.838244
H	-0.816997	-3.085630	-1.779070
H	-1.869964	-2.593924	-3.105305
C	-0.549897	-0.015166	2.176886
C	-0.559441	-1.248672	2.857205
C	-0.540818	-1.294247	4.244061
C	-0.516726	-0.119322	4.992685
C	-0.511519	1.107716	4.332523
C	-0.529328	1.164832	2.945976
H	-0.584551	-2.162370	2.264927
H	-0.546370	-2.259210	4.747973
H	-0.504669	-0.159498	6.079138
H	-0.493917	2.032640	4.906357
H	-0.530135	2.119980	2.422766

m8

E: -850.716091
G: -850.395004
Esol: -850.920562035

Ti	0.231092	-0.163040	-0.000015
N	1.214153	1.142862	1.021377
C	2.145460	-1.488266	-0.108558
C	1.575469	-1.474369	-1.402519
C	0.318809	-2.131719	-1.330552
C	0.118890	-2.541173	0.001549
C	1.239990	-2.132096	0.765210
N	-1.582487	-0.459144	1.086649
N	-1.527201	0.588113	-0.823324
C	-2.308669	0.118996	0.142571
C	-3.802144	0.213994	0.128243
C	-2.149102	-1.251125	2.145160
C	-2.031358	1.308306	-1.959532
H	-4.215822	-0.449582	-0.641405
H	-4.240231	-0.058381	1.091391
H	-4.113597	1.233059	-0.125959
H	-2.703116	-0.641974	2.877234
H	-2.456395	2.286834	-1.683099
H	3.080339	-1.020622	0.179790
H	1.366953	-2.250643	1.837180
H	-0.767825	-3.028838	0.389632
H	-0.383883	-2.246066	-2.147780
H	2.020073	-1.046055	-2.290546
H	-2.808560	0.751138	-2.506642
H	-1.202722	1.492823	-2.649709

H	-1.338861	-1.745295	2.694484
H	-2.831217	-2.037218	1.782184
Si	2.049375	2.464135	0.180353
H	3.113869	1.950243	-0.739383
H	0.728486	0.718733	-1.379683
H	2.732246	3.263689	1.248916
C	0.851214	3.581871	-0.743851
H	-0.041311	3.755421	-0.132289
H	1.318082	4.550572	-0.954562
H	0.541193	3.128987	-1.689651
C	1.637890	0.734300	2.299159
C	0.688232	0.463102	3.296187
C	1.075127	-0.028990	4.537741
C	2.419772	-0.245021	4.823263
C	3.376209	0.051755	3.854580
C	2.994716	0.535459	2.610041
H	-0.358648	0.647236	3.063241
H	0.317678	-0.236730	5.291631
H	2.722804	-0.629381	5.794111
H	4.432389	-0.100184	4.068168
H	3.748958	0.747056	1.851492

tsm7-8

E: -850.693342

G: -850.370449

Esol: -850.897631095

Ti	0.641371	-0.353758	0.306324
N	-0.196976	0.091286	-1.200855
C	2.644058	-0.948073	-0.740110
C	2.547108	-1.751001	0.422167
C	2.617263	-0.899991	1.550130
C	2.756796	0.423815	1.082601
C	2.768083	0.400564	-0.331114
N	0.028233	1.320130	1.418985
N	-0.704426	-0.691387	1.898877
C	-0.972808	0.610190	1.924492
C	-2.287809	1.187488	2.343705
C	-0.128655	2.696355	1.021163
C	-1.669545	-1.675088	2.318447
H	-2.188951	2.232325	2.649056
H	-2.985763	1.148730	1.495456
H	-2.732467	0.615948	3.163353
H	-0.933662	2.848529	0.283626
H	-2.651336	-1.567461	1.827775
H	2.592914	-1.306198	-1.763014
H	2.816954	1.265164	-0.985053
H	2.775013	1.312445	1.701599
H	2.514214	-1.202710	2.585077
H	2.406878	-2.825959	0.437347
H	-1.833013	-1.647176	3.406562
H	-1.290743	-2.672519	2.072025
H	0.802836	3.037025	0.552265

H	-0.318829	3.356058	1.881017
Si	-0.706411	-1.914750	-1.560400
H	-0.261701	-3.367476	-1.594253
H	-0.021061	-1.999471	-0.008134
H	-0.453684	-1.573183	-3.003623
C	-2.548889	-1.893068	-1.153305
H	-2.884775	-0.866149	-0.967526
H	-3.129121	-2.300631	-1.987957
H	-2.759221	-2.498321	-0.265046
C	-0.395641	0.915295	-2.297815
C	0.502519	0.952220	-3.376390
C	0.294691	1.821303	-4.439119
C	-0.812753	2.665782	-4.456487
C	-1.720029	2.625412	-3.401648
C	-1.521539	1.754406	-2.337566
H	1.363456	0.286103	-3.362824
H	1.005094	1.839456	-5.263107
H	-0.970038	3.346292	-5.289736
H	-2.592965	3.275105	-3.408364
H	-2.227752	1.707257	-1.508468

MeSiH2Cl
E: -505.174232
G: -505.146993
Esol: -505.217698109

Si	-0.029435	0.013546	0.630553
H	-0.107912	1.388397	1.182109
H	-1.120308	-0.826814	1.182259
C	0.005567	-0.002577	-1.239282
H	0.111642	-1.026336	-1.610145
H	-0.918667	0.419789	-1.648080
H	0.849045	0.587165	-1.610254
Cl	1.773731	-0.810490	1.322962

m2Cl
E: -1213.350928
G: -1213.041278
Esol: -1213.041278

Ti	-0.326459	-0.601590	-0.097327
N	1.448662	-0.087350	0.354202
N	0.797544	0.648519	1.361624
N	-2.201818	0.348978	0.466213
N	-0.849507	1.267841	-0.966510
Si	3.178730	0.000403	0.007487
C	1.115489	0.228724	2.731536
C	0.905807	2.105174	1.262078
C	-1.953352	1.428465	-0.244506
C	-2.739956	2.703649	-0.229850
C	-3.116413	0.331502	1.577825
C	-0.420712	2.187379	-1.977642
C	0.610470	-1.251075	-2.170911
C	0.700915	-2.361233	-1.294189

C	-0.607378	-2.795662	-1.009232
C	-1.512699	-1.936564	-1.670214
C	-0.756741	-1.005208	-2.414957
H	3.927197	0.158323	1.290332
H	3.548257	-1.286864	-0.641139
H	0.331896	0.597800	3.403114
H	1.131634	-0.859105	2.790492
H	2.086310	0.645911	3.041692
H	0.109581	2.561899	1.864910
H	0.793407	2.421863	0.226048
H	1.876347	2.451328	1.656359
H	-2.144731	3.502327	0.232802
H	-2.974329	3.026444	-1.250372
H	-3.672655	2.605188	0.329071
H	-4.106291	0.733202	1.313880
H	-0.407820	3.234925	-1.630442
H	-1.044078	2.161450	-2.888987
H	0.604625	1.938637	-2.281646
H	-3.246665	-0.700793	1.912207
H	-2.734712	0.902517	2.441884
H	-0.873865	-3.597015	-0.335373
H	-2.592654	-1.970216	-1.595311
H	1.611354	-2.778362	-0.879894
H	1.441788	-0.679367	-2.569442
H	-1.161635	-0.212363	-3.029870
C	3.612173	1.429080	-1.145623
H	4.689557	1.453534	-1.344314
H	3.095430	1.322618	-2.106234
H	3.325329	2.392605	-0.710689
Cl	-0.858449	-1.994559	1.804662

m6Cl
E: -1213.339307
G: -1213.031068
Esol: -1213.54940989

Ti	0.156095	0.058536	0.352334
N	-1.425437	-0.719514	-0.305453
N	-0.659832	-1.875904	-0.486318
C	-0.477716	-2.236761	-1.893927
C	-1.099872	-3.033955	0.293300
C	-0.007360	-0.731486	2.544736
C	0.326145	0.632665	2.685016
C	1.624685	0.826656	2.171027
C	2.108230	-0.423126	1.733667
C	1.101913	-1.389199	1.955660
N	1.693102	-0.397367	-1.080726
N	1.088591	1.658138	-0.707417
C	2.028970	0.881575	-1.207523
C	3.343734	1.364402	-1.732352
C	2.638901	-1.458526	-1.295192
C	1.233645	3.087735	-0.614406
H	4.046397	1.476617	-0.893492

H	3.780957	0.659358	-2.444866
H	3.247680	2.342627	-2.211236
H	2.760691	-1.698398	-2.363823
H	1.271057	3.559647	-1.607601
H	-0.953911	-1.173745	2.833318
H	1.170696	-2.441346	1.704398
H	3.070135	-0.607845	1.268902
H	2.137680	1.778279	2.086752
H	-0.328514	1.405268	3.062179
H	2.141051	3.389498	-0.063828
H	0.362305	3.488965	-0.089837
H	2.278847	-2.371113	-0.802839
H	3.643741	-1.252111	-0.888441
H	0.232828	-3.067895	-1.974564
H	-1.439115	-2.549783	-2.330794
H	-0.087524	-1.372631	-2.435770
H	-0.317768	-3.803382	0.276548
H	-1.291076	-2.733635	1.325154
H	-2.023299	-3.460096	-0.127252
Si	-3.150755	-0.507316	-0.710910
H	-3.927841	-0.100241	0.484144
H	-3.615901	-1.876946	-1.122618
C	-3.333259	0.663636	-2.164612
H	-2.806541	0.254591	-3.034709
H	-4.383317	0.815875	-2.435844
H	-2.885880	1.628612	-1.908819
Cl	-1.508092	1.880912	0.697969

m4Cl

E: -1213.330511

G: -1213.022855

Esol: -1213.53918746

Ti	-0.163169	-0.326488	-0.063723
N	1.384377	0.728475	0.359127
N	1.746370	1.924078	-0.357028
C	1.432505	3.135361	0.377900
C	1.316235	1.995681	-1.744601
C	0.426245	-2.146625	1.277881
C	-0.690360	-2.567730	0.514419
C	-1.800713	-1.798927	0.906532
C	-1.373878	-0.897756	1.910597
C	-0.000557	-1.123081	2.152796
N	-1.385095	1.415802	0.246168
N	-1.712642	0.061212	-1.425874
C	-2.251761	1.005185	-0.666992
C	-3.673959	1.453500	-0.759454
C	-1.766732	2.267280	1.339955
C	-2.450368	-0.696816	-2.400370
H	-3.805243	2.468252	-0.374295
H	-4.040187	1.407818	-1.788810
H	-4.301340	0.781000	-0.156119
H	-1.948850	3.304240	1.014879

H	-2.829679	-0.062842	-3.215151
H	1.436934	-2.523727	1.169632
H	0.619643	-0.572302	2.848962
H	-1.990364	-0.155341	2.402662
H	-2.794577	-1.846824	0.474094
H	-0.669859	-3.300411	-0.282189
H	-3.309629	-1.237147	-1.966236
H	-1.773107	-1.432809	-2.845044
H	-0.948405	2.298674	2.069039
H	-2.672351	1.927352	1.872428
H	1.978374	3.971869	-0.075888
H	0.356133	3.372189	0.361941
H	1.760130	3.031396	1.417607
H	1.809466	2.859374	-2.206638
H	1.621568	1.088780	-2.273382
H	0.223698	2.120976	-1.854107
Si	3.004905	0.259926	0.959823
H	2.869608	-0.840440	1.964711
H	3.596583	1.433923	1.669125
C	4.098714	-0.310616	-0.453636
H	4.244876	0.501026	-1.173099
H	5.079501	-0.631545	-0.086125
H	3.623218	-1.148945	-0.975337
Cl	0.838967	-1.454672	-1.895580

tsm1-4Cl

E : -1213.290339

G : -1212.980292

Esol : -1213.49746372

C	-1.442618	2.440710	0.281177
C	-1.765581	2.024440	-1.034073
C	-0.648512	2.289092	-1.859620
C	0.373381	2.840584	-1.058470
C	-0.124224	2.941365	0.261484
Ti	-0.049779	0.616252	-0.284806
N	1.940751	-0.088554	-0.676430
C	2.758875	-0.797847	-1.626960
N	-1.092552	-0.529830	0.530817
Si	-0.512696	-2.441916	-0.662485
Cl	-0.511182	-0.866398	-2.353232
N	-2.097210	-0.989486	1.341186
C	-1.965549	-0.512850	2.705727
C	-3.418474	-0.734855	0.787162
C	0.637417	-2.859320	0.782349
C	2.311101	0.112162	0.581571
N	1.398641	0.797883	1.254172
C	1.411791	0.900849	2.684536
C	3.562708	-0.414973	1.213873
H	4.075518	0.373917	1.774924
H	3.305675	-1.206004	1.931182
H	4.254620	-0.830803	0.478193
H	1.214036	-0.062035	3.188800

H	2.926157	-1.853993	-1.352080
H	-2.688495	1.551482	-1.349773
H	-2.083721	2.363824	1.151707
H	0.436637	3.292049	1.119096
H	1.375827	3.094191	-1.382246
H	-0.567633	2.040070	-2.911517
H	3.744097	-0.327915	-1.766120
H	2.254256	-0.798995	-2.597553
H	0.629453	1.599578	3.007231
H	2.369371	1.283061	3.071622
H	0.017390	-3.406146	-1.692131
H	-1.944783	-2.773913	-0.498789
H	0.321426	-2.404927	1.724950
H	0.662272	-3.952265	0.880024
H	1.655037	-2.528349	0.544551
H	-2.732452	-0.986118	3.329513
H	-0.977744	-0.783320	3.092284
H	-2.077231	0.586324	2.777492
H	-4.172667	-1.251101	1.391678
H	-3.656372	0.344644	0.766838
H	-3.462805	-1.117495	-0.237714

tsm5-6Cl
E: -1213.297311
G: -1212.989722
Esol: -1213.50510654

Ti	-0.096915	0.259408	0.092169
N	0.189761	-0.684092	-1.405501
N	-1.017935	-1.294823	-1.029520
C	-0.872618	-2.701780	-0.641385
C	-2.103500	-1.148428	-2.003688
C	-1.174155	2.082139	-0.875982
C	-0.178672	2.627329	-0.030729
C	-0.538146	2.355983	1.309320
C	-1.741839	1.624257	1.299750
C	-2.134572	1.449302	-0.048671
N	-0.220048	-0.976880	1.800077
N	1.578169	0.197337	1.348813
C	0.918688	-0.484640	2.275978
C	1.358619	-0.589902	3.702395
C	-1.214552	-1.603951	2.625979
C	2.742608	0.990218	1.637504
H	1.092805	0.334395	4.234498
H	0.880215	-1.426814	4.217612
H	2.444192	-0.705381	3.774769
H	-0.894531	-2.590099	2.998195
H	3.538572	0.402550	2.117725
H	-1.173430	2.122701	-1.959685
H	-3.018858	0.918804	-0.383914
H	-2.256930	1.226535	2.167034
H	0.049430	2.607128	2.186546

H	0.720330	3.135567	-0.361282
H	2.523182	1.853401	2.290232
H	3.149897	1.376812	0.697383
H	-2.117671	-1.765629	2.024630
H	-1.509526	-0.997936	3.499330
H	-1.812472	-3.061807	-0.204932
H	-0.628577	-3.313926	-1.522794
H	-0.070984	-2.785934	0.094835
H	-3.056347	-1.434767	-1.541586
H	-2.159655	-0.113827	-2.347196
H	-1.922580	-1.795418	-2.875802
Si	1.267477	-0.227962	-3.391713
H	2.086284	0.288351	-4.550246
H	-0.113643	0.172839	-3.786842
C	1.737349	-2.054932	-3.305673
H	0.834394	-2.674045	-3.254134
H	2.341268	-2.358280	-4.167006
H	2.304511	-2.230419	-2.385354
Cl	2.228385	1.145296	-1.993061

m8Cl
E: -1310.37268783
G: -1310.056393
Esol: -1310.6048517

C	3.260413	0.454157	2.195168
C	1.877902	0.374215	2.412240
C	1.417066	-0.031756	3.671543
C	2.314121	-0.386327	4.672543
C	3.685883	-0.325567	4.441565
C	4.153146	0.101515	3.202125
N	0.963761	0.728794	1.388831
Si	0.716922	2.500761	1.431542
C	-0.695750	3.098517	0.340419
Ti	0.302198	-0.259779	-0.123400
C	-2.152481	0.332034	-0.515634
C	-3.484730	0.979179	-0.724419
C	1.916754	-1.897382	0.216911
C	1.478274	-2.037638	-1.119677
C	0.117991	-2.410225	-1.095201
C	-0.281049	-2.518949	0.257983
C	0.830239	-2.207181	1.069222
N	-1.649805	-0.084900	0.637066
C	-2.235489	0.021522	1.937995
N	-1.276446	0.126047	-1.486592
C	-1.458558	0.574013	-2.839894
H	-4.082945	0.394408	-1.432479
H	-4.048292	1.085908	0.205143
H	-3.344697	1.974962	-1.162487
H	-1.862476	0.897306	2.495282
H	-1.291335	1.656704	-2.957582
H	2.896641	-1.561377	0.535655

H	0.837649	-2.141864	2.151633
H	-1.280879	-2.741746	0.609332
H	-0.526089	-2.524163	-1.958463
H	2.061570	-1.815696	-2.003823
H	-2.464657	0.339432	-3.218375
H	-0.730826	0.070185	-3.484837
H	-1.975144	-0.866847	2.531487
H	-3.332421	0.080538	1.908127
H	1.992621	3.162614	1.036319
Cl	1.573071	1.015882	-1.648070
H	0.405845	2.858296	2.850771
H	-1.662560	2.741809	0.711369
H	-0.706982	4.194152	0.366238
H	-0.563227	2.785871	-0.700892
H	0.341182	-0.064163	3.843851
H	1.938451	-0.707086	5.642063
H	4.386314	-0.602658	5.225646
H	5.223142	0.163348	3.014854
H	3.612013	0.795893	1.221376

tsm7-8Cl
E: -1310.32322631
G: -1310.008141
Esol: -1310.55529441

C	-0.615870	2.550107	0.290245
C	-0.496536	2.424746	-1.113313
C	0.864127	2.614247	-1.452647
C	1.588078	2.854177	-0.261429
C	0.669909	2.820018	0.810532
Ti	0.695277	0.653364	-0.174040
N	2.553025	-0.293875	0.118611
C	3.605548	-0.995744	-0.573367
N	-0.759468	-0.389184	-0.214303
Si	-0.271285	-2.125412	-1.444540
Cl	0.969889	-0.460292	-2.488823
C	-2.119525	-0.301775	0.056315
C	-2.604032	-0.512310	1.358196
C	-3.960335	-0.394823	1.639704
C	-4.865733	-0.071078	0.633439
C	-4.399735	0.129838	-0.663727
C	-3.047405	0.009198	-0.954275
C	0.302508	-3.018771	0.121070
C	2.313396	-0.455369	1.418617
N	1.287043	0.279947	1.813631
C	0.647027	0.103356	3.085831
C	3.043922	-1.400706	2.320271
H	3.310165	-0.909571	3.262227
H	2.391259	-2.248273	2.569045
H	3.952386	-1.793067	1.858087
H	0.124782	-0.865567	3.170627
H	3.419201	-2.080004	-0.653932

H	-1.297671	2.171659	-1.797774
H	-1.525470	2.409406	0.864735
H	0.922229	2.916126	1.859260
H	2.660852	2.981005	-0.178244
H	1.284568	2.529442	-2.448212
H	4.583609	-0.854956	-0.091068
H	3.684139	-0.611148	-1.593480
H	-0.101775	0.892539	3.226479
H	1.356918	0.173682	3.923977
H	0.314256	-3.030078	-2.502899
H	-1.714667	-2.107341	-1.797413
H	-0.286717	-2.732172	0.998185
H	0.258049	-4.102719	-0.032538
H	1.351561	-2.751259	0.303977
H	-2.680444	0.158473	-1.969552
H	-5.098344	0.379212	-1.459913
H	-5.925681	0.021653	0.856991
H	-4.312276	-0.557335	2.656669
H	-1.889260	-0.761372	2.141330

EtBr
E: -92.5158967319
G: -92.477556
Esol: -2653.20311764
C,0,2.0629856405,2.0157756692,-0.0000002761
H,0,2.4109391539,2.5558858872,0.8859821939
H,0,2.4109387282,2.5558856514,-0.8859830463
H,0,0.9659045131,2.0286472224,-0.0000000271
C,0,2.5524596072,0.591096514,-0.0000002138
H,0,2.2432414079,0.0379250807,-0.8893592923
H,0,2.2432417257,0.0379252515,0.8893590888
Br,0,4.5173133136,0.5159089035,-0.0000006185

tsm5-9Br
E: -800.579084849
G: -800.263667
Esol: -3361.42740336
Ti,0,-0.2563842036,0.1604037116,0.4174301653
N,0,1.2061233942,1.0954220914,-0.1358281392
N,0,0.3865317042,2.2125864835,0.0043255786
C,0,0.0816906801,2.904584339,-1.2493950284
C,0,0.8388001034,3.1687905872,1.0165348865
C,0,-0.0730877421,0.3241604344,2.7439712789
C,0,-0.3898583758,-1.0366678055,2.527171035
C,0,-1.7035134507,-1.1103877982,2.0199516457
C,0,-2.2079005658,0.2028153734,1.9264808361
C,0,-1.2049930815,1.0923098896,2.3711087999
N,0,-1.8453692889,0.6579435582,-0.9340682281
N,0,-0.9612258996,-1.3436801747,-0.9440679725
C,0,-2.017799608,-0.6161027972,-1.2646172661
C,0,-3.2981336777,-1.1767193563,-1.8021608728

C,0,-2.919151413,1.6122144849,-0.9712660811
C,0,-0.9778430596,-2.7806309866,-1.0353519149
H,0,-3.1213455473,-2.0576299846,-2.4252671398
H,0,-3.9328386125,-1.4899537841,-0.9596643494
H,0,-3.8550263813,-0.4359333851,-2.3829322119
H,0,-3.0887111987,2.0131797706,-1.9840831079
H,0,-1.0422264485,-3.1285857819,-2.0777384161
H,0,0.8725421854,0.6955024433,3.1221474403
H,0,-1.293456322,2.172162106,2.4125433696
H,0,-3.183407499,0.4862061676,1.54688681
H,0,-2.2152046586,-2.0161528146,1.7114908242
H,0,0.2775812411,-1.8730618791,2.6894730308
H,0,-1.8122009745,-3.2413719415,-0.4779610924
H,0,-0.0425121147,-3.1692107141,-0.6187845384
H,0,-2.660212944,2.4652301407,-0.3299918737
H,0,-3.883934381,1.2182288736,-0.6085483449
H,0,-0.7056047615,3.6520496203,-1.0901613868
H,0,0.9842679316,3.4185910703,-1.6181955749
H,0,-0.2539912913,2.1712327613,-1.9850143744
H,0,0.0502999798,3.9043346298,1.2223677823
H,0,1.0915381466,2.6357668474,1.9347917249
H,0,1.7352836663,3.7013760661,0.6603025745
H,0,3.9947611736,-0.4541981302,-0.6082281342
H,0,3.4921178643,1.2802372874,-0.356870961
C,0,2.8547873334,0.3777915339,-2.290677758
H,0,2.4525770785,1.3535828496,-2.5721282413
H,0,3.6784095526,0.0939000271,-2.9649559295
H,0,2.060070702,-0.3643602972,-2.4352706955
C,0,3.3385856279,0.3572753523,-0.8989223615
Br,0,1.9544071363,-1.5506328697,0.4049962122

m9
E: -800.699005547
G: -800.377763
Esol: -3361.54913589
Ti,0,-0.1265540671,0.0114285459,0.2932276973
N,0,1.3598701221,0.9560803258,-0.3417457482
N,0,0.6959942126,2.1202665115,0.0633833847
C,0,0.318262089,3.0079573656,-1.038142471
C,0,1.3596717806,2.8729252891,1.1282738642
C,0,0.2879394379,0.0075623099,2.5912152883
C,0,-0.1229300726,-1.3147726998,2.3154514229
C,0,-1.4713351077,-1.2828444025,1.9061176229
C,0,-1.9081459957,0.0566462278,1.9575247918
C,0,-0.8248556503,0.8597164374,2.3758435495
N,0,-1.76984867,0.9299238312,-0.7393684297
N,0,-1.2300740423,-1.1468563827,-1.126696028
C,0,-2.1719381897,-0.2320932944,-1.2443049953
C,0,-3.5513519018,-0.4935794541,-1.7608148614
C,0,-2.6961255869,2.0000196526,-0.4814454023
C,0,-1.458201859,-2.5215654248,-1.4948254339
H,0,-3.5479101176,-1.2624646922,-2.5378502998

H,0,-4.1806877751,-0.8615639036,-0.937024693
H,0,-4.0148391826,0.413493877,-2.1581532048
H,0,-2.9277380988,2.5802145557,-1.3891321141
H,0,-1.6581590137,-2.6271397179,-2.5715076076
H,0,1.2820633446,0.2954428907,2.9128582661
H,0,-0.8452136997,1.9371803688,2.4918851756
H,0,-2.8941571442,0.4150518046,1.6846688687
H,0,-2.0518168505,-2.1355324585,1.5714835876
H,0,0.5060765612,-2.1920102263,2.3598687132
H,0,-2.3050486396,-2.9724097215,-0.9495319452
H,0,-0.5575666015,-3.097279576,-1.2665102358
H,0,-2.2515500813,2.6984513514,0.2387490811
H,0,-3.6562279489,1.6671122819,-0.0512178938
H,0,-0.3346062444,3.8037500955,-0.660175357
H,0,1.2118592978,3.4740737854,-1.4832611096
H,0,-0.2151604945,2.4272215104,-1.7936156125
H,0,0.6490852684,3.585843012,1.5643129627
H,0,1.7093817142,2.1874496998,1.9026883984
H,0,2.2207214268,3.4420759534,0.7447436486
H,0,3.3066669255,0.2692886596,-0.4485652485
H,0,3.1334486657,2.0150882491,-0.7012349191
C,0,2.6620845195,0.7902810984,-2.4322546032
H,0,2.0754653493,1.5530553712,-2.9576973524
H,0,3.6782349624,0.794788529,-2.8435742937
H,0,2.2112585446,-0.1883336392,-2.6304172722
C,0,2.6870537465,1.0349725327,-0.93237517
Br,0,1.6096040672,-1.9794135303,-0.1543960218

m11-H+

E: -708.544898
G: -708.27627
Esol: -708.74547864

Ti	10.874576	4.328663	8.502319
N	12.063051	5.234555	9.624729
N	10.915334	6.008128	9.788013
N	8.944936	4.866471	8.003555
N	9.467134	3.427618	9.603762
C	10.913797	7.299007	9.094542
C	10.353911	6.070946	11.140225
C	8.481315	3.992580	8.887228
C	7.044646	3.617761	9.038255
C	8.132000	5.482237	6.980055
C	9.255253	2.355992	10.548513
C	11.732462	4.132416	6.353433
C	10.729308	3.137266	6.489744
C	11.146491	2.230261	7.487154
C	12.407396	2.661982	7.970315
C	12.777997	3.823616	7.252570
H	12.957770	5.692546	9.794534
H	9.900278	7.712438	9.108600
H	11.602862	8.007798	9.576152

H	11.224357	7.161428	8.050796
H	9.292339	6.334086	11.075530
H	10.876656	6.828354	11.740029
H	10.460200	5.092976	11.613007
H	6.382932	4.412930	8.686875
H	6.831353	2.714814	8.451442
H	6.805980	3.393766	10.081608
H	7.464934	6.250700	7.393945
H	8.703654	2.697700	11.435543
H	9.793873	3.103077	5.943524
H	11.700745	4.980276	5.675870
H	13.685007	4.397454	7.397675
H	12.982936	2.196648	8.763040
H	10.587640	1.373626	7.845605
H	10.227323	1.988245	10.891225
H	8.708567	1.508927	10.110395
H	8.786560	5.978106	6.255221
H	7.517715	4.754438	6.431378

m11-Me+
E: -747.827074
G: -747.532861
Esol: -748.036406645

Ti	0.110588	-0.085120	-0.547739
N	1.738017	-0.816498	-1.066460
N	2.121038	-0.149967	0.103630
N	-0.294743	1.185563	1.037920
N	-0.526336	-1.017204	1.111298
C	2.876960	1.092609	-0.085732
C	2.647110	-0.987949	1.183708
C	-0.734155	0.149649	1.741882
C	-1.445860	0.252639	3.049765
C	-0.601713	2.558593	1.368716
C	-0.972289	-2.290680	1.624768
C	-0.925904	1.257466	-2.144007
C	-1.956811	0.698886	-1.343212
C	-1.937903	-0.700145	-1.518849
C	-0.891517	-1.012856	-2.422559
C	-0.282465	0.201676	-2.825294
H	2.849224	1.666948	0.845565
H	3.924306	0.894878	-0.354476
H	2.414710	1.689761	-0.883138
H	2.543366	-0.451520	2.133141
H	3.709523	-1.215829	1.017600
H	2.071395	-1.915154	1.225629
H	-1.247512	1.205084	3.545874
H	-2.529010	0.170520	2.890368
H	-1.154447	-0.561307	3.720082
H	-0.104361	2.881794	2.293109
H	-0.457868	-2.557390	2.558871
H	-2.616647	1.253476	-0.685894
H	-0.674676	2.311417	-2.211461

H	0.562152	0.295988	-3.498482
H	-0.600709	-2.006818	-2.744317
H	-2.583071	-1.414694	-1.020929
H	-0.742470	-3.069727	0.891295
H	-2.055122	-2.313624	1.813594
H	-0.240412	3.209410	0.565852
H	-1.681247	2.734898	1.482550
C	2.744224	-1.238839	-2.010891
H	3.309216	-0.390399	-2.425110
H	3.452460	-1.939196	-1.546777
H	2.246793	-1.758252	-2.834826

m11-SiH2Me+

E: -752.939668

G: -752.630741

Esol: -753.14999075

Ti	0.115333	-0.120094	-0.559821
N	1.722288	-0.913096	-1.106524
N	2.099323	-0.267466	0.080713
N	-0.215226	1.161342	1.041548
N	-0.561102	-1.026844	1.095380
C	2.895416	0.953636	-0.080395
C	2.571166	-1.119729	1.175521
C	-0.719203	0.147226	1.730494
C	-1.455625	0.281111	3.021750
C	-0.447963	2.546535	1.381221
C	-1.102809	-2.272855	1.583331
C	-0.913358	1.267334	-2.127140
C	-1.942663	0.740072	-1.304121
C	-1.976817	-0.657767	-1.489705
C	-0.968179	-1.000632	-2.424628
C	-0.329698	0.194218	-2.835852
H	2.901526	1.500456	0.867891
H	3.929803	0.720891	-0.374566
H	2.447830	1.587860	-0.856777
H	2.428652	-0.593414	2.125878
H	3.638680	-1.349848	1.054186
H	1.993984	-2.046478	1.180745
H	-1.214457	1.217590	3.529336
H	-2.537460	0.266420	2.833664
H	-1.231674	-0.553605	3.692335
H	0.032078	2.824546	2.329189
H	-0.622534	-2.586201	2.520982
H	-2.564225	1.311638	-0.624215
H	-0.628909	2.312586	-2.199418
H	0.488158	0.270291	-3.543802
H	-0.717893	-2.000261	-2.762283
H	-2.632982	-1.353022	-0.978621
H	-0.913916	-3.056097	0.842534
H	-2.187868	-2.225235	1.755767
H	-0.014587	3.183748	0.603394
H	-1.517713	2.791132	1.457719

Si	2.845775	-1.459244	-2.397444
H	3.466745	-0.251582	-3.013184
H	1.936235	-2.117553	-3.366801
C	4.146695	-2.610832	-1.701378
H	4.860385	-2.080269	-1.062097
H	3.691481	-3.421045	-1.122829
H	4.717717	-3.060910	-2.520555

m10-H+

E: -708.520589

G: -708.253958

Esol: -708.72152851

Ti	0.081175	-0.018004	-0.076844
N	-0.952336	0.158591	1.448711
N	-0.832093	0.258590	2.832744
C	-1.478341	-0.875247	3.482788
C	-1.370993	1.530415	3.299376
C	1.761800	-0.689334	1.389729
C	1.843943	0.717386	1.247922
C	2.151924	1.004978	-0.101888
C	2.259698	-0.225640	-0.795865
C	2.016637	-1.272569	0.127813
N	-0.770246	-1.213371	-1.434817
N	-0.684487	1.022631	-1.603201
C	-1.048028	-0.132691	-2.180763
C	-1.656733	-0.220711	-3.538454
C	-0.973286	-2.569266	-1.899702
C	-0.811489	2.313171	-2.247833
H	-0.866407	-0.403660	-4.278274
H	-2.362897	-1.052531	-3.600182
H	-2.168762	0.703227	-3.814654
H	-2.038861	-2.801273	-2.024479
H	-1.862070	2.614778	-2.347319
H	1.491014	-1.206114	2.302736
H	1.993776	-2.331318	-0.107708
H	2.448081	-0.344034	-1.857383
H	2.249632	1.991305	-0.542934
H	1.649527	1.434205	2.036966
H	-0.346585	2.328827	-3.241760
H	-0.311528	3.064534	-1.631630
H	-0.574546	-3.261794	-1.154578
H	-0.460335	-2.761714	-2.850916
H	-1.328323	-0.799398	4.563682
H	-2.565691	-0.904515	3.281051
H	-1.028567	-1.808369	3.129813
H	-1.220016	1.606510	4.380151
H	-0.843602	2.355863	2.811502
H	-2.453227	1.624099	3.089212
H	-1.948022	0.182521	1.142697

m10-Me+

E: -747.796137

G: -747.502734
Esol: -748.004888754

Ti	-0.098450	0.203452	-0.047013
N	1.511897	-0.716302	-0.174080
N	2.865064	-0.386607	-0.021602
C	3.646763	-0.629997	-1.226978
C	3.456163	-1.008995	1.156405
C	1.190117	2.106916	-0.416729
C	1.067922	1.913062	0.979657
C	-0.299537	2.045598	1.322456
C	-1.020791	2.321799	0.135222
C	-0.099179	2.352685	-0.939349
N	-1.645779	-0.403508	-1.188750
N	-1.481378	-0.824820	1.002725
C	-2.276494	-0.808424	-0.072517
C	-3.732054	-1.128134	-0.048173
C	-2.374299	-0.055123	-2.390654
C	-1.954268	-1.120154	2.339585
H	-4.310111	-0.204466	-0.183168
H	-3.994620	-1.795369	-0.875047
H	-4.037052	-1.591243	0.891273
H	-2.990369	-0.888793	-2.749339
H	-2.371919	-2.132149	2.406566
H	2.111205	2.022060	-0.979624
H	-0.349206	2.503056	-1.984518
H	-2.097245	2.434890	0.052478
H	-0.728640	1.926932	2.311759
H	1.882260	1.662885	1.648908
H	-2.715932	-0.404877	2.679307
H	-1.109853	-1.069432	3.031294
H	-1.662370	0.188947	-3.182494
H	-3.029747	0.816182	-2.238976
H	4.629442	-0.165190	-1.100224
H	3.804702	-1.701446	-1.441028
H	3.151529	-0.165122	-2.086443
H	4.441354	-0.562925	1.324892
H	2.828476	-0.808756	2.031059
H	3.592250	-2.100144	1.056088
C	1.208227	-2.121461	-0.513811
H	1.577201	-2.800676	0.265162
H	0.124348	-2.273106	-0.589034
H	1.639720	-2.400064	-1.482908

m10-SiH2Me+
E: -752.907329
G: -752.598668
Esol: -753.117020549

Ti	0.171501	0.022836	0.025588
N	-1.093670	0.064741	-1.337587
N	-0.973524	-0.109689	-2.733131
C	-1.476266	1.008831	-3.512726
C	-1.470481	-1.399210	-3.190111

C	1.734040	0.667927	-1.571278
C	1.726048	-0.746592	-1.528274
C	2.160369	-1.148780	-0.244607
C	2.436338	0.017962	0.508507
C	2.171436	1.141562	-0.312821
N	-0.364894	1.112003	1.599784
N	-0.401894	-1.126746	1.584874
C	-0.719037	-0.018321	2.248625
C	-1.450750	0.015119	3.545354
C	-0.580408	2.429352	2.155158
C	-0.784958	-2.458874	2.000350
H	-0.940517	0.669631	4.259633
H	-2.451528	0.435436	3.379617
H	-1.559322	-0.977219	3.985047
H	-1.650058	2.651660	2.285404
H	-1.870562	-2.611633	1.928519
H	1.410258	1.267031	-2.413776
H	2.251112	2.180297	-0.009683
H	2.736977	0.047012	1.549787
H	2.230011	-2.167878	0.120358
H	1.396391	-1.391585	-2.333814
H	-0.465920	-2.677881	3.026613
H	-0.299674	-3.186183	1.344185
H	-0.164303	3.175593	1.471991
H	-0.082568	2.554450	3.125429
H	-1.167878	0.871957	-4.554301
H	-2.578505	1.098527	-3.502406
H	-1.036574	1.941388	-3.141655
H	-1.187493	-1.524286	-4.240555
H	-1.004138	-2.199602	-2.606678
H	-2.566727	-1.500398	-3.116140
Si	-2.788738	0.471021	-0.713303
H	-3.731083	-0.199136	-1.642335
H	-2.899405	-0.152281	0.636272
C	-3.061859	2.324186	-0.616726
H	-3.936308	2.546600	0.004992
H	-2.192518	2.819225	-0.168854
H	-3.232563	2.765109	-1.603358

m12-H+

E: -708.507561

G: -708.239974

Esol: -708.710498339

Ti	-0.045996	0.249313	-0.039825
N	-1.521565	-0.661027	-0.190282
N	-2.901246	-0.863556	-0.314398
C	-3.594251	-0.734655	1.004534
C	-3.178758	-2.195044	-0.940149
C	-1.224327	2.270364	-0.187447
C	-0.229327	2.280895	-1.191147
C	1.036553	2.282276	-0.553333
C	0.823559	2.254956	0.841463

C	-0.575526	2.231889	1.070083
N	1.282400	-0.715065	1.156087
N	1.463760	-0.650793	-1.062943
C	2.006109	-1.056449	0.086530
C	3.312614	-1.774944	0.180043
C	1.716939	-0.943053	2.513049
C	2.113542	-0.782021	-2.344371
H	4.123173	-1.052649	0.341836
H	3.317073	-2.470624	1.023303
H	3.533162	-2.327469	-0.736197
H	1.665052	-2.004144	2.793658
H	2.146767	-1.825010	-2.688243
H	-2.296453	2.283270	-0.351367
H	-1.062380	2.194497	2.039205
H	1.591728	2.214242	1.604929
H	1.997352	2.264936	-1.054504
H	-0.402253	2.278116	-2.262255
H	3.140323	-0.389674	-2.336638
H	1.548269	-0.212365	-3.088299
H	1.060487	-0.393265	3.194534
H	2.743340	-0.591297	2.689215
H	-4.669637	-0.881148	0.871768
H	-3.173251	-1.495685	1.664441
H	-3.380089	0.259593	1.400832
H	-4.257430	-2.323924	-1.062720
H	-2.664218	-2.226154	-1.900716
H	-2.763986	-2.953754	-0.274001
H	-3.293692	-0.145881	-0.939521

m12-Me+

E: -747.790577

G: -747.49571

Esol: -748.001105582

Ti	0.249534	-0.001268	-0.125296
N	-0.480178	0.038455	1.444447
N	-0.742739	0.090749	2.819650
C	-0.568393	-1.271231	3.420258
C	-2.160714	0.539673	3.016920
C	2.441183	-0.276752	0.651727
C	2.297338	1.052713	0.182200
C	2.088087	0.999614	-1.219426
C	2.079647	-0.356247	-1.607664
C	2.285736	-1.145902	-0.449590
N	-0.809763	-1.211139	-1.382656
N	-0.963222	1.010824	-1.414251
C	-1.302976	-0.135944	-2.003590
C	-2.090970	-0.211806	-3.270616
C	-0.841342	-2.530209	-1.968059
C	-1.303989	2.308301	-1.946644
H	-1.409292	-0.179401	-4.130861
H	-2.657929	-1.144001	-3.331460
H	-2.782949	0.628660	-3.363186

H	-1.862455	-2.930051	-2.035454
H	-2.385282	2.499993	-1.910744
H	2.624222	-0.577416	1.676532
H	2.307399	-2.230054	-0.415598
H	1.897253	-0.734624	-2.607289
H	1.922902	1.850466	-1.870654
H	2.352557	1.952578	0.785461
H	-0.967686	2.438895	-2.985454
H	-0.817902	3.080325	-1.343031
H	-0.269568	-3.216414	-1.336709
H	-0.398733	-2.554798	-2.975403
H	-0.805786	-1.233846	4.487525
H	-1.239605	-1.951124	2.893014
H	0.468046	-1.576221	3.263285
H	-2.383234	0.582873	4.087096
H	-2.263479	1.522212	2.553628
H	-2.807468	-0.177036	2.508833
C	0.179471	1.059927	3.492973
H	-0.060902	1.114350	4.558725
H	1.202937	0.709226	3.348121
H	0.046306	2.031853	3.013816

m12-SiH2Me+

E: -752.898619659

G: -752.59368

Esol: -753.109134522

Ti	-0.617443	0.390843	0.074016
N	1.003465	0.051535	0.565952
N	2.390049	-0.000908	0.772896
C	2.681971	-0.840292	1.972756
C	2.953507	1.365586	0.960939
C	-0.191886	2.363525	-1.100282
C	-0.631870	2.712641	0.201446
C	-1.982197	2.304903	0.327948
C	-2.372309	1.700606	-0.887340
C	-1.264540	1.729155	-1.766265
N	-1.358957	-1.262185	-0.870683
N	-1.917911	-0.703329	1.213735
C	-2.190078	-1.468086	0.155874
C	-3.365290	-2.386762	0.078683
C	-1.611100	-1.782612	-2.191776
C	-2.772852	-0.639231	2.375662
H	-4.189284	-1.878008	-0.440376
H	-3.127856	-3.289388	-0.490367
H	-3.719712	-2.675768	1.070070
H	-1.726575	-2.874511	-2.194129
H	-2.854148	-1.610730	2.881238
H	0.794998	2.540216	-1.512105
H	-1.239217	1.316799	-2.769374
H	-3.334033	1.240863	-1.091191
H	-2.599804	2.407215	1.213782
H	-0.038172	3.203656	0.964232

H	-3.789540	-0.293283	2.134039
H	-2.345369	0.062823	3.096818
H	-0.758564	-1.547535	-2.836991
H	-2.511204	-1.345277	-2.654497
H	3.764194	-0.900824	2.125866
H	2.198010	-0.373168	2.835719
H	2.251880	-1.831700	1.813282
H	4.029990	1.301017	1.147916
H	2.756962	1.953669	0.060936
H	2.445899	1.824798	1.815476
Si	2.982531	-0.829557	-0.836103
H	2.509207	0.128915	-1.858627
H	2.245044	-2.106719	-0.820807
C	4.839430	-1.005871	-0.769926
H	5.186963	-1.453977	-1.708087
H	5.341205	-0.038089	-0.668364
H	5.164209	-1.662900	0.043011