Supplementary Information

Bis(pentalene)dititanium Chemistry: C-H, C-X and H-H Bond Activation

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General considerations: All manipulations were carried out in a MBraun glovebox under N_2 or Ar (O_2 and H_2O <1 ppm) or by using standard Schlenk techniques under Ar (BOC pureshield) passed through a column containing BASF R3-11(G) catalyst and activated molecular sieves (4 Å). All glassware was dried at 160 °C overnight prior to use. Filter cannulas were prepared using Whatman 25 mm glass microfiber filters and were pre-dried at 160 °C overnight. Toluene was dried over molten K, distilled under a N_2 atmosphere and kept in a Young's ampules over a potassium mirror under Ar. Hydrocarbons were dried over NaK, distilled under a N_2 atmosphere, and kept in Young's ampules over a potassium mirror under Ar. Et_2O was dried over NaK, distilled under a N_2 atmosphere, and kept in Young's ampules over activated molecular sieves (4 Å) under Ar. Deuterated toluene, benzene were degassed by three freeze−thaw cycles, dried by refluxing over molten K for 3 days, vacuum distilled, and kept in Young's ampoules in the glovebox under N_2. (**1**)[i] and (**3**)[ii] were prepared according to a published procedure and stored in a glovebox freezer (-35 ºC) under N_2. Samples of (**4**) or (**4-D**) were prepared *in-situ* prior to use according to a published procedure.[ii] ^{t}BuCCD was prepared according to a published procedure and was vacuum transferred into an ampoule containing activated 4 Å molecular sieves and freeze-thaw-degassed three times prior to use.[iii] 2,6-lutidine and 2,6-Cl_2-pyridine were purchased from commercial suppliers; the former was freeze-thaw-degassed three times prior to use and stored over activated molecular sieves overnight, while the latter was kept in a N_2 glovebox and used as received. HCl 2.0 M in Et_2O was purchased by Sigma-Aldrich in a SureSeal bottle and was stored in a Young's ampule at 5 ºC. ^{1}H-NMR, ^{13}C{^{1}H}-NMR, DEPT135, ^{29}Si{^{1}H}-NMR, deuterium spectra, correlation experiments, and variable temperature experiments were recorded on a Varian VNMR S400 spectrometer operating at 400 MHz (^{1}H) at 30 °C unless otherwise stated. The spectra were referenced internally to the residual protic solvent (^{1}H) or the signals of the solvent (^{13}C). ^{29}Si{^{1}H} NMR spectra were referenced externally relative to $SiMe_4$. EI-MS mass spectra were recorded on a VG-Autospec Fisons instrument at the University of Sussex unless otherwise stated. IR spectra were recorded on a Perkin Elmer 100 instrument as thin films. Elemental analyses were performed by MicroAnalytisches Labor Pascher.

Preparation of (**5**): In an Ar filled glovebox 50 mg (0.053 mmol) of (**2**) were dissolved in n-pentane (*ca* 10 mL) in a Young's ampoule with vigorous stirring. The crimson red solution was treated with 4.4 µL (1.02 mol eq) of pyridine and immediate color change to brown occurred. Volatiles were removed to give a brown residue which was thoroghly dried. It was then dissolved in the minimum amount of n-pentane (*ca* 1 mL) and let to slowly evaporate to ca half in an Ar glovebox to start crystallization, before placing in a -35 ˚C freezer overnight. The light brown crystals (suitable for single crystal XRD) were removed from the mother-liquor *via* a drawn-out pipette. Yield: 20 mg (38%)

Preparation of (**6**): In a N_2 filled glovebox a Young's NMR tube was charged with 31 mg (0.033 mmol) of (**1**) and 5 mg (1 mol eq) of 2,6-Cl_2-pyridine. C_6D_6 was added to the two solids to produce a bright red solution which proved to be (**6**) by NMR spectroscopy in 100% spectroscopic yield. Volatiles were removed in vacuum and the red microcrystalline material was extracted in the minimum amount of pentane (*ca* 2 ml) filtered and cooled in a glovebox freezer (-35 ºC) to yield the title compound as crystals suitable for XRD. Yield: 25 mg (69.5 %) ^{1}H-NMR δ(C_6D_6): 10.02 (1H, d, $^3J_{HH}$ = 7.01 Hz, py*H*), 7.91, (1H, d, $^3J_{HH}$ = 3.11 Hz, Pn*H*), 7.87 (1H, d, $^3J_{HH}$ = 2.73 Hz, Pn*H*), 7.27 (1H, d, $^3J_{HH}$ = 3.50 Hz, Pn*H*), 6.88 (1H, d, $^3J_{HH}$ = 3.11 Hz, Pn*H*), 6.82 (1H, d, $^3J_{HH}$ = 7.79 Hz, py*H*) 6.75 (1H, dd, $^3J_{HH}$ = 7.79 Hz, $^3J_{HH}$ = 7.40 Hz, py*H*), 6.64 (1H, d, $^3J_{HH}$ = 3.50 Hz, Pn*H*), 6.04 (1H, d, $^3J_{HH}$ = 2.73 Hz, Pn*H*), 5.74 (1H, d, $^3J_{HH}$ = 3.11 Hz, Pn*H*), 5.67 (1H, d, $^3J_{HH}$ =

3.11 Hz, Pn*H*), 1.55-1.66 (12H, m, C*H*$(CH_3)_3$), 1.28 (11H, d, $^3J_{HH}$ = 7.40 Hz, CH(C*H*$_3$)$_3$), 1.23 (16H, d, $^3J_{HH}$ = 7.40 Hz, CH(C*H*$_3$)$_3$), 1.11 (20H, two overlapping d, $^3J_{HH}$ = 5.84 Hz, CH(C*H*$_3$)$_3$), 0.98 (11H, d, $^3J_{HH}$ = 7.40 Hz, CH(C*H*$_3$)$_3$), 0.88 (16H, dd, J_{HH} = 2.72 Hz, $^3J_{HH}$ = 7.40 Hz, CH(C*H*$_3$)$_3$); $^{13}C\{^1H\}$-NMR δ(C_6D_6): 204.7 (q), 157.29(q), 144.40 (CH), 142.07,138.49 (CH), 137.75 (q), 136.34(CH), 133.32 (CH), 131.63 (CH), 128.68 (CH, obscured by C_6D_6 but present in DEPT135), 125.99 (q), 123.31 (q), 123.01 (CH), 118.65 (CH), 116.06 (q), 115.37 (CH), 113.91 (CH), 108.91 (CH), 104.29 (q), 103.52 (q), 100.78 (q), 20.50,20.29, 20.06, 19.80, 19.62, 14.85, 14.72, 13.23, 12.75 (*TIPS*); $^{29}Si\{^1H\}$-NMR δ(C_6D_6): 2.20, 2.25, 2.60, 3.73 (*Si*^{i}Pr$_3$). Elemental Analysis: Calcd for $C_{62}H_{107}Cl_2NSi_4Ti_2$ (**6**).C_5H_{12}: C 65.01, H 9.42, N 1.22; Found: C 64.90, H 8.95, N 1.23; No molecular ion could be observed in EI.

Preparation of (**7**): In an Ar filled glovebox 30 mg (0.029 mmol) of (**3**) were dissolved in 0.5-0.7 mL of C_6D_6 and the resultant pine green solution was treated at RT with 3.5 µL (1 mol eq) of ^{t}BuCCH and the reaction mixture was shaken vigorously to produce a homogeneous deep green solution. After NMR spectroscopy (100% spectroscopic yield), the solution was lyophilised to produce a deep green solid which was extracted in the glovebox with n-pentane (*ca* 1 mL) and refrigerated overnight (-35 ºC) to give the title compound as green needles suitable for single crystal XRD. Yield: 22 mg (*ca* 69%). ^{1}H-NMR δ(C_6D_6): 7.78 (1H, d, $^3J_{HH}$ = 3.30 Hz, Pn*H*), 7.63 (1H, d, $^3J_{HH}$ = 2.75 Hz, Pn*H*), 7.43 (1H, d, $^3J_{HH}$ = 2.93 Hz, Pn*H*), 6.78 (1H, d, $^3J_{HH}$ = 3.30 Hz, Pn*H*), 6.12 (1H, d, $^3J_{HH}$ = 3.12 Hz, Pn*H*), 6.05 (1H, d, $^3J_{HH}$ = 2.75 Hz, Pn*H*), 5.85 (1H, d, $^3J_{HH}$ = 2.75 Hz, Pn*H*), 5.38 (1H, d, $^3J_{HH}$ = 2.93 Hz, Pn*H*), 4.18 (3H, s, NC*H*$_3$), 2.15-2.09 (4H, m, C*H*$(CH_3)_2$), 1.68-1.51 (10H, m, C*H*$(CH_3)_2$ and NC*H*$_3$), 1.49-1.51 (17H, m, CH(C*H*$_3$)$_2$), 1.37 (9H, s, *^{t}Bu*CC), 1.34-1.29 (39H, m, CH(C*H*$_3$)$_2$), 1.18-1.00 (23H, m, CH(C*H*$_3$)$_2$), -8.83 (1H, s, Ti*H*Ti); $^{13}C\{^1H\}$-NMR δ(C_6D_6): 196.74 (N*C*N), 135.64 (q), 134.62 (*C*H Pn), 133.86, 133.10(q), 131.32 (*C*H, Pn), 129.19 (q), 126.89 (*C*H, Pn), 126.38 (q), 125.91 (*C*H, Pn), 125.19 (q), 120.74 (q), 118.75 (q), 116.60 (*C*H, Pn), 108.28 (*C*H, Pn), 104.71 (*C*H, Pn), 102.80 (*C*H, Pn), 101.57 (q), 100.01 (q), 94.10 (^{t}Bu*CC*), 93.12 (^{t}Bu*CC*), 39.20 (N*C*H$_3$), 35.00, 33.00 ((*C*H$_3$)$_3$CCC), 29.83 ((CH$_3$)$_3$*C*CC), 20.94, 20.88, 20.79, 20.68, 20.46, 20.31, 15.05, 14.83, 13.56, 12.98, 9.36, 8.75; $^{29}Si\{^1H\}$-NMR δ(C_6D_6): 1.61, 1.85, 2.28, 3.22 (*Si*^{i}Pr$_3$). Elemental Analysis: Calcd for $C_{65}H_{114}N_2Si_4Ti_2$: C 66.98, H 10.15, N 2.48; Found: C 66.84, H 9.73, N 2.25; No molecular ion could be observed in EI.

Preparation of (**7-D**): In a similar manner to (**7**) starting from 25 mg (*ca* 0.024 mmol) of (**3**) and 3 µL (1 mol eq) of ^{t}BuCCD in C_6H_6 with a few drops of C_6D_6 for ^{2}H NMR or in C_6D_6 for full characterization.

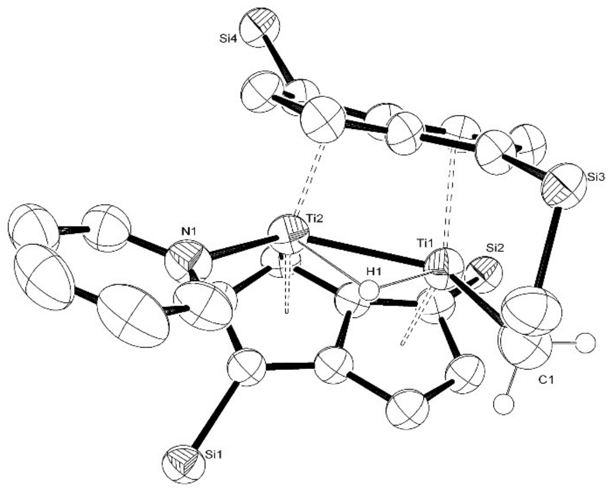
Preparation of (**9**): A Young's ampule was charged in a N_2 filled glovebox with 28 mg (0.0266 mmol) of (**3**), which was subsequently dissolved in 5 mL of Et_2O with stirring and cooled at 0 ºC using an ice bath. To this 13.3 µL of a 2.0 M HCl solution in Et_2O (1 mol eq.) were added in one go *via* a microsyringe under a current of Ar and the reaction mixture was allowed to stir at this temperature for *ca* 5 minutes. The ice bath was then removed and after 10 minutes volatiles were removed and the dark green film was dried in vacuum to give the title compound in 100 % spectroscopic yield as judged by NMR spectroscopy in C_6D_6. C_6D_6 was then removed *via* lyophilization and the residue was extracted in am Ar filled glovebox with n-pentane (*ca* 2 mL), filtered, the volume reduced at ambient temperature to *ca* half and finally refrigerated (-35 ºC) to furnish the title compound as dichroic green brown needles. Yield: 20 mg (64.5%) ^{1}H-NMR δ(C_6D_6): 7.73 (1H, d, $^3J_{HH}$ = 3.44 Hz, Pn*H*)*,* 7.50 (1H, d, $^3J_{HH}$ = 2.95 Hz, Pn*H*)*,* 7.47 (1H, d, $^3J_{HH}$ = 2.90 Hz, Pn*H*)*,* 6.90 (1H, d, $^3J_{HH}$ = 3.20 Hz, Pn*H*)*,* 6.65 (1H, d, $^3J_{HH}$ = 3.02 Hz, Pn*H*)*,* 6.47 (1H, d, $^3J_{HH}$ = 3.40 Hz, Pn*H*)*,* 5.82 (1H, d, $^3J_{HH}$ = 2.95 Hz, Pn*H*)*,* 5.42 (1H, d, $^3J_{HH}$ = 3.10 Hz, Pn*H*)*,* 4.08 (3H, s, NC*H*$_3$), 1.70-0.95 (m, 93H, CH(C*H*$_3$)$_2$ C*H*$(CH_3)_2$ and C*H*$_3$ of ylidene) -8.6 (1H, s, Ti*H*Ti); $^{13}C\{^1H\}$-NMR δ(C_6D_6): 195.13 (N*C*N), 138.13 (*C*H, Pn), 136.71 (q) 134.68 (q), 133.43 (*C*H, Pn), 126.95 (*C*H, Pn), 125.54 (*C*H, Pn), 126.39 (q), 125.04 (q), 129.07 (q), 120.07 (*C*H, Pn) 119.36 (q), 116.92 (q), 110.94 (q), 107.30 (*C*H, Pn), 105.19 (*C*H, Pn), 103.27 (*C*H, Pn), 97.47 (q), 94.74 (q), 38.62 (N*C*H_3), 34.76 (N*C*H_3), 20.55, 2045, 20.38, 20.27, 20.16, 20.05, 19.89, 14,67, 14,37, 13,21m 12,92, 8.97, 8.44 (CH(*C*H_3)$_2$ and *C*H(CH$_3$)$_2$; ^{29}Si{^{1}H}-NMR δ(C_6D_6): 3.27, 2.61, 2.13 and 2.01 (*Si*^{i}Pr$_3$); Elemental Analysis: Calcd for $C_{59}H_{105}ClN_2Si_4Ti_2$: C 65.25 H 9.75 N 2.58; Found C 65.17, H 9.66, N 2.22; No molecular ion could be observed in EI

Preparation of (**10**): In an Ar filled glovebox 50 mg (0.048 mmol) of (**3**) were combined with 20 mg of [NEt$_3$H]BPh$_4$ (1 mol eq) in a Young's ampule and benzene (*ca* 5 mL) was added at RT. After *ca* 10 minutes stirring at RT volatiles were removed and the dark turquoise residue dried extensively. NMR spectroscopy (C_7D_8) showed that (**10**) is produced in 100 % spectroscopic yield. Layering this toluene solution (*ca* 1 mL) with n-heptane and leaving undisturbed for 1 week produces crystals (20 mg) suitable for XRD of the title compound along with an oily residue which can be separated from the crystals with a drawn-out pipette. The latter can be separated from its mother-liquor *via* careful decantation, washed with n-pentane, and dried in vacuum to produce a turquoise film that is of the same purity as the crystalline material. Combined yield: 43 mg (*ca* 68%) ^{1}H-NMR δ(C_7D_8): 7.92 (8H, broad B(C_6*H_5*)$_4^-$), 7.50 (1H, d, $^3J_{HH}$ = 3.07 Hz, Pn*H*), 7.38 (1H, d, $^3J_{HH}$ = 2.63 Hz, Pn*H*), 7.25 (8H, virtual t, B(C_6*H_5*)$_4^-$), 7.13 (1H, d, $^3J_{HH}$ = 3.29 Hz, Pn*H*), 7.10 (4H, virtual t, B(C_6*H_5*)$_4^-$), 7.01 (1H, broad s, Pn*H*), 6.47 (1H, d, $^3J_{HH}$ = 3.07 Hz, Pn*H*), 5.93 (1H, d, $^3J_{HH}$ = 2.85 Hz, Pn*H*), 5.82 (1H, d, $^3J_{HH}$ = 3.29 Hz, Pn*H*), 5.75 (1H, d, $^3J_{HH}$ = 3.07 Hz, Pn*H*), 3.57 (3H, s, NC*H_3*), 1.48 (3H, s, NC*H_3*), 1.42-1.31 (6H, m, C*H*(CH$_3$)$_2$), 1.22-1.15 (13H m), 1.1-0.98 (50H, m, CH(C*H_3*)$_2$), 0.97-0.9 (6H, m, C*H*(CH$_3$)$_2$), 0.86 (3H, br s, CH(C*H_3*)$_2$), 0.71 (6H, d, $^3J_{HH}$ = 7.24 Hz, CH(C*H_3*)$_2$), 0.22 (6H, d, $^3J_{HH}$ = 7.23 Hz, CH(C*H_3*)$_2$), -5.72 (1H, s, Ti*H*Ti); ^{13}C{^{1}H}-NMR δ(C_7D_8): 185.41 (N*C*N), 165.23 (q, B(*C*$_6$H$_5$)$_4^-$, $^1J_{BC}$ = 49.6 Hz), 140.67 (q), 139.19 (q), 137.20 (B(C_6H_5)$_4^-$), 136.75 (*C*H, Pn), 134.07 (*C*H, Pn), 133.79 (*C*H, Pn), 133.64(*C*H, Pn), 129.14 (*C*H, Pn, located by DEPT 135), 128.21 (*C*H, Pn, located by DEPT 135), 125.89 (B(*C*$_6$H$_5$)$_4^-$), 121.89 (B(*C*$_6$H$_5$)$_4$), 121.62 (q), 117.48 (q), 116.15 (q), 112.44 (*C*H, Pn), 112.24 (*C*H, Pn), 111.25 (q), 106.74 (*C*H, Pn), 105.52 (*C*H, Pn), 104.12 (q), 100.66 (q), 37.64 (N*C*H_3), 34.50, 33.83, 22.75, 19.99, 19.97, 19.79, 19.56, 19.52, 18.52, 17.35, 14.39, 14.23, 14.19, 14.14, 13, 8.88, 8.40 (*C*H(*C*H$_3$)$_2$ and NHC *C*H$_3$); ^{29}Si{^{1}H}-NMR δ(C_7D_8): 4.31, 4.14, 4.03, 3.73 (*Si*^{i}Pr$_3$); ^{11}B{^{1}H}-NMR δ(C_7D_8): -6.75 (*B*(C_6H_5)$_4^-$); IR (thin film): 2753 cm^{-1} (agostic C-H); Elemental Analysis: Calcd for $C_{97}H_{157}BN_2Si_4Ti_2$ (**10**).C_7H_{16}: C 73.54, H 9.67, N 1.92; Found C 73.67, H 9.30 N 1.95; No molecular ion could be observed in ESI$^+$

X-ray Crystallography: Data for all compounds were collected using an Agilent Gemini Ultra diffractometer using with an Enhance Ultra (Cu *Kα*), equipped with an Eos CCD area detector, operating in ω scanning mode to fill the Ewald sphere. All collections were carried out at 173 K. Control, integration and absorption correction were handled by the CrysAlis^{Pro} software. The crystals were mounted on MiTiGen loops, from dried vacuum oil kept over 4Å in an MBraun glovebox under Ar. All solutions and refinements were performed using the WinGX package and all software packages within. All non-hydrogen atoms were refined using anisotropic thermal parameters, and hydrogens were added using a riding model, except in the case of the Ti-H bonds that were found in the difference map and refined freely. In the case of (**7**), twinning was handled from the CrysAlis^{Pro} software suite that produced the .hkl4 reflection file which was used for the refinement of the model. In the case of (**10**) the hydrogen atoms on carbon atom C9 were found in the difference map and refined freely. Crystal structure, data collection and refinement details are given in the following table of this Supporting Information.

In the case of (**5**) and **(9)** data were collected on a Rigaku FR-E rotating Cu *Kα* anode at 100K equipped with a Saturn 724+ CCD area detector. The brown-green dichroic crystals of (**9**) were found to have high mosaicity (4°) on one direction, thus hindering the acquisition of data with the desired resolution. Our efforts were further hampered by decomposition of the crystals upon extended exposures (the best crystals were found to be very thin needles). Nevertheless, connectivity could be established and the data-set could be solved from the 'What is this' pre-experiment routine in CrysAlis Pro. Although these data do not provide the level of confidence regarding bond lengths and angles, they completely agree with our spectroscopic and analytical data. The structure contains large solvent accessible voids although no crystallisation solvent could be located and hints as to the high mosaicity of the crystals. Parameters of this pre-collection experiment, along with information regarding refinement details are provided in reference 32 of the main text. In the case of **(5)** data were collected to a resolution of 0.9 Å. All this data is available free of charge at the Cambridge Crystallographic Database depository with the following codes: (**5**): CCDC-1861427 (**6**): CCDC-1850106; (**7**): CCDC-1850107; (**9**): CCDC-1850109; (**10**): CCDC-1850108.

Compound	**5**	**6**	**7**	**10**
Colour, Habit	Light Brown, Plate	Dark Orange, Plate	Green, Plate	Green, Block
Size/mm	0.08 x 0.08 x 0.01	0.08 x 0.05 x 0.01	0.08 x 0.1 x 0.2	0.3 x 0.3 x 0.1
Empirical Formula	$C_{57}H_{97}NSi_4Ti_2$. ½ C_5H_{12}	$C_{57}H_{95}Cl_2NSi_4Ti_2$	$C_{65}H_{114}N_2Si_4Ti_2$	$C_{81}H_{121}BN_2Si_4Ti_2$ .0569 C_7H1_6 .0.431 C_7H_8
M	1040.58	1073.39	1131.69	1368.80
Crystal System	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space Group	*P-1*	$P\ 2_1/n$	$P\ 2_1/c$	$P\ 2_1/c$
a/Å	12.7393(6)	13.5335(10)	17.0419(13)	21.4972(3)
b/Å	12.9078(8)	29.979(2)	14.2566(11)	13.1075(2)
c/Å	21.1087(11)	14.6437(12)	27.6286(16)	30.6056(5)
α/°	77.484(5)	90	90	90
β/°	87.578(4)	95.841(7)	94.809(7)	95.6200(10)
γ /°	61.137(5)	90	90	90
V/ $Å^3$	2959.7(3)	5910.4(8)	6689.0(8)	8582.4(2)
Z	2	4	4	4
μ/mm^{-1}	3.329	4.163	2.987	2.435
T (K)	100	173	173	173
θmin/max	3.973/51.756	4.232/68.251	3.961/67.079	3.393/ 67.076
Completeness	97.5 to 51.756	99.0 to 68.251	98.2 to 67.079	99.5 to 67.076
Reflections Total/Independent	6384/5407	10719/6778	11727/5273	16184/13455
R_{int}	0.0404	0.0646	0.1048	0.0276
Final *R1* and *wR2*	0.0562/0.1577	0.0707/0.1737	0.0793/0.2566	0.0549/0.1616
Goof	1.027	1.075	0.898	1.025
Largest peak hole/ e.$Å^{-3}$	0.52 and -0.48	0.5 and -0.4	0.66 and -1.12	1.0 and -0.42
ρ_{calc}/g.cm^{-3}	1.168	1.206	1.124	1.135



Molecular structure of (**5**) showing 50% probability ellipsoids. ^{i}Pr and H atoms (except the bridging hydride and the hydrogens on the cyclo-metallated ^{i}Pr group (atom C1)) have been removed for clarity. Selected bond lengths (Å) and angles (˚): C1-Ti1: 2.243(5), Ti1-Ti2: 2.5362(11), Ti1-H1: 1.82(3), Ti2-H1: 1.91(4), N1-Ti2: 2.266(3); N1-Ti2-Ti1: 129.15(10), N1-Ti2-H1: 83.6(10), Ti1-Ti2-H1: 45.5(10), Ti1-H1-Ti2: 85.8(18), C1-Ti1-H1: 75.4(11)

Computational Details: Density functional calculations were carried using the Amsterdam Density Functional package (version ADF2016.107).[iv] The Slater-type orbital (STO) basis sets were of triple-ζ quality augmented with a one polarization function (ADF basis TZP). Core electrons were frozen (C, N 1s; Ti 2p) in the model of the electronic configuration for each atom. The local density approximation (LDA) by Vosko, Wilk and Nusair (VWN)[v] was used together with the exchange correlation corrections of Becke and Perdew (BP86).[vi,vii] Local minima and transition states were confirmed by frequency calculations.

Cartesian coordinates for optimised structures.

H_2

H	-3.58553509	4.51453437	1.87556790
H	-3.12634177	3.97014110	1.63679021

3

C	0.83011677	0.96303980	0.82833386
C	1.34089322	0.42486982	-0.42161795
C	1.55446477	1.52743717	-1.32533549
C	1.29531005	2.71784788	-0.59286281
C	0.76761254	2.40082055	0.69490697
C	1.48309736	-0.99960278	-0.25766878
C	0.67477809	-0.14081366	1.75553397
C	1.16936372	-1.30863507	1.09923305
H	1.93337060	1.47599046	-2.34003861
H	1.41939209	3.72516049	-0.98683587
H	0.51741983	3.11505595	1.47225595
H	1.87906937	-1.69598856	-0.99032454
H	0.40806918	-0.06995107	2.80475510
H	1.27662313	-2.28948717	1.55880455

C	-2.47948715	1.04336584	0.80713733
C	-2.99994660	0.53524534	-0.45139619
C	-3.14531251	1.64982981	-1.35394400
C	-2.83523727	2.82339543	-0.61398172
C	-2.34216254	2.47636604	0.67959090
C	-3.21561050	-0.88088878	-0.29418351
C	-2.39269114	-0.06958948	1.73276137
C	-2.93653351	-1.20915153	1.06565093
C	-0.89147581	-2.35692020	-1.37021305
H	-2.90234409	3.83685118	-1.00628677
H	-2.06518952	3.17459068	1.46244934
H	-3.63433507	-1.55490091	-1.03503849
H	-2.13849092	-0.01474169	2.78602727
H	-3.09925795	-2.18474628	1.52000163
Ti	-0.79756343	1.64618026	-0.87270091
Ti	-0.86137113	-0.66158760	0.08408932
H	-0.95324965	-5.47888821	-2.50957229
H	-0.89179026	-3.51927412	-4.47919894
H	-0.94176180	-4.15685299	-0.30685596
N	-0.87730100	-2.22243365	-2.72801000
C	-0.89911816	-3.43614024	-3.39916969
C	-0.92928619	-4.39845598	-2.43395707
N	-0.92361339	-3.71682794	-1.22034674
H	-0.85213397	-1.28928929	-3.13934015
H	-3.51287511	1.62101303	-2.37370869
H	-0.83353833	0.01939775	-1.59499020
H	-0.78400459	1.75351555	-2.62109899

TS1

C	0.86362200	0.81625200	0.89198900
C	1.39479200	0.32844100	-0.36795200
C	1.58045100	1.47815200	-1.22816100
C	1.32635200	2.63851400	-0.45242500
C	0.75146500	2.25909800	0.79697500
C	1.45962700	-1.09104400	-0.30559600
C	0.61821700	-0.31577200	1.73293700
C	1.01433300	-1.50501800	1.01133200
H	1.99920200	1.47305100	-2.23171700
H	1.51361200	3.65826700	-0.76974100
H	0.51982500	2.94228300	1.60846500
H	1.84102700	-1.74986800	-1.08003500
H	0.30281600	-0.29137900	2.77041900
H	1.17860600	-2.48273200	1.45740900
C	-2.43257500	1.06259600	0.76786900
C	-3.00072600	0.56895600	-0.47206200
C	-3.21176400	1.70439600	-1.33590400
C	-2.92031800	2.87447500	-0.58118800
C	-2.35132600	2.50662700	0.67580200
C	-3.18100900	-0.85027000	-0.34022400
C	-2.29917100	-0.06454200	1.67132800

C	-2.85890200	-1.19961500	1.00921100
C	-0.86097800	-2.37691800	-1.39614800
H	-3.05063700	3.89382600	-0.93255400
H	-2.06730300	3.19434700	1.46499400
H	-3.62178800	-1.51592700	-1.07574800
H	-2.03045100	-0.01522800	2.72013900
H	-3.01666100	-2.17807300	1.45623600
Ti	-0.85500900	1.85149000	-0.93739300
Ti	-0.80785800	-0.63085800	-0.02277500
H	-0.50642600	-5.58039900	-2.21184000
H	-1.23151600	-3.92138100	-4.31773800
H	-0.34111600	-3.98244500	-0.18530200
N	-1.14360000	-2.42147800	-2.73444400
C	-1.04535000	-3.69854600	-3.27399100
C	-0.68850000	-4.51287300	-2.24037000
N	-0.59096100	-3.68947700	-1.12469300
H	-1.35947500	-1.57256600	-3.24770700
H	-3.62329900	1.68931000	-2.34199400
H	-0.82467100	0.22370500	-1.72071600
H	-0.61459200	3.50646800	-1.55673900
H	-0.71140300	2.26497300	-3.69531100
H	-0.73915400	1.53715100	-3.47003900

INT

C	0.87576600	0.81617500	0.89034500
C	1.39230400	0.32532600	-0.37401600
C	1.57357600	1.47494100	-1.24112000
C	1.32339000	2.63551100	-0.45979900
C	0.75764300	2.25674000	0.79091700
C	1.45674400	-1.09520900	-0.30411600
C	0.63714100	-0.31098600	1.73837600
C	1.02300800	-1.50298400	1.01809500
H	2.01721900	1.46938800	-2.23352100
H	1.51461500	3.65603500	-0.77336200
H	0.51655200	2.94205600	1.59789600
H	1.83191500	-1.75949900	-1.07703700
H	0.32713700	-0.28126900	2.77749100
H	1.18164100	-2.48139000	1.46419500
C	-2.43390400	1.06189400	0.76191000
C	-2.99556300	0.55066200	-0.47423600
C	-3.21444500	1.67731000	-1.35164900
C	-2.93315300	2.85518100	-0.60313400
C	-2.36303900	2.50361500	0.65477200
C	-3.17175900	-0.86781900	-0.32303400
C	-2.29251300	-0.05317400	1.67756800
C	-2.84499700	-1.20225700	1.02878800
C	-0.86283400	-2.36171100	-1.39708000
H	-3.07395400	3.87154700	-0.95984100
H	-2.07685900	3.20234200	1.43355000
H	-3.60781800	-1.54388600	-1.05198400

H	-2.02200300	0.01060800	2.72526100
H	-3.00066500	-2.17492100	1.48873900
Ti	-0.85453800	1.83434600	-0.96882400
Ti	-0.80628100	-0.62575700	-0.00865200
H	-0.60135000	-5.57490700	-2.20700900
H	-1.16415400	-3.88422500	-4.33709700
H	-0.45786600	-3.98696700	-0.17008700
N	-1.08721000	-2.39168100	-2.74606600
C	-1.01634300	-3.67084000	-3.28533600
C	-0.73927100	-4.50096500	-2.24007400
N	-0.65740100	-3.68361400	-1.11828900
H	-1.25094500	-1.53333000	-3.26341000
H	-3.64993100	1.65150400	-2.34697900
H	-0.82149400	0.21623800	-1.72775300
H	-0.63401700	3.55989500	-1.43364800
H	-0.73672900	2.49455300	-2.79085600
H	-0.79330600	1.69215700	-2.90842700

TS2

C	0.82813800	0.89607500	0.83737300
C	1.36202900	0.38932400	-0.41343400
C	1.59387200	1.53138300	-1.27518500
C	1.35941800	2.70064800	-0.49945000
C	0.77659800	2.33966900	0.74876200
C	1.44819100	-1.03417400	-0.31262600
C	0.60326700	-0.22794300	1.70946900
C	1.05514800	-1.41085200	1.02366500
H	2.03611100	1.51332100	-2.26781900
H	1.55041400	3.71818900	-0.82606700
H	0.52975500	3.03096000	1.54797900
H	1.84381700	-1.70748600	-1.06705400
H	0.31116900	-0.17945900	2.75248300
H	1.20589200	-2.38711400	1.47598500
C	-2.46229100	0.99229000	0.80046000
C	-3.00202300	0.51207700	-0.45820800
C	-3.16641400	1.66345300	-1.32219700
C	-2.88655500	2.82027800	-0.54237700
C	-2.34328000	2.43190800	0.71548300
C	-3.16594000	-0.90572000	-0.35572900
C	-2.31543200	-0.14155800	1.67964200
C	-2.82475600	-1.29553100	0.98888600
C	-0.88315300	-2.37531900	-1.39893800
H	-3.01905100	3.84585700	-0.87331400
H	-2.07236100	3.10998800	1.51808000
H	-3.58428700	-1.55992000	-1.11460900
H	-2.04229100	-0.10623600	2.72820600
H	-3.02388700	-2.26575900	1.43536900
Ti	-0.78710700	1.82752200	-0.94401600
Ti	-0.84911400	-0.62672500	-0.02050300
H	-0.90649200	-5.61390300	-2.14932400

H	-0.95998400	-3.91452500	-4.34550700
H	-0.85666400	-4.00949000	-0.12009400
N	-0.91768800	-2.40832500	-2.76604000
C	-0.93248600	-3.69789100	-3.28429400
C	-0.90614500	-4.53212500	-2.20660100
N	-0.87828100	-3.70553100	-1.08873600
H	-0.92588600	-1.54757400	-3.30512000
H	-3.59151600	1.66687400	-2.32242400
H	-0.81628300	0.23033900	-1.73577800
H	-0.72180500	3.58083900	-1.40149500
H	-0.74652000	2.54125800	-2.73325900
H	-0.76913500	1.73727800	-2.87670600

10

C	10.39722577	-1.33506048	19.76269913
C	13.18315022	1.06446157	20.88767541
C	12.79334318	0.45179187	19.64927598
C	12.00477620	1.40312979	18.93995895
H	11.63168799	1.26648168	17.92696902
C	11.74607630	2.53505669	19.76140500
H	11.22243931	3.43429931	19.45543524
C	12.53325932	2.36226519	20.96258012
C	13.00427394	3.02447906	22.15965164
C	13.96381238	2.15902116	22.76507948
H	14.56080522	2.40267936	23.64146497
C	13.99779015	0.91512011	22.06724425
H	14.62874005	0.06638866	22.31667500
C	10.38629116	2.94601297	23.49459018
H	10.65107073	3.99731902	23.46297826
C	10.47959331	2.09800260	24.63308950
H	10.90568445	2.40237648	25.58712121
C	9.97538790	0.77705492	24.34336071
C	9.40923178	0.87740994	23.00863036
C	9.67745728	2.20545314	22.48003364
C	9.05006333	2.31474822	21.18132624
C	8.34083074	1.09552628	20.97775134
H	7.67377788	0.89546365	20.14338749
C	8.64569763	0.16938252	22.01001139
H	8.26046879	-0.84224865	22.08343088
H	11.99955785	-5.05434883	18.92105735
H	9.10429052	0.46288981	18.38046717
C	11.91887063	-2.28145302	26.91283836
H	11.25669506	-2.37311145	27.78511324
Si	9.88279188	-0.60494657	25.65753364
H	12.95386760	-2.37138910	27.27780413
Ti	10.68769044	0.69403916	20.78774056
H	13.13525811	-0.50036709	19.25826929
C	9.60572342	-2.87621066	18.24182693
N	10.94837001	-2.57237129	19.97691927
H	11.43141634	-0.31794929	22.09947537

H	11.72745770	-3.14431219	26.25899803
H	11.67192823	-3.72542616	21.58620872
H	8.94751308	3.21671715	20.58740057
H	8.95669918	-4.44513068	16.95245240
N	9.58139501	-1.54675261	18.67925055
Ti	11.83500834	1.21581961	22.97037216
C	10.47900881	-3.52902497	19.06884779
C	8.96650154	-2.11860170	24.91169504
H	8.07338949	-1.66918530	24.43813712
C	9.75296811	-2.85273336	23.81168654
H	10.10016772	-2.17056541	23.02344512
H	9.12690804	-3.62582627	23.33666981
H	10.63424547	-3.36523188	24.22606259
C	8.45867471	-3.12011913	25.96912033
H	7.81311084	-2.64637831	26.72018575
H	9.28781627	-3.60727457	26.50199299
H	7.86989939	-3.91684607	25.48790514
C	9.51700481	1.17378281	27.95818823
H	10.54156035	0.94605659	28.28508794
H	8.92827611	1.38732697	28.86388956
H	9.54208216	2.10429971	27.37230747
C	8.87276902	0.02439503	27.16203209
H	8.82528159	-0.85227823	27.83499228
C	7.42999392	0.39021195	26.76074225
H	6.90430745	-0.43976824	26.26766503
H	7.41683555	1.24891549	26.07261188
H	6.84000684	0.67138657	27.64666667
C	12.68822837	-0.80035111	24.99656838
H	12.78190323	0.27571748	24.70656178
H	12.40421292	-1.40868568	24.12587451
H	13.71619216	-1.08509070	25.27437156
C	11.70837905	-0.94439326	26.17548220
H	11.95206173	-0.13990138	26.89224945
H	12.81329568	4.05165411	22.44855033
H	12.92047495	-3.15008127	20.44563930
C	8.79932224	-3.36926144	17.08951685
H	7.72184290	-3.20821547	17.24332533
H	9.07939836	-2.87315730	16.14773946
C	8.81246602	-0.51662461	17.99011363
H	9.02593731	-0.54632697	16.91421055
H	7.73395212	-0.66097582	18.14020817
C	10.91686087	-4.95385839	19.09042748
H	10.68380720	-5.43949601	20.04989096
H	10.40570205	-5.51813936	18.30212720
C	11.98423440	-2.88446773	20.95550928
H	12.14194287	-2.00013174	21.57894451

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