

## Synthesis, solid state and DFT structure and olefin polymerization capability of a unique base-free dimeric methyl titanium dication

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### Supporting information

#### Synthesis and characterising data for Cp\*Ti{NC(Ar<sup>F2</sup>)N<sup>i</sup>Pr<sub>2</sub>}Me<sub>2</sub> (1).

To a solution of diisopropylamine (2.50 g, 24.8 mmol) in toluene (60 mL) was added a solution of ethylmagnesium bromide in ether (8.0 mL, 3.0 M, 24 mmol) at 50°C. The mixture was stirred for 1 h and a white precipitate formed. Then, the mixture was cooled to 0°C and 2,6-difluorobenzonitrile (3.34 g, 24 mmol) was added. The mixture was allowed to warm to room temperature and was stirred for another 16 h. The mixture was quenched with an aqueous NH<sub>4</sub>Cl solution (100 mL of a 1 wt.% solution). The organic phase was separated from the aqueous phase and the latter was extracted twice with diethylether (200 mL). The combined organic phases were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and the solvents were removed under reduced pressure resulting in 5.40 g (91%) of solid N,N-diisopropyl-2,6-difluorobenzamidine.

N,N-diisopropyl-2,6-difluorobenzamidine (6.05 g, 25.2 mmol) and Cp\*TiCl<sub>3</sub> (7.24g, 25 mmol) were dissolved in toluene (150 mL). Triethylamine (4.0 mL, 2.9 g, 29 mmol) was added and the reaction mixture was stirred for 18 hours. The reaction mixture was filtered and the residue was rinsed once with toluene (60 mL). The solvent of the combined organic phases was removed in vacuo. The residue was washed with hexane (60 mL) once resulting in 12.18 g (99%) of an orange powder. Anal. for C<sub>23</sub>H<sub>32</sub>Cl<sub>2</sub>F<sub>2</sub>N<sub>2</sub>Ti Calcd.: C, 56.00; H, 6.54; N, 5.68; Found: C, 56.24; H, 6.59; N, 5.65 %. To a solution of Cp\*Ti{NC(Ar<sup>F2</sup>)N<sup>i</sup>Pr<sub>2</sub>}Cl<sub>2</sub> (12.2 g, 24.7mmol) in toluene (100 mL) was added a solution of methylmagnesium bromide (16.5 mL, 3.0M solution in diethylether, 49.5 mmol) at -78°C. The reaction mixture was stirred at room temperature for 18 hours. The reaction mixture was filtered and the solvent was removed in vacuo. The product was dissolved in hexanes and filtered once more. This resulted in 10.9 g of a yellow powder (97%). Single crystals could be obtained by crystallizing the product from a hexanes solution at -20 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 0.0 (s, 6H), 1.3 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 6H), 1.8 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 6H), 1.9 (s, 15H), 3,8 (sept, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 1H), 4.0 (bs, 1H), 7.0 (m, 2H), 7.8 (m, 1H). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>5</sub>Cl, 282 MHz): δ -111 (Ar<sup>F2</sup>). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.4): δ 10.3 (C<sub>5</sub>Me<sub>5</sub>), 20.1, 19.4 (2 x CHMe<sub>2</sub>), 47.1, 45.9 (2 x CHMe<sub>2</sub>), 50.5 (2 x Ti-Me), 110.3 (Ar, dd, <sup>2</sup>J<sub>CF</sub>=18 Hz, <sup>4</sup>J<sub>CF</sub>=7 Hz), 117.2 (Ar, t, <sup>2</sup>J<sub>CF</sub> = 25 Hz), 118.7 (C<sub>5</sub>Me<sub>5</sub>, s), 127.1 (Ar, t, <sup>3</sup>J<sub>CF</sub>=10 Hz), 146.5, (C=N, t, <sup>3</sup>J<sub>CF</sub>=10 Hz), 157.3 (Ar-CF, dd,

$^1J_{CF} = 248$  Hz and  $^2J_{CF} = 8$  Hz). Anal. for  $C_{25}H_{38}F_2Cl_2Ti$  Calcd.: C, 66.37; H, 8.47; N, 6.19; Found: C, 66.23; H, 8.31; N, 6.07 %.

**Synthesis and characterising data for  $[Cp^*Ti\{NC(Ar^{F2})N^iPr_2\}Me(OPPh_3)][BF_2O]$  (**2-BF<sub>20</sub>**).**

Solid **1** (0.58g, 1.3 mmol) and trityl tetrakis(pentafluorophenyl)borate (1.19 g, 1.3 mmol) were mixed at room temperature in a Schlenk vessel and 30 mL of fluorobenzene were added. A dark brown to reddish solution was formed. One equivalent of triphenylphosphinoxide was added after one hour of stirring at room temperature and immediately turned the solution yellow. After 1 hour of stirring at room temperature all volatiles were removed and the solid was washed twice with 20 mL of toluene and dried *in vacuo*.

$^1H$  NMR ( $C_6D_5Cl$ , 300 MHz):  $\delta$  0.52 (s, 3H, TiMe), 1.07 (d,  $^3J_{HH} = 6.0$  Hz, 3H,  $CHMe_2$ ), 1.10 (d,  $^3J_{HH} = 6.0$  Hz, 3H,  $CHMe_2$ ), 1.32 (d,  $^3J_{HH} = 6.0$  Hz, 3H,  $CHMe_2$ ), 1.52 (br d,  $^3J_{HH} = 6.0$  Hz, 3H,  $CHMe_2$ ), 1.78 (s, 15H, Cp\*), 3.66 (sept,  $^3J_{HH} = 6.0$  Hz, 1H,  $CHMe_2$ ), 3.92 (br sept, 1H,  $CHMe_2$ ), 6.55 (t,  $^3J_{HH} = 7.8$  Hz, 1H,  $Ar^{F2}$ ), 6.88 (t,  $^3J_{HH} = 7.8$  Hz, 1H,  $Ar^{F2}$ ), 7.1-7.9 (series of m overlapping with residual protio solvent,  $Ar^{F2}$ ,  $OPPh_3$ ).  $^{19}F$  NMR ( $C_6D_5Cl$ , 282 MHz):  $\delta$  -111 and -112 (2 x 1F,  $Ar^{F2}$ ), -133 (m, 8F, 2- $C_6F_5$ ), -163 (m, 4F, 4- $C_6F_5$ ), -167 (m, 8F, 3- $C_6F_5$ ).  $^{31}P$ - $\{^1H\}$  NMR ( $C_6D_5Cl$ , 121.5 MHz): 64.6 (s,  $POPh_3$ ).  $^{13}C$ - $\{^1H\}$  NMR ( $C_6D_5Cl$ , 75.4 MHz):  $\delta$  12.0 ( $C_5Me_5$ ), 20.6, 20.9, 21.1 and 21.3 (4 x  $CHMe_2$ ), 48.6 (TiMe), 52.4, 52.9 (2 x  $CHMe_2$ ). The  $Ar^{F2}$ ,  $C_5Me_5$ , and  $C_6F_5$  carbon atoms could not be assigned individually. Anal. for  $C_{66}H_{50}BF_{22}ON_2PTi$ : calcd. C, 43.73; H, 2.78; N, 1.55 %; found C, 44.03; H, 2.60, N: 1.21 %.

**Synthesis and characterising data for  $[Cp^*_2Ti_2\{NC(Ar^{F2})N^iPr_2\}_2(\mu-Me)_2][BF_2O]_2$  (**3-[BF<sub>20</sub>]<sub>2</sub>**).**

To a solid mixture of **1** (0.50g, 1.1 mmol) and trityl tetrakis(pentafluorophenyl)borate (1.02g, 1.1 mmol) was added fluorobenzene (20 mL) at room temperature. The mixture was stirred for 30 minutes and the magnetic stirring bar was removed. Dark red crystals of **4** (0.63 g, 53%) were obtained by cooling the solution to  $-20^\circ C$  for 3 days.

$^1H$  NMR ( $C_6D_5Cl$ , 300 MHz):  $\delta$  1.20 (s, 6H, TiMe) 1.22 (d,  $^3J_{HH} = 6.0$  Hz, 12H,  $CHMe_2$ ); 1.52 (d,  $^3J_{HH} = 6.0$  Hz, 12H,  $CHMe_2$ ), 2.00 (s, 30H, Cp\*), 3.82 (septet,  $^3J_{HH} = 6.0$  Hz, 2H,  $CHMe_2$ ), 4.12 (sept,  $^3J_{HH} = 6.0$  Hz, 2H,  $CHMe_2$ ), 7.01 (m, 4H,  $Ar^{F2}$ ), 7.25 (m, 2H,  $Ar^{F2}$ ).  $^{19}F$  NMR ( $C_6D_5Cl$ , 282 MHz):  $\delta$  -112 (4F,  $Ar^{F2}$ ), -133 (m, 16F, 2- $C_6F_5$ ), -163 (m, 8F, 4- $C_6F_5$ ), -167 (m, 16F, 3- $C_6F_5$ ). The compound was insufficiently soluble to obtain a  $^{13}C$  NMR spectrum. Anal. for  $C_{96}H_{70}B_2F_{44}N_4Ti_2$ : calcd. C, 51.64; H, 3.16; N, 2.51 %; Found C, 51.57; H, 3.06; N, 2.41 %.

### Synthesis and characterising data for $[\text{Cp}^*_2\text{Ti}_2\{\text{NC}(\text{Ar}^{\text{F}2})\text{N}^i\text{Pr}_2\}_2\text{Me}_2(\mu\text{-Me})][\text{BF}_2\text{O}]$ (**4-BF<sub>20</sub>**).

To a *d*<sub>5</sub>-chlorobenzene (0.5 mL) solution of **3**, which was *in situ* prepared by mixing 28 mg (3.0 μmol) of trityl tetrakis(pentafluorophenyl)borate and 15 mg (3.3 μmol) of *N,N*-diisopropyl-2,6-difluorobenzamidinate) titaniumdimethyl (**1**) and analyzed with <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy, an additional 12 mg (2.7 μmol) of *N,N*-diisopropyl-2,6-difluorobenzamidinate) titaniumdimethyl was added. Cation **4**<sup>+</sup> exists as a mixture of diastereoisomers (“a” and “b”) in a 2:3 ratio. Only the <sup>1</sup>H and <sup>19</sup>F NMR spectra could be meaningfully assigned. The overlapping nature of the spectra and the similar relative concentrations of isomer “a” and “b” caused some assignments to be ambiguous. The quoted intensities given are self-consistent within each isomer. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>5</sub>Cl, 300 MHz): δ -0.54 (s, 3H, Ti-Me-Ti, isomer “a”), -0.38 (s, 3H, Ti-Me-Ti, isomer “b”), 0.65 (s, 6H, Ti-Me, isomer “b”), 0.71 (s, 6H, Ti-Me, isomer “a”), 1.25 (br m, 12H, CHMe<sub>2</sub>, isomer “a” or “b”), 1.62 (br m, 6H, CHMe<sub>2</sub>, isomer “a” or “b”), 1.76 (br m, 6H, CHMe<sub>2</sub>, isomer “a” or “b”), 1.99 (s, 15H, Cp\*, isomer “a”), 2.04 (s, 15H, Cp\*, isomer “b”), 3.84 (m, 4H, CHMe<sub>2</sub>, isomer “a” or “b”), 4.1-4.4 (overlapping 2 x br m, 4H, CHMe<sub>2</sub>, isomer “a” or “b”), 6.95-7.05 (overlapping 2 x t, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 2 x 2H, Ar<sup>F2</sup>, isomer “a” and “b”), 7.2-7.5 (overlapping br m, 4H, Ar<sup>F2</sup>, isomer “a” and “b”). <sup>19</sup>F NMR (C<sub>6</sub>D<sub>5</sub>Cl, 282 MHz): δ -111 and -112 (2 x 2F, Ar<sup>F2</sup>, isomer “a” and “b”), -132 (m, 8F, 2-C<sub>6</sub>F<sub>5</sub>), -163 (m, 4F, 4-C<sub>6</sub>F<sub>5</sub>), -167 (m, 8F, 3-C<sub>6</sub>F<sub>5</sub>). On scale up compound **4-BF<sub>20</sub>** was obtained as a waxy solid and a satisfactory elemental analysis was not obtained.

### DFT calculations

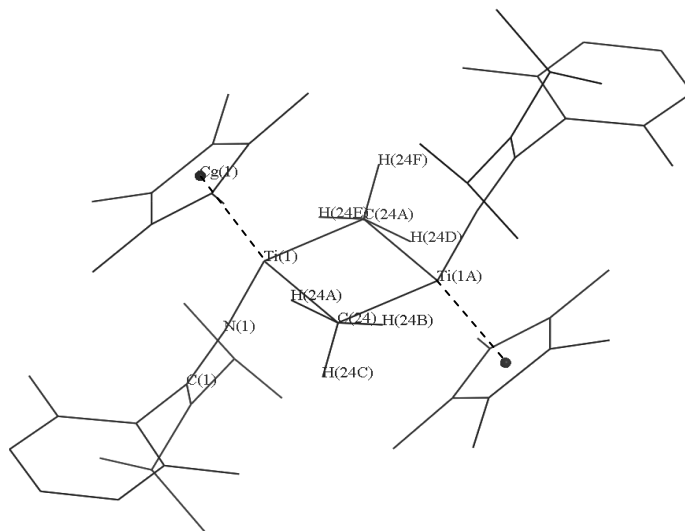
Calculations have been performed with the TURBOMOLE program<sup>S1</sup> using the hybrid functional b3-lyp<sup>S2</sup> in combination with the standard SV(P) basis sets<sup>S3</sup> and an effective core potential with 28 core electrons for Zr.<sup>S4</sup> Full optimizations without any symmetry constraints were carried out. Frequency calculations confirmed that the DFT structures are true energy minima. In the case of **6**<sup>2+</sup> no imaginary frequencies were found for the minimised structure. For **3**<sup>2+</sup> there were two imaginary frequencies corresponding to rotation of the Cp\* ligand methyl groups. These small residual rotational modes are well-known for large structures such as **3**<sup>2+</sup> featuring many methyl groups. Since they are of no structural or chemical significance regarding the unique Ti<sub>2</sub>(μ-CH<sub>3</sub>)<sub>2</sub> core of **3**<sup>2+</sup> they can be safely ignored.

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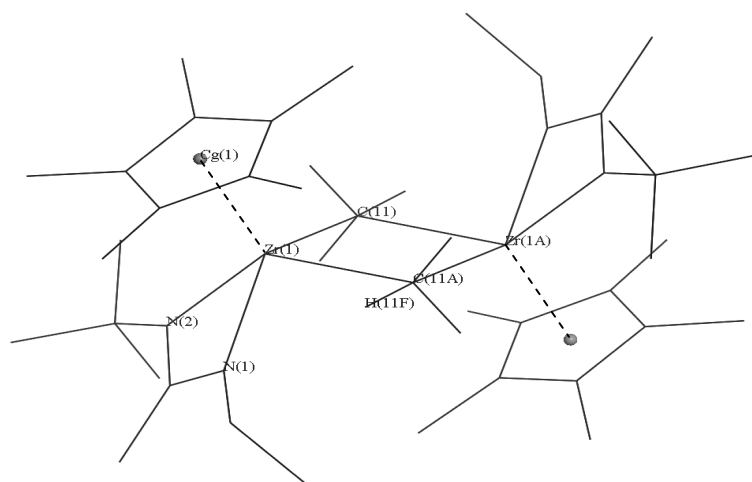
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**Figure S1.** DFT-calculated structure of  $[\text{Cp}^*_2\text{Ti}_2\{\text{NC}(\text{Ar}^{\text{F}2})\text{N}^i\text{Pr}_2\}_2(\mu\text{-Me})_2]^{2+}$  ( $\mathbf{3}^{2+}$ ).  $\text{Ti}(1)\text{-N}(1) = 1.794$ ,  $\text{Ti}(1)\text{-Cg}(1) = 2.094$ ,  $\text{Ti}(1)\text{-C}(24) = 2.275$ ,  $\text{Ti}(1)\text{-C}(24\text{A}) = 2.275$ ,  $\text{Ti}(1)\cdots\text{H}(24\text{A}) = 2.220$ ,  $\text{Ti}(1)\cdots\text{H}(24\text{E}) = 2.342$ ,  $\text{Ti}(1)\text{-N}(1)\text{-C}(1) = 168.4$ ,  $\text{Cg}(1)\text{-Ti}(1)\text{-N}(1) = 119.9$ ,  $\text{Cg}(1)\text{-Ti}(1)\text{-C}(24) = 121.0$ ,  $\text{C}(24)\text{-Ti}(1)\text{-C}(24\text{a}) = 93.3$ ,  $\text{Ti}(1)\text{-C}(24)\text{-Ti}(1\text{A}) = 86.7$ . Cg represents the Cp\* centroid.



**Figure S2.** DFT-calculated structure of  $\text{Cp}^*_2\text{Zr}_2\{\text{MeC}(\text{N}^t\text{Bu})(\text{NEt})\}_2(\mu\text{-Me})_2]^{2+}$  ( $\mathbf{6}^{2+}$ ).  $\text{Zr}(1)\text{-N}(1) = 2.180$ ,  $\text{Zr}(1)\text{-N}(2) = 2.295$ ,  $\text{Zr}(1)\text{-Cg}(1) = 2.262$ ,  $\text{Zr}(1)\text{-C}(11\text{A}) = 2.451$ ,  $\text{Zr}(1)\text{-C}(11) = 2.414$ ,  $\text{Zr}(1)\cdots\text{H}(11\text{F}) = 2.526$ ,  $\text{N}(1)\text{-Zr}(1)\text{-N}(2) = 60.0$ ,  $\text{Cg}(1)\text{-Zr}(1)\text{-N}(1) = 113.1$ ,  $\text{Cg}(1)\text{-Zr}(1)\text{-C}(11\text{A}) = 104.7$ ,  $\text{C}(11\text{A})\text{-Zr}(1)\text{-C}(11) = 85.9$ ,  $\text{Zr}(1)\text{-C}(11\text{A})\text{-Zr}(1\text{A}) = 94.1$ . Cg(1) represents the Cp\* centroid.



**X-ray crystal structure determination of [Cp\*<sub>2</sub>Ti<sub>2</sub>{NC(Ar<sup>F2</sup>)N<sup>i</sup>Pr<sub>2</sub>}<sub>2</sub>(μ-Me)<sub>2</sub>][BF<sub>20</sub>]<sub>2</sub> (3-[BF<sub>20</sub>]<sub>2</sub>).**  
[C<sub>48</sub>H<sub>70</sub>F<sub>4</sub>N<sub>4</sub>Ti<sub>2</sub>](C<sub>24</sub>BF<sub>20</sub>)<sub>2</sub> + disordered solvent, Fw = 2232.98,<sup>\*</sup> dark red plate, 0.66 x 0.51 x 0.18 mm, triclinic, P  $\bar{1}$  (no. 2), a = 13.1212(4), b = 13.2408(3), c = 18.5640(3) Å, α = 105.738(1), β = 105.857(2), γ = 96.491(2)°, V = 2924.53(13) Å<sup>3</sup>, Z = 1, D<sub>x</sub> = 1.268 g/cm<sup>3</sup>,<sup>\*</sup> μ = 0.25 mm<sup>-1</sup>.<sup>\*</sup> 53377 Reflections were measured on a Nonius KappaCCD diffractometer with rotating anode (graphite monochromator, λ = 0.71073 Å) up to a resolution of (sin θ/λ)<sub>max</sub> = 0.65 Å<sup>-1</sup> at a temperature of 150(2) K. Intensity integration was performed with Eval15.<sup>S5</sup> The SADABS<sup>S6</sup> program was used for absorption correction and scaling based on multiple measured reflections (0.60-0.75 correction range). 12979 Reflections were unique (R<sub>int</sub> = 0.021), of which 11363 were observed [I > 2σ(I)]. The structure was solved with Direct Methods using the program SHELXS-97<sup>S7</sup> and refined with SHELXL-97<sup>S7</sup> against F<sup>2</sup> of all reflections. Non hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were introduced in calculated positions and refined with a riding model. The crystal structure contains solvent accessible voids (808.5 Å<sup>3</sup> / unit cell) filled with severely disordered solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON<sup>S8</sup> resulting in 69 electrons / unit cell. 685 Parameters were refined with 6 restraints concerning the C-H distances and H-C-H angles of the bridging methyl ligand. R<sub>1</sub>/wR<sub>2</sub> [I > 2σ(I)]: 0.0415 / 0.1335. R<sub>1</sub>/wR<sub>2</sub> [all refl.]: 0.0465 / 0.1388. S = 1.074. Residual electron density between -0.39 and 0.59 e/Å<sup>3</sup>. Geometry calculations and checking for higher symmetry was performed with the PLATON program.<sup>S8</sup>

\* Derived values do not contain the contribution of the disordered solvent.

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