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

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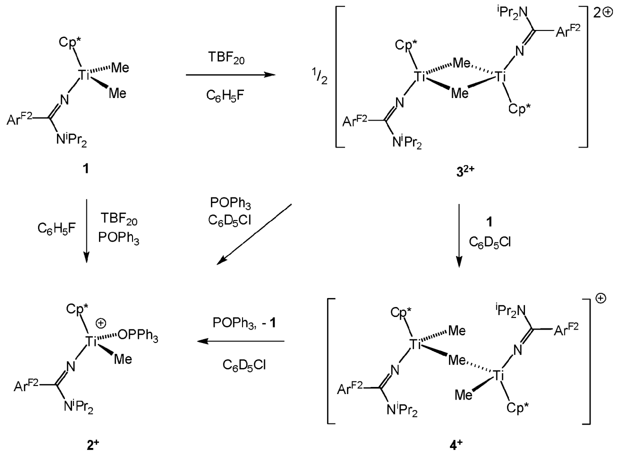
Reaction of Cp*Ti{NC(Ar^{F_2})N^iPr_2}Me_2 (1, Ar^{F_2} = 2,6-$C_6H_3F_2$) with [Ph_3C][B(C_6F_5)$_4$] gave the base-free structurally authenticated dication [Cp*$_2$Ti$_2${NC(Ar^{F_2})N^iPr_2}$_2$(μ-Me)$_2$][B(C_6F_5)$_4$]$_2$ (3-[BF_{20}]$_2$) containing two doubly α-agostic bridging methyl groups. 3-[BF_{20}]$_2$ is a highly effective ethylene–propylene polymerization catalyst at 90 °C, and its performance is identical to the catalyst generated *in situ* from 1 and [Ph_3C][B(C_6F_5)$_4$].

Following the spectacular success of Group 4 metallocenes as single-site olefin polymerization catalysts,[1–4] numerous half-sandwich and non-cyclopentadienyl systems have been developed by replacing one or both cyclopentadienyl ligands by heteroatom donor moieties.[4–11] An essential feature of Group 4 (and most other) metal catalysts is a highly electron-deficient alkyl cation $[(L)M–R]^+$ (R = initiating group or polymeryl chain) which is the initiating or active species. The nature of these cations and other species which may be formed prior to or during the polymerization process continues to be a topic of considerable interest and importance.[4,12–16]

Half-sandwich Group 4 complexes have proven to be highly efficient co-polymerization catalysts.[5–8] DSM recently introduced (as Keltan ACE™)[17] a new class of half-sandwich κ^1-amidinate titanium complexes of the type (η-C_5R_5)Ti{NC(Ar)NR′$_2$}X_2 (X = Me or Cl), which are extremely active pre-catalysts for the commercial homo- and co-polymerization of olefins.[18,19] One example is Cp*Ti{NC(Ar^{F_2})N^iPr_2}Me_2 (**1**, Ar^{F_2} = 2,6-$C_6H_3F_2$; Cp* = η-C_5Me_5, Scheme 1). While investigating the underlying chemistry of this compound we prepared the first base-free, isolable and highly stable Group 4 μ-methyl dication dimer that is as active a pre-catalyst for olefin polymerization as the system obtained by *in situ* activation of the corresponding dimethyl pre-catalyst. We describe here our preliminary results.

Reaction of Cp*Ti{NC(Ar^{F_2})N^iPr_2}Me_2 (**1**) with [Ph_3C][B(C_6F_5)$_4$] (TBF_{20}) in fluorobenzene in the presence of $POPh_3$ resulted in good yields of [Cp*Ti{NC(Ar^{F_2})N^iPr_2}Me($OPPh_3$)][BF_{20}] (**2-BF$_{20}$**), which was characterised on the basis of spectroscopic data and combustion analysis.† The NMR data are fully consistent with the presence of the base-stabilized titanium methyl monocation **2**$^+$ (depicted in Scheme 1) and a separated $[BF_{20}]^-$ anion. A number of half-sandwich, base-stabilized Group 4 alkyl cations have been reported previously.[4]



Scheme 1 Synthesis of the new titanium methyl cations derived from Cp*Ti{NC(Ar^{F_2})N^iPr_2}Me_2 (**1**). $[BF_{20}]^-$ anions omitted.

Reaction of **1** with TBF_{20} in C_6H_5F in the absence of added Lewis base, followed by cooling to −20 °C, gave red crystals of [Cp*$_2$Ti$_2${NC(Ar^{F_2})N^iPr_2}$_2$(μ-Me)$_2$][BF_{20}]$_2$ (**3-[BF$_{20}$]$_2$**) in 53% isolated yield.† Compound **3-[BF$_{20}$]$_2$** contains a dinuclear methyl-bridged *dication* and two separated $[BF_{20}]^-$ anions according to X-ray crystallography (see below).‡ When followed by ^1H and ^{19}F NMR *in situ* in C_6D_5Cl, **3-[BF$_{20}$]$_2$** forms quantitatively from **1** and TBF_{20}. As expected, addition of $POPh_3$ to either isolated or *in situ* generated **3-[BF$_{20}$]$_2$** in C_6D_5Cl formed **2-BF$_{20}$** in quantitative yield.

Addition of Cp*Ti{NC(Ar^{F_2})N^iPr_2}Me_2 (**1**, 2 equiv.) to **3-[BF$_{20}$]$_2$** in C_6D_5Cl formed [Cp*$_2$Ti$_2${NC(Ar^{F_2})N^iPr_2}$_2$–Me_2(μ-Me)][BF_{20}] (**4-BF$_{20}$**, Scheme 1) in quantitative yield. This compound contains a dimeric monocation (**4**$^+$) with one bridging methyl group and terminal methyl groups. No evidence for separated **1** and **3**$^{2+}$ was found in the NMR spectra of **4-BF$_{20}$**. According to ^1H and ^{19}F NMR spectroscopy, cation **4**$^+$ exists as a mixture of diastereoisomers (arising from different orientations of the amidinate N^iPr_2 and Ar^{F_2} substituents) in a *ca.* 2 : 3 ratio. Nonetheless, addition of 1 equiv. $POPh_3$ quantitatively formed **1** and **2-BF$_{20}$**. As has been found for several compounds of the type $[(L)_2M_2Me_2(\mu\text{-}Me)]^+$ (M = Group 4 metal),[14a,15c,20] **4-BF$_{20}$** can also be made on the preparative scale by the addition of 0.5 equiv. TBF_{20} to **1**.

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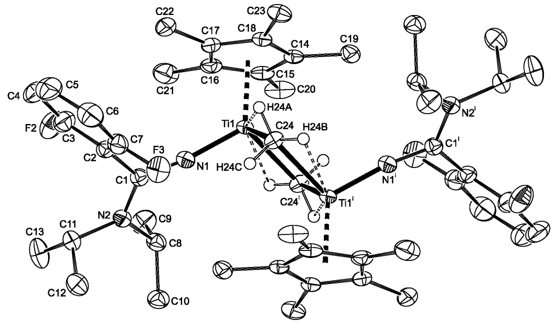
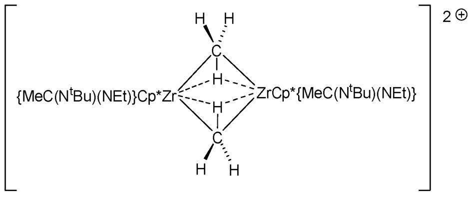


Fig. 1 Displacement ellipsoid plot (50% probability level) of $\mathbf{3^{2+}}$. Hydrogen atoms, others than those of the μ-Me groups omitted. Selected distances (Å) and angles (°): Ti1–N1 1.7913(13), Ti1–Cg1 2.042(1), Ti1–C24 2.2575(15), Ti1–C24^{i} 2.2838(15), Ti1–H24A 2.14(2), Ti1–H24B^{i} 2.27(2), Ti1–N1–C1 170.97(12), Cg1–Ti1–C24 118.83(5), Cg1–Ti1–C24^{i} 114.49(5), C24–Ti1–C24^{i} 94.83(5), Ti1–C24–Ti1^{i} 85.18(5). Cg1 represents the computed Cp* centroid. Symmetry operation i = −*x*, −*y*, −*z*.



$\mathbf{6^{2+}}$

Fig. 2 The structure of $[Cp^*{}_2Zr_2\{MeC(N^tBu)(NEt)\}_2(\mu\text{-}Me)_2]^{2+}$ ($\mathbf{6^{2+}}$) emphasising the unusual μ-methyl group geometry.[23]

Unfortunately, $\mathbf{4\text{-}BF_{20}}$ forms as a waxy solid when isolated and its solid state structure could not be determined.

The remarkable solid state structure of the centrosymmetric dication $[Cp^*{}_2Ti_2\{NC(Ar^{F2})N^iPr_2\}_2(\mu\text{-}Me)_2]^{2+}$ ($\mathbf{3^{2+}}$) is shown in Fig. 1. $\mathbf{3^{2+}}$ contains pseudo-tetrahedral titanium centres, each bound to an amidinate and Cp* ligand and two approximately symmetrically bridging methyl groups. The H atoms of the latter were located from a Fourier map and positionally refined. Each μ-methyl group in $\mathbf{3^{2+}}$ forms two α-agostic contacts, one to each Ti. The Ti–Me distances in $\mathbf{3^{2+}}$ (2.2575(15) and 2.2838(15) Å) are much longer than in **1** (avg. 2.119 Å). This is expected since the Ti–Me–Ti bonding in $\mathbf{3^{2+}}$ is based only on 3-centre, 2-electron interactions, and there is also substantial coulombic repulsion between the two cationic centres.

As mentioned, the nature of the species present in Ziegler–Natta polymerization catalysis is a topic of considerable interest.[4,12–16] Although *neutral* homobimetallic complexes of the type (L)M(μ-Me)$_2$M(L) have been structurally authenticated,[21] none has been reported for Group 4. The only structurally authenticated Lewis base- or coordinated anion-free titanium analogue of $\mathbf{3^{2+}}$ is the very recently reported AlMe$_3$-stabilized heterobimetallic monocation $[Ti(Me_3[9]aneN_3)(N^tBu)(\mu\text{-}Me)_2\text{-}AlMe_2]^+$ ($\mathbf{5^+}$).[16] Like $\mathbf{3^{2+}}$, this has two square based pyramidal μ-methyl groups, each forming an α-agostic contact to Ti (H atoms positionally refined). The DFT computed structure of $\mathbf{5^+}$ confirmed the one determined crystallographically. Coordination of AlMe$_3$ to $[Ti(Me_3[9]aneN_3)(N^tBu)Me]^+$ significantly inhibits polymerization activity.[22]

Despite the aforementioned intense international efforts around the chemistry of alkyl cations over the last two decades, only one dicationic analogue of $\mathbf{3^{2+}}$ has been reported, namely Sita's dizirconium dication $[Cp^*{}_2Zr_2\{MeC(N^tBu)(NEt)\}_2(\mu\text{-}Me)_2]^{2+}$ ($\mathbf{6^{2+}}$, Fig. 2).[23] The structure of $\mathbf{6^{2+}}$ has attracted much attention owing to postulated implications for Ziegler–Natta catalysis, and also the very unusual reported arrangement of the Zr$_2$(μ-Me)$_2$ hydrogens. Each μ-methyl group was described as having a trigonal bipyramidal geometry and an unprecedented *doubly-bridging* agostic C–H bond (Fig. 2; none of the H atoms were positionally refined). Remarkably, close examination of the reported data finds the H···H separation between the agostic hydrogens to be only 1.32 Å (sum of the van der Waals radii = 2.40 Å).

Because the arrangement of the μ-methyl group hydrogens in $\mathbf{6^{2+}}$ is very much at odds with those in $\mathbf{3^{2+}}$ and $\mathbf{5^+}$ (and neutral analogues [(L)M(μ-Me)$_2$M(L)]), we sought to gain further information on these systems by carrying out DFT calculations on both $\mathbf{3^{2+}}$ and $\mathbf{6^{2+}}$.† The minimum energy structure for the titanium dication showed excellent agreement with experiment (*e.g.*, Ti–N: calcd 1.794, found 1.7913(13) Å; avg. Ti–Me: calcd 2.272, found 2.2575(15) and 2.2838(15) Å; avg. Ti–H$_{\text{agostic}}$: calcd 2.20, found 2.14(2) and 2.27(2) Å). On the other hand, regardless of the starting μ-CH$_3$ group geometry, the DFT structure of $\mathbf{6^{2+}}$ minimized to be analogous to the μ-CH$_3$ geometry in $\mathbf{3^{2+}}$ and $\mathbf{5^+}$. Note that apart from the differing arrangements of these H atoms, the computed and experimental parameters for $\mathbf{6^{2+}}$ were in excellent agreement (*e.g.*, avg. Zr–Me: calcd 2.432, found 2.447 Å). On the basis of the structures of $\mathbf{3^{2+}}$ and $\mathbf{5^+}$ and the DFT calculations the μ-Me geometries of $\mathbf{3^{2+}}$ are without doubt "normal" with regard to other compounds of the type (L)M(μ-Me)$_2$M(L). The unusual geometry reported for $\mathbf{6^{2+}}$ is inconsistent with these other results.

Although it was speculated previously[23] that $\mathbf{6^{2+}}$ could have relevance to catalysis, this was not demonstrated, the precursor solutions decomposing at ambient temperature. The solution stability of $[Cp^*{}_2Ti_2\{NC(Ar^{F2})N^iPr_2\}_2(\mu\text{-}Me)_2][BF_{20}]_2$ ($\mathbf{3\text{-}[BF_{20}]_2}$) offered a unique opportunity to assess the polymerization initiating capability of a non-stabilized dialkyl-dication for the first time.

Table 1 compares the ethylene–propylene co-polymerization capability at 90 °C of *in situ* activated $Cp^*Ti\{NC(Ar^{F2})N^iPr_2\}Me_2$ (**1**) (using TBF$_{20}$) and that of *isolated* $[Cp^*{}_2Ti_2\{NC(Ar^{F2})\text{-}N^iPr_2\}_2(\mu\text{-}Me)_2][BF_{20}]_2$ ($\mathbf{3\text{-}[BF_{20}]_2}$) and $[Cp^*{}_2Ti_2\{NC(Ar^{F2})\text{-}N^iPr_2\}_2Me_2(\mu\text{-}Me)][BF_{20}]$ ($\mathbf{4\text{-}BF_{20}}$). All three have overall comparable productivities, and key polymer characteristics such as molecular weight, molecular weight distribution and composition (ethylene and propylene content) are indistinguishable within experimental error. It is evident that both the *in situ* **1** + TBF$_{20}$ and isolated $\mathbf{3\text{-}[BF_{20}]_2}$ catalyst systems give rise to the same equilibrium level amounts of the same monomeric active species $[Cp^*Ti\{NC(Ar^{F2})N^iPr_2\}R]^+$ (R = polymeryl chain), in the same way that $[Cp^*Ti\{NC(Ar^{F2})N^iPr_2\}Me(OPPh_3)][BF_{20}]$ ($\mathbf{2\text{-}BF_{20}}$) can be formed from all three systems **1** + TBF$_{20}$, $\mathbf{3\text{-}[BF_{20}]_2}$ and $\mathbf{4\text{-}[BF_{20}]}$ (Scheme 1).

In conclusion, we have reported a base-free single site Ziegler–Natta catalyst system of commercial relevance that can be isolated and stabilized in the solid state. The solid state μ-methyl group geometry of $[Cp^*{}_2Ti_2\{NC(Ar^{F2})N^iPr_2\}_2(\mu\text{-}Me)_2]^{2+}$ ($\mathbf{3\text{-}[BF_{20}]_2}$)

Table 1 Ethylene–propylene co-polymerization data using compounds Cp*Ti{NC(Ar^{F_2})N^{i}Pr$_2$}Me$_2$ (**1**), [Cp*$_2$Ti$_2${NC(Ar^{F_2})N^{i}Pr$_2$}$_2$(μ-Me)$_2$][BF$_{20}$]$_2$ (**3-[BF$_{20}$]$_2$**) and [Cp*$_2$Ti$_2${NC(Ar^{F_2})N^{i}Pr$_2$}$_2$Me$_2$(μ-Me)][BF$_{20}$] (**4-BF$_{20}$**)[a]

					Polymer composition[b] (wt%)		Molar mass distribution (GPC, g mol^{-1})	
Entry	Compound	Co-catalyst	Catalyst dosing (μmol Ti)	Polymer yield/g	C$_2$	C$_3$	M_n	M_w/M_n
1	**1**	TBF$_{20}$	0.20	10.7[c]	48	52	215 000	2.0
2	**3-[BF$_{20}$]$_2$**	None	0.20	12.5[d]	47	53	210 000	2.0
3	**4-BF$_{20}$**	None	0.40	8.95[e]	50	50	213 000	2.3

[a] Experimental conditions: total pressure 8 bar, T = 90 °C, reaction time 10 min, solvent pentamethylheptane (1 L). Al^{i}Bu$_3$ scavenger (Al : Ti ratio = 2250 modified by 4-methyl-2,6-di-*tert*-butylphenol (1 : 1 molar ratio). The ethylene : propylene molar ratio in the head space was kept at 1 : 2 by continuously feeding the gas to the reactor equipped with a purge to prevent polymer composition drift. After polymerization 500 ppm of Irganox 1076 stabilizer was added to the solution. Volatiles were removed under reduced pressure at 100 °C. [b] C$_2$ = ethylene content, C$_3$ = propylene content, as determined by FT-IR spectroscopy. [c] Equivalent to 4.01 × 10^4 kg (polymer) mol(Ti)$^{-1}$ h^{-1} (total pressure/bar)$^{-1}$. [d] Equivalent to 4.69 × 10^4 kg (polymer) mol(Ti)$^{-1}$ h^{-1} (total pressure/bar)$^{-1}$. [e] Equivalent to 3.36 × 10^4 kg (polymer) mol(Ti)$^{-1}$ h^{-1} (total pressure/bar)$^{-1}$.

(supported by DFT calculations for **3**$^{2+}$) suggests that the unusual structure reported for the dizirconium system **6**$^{2+}$ may warrant further investigation.

Notes and references

‡ Crystal data for **4**: [C$_{48}$H$_{70}$F$_4$N$_4$Ti$_2$](C$_{24}$BF$_{20}$)$_2$ + disordered solvent, Fw = 2232.98 [*], triclinic, $P\bar{1}$, 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^3, T = 150(2) K, 53 377/12 979 measured/unique refl., R_{int} = 0.021, Z = 1, D_x = 1.268 g cm^{-3} [*], μ = 0.25 mm^{-1} [*]. R_1/wR_2 [I > 2σ(I)]: 0.0415/0.1335. R/wR_2 [all refl.]: 0.0465/0.1388. S = 1.074. [*] derived values do not contain the contribution of the disordered solvent treated using the SQUEEZE routine of PLATON.[24]

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