Well-defined imidotitanium alkyl cations: agostic interactions, migratory insertion vs. [2+2] cycloaddition, and the first structurally authenticated AlMe₃ adduct of any transition metal alkyl cation†

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The imidotitanium alkyl cations $[Ti(N^tBu)(Me_3[9]aneN_3)R]^+$ (R = Me (3^+) or CH_2SiMe_3 (4^+)) possess either a very weak α-agostic or β-Si–C agostic interactions, respectively, according to ^{13}C and ^{29}Si NMR and DFT studies; reaction of 4^+ with $^iPrNCN^iPr$ gives totally selective insertion into the Ti–alkyl bond; reaction of 3^+ with AlMe₃ gives the first structurally characterised AlMe₃ adduct of a transition metal alkyl cation $(Me_3[9]aneN_3 = 1,4,7$-trimethyltriazacyclononane).

Substantial effort has been made over the past 10–15 years to develop early transition metal 'post-metallocene' Ziegler type olefin polymerisation catalysts,[1] and imido compounds $(L_nM=NR)[2]$ have also been extensively studied in this regard.[3] We recently reported that certain macrocycle-supported imidotitanium dichlorides $[Ti(NR)(Me_3[9]aneN_3)Cl_2]$ (I–R, Chart 1), isolobal with Group 4 metallocene dichlorides II, form (for bulky alkyl groups R) extremely active ethylene polymerisation catalysts with methyl aluminoxane (MAO).[4] Activation of the dialkyls $[Ti(N^tBu)(Me_3[9]aneN_3)R_2]$ (R = Me (1) or CH_2SiMe_3 (2)) with $[CPh_3][BAr^F_4]$ (TB, $Ar^F = C_6F_5$) also afforded very active species. The catalyst systems I-^tBu/MAO and 1/TB are the most active imido-supported Ziegler catalysts described to date.

Remarkably, despite the many detailed studies of metallocenium and non-metallocenium alkyl cations (deemed to be the active species in Ziegler polymerisation),[1,5] very little is known about catalytically-active imido-supported alkyl cations (imido compounds themselves have been of enormous interest for over 20 years[2]). The only report to date is from Gibson who described NMR evidence for the bis(imido)chromium benzyl cation $[Cr(N^tBu)_2(CH_2Ph)]^+$ (III) and its PMe₃ adduct.[6] In this contribution we report our initial studies of well-defined imidotitanium alkyl cations.

Reaction of $[Ti(N^tBu)(Me_3[9]aneN_3)R_2]$ (R = Me (1) or CH_2SiMe_3 (2)) with TB in C_6D_5Br gave the cations $[Ti(N^tBu)(Me_3[9]aneN_3)R]^+$ (R = Me (3^+) or CH_2SiMe_3 (4^+)) whose NMR data suggest they exist as solvent separated ion pairs.[7]† The corresponding reaction of 1 with TB in CD_2Cl_2 led to decomposition, but for 2 the formally 14 valence electron cation 4^+ was again quantitatively formed and, remarkably, is stable for *days* at room temperature in CD_2Cl_2. The reaction between 2 and TB followed by Ph₃PO gave the fully characterised adduct $[Ti(N^tBu)(Me_3[9]aneN_3)(CH_2SiMe_3)(Ph_3PO)][BAr^F_4]$ (5-BAr^F_4) in 66% isolated yield (Scheme 1).†

The formally 14 valence electron 3^+ and 4^+ are isolobal[8] analogues of Group 4 metallocenium cations $[Cp_2MR]^+$, active species in Ziegler–Natta olefin polymerisation.[1,5] The electron-deficient nature of 3^+ and 4^+ raises the possibility of agostic interactions[9] and so further NMR studies were carried out, together with DFT calculations† on the model dialkyl compounds $[Ti(NMe)(H_3[9]aneN_3)R_2]$ (R = Me (1a) or CH_2SiMe_3 (2a)) and cations $[Ti(NMe)(H_3[9]aneN_3)R]^+$ (R = Me ($3a^+$) or CH_2SiMe_3 ($4a^+$)). Calculations on $3a^+$ found a very weak α-C–H agostic interaction with one Ti–C–H angle of 105.9° and two of 115.7° and 113.8° (similar interactions have been found in metallocenium methyl cations[10]) which resulted in a 5.5 Hz increase in the calculated average $^1J_{CH}$ for the Ti–Me ligand (107.5 Hz) compared to that in model dimethyl 1a (102 Hz). Constraining the Ti–Me moiety in $3a^+$ to be non-agostic (only *ca.* 2 kJ mol⁻¹ less stable) with equivalent Ti–C–H angles of 109.5° gave an average $^1J_{CH}$ that was 11 Hz greater than that in 1a.[11a] The observed (C_6D_5Br) $^1J_{CH}$ for 1 and 3^+ of 111 and 116 Hz $(\Delta^1J_{CH} = 5$ Hz) are consistent with the agostic structure computed by DFT.[7] However, given the weak nature of the α-agostic interaction this conclusion is only tentative and calculations on extended systems are in progress. There are few reports of calculations of spin–spin coupling constants within ligands of transition metal complexes.[11b] The experience gained on organic systems indicates that hybrid functionals (B3PW91 in the calculations reported herein) are particularly efficient. Accuracies

Chart 1

Scheme 1 Reactions of $[Ti(N^tBu)(Me_3[9]aneN_3)(CH_2SiMe_3)]^+$ (4^+). $[BAr^F_4]^-$ anion is omitted. All reactions in CH_2Cl_2.
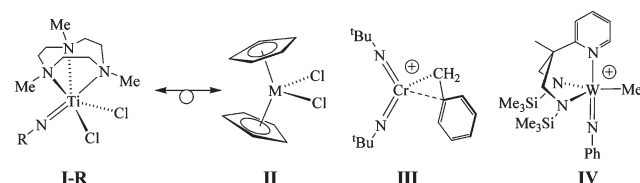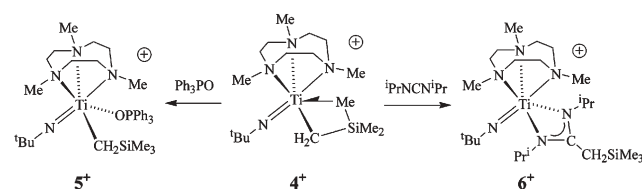
† Electronic supplementary information (ESI) available: characterising data and details of the DFT calculations; molecular structure of 6-BAr^F_4. See http://www.rsc.org/suppdata/cc/b5/b504567c/

of better than 10% (with respect to experimental values) are considered to be excellent.[11c,d]

The observed ^{29}Si NMR shifts (CD$_2$Cl$_2$) of δ -1.8 and -0.7 ppm in the six-coordinate complexes **2** and **5**$^+$ are within normal ranges but the high-field value of -15.9 ppm in **4**$^+$ is very unusual. The DFT calculated structure of **4a**$^+$ (Fig. 1) shows a clear β-Si–C···Ti interaction, and the calculated ^{29}Si NMR shift of δ -17.6 ppm for **4a**$^+$ agrees well with that for the experimental system, as does that for the neutral dialkyl **2a** (calcd. -1.2 ppm *vs.* -1.8 ppm found for **2**). Horton has observed upfield shifted ^{29}Si resonances in the isolated cationic zirconocene vinyl complex [Cp$_2$Zr{C(=CMe$_2$)SiMe$_3$}]$^+$ which features a β-Si–C···Zr contact,[12a] and β-Si–C interactions are well-known in neutral Group 3 complexes containing CH(SiMe$_3$)$_2$ and N(SiMe$_3$)$_2$ ligands.[9c,12b]

Imido-supported transition metal alkyl cations have at least two potential sites for reaction with unsaturated substrates. Jensen and Børve have suggested that ethylene addition to one of the Cr=NR bonds in catalytically relevant species akin to **III** can be preferred over insertion into the Cr–alkyl bond,[13] raising fundamental questions of site selectivity and mechanism in imido-based Ziegler catalysts (note that M=NR bonds for Ti and Zr in particular undergo a wide range of cycloaddition reactions[2]). Legzdins *et al.* have reported that neutral bis(imido)tungsten alkyls also react preferentially at a W=NR bond.[14] In an attempt to address these issues we very recently undertook detailed experimental and DFT studies of the reactions of the well-defined imidotungsten methyl cation [W(N$_2$N$_{py}$)(NPh)Me]$^+$ **IV** (Chart 1) with unsaturated substrates (N$_2$N$_{py}$ = (2-NC$_5$H$_4$)C(Me)(CH$_2$NSiMe$_3$)$_2$).[15] Unfortunately, experimental tests of the DFT-predicted preference for insertion into W–Me instead of cycloaddition to W=NPh were frustrated by the reactivity of the N$_{amide}$ lone pairs of the supporting ligand which offered an alternative, kinetically favoured pathway.

The well-defined, metallocenium-like cations **3**$^+$ and **4**$^+$ provide a unique opportunity for addressing experimentally the fundamental question of site-selectivity in imido-supported Ziegler catalysts. Since both Group 4 imido compounds [L$_n$M=NR] and metal–alkyl cations [L$_n$M–R]$^+$ are known to react with carbodiimides RNCNR to form [2+2] cycloaddition[2b,c] or alkyl migratory insertion products respectively, ^{i}PrNCN^{i}Pr was selected as a

model substrate. The bulkier alkyl cation **4**$^+$ was chosen so that the competing Ti=NCMe$_3$ and Ti–CH$_2$SiMe$_3$ reactive sites would be as sterically equivalent as possible.

Cation **4**$^+$ reacts quantitatively on an NMR tube scale to form the migratory insertion product [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)-{Me$_3$SiCH$_2$C(N^{i}Pr)$_2$}]$^+$ (**6**$^+$) which was isolated as **6**-BAr$^F_4$ in 31 % yield, Scheme 1).† The molecular structure†‡ of **6**$^+$ unambiguously confirms the site of attack of the carbodiimide substrate and the formation of a trimethylsilylmethyl-substituted diisopropylformamidinate moiety.

Cationic alkyl complexes "[L$_n$M–R]$^+$" are generally accepted as being the active species in Ziegler-type olefin polymerisation catalysis. However, in systems activated by MAO (typically containing up to 15 wt% "AlMe$_3$") the catalyst resting state is probably a cationic bimetallic species of the type [L$_n$M(μ-R)AlR$_2$]$^+$.[16] Such species are also important in chain transfer (to aluminium) and catalyst deactivation. Although cationic Group 4 (or later) bimetallic cations of this type have been isolated and studied spectroscopically and computationally, none has been structurally authenticated to date.[17] We showed previously[4] that the presence of "AlMe$_3$" is probably important in chain transfer and molecular weight distributions in the catalyst system **I**/MAO, and Gibson has correlated chain transfer to aluminium with the presence of bimetallic complexes [L$_n$M(μ-R)$_2$AlR$_2$]$^{n+}$ as catalyst resting states.[5c]

$$ \text{(1)} $$
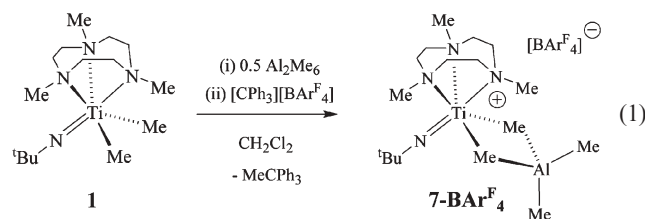
Reaction of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)Me]$^+$ (**3**$^+$) with Al$_2$Me$_6$ (0.5 equiv., C$_6$D$_5$Br) quantitatively formed the heterobimetallic cation [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)(μ-Me)$_2$AlMe$_2$]$^+$ (**7**$^+$); addition of TB to a solution of **1** and Al$_2$Me$_6$ in CH$_2$Cl$_2$ afforded **7**-BAr$^F_4$ in 53 % isolated yield (eqn. 1). The molecular structure†‡ (Fig. 2)
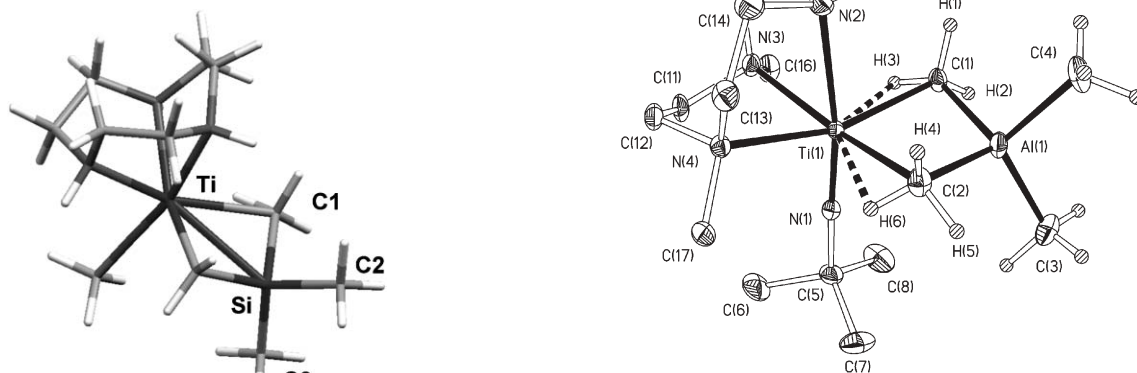

Fig. 1 DFT(B3PW91) calculated structure of [Ti(NMe)(H$_3$[9]-aneN$_3$)(CH$_2$SiMe$_3$)]$^+$ **4a**$^+$. Ti–CH$_2$ 2.100; Ti···C1 2.534; Si–C1 1.973; Si–C2 1.893; Si–C3 1.883 Å; Ti–CH$_2$–Si 90.7°, CH$_2$–Si–C1 106.4°, CH$_2$–Si–C2 112.9°, CH$_2$–Si–C3 114.6°.

Fig. 2 Molecular structure of [Ti(N^{t}Bu)(Me$_3$[9]aneN$_3$)(μ-Me)$_2$AlMe$_2$]$^+$ (**7**$^+$). Selected H atoms and [BAr$^F_4$]$^-$ anion are omitted. H atoms shown as spheres of arbitrary radius. Ti(1)–C(1) 2.344(2); Ti(1)–C(2) 2.335(2); Ti(1)–N(1) 1.6978(16); Ti(1)···H(3) 2.17(3), Ti(1)···H(6) 2.17(3), Al(1)–C(1) 2.081(2); Al(1)–C(2) 2.075(2); Al(1)–C(3) 1.963(3); Al(1)–C(4) 1.981(3) Å.

shows the presence of pentacoordinate bridging methyl groups Ti(μ-Me)Al and terminal Al–Me groups which are also clearly distinguished in the ^{1}H and ^{13}C NMR spectra.†

The cation 7^+ possesses an approximately tetrahedral Al centre and an octahedral Ti (ignoring any bridging H atoms). The Ti–N and terminal Al–C distances are within usual ranges and we will focus our discussion on the central Ti(μ-Me)$_2$Al moiety, the point of most interest. As expected, the Ti–C distances (av. 2.339 Å) are significantly lengthened in comparison with those for the dimethyl precursor **1** (av. 2.213 Å).[4] The bridging Al–Me distances are also longer (av. 2.078 Å) than the terminal ones (av. 1.972 Å). The H atoms for the μ-Me and Al–Me groups were located from a Fourier difference map and refined positionally and isotropically. Notwithstanding the inherent imprecisions concerning H atom location using X-ray diffraction, the geometry at the two μ-Me ligands is much better described as the approximately square based bipyramidal geometry found by neutron diffraction for the μ-Me ligands in Al$_2$Me$_6$[18] rather than the trigonal bipyramidal geometry found for the Nd(μ-Me)$_2$Al groups in [Nd(AlMe$_4$)$_3$][17a] (again by neutron diffraction). There is no statistically significant lengthening of individual C–H bonds of the bridging methyl groups, nor is the average C–H distance significantly different between the terminal and bridging ligands (in line with the measured $^1J_{CH}$ values mentioned above). Furthermore, only *one* H atom per μ-Me ligand forms a close contact to titanium (Ti(1)···H(3) = Ti(1)···H(6) = 2.17(3) Å) in contrast to the structures found for neutral yttrium or lanthanide compounds with M(μ-Me)$_2$AlMe$_2$ or related units which have *two* close M···H contacts per μ-Me group (note again the neutron diffraction study of [Nd(AlMe$_4$)$_3$][17a]). DFT calculations on a model of 7^+ (namely [Ti(NMe)(H$_3$[9]aneN$_3$)(μ-Me)$_2$AlMe$_2$]$^+$) reproduced the experimental structure very well, including the μ-Me group H atom positions and the geometry at these carbon atoms; an alternative structure with two close M···H contacts for one μ-Me group was found to be 10.7 kJ mol^{-1} higher in energy and corresponds to the transition state for H exchange within this bridging Me group. It appears that the modeling of transition metal cations [L$_n$M(μ-Me)$_2$AlMe$_2$]$^+$ by neutral rare earth analogues is appropriate only to a first approximation, and that the geometry and orientation of the μ-methyl ligands can differ.[19]

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Notes and references

‡ Crystal data for **6**-BAr$^F_4$: C$_{48}$H$_{55}$BF$_{20}$N$_6$SiTi, M_w = 1182.76, triclinic, $P\bar{1}$, a = 11.9619(2), b = 12.7619(2), c = 17.9840(2) Å, α = 75.5723(5), β = 80.1952(5), γ = 86.9238(5)°, U = 2619.78(7) Å^3, Z = 2, T = 150 K, μ = 0.299 cm^{-1}, 7976 reflections $I > 3\sigma(I)$, R_{int} = 0.049 R = 0.0402, R_w = 0.0476. Data for **7**-BAr$^F_4$·CH$_2$Cl$_2$: C$_{41}$H$_{42}$AlBF$_{20}$N$_4$Ti·CH$_2$Cl$_2$,

M_w = 1141.40, monoclinic, P 2$_1$/n, a = 13.7837(2), b = 19.5766(3), c = 18.6673(2) Å, α = 90, β = 109.7558(7), γ = 90°, U = 4740.67(11) Å^3, Z = 4, T = 150 K, μ = 0.428 cm^{-1}, 7266 reflections $I > 3\sigma(I)$, R_{int} = 0.047, R = 0.0359, R_w = 0.0371. CCDC 268643 and 268644. See http://www.rsc.org/suppdata/cc/b5/b504567c/ for crystallographic data in CIF or other electronic format.

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