7.75 (s, 1H, $H_{5'}$), 7.76 (s, 1H, $H_{6'}$), 7.80 (s, 2H, $H_{5,6}$), 7.99 (s, 1H, $H_{4'}$), 8.07 (s, 1H, $H_{7'}$), 8.12 (d, $J = 8.3$ Hz, 2H, $H_{3,8}$), 8.31 (d, $J = 8.3$ Hz, 2H, $H_{4,7}$), 8.43 (d, $J = 8.8$ Hz, 4H, H_o); FAB-MS: m/z calcd for $C_{65}H_{55}N_4O_8^+$: 1019.4; found: 1019.5.

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[11] $\mathbf{2}^{2+}$: ^1H NMR (400 MHz, CD_2Cl_2/CD_3CN): $\delta = 2.00$ and 2.09 (2s, 12H, CH_3), 3.35–3.89 (m, 32H, $H_{\alpha,\beta,\delta,\gamma}$), 4.96 (s, 4H, $ArOCH_2Ar$), 5.94 (d, $J = 8.6$ Hz, 8H, H_m), 6.62 (d, $J = 2.2$ Hz, 4H, H_b), 6.65 (t, $J = 2.2$ Hz, 2H, H_a), 6.85 (d, $J = 8.8$ Hz, 4H, $H_{m''}$), 6.96 and 7.12 (2d, $J = 8.2$ Hz, 8H, $H_{m'}$, $H_{o'}$), 7.06 (s, 2H, OH), 7.15 (d, $J = 8.5$ Hz, 4H, $H_{o''}$), 7.43 (d, $J = 8.6$ Hz, 8H, H_o), 7.99 (s, 2H, $H_{4'}$), 8.01 and 8.18 (2d, $J = 8.6$ Hz, 4H, $H_{5'}$, $H_{6'}$), 8.06 (d, $J = 8.5$ Hz, 4H, $H_{3,8}$), 8.09 (s, 4H, $H_{5,6}$), 8.18 (d, $J = 8.6$ Hz, 2H, $H_{5'}$), 8.24 (s, 2H, $H_{7'}$), 8.64 (d, $J = 8.3$ Hz, 4H, $H_{4,7}$); ESI-MS: m/z calcd for $Cu_2C_{130}H_{108}N_8O_{16}PF_6^+$: 2310.3; found: 2310.3; $M/2$ calcd for $Cu_2C_{130}H_{108}N_8O_{16}^{2+}$: 1082.7; found: 1082.7.

[12] X-ray crystallography for $\mathbf{2}^{2+}$. Deep red single crystals of $\mathbf{2}^{2+} \cdot 2PF_6^- \cdot 2CH_3OH$ were obtained as described above. $C_{67}H_{61}O_{10}N_4PF_6Cu$, $M_r = 1290.76$, monoclinic, $a = 25.543(1)$, $b = 20.870(1)$, $c = 27.869(1)$ Å, $\beta = 116.96(2)°$, $V = 13242(2)$ Å^3, space group $C2/c$, $Z = 4$, $\rho_{calcd} = 1.295$ g cm^{-3}, $\mu = 4.296$ mm^{-1}. Data were collected at -100 °C on a Nonius Kappa CCD diffractometer by using the standard data-collection procedures ($2.5 < \theta < 30°$) and graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) on a crystal of dimensions $0.30 \times 0.30 \times 0.20$ mm^3. 21423 data collected; 7329 with $I > 3\sigma(I)$. The structure was solved by direct methods. The diffraction power of the crystals was very poor, and the data of four samples were collected with the same results. It was therefore not possible to fully resolve the disorder of one of the PF_6^- ions and to locate all solvent molecules, even by refining on F^2 and using all data with $I > 2\sigma(I)$. Nevertheless, the core of the molecule is correct and refines normally. Final results: $R = 0.142$, $Rw = 0.193$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-135902. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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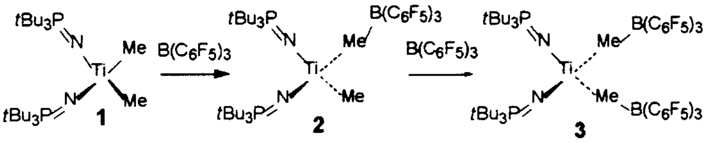
Synthesis and Structure of the Dicationic Bisborate Adduct $[(tBu_3PN)_2Ti\{\mu\text{-}MeB(C_6F_5)_3\}_2]$[**]

Frédéric Guérin and Douglas W. Stephan[*]

Complexes of nitrogen-based ligands have been the focus of much attention in the quest for new olefin polymerization catalysts. For example, Brookhart and co-workers[1–4] and Gibson and co-workers [5, 6] have recently reported unprecedented Fe- and Cr-based polymerization catalysts containing Schiff-base ligands, while McConville and co-workers[7, 8] observed living olefin polymerization using a Ti–amide catalyst. Recently, we described titanium compounds containing phosphanimide ligands of the form $[CpTi(NPR_3)Me_2]$ (R = *t*Bu, *i*Pr, Cy; Cp = C_5H_5) and $[(tBu_3PN)_2TiMe_2]$ (**1**).[9, 10] These species are catalyst precursors for olefin polymerization, and in fact **1** is highly active under both laboratory screening (1 atm, 25 °C) and commercially relevant (103 bar, 160 °C) polymerization conditions. The interaction of the precursors with Lewis acid activators is of fundamental importance. Marks,[11–15] Jordan,[16–18] and Bochmann[19] and their groups have elucidated the interaction of metallocenes with Lewis acid activators. The analogous chemistry of non-metallocene catalysts with Lewis acids has drawn lesser attention. Herein, we describe reactions of **1** with the Lewis acid $B(C_6F_5)_3$. In the reaction with excess borane $B(C_6F_5)_3$, a bis-borate zwitterionic species is obtained.

We have previously described the stoichiometric reaction of **1** with $B(C_6F_5)_3$ which generates the zwitterionic species $[(tBu_3PN)_2TiMe(\mu\text{-}Me)B(C_6F_5)_3]$ (**2**) (Scheme 1).[9] This isolated species is an active catalyst for ethylene polymerization.[9] While single-component catalysts are of interest, in situ generation of catalysts by the combination of precursor complex and co-catalyst is a more common practice. In the generation of **2** in situ for ethylene polymerization experiments, we noted that the order of addition of the reagents had a dramatic effect on the activity. Initially, **2** was generated by adding **1** to a solution of $B(C_6F_5)_3$ at 25 °C under an ethylene atmosphere. This led to poor activity and thus to only a small amount of polyethylene (PE; < 50 g of PE per mmol per hour). In contrast, addition of $B(C_6F_5)_3$ to a solution of **1** gave significantly increased catalyst activity[20] (265 g PE mmol^{-1} h^{-1}).



Scheme 1. Generation of **2** and **3** through reaction of **1** with $B(C_6F_5)_3$.

In probing these observations, we examined the reaction of **1** in the presence of excess $B(C_6F_5)_3$ in CH_2Cl_2 under an N_2 atmosphere. Upon addition of **1**, a yellow crystalline product **3** was formed immediately, which was isolated in 95 % yield. ^1H, ^{13}C, ^{19}F, ^{11}B, and ^{31}P NMR spectroscopic data confirmed the presence of the B and Ti moieties. The observation of a distinct ^{31}P chemical shift indicated that this new product **3** was not the 1:1 zwitterionic species **2**. Moreover, the presence of a single, temperature-invariant, Ti–methyl environment suggested the formation of a bis-$B(C_6F_5)_3$ adduct.

Crystals of $\mathbf{3} \cdot 2CH_2Cl_2$ were isolated from CH_2Cl_2. A crystallographic study[21] confirmed that $[(tBu_3PN)_2Ti\{\mu\text{-}MeB(C_6F_5)_3\}_2]$ (**3**), an unprecedented di-zwitterionic species, sits on a position with crystallographically imposed twofold symmetry (Figure 1). The pseudo-tetrahedral coordination sphere about Ti comprises the nitrogen atoms of the

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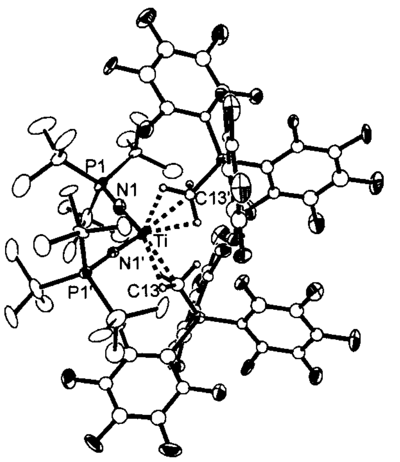

Figure 1. ORTEP drawing of **3** (30% thermal ellipsoids are shown). All hydrogen atoms except those of the B-bound methyl groups are omitted for clarity.

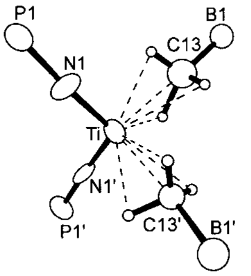

Figure 2. Molecular structure of the core of **3**. Selected bond lengths [Å] and angles [°]: Ti–N1 1.757(5), Ti–C13 2.333(7), P1–N1 1.628(5); N1-Ti-N2 115.4(3), N1-Ti-C13 109.1(2), C13-Ti-C13′ 104.6(4), P1-N1-Ti 176.3(3), B1-C13-Ti 175.0(5).

phosphanimide ligands and the carbon atoms of the two methyl groups of the two borate anions (Figure 2). The geometry about N is nearly linear, similar to that observed in other phosphanimide complexes.[9, 10] However, the Ti–N distance is 1.757(5) Å, which is significantly shorter than the corresponding Ti–N distance of 1.827(2) Å seen in the neutral precursor **1**. In addition, the P–N distance of 1.628(5) Å is longer than that in **1** (1.561(2) Å). These data are consistent with strengthened Ti–N bonds attributable to the formal +2 charge at the Ti center. It is noteworthy that the N-Ti-N angle of 115.4(3)° in **3** is significantly smaller than the Cp-Ti-N angle of 131.2° seen in the zwitterionic species [CpTi(NP*t*Bu$_3$)Me{μ-MeB(C$_6$F$_5$)$_3$}] (**4**).[10] The Ti–C distance in **3** is 2.333(7) Å, which compares to the longer Ti–C(borate) distance of 2.404(4) Å in **4**, and the Zr–C(borate) distances of 2.549(3) and 2.667(5) Å in [(C$_5$H$_3$Me$_2$)$_2$ZrMe{μ-MeB(C$_6$F$_5$)$_3$}] (**5**)[12] and [{C$_5$H$_3$(SiMe$_3$)$_2$}$_2$ZrMe{μ-MeB(C$_6$F$_5$)$_3$}] (**6**),[19] respectively. The nearly linear Ti-C-B angle in **3** (Ti-C-B$_{\mathrm{av}}$ 175.0(5)°) is significantly larger than the corresponding M-C-B angles in **4**–**6** of 167.2(3)°, 161.8(2)°, and 170.5(3)°, respectively. The positions of the hydrogen atoms of the B-bound methyl groups in **3** were located and refined. For the methyl group, two of the three protons were slightly closer to the metal center than the third, reminiscent of the M–methyl interactions in **4**–**6**. The range of the Ti–H distances in **3** (2.201–2.351 Å; Figure 2) is comparable to that of the Ti–H distances in the related zwitterionic species **4** (2.197–2.435 Å).[10] The close approach of the methyl group to the Ti center reflects the formal +2 charge at Ti in **3**. While donor-[22–26] or metal-arene-stabilized[27] dicationic complexes are known, **3** represents an unprecedented example of a zwitterionic dicationic complex.

The gross structural features of **3** support the view that phosphanimide ligands provide a sterically protective shell, which is remote from the metal center. While it may be postulated that a bisphosphanimide metal fragment provides a steric analogy to a metallocene, the more remote nature of the steric demands in phosphanimide ligands appears to permit greater access to the metal coordination sphere. This proposition is supported by the close approach of the borate anions to Ti in **3**. Moreover, this view is consistent with our observation that the complexes [Cp$_2$ZrMe$_2$], [Cp$_2$TiMe$_2$], [CpTi(NP*t*Bu$_3$)Me$_2$], and [(C$_5$H$_4$SiMe$_2$N*t*Bu)TiMe$_2$] fail to react with more than one equivalent of B(C$_6$F$_5$)$_3$. Presumably, steric congestion closer to the metal center precludes reactivity, although these species are expected to be more nucleophilic than **1**.

Compound **3** exhibits negligible polymerization activity when placed in solution under an atmosphere of ethylene. In addition, **3** is stable with respect to conproportionation, undergoing no reaction with added **1**. This stability of **3** is not surprising given the steric crowding and the formal +2 charge at the Ti center and is consistent with the observed dependence of catalytic activity on the order of addition of **1** and B(C$_6$F$_5$)$_3$. Moreover, these observations demonstrate that while B(C$_6$F$_5$)$_3$ activates **1** to generate the active catalyst **2**, excess B(C$_6$F$_5$)$_3$ acts to poison **2** affording the inactive compound **3**. This is the first such evidence of this duality for B(C$_6$F$_5$)$_3$.

In conclusion, the reaction of **1** with an excess of the Lewis acid B(C$_6$F$_5$)$_3$ yields the first bis-borate-zwitterionic species **3**. The isolation and characterization of **3** clearly defines a deactivation pathway for the active catalyst **2** in the presence of excess B(C$_6$F$_5$)$_3$. Moreover, this work demonstrates the importance of the order of addition for the pre-catalyst and activator as this is the first evidence, to our knowledge, that B(C$_6$F$_5$)$_3$ may act as a catalyst poison.

Experimental Section

3: A solution of complex **1** (0.200 g, 0.392 mmol) in CH$_2$Cl$_2$ (2 mL) was added to a solution of B(C$_6$F$_5$)$_3$ (0.421 g, 0.822 mmol) in the same solvent (2 mL). The solution turned bright yellow within seconds, and was stirred for 30 min at room temperature. The solvent was removed under vacuum to yield light yellow **3** (0.570 g, 0.371 mmol, 95%). ^{1}H NMR (CD$_2$Cl$_2$, 25°C): $\delta = 1.52$ (d, $^3J_{\mathrm{P,H}} = 14.6$ Hz, 52H; PCMe$_3$), 0.49 (s, 6H; MeB); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$, 25°C): $\delta = 150.4$, 147.3, 139.1, 135.2, 39.9 ($^1J_{\mathrm{P,C}} = 39.0$ Hz), 29.9 (br), 29.5; ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 25°C): $\delta = 60.57$; ^{11}B{^{1}H} NMR (CD$_2$Cl$_2$, 25°C): $\delta = -15.22$; ^{19}F{^{1}H} NMR (CD$_2$Cl$_2$, 25°C): $\delta = -55.80$ (d, $^3J_{\mathrm{FF}} = 22.0$ Hz), -87.87 (d, $^3J_{\mathrm{FF}} = 20.6$ Hz), -90.44 (d, $^3J_{\mathrm{FF}} = 21.0$ Hz); elemental analysis (%) calcd for $C_{62}H_{60}B_2F_{30}N_2P_2Ti$: C 47.06; H 3.82; N 1.77; found: C 46.86, H 3.69, N 1.73.

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[21] Crystal structure analysis of **3**: monoclinic, space group $C2/c$, $a = 23.417(9)$, $b = 14.776(6)$, $c = 22.678(8)$ Å, $\beta = 109.98(3)^{\circ}$, $V = 7374.2(49)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.535$, $\mu = 0.421$, 5661 reflections, 486 parameters, $R = 0.0823$, $Rw = 0.1827$, GOF = 1.002. Diffraction experiments were performed on a Siemens SMART System CCD diffractometer, and the structure was solved with the SHELX-TL software package. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134941. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
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A G-Quartet Formed in the Absence of a Templating Metal Cation: A New 8-(*N*,*N*-dimethylaniline)guanosine Derivative[**]

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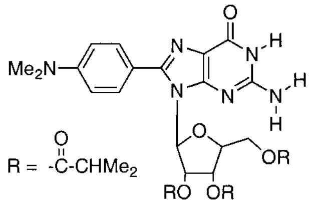
Katherine Doerr, Vincent Lynch, and
Khalil A. Abboud

Dedicated to Professor Jean-Marie Lehn
on the occasion of his 60th birthday

Self-assembly is one of the more intriguing subfields within the general area of molecular recognition. Indeed, quite a number of natural and unnatural molecules form ordered supramolecular ensembles by self-assembly.[1] Notable among these is guanosine, a compound known to self-assemble into dimeric,[2] tetrameric,[3] ribbonlike,[4] and helical structures[5] as the result of Watson–Crick and Hoogsteen base-pairing interactions. The tetrameric forms of guanosine, known also as G-quartets, have drawn considerable attention over the past three decades. They have been implicated in a variety of biological functions[6] and have seen application in a range of nonbiological areas such as ionophores[7] and phase-transfer catalysts.[8] X-ray analyses of crystals obtained from aqueous solutions of 5′- and 3′-guanosine monophosphate revealed that the constituent bases adopt a tetrameric planar arrangement, which then stacks in a helical fashion with other tetramers to form columnar aggregates.[9]

Currently, it is believed that templating alkali metal cations such as Na^+ and K^+ are needed to stabilize the formation of G-quartets.[10] The need for such cations to stabilize self-assembled and higher order aggregates formed from lipophilic deoxyguanosine derivatives in chlorinated organic solvents (that is, G-quartet model systems) has also been explicitly noted.[4, 7] Indeed, in the absence of alkali metal cations these compounds were found to adopt a ribbonlike structure (but not G-quartets) in both chloroform solution[4a] and in the solid state.[4b] Here, we report the synthesis of the new (*N*,*N*-dimethylaniline)guanosine derivative **1** that forms a G-quartet in the absence of alkali metal



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