Novel zwitterionic complexes of Ti(IV) *via* reaction of Lewis acids $M(C_6F_5)_3$ (M = B, Al) with a titanium diene complex (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(1,3-pentadiene)

Alan H. Cowley,* Gregory S. Hair, Brian G. McBurnett and Richard A. Jones*

Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, Texas 78712, USA.
E-mail: cowley@mail.utexas.edu

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The reaction of (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(1,3-pentadiene) with $B(C_6F_5)_3$ or $Al(C_6F_5)_3$ in 1 : 1 mole ratio in hexane solution at room temperature results in the formation of titanium borate or aluminate zwitterions which both feature stabilisation of the Ti(IV) centre by two agostic Ti···H–C interactions.

It has been demonstrated recently that Cp_2Zr(butadiene) reacts readily with $B(C_6F_5)_3$ to afford a zirconium borate zwitterion (**1**) that is an active catalyst for α-olefin polymerization.[1] An important structural facet of this zwitterion is the presence of a weak dative interaction between an *ortho*-fluorine of one of the BC_6F_5 groups and an otherwise vacant coordination site on zirconium.[2] We report here (i) the first structurally characterised example of a new type of titanium borate zwitterion that does not involve intramolecular F→metal stabilisation,† and (ii) the first example of an analogous titanium aluminate zwitterion. In addition, both complexes feature stabilisation of the Ti(IV) metal centre by two agostic C–H···Ti interactions.

It has been reported[3] that, when treated with $B(C_6F_5)_3$, the bridged monocyclopentadienyl titanium diene complex (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(1,3-pentadiene) **2** forms an active olefin polymerization catalyst. We have found that the reaction of **2** with an equimolar quantity of $B(C_6F_5)_3$ in hexane at 25 °C affords a virtually quantitative yield of a dark green crystalline solid (mp 156–157 °C) with an empirical composition (η^5-$C_5Me_4SiMe_2N^tBu$)Ti(1,3-pentadiene)·$B(C_6F_5)_3$ **3**.‡ An X-ray diffraction study of **3** (Fig. 1)§ revealed a zwitterionic structure in which the $B(C_6F_5)_3$ group is bound to the terminal $-CH_2$ carbon atom (C(1)) of the original pentadiene ligand. The C(2)–C(3) and C(3)–C(4) bond distances and the C(2)–C(3)–C(4) bond angle of the coordinated diene are similar to those reported by Erker *et al.*[1] for **1** hence the C(2)–C(3)–C(4) moiety can be regarded as being η^3-attached to the metal. However, the metal–C(2)–C(1) bond angle in **3** is considerably more acute (74.08(10)°) than the corresponding bond angle in **1** such that the Ti–C(1)–B fragment is almost linear (Ti–C(1)–B = 174.1(1)°), the Ti–C(1) distance is short (2.360(2) Å), and the C(1)–B distance is longer in **3** (1.705(3) Å) than in **1** (1.633(9) Å). Collectively, the foregoing structural features strongly suggested the presence of agostic C–H···Ti interactions for the CH_2 hydrogens of C(1). This surmise was confirmed in the later stages of refinement of the X-ray structure. Both hydrogen atoms attached to C(1) were located and refined with isotropic thermal parameters and show relatively short Ti···H distances (Ti–H(1A) = 2.20(2); Ti–H(1B) = 2.27(2) Å). Further support for the existence of the proposed agostic interactions stemmed from the observation of a C–H stretching frequency at 2669 cm^{-1} in the IR spectrum (Nujol mull). ^1H, ^{13}C, and ^{11}B NMR spectroscopic data¶ are also consistent with the X-ray analysis, thus implying that the solid state structure persists in solution. The ^{11}B chemical shift for **2** (δ −8.4) falls in the region observed for four-coordinate boron.[4] Three additional points are worth noting regarding the NMR data. Firstly, a two-dimensional ^1H–^{13}C study (at 500 and 125 MHz) revealed that the N–^tBu and *Me*CHCHCHCH$_2$ signals overlap at δ −1.05. Secondly, the carbon attached to boron, C(1), is not observed in the ^{13}C NMR spectrum, and finally there is a ≈ 1.0 ppm difference in the ^1H chemical shifts for the C(1) methylene protons. The primary cause of this difference in chemical shifts is probably the existence of the chiral centre at titanium. However, other possible contributors include (i) the influence of the ring current from the tetramethylcyclopentadienyl group and (ii) only one H atom may be agostic in solution.

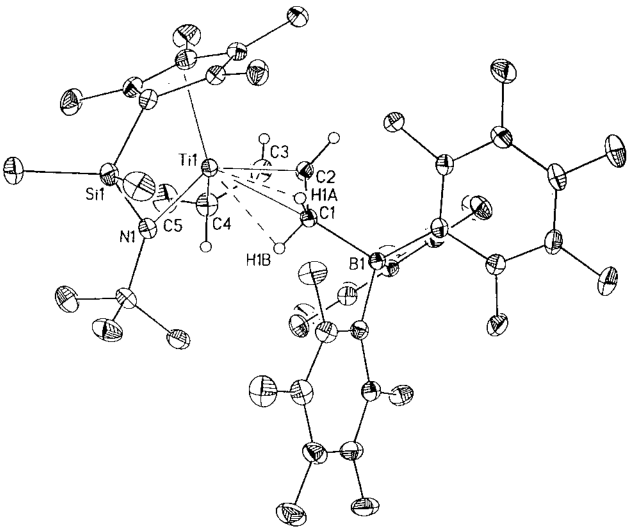

Fig. 1 X-Ray crystal structure of **3**. Selected bond distances (Å) and angles (°) for **3** (the corresponding values for **4** are shown in parentheses with Al(1) replacing B(1)): Ti(1)–C(1) 2.360(2) (2.355(2)), Ti(1)–C(2) 2.282(2) (2.261(3)), Ti(1)–C(3) 2.327(2) (2.344(3)), Ti(1)–C(4) 2.233(2) (2.271(3)), Ti(1)–H(1A) 2.20(2) (2.27(3)), Ti(1)–H(1B) 2.27(2) (2.45(3)), C(1)–B(1) 1.706(3) (2.052(3)), C(1)–C(2) 1.494(3) (1.479(5)), C(2)–C(3) 1.382(3) (1.386(5)), C(3)–C(4) 1.413(3) (1.416(5)), C(4)–C(5) 1.505(3) (1.512(5)), B(1)–C(1)–C(2) 116.8(2) (108.3(2)), C(1)–C(2)–C(3) 125.8(2) (126.6(3)), C(2)–C(3)–C(4) 125.8(2) (125.4(3)), C(3)–C(4)–C(5) 121.9(2) (120.3(3)). Thermal ellipsoids are drawn at the 30% level.

The reaction of **2** with $Al(C_6F_5)_3$ in hexane solution at 25 °C afforded high yields of **4**, the aluminium analogue of **3**.‡ To our knowledge, this represents the first example of a titanium aluminate zwitterion of this type. Structural authentication was provided by an X-ray crystallographic study§ which demonstrated that the geometry of **4** is very similar to that of **3** (Fig. 2). Two agostic Ti–H–C interactions are present with Ti–H(1A) and Ti–H(1B) distances of 2.27(3) and 2.45(3) Å, respectively. As in the case of **3**, NMR spectroscopic data indicate that the solution and solid state structures are very similar. The only significant difference in the ^1H and ^{13}C NMR spectra for **3** and **4** is that in the latter there is no overlap of the N–^tBu and diene methyl ^1H resonances.

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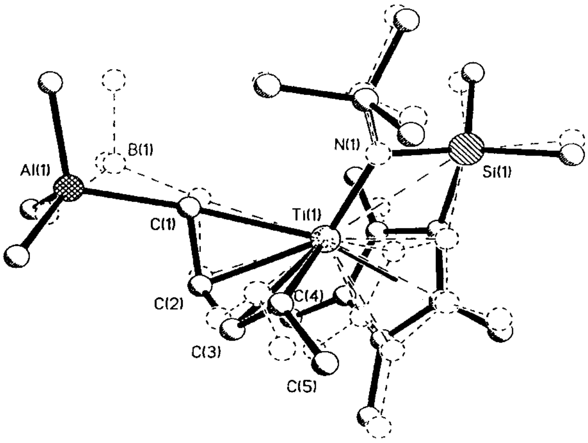

Fig. 2 Comparison of the ball-and-stick structures of **3** and **4**.

Notes and references

† A referee has suggested that the structural differences between the title compounds and the zirconium borate zwitterion (**1**) may be due to the greater electron deficiency at titanium.

‡ *Experimental procedures*: **3**: all manipulations were performed under an atmosphere of dry nitrogen or under vacuum using a Vacuum Atmospheres drybox or standard Schlenk techniques. All solvents were dried prior to use. A solution of $B(C_6F_5)_3$ (1.06 g, 2.07 mmol) in hexane (75 ml) was added to a solution of **2** (0.754 g, 2.06 mmol) in hexane at 25 °C with stirring. A dark green precipitate of **3** formed immediately and was collected and dried under vacuum. X-Ray quality crystals of **3** were grown by slow cooling of concentrated hexane solutions from 50 °C to room temperature. Isolated yield: 1.43 g, 80%; ^{1}H NMR assay indicated that the reaction is essentially quantitative. (Found: C, 52.02; H, 4.19; Ti, 5.45. Calc. for $C_{38}H_{35}BF_{15}NSiTi$: C, 52.02; H, 4.02; Ti 5.46%). Compound **4** was prepared in a similar fashion to that described for **3**.

§ *Crystal data*: **3**, $C_{38}H_{35}BF_{15}NSiTi$, M = 877.47, triclinic, space group $P\bar{1}$, a = 10.243(1), b = 11.376(1), c = 16.419(2) Å, α = 78.67(1), β = 79.45(1), γ = 84.85(1)°, U = 1841.3(3) Å^3, Z = 2, μ = 3.72 cm^{-1}, D_c = 1.583 Mg m^{-3}, $F(000)$ = 892, λ = 0.71073 Å, T = 183 K. Data for **3** and **4** were collected on a Siemens P4 diffractometer. Of a total of 9281 collected reflections, 8284 were unique. The structure was solved by direct methods. The hydrogens on the coordinated diene were located; the remaining hydrogens were placed in calculated positions (C–H, 0.96 Å). Refinement was by full matrix least squares on F^2 with anisotropic displacement parameters for the non-located H atoms. Final R indices [$I > 2\sigma(I)$], $R1$ = 0.0410, $wR2$ = 0.1092.

4, $C_{45}H_{43}AlF_{15}NSiTi$, M = 985.77, monoclinic, space group $P2_1/n$, a = 10.879(3), b = 38.665(6), c = 11.069(2) Å, β = 107.19(2)°, U = 4448(1) Å^3, Z = 4, μ = 3.36 cm^{-1}, D_c = 1.472 Mg m^{-3}, $F(000)$ = 2016, λ = 0.71073 Å, T = 183 K. Of a total of 12 132 collected reflections, 10 205 were unique. The structure was solved by direct methods. The hydrogens on the coordinated diene were located; the remaining hydrogens were placed in calculated positions (C–H, 0.96 Å). Refinement was by full matrix least squares on F^2 with anisotropic displacement parameters for the non-located H atoms. Final R indices [$I > 2\sigma(I)$], $R1$ = 0.0536, $wR2$ = 0.1116. CCDC 182/1160. See http://www.rsc.org/suppdata/cc/1999/437/ for crystallographic files in .cif format.

¶ NMR data for **3**: ^{1}H NMR (500 MHz, C_6D_6) δ −0.37 (s, CH_2-diene, 1H), 0.35 (br s, $SiCH_3$, 3H), 0.58 (s, SiMe, 3H), 0.88 (br s, CH_2-diene, 1H), 1.05 (s, N^{t}Bu + CH_3-diene, 12H), 1.22 (s, CpMe, 3H), 1.28 (s, CpMe, 3H), 1.29 (s, CpMe, 3H), 1.85 (s, CpMe, 3H), 3.26 (m, CH-diene, 1H), 3.90 (m, CH-diene, 1H), 4.91 (m, CH-diene, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6) δ 6.42 (s, $SiCH_3$), 6.81 (s, $SiCH_3$), 10.83 (s, $CpCH_3$), 12.19 (s, $CpCH_3$), 14.37 (s, $CpCH_3$), 14.46 (s, $CpCH_3$), 18.74 (s, CH_3(diene)), 33.79 (s, CH_3-^{t}Bu), 61.42 (s, C-^{t}Bu), 90.32 (s, CH-diene), 110.52 (s, C(Cp)), 112.04 (s, CH-diene), 127.45 (s, CpMe(Cp)), 130.56 (s, CH-diene), 132.75 (s, CMe(Cp)), 134.85 (s, CMe(Cp)), 137.88 (s, CMe(Cp)), 136.50 (m, C(C_6F_5)), 138.50 (m, CF), 147.69 (m, CF), 149.55 (m, CF). ^{19}F NMR (282 MHz, C_6D_6) δ −129.0 (m, *o*-F, 6F), −157.9 (m, *p*-F, 3F), −163.1 (m, *m*-F, 6F). ^{11}B NMR (96 MHz, C_6D_6) δ −8.4.

NMR data for **4**: ^{1}H NMR (500 MHz, C_6D_6) δ −0.09 (d, CH_2-diene, 1H, ^3J = 3.8), 0.33 (s, $SiCH_3$, 3H), 0.54 (s, $SiCH_3$, 3H), 0.72 (d, CH_2-diene, 1H, ^3J = 15.5), 1.05 (s, N^{t}Bu, 9H), 1.12 (d, CH_3-diene, 3H, ^3J = 5.8), 1.15 (s, $CpCH_3$, 3H), 1.18 (s, $CpCH_3$, 3H), 1.31 (s, $CpCH_3$, 3H), 1.73 (s, $CpCH_3$, 3H), 3.02 (qd, CH-diene, 1H), 4.14 (m, CH-diene, 1H), 4.69 (dd, CH-diene, 1H, ^3J = 9.93, 13.75). $^{13}C\{^1H\}$ NMR (125 MHz, C_6D_6) δ 6.26 (s, $SiCH_3$), 7.36 (s, $SiCH_3$), 10.71 (s, $CpCH_3$), 11.84 (s, $CpCH_3$), 14.02 (s, $CpCH_3$), 14.98 (s, $CpCH_3$), 18.87 (s, CH_3-diene), 33.93 (s, CH_3^{t}Bu), 60.91 (s, C-^{t}Bu), 89.83 (s, CH-diene), 109.36 (s, C(Cp)), 112.44 (s, CH-diene), 127.45 (s, CH-diene), 130.75 (s, CMe(Cp)), 133.12 (s, CMe(Cp)), 135.49 (s, CMe(CP)), 136.20 (m, CF), 138.25 (s, CMe(Cp)), 149.47 (m, CF). ^{19}F NMR (282 MHz, C_6D_6) δ −121.9 (m, *o*-F, 6F), −153.9 (m, *p*-F, 3F), −161.9 (m, *m*-F, 6F).

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