Formation and reactivity of cationic alkyl derivatives of titanium containing *ortho*-(1-naphthyl)phenoxide ligation

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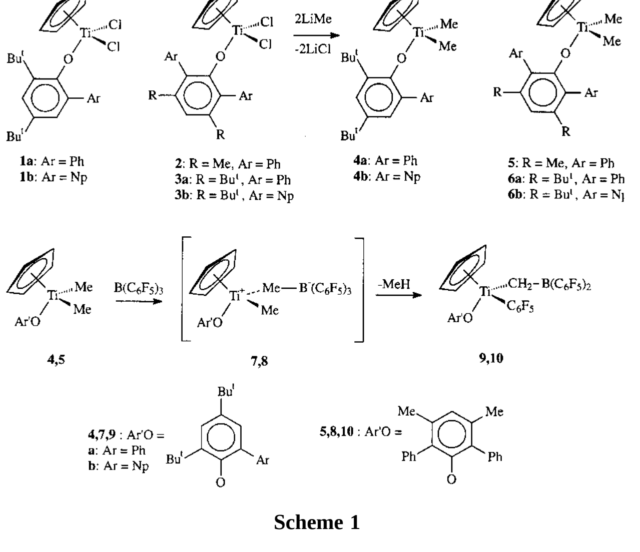
A series of dimethyl compounds of Ti(IV) have been isolated containing both cyclopentadiene and *ortho*-arylphenoxide ligation; reaction with [B(C_6F_5)$_3$] generates corresponding cationic methyl species which eliminate methane and form [Cp(ArO)Ti{$CH_2B(C_6F_5)_2$}(C_6F_5)] derivatives.

There is continued research interest in the chemistry of cationic Group 4 metal alkyl compounds.[1] We have recently isolated a series of titanium chloride compounds containing both cyclopentadiene and *o*-arylphenoxide ligation.[2,3] We report here on the structure, dynamics and reactivity of the corresponding neutral and cationic methyl derivatives.[4,5]

Treatment of **1**–**3** with LiMe leads to the corresponding dimethyl compounds **4**–**6** as yellow solids (Scheme 1, Np = 1-naphthyl).† The solid state structure of **4b** is shown in Fig. 1.‡ The Ti–Me distances of 2.076(4) and 2.091(4) Å are intermediate between those reported for [Cp_2TiMe_2],[6] 2.170(2) and 2.181(2) Å, and values of 2.052(2) and 2.069(2) Å found in [Ti($OC_6H_3Ph_2$-2,6)$_2$Me$_2$].[7] There is also a corresponding opening up of the Me–Ti–Me angle upon replacing Cp by OAr; *c.f.* 91.3(1)° for [Cp_2TiMe_2], 97.5(2)° in **4b** and 103.9(1)° in [Ti($OC_6H_3Ph_2$-2,6)$_2$Me$_2$]. In the solution NMR spectra of **4a**, **5** and **6a**, only one signal is present for the Ti–Me groups in the ^{1}H and ^{13}C NMR spectra. This indicates in the case of **4a** that rotation about the Ti–O–Ar bonds is fast on the NMR timescale. In contrast two well-resolved Ti–Me resonances are observed for the *o*-(1-naphthyl) derivatives **4b** and **6b**. In the case of **6b** this is consistent with the presence of the chiral, *dl*-form of the ligand. Variable temperature NMR studies of **4b** show that the two methyl signals remain sharp even at 90 °C (toluene-d_8), indicating slow naphthyl rotation on the NMR timescale at this temperature.

Addition of [B(C_6F_5)$_3$][8] to **4**,**5** in benzene or toluene solvent leads to the rapid (NMR) formation of the thermally unstable (*vide infra*) cationic **7**,**8**. Variable temperature spectra of these species are highly informative. Low temperature ^{1}H and ^{13}C NMR spectra of **7a** and **8** show a single set of Cp and OAr resonances along with resolved Ti-Me (sharp) and Ti-Me-B (broad) resonances. Spectra obtained for **7a** at ambient temperature show broadening of these methyl signals, but the thermal instability precludes obtaining limiting high temperature spectra. We interpret this broadening as due to exchange of the boron between methyl groups (boron exchange) which is becoming fast on the NMR time scale. For **7b**, two broad methyl signals and a single, sharp Cp resonance are present at room temperature. At −10 °C (toluene-d_8) the Ti-Me and Ti-Me-B signals sharpen up, but there is still only a single Cp resonance. At −30 °C the Cp resonance splits into two signals in the ratio of 80 : 20 representing the two, diastereoisomeric forms. The methyl signals also split into two large, equal intensity signals and one resolvable smaller peak (presumably the second methyl signal is obscured by OAr resonances). We interpret these changes as representing two distinct dynamic processes. The faster process involves exchange between the two diastereoisomers (80 : 20 ratio) of **7b** (Scheme 2) without methyl exchange. This process involves cation–anion dissociation and rearrangement and can only be detected using the chiral *o*-(1-naphthyl)phenoxide. An alternative process for exchange of diastereoisomers would involve naphthyl rotation. However, the variable temperature NMR studies on **4b** and data presented below show that this process is too slow to account for the observed process. The slower process in **7b**, which is also detected for **7a** and **8**, involves Ti-Me/Ti-Me-B exchange. In the case of **7b** this process alone cannot lead to exchange of methyl signals in the NMR spectra. However, when coupled with the faster ion-pair dissociation, it leads to methyl exchange (Scheme 2). Previous work by Marks *et al.* has shown similar dynamics are present in [Cp′$_2$Zr(Me)-{MeB(C_6F_5)$_3$}] species.[8] Based upon the spectra obtained for **7b** we estimate the free energy of activation for ion-pair dissociation to be 12.4(5) kcal mol^{-1} at −25 °C (Cp



Scheme 1

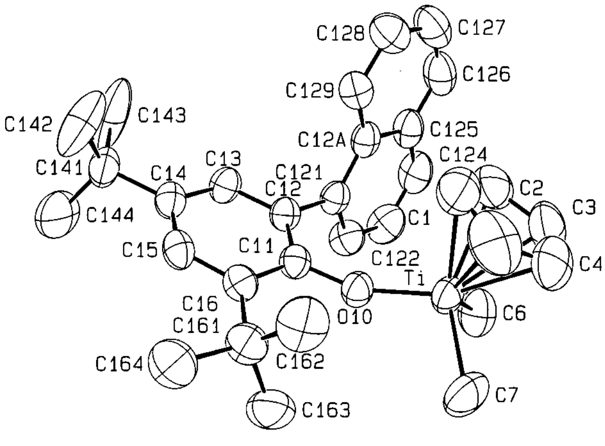
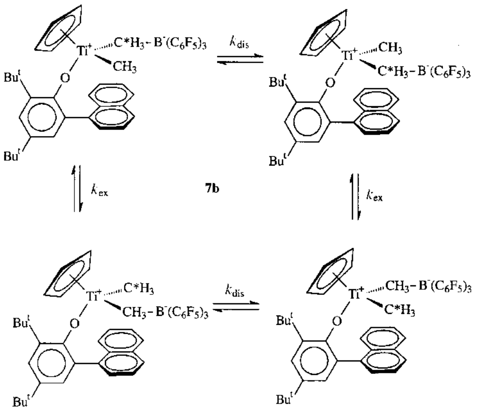


Fig. 1 Molecular structure of **4b** showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ti–O(10) 1.815(2), Ti–C(6) 2.076(4), Ti–C(7) 2.091(4), C(6)–Ti–C(7) 97.5(2), Cp–Ti–O(10) 123.7(2), Ti–O(10)–C(11) 158.8(2).



Scheme 2

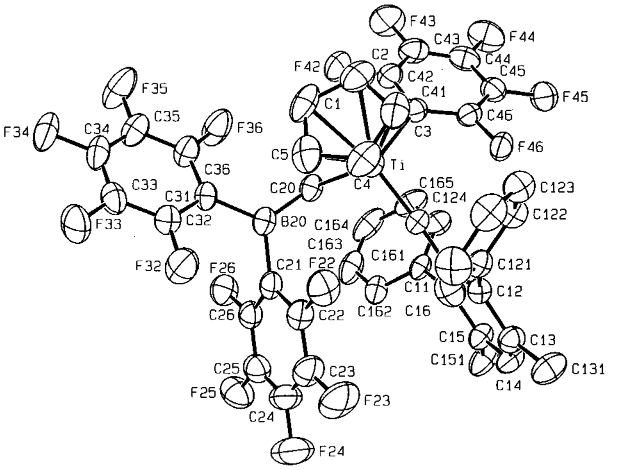


Fig. 2 Molecular structure of **10** showing the atomic numbering scheme. Selected interatomic distances (Å) and angles (°): Ti–O(10) 1.770(2), Ti–C(20) 2.115(2), Ti–C(41) 2.176(2), Cp–Ti–O(10) 126.9(1), C(20)–Ti–C(41) 98.73(8), Ti–O(10)–C(11) 176.2(1).

coalescence temperature at 300 MHz) while that for the methyl exchange is 15.0(5) kcal mol^{-1} at −35 °C.

When monitored by ^{1}H NMR, solutions of **7**,**8** at ambient temperatures over hours eliminate methane and form the neutral species **9**,**10** (Scheme 2). The solid state structure of **10** (Fig. 2) confirms the molecular structure and shows that the boron atom is trigonal planar with no interaction present with the adjacent Ti-C_6F_5 unit.[9] In the ^{1}H NMR spectra of **9a** and **10**, a single set of Cp and OAr resonances are present along with well-resolved diastereotopic Ti-CH_2-B protons. In the case of **9b** containing the chiral *o*-(1-naphthyl) ligand, two sets of sharp NMR signals are present representing a 70 : 30 mixture of the two possible diastereoisomers. The fact that exchange of these isomers is slow on the NMR timescale at ambient temperature confirms that naphthyl rotation cannot account for the observed fluxionality in **7b**.

Notes and references

† *Selected spectroscopic data*: aromatic signals unless indicated: ^{1}H NMR (C_6D_6, 30 °C, unless otherwise stated) **4a**: δ 6.70–7.60; 5.57 (s, C_5H_5); 1.68 (s), 1.32 [s, $C(CH_3)_3$]; 0.85 (s, CH_3). **4b**: δ 7.10–8.00; 5.41 (s, C_5H_5); 1.64 (s), 1.26 [s, $C(CH_3)_3$]; 0.58 (s), 0.15 [s, CH_3]. **5**: δ 7.07–7.29; 6.82 (s, *para*-H); 5.63 (s, C_5H_5); 2.09 (s, *meta*-CH_3); 0.26 (s, Ti-CH_3). **6a**: δ 7.71 (s, *para*-H); 7.31–7.02 (m); 5.75 (s, C_5H_5); 1.29 [s, $C(CH_3)_3$]; 0.10 (s, CH_3). **6b**: δ 7.90 (s, *para*-H); 7.62–7.15 (m); 5.17 (s, C_5H_5); 1.21 [s, $C(CH_3)_3$]; −0.35, −0.81, (s, CH_3). **7a**: δ 6.87–7.45; 5.44 (s, C_5H_5); 1.43 (br, Ti-CH_3); 1.34 (s), 1.19 [s, $C(CH_3)_3$]; 0.90 (br, B-CH_3). (C_7D_8, −10 °C): δ 6.91–7.40; 5.37 (s, C_5H_5); 1.52 (s, Ti-CH_3); 1.32 (s), 1.16 [s, $C(CH_3)_3$]; 0.94 (br, B-CH_3). **7b**: δ 7.05–7.68; 5.36 (s, C_5H_5); 1.32 (s), 1.19 [s, $C(CH_3)_3$]; 0.91 (br, Ti-CH_3); 0.81 (br, B-CH_3). (C_7D_8, −10 °C): δ 6.97–7.68; 5.27 (s, C_5H_5); 1.31 (s), 1.15 [s, $C(CH_3)_3$]; 0.96 (br, Ti-CH_3); 0.77 (br, B-CH_3). ^{1}H NMR (C_7D_8, −30 °C): δ 6.96–7.67; 5.23 (s, C_5H_5-major); 5.14 (s, C_5H_5-minor); 1.31 (s), 1.21 [s, $C(CH_3)_3$]; 0.95 (br, Ti-CH_3-major); 0.76 (br, B-CH_3-major); 0.54 (br, B-CH_3-minor). **8**: δ 6.80–7.32; 6.74 (s, *para*-H); 5.44 (s, C_5H_5); 1.90 (s, *meta*-CH_3); 0.68 (br, Ti-CH_3); 0.53 (br, B-CH_3). (C_7D_8, −20 °C): δ 6.63–7.14; 5.39 (s, C_5H_5); 1.87 (s, *meta*-CH_3); 0.67 (s, Ti-CH_3); 0.46 (br, B-CH_3). **9a**: δ 7.56 (d), 7.13 [d, $^4J(^1H–^1H)$ = 2.5 Hz, *meta*-H]; 6.10 (s, C_5H_5); 4.21 (br), 3.23 (br, Ti-CH_2-B); 1.62 (s), 1.26 [s, $C(CH_3)_3$]. **9b**: δ 6.72–7.86; 6.24 (s), 5.80 (s, C_5H_5); 4.16 (br), 4.14 (br), 3.00 (m, Ti-CH_2-B); 1.60 (s), 1.57 (s), 1.19 (s), 1.15 [s, $C(CH_3)_3$]. **10**: δ 6.85–7.18; 6.68 (s, *para*-H); 5.65 (s, C_5H_5); 3.56 (br), 2.67 (br, Ti-CH_2-B); 1.84 (s, *meta*-CH_3). ^{13}C NMR (C_6D_6, 30 °C) **4a**: δ 160.8 (Ti-O-C); 114.4 (C_5H_5); 58.4, (Ti-CH_3); 35.8, 34.5 [$\mathit{C}(CH_3)_3$]; 31.7, 30.5 [$C(\mathit{C}H_3)_3$]. **4b**: δ 161.6 (Ti-O-C); 114.1 (C_5H_5); 58.4, 57.8 (Ti-CH_3); 35.8, 34.6 [$\mathit{C}(CH_3)_3$]; 31.7, 30.6 [$C(\mathit{C}H_3)_3$]. **5**: δ 161.1 (Ti-O-C); 113.7 (C_5H_5); 56.1, (Ti-CH_3); 20.8 (*meta*-CH_3). **6a**: δ 163.0 (O-C); 147.5, 140.8, 132.6, 130.9, 128.3, 126.9, 118.7; 113.5 (C_5H_5); 56.9 (CH_3); 37.4, [$\mathit{C}(CH_3)_3$]; 33.1 [$C(\mathit{C}H_3)_3$]. **6b**: δ 163.6 (O-C); 152.0, 148.7, 138.9, 135.1, 134.0, 129.7, 126.0, 125.3, 119.9; 113.3 (C_5H_5); 56.5, 56.1 (CH_3); 37.7, [$\mathit{C}(CH_3)_3$]; 32.0 [$C(\mathit{C}H_3)_3$]. **7a**: δ 163.0 (Ti-O-C); 120.4 (C_5H_5); 113.0 (br, B-CH_3); 77.7 (br, Ti-CH_3); 35.1, 34.4 [$\mathit{C}(CH_3)_3$]; 30.8, 29.7 [$C(\mathit{C}H_3)_3$]. (C_7D_8, −10 °C): δ 163.2 (Ti-O-C); 120.7 (C_5H_5); 112.9 (br, B-CH_3); 77.4 (s, Ti-CH_3); 35.4, 34.7 [$\mathit{C}(CH_3)_3$]; 31.1, 30.0 [$C(\mathit{C}H_3)_3$]. **7b**: δ 163.3 (Ti-O-C); 119.9 (C_5H_5); 113.1 (br, B-CH_3); 79.4 (br, Ti-CH_3); 35.1, 34.4 [$\mathit{C}(CH_3)_3$]; 30.9, 30.0 [$C(\mathit{C}H_3)_3$]. **8**: δ 162.5 (Ti-O-C); 119.3 (C_5H_5); 113.0 (br, B-CH_3); 77.8 (Ti-CH_3); 19.9 (*meta*-CH_3). **9a**: δ 163.7 (Ti-O-C); 119.4 (C_5H_5); 107.1 (br, Ti-CH_2-B); 35.8, 34.7 [$\mathit{C}(CH_3)_3$]; 31.4, 30.6 [$C(\mathit{C}H_3)_3$]. **9b**: δ 164.4, 164.3 (Ti-O-C); 119.2, 119.0 (C_5H_5); 107.0, 105.5 (br, Ti-CH_2-B); 35.9, 35.8, 34.7, 34.7 [$\mathit{C}(CH_3)_3$]; 31.4, 31.4, 30.7, 30.6 [$C(\mathit{C}H_3)_3$]. **10**: δ 162.3 (Ti-O-C); 118.1 (C_5H_5); 114.2 (br, Ti-CH_2-B); 20.1 (*meta*-CH_3).

‡ *Crystal data* for **4b** at 296 K: $TiOC_{31}H_{38}$, M = 474.55, space group $P2_1/c$ (no. 14), a = 13.1917(8), b = 11.7251(6), c = 18.788(1) Å, β = 107.115(2)°, V = 2777.4(5) Å^3, D_c = 1.135 g cm^{-3}, Z = 4. Of the 6750 unique reflections collected ($4.54 \leqslant 2\theta \leqslant 61.36°$) with Mo-K$\alpha$ (λ = 0.71073 Å), the 6750 with $F_o^2 > 2\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o)$ = 0.064 and $R_w(F_o^2)$ = 0.166. For **10** at 203 K: $TiF_{15}OC_{44}BH_{24}$, M = 912.37, space group $P\bar{1}$ (no. 2), a = 12.2084(5), b = 12.3668(2), c = 13.7876(5) Å, α = 71.440(2), β = 84.811(1), γ = 83.982(2)°, V = 1958.9(2) Å^3, D_c = 1.547 g cm^{-3}, Z = 2. Of the 9835 unique reflections collected ($8.00 \leqslant 2\theta \leqslant 61.10°$) with Mo-K$\alpha$ (λ = 0.71073 Å), the 9835 with $F_o^2 > 2\sigma(F_o^2)$ were used in the final least-squares refinement to yield $R(F_o)$ = 0.052 and $R_w(F_o^2)$ = 0.126. CCDC 182/996.

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