DALTON

Synthesis of a series of new, highly electrophilic, monocyclopentadienyltitanium olefin polymerization initiators†

Mark J. Sarsfield, Sean W. Ewart, Tracey L. Tremblay, Aleksander W. Roszak and Michael C. Baird*

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L3N6

The new compounds $Ti(\eta-C_5Me_5)Me_2E$ ($E = C_6F_5$ or OC_6F_5) and $Ti(\eta-C_5Me_5)Me(OC_6F_5)_2$ have been synthesized and characterized by a variety of techniques, including $^{47/49}Ti$ NMR spectroscopy. All three compounds react with the borane $B(C_6F_5)_3$ to form the highly electrophilic but thermally unstable species $Ti(\eta-C_5Me_5)Me(E)(\mu-Me)B(C_6F_5)_3$ and $[(\eta-C_5Me_5)Ti(OC_6F_5)_2][BMe(C_6F_5)_3]$, the solution structures and dynamics of which are investigated and compared with those of the known compound $Ti(\eta-C_5Me_5)Me_2(\mu-Me)B(C_6F_5)_3$. Interestingly, $Ti(\eta-C_5Me_5)Me(C_6F_5)(\mu-Me)B(C_6F_5)_3$ undergoes neither significant ion-pair dissociation to the solvent separated ions $[(\eta-C_5Me_5)TiMe(C_6F_5)]^+$ and $[BMe(C_6F_5)_3]^-$ nor borane dissociation to its precursors $(\eta-C_5Me_5)TiMe_2(C_6F_5)$ and $B(C_6F_5)_3$; indeed, both rotation about the $Ti-C_6F_5$ bond and inversion at the chiral metal are slow on the NMR time-scale. In contrast, $Ti(\eta-C_5Me_5)Me(OC_6F_5)(\mu-Me)B(C_6F_5)_3$ is more labile and, like $Ti(\eta-C_5Me_5)Me_2(\mu-Me)B(C_6F_5)_3$, undergoes ion-pair dissociation, while $[(\eta-C_5Me_5)Ti(OC_6F_5)_2][BMe(C_6F_5)_3]$ exists in solution as the solvent separated ion species $[(\eta-C_5Me_5)Ti(OC_6F_5)_2]^+$ and $[BMe(C_6F_5)_3]^-$ in equilibrium with its precursors, $(\eta-C_5Me_5)TiMe(OC_6F_5)_2$ and $B(C_6F_5)_3$.

Since the early 1980s, there has been extensive research into the use of Group 4 metallocene compounds as homogeneous catalysts for olefin polymerization. The most successful catalysts are the formally 14-electron, cationic complexes $[Cp'_2MR]^+$ (Cp' = functionalized cyclopentadienyl; M = Ti, Zr or Hf; R = alkyl or H),[1–3] which contain a vacant co-ordination site and an alkyl ligand and which can therefore readily take part in co-ordination polymerization (Ziegler–Natta) processes with a variety of olefins. However, these complexes can also co-ordinate counter anions[2] and Lewis bases,[2] and are sometimes found to react with solvents,[4] all processes which can reduce the activity of the cationic moiety, and thus judicious choice of polymerization conditions is oft imperative. Of great relevance here, crystallographically characterized compounds of the type $Cp'_2MMe(\mu-Me)B(C_6F_5)_3$ have been studied intensively as precursors for the above-mentioned cationic species $[Cp'_2MR]^+$, and have provided valuable information concerning the optimal requirements of non-co-ordinating counter anions.[5–11]

Another family of compounds which satisfy the above requirements for Ziegler–Natta catalysis are 10-electron, monocyclopentadienyl complexes of the type $[Cp'MR_2]^+$. These electronically less saturated and sterically less hindered complexes might be expected to exhibit even higher reactivities than their metallocene counterparts, and we[12–20] have investigated several such systems in detail. Thus reaction of $Ti(\eta-C_5Me_5)Me_3$ with the strong Lewis acid $B(C_6F_5)_3$ results in the formation of the methyl-bridged complex $Ti(\eta-C_5Me_5)Me_2(\mu-Me)B(C_6F_5)_3$, which dissociates in solution to form $[Ti(\eta-C_5Me_5)Me_2]^+$,[17] an extremely active initiator for both carbocationic [isobutylene,[21] vinyl ethers,[15] styrene (below 0 °C)[16]] and Ziegler–Natta (ethylene,[16] hex-1-ene,[14] styrene[16,22] and propylene[19]) polymerization processes. Furthermore, while metallocene complexes permit catalyst fine tuning only *via* functionalizing of the cyclopentadienyl ring and changes in the counter anion, monocyclopentadienyl complexes contain a 'spectator' anionic ligand {methyl in the case of $[Ti(\eta-C_5Me_5)Me_2]^+$} and thus also offer the opportunity to alter the steric and electronic properties of the initiator system by changing the 'spectator' ligand.

The research described here began with the hypothesis that, since cationic complexes generally form more active polymerization catalysts than do neutral species,[1–3] it seemed possible that substitution of one of the methyl groups of $[Ti(\eta-C_5Me_5)Me_2]^+$ with a more electron-withdrawing ligand could result in the formation of more active initiators. This expectation is contrary to current conventional wisdom for metallocene systems, since incorporation of electron-withdrawing groups on the Cp' rings of some metallocenes has been reported to result in both decreased activity and reduced polymer molecular weights.[23] However, the relative rates of initiation, propagation, termination and chain transfer are all affected unpredictably by ligand substitution, and the reasons for the observed deactivation were not assessed in detail.[23] In addition, as has been shown,[5–11] enhanced Lewis acidity of the metal can result in stronger binding of the counter anion, possibly resulting in both inhibition of monomer co-ordination and more facile termination of polymer growth *via* olefin ligand substitution. Utilization of a counter anion which for steric or electronic reasons could not co-ordinate would obviate the latter modes of deactivation, and thus the effects of increased metal ion electrophilicity on overall initiator activity arguably remain moot.

While complexes of the type $[Ti(\eta-C_5Me_5)Me(OR)]^+$ have previously been synthesized and shown to be less active than $[Ti(\eta-C_5Me_5)Me_2]^+$,[16,24] the lower activities were probably a result of *decreased* electrophilicity of the metal because of π-electron donation of the alkoxy oxygen lone pairs to the empty d orbitals of the metal and/or dimerisation *via* bridging alkoxy ligands. Extending this work, we now describe the synthesis, characterization and solution chemistry of the compounds $Ti(\eta-C_5Me_5)Me_2E$ ($E = C_6F_5$ or OC_6F_5) and $Ti(\eta-C_5Me_5)Me(OC_6F_5)_2$, which contain highly electronegative, poor π-electron donors ligands. When reacted with $B(C_6F_5)_3$, these form respectively the anticipated species $Ti(\eta-C_5Me_5)MeE(\mu-Me)B(C_6F_5)_3$ and $[(\eta-C_5Me_5)Ti(OC_6F_5)_2][BMe(C_6F_5)_3]$, which exhibit interesting solution chemistry. Successful efforts to utilize these complexes as olefin polymerization catalysts will be described elsewhere.

---

† Dedicated to the memory of Geoff Wilkinson, a generous mentor in whose laboratory M. C. B. spent a very fruitful eighteen months.

Experimental

All manipulations were carried out, under dry, prepurified grade dinitrogen, using conventional Schlenk techniques, a Vacuum Atmospheres glove box and dried, thoroughly deoxygenated solvents. Proton, ^{13}C-{^{1}H} and ^{19}F NMR spectra were run using a Bruker AM 400 spectrometer operating at 400.14 MHz, 100.6 MHz and 376.5 MHz respectively; ^{1}H and ^{13}C-{^{1}H} NMR spectra are referenced with respect to internal SiMe$_4$ using residual proton resonances or carbon resonances, respectively, of the solvents, while ^{19}F spectra are referenced to external CFCl$_3$. Titanium-47,49 NMR spectra (Table 1) were obtained (50,000–100,000 transients were acquired on 1 M samples) on a Bruker AM400 spectrometer with a 10 mm diameter broad-band probe at ambient temperature, and are referenced to external TiCl$_4$. A Hewlett-Packard 8452A diode array spectrophotometer was used for measuring UV/VIS spectra. Elemental analyses for carbon and hydrogen were carried out by Canadian Microanalytical Services, Delta, British Columbia. The compounds Ti(η-C$_5$Me$_5$)Cl$_3$,[25] Ti(η-C$_5$Me$_5$)MeCl$_2$,[26] Ti(η-C$_5$Me$_5$)Me$_2$Cl,[26] Ti(η-C$_5$Me$_5$)Me$_3$[27] B(C$_6$F$_5$)$_3$[28a] and LiC$_6$F$_5$[28b] were prepared by literature methods.

Syntheses

Ti(η-C$_5$Me$_5$)Me$_2$(C$_6$F$_5$) 1. A solution of Ti(η-C$_5$Me$_5$)Me$_2$Cl (4.01 g, 16.1 mmol) in hexanes (200 cm^3) was added to a solution of LiC$_6$F$_5$ (18.8 mmol) in diethyl ether (30 cm^3) cooled to −78 °C. After stirring at −78 °C for 2 h, the resulting suspension was allowed to warm to room temperature before filtering through Celite. The deep red filtrate was concentrated *in vacuo* to a red oil before being recrystallised twice from hexanes at −78 °C. Yield 58% (Found: C, 56.43; H, 5.99. Calc. for C$_{18}$H$_{21}$F$_5$Ti: C, 56.86; H, 5.57%). ^{1}H NMR (CDCl$_3$): δ 1.98 (s, 15 H, C$_5$Me$_5$), 1.41 [t, 6 H, ^4J(HF) = 2 Hz, TiMe]. ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 127.0 (*C*$_5$Me$_5$), 80.0 [t, ^3J(CF) = 3 Hz, TiMe], 12.4 (C$_5$*Me*$_5$). ^{19}F NMR (C$_6$H$_6$): δ −121.4 (m, 2 F, *o*-F), −155.6 (t, 1 F, *p*-F), −163.0 (m, 2 F, *m*-F).

Ti(η-C$_5$Me$_5$)Me$_2$(OC$_6$F$_5$) 2. A solution of Ti(η-C$_5$Me$_5$)Me$_2$Cl (4.0 g, 16.1 mmol) and LiOC$_6$F$_5$ (3.1 g, 16.1 mmol) in hexanes (200 cm^3) was stirred at 0 °C for 4 h and then warmed to room temperature. The yellow suspension was filtered through Celite and dried under vacuum. The bright yellow solid was isolated pure after recrystallizing twice from hexanes at −78 °C. Yield 71% (Found: C, 54.34; H, 5.33. Calc. for C$_{18}$H$_{21}$F$_5$OTi: C, 54.56; H, 5.34%). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.86 (s, 15 H, C$_5$Me$_5$), 0.55 (s, 6 H, TiMe). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 141.1 [d, *J*(CF) = 231, *o*-CF], 138.7 [d, *J*(CF) = 241, *m*-CF], 135.5 [d, *J*(CF) = 241 Hz, *p*-CF], 124.2 (*C*$_5$Me$_5$), 59.0 (TiMe), 12.1 (C$_5$*Me*$_5$). ^{19}F NMR (CD$_2$Cl$_2$): δ −160.1 (m, 2 F, *o*-F), −167.0 (m, 2 F, *m*-F), −171.3 (t, 1 F, *p*-F).

Ti(η-C$_5$Me$_5$)Me(OC$_6$F$_5$)$_2$ 3. A solution of Ti(η-C$_5$Me$_5$)MeCl$_2$ (0.50 g, 1.85 mmol) and LiOC$_6$F$_5$ (0.70 g, 3.72 mmol) in hexanes (50 cm^3) was stirred at 0 °C for 4 h and then warmed to room temperature. The yellow suspension was filtered through Celite and dried under vacuum. The bright yellow solid proved difficult to purify and could only be isolated with small amounts of impurities of Ti(η-C$_5$Me$_5$)(OC$_6$F$_5$)$_3$. Yield 40% (Found: C, 48.00; H, 3.49. Calc. for C$_{23}$H$_{18}$F$_{10}$O$_2$Ti: C, 48.86; H, 3.22%). ^{1}H NMR (CD$_2$Cl$_2$): δ 1.89 (s, 15 H, C$_5$Me$_5$), 1.17 (3 H, TiMe). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 139.9 [d, *J*(CF) = 251, *o*-CF], 138.1 [d, *J*(CF) = 241, *m*-CF], 135.2 [d, *J*(CF) = 251 Hz, *p*-CF], 127.0 (*C*$_5$Me$_5$), 61.5 (TiMe), 10.9 (C$_5$*Me*$_5$). ^{19}F NMR (CD$_2$Cl$_2$): δ −162.0 (m, 2 F, *o*-F), −167.2 (m, 2 F, *m*-F), −171.7 [t, ^2J(FF) = 21 Hz, 1 F, *p*-F].

Ti(η-C$_5$Me$_5$)(OC$_6$HF$_4$-*p*)$_3$ 4. A solution of Ti(η-C$_5$Me$_5$)Cl$_3$ (1.00 g, 3.45 mmol) and LiOC$_6$HF$_4$-*p* (1.79 g, 10.40 mmol) in toluene (40 cm^3) was stirred at 0 °C for 1 h before being warmed to room temperature and stirred for a further 5 h. The orange suspension was filtered through Celite affording a clear orange solution. The solvent was removed *in vacuo* and crystals were grown from a toluene–hexanes solution at −10 °C. Yield 66% (Found: C, 50.18; H, 3.11. Calc. for C$_{28}$H$_{18}$F$_{12}$O$_3$Ti: C, 50.03; H, 2.90%). ^{1}H NMR (C$_6$D$_6$): δ 1.85 (s, 15 H, C$_5$Me$_5$), 5.92 [tt, ^4J(HF) = 6.1, 1.9 Hz, 3 H, *p*-H]. ^{13}C-{^{1}H} NMR (C$_6$D$_6$): δ 140.1 [d, *J*(CF) = 247, *o*-CF], 139.4 [d, *J*(CF) = 248 Hz, *m*-CF], 135.3 (*p*-CH), 128.3 (*C*$_5$Me$_5$), 14.0 (C$_5$*Me*$_5$), 14.0 (C$_5$*Me*$_5$). ^{19}F NMR (C$_6$D$_6$): δ −141.5 [d, *J*(CF) = 20.3, 2 F, *o*-F], −159.7 [d, *J*(CF) = 20.3 Hz, 2 F, *m*-F].

{Ti(η-C$_5$Me$_5$)(OC$_6$HF$_4$-*p*)$_2$}$_2$(μ-O) 5. While attempting to grow crystals of Ti(η-C$_5$Me$_5$)(OC$_6$HF$_4$-*p*)$_3$ in toluene, slow hydrolysis by adventitious water gave orange crystals of **5**. In a separate experiment, a toluene solution of Ti(η-C$_5$Me$_5$)(OC$_6$HF$_4$-*p*)$_3$ was left to stir in air overnight. The solvent was removed *in vacuo* to give an orange powder of **5**, ^{1}H NMR (C$_6$D$_6$) δ 1.89 (15 H, C$_5$Me$_5$), 5.96 (m, 3 H, *p*-H), which was characterized crystallographically (see below).

The following compounds could not be isolated as pure solids, and all work with them involved synthesis and spectroscopic characterization *in situ* on NMR scale samples prepared in NMR tubes.

Ti(η-C$_5$Me$_5$)Me(C$_6$F$_5$)(μ-Me)B(C$_6$F$_5$)$_3$ 9. A solution of B(C$_6$F$_5$)$_3$ (31 mg, 0.06 mmol) in CD$_2$Cl$_2$ (0.3 cm^3) was added to a solution of Ti(η-C$_5$Me$_5$)Me$_2$(C$_6$F$_5$) (23 mg, 0.06 mmol) in CD$_2$Cl$_2$ (0.4 cm^3) cooled to −78 °C. The red solution was maintained at −78 °C for a few minutes, then placed in the probe of an AM-400 NMR spectrometer at −50 °C where it was examined by ^{1}H, ^{13}C-{^{1}H} and ^{19}F NMR spectroscopy. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.61 [d, ^4J(HF) = 3 Hz, 3 H, TiMe], 2.10 (15 H, C$_5$Me$_5$), 1.36 (br s, 3 H, μ-Me). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 138.2 (*C*$_5$Me$_5$), 109.9 (TiMe), 13.6 (C$_5$*Me*$_5$). ^{19}F NMR (CD$_2$Cl$_2$): δ −118.6 (m, 1 F, *o*-F of TiC$_6$F$_5$), −124.3 (m, 1 F, *o*-F of TiC$_6$F$_5$), −135.1 (m, 6 F, *o*-F of BC$_6$F$_5$), −150.1 (t, 1 F, *p*-F of TiC$_6$F$_5$), −160.3 (m, 1 F, *m*-F of TiC$_6$F$_5$), −160.8 (t, 3 F, *p*-F of BC$_6$F$_5$), −161.7 (m, 1 F, *m*-F of TiC$_6$F$_5$), −166.0 (m, 6 F, *m*-F of BC$_6$F$_5$).

Ti(η-C$_5$Me$_5$)Me(OC$_6$F$_5$)(μ-Me)B(C$_6$F$_5$)$_3$ 10. In an NMR experiment carried out as above, B(C$_6$F$_5$)$_3$ (31 mg, 0.06 mmol) in CD$_2$Cl$_2$ (0.3 cm^3) was added to a solution of Ti(η-C$_5$Me$_5$)Me$_2$(OC$_6$F$_5$) (24 mg, 0.06 mmol) in CD$_2$Cl$_2$ (0.4 cm^3) cooled to −78 °C providing an orange solution. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.04 (15 H, C$_5$Me$_5$), 1.89 (3 H, TiMe), 0.62 (br s, 3 H, μ-Me). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 134.3, (*C*$_5$Me$_5$), 82.2 (TiMe), 12.2 (C$_5$*Me*$_5$). ^{19}F NMR (CD$_2$Cl$_2$): −135.4 (m, 6 F, *o*-F of BC$_6$F$_5$), −159.7 (m, 2 F, *o*-F of TiOC$_6$F$_5$), −160.9 (t, 3 F, *p*-F of BC$_6$F$_5$), −164.5 (m, 2 F, *m*-F of TiOC$_6$F$_5$), −165.0 (t, 1 F, *p*-F of TiOC$_6$F$_5$), −166.0 (m, 6 F, *m*-F of BC$_6$F$_5$).

[{Ti(η-C$_5$Me$_5$)Me(OC$_6$F$_5$)}$_2$(μ-Me)][BMe(C$_6$F$_5$)$_3$] 11. In an NMR experiment carried out as above, B(C$_6$F$_5$)$_3$ (15 mg, 0.03 mmol) in CD$_2$Cl$_2$ (0.3 cm^3) was added to a solution of Ti(η-C$_5$Me$_5$)Me$_2$(OC$_6$F$_5$) (24 mg, 0.06 mmol) in CD$_2$Cl$_2$ (0.4 cm^3) cooled to −78 °C providing an orange solution. ^{1}H NMR (CD$_2$Cl$_2$): δ 2.01 (30 H, C$_5$Me$_5$), 1.50 (3 H, TiMe), 1.47 (3 H, TiMe), 0.34 (br s, 3 H, BMe), −0.31 (3 H, μ-Me). ^{13}C-{^{1}H} NMR (CD$_2$Cl$_2$): δ 132.0 and 131.9 (*C*$_5$Me$_5$), 79.7 and 79.3 (TiMe), 12.3 and 12.2 (C$_5$*Me*$_5$). ^{19}F NMR (CD$_2$Cl$_2$): −134.3 (m, 6 F, *o*-F of BC$_6$F$_5$), −159.4 and −159.6 (m, 4 F, *o*-F of TiOC$_6$F$_5$), −163.6 and −164.1 (m, 4 F, *m*-F of TiOC$_6$F$_5$), −165.0 (m, 2 F, *p*-F of TiOC$_6$F$_5$), −165.0 (m, 3 F, *p*-F of BC$_6$F$_5$), −167.7 (m, 6 F, *m*-F of BC$_6$F$_5$).

Table 1 Crystallographic data for compounds **4** and **5**

Compound	**4**	**5**
Empirical formula	$C_{28}H_{18}F_{12}O_3Ti$	$C_{44}H_{34}F_{16}O_5Ti_2$
M	678.32	1042.51
Crystal symmetry	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	8.196(2)	11.3152(17)
b/Å	10.583(2)	12.6242(20)
c/Å	15.997(2)	17.7777(19)
α/°	91.939(12)	106.297(9)
β/°	95.066(12)	90.171(11)
γ/°	87.123(12)	113.476(13)
U/Å^3	1379.9(4)	2216.6(5)
Z	2	2
D_c/g cm^{-3}	1.633	1.562
μ(Mo-Kα)/mm^{-1}	0.422	0.472
Crystal dimensions/mm	0.35 × 0.25 × 0.10	0.40 × 0.25 × 0.15
Crystal color	Orange	Yellow-brown
λ(Mo-Kα)/Å	0.710 69	0.710 69
Data collected	$-8 \leqslant h \leqslant 8, 0 \leqslant k \leqslant 11, -17 \leqslant l \leqslant 17$	$0 \leqslant h \leqslant 12, -14 \leqslant k \leqslant 13, -20 \leqslant l \leqslant 20$
θ Scan range/°	1.2–23.0	1.2–24.0
T/K	298(2)	298(2)
No. of reflections	4432	7327
No. of independent reflections	3818	6924
Final R	0.0477	0.0514
a, b in weighting scheme[a]	0.051, 0.27	0.0204, 0.938
R,[b] $wR2$,[c] all independent reflections	0.0876, 0.1460	0.1034, 0.1280
Goodness of fit indicator[d]	1.148	1.327
Maximum shift/error, final cycle	0.003	0.004
Maximum resid. electron dens./e Å^{-3}	0.288	0.505
Minimum resid. electron dens./e Å^{-3}	−0.252	−0.406

[a] $w = 1/[\sigma^2(F_o^2) + aP^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. [b] $R = \Sigma\left||F_o| - |F_c|\right|/\Sigma|F_o|$. [c] $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/[\Sigma w(F_o^2)^2]\}^{\frac{1}{2}}$. [d] Goodness-of-fit on F^2, $S = \{[\Sigma w(F_o^2 - F_c^2)^2]/(N_o - N_v)\}^{\frac{1}{2}}$, all independent data.

{Ti(η-C_5Me_5)(OC_6F_5)$_2$}{BMe(C_6F_5)$_3$} 12. In an NMR experiment carried out as above, B(C_6F_5)$_3$ (31 mg, 0.06 mmol) in CD_2Cl_2 (0.3 cm^3) was added to a solution of Ti(η-C_5Me_5)-Me(OC_6F_5)$_2$ (34 mg, 0.06 mmol) in CD_2Cl_2 (0.4 cm^3) cooled to −78 °C to give a red solution. ^{1}H NMR (CD_2Cl_2): δ 2.17 (15 H, C_5Me_5), 0.37 (br s, 3 H, BMe). ^{13}C-{^{1}H} NMR (CD_2Cl_2): δ 139.3 (C_5Me$_5$), 12.3 (C_5*Me*$_5$). ^{19}F NMR (CD_2Cl_2): −134.7 (m, 6 F, *o*-F of BC_6F_5), −159.7 (m, 4 F, *o*-F of TiOC_6F_5), −165.1 (t, 2 F, *p*-F of TiOC_6F_5), −164.2 (m, 4 F, *m*-F of TiOC_6F_5), −166.4 (m, 3 F, *p*-F, of BC_6F_5), −169.0 (m, 6 F, *m*-F of BC_6F_5).

Table 2 Selected bond lengths (Å) and angles (°) for complex **4***

Ti−Cg	2.023(3)	Ti−O(1)	1.867(3)
Ti−O(2)	1.826(3)	Ti−O(3)	1.830(3)
O(1)−C(11)	1.339(5)	O(2)−C(21)	1.330(5)
O(3)−C(31)	1.317(5)		
Ti−O(1)−C(11)	137.1(3)	Ti−O(2)−C(21)	165.0(3)
Ti−O(3)−C(31)	156.6(3)	O(1)−Ti−Cg	111.14(12)
O(2)−Ti−Cg	116.49(13)	O(3)−Ti−Cg	118.39(13)
O(1)−Ti−O(2)	106.2(2)	O(1)−Ti−O(3)	100.59(14)
O(2)−Ti−O(3)	102.2(2)		

* Cg is the center of gravity of the (η-C_5Me_5) ring.

Table 3 Selected bond lengths (Å) and angles (°) for complex **5***

Ti(1)−Cg(1)	2.042(3)	Ti(2)−Cg(2)	2.038(3)
Ti(1)−O(1)	1.814(3)	Ti(2)−O(1)	1.823(3)
Ti(1)−O(2)	1.838(3)	Ti(2)−O(4)	1.844(3)
Ti(1)−O(3)	1.883(3)	Ti(2)−O(5)	1.875(3)
Ti(1)−O(1)−Ti(2)	160.2(2)	O(1)−Ti(2)−Cg(2)	116.82(15)
O(1)−Ti(1)−Cg(1)	118.23(15)	O(4)−Ti(2)−Cg(2)	116.24(16)
O(2)−Ti(1)−Cg(1)	114.48(14)	O(5)−Ti(2)−Cg(2)	110.31(15)
O(3)−Ti(1)−Cg(1)	110.29(14)	O(1)−Ti(2)−O(4)	103.45(13)
O(1)−Ti(1)−O(3)	104.58(13)	O(1)−Ti(2)−O(5)	102.63(14)
O(1)−Ti(1)−O(2)	102.51(13)		

* Cg is the center of gravity of the (η-C_5Me_5) ring.

Crystallography: structure solution and refinement

The structure of complex **4** was solved by direct methods using the program SHELXS 86,[29] and that of complex **5** by Patterson and Fourier methods using the program SHELXS 86.[29] The pertinent crystallographic data are given in Table 1. For both structures full-matrix least-squares refinement on F^2 data with the anisotropic displacement parameters for all non-H atoms was performed using the program SHELXL 93[30] (the neutral-atom scattering factors and anomalous dispersion corrections used are taken from ref. 31).

In structure **4** the aromatic hydrogen atoms were placed in calculated positions with C−H distances of 0.93 Å, and those of (η-C_5Me_5) methyl groups with C−H 0.96 Å and orientations based on features of the Fourier-difference map. In the refinement, all H atoms were riding on the carbon atoms to which they are attached with their isotropic thermal displacement parameters kept as $U_{iso}(H) = 1.2U_{eq}(C)$. The refinement for structure **4** converged at the final R (conventional, based on F) of 0.0477. There was no residual solvent accessible area in this structure. Selected bond lengths and bond angles are listed in Table 2.

In structure **5** atoms C(54), C(55), F(55), C(56) and F(56) of one of the tetrafluorophenyl rings show large anisotropy consistent with some slight disorder. The aromatic hydrogen atoms were placed in calculated positions with C−H distances of 0.93 Å, and those of (η-C_5Me_5) methyl groups with C−H 0.96 Å and orientations based on features of the Fourier-difference map. In the refinement, all H atoms were riding on the carbon atoms to which they are attached with their isotropic thermal displacement parameters kept as $U_{iso}(H) = 1.2U_{eq}(C)$. The refinement for structure **5** converged at the final R (conventional, based on F) of 0.0514. There was no residual solvent accessible area in this structure. Selected bond lengths, and bond angles are listed

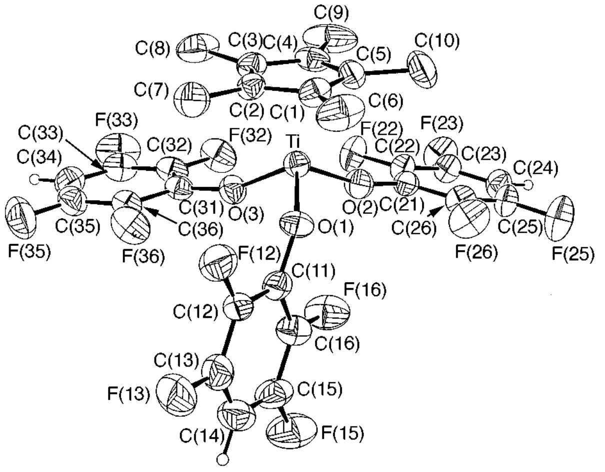

Fig. 1 An ORTEP plot of complex **4**

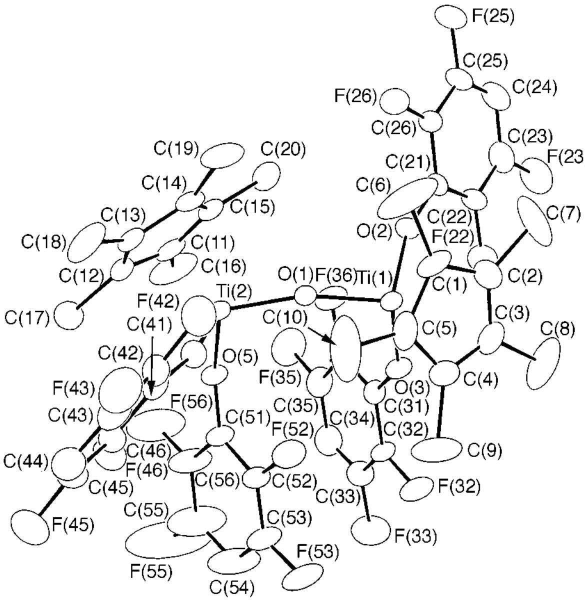

Fig. 2 An ORTEP plot of complex **5**

in Table 3. The geometrical analysis of the structures was done with programs SHELXL 93[30] and PLATON.[32]

The ORTEP[33] drawings of molecules **4** and **5**, with the atom numbering schemes, are given in Figs. 1 and 2 respectively.

CCDC reference number 186/641.

Results and Discussion

Preparations and general characterization

There are several synthetic routes which one can take to synthesize derivatives of Ti(η-C_5Me_5)Me_3. For instance, addition of aldehydes or ketones to Ti(η-C_5Me_5)Me_3 results in insertion of a C=O group into a Ti–Me bond to produce secondary and tertiary alkoxy compounds, respectively [equations (1) and (2)].[24] Protonolysis of Ti(η-C_5Me_5)Me_3 by alcohols gives similar

$$\mathrm{Ti(\eta\text{-}C_5Me_5)Me_3 + MeCHO \longrightarrow Ti(\eta\text{-}C_5Me_5)Me_2(OCHMe_2)} \quad (1)$$

$$\mathrm{Ti(\eta\text{-}C_5Me_5)Me_3 + Me_2CO \longrightarrow Ti(\eta\text{-}C_5Me_5)Me_2(OCMe_3)} \quad (2)$$

products [equation (3)], but all three processes are quite

$$\mathrm{Ti(\eta\text{-}C_5Me_5)Me_3} + n\mathrm{ROH} \longrightarrow \mathrm{Ti(\eta\text{-}C_5Me_5)Me}_n\mathrm{(OR)}_{3-n} + n\mathrm{CH_4} \quad (3)$$

unselective, giving inseparable mixtures of mono-, di- and tri-substituted compounds. Often the final product can only be recovered pure when all three Ti–Me bonds are transformed, and facile formation of Ti(η-C_5Me_5)Me_2(OR) *via* protonolysis has been limited to alcohols ROH with bulky R groups ($SiPh_3$,[34] CPh_3,[24] Bu^t[24] or Pr^i[24]).

As an alternative, more selective methodology Royo and coworkers[34,35] have described the isolation of partially methylated titanium derivatives Ti(η-C_5Me_5)Me_nCl_{3-n} (n = 1–3) by treating Ti(η-C_5Me_5)Cl_3 with methyllithium or MeMgX (X = Cl or Br) [equation (4)]. We have used this latter route to synthesize the

$$\mathrm{Ti(\eta\text{-}C_5Me_5)Cl_3} + n\mathrm{MeLi} \longrightarrow \mathrm{Ti(\eta\text{-}C_5Me_5)Me}_n\mathrm{Cl}_{3-n} + n\mathrm{LiCl} \quad (4)$$

desired substituted complexes Ti(η-C_5Me_5)$Me_{3-n}E_n$. Treatment of Ti(η-C_5Me_5)Cl_3 with 1 equivalent of MeLi in hexanes provides the yellow complex Ti(η-C_5Me_5)$MeCl_2$, while addition of 2 equivalents in tetrahydrofuran (thf) gives the orange compound Ti(η-C_5Me_5)Me_2Cl.[34,35] We also find that reacting Ti(η-C_5Me_5)Cl_3 with Ti(η-C_5Me_5)Me_3 in a molar ratio of 1 : 2 at room temperature in hexanes provides a clean, high yield route to Ti(η-C_5Me_5)Me_2Cl *via* comproportionation. Subsequent replacement of the chloride ligands in Ti(η-C_5Me_5)$Me_{3-n}Cl_n$ is then easily achieved by addition of an appropriate amount of the lithium salt of the desired substituent ELi in hexanes, resulting in LiCl precipitation and the formation of Ti(η-C_5Me_5)$Me_{3-n}E_n$ (n = 1, E = C_6F_5 **1** or OC_6F_5 **2**; n = 2, E = OC_6F_5 **3**; n = 3, E = OC_6HF_4-*p* **4**) [equation (5)].

$$\mathrm{Ti(\eta\text{-}C_5Me_5)Me}_{3-n}\mathrm{Cl}_n + n\mathrm{ELi} \longrightarrow \mathrm{Ti(\eta\text{-}C_5Me_5)Me}_{3-n}\mathrm{(E)}_n + \mathrm{nLiCl} \quad (5)$$

Compounds **1**–**4** have been fully characterized by elemental analyses and spectroscopic methods. Of some interest is the observation of long range spin–spin coupling (2 Hz) between the Ti–Me resonances and the *ortho* fluorine atoms of **1**. While the chemical shifts of the C_5Me_5 resonances of this series of compounds vary little (<0.1 ppm), the TiMe resonances do. Indeed, substitution of one of the TiMe methyl groups of Ti(η-C_5Me_5)Me_3 by the much more electronegative ligand C_6F_5 results in a downfield shift of 0.52 ppm. In contrast, substitution by the OC_6F_5, OPr^i and OBu^t groups results in upfield shifts of 0.11, 0.70 and 0.75 ppm, respectively, presumably because of π donation from the oxygen lone pairs to the vacant d orbitals of the titanium centre. Previous studies show that alkoxy[36] and aryloxy[34] ligands readily donate electrons to the titanium center with their lone pair orbitals conveniently situated to overlap with empty metal d orbitals, forming partial double bonds. For the more electronegative OC_6F_5 ligand, the donating ability of the oxygen is apparently suppressed, resulting in a more electrophilic metal centre with respect to the non-fluorinated alkoxy compounds.

Titanium NMR spectroscopy

Titanium NMR spectroscopy is becoming increasingly useful as an investigative tool for assessing electronic effects of ligand substitution in titanium compounds,[6,37–46] including systems of interest in catalytic processes.[6,44–46] Although spectral acquisition of the NMR active ^{47}Ti and ^{49}Ti nuclei is generally hindered by low natural abundances (7.75%, 5.51%, respectively) and low sensitivities (both $\approx 10^{-3}$ that of ^{1}H), as well as by quadrupolar broadening of resonances of these two nuclei ($I = \frac{5}{2}, \frac{7}{2}$ respectively), useful spectra of titanium(IV) complexes containing a wide variety of ligands have been reported.[6,37–46] Since the ^{47}Ti and ^{49}Ti nuclei have almost identical magnetogyric ratios, resonances of both are readily apparent in the spectra of most compounds, with separations $\approx$266 ppm. In practice the ^{49}Ti resonances are easier to observe because of greater quadrupolar broadening of the ^{47}Ti resonances, although the chemical shifts of both are of course identical when referenced to the corresponding isotopomer of $TiCl_4$, the usual reference.

Chemical shifts are usually described by the Ramsey equation, which describes the overall shielding σ as in equation (6);

$$\sigma = \sigma_d + \sigma_p + \sigma_o \qquad (6)$$

here σ_d is the diamagnetic shielding, σ_p is the paramagnetic shielding and σ_o is a contribution from other atoms.[47] However, σ_p seems generally to dominate the chemical shifts of transition-metal nuclei, and equation (6) has been simplified to the form shown in equation (7). Here A and B are constants

$$\sigma = A - (B/\Delta) \qquad (7)$$

for complexes with similar ligands and Δ is the average energy difference between the ground state and low-lying electronic excited states.[47] To date, most $^{47/49}$Ti NMR chemical shift data have been interpreted in terms of equation (7),[6,37–46] with linear relationships between the chemical shifts and the longest wavelength transition in the electronic spectra being observed for several series of compounds.[6,37,38,46]

Indeed, reasonably linear correlations between $^{47/49}$Ti chemical shifts and the longest wavelength electronic transitions have been found for each of the series of compounds TiX_4 (X = Cl, Br, I, OPr^i or NEt_2),[37,38] Cp'_2TiX_2 ($Cp' = C_5H_5$ or substituted C_5H_5; X = F, Cl, Br, I, N_3 or NCS)[38,44,46] and (ind′)$TiCl_3$ (ind′ = substituted indenyl),[6] although the three series of compounds do not exhibit the *same* relationship. Differences in the nature of the ligands apparently result in significant variations in A and/or B of equation (7).[45,46] However, for the individual series TiX_4 and Cp'_2TiX_2, equation (7) does generally apply and results in chemical shifts becoming less shielded in the order X = F > Cl > Br > I.[47] These various types of Ti^{IV} complexes thus apparently exhibit a direct correlation between $^{47/49}$Ti shielding and ligand electronegativities, a relationship which may possibly be fortuitous but which has now been utilized extensively. Indeed, several correlations of titanium chemical shifts with electron-donating properties of Cp′ ring substituents have recently been reported.[6,40,45,46]

With a view to possibly assessing futher the relative electrophilicities of the compounds $Ti(\eta\text{-}C_5Me_5)Me_2E$ and related species, we have obtained $^{47/49}$Ti NMR data for several of the compounds reported here. As yet, few Ti NMR data have been available for monocyclopentadienyl titanium compounds of the type $Cp'TiX_3$[6,40,44,45] and, in general, chemical shifts of substituted cyclopentadienyl compounds $Cp'TiCl_3$ are found in the region δ −270 to −390.[44,45] However, chemical shifts of similar indenyl compounds are found in the range δ −114 to −269,[6] that of $Ti(\eta\text{-}C_5Me_5)Cl_3$ at δ −85.[44,45] Only a single report for alkyltitanium compounds has appeared, the chemical shifts of the compounds $TiMeCl_3$ and $TiMeBr_3$ being reported at δ 618 and δ 825, respectively,[43] intermediate between those of $TiBr_4$ and TiI_4.[38] We have also, therefore, in the course of this work obtained further information on the effects of alkyl ligands on $^{47/49}$Ti chemical shifts.

The $^{47/49}$Ti NMR data obtained for the series of compounds $Ti(\eta\text{-}C_5Me_5)Me_2E$ (E = Me **6**, Cl **7**, OC_6F_5 **2** or C_6F_5 **1**), $Ti(\eta\text{-}C_5Me_5)MeE_2$ (E = Cl **8**, OC_6F_5 **3**) and $Ti(\eta\text{-}C_5Me_5)Cl_3$ are shown in Table 4. The individual ^{47}Ti and ^{49}Ti resonances were observed in most cases, the former being relatively broad, and there is good agreement between the observed $^{47/49}$Ti chemical shift and linewidths ($\Delta\nu_{\frac{1}{2}}$) of $Ti(\eta\text{-}C_5Me_5)Cl_3$ and previously published values.[45] The λ_{max} values for the lowest energy electronic transitions of $Ti(\eta\text{-}C_5Me_5)Cl_3$ and the compounds **1**–**3** and **6**–**8** are also listed in Table 4, and a plot of chemical shifts *vs.* λ_{max} is shown in Fig. 3. As can be seen, the expected relationship between δ(^{49}Ti) and λ_{max} is not observed for these compounds, suggesting that the relationship shown in equation (7) does not apply well. In fact, the plot in Fig. 3 illustrates a large downfield shift for the trimethyl compound **6** (δ 551) and a linear *decrease* in the chemical shift with an increase in λ_{max} as methyl ligands are substituted by chloride, a ligand of lower ligand field strength. The opposite trend is found for the series of compounds TiX_4,[36,37] Cp'_2TiX_2[38,44,46] and (ind′)$TiCl_3$,[6] as well as for many other types of transition-metal systems where strong field ligands generally result in shifts to higher field.[47]

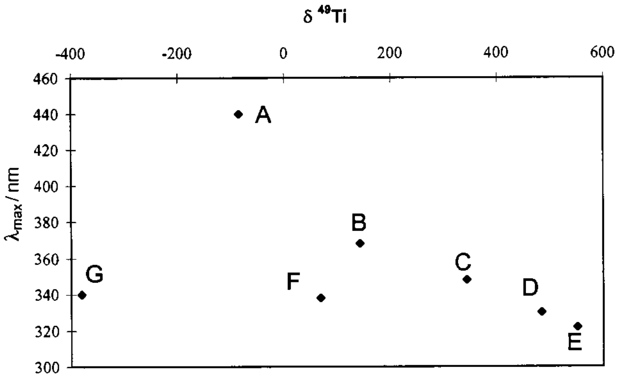

Fig. 3 Plot of λ_{max} against δ^{49}Ti: A = $Ti(\eta\text{-}C_5Me_5)Cl_3$, B = $Ti(\eta\text{-}C_5Me_5)MeCl_2$, C = $Ti(\eta\text{-}C_5Me_5)Me_2Cl$, D = $Ti(\eta\text{-}C_5Me_5)Me_2(C_6F_5)$, E = $Ti(\eta\text{-}C_5Me_5)Me_3$, F = $Ti(\eta\text{-}C_5Me_5)Me_2(OC_6F_5)$, G = $Ti(\eta\text{-}C_5Me_5)Me(OC_6F_5)_2$

Table 4 Titanium-47/49 NMR data*

Compound	δ^{49}Ti	$\Delta\nu_{\frac{1}{2}}$^{49}Ti	δ^{47}Ti	$\Delta\nu_{\frac{1}{2}}$^{47}Ti	λ_{max}
6 $Ti(\eta\text{-}C_5Me_5)Me_3$	551	317	288	902	322
1 $Ti(\eta\text{-}C_5Me_5)Me_2(C_6F_5)$	484	1664	nd	nd	330
7 $Ti(\eta\text{-}C_5Me_5)Me_2Cl$	343	567	−121	1056	348
8 $Ti(\eta\text{-}C_5Me_5)MeCl_2$	143	143	nd	nd	368
2 $Ti(\eta\text{-}C_5Me_5)Me_2(OC_6F_5)$	69	620	nd	nd	338
$Ti(\eta\text{-}C_5Me_5)Cl_3$	−88	11	−354	27	440
3 $Ti(\eta\text{-}C_5Me_5)Me(OC_6F_5)_2$	−380	460	nd	nd	340

* nd = Not determined.

While the reasons for the anomalies are not known, we note that ^{195}Pt chemical shifts also often exhibit a poor correlation which is attributed to a number of influences, mainly the variation of B with ligand substitution.[48–51] The term B relates to the angular momentum of valence orbitals, and is very sensitive to changes in the distance of the d electrons/orbitals from the metal nucleus ($B \propto \langle r^{-3}\rangle_d$).[48]

As a group, the methyl-substituted complexes **6**, **7** and **8** are the most deshielded of any titanium compounds yet known, more so even than the sulfur-bound compounds $TiCl_x(S_2CNR_2)_{4-x}$ (x = 2–0).[42] Substituting methyl ligands with the oxygen-donor ligand OC_6F_5 causes an upfield shift **6** (551) > **2** (69) > **3** (−380 ppm). Such an upfield shift upon increasing the number of oxygen-donor ligands is also apparent for the compounds $CpTiCl_3$ (δ −390) and $CpTi(2\text{-}PrO)_2Cl$ (δ −917),[44] and for the series of compounds $TiCl_x(OEt)_{4-x}$ [x = 4 (δ 0), 3 (−360), 2 (−560), 1 (−750) or 0 (−825)].[42]

Crystal structures of $Ti(\eta\text{-}C_5Me_5)(OC_6HF_4\text{-}p)_3$ 4 and $\{Ti(\eta\text{-}C_5Me_5)(OC_6HF_4\text{-}p)_2\}_2(\mu\text{-}O)$ 5

Compound **4** was characterized crystallographically because we wished to assess the possibility of alkoxy ligand π donation in compounds of this type but could not obtain satisfactory crystals of $Ti(\eta\text{-}C_5Me_5)(OC_6F_5)_3$. The structure of **5** was obtained because our initial attempt to grow crystals of **4** produced instead **5**, the product of hydrolysis by adventitious water; the structure is reported because it was thus available for purposes of comparison and complements the structure of **4**. Fig. 1 shows a perspective of the molecular structure of **4**, Table 2 most important bond distances and angles. Compound **4** is monomeric, and assumes a classical three-legged piano stool structure. The ($\eta\text{-}C_5Me_5$ centroid)–Ti–O angles vary from

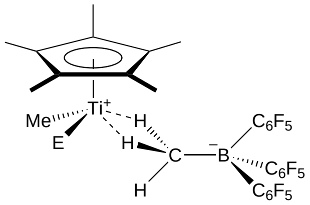

Fig. 4 Structure proposed for Ti(η-C_5Me_5)MeE(μ-Me)B$(C_6F_5)_3$ (E = Me, C_6F_5 or OC_6F_5)

111.14 for O(1) to 118.4° for O(3), similar to those found for Ti(η-C_5Me_5)$(NMe_2)_3$, where the (η-C_5Me_5 centroid)–Ti–N angles range from 112 to 119°.[52] The O–Ti–O angles lie between 100.59(14) and 106.2(2)°, while the Ti–C (C_5Me_5) distances are in the normal range. The angles between titanium, oxygen and the *ipso* carbon of the aryl rings vary significantly, *i.e.* Ti–O(3)–C(31) = 156.6(3), Ti–O(2)–C(21) = 165.0(3), Ti–O(1)–C(11) = 137.1(3)°.

Large Ti–O–C (aryl) angles and short Ti–O (aryl) distances would be indicative of double bond character for the Ti–O bond due to π-electron donation from the alkoxy ligands.[53] Indeed, the Ti–O bond in Ti(η-C_5Me_5)Cl_2($OC_6H_3Me_2$-2,6) [1.785(2) Å, 162.3°][34] is believed to have significant multiple character in contrast to that of Ti(η-C_5Me_5)$_2${$OC_6H_2Bu^t$-2,6-Me-4} [1.892(2) Å, 142.3°].[53] However, the Ti–O–aryl bond angles of **4** vary considerably, and it appears distortions are very facile, possibly because of the steric effects, and it would seem that the effects of π-electron donation in **4** must be minimal. All other bond lengths and angles are normal.[54]

Fig. 2 shows a perspective of the molecular structure, Table 3 the most important bond distances and angles of the oxygen bridged compound {Ti(η-C_5Me_5)(OC_6HF_4-*p*)$_2$}$_2$(μ-O) **5**. The molecular structure of **5** consists of two identical Ti(η-C_5Me_5)(OC_6HF_4-*p*)$_2$ units bridged by an oxygen atom situated such that there is a *trans* arrangement of the (η-C_5Me_5) rings. As with **4**, the OR ligands in **5** exhibit quite different Ti–O–R bond angles [Ti(1)–O(2)–C(21) = Ti(1)–O(4)–C(41) ≈161, Ti(2)–O(3)–C(31) = Ti(2)–O(5)–C(51) ≈144°]. Significant π bonding involving the μ-O ligand might also be anticipated, and would be implied by shortened Ti–O bonds and a linear or near linear arrangement of the Ti–O–Ti bonds.[55] However the Ti–O bond lengths and Ti–O–Ti bond angles in {Ti(η-C_5H_5)$_2$(CN)}$_2$(μ-O) [1.840(2) Å, 174.3(1)°],[56] {Ti(η-C_5H_5)$_2$(Et)}$_2$(μ-O) [1.840(3) Å, 173.7(2)°],[57] {Ti(η-C_5H_5)$_2$}$_2$(μ-O) [1.838(1) Å, 170.9(4)°][58] and {Ti(η-C_5H_5)$_2$(Cl)$_2$}$_2$(μ-O) [1.809(9) Å, 167.5(6)°][59] do not correlate as expected, and thus the deviation of the Ti(1)–O(1)–Ti(2) bond angle (160.2°) from a linear arrangement and the titanium–oxygen distances of 1.814 Å for Ti(1)–O(1) and 1.823 Å for Ti(2)–O(1) are in the range expected for titanium–oxo bridged dimers (1.820 Å),[54] and little can be said about the Ti–O bonding. All other bond lengths and angles are normal.[54]

Zwitterionic complexes

Treatment of solutions of Ti(η-C_5Me_5)Me_2(C_6F_5) **1** and Ti(η-C_5Me_5)Me_2(OC_6F_5) **2** with 1 equivalent each of the borane B$(C_6F_5)_3$ in CD_2Cl_2 at −78 °C results in immediate colour changes from yellow to red and the formation of the zwitterionic complexes Ti(η-C_5Me_5)MeE(μ-Me)B$(C_6F_5)_3$ (E = C_6F_5 **9**, OC_6F_5 **10**) (Fig. 4). These complexes decompose above 10 °C and could not be isolated, but were characterized by ^1H, ^{13}C and ^{19}F NMR spectroscopic studies (CD_2Cl_2, −50 to 10 °C); the structure proposed, with two bridging hydrogen atoms, is based on metallocene precedents.[2,9] Unfortunately, $^{47/49}Ti$ resonances could not be detected, presumably because of severe quadrupolar broadening.[60] Compounds **9** and **10** were also readily identified on the basis of comparison with the previously characterized Ti(η-C_5Me_5)Me_2(μ-Me)B$(C_6F_5)_3$.[17] The broadened μ-MeB resonances of all three compounds are especially characteristic of the proposed zwitterionic structures because of their linewidths, a consequence of quadrupolar relaxation by the $^{10,11}B$ nuclei.[60] Shielding of the terminal methyl protons of the compounds Ti(η-C_5Me_5)MeE(μ-Me)B$(C_6F_5)_3$ clearly decreases in the order E = Me (δ 1.53) > OC_6F_5 (1.89) > C_6F_5 (2.61), consistent with the relative electronegativities of the groups E and strongly implying a high degree of electrophilicity of the metal in compounds **9** and **10**. However, while shielding of the MeB protons decreases in a different order, E = OC_6F_5 (δ 0.62) Me > (1.19) > C_6F_5 (1.35), solution and crystallographic studies of the similar methylzirconocene compounds Cp'_2ZrMe(μ-Me)B$(C_6F_5)_3$ indicate that the MeB resonances become increasingly deshielded as the strength of the borate–zirconium interaction, affected by both electronic and steric factors, increases. Thus it seems likely that the metal–borate interaction in **10** may be weakened by steric interactions.

Spin saturation experiments have previously been carried out on a solution of Ti(η-C_5Me_5)Me_2(μ-Me)B$(C_6F_5)_3$, the Ti–Me and μ-Me resonances being irradiated and difference spectra being inspected for transfer of magnetization.[17] Interestingly, while no transfer between these two resonances was observed, implying that the B$(C_6F_5)_3$ does not 'hop' from one methyl group to another, irradiation of the μ-Me resonance resulted in enhancement of a vanishingly weak resonance at δ ≈0.38, the chemical shift of free borate anion. It follows that the borate anion, $[BMe(C_6F_5)_3]^-$, of Ti(η-C_5Me_5)Me_2(μ-Me)B$(C_6F_5)_3$ dissociates to some extent in solution, and that a low, steady-state concentration of the (possibly solvated) cation [Ti(η-C_5Me_5)$Me_2]^+$ exists in solution. Similar NMR experiments performed on **9** and **10** over the temperature range −50 to −10 °C provided no evidence for borate dissociation in the former but did result in magnetization transfer, and hence evidence for free borate ion, in the spectrum of **10**. This result indicates an equilibrium between the methyl-bridged species and the solvent separated ions, [Ti(η-C_5Me_5)Me(OC_6F_5)$]^+$ and $[BMe(C_6F_5)_3]^-$, in the case of **10**. Thus the strength of the titanium–borate interaction in the compounds Ti(η-C_5Me_5)MeE(μ-Me)B$(C_6F_5)_3$ decreases in the order E = C_6F_5 > OC_6F_5 = Me, correlating reasonably well with the apparent electrophilicities of the complexes [Ti(η-C_5Me_5)MeE$]^+$ and providing an indication of the relative amounts present in solution of these cations, believed to be the active species in olefin polymerizations.[1,2,9]

The ^{19}F NMR spectrum of complex **9** at −50 °C exhibits five resonances of equal intensity and assignable to five magnetically inequivalent fluorine environments in the C_6F_5 ligands. The *ortho* and *meta* resonances broaden as the temperature is raised but the compound decomposes before coalescence is reached, preventing acquisition of accurate site exchange data. However, using the dynamic NMR simulation program DNMR 5,[61] the spectra were fitted for a number of temperatures and the data did provide activation data for the dynamic process(es) involved,[62] and a least-squares fitting of the data resulted in determination of activation enthalpies and entropies: $\Delta H^\ddagger = 4.5 \pm 0.1$ kcal mol^{-1} (cal = 4.184 J) and $\Delta S^\ddagger = -25.8 \pm 0.8$ cal K^{-1} mol^{-1} for the *ortho* F resonances; $\Delta H^\ddagger = 3.2 \pm 0.1$ kcal mol^{-1} and $\Delta S^\ddagger = -32.6 \pm 0.8$ cal K^{-1} mol^{-1} for the *meta* F resonances. The coalescence temperatures for the exchange of the *ortho* and *meta* fluorines are 11.7 ± 1 °C and 1.0 ± 1 °C, respectively and, using equation (8) for an equally

$$\Delta G_c^\ddagger = aT[9.972 + \log(T/\delta\nu)] \qquad (8)$$

populated two-site system, good agreement was obtained for the two calculated free energy of activation values: $\Delta G_c^\ddagger = 11.8 \pm 0.4$ kcal mol^{-1} and 12.2 ± 0.2 kcal mol^{-1} respectively.

Possible reasons for the non-equivalences are restricted rotation of the C_6F_5 ring about the Ti–C_6F_5 bond and/or borate ligand dissociation/reorganisation; the latter is observed to

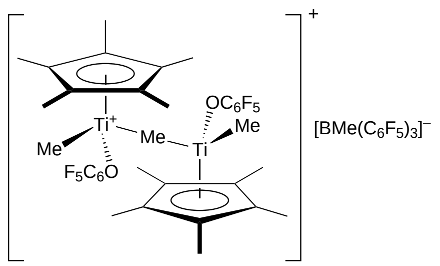

Fig. 5 Structure proposed for $[\{Ti(\eta\text{-}C_5Me_5)Me(OC_6F_5)\}_2(\mu\text{-}Me)][BMe(C_6F_5)_3]$

occur at higher temperatures for the metallocenes $Cp'_2MMe(\mu\text{-}Me)B(C_6F_5)_3$ (Cp′ = substituted cyclopentadienyl, M = Zr or Hf), with free energies of activation of 13.5 to >19 kcal mol^{-1}.[7,10,11] Since, as shown above, spin saturation transfer experiments on **9** show no sign of TiMe–MeB methyl exchange, it seems that the site exchange phenomenon observed is a result of restricted rotation of the C_6F_5 ring rather than an intra/intermolecular methyl exchange between the borane and the metal.

Addition of 0.5 equivalent of borane to **2** or of 1 equivalent of **2** to **10** results in formation of an unstable species which, on the basis of its NMR spectrum, is the dititanium complex $[\{Ti(\eta\text{-}C_5Me_5)Me(OC_6F_5)\}_2(\mu\text{-}Me)][BMe(C_6F_5)_3]$ **11** (Fig. 5); this contains two chiral titanium centres and thus exists as diastereomers. The bridged methyl resonance of **11** is shifted upfield by 2 ppm relative to the terminal TiMe resonance of **10**, a characteristic of Group 4 metal methyl-bridged compounds of the type $Cp'_2ZrMe(\mu\text{-}Me)ZrMeCp'_2$.[8,17,63,64] The diastereomeric nature of **11** is attested to by the ^1H NMR TiMe resonances at δ 1.50 and 1.47, and by pairs of resonances in the $^{13}C\text{-}\{^1H\}$ NMR spectrum: C_5Me$_5$ (δ 132.0 and 131.9), TiMe (δ 79.7 and 79.3), C_5Me_5 (δ 12.3 and 12.2). The ^{19}F NMR spectrum also shows pairing of resonances for both the *o*-fluorines (δ −159.4 and −159.6) and the *m*-fluorines of $TiOC_6F_5$ (δ −163.6 and −164.1) although the *p*-fluorine resonance is obscured by that of $MeB(C_6F_5)_3$. The pairs of diastereomers occur in about a 1 : 1 ratio, as all of the above-mentioned pairs of resonances are of equal intensity. Irradiation experiments (−50 °C, CD_2Cl_2) show the bridged and terminal methyl groups to be in exchange, a result found for the similar system $[\{Ti(\eta\text{-}C_5Me_5)Me_2\}_2(\mu\text{-}Me)][BMe(C_6F_5)_3]$.[17]

Treatment of $Ti(\eta\text{-}C_5Me_5)Me(OC_6F_5)_2$ **3** with 1 equivalent of $B(C_6F_5)_3$ (−50 °C, CD_2Cl_2) results in an immediate colour change from yellow to deep red. The ^1H NMR spectrum shows the formation of the complex $[Ti(\eta\text{-}C_5Me_5)(OC_6F_5)_2][BMe(C_6F_5)_3]$ **12**, with a downfield shift of the $(\eta\text{-}C_5Me_5)$ resonance of **3** (δ 1.89) to δ 2.17 and a broad methyl resonance at δ 0.37, attributable to free borate, $[BMe(C_6F_5)_3]^-$. Thus, in contrast to the methyl-bridged complexes **9** and **10**, complex **12** shows no co-ordination of the methyl group to the metal, surprising given the apparent eletrophilic nature of the titanium centre. Thus the inability of $[Ti(\eta\text{-}C_5Me_5)(OC_6F_5)_2]^+$ to bind the borate anion must be attributed to steric hindrance by the three bulky ligands on the titanium, which would arguably have greater steric requirements than the ligands of **9** and **10**. Interestingly, warming the solution results in the reappearance of the resonances of **3**, and at −10 °C there are substantial amounts of both species present. Spin saturation transfer and variable-temperature experiments show them to be in equilibrium [equation (9)], with $\Delta H = -1.25 \pm 0.1$ kJ mol^{-1} and $\Delta S =$

$$\mathbf{3} + B(C_6F_5)_3 \rightleftharpoons [Ti(\eta\text{-}C_5Me_5)(OC_6F_5)_2][BMe(C_6F_5)_3] \quad (9)$$

$-46 \pm$ J K^{-1} mol^{-1}.

The ability of **12** to engage in Ti–Me/B–Me exchange is unique among the mono(η-C_5Me_5) compounds studied here, and also stands in contrast to some zirconocene systems,[5,7–10] for which rather similar exchange is implied by variable-temperature NMR studies although not the type of shift in equilibrium found here. As pointed out above, $[(\eta\text{-}C_5Me_5)Ti(OC_6F_5)_2]^+$ is expected to be a relatively strong Lewis acid and its apparently unusual disinclination to bind the $[BMe(C_6F_5)_3]^-$ anion is to be attributed to steric hindrance by the three bulky ligands on the titanium hindering co-ordination of the latter. Indeed, it appears that the strong but sterically hindered Lewis acid $[(\eta\text{-}C_5Me_5)Ti(OC_6F_5)_2]^+$ effectively competes with $B(C_6F_5)_3$ for possession of the methyl group, presumably *via* a transient methyl-bridged species although none was detected in the spin saturation experiments.

The results reported here are in accord with the findings of Marks and co-workers[5,7–10] that bulky substituents at a metal center can result in reduced [metal cation]–anion interactions in spite of the intrinsic electrophilicity of the metal center. Compound **12** presents an extreme case where the steric effects completely overcome any strong electrostatic interactions.

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada (Research and Strategic Grants to M. C. B. and Graduate Scholarship to S. W. E.) and Alcan (Graduate Scholarship to S. W. E.) for financial support.

References

1 H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1143.
2 M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1996, 255.
3 P. C. Möhring and N. J. Coville, *J. Organomet. Chem.*, 1994, **479**, 1.
4 S. L. Borkowsky, N. C. Brenzinger and R. F. Jordan, *Organometallics*, 1993, **12**, 486.
5 L. Jia, X. Yang, C. L. Stern and T. J. Marks, *Organometallics*, 1997, **16**, 842.
6 Y. Kim, B. H. Koo and Y. Do, *J. Organomet. Chem.*, 1997, **527**, 155.
7 C. Sishta, R. M. Hathorn and T. J. Marks, *J. Am. Chem. Soc.*, 1992, **114**, 1112.
8 M. A. Giardello, M. S. Eisen, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1995, **117**, 12 114.
9 X. Yang, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10 015.
10 P. A. Deck and T. J. Marks, *J. Am. Chem. Soc.*, 1995, **117**, 6128.
11 A. R. Siedle and R. A. Newmark, *J. Organomet. Chem.*, 1995, **497**, 119.
12 D. J. Gillis, M.-J. Tudoret and M. C. Baird, *J. Am. Chem. Soc.*, 1993, **115**, 2543.
13 D. J. Gillis, R. Quyoum, M.-J. Tudoret, Q. Wang, D. Jeremic, A. W. Roszak and M. C. Baird, *Organometallics*, 1996, **15**, 3600.
14 M. C. Murray and M. C. Baird, *J. Mol. Catal.*, in the press.
15 Q. Wang and M. C. Baird, *Macromolecules*, 1995, **28**, 8021.
16 Q. Wang, R. Quyoum, D. J. Gillis, M.-J. Tudoret, D. Jeremic, B. K. Hunter and M. C. Baird, *Organometallics*, 1996, **15**, 693.
17 Q. Wang, R. Quyoum, D. J. Gillis, D. Jeremic and M. C. Baird, *J. Organomet. Chem.*, 1997, **527**, 7.
18 R. Quyoum, Q. Wang, M.-J. Tudoret, M. C. Baird and D. J. Gillis, *J. Am. Chem. Soc.*, 1994, **116**, 6435.
19 S. W. Ewart, M. J. Sarsfield, T. L. Tremblay, A. W. Roszak and M. C. Baird, unpublished work.
20 T. L. Tremblay, S. W. Ewart, M. J. Sarsfield and M. C. Baird, *Chem. Commun.*, 1997, 831.
21 F. Barsan and M. C. Baird, *J. Chem. Soc., Chem. Commun.*, 1995, 1065.
22 C. Pellecchia, D. Pappalardo, L. Oliva and A. Zambelli, *J. Am. Chem. Soc.*, 1995, **117**, 6593.
23 I. M. Lee, W. J. Gauthier, J. M. Ball, B. Iyengar and S. Collins, *Organometallics*, 1992, **11**, 2115.
24 D. J. Gillis, Ph.D. Thesis, Queens University, Kingston, 1993.
25 G. Hidalgo-Llinás, M. Mena, F. Palacios, P. Royo and R. Serrano, *J. Organomet. Chem.*, 1988, **340**, 37.
26 A. Martín, M. Mena, M. A. Pellinghelli, P. Royo, R. Serrano and A. Tiripicchio, *J. Chem. Soc., Dalton Trans.*, 1993, 2117.
27 M. Mena, P. Royo, R. Serrano, M. A. Pellinghelli and A. Tiripicchio, *Organometallics*, 1989, **8**, 476.
28 (*a*) A. G. Massey and A. J. Park, *J. Organomet. Chem.*, 1964, **2**, 245; (*b*) R. Uson and A. Laguna, *Inorg. Synth.*, 1982, **21**, 72.

29 G. M. Sheldrick, SHELXS 86, Program for the Solution of Crystal Structures, University of Göttingen, 1985.
30 G. M. Sheldrick, SHELXS 92, Program for the Refinement of Crystal Structures, University of Göttingen, 1992.
31 A. J. C. Wilson, in *International Tables for Crystallography*, ed. A. J. C. Wilson, Kluwer, Dordrecht, 1992.
32 A. L. Speck, *Acta Crystallogr.*, *Sect. A*, 1990, **46** (Suppl.), C34.
33 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
34 P. M. Gómez-Sal, M. Mena, P. Royo and R. Serrano, *J. Organomet. Chem.*, 1988, **358**, 147.
35 P. M. Gómez-Sal, A. Martín, M. Mena, P. Royo and R. Serrano, *J. Organomet. Chem.*, 1991, **419**, 77.
36 J. C. Huffman, K. G. Maloy, J. A. Marsella and K. G. Caulton, *J. Am. Chem. Soc.*, 1980, **102**, 3009.
37 R. G. Kidd, R. W. Mathews and H. G. Spinney, *J. Am. Chem. Soc.*, 1972, **94**, 6686.
38 N. Hao, B. G. Sayer, G. Denes, D. F. Bickley and M. J. McGlinchey, *J. Magn. Reson.*, 1982, **50**, 50.
39 P. G. Gassmann, W. H. Campbell and D. W. Macomber, *Organometallics*, 1984, **3**, 385.
40 A. Dormond, M. Fauconet, J. C. Leblanc, and C. Moise, *Polyhedron*, 1984, **3**, 897.
41 K. M. Chi, S. R. Frerichs, S. B. Philson and J. E. Ellis, *J. Am. Chem. Soc.*, 1988, **110**, 303.
42 P. R. Trail and C. G. Young, *J. Magn. Reson.*, 1990, **90**, 551.
43 S. Berger, W. Bock, C. F. Marth, B. Raguse and M. T. Reetz, *Magn. Reson. Chem.*, 1990, **28**, 559.
44 A. Hafner, R. O. Duthaler, R. Marti, G. Rihis, P. Rothe-Streit and F. Schwarzenbach, *J. Am. Chem. Soc.*, 1992, **114**, 2321.
45 A. Hafner and J. Okuda, *Organometallics*, 1993, **12**, 949.
46 W. C. Finch, E. W. Anslyn and R. H. Grubbs, *J. Am. Chem. Soc.*, 1988, **110**, 2406.
47 J. J. Dechter, *Prog. Inorg. Chem.*, 1985, **33**, 393.
48 R. G. Kidd, *Annu. Rep. NMR Spectrosc.*, 1980, **10**, 1.
49 R. R. Dean and J. C. Green, *J. Chem. Soc. A*, 1968, 3047.
50 P. L. Goggin, R. J. Goodfellow, S. R. Haddock, B. F. Taylor and R. H. Marshall, *J. Chem. Soc.*, *Dalton Trans.*, 1976, 459.
51 A. Pidcock and R. E. Richards, *J. Chem. Soc. A*, 1968, 1970.
52 A. Martin, M. Mena, C. Yelamos, R. Serrano and P. R. Raithby, *J. Organomet. Chem.*, 1994, **467**, 79.
53 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.
54 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc.*, *Dalton Trans.*, 1989, S1.
55 B. Cetinkaya, P. B. Hitchcock, M. L. Lappert, S. Torroni, J. L. Atwood, W. E. Hunter and M. J. Zaworotko, *J. Organomet. Chem.*, 1980, **188**, C31.
56 U. Thewalt and W. Nuding, *J. Organomet. Chem.*, 1996, **512**, 127.
57 H. G. Alt, K.-H. Schwind, M. D. Rausch and U. Thewalt, *J. Organomet. Chem.*, 1988, **349**, C7.
58 B. Honold, U. Thewalt, M. Herberhold, H. G. Halt, L. B. Kool and M. D. Rausch, *J. Organomet. Chem.*, 1986, **314**, 105.
59 P. Gowik, T. Klapötke and J. Prickardt, *J. Organomet. Chem.*, 1990, **393**, 343.
60 R. K. Harris, in *Nuclear Magnetic Resonance Spectroscopy*, Pitman, London, 1983.
61 D. S. Stephenson and G. Binsch, *Quantum Chemistry Program Exchange*, 1978, **11**, 365.
62 J. Sandström, *Dynamic NMR Spectroscopy*, Academic Press, New York, London, 1982, pp. 93–100.
63 M. Bochmann and S. J. Lancaster, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1634.
64 M. Bochmann and S. J. Lancaster, *J. Organomet. Chem.*, 1992, **434**, C15.

Received 6*th May* 1997; *Paper* 7/03112B