Solution structures and exchange phenomena of the new alkene polymerization initiators (η-C_5Me_5)TiMe(E)(μ-Me)B$(C_6F_5)_3$ (E = C_6F_5, OC_6F_5) and [(η-C_5Me_5)Ti$(OC_6F_5)_2$][BMe$(C_6F_5)_3$]

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The solution structures and dynamics of the new alkene polymerization initiators (η-C_5Me_5)TiMe(C_6F_5)(μ-Me)B$(C_5F_5)_3$ 2, (η-C_5Me_5)TiMe(OC_6F_5)(μ-Me)B$(C_6F_5)_3$ 3 and [(η-C_5Me_5)Ti$(OC_6F_5)_2$][BMe$(C_5F_5)_3$] 4 are compared and contrasted with those of the known initiator (η-C_5Me_5)-TiMe$_2$(μ-Me)B$(C_6F_5)_3$ 1; compound 2 undergoes neither spontaneous ion-pair dissociation to the solvent separated [(η-C_5Me_5)TiMe(C_6F_5)]$^+$ and [BMe$(C_6F_5)_3$]$^-$ nor borane dissociation to its precursors (η-C_5Me_5)TiMe$_2$(C_6F_5) and B$(C_6F_5)_3$; in contrast, 3 is more labile and does undergo ion-pair dissociation, while 4 exists in solution as the separated ion species in equilibrium with its precursors, (η-C_5Me_5)TiMe$(OC_6F_5)_2$ and B$(C_6F_5)_3$.

There is currently considerable interest in the utilization of group 4 metal complexes of the types [(Cp′)$_2$MMe]$^+$X$^-$ and [(Cp′)MMe$_2$]$^+$X$^-$ (Cp′ = substituted cyclopentadienyl; M = Ti, Zr, Hf; X$^-$ = poorly coordinating anion) as initiators for alkene polymerization.[1–3] Since most of the more active molecular alkene polymerization initiators are cationic rather than neutral,[1–3] one might anticipate that increasing the Lewis acidity of the metal atoms by incorporation of more electron-withdrawing ligands would result in even hgher activities. However, binding of X$^-$ to the cationic species [(Cp′)$_2$MMe]$^+$ and [(Cp′)MMe$_2$]$^+$ may also be enhanced by increasing the Lewis acidity,[4] resulting in inhibition of monomer coordination, while the relative rates of initiation, propagation, termination and chain transfer are affected unpredictably by ligand substitution.[1,5] The result is that electron-withdrawing ligands sometimes result in both decreased catalytic activity and reduced polymer molecular masses.[5]

Although detailed studies of ion-pairing phenomena and their effects on catalytic activities of some metallocene systems [(Cp′)$_2$MMe]$^+$X$^-$ are available,[4] relatively little is known as yet of the behaviour of monocyclopentadienyl systems [(Cp′)M-Me$_2$]$^+$X$^-$. Interestingly, it has been shown that the zwitterionic compound (η-C_5Me_5)TiMe$_2$(μ-Me)B$(C_6F_5)_3$ **1** (Fig. 1, E = Me), formed by treating (η-C_5Me_5)TiMe$_3$ with B$(C_6F_5)_3$ [eqn. (1)],[3] undergoes facile displacement of borate anion,

$$(\eta\text{-}C_5Me_5)TiMe_2E + B(C_6F_5)_3 \rightleftharpoons (\eta\text{-}C_5Me_5)TiMeE(\mu\text{-}Me)B(C_6F_5)_3 \quad (1)$$
$$E = Me\ \mathbf{1},\ C_6F_5\ \mathbf{2},\ OC_6F_5\ \mathbf{3}$$

[BMe$(C_6F_5)_3$]$^-$, on reaction with other ligands.[3] Furthermore, magnetization transfer experiments have demonstrated a low degree of reversible borate dissociation from **1** at 223 K [eqn. (2); E = Me][3] but no exchange between terminal and bridging methyl groups was detected, *i.e.* the borane in **1** does not 'hop' from one methyl to another [reverse of eqn. (2)],

$$(\eta\text{-}C_5Me_5)TiMeE(\mu\text{-}Me)B(C_6F_5)_3 \rightleftharpoons [(\eta\text{-}C_5Me_5)TiMeE]^+[BMe(C_6F_5)_3]^- \quad (2)$$

as occurs in some metallocene systems.[4a–d]

In order to better understand the effects of ligand electronic properties on catalytic activities of this class of compounds, we have extended our investigation to the methyl-bridged chiral compounds (η-C_5Me_5)TiMe(C_6F_5)(μ-Me)B$(C_6F_5)_3$ **2** and (η-C_5Me_5)TiMe(OC_6F_5)(μ-Me)B$(C_6F_5)_3$ **3**, and to the achiral, apparently ionic compound [(η-C_5Me_5)Ti$(OC_6F_5)_2$][BMe$(C_6F_5)_3$] **4**. The new zwitterionic complexes **2** and **3**, in which one of the methyl ligands of **1** has been replaced by the more electronegative ligands C_6F_5 and OC_6F_5, formed cleanly on treatment of solutions of (η-C_5Me_5)TiMe$_2$(C_6F_5)† and (η-C_5Me_5)TiMe$_2$(OC_6F_5)† with 1 equiv. each of the borane B$(C_6F_5)_3$ in CD_2Cl_2 at 195 K [eqn. (1)]. These complexes decompose above 283 K and could not be isolated, but have been fully characterized by ^{1}H, ^{13}C and ^{19}F NMR spectroscopic studies (CD_2Cl_2, 223–283 K).†

The ^{1}H, ^{19}F and ^{13}C{^{1}H} NMR spectra† of **2** and **3** are all consistent with structures as in Fig. 1, sharp terminal Ti–Me and broadened μ-MeB resonances being especially characteristic of the zwitterionic structures proposed.[3] Interestingly, however, the ^{1}H NMR spectrum of **2** at 223 K exhibits a doublet Ti–Me resonance because of long-range coupling with one of the *o*-fluorine atoms of the Ti–C_6F_5 ligand (J_{HF} 3.1 Hz), while the ^{19}F spectrum of **2** at 223 K exhibits five equal intensity resonances attributable to the Ti–C_6F_5 group, On warming, the pairs of *o*- and *m*-^{19}F resonances broaden and coalesce at *ca.* 293 and 273 K, respectively, although the *p*-fluorine resonance and all of the borate fluorine resonances remain well resolved in the temperature range 223–283 K. These observations require that both rotation about the Ti–C_6F_5 bond and inversion at the chiral metal (involving ion-pair dissociation–recombination[4a–d]) be slow on the NMR timescale at 223 K, while consideration of the coalescence temperatures suggests an approximate $\Delta G^\ddagger$ of 50.6 ± 2.1 kJ mol^{-1} for the exchange process(es).[7] This would represent a lower limit for both processes, and is to be compared with *ca.* 58 ± 19 kJ mol^{-1} for ion-pair dissociation–reorganization processes of similar zirconocene and hafnocene complexes.[4a–d]

Consistent with this interpretation and in contrast to **1**,[3] attempted magnetization transfer experiments provided no evidence in the ^{1}H NMR spectrum of **2** for dissociation of the borate anion [BMe$(C_6F_5)_3$]$^-$; thus the (μ-Me)B(C_6F_5) moiety is relatively strongly bound to the titanium centre in **2**. In contrast, irradiation of the μ-Me resonance of **3** did result in magnetization transfer and appearance of a weak free borate resonance, indicating an equilibrium between solvent separated ion pairs and the methyl bridged species, as with **1**.[3] With neither **2** nor **3**

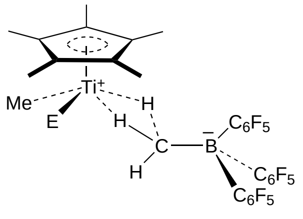

Fig. 1 Proposed structure for **1** (E = Me), **2** (E = C_6F_5) and **3** (E = OC_6F_5)

was there evidence from spin-transfer experiments for Ti–Me/B–Me exchange, as occurs in zirconocene systems.[4a–d]

Compounds **1**,[3] **2** and **3** all behave as ethene and propene polymerization catalysts under strictly anhydrous conditions in toluene. While the polyethylene formed is generally too insoluble for even high-temperature GPC measurements, the molecular masses of the polypropylene formed at 195 K decrease in the order **2** ($M_\mathrm{w} = 2.3 \times 10^6$, $M_\mathrm{w}/M_n = 1.7$) > **3** ($M_\mathrm{w} = 2.0 \times 10^6$, $M_\mathrm{w}/M_n = 1.7$) > **1** ($M_\mathrm{w} = 0.3 \times 10^6$, $M_\mathrm{w}/M_n = 1.3$). The low dispersities observed are consistent with single site catalysts in all cases,[1] but the most Lewis acidic catalyst gives the highest molecular mass polymer, just the opposite to apparent trends in metallocene systems.[5] On the other hand, the yields of polymers obtained with **2** and **3** are about 30% lower than those obtained with **1**, consistent with stronger borate coordination to the more Lewis acidic catalytic sites. Thus combination of the types of Lewis acidic complexes described here with counter anions which, perhaps for steric reasons,[8] coordinate less weakly than $[\mathrm{BMe(C_6F_5)_3}]^-$, may well lead to alkene polymerization catalysts of high activity.

The solution behaviour observed for **4** was most unexpected. The methyl abstraction reaction of $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{TiMe(OC_6F_5)_2}$ with 1 equiv. of $\mathrm{B(C_6F_5)_3}$ in $\mathrm{CD_2Cl_2}$ was monitored by ^{1}H and ^{19}F NMR spectroscopy in the temperature range 223–298 K, and it was found that the ^{1}H and ^{19}F spectra at 223 K exhibited resonances attributable only to the solvent separated species of **4**, $[(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ti(OC_6F_5)_2}]^+$ and $[\mathrm{BMe(C_6F_5)_3}]^-$; none were attributable to coordinated borate as in **1–3**. Remarkably, warming the NMR solution of **4** resulted in the reversible reappearance of the resonances of the neutral precursor $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{TiMe(OC_6F_5)_2}$, and at 263 K there was a substantial amount of both species present. Spin saturation transfer and variable-temperature experiments showed them to be in equilibrium, with $\Delta H = -1.25 \pm 0.1$ kJ mol^{-1}, $\Delta S = -46 \pm 4$ J K^{-1} mol^{-1} for conversion to the non-ionic species. The ability of **4** to engage in Ti–Me/B–Me exchange stands in contrast to **1**–**3** and even to methylzirconocene systems,[4a–d] for which variable-temperature NMR studies imply similar exchange but not the major shift in equilibrium noted here. Since $[(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ti(OC_6F_5)_2}]^+$ is expected to be a relatively strong Lewis acid, its unusual disinclination to bind the borate anion must be attributed to steric hindrance by the three bulky ligands on the titanium hindering close approach of the borate anion. In **4**, moreover, it appears that the strong but sterically hindered Lewis acid $[(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ti(OC_6F_5)_2}]^+$ effectively competes with $\mathrm{B(C_6F_5)_3}$ for possession of the methyl group, presumably *via* a transient methyl bridged species although none was detected in the spin saturation experiments. An alternative structure for **4** such as $\{[(\eta\text{-}\mathrm{C_5H_5})\mathrm{Ti(OC_6F_5)}(\mu\text{-}\mathrm{OC_6F_5})]_2\}^{2+}$ seems unlikely since (*a*) the pentafluorophenoxy groups are equivalent in the ^{19}F NMR spectrum and (*b*) **3** clearly does not contain such a μ-$\mathrm{OC_6F_5}$ group.

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Footnotes

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† Reactions of the compounds $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{TiCl_2Me}$[6] and $(\eta\text{-}\mathrm{C_5Me_5})$-$\mathrm{TiMe_2Cl}$[6] with appropriate amounts of $\mathrm{LiC_6F_5}$ or $\mathrm{LiOC_6F_5}$ in hexanes yielded the thermally robust, yellow compounds $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{TiMe_2(C_6F_5)}$, $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{TiMe_2(OC_6F_5)}$ and $(\eta\text{-}\mathrm{C_5Me_5})\mathrm{TiMe(OC_6F_5)_2}$, all of which have been fully and satisfactorily characterized by elemental analyses and spectroscopic methods.

$(\eta\text{-}\mathrm{C_5Me_5})\mathrm{TiMe_2(C_6F_5)}$. ^{1}H NMR ($\mathrm{CDCl_3}$, 298 K), δ 1.98 (s, 15 H, $\mathrm{C_5Me_5}$), 1.41 (t, 6 H, Ti–Me, J_HF 2.0); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CDCl_3}$, 298 K); δ 127.0 ($C_5\mathrm{Me_5}$), 80.0 (t, Ti–Me, J_CF 3.3 Hz), 12.4 ($\mathrm{C_5}Me_5$); ^{19}F NMR ($\mathrm{C_6D_6}$, 298 K, ref. $\mathrm{CFCl_3}$), δ −121.4 (m, 2 F, *o*-F), −155.6 (t, 1 F, *p*-F), −163.0 (m, 2 F, *m*-F).

$(\eta\text{-}\mathrm{C_5Me_5})\mathrm{TiMe_2(OC_6F_5)}$. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 223 K), δ 1.86 (s, 15 H, $\mathrm{C_5Me_5}$), 0.55 (s, 3 H, Ti–Me); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$, 223 K), δ 141.1 (d, *o*-CF, J_CF 231.5 Hz), 138.7 (d, *m*-CF, J_CF 241.5 Hz), 135.5 (d, *p*-CF, J_CF 241.5 Hz), 124.2 ($C_5\mathrm{Me_5}$), 59.0 (Ti–Me), 12.1 ($\mathrm{C_5}Me_5$); ^{19}F NMR ($\mathrm{CD_2Cl_2}$, 298 K, ref. $\mathrm{CFCl_3}$), δ −160.1 (m, 2 F, *o*-F), −167.0 (m, 2 F, *m*-F), −171.3 (t, 1 F, *p*-F).

$(\eta\text{-}\mathrm{C_5Me_5})\mathrm{TiMe(OC_6F_5)_2}$. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 223 K), δ 1.89 (s, 15 H, $\mathrm{C_5Me_5}$), 1.09 (s, 3 H, Ti–Me); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$, 223 K), δ 139.9 (d, *o*-CF, J_CF 251.5 Hz), 138.1 (d, *m*-CF, J_CF 241.5 Hz), 135.2 (d, *p*-CF, J_CF 251.5 Hz), 127.0 ($C_5\mathrm{Me_5}$), 61.5 (Ti–Me), 10.9 ($\mathrm{C_5}Me_5$); ^{19}F NMR ($\mathrm{CD_2Cl_2}$, 223 K), δ −161.4 (m, 2 F, *o*-F), −167.0 (m, 2 F, *m*-F), −171.3 (t, 1 F, *p*-F).

$(\eta\text{-}\mathrm{C_5Me_5})\mathrm{TiMe(C_6F_5)}(\mu\text{-}\mathrm{Me})\mathrm{B(C_6F_5)_3}$ **2**. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 223 K), δ 2.61 (d, 3 H, Ti–Me, J_HF 3.1), 2.10 (s, 15 H, $\mathrm{C_5Me_5}$), 1.36 (br s, 3 H, μ-Me); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ ($\mathrm{CD_2Cl_2}$, 223 K), δ 138.2 ($C_5\mathrm{Me_5}$), 109.9 (Ti–Me), 13.6 ($\mathrm{C_5}Me_5$); ^{19}F ($\mathrm{CD_2Cl_2}$, 223 K), δ −118.6 (m, 1 F, *o*-F of Ti–$\mathrm{C_6F_5}$), −124.3 (m, 1 F, *o*-F of Ti–$\mathrm{C_6F_5}$), −135.1 (m, 6 F, *o*-F of B–$\mathrm{C_6F_5}$), −150.1 (t, 1 F, *p*-F of Ti–$\mathrm{C_6F_5}$), −160.3 (m, 1 F, *m*-F of Ti–$\mathrm{C_6F_5}$), −160.8 (t, 3 F, *p*-F of B–$\mathrm{C_6F_5}$), −161.7 (m, 1 F, *m*-F of Ti–$\mathrm{C_6F_5}$), −166.0 (m, 6 F *m*-F of B–$\mathrm{C_6F_5}$).

$(\eta\text{-}\mathrm{C_5Me_5})\mathrm{TiMe(OC_6F_5)}(\mu\text{-}\mathrm{Me})\mathrm{B(C_6F_5)_3}$ **3**. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 223 K), δ 2.04 (s, 15 H, $\mathrm{C_5Me_5}$), 1.89 (s, 3 H, Ti–Me), 0.62 (br s, 3 H, μ-Me); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ ($\mathrm{CD_2Cl_2}$, 223 K), δ 134.3 ($C_5\mathrm{Me_5}$), 82.2 (Ti–Me), 12.2 ($\mathrm{C_5}Me_5$); ^{19}F ($\mathrm{CD_2Cl_2}$, 223 K), δ −135.4 (m, 6 F, *o*-F of B–$\mathrm{C_6F_5}$), −159.7 (m, 2 F, *o*-F of Ti–$\mathrm{OC_6F_5}$), −160.9 (t, 3 F, *p*-F of B–$\mathrm{C_6F_5}$), −164.5 (m, 2 F, *m*-F of Ti–$\mathrm{OC_6F_5}$), −165.0 (m, 2 F, *m*-F of Ti–$\mathrm{OC_6F_5}$), −166.0 (m, 6 F, *m*-F of B–$\mathrm{C_6F_5}$).

$[(\eta\text{-}\mathrm{C_5Me_5})\mathrm{Ti(OC_6F_5)_2}][\mathrm{BMe(C_6F_5)_3}]$ **4**. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 223 K), δ 2.17 (s, 15 H, $\mathrm{C_5Me_5}$), 0.37 (br s, 3 H, B–Me); $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$, 223 K), δ 139.3 ($C_5\mathrm{Me_5}$), 12.3 ($\mathrm{C_5}Me_5$), ^{19}F NMR ($\mathrm{CD_2Cl_2}$, 223 K), δ −133.7 (m, 6 F, *o*-F of B–$\mathrm{C_6F_5}$), −159.2 (m, 4 F, *o*-F of O–$\mathrm{C_6F_5}$), −165.1 (t, 3 F, *p*-F of B–$\mathrm{C_6F_5}$), −163.5 (m, 4 F, *m*-F of O–$\mathrm{C_6F_5}$), −162.4 (t, 2 F, *p*-F of O–$\mathrm{C_6F_5}$), −168.4 (m, 6 F, *m*-F of B–$\mathrm{C_6F_5}$).

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