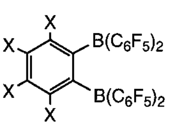
Activation of $[Cp_2ZrMe_2]$ with New Perfluoroaryl Diboranes: Solution Chemistry and Ethylene Polymerization Behavior in the Presence of $MeAl(BHT)_2$**

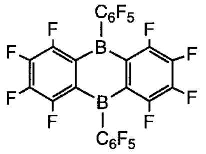
V. Clifford Williams, Chaoyang Dai, Zengmin Li,
Scott Collins,* Warren E. Piers,* William Clegg,
Mark R. J. Elsegood, and Todd B. Marder

Perfluoroaryl-substituted boranes[1] and alanes[2] are potent Lewis acids which are able to abstract alkide groups (e.g. CH_3^-, methide) from organotransition metal complexes, forming highly reactive cationic complexes.[3] This is done most often within the context of olefin polymerization catalysis and perfluoroaryl-substituted boranes $B(Ar_F)_3$ have become important as cocatalysts in commercial processes. Effects of counterions on the activity and thermal stability of the catalysts are profound and depend to a large degree on the nature and strength of the ion–ion interaction in solution.[4]

Marks et al. have suggested that one way to ameliorate these interactions is to distribute the negative charge of the anion over more atoms through the use of bifunctional Lewis acids.[5] To this end, we have recently reported the synthesis of the novel diboranes **1** and **2**.[6] While developing the synthetic route to **1**, we prepared the 9,10-boraanthracene compound 9,10-$Cl_2C_{12}B_2F_8$, which can be converted smoothly into the perfluorophenyl substituted analogue **3** by use of $Zn(C_6F_5)_2$[7] as a C_6F_5 transfer agent. Diboraanthracene **3** has been prepared and disclosed independently by Marks et al.[8]



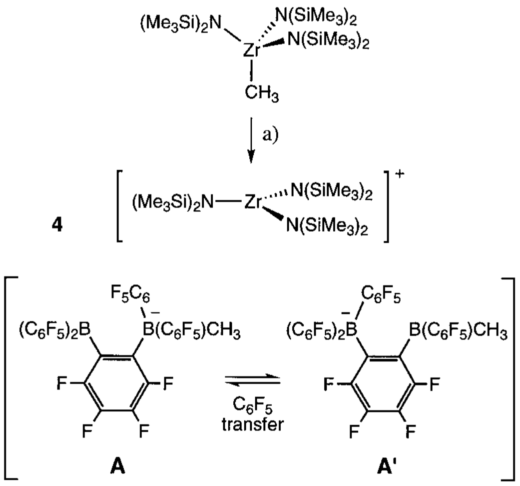
1, X = F
2, X = H



3

Herein we report the methide abstraction reactions of **1** with organozirconium compounds and a comparative assessment of $B(C_6F_5)_3$ and diboranes **1**–**3** as olefin polymerization initiators. In addition, we describe the behavior of these various activators in the presence of $MeAl(BHT)_2$ (MAD; BHT = 2,6-di-*tert*-butyl-4-methylphenoxide), a monomeric alkylaluminum compound[9] which appears to be an example of a "noninteracting" scrubbing agent of use in olefin polymerization.[10]

To assess the solution and solid-state structure of the anion formed upon methide abstraction by **1**, we employed the tris-amido zirconium complex $[MeZr\{N(SiMe_3)_2\}_3]$[11] as a CH_3^- source. In C_6D_5Br, reaction of **1** and $[MeZr\{N(SiMe_3)_2\}_3]$ in a 1:1 ratio cleanly formed a stable ion pair (**4**, Scheme 1).



Scheme 1. Synthesis of the stable ion pair **4**. a) **1** (1 equiv), C_6D_5Br.

The solution structure of the anionic portion of **4** was investigated by 1D and 2D ^{19}F NMR experiments. The ^{19}F NMR spectrum (282.4 MHz) collected at room temperature is shown in Figure 1. The anion comprises two species as indicated by the two signals at $\delta = -146.9$ (major) and

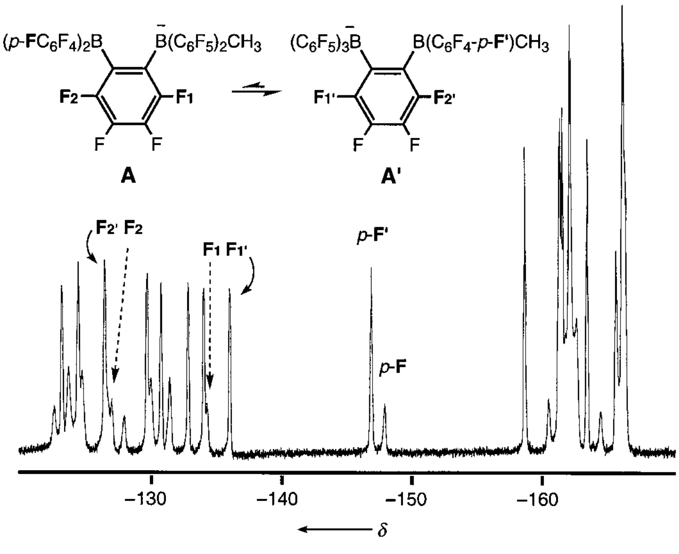


Figure 1. ^{19}F NMR spectrum (282.4 MHz) of **4** recorded in CD_2Cl_2 at room temperature.

---

[*] Prof. S. Collins, Dr. C. Dai, Dr. Z. Li
Department of Chemistry, University of Waterloo
Waterloo, ON, N2L3G1 (Canada)
Fax: (+1)519-746-0435
E-mail: scollins@uwaterloo.ca

Prof. W. E. Piers, Dr. V. C. Williams
Department of Chemistry, University of Calgary
2500 University Drive NW
Calgary, AB, T2N1N4 (Cananda)
Fax: (+1)403-289-9488
E-mail: wpiers@ucalgary.ca

Prof. W. Clegg, Dr. M. R. J. Elsegood
Department of Chemistry, University of Newcastle
Newcastle upon Tyne, NE17RU (England)

Prof. T. B. Marder
Department of Chemistry, University of Durham
Durham, DH1 3LE (England)

[**] Financial support for this work was provided by the Natural Sciences and Engineering Council of Canada's Strategic Projects program (STR192869) and the EPSRC (UK). Technical and in-kind support from Nova Chemicals of Calgary, Alberta, is also acknowledged. W.E.P. thanks the Alfred P. Sloan Foundation for a Research Fellowship (1996–2000). BHT = 2,6-di-*tert*-butyl-4-methylphenoxide.

-147.9 (minor), which are characteristic of *para*-fluorine atoms on a C_6F_5 ring bound to a neutral borane center (p-**F′** and p-**F**, respectively).[12] The presence of the two resonances suggests that there are two different neutral borane centers in the anion, related by reversible C_6F_5 transfer (Scheme 1). ^{19}F COSY 45 experiments allow for assignment of the *ortho*-fluorine atoms of the central ring; the resonances at $\delta = -136.0$ and -126.5 are ascribed to the fluorine atoms *ortho* to the borate and borane centers, respectively, of the major species (**F1′** and **F2′**); the less intense resonances at $\delta = -134.3$ and -127.1 are the analogous peaks for the minor species (**F1** and **F2**). Since the signals at $\delta = -136.0$ (major species, *ortho*-borate fluorine) and $\delta = -146.9$ (major species, *para*-C_6F_5) integrate in a 1:1 ratio, we assign the major solution species the structure **A′**, formed by C_6F_5 transfer from the (presumably) kinetically formed minor species **A** (see Scheme 1). Comparison of the two distinct *para*-fluorine resonances suggests that **A′** predominates over **A** in approximately a 6:1 ratio.

The ^{19}F EXSY experiments show that exchange of the C_6F_5 groups in the anion is extensive. Particularly informative is the EXSY map of the well-resolved *ortho* region of the spectrum, which indicates that at least two processes are operative. The first, manifested by exchange between *ortho* fluorine atoms of the major species, can be explained on the basis of rotation about the B–C_6F_5 and C_6F_4–B axes, which is restricted at room temperature in this sterically crowded system. Cross-peaks in the EXSY map between peaks ascribed to the *ortho*-fluorine atoms of **A** and the *ortho*-fluorine atoms of **A′** can only arise by transfer of a C_6F_5 ring between boron centers; in this fashion, all the C_6F_5 rings are scrambled. A correlation between the peaks ascribed to the *para*-fluorine atoms of the C_6F_5 rings bound to neutral three-coordinate borane centers is also consistent with this process.

Layering a solution of **4** in CH_2Cl_2 with hexanes produced crystals suitable for X-ray analysis.[13] The cationic portion of the molecule is nearly identical to that reported by Green and co-workers;[14] the structure of the anion in **4** is given in Figure 2. The anion's solid-state structure corresponds to that of the major isomer in solution, that is, **A′**. While the B1-C1-C6-B2 dihedral angle is 19.9(2)° in free borane **1**,[6] these atoms are essentially coplanar in the anion of **4**, suggesting an alignment of the borate negative charge with the neutral borane center at B2. Steric tension is evident, however, in the large B2-C6-C1 and B1-C1-C6 angles of 131.5(2)° and 127.2(2)°, respectively.

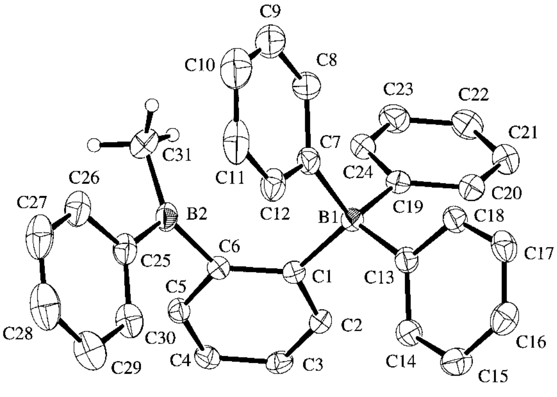
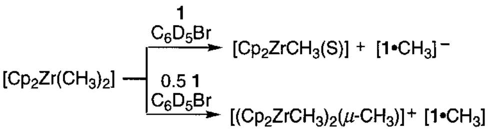


Figure 2. Molecular structure of the anion in **4**. Selected bond distances [Å] and angles [°]: B1–C1 1.650(4), B1–C7 1.662(4), B1–C13 1.657(4), B1–C19 1.674(4), B2–C6 1.601(4), B2–C25 1.590(5), B2–C31 1.565(5); B1-C1-C6 127.2(2), B1-C1-C2 117.3(2), B2-C6-C1 131.5(2), B2-C6-C5 110.1(2), C1-B1-C7 109.2(2), C1-B1-C13 115.6(2), C1-B1-C19 104.2(2), C6-B2-C25 119.4(3), C6-B2-C31 117.3(3), C25-B2-C31 121.5(3).

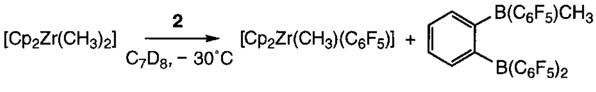
Diborane **1** readily abstracts a methide group from $[Cp_2ZrMe_2]$. Reactions in toluene yield immiscible oils; in C_6D_5Br, however, the products are soluble and stable for several hours. In the 1:1 (**1**:Zr) reaction the major species (≈90%) is a monomeric, solvent-separated ion pair [Eq. (1a); S = solvent] that slowly ($t_{1/2} \approx 2$ d) decomposes to an unknown product. The 1:2 reaction produces a μ-methyl zirconium dimer[3a, 15] [Eq. (1b)], as indicated by the appearance of signals at $\delta = 0.07$ and -1.05 in a 2:1 ratio, assigned to the terminal and bridging methyl groups, respectively. The ^1H, ^{11}B, and ^{19}F NMR data for the monomeric and dimeric compounds indicate that the structure of the counteranion in these systems is the same as that found in **4**. In the ^1H NMR spectra of these complexes, broad signals at $\delta = 1.19$ and 1.67 (≈5:1) are a consistent feature and are assigned to $B_{neutral}CH_3$ of **A′** and $B_{borate}CH_3$ of **A**, respectively.



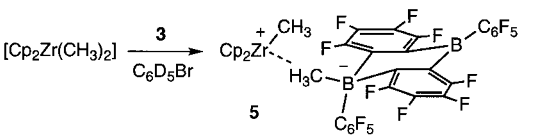
(1a)

(1b)

Diborane **2** appears to react with $[Cp_2ZrMe_2]$ in an analogous fashion [Eq. (2)], although the ion pair is thermally unstable, even at $-30\,^{\circ}C$ in [D$_8$]toluene; the major products observed result from C_6F_5 transfer[15d] from the counterion to Zr. In contrast, diboraanthracene **3** reacts with $[Cp_2ZrMe_2]$ to furnish the stable ion pair **5** [Eq. (3)], in which there is restricted rotation about both exocyclic B–C_6F_5 bonds. The ^1H chemical shift of BCH_3 ($\delta = 0.12$) is consistent with a contact ion pair structure.[3a] Interestingly, further addition of one equivalent of $[Cp_2ZrMe_2]$ to solutions of **5** led to the formation of a precipitate, with complete disappearance of all NMR signals due to **5** (and $[Cp_2ZrMe_2]$). The precipitate is insoluble/unstable in common NMR solvents, and may be a diboraanthracene species such as $[Cp_2ZrMe]_2[9,10\text{-}Me_2C_{12}B_2F_8]$.[8]



(2)



(3)

To assess the suitability of these diboranes as cocatalysts, ethylene polymerizations were conducted in toluene slurry using $[Cp_2ZrMe_2]$ and each of the cocatalysts $B(C_6F_5)_3$ and **1**–**3**. Initially, experiments were conducted by mixing $[Cp_2ZrMe_2]$ (1.0 equiv) with the cocatalyst (1.2 equiv) in a small volume of toluene just prior (i.e., contact time < 1 min) to delivery to the reactor, which was presaturated with ethylene and contained $AlMe_3$ as a scrubbing agent (≈30 μM).

As shown in Table 1 (entries 1–3) the order of polymerization activity under these conditions is $B(C_6F_5)_3 > \mathbf{1} > \mathbf{2}$. The lower activity of the ion pair derived from **2** and $[Cp_2ZrMe_2]$ may be a reflection of the limited stability of this species at room temperature (or even at low temperature, see above); we have noted elsewhere that even ion pairs with limited thermal stability can be competent polymerization catalysts when generated in situ.[15d] The lower polymerization activity of the ion pair derived from **1**, compared to that formed from $B(C_6F_5)_3$, is surprising in view of both the thermal stability of the ion pair derived from **1** and $[Cp_2ZrMe_2]$ in bromobenzene and the fact that the major species appears to be a solvent-separated ion pair

Table 1. Ethylene polymerization using $[Cp_2ZrMe_2]$ and various cocatalysts.[a]

Entry	Cocatalyst	AlR_3 (conc. [μM])	Act.[b]	M_w	M_w/M_n
1	$B(C_6F_5)_3$	$AlMe_3$ (30)	4.4	340	2.17
2	**1**	$AlMe_3$ (30)	3.3	290	2.08
3	**2**	$AlMe_3$ (30)	2.8	370	1.83
4	$B(C_6F_5)_3$	MAD (50)	1.5	–	–
5	$B(C_6F_5)_3$	MAD (100)	1.6	–	–
6	$B(C_6F_5)_3$	MAD (200)	13.9	270	2.18
7[c]	$B(C_6F_5)_3$	MAD (300)	13.4	260	2.00
8[c,d]	$[Ph_3C][B(C_6F_5)_4]$	MAD (300)	48.9	240	2.06
9[c–e]	$[Ph_3C][B(C_6F_5)_4]$	MAD (300)	30.1	340	2.24
10[c,d,f]	$[Ph_3C][B(C_6F_5)_4]$	MAD (300)	10.8	250	2.18
11	**1**	MAD (300)	5.0	260	1.98
12	**2**	MAD (300)	3.8	200	2.04
13[g]	**2**	MAD (300)	0.39	–	–
14[c]	**3**	MAD (300)	1.5	280	2.23
15[h]	**3**	MAD (300)	1.8	260	1.98

[a] Conditions: 500 mL of toluene, 30 °C, 20 psi (1.38 bar) C_2H_4, 1000 rpm with $c([Cp_2ZrMe_2]) = 10$ μM and $c(\text{cocatalyst}) = 12$ μM, except where noted. The cocatalyst was added to the reactor, presaturated with monomer and containing scrubbing agent, followed immediately by the addition of $[Cp_2ZrMe_2]$ except where noted. [b] Activity in 10^6 g of polyethylene per mol Zr per hour. [c] $c([Cp_2ZrMe_2]) = 2.0$ μM, $c(\text{cocatalyst}) = 2.2$ μM. [d] 30 psi (2.07 bar) C_2H_4. [e] $[Cp_2ZrMe_2]$ was added 5 min after the cocatalyst. [f] $[Cp_2ZrMe_2]$ was added 10 min after the cocatalyst. [g] $[Cp_2ZrMe_2]$ and **2** were premixed in toluene (20 mL) for 5 min at 25 °C. [h] $c([Cp_2ZrMe_2]) = 4.0$ μM, $c(\text{cocatalyst}) = 2.0$ μM

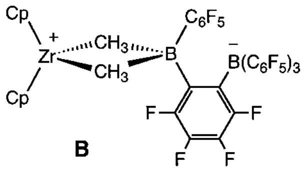
It is known that simple scrubbing agents such as $AlMe_3$ or $Al\mathit{i}Bu_3$ can be incompatible with neutral boranes, such as $B(C_6F_5)_3$,[16] or other common cocatalysts, such as $[Ph_3C][B(C_6F_5)_4]$.[2b] This complexity makes interpretation of polymerization experiments conducted under conditions such as those reported here (i.e., continuous in monomer and with effective stirring) difficult, as the different activities observed using the different activators might be entirely due to differences in the concentration of activator (or even the nature of the activator) and thus ultimately the catalytically active species [Zr*].

We have discovered that MAD appears to be an example of a "noninteracting" scrubbing agent, at least with $B(C_6F_5)_3$. This compound is unreactive towards $[Cp_2ZrMe_2]$, $B(C_6F_5)_3$, or the ion pair derived from these compounds in toluene at room temperature, as revealed by ^1H and ^{19}F NMR spectroscopy.[17]

As shown in Table 1, substitution of $AlMe_3$ by MAD leads to pronounced improvements in catalytic activity of $[Cp_2ZrMe_2]$ and $B(C_6F_5)_3$ (entries 4–7). Having said that, MAD appears to be a less effective scrubbing agent than $AlMe_3$ in the sense that higher concentrations (and longer contact times) are required to effectively remove impurities from solvent and monomer. However, unlike the situation with $AlMe_3$, which can have an inhibitory effect at high concentrations,[15a] MAD is much more convenient to use as a scrubbing agent as the amount employed (above the threshold value required to remove impurities) does not seem to influence polymerization activity.

While MAD is unreactive towards $B(C_6F_5)_3$, it does react slowly with $[Ph_3C][B(C_6F_5)_4]$ at room temperature in [D$_5$]chlorobenzene ($t_{1/2} \approx 1$ h with $c(\text{MAD}) = c([Ph_3C][B(C_6F_5)_4]) \approx 0.05$ M). The principal reaction appears to involve hydride (rather than CH_3^-)[2b] abstraction from MAD, as revealed by the formation of Ph_3CH. The nature of the aluminum-containing products has not yet been determined, but the AlMe moiety appears to remain intact. As the polmerization results using $[Ph_3C][B(C_6F_5)_4]$ demonstrate (Table 1, entries 8–10), incompatibility of the cocatalyst and the scrubbing agent can have definite consequences on polymerization activity when $[Cp_2ZrMe_2]$ introduction is delayed.

Even with MAD, the same activity order is observed using these diborane cocatalysts. Indeed, the activity of **1**/$[Cp_2ZrMe_2]$ is not as dramatically improved compared with the use of $B(C_6F_5)_3$/$[Cp_2ZrMe_2]$ in the presence of MAD. These results suggest that the lower activity of the ion pair resulting from **1**/$[Cp_2ZrMe_2]$ may be intrinsic, despite the apparent lower coordinating ability of the counteranion in bromobenzene. One possible explanation is that the counterion does coordinate to Zr in toluene, but the interaction involves the borane moiety, rather than the perfluoroarylborate portion of the molecule (e.g. **B**).[18] The resulting adduct would be analogous to those formed from metallocenium ions and $AlMe_3$[15a] and would be expected to have lower activity.



B

As might be expected, premixing **2** and $[Cp_2ZrMe_2]$ in toluene, prior to polymerization, leads to a tenfold decrease in activity compared to in situ generation (Table 1, entry 13 versus 12), demonstrating that ion pair stability effects [Eq. (2)] are important. Interestingly, **3** is an effective cocatalyst, even when the Zr:B ratio is 1:1 instead of 1:2 (entry 15 versus 14).[8] In light of the solution chemistry reported for **3**/$[Cp_2ZrMe_2]$ (see above), in the latter case (Zr:B = 1:2) the likely species present is the ion pair **5**.

Experimental Section

General techniques have been described in detail elsewhere.[15d] ^1H NMR spectra acquired in C_6D_5Br were referenced to the residual *meta*-protons at $\delta = 6.90$.

Synthesis of **4**: Hexane (20 mL) was condensed into a flask containing $[MeZr\{N(SiMe_3)_2\}_3]$ (0.12 g, 0.21 mmol) and diborane **1** (0.18 g, 0.21 mmol) at −78 °C. The solids slowly dissolved as the sample was warmed to room temperature, forming a colorless oil. Trituration afforded a white powder, which was isolated by filtration and dried in vacuo (0.35 g, 95 %). ^{1}H NMR (200 MHz, CD_2Cl_2, 25 °C, TMS): $\delta = 0.17$ (s, $SiCH_3$); ^{11}B NMR (96.29 MHz, CD_2Cl_2): $\delta = -15$ (borane signal not observed); see Figure 1 for the ^{19}F NMR spectrum; elemental analysis calcd for $C_{49}H_{57}B_2F_{24}N_3Si_6Zr$: C 41.3, H 4.0, N 2.9; found: C 41.2, H 3.9, N 2.8.

Generation of metallocenium cations from $[Cp_2ZrMe_2]$ and **1**: Monomeric and dimeric metallocenium cations were generated in situ by adding a solution of **1** in C_6D_5Br to a solution of $[Cp_2ZrMe_2]$ in a 1:1 or a 1:2 (**1**:Zr) stoichiometry. The solutions were then assayed by ^{1}H, ^{11}B, and ^{19}F NMR spectroscopy; the results of the latter two were essentially identical to that found for **4**. ^{1}H NMR for $[Cp_2ZrCH_3(S)]^+[\mathbf{A'}/\mathbf{A}]^-$ (S = solvent; 200 MHz, C_6D_5Br, 25 °C): $\delta = 5.83$ (s, C_5H_5), 1.67 (br s, $B_{borate}CH_3$), 1.19 (br s, $B_{borane}CH_3$), 0.48 (s, $ZrCH_3$); ^{13}C NMR (100.61 MHz, C_6D_5Br): $\delta = 115.3$ (C_5H_5), 53.8 ($ZrCH_3$), 17.3 ($B_{borate}CH_3$), 15.0 ($B_{borane}CH_3$). ^{1}H NMR for $[(Cp_2ZrCH_3)_2(\mu\text{-}CH_3)]^+[\mathbf{A'}/\mathbf{A}]^-$ (200 MHz, C_6D_5Br, 25 °C): $\delta = 5.89$ (s, 20 H, C_5H_5), 1.67 (br s, $B_{borate}CH_3$ of **A**), 1.19 (br s, $B_{borane}CH_3$ of **A′**), 0.07 (s, 6 H, $ZrCH_3$), −1.05 (s, 3 H, $ZrCH_3Zr$).

Generation of metallocenium cations from $[Cp_2ZrMe_2]$ and **3**: Ion pair **5** was generated in situ by mixing $[Cp_2ZrMe_2]$ and diborane **3** in C_6D_5Br. ^{1}H NMR (200 MHz, C_6D_5Br, 25 °C): $\delta = 5.74$ (s, 10 H, C_5H_5), 0.36 (s, 3 H, $ZrCH_3$), 0.12 (br s, 3 H, $B_{borate}CH_3$); ^{19}F{^{1}H} NMR (C_6D_5Br, 25 °C): $\delta = -124.74$ (br m, 2 F), −133.8 and −136.8 (2 × br m, total 2 F, *o*-F), −134.4 (m, 2 F), −135.8 (br m, 2 F, *o*-F), −146.6 (br m, 2 F), −156.4 (t, J(F,F) = 20.7 Hz, *p*-F), −159.8 (br m, 2 F, *m*-F), −160.9 (br m, 1 F, *p*-F), −163.2 and −163.8 (2 × br m, total 2 F, *m*-F), −165.2 (br m, 2 F).

Received: July 2, 1999
Revised version: September 10, 1999 [Z 13671 IE]
German version: *Angew. Chem.* **1999**, *111*, 3922–3926

Keywords: boranes · fluorine · metallocenes · polymerizations

---

[1] a) L. Li, T. J. Marks, *Organometallics* **1998**, *17*, 3996; b) Y.-X. Chen, C. L. Stern, S. Yang, T. J. Marks, *J. Am. Chem. Soc.* **1996**, *118*, 12451; c) D. J. Parks, W. E. Piers, G. P. A. Yap, *Organometallics* **1998**, *17*, 5492; d) A. G. Massey, A. J. Park, *J. Organomet. Chem.* **1964**, *2*, 245.

[2] a) Y.-X. Chen, C. L. Stern, T. J. Marks *J. Am. Chem. Soc.* **1997**, *119*, 2582; b) M. Bochmann, M. J. Sarsfield, *Organometallics* **1998**, *17*, 5908.

[3] a) Y.-X. Chen, M. V. Metz, L. Li, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **1998**, *120*, 6287, and references therein; b) R. E. v. H. Spence, W. E. Piers, Y. Sun, M. Parvez, L. R. MacGillivray, M. J. Zaworotko, *Organometallics* **1998**, *17*, 2459.

[4] a) P. A. Deck, C. L. Beswick, T. J. Marks, *J. Am. Chem. Soc.* **1998**, *120*, 1772, and references therein; b) Y. Sun, R. E. v. H. Spence, W. E. Piers, M. Parvez, G. P. A. Yap, *J. Am. Chem. Soc.* **1997**, *119*, 5132; c) L. Luo, T. J. Marks, *Top. Catal.* **1999**, *7*, 97.

[5] a) L. Jia, X. Yang, C. L. Stern, T. J. Marks, *Organometallics* **1994**, *13*, 3755; b) T. J. Marks, L. Jia, X. Yang (Northwestern University), US Patent 5447895, **1995**.

[6] V. C. Williams, W. E. Piers, W. Clegg, M. R. J. Elsegood, S. Collins, T. B. Marder, *J. Am. Chem. Soc.* **1999**, *121*, 3244.

[7] Y. Sun, W. E. Piers, M. Parvez, *Can. J. Chem.* **1998**, *76*, 513.

[8] a) M. V. Metz, D. J. Schwartz, C. L. Beswick, C. L. Stern, T. J. Marks, *Inorganic Abstracts of the 217th ACS National Meeting* (Anaheim, CA), **1999**, abstract no. 15; b) M. H. Mcadon, P. N. Nickias, T. J. Marks, D. J. Swartz (Northwestern University and the Dow Chemical Co.) WO 99/06413, **1999**.

[9] M. D. Healey, D. A. Wierda, A. R. Barron, *Organometallics* **1988**, *7*, 2543.

[10] The use of MAD in combination with $[Cp_2ZrMe_2]$ and methylaluminoxane (MAO) in ethylene polymerizations and as a cocatalyst in styrene polymerizations using Ti–alkoxide initiators has been reported: a) S. S. Reddy, S. Shashidhar, S. Sivaram, *Macromolecules* **1993**, *26*, 1180; b) S. S. Reddy, S. Shashidhar, *Eur. Polym. J.* **1997**, *33*, 583; for use of $R_2Al(BHT)$ and related compounds as scrubbing agents, see R. K. Rosen, J. C. Stevens, J. C. Tracy (Dow Chemical Co.), WO 97/27228, **1997**.

[11] R. Andersen, *Inorg. Chem.* **1979**, *18*, 1724.

[12] A. D. Horton, J. de With, *Organometallics* **1997**, *16*, 5424.

[13] Crystal data for **4** ($C_{49}H_{57}B_2F_{24}N_3Si_6Zr$): $M_r = 1425.4$, monoclinic, space group $P2_1/c$, $a = 12.942(2)$, $b = 22.372(4)$, $c = 22.345(4)$ Å, $\beta = 95.403(4)°$, $V = 6441.0(19)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.470$ g cm^{-3}, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 275(2)$ K; of 35107 measured reflections, 15491 were unique, $R_{int} = 0.0361$; 9019 reflections with $I_{net} > 2.0\,\sigma(I_{net})$, $\mu = 3.87$ cm^{-1}, min./max. transmission 0.752 and 0.913, $R = 0.0441$ ($I > 2\sigma$), $Rw = 0.1069$ (F^2, all data), GOF = 0.922, no. of parameters 785, final difference map within ± 0.52 e Å^{-3}. 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-127481. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; email: deposit@ccdc.cam.ac.uk.

[14] J. R. Galsworthy, M. L. H. Green, N. Maxted, M. Müller, *J. Chem. Soc. Dalton Trans.* **1998**, 387.

[15] a) M. Bochmann, S. L. Lancaster, *Angew. Chem.* **1994**, *106*, 1715; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1634; b) X. Yang, C. L. Stern, T. J. Marks, *Organometallics* **1991**, *10*, 840; c) S. Beck, M.-H. Prosenc, H. H. Brintzinger, R. Goretzki, N. Herfert, G. Fink, *J. Mol. Catal. A* **1996**, *111*, 67; d) K. Köhler, W. E. Piers, S. Xin, Y. Feng, A. M. Bravakis, A. P. Jarvis, S. Collins, W. Clegg, G. P. A. Yap, T. B. Marder, *Organometallics* **1998**, *17*, 3557.

[16] C. H. Lee, S. J. Lee, J. W. Park, K. H. Kim, B. Y. Lee, J. S. Oh, *J. Mol. Catal. A* **1998**, *132*, 231.

[17] Although degenerate Me exchange can occur between MAD and $[Cp_2ZrMe_2]$ or the ion pair formed from $[Cp_2ZrMe_2]$ and $B(C_6F_5)_3$, these processes are slow on the NMR time scale at 25 °C in [D$_8$]toluene. For quantitative studies on Me exchange between alkylmetallocenes and MAD in toluene, see A. R. Siedle, R. A. Newmarks, W. M. Lamanna, J. N. Schroepfer, *Polyhedron* **1990**, *9*, 301.

[18] The 2D ^{1}H–^{1}H EXSY spectra of the ion pair derived from $[Cp_2ZrMe_2]$ and **1** in bromobenzene revealed the presence of weak crosspeaks between the ZrMe resonance and the neutral BMe resonance of the major counteranion, suggesting slow Me exchange under these conditions. The limited solubility of this ion pair in toluene precluded analogous experiments in this solvent.

Titanium – Thiolate – Aluminum – Carbide Complexes by Multiple C–H Bond Activation[**]

Frédéric Guérin and Douglas W. Stephan[*]

Much of early transition metal thiolate chemistry is based on metallocene derivatives.[1] More recently, interest has focused on related monocyclopentadienyl analogues as such systems have proved to be more reactive, often affording novel reactivity and products.[2–13] For example, we have observed that CpTi–thiolate species undergo either β-C–H or C–S bond activation of the thiolate ligands depending on the reaction conditions.[3–7] An interesting aspect of early transition metal chemistry in general involves the perturba-

---

[*] Prof. D. W. Stephan, Dr. F. Guérin
School of Physical Sciences, Chemistry and Biochemistry
University of Windsor
Ontario, N9P 3P4 (Canada)
Fax: (+1) 519-973-7098
E-mail: stephan@uwindsor.ca

[**] Financial support from NSERC of Canada is gratefully acknowledged. F.G. is grateful for the award of an NSERC Postdoctoral Fellowship.