Generation of Cationic [Zr-{*tert*-Butyl Enolate}] Reactive Species: Methyl Abstraction versus Hydride Abstraction

Bing Lian,[a] Loïc Toupet,[b] and Jean-François Carpentier*[a]

Abstract: Treatment of the neutral methyl–Zr–enolate $[Cp_2Zr(Me)\{O(tBuO)C{=}CMe_2\}]$ (**1**) with one equivalent of $B(C_6F_5)_3$ or $[HNMe_2Ph][B(C_6F_5)_4]$ as a methyl abstractor in THF at 0 °C leads to the selective formation of the free ion pair complex $[Cp_2Zr(THF)\{O(tBuO)C{=}CMe_2\}]^+$ $[anion]^-$ (**2**) (anion = $MeB(C_6F_5)_3^-$, $B(C_6F_5)_4^-$), which is relevant to the controlled polymerization of methacrylates. Cation **2** rapidly decomposes at 20 °C in THF with release of one equivalent of isobutene to form the cationic Zr–carboxylate species $[Cp_2Zr(THF)(O_2CiPr)]^+$ (**3**), through a proposed intramolecular proton transfer process from the *tert*-butoxy group to the enolate. The reaction of **1** with one equivalent of $B(C_6F_5)_3$ or $[HNMe_2Ph][B(C_6F_5)_4]$ in CH_2Cl_2 leads to the direct, rapid formation of the dimeric μ-isobutyrato–Zr dicationic species $[\{Cp_2Zr[\mu\text{-}(O_2CiPr)]\}_2]^{2+}$ (**4**), which gives **3** upon dissolution in THF. Contrastingly, when $[Ph_3C][B(C_6F_5)_4]$ is used to generate the cationic Zr–enolate species from **1** in CD_2Cl_2, a 15:85 mixture of dicationic complexes **4** and $[\{Cp_2Zr[\mu\text{-}(O_2C{-}C(Me){=}CH_2)]\}_2]^{2+}$ $[B(C_6F_5)_4]_2^-$ (**5**-$[B(C_6F_5)_4]_2$) is obtained quantitatively. The formation of **5** is proposed to arise from initial hydride abstraction from a methyl enolate group by Ph_3C^+, as supported by the parallel production of Ph_3CH, and subsequent elimination of methane and isobutene. In addition to standard spectroscopic and analytical characterizations for the isolated complexes **2**–**5**, complexes **4** and **5** have also been structurally characterized by X-ray diffraction studies.

Keywords: boranes · C–H activation · enolates · methyl abstraction · zirconium

Introduction

Cationic Group 4 metal species play an important role in the homogeneous polymerization of olefins,[1,2] and the characterization of these species and observable models thereof, is of high interest for understanding catalyst structure–reactivity relationships.[3] The Zr-mediated living polymerization of methyl methacrylate (MMA) was achieved by Collins and co-workers by using a two-component system consisting of the neutral enolate complex $[Cp_2ZrMe\{O(OtBu)C{=}CMe_2\}]$ as initiator and cationic complex $[Cp_2Zr(THF)Me]^+[BPh_4]^-$ as catalysts.[4] The isolation of the *neutral* zirconocene enolate in its pure form enabled them to establish unambiguously, via detailed kinetic studies, a group-transfer-type bimetallic propagating mechanism. Gibson and co-workers reported that Zr-mediated MMA living polymerization can be realized just using the one-component system $[Cp_2ZrMe_2]$/abstractor, which gives high molecular weight and narrow PDI, but still apparently involves two metal atoms per polymer chain.[5] Isolation of elusive *cationic* Zr–enolate species, which may act as key intermediates/models in the Zr-mediated polymerization of MMA, is therefore a central objective.[2] In the course of the preparation of this article, Chen and co-workers have reported the isolation of the cationic *ansa*-zirconocene ester enolate complex $[rac\text{-}(EBI)Zr^+(THF)\{O(OiPr)C{=}CMe_2\}][MeB(C_6F_5)_3]^-$ (EBI = ethylenebis(indenyl)) and the generation of the cationic "constrained geometry" Ti ester enolate complex, $[(CGC)Ti^+(THF)\{O(OiPr)C{=}CMe_2\}][MeB(C_6F_5)_3]^-$ (CGC = $Me_2Si(Me_4C_5)(tBuN)$), which were both shown to be highly active for the polymerization of MMA.[2c,d] Here, we report complementary studies devoted to the generation of the ionic species $[Cp_2Zr(THF)\{O(tBuO)C{=}CMe_2\}]^+[anion]^-$ from the neutral Zr–enolate $[Cp_2Zr(Me)\{O(tBuO)C{=}CMe_2\}]$ (**1**) by using three different discrete abstractors ($B(C_6F_5)_3$, $[HNMe_2Ph][B(C_6F_5)_4]$, and $[Ph_3C][B(C_6F_5)_4]$). Unprecedented transformations of the cationic Zr–enolate reactive species are evidenced, for which a reaction mecha-

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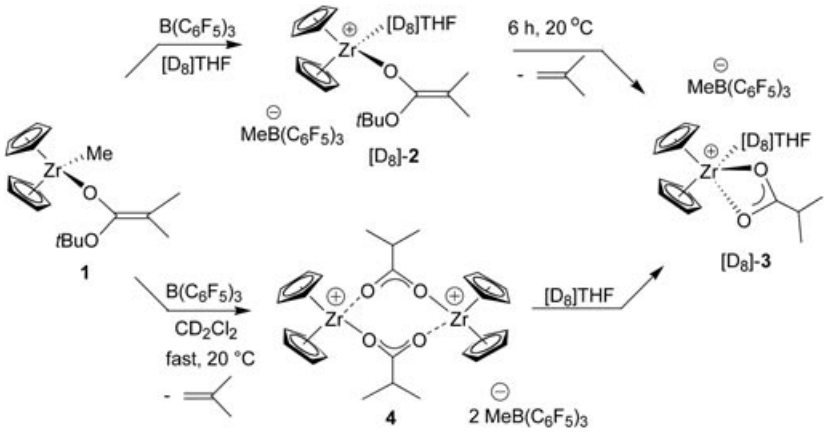
 DOI: 10.1002/chem.200400473

nism is proposed based on the competition between methyl abstraction and hydride abstraction.

Results and Discussion

The new Zr–enolate cationic species [D_8]-**2** was cleanly generated in [D_8]THF by the addition of one equivalent of $B(C_6F_5)_3$ to the neutral methyl–Zr–enolate **1** (Scheme 1).



Scheme 1.

Monitoring by NMR spectroscopy showed that [D_8]-**2** is stable for several days at 0 °C. However, it transforms rapidly at 20 °C to yield quantitatively the new cationic Zr–isobutyrate species [D_8]-**3**, with concomitant release of one equivalent of isobutene (Scheme 1).[2c,6] The ionic complex [D_8]-**3** was fully characterized in solution by 1D and 2D ^{1}H and ^{13}C NMR experiments, which established in particular that the anion is free. Also, the ^{1}H NMR spectrum in CD_2Cl_2 of the analogous complex **3**, generated from THF instead of [D_8]THF, showed the unambiguous coordination of one THF molecule ($\delta = 4.10$ and 2.17 ppm versus $\delta = 3.82$ and 1.96 ppm for free THF).

When the cationic Zr species was generated by addition of $B(C_6F_5)_3$ to **1** using CD_2Cl_2 as the solvent, a large amount of white crystals formed rapidly from the solution. An X-ray diffraction analysis revealed that this product, which was isolated in 78% yield, is the new dimeric μ-isobutyrato–Zr dicationic species (**4**) that features in the solid state a C_2-symmetric dication with bridging carboxylate groups (Figure 1 and Table 1) and two independent borate anions.

Table 1. Selected bond lengths [Å] and angles [°] for the dication **4**.[a]

Zr1–O1	2.093(3)	O1-Zr1-O2	96.38(12)
Zr1–O2	2.084(3)	Zr1-O1-C11	154.9(3)
O1–C11	1.241(5)	O1-C11-O1_1	120.5(4)
C11–O1_1	1.269(5)	O1-C11-C12	120.4(4)
C11–C12	1.504(6)	C13-C12-C14	113.9(5)
C12–C13	1.512(7)	C11-C12-C13	112.0(4)
C12–C14	1.516(7)	C11-C12-C14	112.4(4)
Zr1–Ct1	2.184(4)	Ct1-Zr1-Ct2	132.06
Zr1–Ct2	2.194(4)		

[a] Ct1 is the centroid of the C1–C5 ring; Ct(2) is the centroid of the C6–C10 ring.

Consistent with its ionic nature, complex **4** is insoluble in CD_2Cl_2 and toluene, and readily soluble in THF. The ^{1}H and ^{13}C NMR spectra of **4** in [D_8]THF are identical to those of [D_8]-**3**, showing that the dimer readily cleaves in a donor solvent (Scheme 1).

The above observations suggest that transformation of the cationic Zr–enolate complex [D_8]-**2** to a carboxylate species (**3**) proceeds much faster in a weakly coordinating solvent such as CD_2Cl_2 than in [D_8]THF. Accordingly, we propose two possible decomposition pathways that involve both the "base-free" cationic Zr–enolate species **2**[7] (Scheme 2). The first mechanism implies direct elimination of isobutene from the coordinated *tert*-butoxy group of **2** and formation of a carboxylato species[2c] which would rapidly dimerize to **4** (mechanism 1). Alternatively, it is also possible to envision from the Zr–enolato species **2** a β-*tert*-butoxy elimination with release of ketene ($Me_2C{=}C{=}O$, not observed) to form a transient cationic *tert*-butoxy–Zr complex

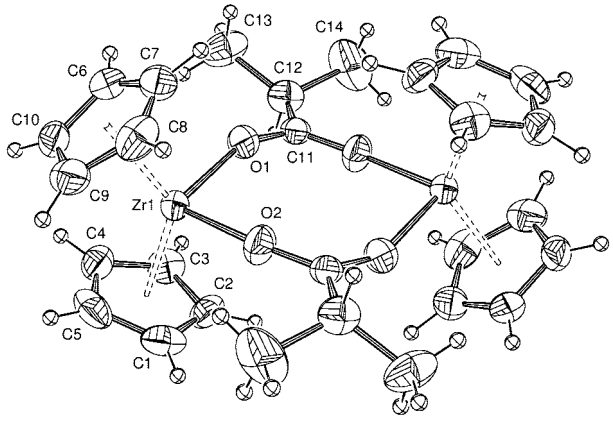
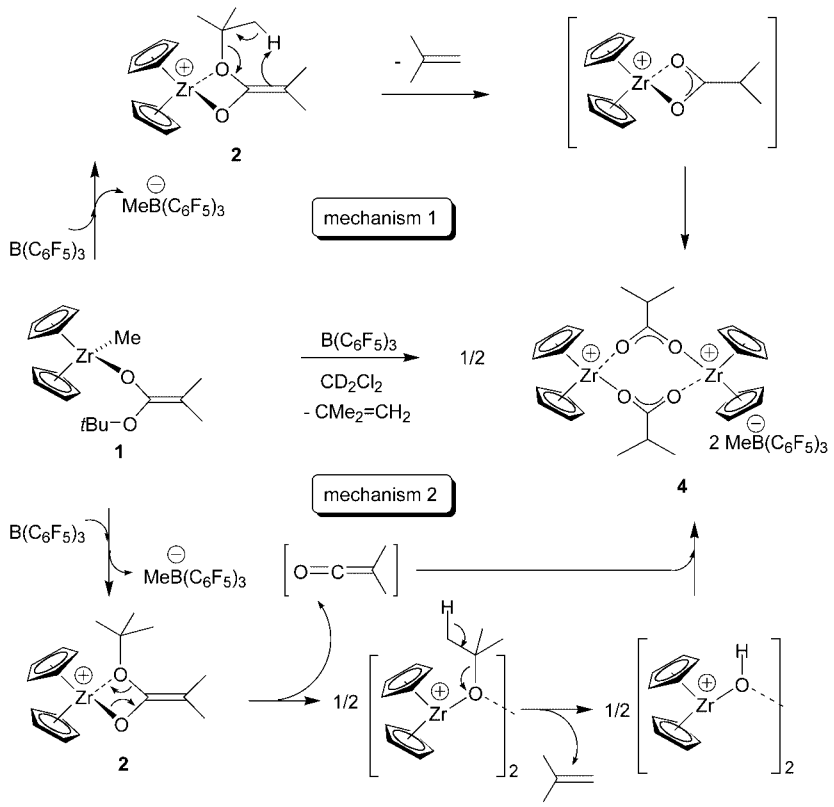


Figure 1. Molecular structure of the dication $[\{Cp_2Zr(\mu\text{-}(O_2CiPr))\}_2]^{2+}$ (**4**; ellipsoids at 50% probability).

(mechanism 2).[8] The latter species has been shown recently by Jordan et al. to decompose by elimination of isobutene to generate a dimeric μ-hydroxy–Zr complex,[9] which would then trap the ketene initially released into the Zr–OH bond to yield the dimeric μ-carboxylato complex **4.** As variable temperature NMR experiments did not reveal the intermediates in this process, it is not possible to verify the operation of these two mechanisms. However, the concerted process (mechanism 1) might better account for this high-yield transformation of **1** to **4**.[2c]

The reaction of **1** with one equivalent of $[HNMe_2Ph][B(C_6F_5)_4]$ as the methyl abstractor in CD_2Cl_2 proceeds similarly as for $B(C_6F_5)_3$, with rapid formation of colorless crystals and release of one equivalent of CH_4, free NMe_2Ph, and



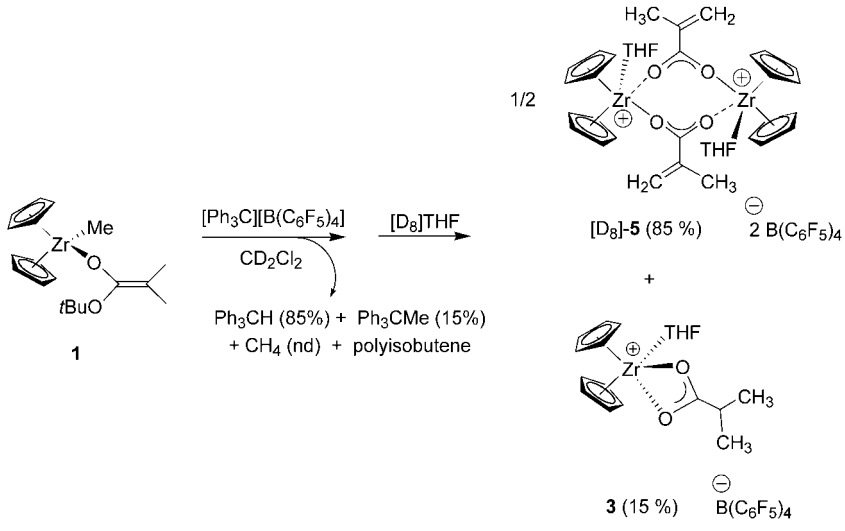
Scheme 2. Possible pathways for the formation of complex **4**.

isobutene. ^{1}H NMR spectra of the white crystals in [D$_8$]THF indicated the selective formation of [D$_8$]-**3** (note in this case that the anion is B(C$_6$F$_5$)$_4^-$).

On the other hand, when [Ph$_3$C][B(C$_6$F$_5$)$_4$] was used to generate the cationic Zr–enolate species in CD_2Cl_2, the solution turned immediately yellow and a large amount of yellow crystals, along with a small amount of colorless crystals, formed over 5 to 20 min. Both types of crystals are insoluble in benzene and toluene, but readily soluble in THF at room temperature, indicative of their ionic nature. When [D$_8$]THF was added to the solid material, the color of the solution faded immediately to colorless, and ^{1}H NMR spectra of the solution revealed it is a mixture of the new compound [D$_8$]-**5** (85%) and compound [D$_8$]-**3** (15%; note in this case that the anion is B(C$_6$F$_5$)$_4^-$) (Scheme 3). This indicates that the minor amount of colorless crystals present in the solid material corresponds to **4**.

The ^{1}H NMR spectrum of [D$_8$]-**5**[10] in [D$_8$]THF features no dynamic phenomenon in the temperature range −80 to 30 °C and is quite simple. It comprises one singlet for the 20 Cp protons ($\delta = 6.53$ ppm at 20 °C), one high-field singlet ($\delta = 1.92$ ppm) attributed to two equivalent Me groups, and two relatively sharp, low-field multiplets ($\delta = 6.24$ and 5.81 ppm) that integrate each for 2H. The ^{1}H–^{1}H COSY spectrum shows a strong intensity cross-peak between the two low-field signals as well as a less intense cross-peak between each of those signals with the methyl protons. Also, the ^{13}C NMR spectrum of [D$_8$]-**5** features only four resonances other than those belonging to the Cp rings and the anion. Such a pattern is indicative of an allylic CH_3–C(CO$_2$)=C*HH* system as shown in Scheme 3. This assignment is supported by 2D ^{1}H–^{13}C experiments; key data include a correlation in the HMQC experiment between the two low-field ^{1}H resonances and a ^{13}C resonance ($\delta = 128.7$ ppm, *C*HH=C), and correlations in the HMBC experiment between those two low-field ^{1}H resonances with three ^{13}C resonances ($\delta = 180.4$ ppm, CH_3–C(*C*O$_2$)=CHH; $\delta = 135.6$ ppm, CH_3–*C*(CO$_2$)=CHH, and $\delta = 15.4$ ppm, *C*H$_3$–C(CO$_2$)=CHH).

The solid-state structure of **5**-[B(C$_6$F$_5$)$_4$]$_2$ confirms two borate anions with an independent dication composed of two Cp$_2$Zr fragments bridged by two carboxylate groups (Figure 2 and Table 2). A C_2 axis passes through both the carbon atoms of the carboxylate groups (C35, C38) and the both carbon atoms attached to the latter (C36, C39). The C36 and C39 carbon atoms are obviously sp^2 hybridized



Scheme 3.

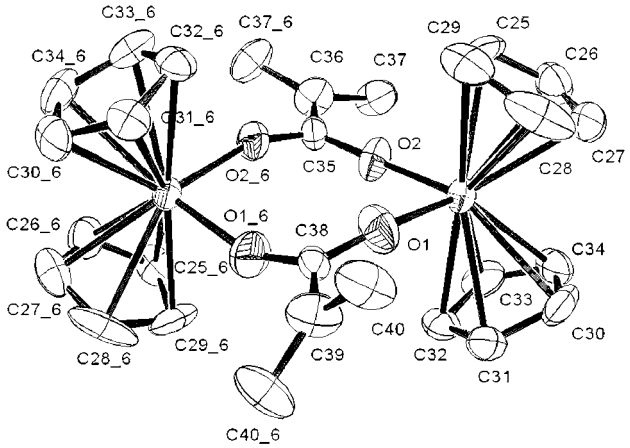


Figure 2. Solid-state structure of the dication **5** (ellipsoids at 50% probability).

Table 2. Selected bond lengths [Å] and angles [°] for the dication **5**.[a]

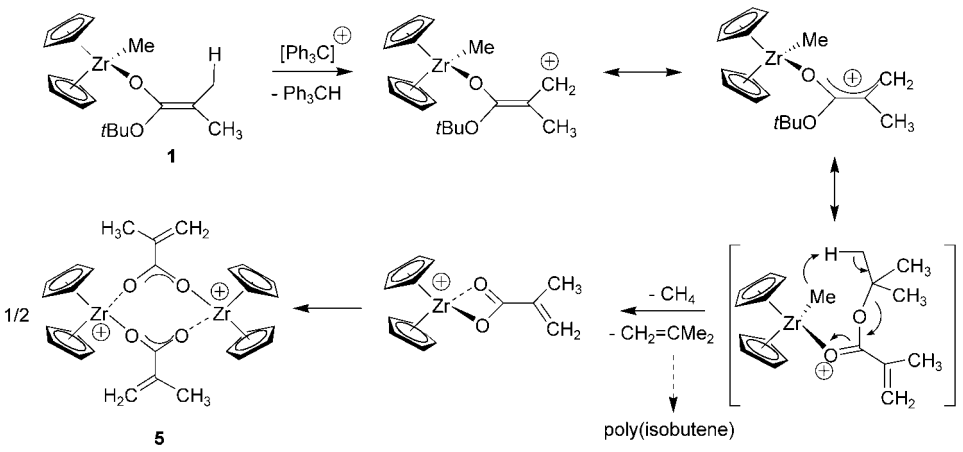
Zr1–O1	2.095(8)	O1(Zr1(O2	94.3(3)
Zr1–O2	2.090(7)	C35-O2-Zr1	158.6(8)
O2–C35	1.252(9)	C38-O1-Zr1	157.0(8
C35–C36	1.41(2)	C35-C36-C37	120.3(8)
C36–C37	1.439(12	C37-C36-C37_6	119.3(15)
C36–C37_6	1.439(12)	C35-C36-C37_6	120.3(8)
O1–C38	1.233(9)	C38-C39-C40	117.9(8)
C38–C39	1.44(2)	C40-C39-C40_6	124.2(16)
C39–C40	1.356(12)	C40_6-C39-C38	117.9(8)
C39–C40_6	1.356(12)	Ct1-Zr1-Ct2	130.04
Zr1–Ct1	2.173(11)	O1-Zr1-Ct2	107.57
Zr1–Ct2	2.166(11)	O1-Zr1-Ct1	106.32

[a] Ct1 is the centroid of the C25–C29 ring; Ct2 is the centroid of the C30–C34 ring.

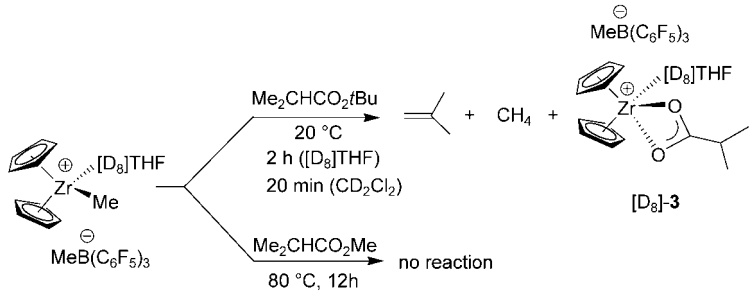
(sum of the angles 359.9 and 360.0°, respectively). Also, the C–C bond lengths in the residues on the both carboxylate groups in **5** (1.36(1)–1.44(2) Å) are significantly shorter than those in **4** (1.504(6)–1.516(7) Å). These observations are consistent with the structure observed in THF solution. However, the residues on the both carboxylate groups are not similar. In the C35 moiety, the C35–C36 bond length (1.41(2) Å) is, within experimental errors, very similar to the C36–C37 and C36–C37_6 (1.439(12) Å) bond lengths. In the C38 moiety, the C39–C40 and C39–C40_6 (1.356(12) Å) bond lengths are unusually short and shorter than the C38–C39 bond length (1.44(2) Å). This overall situation in the solid state is indicative of a very delocalized structure, which is possibly complicated by disorder problems.

The ^{1}H and ^{13}C NMR spectra of the mother CD_2Cl_2 solution from which the crystals of **4**-$[MeB(C_6F_5)_4]_2$ and **5**-$[B(C_6F_5)_4]_2$ were grown established the parallel formation of Ph_3CMe (15%) and Ph_3CH (85%), as well as the presence of CH_4 (not quantified) and resonances characteristic for polyisobutene (64% based on Ph_3CMe) (Scheme 3). In view of the similar amounts of the complexes $[D_8]$-**3**(**4**)/$[D_8]$-**5**(**5**) (15:85) and the above organic products arising from the trityl activator (15:85), it is reasonable to consider that two distinct, competitive pathways take place for the formation of the Zr cationic species **4** and **5**, that involve methyl abstraction and hydride abstraction, respectively, from the neutral methyl–Zr–enolate **1**. We assume that **4** is formed from the **2**/$[Ph_3C][B(C_6F_5)_4]$ mixture in a similar way to that in the presence of $B(C_6F_5)_3$, via methyl abstraction (Scheme 2). On the other hand, we propose that the formation of **5** involves a preliminary hydride abstraction from an enolate methyl group by the trityl cation[11] (Scheme 4). The resulting cation would then eliminate in a concerted fashion methane and isobutene to generate a propenyl-2-carboxylato cation that would dimerize to **5**. No isobutene is observed because this compound obviously polymerizes rapidly in the presence of cationic Zr species under these conditions.[1c]

To support the above mechanism, we mimicked the putative intermediate $[Cp_2Zr(Me)\{tBuO_2C[C(CH_3)=CH_2]\}]^+$ in Scheme 4, starting from $[Cp_2ZrMe_2]$ and $B(C_6F_5)_3$ in $[D_8]$THF to give $[Cp_2Zr([D_8]THF)Me]^+$, and then added one equivalent of $(CH_3)_2CHCO_2tBu$. As expected, $[Cp_2Zr([D_8]THF)Me]^+$ was quantitatively converted following this procedure to give complex $[D_8]$-**3** with release of CH_4 and isobutene (which does not polymerize under these conditions), within 2 h (Scheme 5). When the same reaction of $[Cp_2Zr(THF)Me]^+$ with $(CH_3)_2CHCO_2tBu$ was carried out in CD_2Cl_2 instead of $[D_8]$THF, completion was observed within 20 min. This increase in the reaction rate is consistent with the intermediacy of base(THF)-free species in this transformation process (vide supra). Conversely, no reaction between $[Cp_2Zr(THF)Me]^+$ and Me_2CHCO_2Me takes place, even after 12 h at 80 °C, indicating that this process is not operative under usual conditions for methyl esters.



Scheme 4. Possible mechanism for the formation of complex **5** (the counterion is $B(C_6F_5)_4^-$).



Scheme 5.

Conclusion

We have shown that the cationic zirconocene–*tert*-butyl enolate species $[Cp_2Zr(THF)\{O(t\text{BuO})C{=}CMe_2\}]^+$ (**2**) is cleanly generated through methyl abstraction from the corresponding neutral methyl–Zr–ester enolate **1** and a judiciously chosen solvent and discrete activator, for example, $B(C_6F_5)_3$ or $[HNMe_2Ph][B(C_6F_5)_4]$. Contrastingly, the reaction of **1** with $[Ph_3C][B(C_6F_5)_4]$ in dichloromethane proceeds by a novel pathway, which involves hydride abstraction by the trityl cation, to produce quite selectively an unusual unsaturated Zr–carboxylate dication, after elimination of methane and isobutene. Once generated, the cationic species **2** can be stabilized at 0°C. Preliminary studies in our group have shown that **2** is an effective initiator for MMA polymerization in toluene or THF solution, yielding PMMA with narrow polydispersity ($M_w/M_n < 1.2$), and thereby showing that this species may serve as a simple and valuable structural model of the active propagating species. Complex **2** decomposes, however, readily at room temperature in THF and above all dichloromethane, by elimination of isobutene and formation of a carboxylate–Zr complex. Our observations suggest that the aforementioned decomposition processes are specific to the *tert*-butyl enolate esters studied, but may not affect methyl enolate species involved in MMA polymerization.

Experimental Section

General procedures: All experiments were carried out under purified argon using standard Schlenk techniques or a Vacuum Atmosphere glovebox. Hydrocarbon solvents, diethyl ether, and tetrahydrofuran were distilled from Na/benzophenone, toluene and pentane were distilled from Na/K alloy under nitrogen and degassed by freeze-thaw-vacuum prior to use. Chlorinated solvents were distilled from calcium hydride. Deuterated solvents were purchased from Eurisotop and purified before use. $[Cp_2ZrCl_2]$ (Acros), $[Cp_2ZrMe_2]$ (Aldrich), $B(C_6F_5)_3$ (Boulder: double sublimed before use), $[Ph_3C][B(C_6F_5)_4]$ (Boulder), and $[HNMe_2Ph][B(C_6F_5)_4]$ (Boulder) were used as received. *tert*-Butyl isobutyrate[12] and $[Cp_2Zr(Me)\{O(t\text{BuO})C{=}CMe_2\}]$ (**1**)[13] were prepared following reported procedures. NMR spectra were recorded on Bruker AC-200, AC-300, and AC-500 spectrometers in Teflon-valved NMR tubes at room temperature unless otherwise stated. ^1H and ^{13}C NMR chemical shifts were determined by using residual solvent resonances and are reported versus TMS. ^{19}F and ^{11}B NMR chemical shifts are referenced to external $CFCl_3$ and external $BF_3{\cdot}Et_2O$, respectively. Assignment of signals was made from ^1H–^1H COSY, ^1H–^{13}C HMQC, and ^1H–^{13}C HMBC 2D NMR experiments. Coupling constants are given in Hertz. Elemental analyses (C, H, N) were performed by the Microanalytical Laboratory at the Institute of Chemistry of Rennes and are the average of two independent determinations.

The cationic Zr complexes containing $MeB(C_6F_5)_3^-$ and $B(C_6F_5)_4^-$ are totally dissociated in $[D_8]$THF and CD_2Cl_2 solution, and the NMR resonances for these anions are almost identical. The NMR data are listed below for all the compounds containing for the $MeB(C_6F_5)_3^-$ and $B(C_6F_5)_4^-$ free anions.

Data for $MeB(C_6F_5)_3^-$: ^1H NMR ($[D_8]$THF): $\delta = 0.50$ (br s, 3H; BCH_3). ^1H NMR (CD_2Cl_2): $\delta = 0.54$ ppm (br s, 3H; BCH_3); $^{13}C\{^1H\}$ NMR ($[D_8]$THF): $\delta = 148.5$ (dm, $J_{C,F} = 252$ Hz; *o*-C_6F_5), 137.4 (dm, $J_{C,F} = 247$ Hz; *p*-C_6F_5), 136.2 (dm, $J_{C,F} = 229$ Hz; *m*-C_6F_5), 129.7 (C_{ipso}), 9.7 ppm (br; BCH_3); $^{13}C\{^1H\}$ NMR (CD_2Cl_2): $\delta = 148.3$ (dm, $J_{C,F} = 238$ Hz; *o*-C_6F_5), 137.4 (dm, $J_{C,F} = 257$ Hz; *p*-C_6F_5), 136.4 (dm, $J_{C,F} = 245$ Hz; *m*-C_6F_5), 128.9 (C_{ipso}), 9.9 ppm (br; BCH_3); ^{11}B NMR ($[D_8]$THF): $\delta = -14.8$ ppm (s; BCH_3); ^{11}B NMR (CD_2Cl_2): $\delta = -14.9$ ppm (s; BCH_3); ^{19}F NMR ($[D_8]$THF): $\delta = -134.5$ (d, $^3J_{F,F} = 21$ Hz, 6F; *o*-F), −168.5 (t, $^3J_{F,F} = 21$ Hz, 3F; *p*-F), −170.6 ppm (m, $^3J_{F,F} = 18$ Hz, 6F; *m*-F); ^{19}F NMR (CD_2Cl_2): $\delta = -133.6$ (d, $^3J_{F,F} = 18$ Hz, 6F; *o*-F), −165.6 (t, $^3J_{F,F} = 22$ Hz, 3F; *p*-F), −168.2 ppm (t, $^3J_{F,F} = 22$ Hz, 6F; *m*-F).

Data for $B(C_6F_5)_4^-$: ^{13}C NMR ($[D_8]$THF): $\delta = 148.2$ (dm, $J_{C,F} = 240$ Hz; *o*-C_6F_5), 138.1 (dm, $J_{C,F} = 244$ Hz; *p*-C_6F_5), 136.1 (dm, $J_{C,F} = 247$ Hz; *m*-C_6F_5), 125.1 ppm (C_{ipso}); ^{13}C NMR (CD_2Cl_2): $\delta = 148.1$ (dm, $J_{C,F} = 240$ Hz; *o*-C_6F_5), 138.0 (dm, $J_{C,F} = 244$ Hz, *p*-C_6F_5), 136.2 (dm, $J_{C,F} = 248$ Hz; *m*-C_6F_5), 125.0 ppm (C_{ipso}); ^{11}B NMR ($[D_8]$THF): $\delta = -16.6$ ppm (s; BC_6F_5); ^{11}B NMR (CD_2Cl_2): $\delta = -16.7$ ppm (s; BC_6F_5); ^{19}F NMR ($[D_8]$THF): $\delta = -132.2$ (s, 8F; *o*-F), −163.6 (t, $^3J_{F,F} = 21$ Hz, 4F; *p*-F), −167.3 ppm (s, 8F; *m*-F); ^{19}F NMR (CD_2Cl_2): $\delta = -133.5$ (s, 8F; *o*-F), −164.1 (t, $^3J_{F,F} = 22$ Hz, 4F; *p*-F), −168.0 ppm (t, $^3J_{F,F} = 20$, 8F; *m*-F).

Generation of $[Cp_2Zr([D_8]THF)\{O(t\text{BuO})C{=}CMe_2\}][MeB(C_6F_5)_3]$ ($[D_8]$-2): A solution of complex **1** (15.2 mg, 0.040 mmol) in $[D_8]$THF (ca. 0.5 mL) was prepared in a Teflon-valved NMR tube, and $B(C_6F_5)_3$ (20.5 mg, 0.040 mmol) was added at room temperature. The tube was sealed and agitated for 10 min, and ^1H NMR spectra were recorded. The conversion of **1** to $[D_8]$-**2** was almost quantitative. ^1H NMR ($[D_8]$THF): $\delta = 6.71$ (s, 10H; Cp), 1.62 (s, 6H; $=C(CH_3)_2$), 1.29 ppm (s, 9H; $C(CH_3)_3$); $^{13}C\{^1H\}$ NMR ($[D_8]$THF): $\delta = 155.8$ ($O(t\text{BuO})C{=}$), 116.7 (Cp), 92.4 ($C{=}CMe_2$), 80.3 ($C(CH_3)_3$), 28.5 ($C(CH_3)_3$), 18.3 ($C{=}C(CH_3)_2$), 17.6 ppm ($C{=}C(CH_3)_2$). The NMR data for the free anion $MeB(C_6F_5)_3^-$ were the same as those described above. Complex $[D_8]$-**2** is stable for several days at 0°C, but rapidly decomposes at 20°C as described below.

Transformation of $[Cp_2Zr([D_8]THF)\{O(t\text{BuO})C{=}CMe_2\}][MeB(C_6F_5)_3]$ ($[D_8]$-2) to $[Cp_2Zr([D_8]THF)(O_2Ci\text{Pr})][MeB(C_6F_5)_3]$ ($[D_8]$-3): The above NMR tube was maintained at room temperature for 6 h, and an NMR spectrum was recorded. The ^1H NMR spectrum revealed the complete disappearance of $[Cp_2Zr([D_8]THF)\{O(t\text{BuO})C{=}CMe_2\}]^+$ and the formation of one equivalent of isobutylene and the isobutyrato–Zr cation $[Cp_2Zr([D_8]THF)(O_2Ci\text{Pr})]^+$. NMR data for the cation $[D_8]$-**3**. ^1H NMR ($[D_8]$THF): $\delta = 6.50$ (s, 10H; Cp), 2.53 (m, $^3J = 7.0$ Hz, 1H; $CH(CH_3)_2$), 1.18 ppm (d, $^3J = 7.0$ Hz, 6H; $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR ($[D_8]$THF): $\delta = 192.4$ (O_2C), 116.4 (Cp), 35.2 ($CH(CH_3)_2$), 16.7 ppm ($CH(CH_3)_2$). NMR data for isobutene: ^1H NMR ($[D_8]$THF): $\delta = 4.60$ (m, $^4J = 1.0$ Hz, 2H; $CH_2{=}$), 1.68 ppm (t, $^4J = 1.0$ Hz, 6H; $=C(CH_3)_2$); $^{13}C\{^1H\}$ NMR ($[D_8]$THF): $\delta = 141.6$ ($=C(CH_3)_2$), 111.0 ($CH_2{=}$), 23.2 ppm ($=C(CH_3)_2$).

$[\{Cp_2Zr[\mu\text{-}(O_2Ci\text{Pr})]\}_2][MeB(C_6F_5)_3]_2$ (4-$[MeB(C_6F_5)_3]_2$): Complex **1** (19.7 mg, 0.052 mmol) and $B(C_6F_5)_3$ (26.5 mg, 0.052 mmol) were added in a Teflon-valved NMR tube, and CD_2Cl_2 (ca. 0.5 mL) was vacuum transferred. The tube was sealed and agitated for 5 min, and left at room temperature. White crystals of **4**-$[MeB(C_6F_5)_3]_2$ rapidly formed within 2 min. The solid was washed with pentane (3×1 mL), and dried in vacuum (34 mg, 78%). A suitable crystal of **4**-$[MeB(C_6F_5)_3]_2$ was analyzed by X-ray diffraction, and the NMR data in $[D_8]$THF were the same as those described above. Elemental analysis calcd (%) for $C_{66}H_{40}O_4F_{30}B_2Zr_2$ (1671.06): C 47.44, H 2.41; found: C 47.36, H 2.29.

[Cp$_2$Zr(THF)(O$_2$C*i*Pr)][MeB(C$_6$F$_5$)$_3$] (3): A sample of complex **4**-[MeB(C$_6$F$_5$)$_3$]$_2$ (ca. 30 mg) was dissolved in THF in a Teflon-valved NMR tube. The solvent was removed in vacuum, CD_2Cl_2 (ca. 0.5 mL) was vacuum transferred, and a ^{1}H NMR spectrum was recorded. ^{1}H NMR or the cation **4** (CD_2Cl_2): $\delta = 6.42$ (s, 10H; Cp), 4.10 (m, 4H; OCH_2CH$_2$), 2.58 (m, $^3J = 7.0$ Hz, 1H; CH(CH$_3$)$_2$), 2.17 (m, 4H; OCH$_2$CH_2), 1.24 ppm (d, $^3J = 7.0$ Hz, 6H; CH(CH_3)$_2$); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 193.0$ (O$_2$*C*), 116.1 (Cp), 75.3(OCH$_2$CH$_2$), 35.4 (*C*H(CH$_3$)$_2$), 25.2 (OCH$_2$*C*H$_2$), 17.2 ppm (CH(*C*H$_3$)$_2$). The NMR data for the free anion MeB(C$_6$F$_5$)$_3^-$ were the same as those described above.

Reaction of [Cp$_2$Zr(Me){O(*t*BuO)C=CMe$_2$}] (1) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$]: synthesis of 4-[B(C$_6$F$_5$)$_4$]$_2$: The same procedure than the one described above was used starting from complex **1** (26.2 mg, 0.069 mmol) and [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] (55.3 mg, 0.069 mmol), yielding white crystals of **4**-[B(C$_6$F$_5$)$_4$]$_2$ (43 mg, 63%). The NMR data in [D$_8$]THF were the same as those described above for [D$_8$]-**3**, except the resonances for the anion (B(C$_6$F$_5$)$_4^-$). The NMR data of the CD_2Cl_2 solution from which crystals of **4**-[B(C$_6$F$_5$)$_4$]$_2$ formed indicated the presence of CH_4 (^{1}H NMR: $\delta = 0.26$), isobutene (^{1}H NMR: $\delta = 4.70$ (m, $^4J = 1.0$ Hz, 2H; CH_2=), 1.77 ppm (t, $^4J = 1.0$ Hz, 6H; =C(CH_3)$_2$); ^{13}C{^{1}H} NMR: $\delta = 142.5$ (=*C*(CH$_3$)$_2$), 110.1 (*C*H$_2$=), 23.8 ppm (=C(*C*H$_3$)$_2$)), and free NMe$_2$Ph (^{1}H NMR: $\delta = 7.27$ (m, 2H; Ph), 6.78 (m, 3H; Ph). 2.96 ppm (s, 6H; N(CH_3)$_2$); ^{13}C{^{1}H} NMR: δ 142.5 (Ph), 128.9 (Ph), 119.6 (Ph), 115.9 ppm (Ph), 40.3 ppm (N(*C*H$_3$)$_2$)); elemental analysis calcd (%) for C$_{76}$H$_{30}$O$_4$F$_{40}$B$_2$Zr$_2$ (1971.06): C 46.31, H 1.53; found: C 46.53, H 1.93.

Reaction of [Cp$_2$Zr(Me){O(*t*BuO)C=CMe$_2$}] (1) and [Ph$_3$C][B(C$_6$F$_5$)$_4$]: generation of 4-[B(C$_6$F$_5$)$_4$]$_2$ and 5-[B(C$_6$F$_5$)$_4$]$_2$: [Ph$_3$C][B(C$_6$F$_5$)$_4$] (45.7 mg, 0.050 mmol) and complex **1** (18.8 mg, 0.050 mmol) were charged in a Teflon-valved NMR tube, and CD_2Cl_2 (ca. 0.5 mL) was vacuum transferred. The tube was sealed and agitated for 5 min, and left at room temperature. Yellow crystals rapidly formed over 5 min to 20 min. ^{1}H and ^{13}C NMR analysis of the CD_2Cl_2 solution showed the formation of Ph$_3$CMe (15% versus **1**; ^{1}H NMR: $\delta = 7.36$–7.15 (m, 15H; Ph), 2.22 ppm (s, 3H; CH_3); ^{13}C {^{1}H} NMR: $\delta = 149.1$ (Ph), 129.3 (Ph), 128.3 (Ph), 126.3 (Ph), 52.5 (*C*Me), 30.6 ppm (C*C*H$_3$)) and Ph$_3$CH (85% versus **1**; ^{1}H NMR: $\delta =$ 7.36–7.15 (m, 15H; Ph), 5.55 ppm (s, 1H; C*H*); ^{13}C {^{1}H} NMR: $\delta = 144.0$ (Ph), 129.3 (Ph), 128.3 (Ph), 126.3 (Ph), 56.8 ppm (Ph$_3$*C*H)), as well as the presence of CH_4 ($\delta(^1H) = 0.26$ ppm) and resonances characteristic for polyisobutene. In the glovebox, the solid was removed from the solution, washed with pentane (3 × 1 mL) and dried in vacuum (25.5 mg, 62%). Elemental analysis calcd (%) for C$_{76}$H$_{30}$O$_4$F$_{40}$B$_2$Zr$_2$ (1971.73) (**5**): C 46.29, H 1.57; found: C 46.43, H 1.98. A suitable yellow crystal of **5** was selected for X-ray diffraction analysis. Then, [D$_8$]THF (ca. 0.5 mL) was vacuum transferred to the tube containing the crystalline solid material, and an NMR spectrum was recorded. The NMR data indicated the presence of a main product (85%) that was assigned as compound [D$_8$]-**5**, together with resonances for the cation [D$_8$]-**3** (15%). NMR data for the cation [D$_8$]-**5**: ^{1}H NMR ([D$_8$]THF): $\delta = 6.53$ (s, 20H; Cp), 6.24 (m, 2H; =CH*H*), 5.81 (m, 2H; =*CH*H), 1.92 ppm (s, 6H; CH_3); ^{13}C{^{1}H} NMR ([D$_8$]THF): $\delta = 180.4$ (O$_2$*C*), 135.6 (CH$_2$=*C*(CO$_2$)CH$_3$), 128.7 (*C*H$_2$=C), 116.4 (Cp), 15.4 ppm (*C*H$_3$). The NMR data for the free anion B(C$_6$F$_5$)$_4^-$ were the same as those described above.

Generation of 5·THF: The above mixture of complexes **4** and **5** was dissolved in THF in a Teflon-valved NMR tube. The solvent was removed in vacuum, CD_2Cl_2 (ca. 0.5 mL) was vacuum transferred, and a ^{1}H NMR spectrum was recorded. NMR data for the cation **5**·THF**:** ^{1}H NMR (CD_2Cl_2): $\delta = 6.46$ (s, 20H; Cp), 6.33 (m, 2H; =CH*H*), 5.88 (m, 2H; = *CH*H), 4.14 (m, 8H; OCH_2CH$_2$), 2.18 (m, 8H; OCH$_2$CH_2), 1.98 ppm (s, 6H; CH_3); ^{13}C{^{1}H} NMR ([D$_8$]THF): $\delta = 180.9$ (O$_2$*C*), 135.1 (CH$_2$= *C*(CO$_2$)CH$_3$), 130.3 (*C*H$_2$=C), 116.1 (Cp), 75.5(O*C*H$_2$CH$_2$), 25.4 (OCH$_2$*C*H$_2$), 16.0 ppm (*C*H$_3$). The NMR data for the free anion B(C$_6$F$_5$)$_4^-$ and the cation **3**·THF were the same as those described above.

Generation of [Cp$_2$Zr([D$_8$]THF)Me][MeB(C$_6$F$_5$)$_3$]: B(C$_6$F$_5$)$_3$ (25 mg, 0.049 mmol) was added at room temperature to a solution of [Cp$_2$ZrMe$_2$] (12.3 mg, 0.049 mmol) in [D$_8$]THF (ca. 0.5 mL) in a Teflon-valved NMR tube. The solution was left for 10 min at room temperature to insure the complete formation of [Cp$_2$Zr([D$_8$]THF)Me][MeB(C$_6$F$_5$)$_3$]. NMR data for Cp$_2$ZrMe$_2$: ^{1}H NMR ([D$_8$]THF): $\delta = 6.08$ (s, 10H; Cp), -0.43 (s, 6H; Zr(CH_3)$_2$); ^{1}H NMR (C_6D_6): $\delta = 5.72$ (s, 10H; Cp), -0.13 ppm (s, 6H; Zr(CH_3)$_2$); ^{1}H NMR (CD_2Cl_2): $\delta = 6.16$ (s, 10H; Cp), -0.35 (s, 6H; Zr(CH_3)$_2$). NMR data for [Cp$_2$Zr([D$_8$]THF)Me][MeB(C$_6$F$_5$)$_3$]: ^{1}H NMR ([D$_8$]THF): $\delta = 6.58$ (s, 10H; Cp), 0.77 ppm (s, 3H; ZrCH_3); ^{13}C NMR ([D$_8$]THF): $\delta = 116.5$ (Cp), 41.8 ppm (Zr*C*H$_3$). The NMR data for the free anion MeB(C$_6$F$_5$)$_3^-$ were the same as those described above.

Reaction of [Cp$_2$Zr([D$_8$]THF)Me][MeB(C$_6$F$_5$)$_3$] with (CH$_3$)$_2$CHCO$_2$*t*Bu. Generation of [Cp$_2$Zr([D$_8$]THF)(O$_2$C*i*Pr)][MeB(C$_6$F$_5$)$_3$] ([D$_8$]-3): To the above NMR tube (freshly prepared), (CH$_3$)$_2$CHCO$_2$*t*Bu (7.0 mg, 0.049 mmol) was added by microsyringe. The tube was sealed and ^{1}H NMR spectra were recorded periodically. The complete conversion of [Cp$_2$Zr([D$_8$]THF)Me][MeB(C$_6$F$_5$)$_3$] to [D$_8$]-**3** and release of one equivalent of isobutene and CH_4 was observed within 2 h. NMR data for CH_4: ^{1}H NMR ([D$_8$]THF): $\delta = 0.16$ (s). The NMR data for [D$_8$]-**3** and isobutene were the same as those described above.

Generation of [Cp$_2$Zr(THF)Me][MeB(C$_6$F$_5$)$_3$]: B(C$_6$F$_5$)$_3$ (25.6 mg, 0.05 mmol) was added at room temperature to a solution of [Cp$_2$ZrMe$_2$] (12.6 mg, 0.05 mmol) in THF (ca. 0.5 mL) in a Teflon-valved NMR tube. The solution was left for 10 min at room temperature to insure the complete formation of [Cp$_2$Zr(THF)Me][MeB(C$_6$F$_5$)$_3$]. Then the tube was dried under vacuum and CD_2Cl_2 (ca. 0.5 mL) was vacuum transferred. NMR data for [Cp$_2$Zr(THF)Me][MeB(C$_6$F$_5$)$_3$]: ^{1}H NMR (CD_2Cl_2): $\delta =$ 6.51 (s, 10H; Cp), 3.81 (m, 4H; OCH_2CH$_2$), 1.98 (m, 4H; OCH$_2$CH_2), 0.88 ppm (s, 3H; ZrCH_3). The NMR data for the free anion MeB(C$_6$F$_5$)$_3^-$ were the same as those described above.

Reaction of [Cp$_2$Zr(THF)Me][MeB(C$_6$F$_5$)$_3$] with (CH$_3$)$_2$CHCO$_2$*t*Bu. Generation of [Cp$_2$Zr(THF)(O$_2$C*i*Pr)][MeB(C$_6$F$_5$)$_3$] (3): To the above NMR tube (freshly prepared), (CH$_3$)$_2$CHCO$_2$*t*Bu (7.2 mg, 0.05 mmol) was added by microsyringe. The tube was sealed and ^{1}H NMR spectra were recorded periodically. The complete conversion of [Cp$_2$Zr(THF)Me][MeB(C$_6$F$_5$)$_3$] to **3** and release of one equivalent of isobutene and CH_4 was observed within 20 min. The NMR data for **3**, isobutene and CH_4 were the same as those described above.

X-ray structure determinations of compounds 4-[MeB(C$_6$F$_5$)$_3$]$_2$ and 5-[B(C$_6$F$_5$)$_4$]$_2$: Single crystals of **4**-[MeB(C$_6$F$_5$)$_3$]$_2$ and **5**-[B(C$_6$F$_5$)$_4$]$_2$ were obtained from CD_2Cl_2 at room temperature. Crystal data collection parameters for the two structures are presented in Table 3. The crystal structures

Table 3. Crystal structure data of compounds **4**-[MeB(C$_6$F$_5$)$_3$]$_2$ and **5**-[B(C$_6$F$_5$)$_4$]$_2$.

	4-[MeB(C$_6$F$_5$)$_3$]$_2$·CH$_2$Cl$_2$	**5**-[B(C$_6$F$_5$)$_4$]$_2$
formula	C$_{33.5}$H$_{21}$O$_2$ClF$_{15}$BZr	C$_{38}$H$_{15}$O$_2$F$_{20}$BZr
molecular mass	877.98	985.53
crystal size [mm]	0.30 × 0.05 × 0.05	0.32 × 0.12 × 0.10
crystal system	monoclinic	trigonal
space group	*P*21/*c*	*P*3221
a [Å]	11.0319(2)	12.6595(3)
b [Å]	12.4574(2)	12.6595(3)
c [Å]	24.1694(5)	38.0800(10)
β [°]	95.1220(10)	90
V [Å^3]	3308.31(11)	5285.2(2)
Z	4	6
ρ_{calcd} [g cm^{-3}]	1.763	1.858
diffractometer	NONIUS Kappa CCD	NONIUS Kappa CCD
T [K]	130	120
μ [mm^{-1}]	0.531	0.456
scan method	φ scans	φ scans
2θ(max) [°]	55.00	52.04
total reflections	14708	7218
unique reflections	7594	5724
observed reflections [$I > 2\sigma(I)$]	5294	3610
R_1	0.0558	0.0789
wR_2	0.1417	0.1232
GOF	1.037	1.152
parameters/constraints	496/4	561/0
residual electron density [e Å^{-3}]	< 1.5	< 0.4

were solved by means of the Patterson method, remaining atoms were located from difference Fourier synthesis, followed by full-matrix least-squares refinement based on F^2 (programs SHELXS-97 and SHELXL-97).[14] In both cases, many hydrogen atoms could be found from the Fourier differences. Carbon-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached carbon atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The cell of **4**-$[MeB(C_6F_5)_3]_2$ was found to contain one molecule of crystallization dichloromethane.[15]

Acknowledgement

We thank Total and AtoFina Co. (grant to B. L.) and the Centre National de la Recherche Scientifique for financial support of this work. We thank Prof. R. F. Jordan (University Chicago) for helpful discussions.

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[15] CCDC-225762 (**4**) and CCDC-228823 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Received: May 14, 2004
Published online: July 19, 2004

