Formation of Group 4 Metallocene-Enolate · B(C_6F_5)$_3$ Adducts and Their Role as Initiators in the Rapid Polymerization of the Functionalized Olefin Methyl vinyl ketone

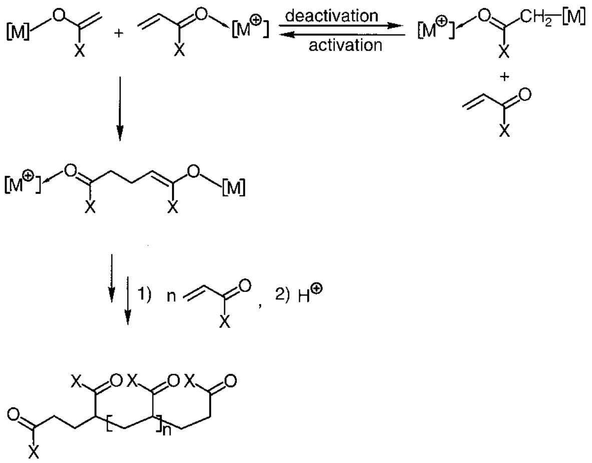
Wolf Spaether, Katrin Klaß, Gerhard Erker,* Frank Zippel, and Roland Fröhlich

Abstract: The Group 4 metallocene bis(enolate) complexes [$Cp_2M(\text{-O-CMe=CH}_2)_2$] (**1**) add one or two molar equivalents of the organometallic Lewis acid $B(C_6F_5)_3$ to form the addition products [$Cp_2M\{\text{-O=CMe-CH}_2B(C_6F_5)_3\}(\text{-O-CMe=CH}_2)$] (**2**) and [$Cp_2M\{\text{-O=CMe-CH}_2B(C_6F_5)_3\}_2$] (**3**), respectively. Complexes **3a** (M = Ti) and **3b** (M = Zr) were characterized by X-ray diffraction. Complexes **2** undergo a thermally induced intramolecular aldol condensation type C–C coupling. Mixtures of **1** and $B(C_6F_5)_3$, in ratios ranging from 1:1 to 1:4, give increasingly active catalyst systems for the polymerization of methyl vinyl ketone which proceeds by a group-transfer mechanism.

Keywords: boron · homogeneous catalysis · polymerizations · reaction mechanisms · sandwich complexes

Introduction

Homogeneous, bent metallocene-derived Ziegler catalysts of Group 4 metals have become enormously important in the polymerization of alkenes. Simple unfunctionalized α-olefins undergo C–C coupling reactions with extremely high regio- and stereoselectivities to selectively yield the various principal types of α-olefin polymers, cyclopolymers and copolymers, depending on the specific metallocene precursor used.[1] A serious limitation in the application of the metallocene Ziegler catalysts at present is their near to general inability to couple functionalized alkenes.[2] There have been a few attempts to circumvent this problem: in the case of the polymerization of α,β-unsaturated carbonyl compounds, the olefin C–C coupling mechanism was changed from a coordination polymerization to a preferred group-transfer polymerization process.[3] The active species in the examples described, for example, by the groups of Yasuda, Collins, Soga, Marks et al.,[4] is probably a metal enolate complex that serves as a carbon nucleophile which attacks an equivalent of the CH_2=CR-COX monomer that is activated by its coordination to an electrophilic metal center. The few specific systems published so far differ in the generation of the active enolate species and the way the electrophilic activation of the incoming monomer is actually carried out. In the systems developed by Collins et al. two zirconocene-derived complexes are used, whereas in the system developed by Soga et al. the combination of a zirconocene with, for example, a diethylzinc component is effective. It appears that a very delicate balance has to be maintained to keep such systems on the active catalytic side because there is always the danger that the direct interaction of the propagating carbon nucleophile with the electrophilic activator compound gives an inactive coupling product or, at least, results in an equilibrium situation that diminishes the overall catalyst activity (Scheme 1). It would be highly desirable to have a variety of systems



Scheme 1. Activation and deactivation equilibrium of metallocene catalysts.

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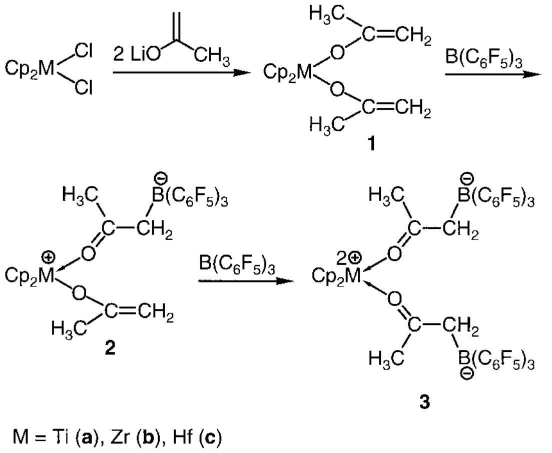
available in which the combination of, for example, an active metal enolate species with an electrophilic activator compound would result in a new system that itself has either an *intrinsic tendency* for rapid carbon–carbon coupling with an incoming activated electrophilic alkene and is thereby capable of actively propagating the polymerization process of a directly functionalized olefin, such as an α,β-unsaturated carbonyl compound, or is in a favorable equilibrium with such an active species. We may have found a principal entry into such a class of Group 4 metallocene-derived catalyst systems, the first examples of which are described herein.

Results and Discussion

Starting materials of our study were the bis(enolato)titanocene, -zirconocene, and -hafnocene complexes **1a–c**. These were prepared by treatment of the respective metallocene dichlorides with two molar equivalents of the lithium enolate of acetone (Scheme 2).[5] Soxhlet extraction with pentane gave the pure product $[Cp_2Zr(OCMe{=}CH_2)_2]$ (**1b**) directly. The related titanocene- and hafnocenebis(enolate) complexes had to be purified by recrystallization from dichloromethane since they seem to have a tendency for complexation with lithium chloride.



Scheme 2. Preparation of **1–3**.

Bis(2-propenolato)zirconocene (**1b**) was treated with one molar equivalent of tris(pentafluorophenyl)borane[6] in $[D_8]$toluene. The ^1H and ^{13}C NMR spectra (600 and 150 MHz, respectively) at 213 K showed that the strong organometallic boron Lewis acid[7] had attached itself to the enolate methylene group[8] of one of the 2-propenolato ligands of **1b** to selectively form the monoadduct **2b**. If the temperature is raised, there is a rapid broadening of the ^1H NMR signals of both the enolate and the borylated enolate ligand and finally coalescence. An equilibrated set of ^1H NMR signals at high temperature indicates a rapid migration (probably intermolecular) of the $B(C_6F_5)_3$ group between [Zr] enolate moieties.

Treatment of **1a** with one equivalent of $B(C_6F_5)_3$ likewise leads to **2a**. Treatment of the enolate complexes **1** with two molar equivalents of the Lewis acid $B(C_6F_5)_3$ results in the clean formation of the bis-adduct. The complexes **3a–c** were isolated as pure monosolvates in reasonable yield after crystallization from dichloromethane. The ^1H NMR spectrum now shows only a single set of signals. The complexes **3a** (Ti) and **3b** (Zr) were both identified by X-ray crystal structure analyses. A view of the molecular geometry of the zirconium complex **3b** is shown in Figure 1.

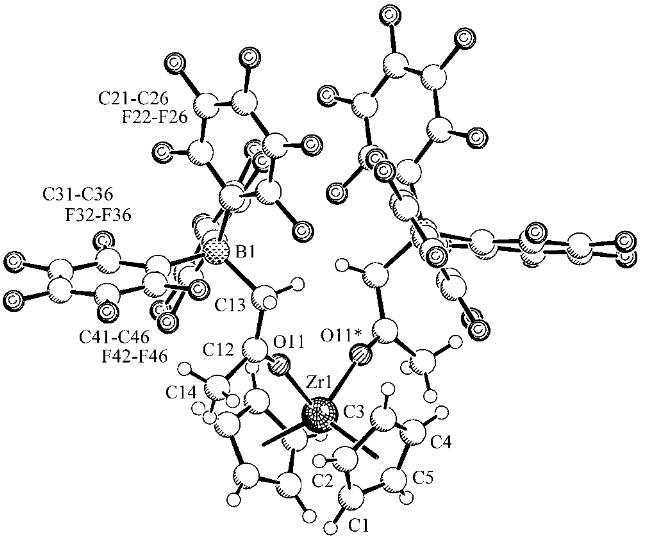


Figure 1. A projection of the molecular structure of complex **3b** with atom numbering scheme. Selected bond lengths [Å] and angles [°]: Zr1–O11 2.081(4), Zr1–C1 2.480(7), Zr1–C2 2.484(7), Zr1–C3 2.512(7), Zr1–C4 2.498(7), Zr1–C5 2.479(7), O11–C12 1.258(7), C12–C13 1.449(8), C12–C14 1.481(9), C13–B1 1.710(9), B1–C21 1.642(9), B1–C31 1.643(10), B1–C41 1.646(10); Zr1-O11-C12 158.4(4), O11-Zr1-O11* 94.7(2), O11-C12-C13 121.0(6), O11-C12-C14 117.5(6), C13-C12-C14 121.5(6), C12-C13-B1 117.3(5), C13-B1-C21 109.5(5), C13-B1-C31 113.1(5), C13-B1-C41 104.2(5), C21-B1-C31 102.9(5), C21-B1-C41 113.2(5), C31-B1-C41 114.1(5).

In the crystal, complex **3b** is C_2-symmetric and thus chiral. The Cp(centroid)-metal-Cp(centroid) angle of the central zirconocene unit is 130.4°. The enolate oxygen atoms are bonded in the σ-ligand plane which bisects the Cp-Zr-Cp bent metallocene wedge to complete the pseudotetrahedral ligand arrangement around the metal atom. The two bulky $-OC(CH_3)CH_2B(C_6F_5)_3$ groups are bonded to zirconium only through oxygen, and their central atoms are arranged C_2-symmetrically in the vicinity of the major bent metallocene σ-ligand plane.[9] As expected, the bulky $B(C_6F_5)_3$ groups are orientated away from the bulky $[Cp_2Zr]$ moiety to avoid unfavorable steric interactions.

The addition of the $B(C_6F_5)_3$ building block to the metal enolate functional group effects a substantial change in the typical bonding parameters of the $M\text{-}OC(CH_3)CH_2$ unit. The Zr1–O11 bond is rather short (2.081(4) Å), and together with the rather large bonding angle at oxygen (Zr1-O11-C12: 158.4(4)°) this indicates some metal–oxygen π interaction.[10] The adjacent C12–O11 bond length is 1.258(7) Å, which is at the high end of the range of C=O double bonds (statistical average 1.21 Å[11]), but is still outside the C–O single bond regime. The C12–C13 bond length is 1.449(8) Å, which is slightly below the typical value expected for a $C(sp^3)-C(sp^2)$

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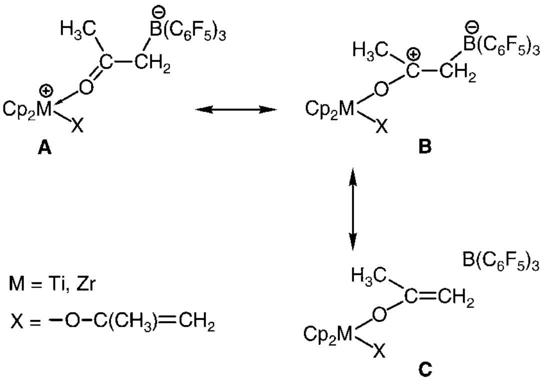
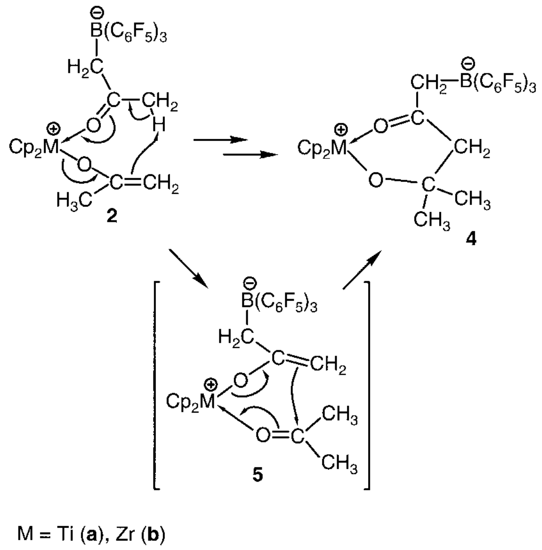
single bond (statistical average: 1.503 Å;[11] but note that the length of the corresponding directly adjacent C12–C14 linkage is only 1.481(9) Å), but clearly greater than a C=C double bond system. Finally, the C13–B1 bond length is 1.710(9) Å, which is slightly longer than the adjacent B–C(arom.) bonds (B1–C21: 1.642(9) Å; B1–C31: 1.643(10) Å; B1–C41: 1.646(10) Å). The corresponding bond angles around C12 and C13 are 117.5(6)° (O11-C12-C14), 121.5(6)° (C13-C12-C14), 121.0(6)° (O11-C12-C13), and 117.3(5)° (C12-C13-B1). The B1-C13-C12-O11 dihedral angle is 104.7(7)°, while the corresponding B1-C13-C12-C14 angle is −76.2(8)°. The structural features of the titanocene complex **3a** are analogous (for details see the Experimental Section).

These very characteristic bonding parameters indicate that the M-enolate-$B(C_6F_5)_3$ addition product exhibits a structural tendency towards a description of a metal complex containing a ketone ligand with a borato group attached to its α-carbon atom. A close inspection of the structural data, however, reveals that the adduct retains a particular metal enolate character. Therefore, the new complexes **3** can best be depicted by a description that includes an ample participation of the resonance formulae **A** and **B**, but some hyperconjugative interaction should probably also be taken into account, as visualized by the arrangement **C**.



Complex **3b** is thermally labile: if it is heated to 60 °C in an aromatic solvent, an intramolecular aldol reaction takes place leading to **4b**.[5b] The product could not be isolated due to a subsequent unspecific decomposition reaction, but it was unequivocally identified by spectroscopy. Apparently, one equivalent of $B(C_6F_5)_3$ is eliminated in the course of the **3b**→**4b** transformation. Consequently, the aldol product has also been generated directly by treatment of the bis(enolate)zirconocene complex **1b** with one equivalent of $B(C_6F_5)_3$ in [D$_6$]benzene at +40 °C. In a series of experiments (see Experimental Section), the amount of $B(C_6F_5)_3$ reagent added was increased stepwise to 2, 2.5, and 6 molar equivalents. As expected, this led to a marked decrease of the rate of formation of the intramolecular carbon–carbon coupling product **4b**. We assume that a coordinated acetone ligand is formed by means of an intramolecular proton transfer reaction to the metal enolate to give the intermediate **5**, which is ideally suited to undergo C–C coupling to yield directly the observed aldol addition product **4** (see Scheme 3). The half-life of the **3b**→**4b** transformation (with the loss of one equivalent of $B(C_6F_5)_3$) is about 30 min at 60 °C. The analogous reaction in the titanium system (**3a**→**4a**) also proceeds at elevated temperatures but is slightly slower.[12]



Scheme 3. Formation of the intramolecular carbon–carbon coupling product **4**.

The metallocene enolate/$B(C_6F_5)_3$ systems were employed as catalysts for the polymerization of the functionalized olefin methyl vinyl ketone. Two series of preliminary experiments were performed. In the first series all three metallocene enolates (**1a**–**c**) were employed as the catalyst precursors. The reactions were performed at ambient temperature with monomer:**1** ratios of ≈1000 and **1**:$B(C_6F_5)_3$ ratios between 1:1 and 1:4. A second series of experiments was carried out under slightly varied conditions using slightly lower monomer:**1** ratios of ≈600. In this case, only **1a** and **1b** were employed as catalyst precursors, and reactions were carried out at three different temperatures.

[Bis(2-propenolato)ZrCp$_2$] (**1b**)/$B(C_6F_5)_3$ in a 1:1 ratio (i.e. the mono-addition product **2b**) catalyzed the polymerization reaction of the monomer in dichloromethane with a moderate activity.[13] The reaction of 4.25 g (5 mL, 60.7 mmol) of methyl vinyl ketone in CH_2Cl_2 (3 mL) with 0.06 mmol of the catalyst system **2b** (derived from 20 mg of **1b**) gave a yield of 200 mg (5 %) of poly(methyl vinyl ketone) after 120 min (Table 1). This amounts to an integral catalyst activity of about 1.7 kg (polymer) per mol **2b** per h. At a **1b**:$B(C_6F_5)_3$ ratio of 1:2 (i.e. formation of the bis-adduct **3b**), the poly(methyl vinyl ketone) was formed with a catalyst activity of about 3.3 (600 mg isolated, 15 % yield) after 180 min under otherwise unchanged conditions. A drastic increase of the catalyst activity was observed when the **2b**:$B(C_6F_5)_3$ ratio was increased beyond the stoichiometric ratio of 1:2. At a 1:3 ratio, the catalyst activity was about 37 [2.2 g polymer (52 %) formed during 60 min]. At a **2b**:$B(C_6F_5)_3$ ratio of 1:4 the catalyst activity was as high as about 50 (3.0 g, 71 % isolated). The ^1H and ^{13}C NMR spectra revealed that the poly(methyl vinyl ketone) formed under these conditions with the metallocene-enolate/$B(C_6F_5)_3$ catalyst system is close to atactic [well-separated mm, mr, and rr ^1H NMR methylene triad signals at $\delta = 1.8$, 1.5, and 1.0 as well as the corresponding ^{13}C

Table 1. Methyl vinyl ketone polymerization with a variety of **1a–c**/$B(C_6F_5)_3$ catalyst combinations.[a]

	1 [mmol]	**1**:$B(C_6F_5)_3$	g (monomer)	t_R[b]	Yield[c]	Activity[d]
1a (Ti)	0.07	1:2	4.25	120	1.6 (38)	11.4
	0.07	1:4	4.25	90	3.0 (71)	28.6
	0.14[e]	1:4	6.80	5	4.6 (68)	394.3
1b (Zr)	0.06	1:1	4.25	120	0.2 (5)	1.7
	0.06	1:2	4.25	180	0.6 (15)	3.3
	0.06	1:3	4.25	60	2.2 (52)	36.7
	0.06	1:4	4.25	60	3.0 (71)	50.0
1c (Hf)	0.06	1:2.4	4.25	90	2.4 (56)	26.7
	–	30 mg[f]	4.25	120	–[g]	–[g]
	–	100 mg[f]	4.25	90	–[g]	–[g]

[a] Reactions all carried out in CH_2Cl_2 (3 mL) at room temperature; the resulting polymer was atactic. [b] Total reaction time in min. [c] Yield of polymer in g (%). [d] Overall activity in kg (polymer) per mol **1** per h. [e] Reaction in CH_2Cl_2 (10 mL). [f] Control experiments. [g] No polymer formed.

NMR carbonyl resonances at $\delta = 210.7$, 210.4, and 210.1 (in $CDCl_3$)[14–17]].

The hafnium system **1c**/$B(C_6F_5)_3$ is similarly active. At a B:Hf ratio of 2.4, atactic poly(methyl vinyl ketone) was formed with an overall catalyst activity of about 27 (56% isolated after a reaction time of 90 min) (see Table 1). The titanocene-derived catalyst system responded strongly to alteration of the B:Ti ratio: at 2:1 (i. e. stoichiometric formation of **2a**) a catalyst activity of ≈ 11 was obtained (1.6 g, 38% polymer recovered), whereas at a 4:1 ratio the reaction had become so fast that it was already close to completion after a period of 5 min (4.6 g, 68% of atactic poly(methyl vinyl ketone) isolated). This amounts to an integral catalyst activity of ≈ 400 for the [bis(2-propenolate)titanocene]/$B(C_6F_5)_3$ catalyst system (1:4 molar ratio) for the polymerization of methyl vinyl ketone in CH_2Cl_2 (monomer:[Ti] molar ratio ≈ 700) at ambient temperature ($t_R = 5$ min).

In a second series of polymerization reactions we activated each of the compounds **1a** and **1b** with $B(C_6F_5)_3$ (1:1 to 1:4 ratio, the values corresponding to both the low and the high metal:boron ratio are listed in Table 2) in dichloromethane. The polymerization reaction was then started by adding methyl vinyl ketone at a preset temperature (monomer:catalyst ratio ≈ 600). After 10 min, 25% of the reaction mixture was removed by syringe, quenched, and the polymer isolated. The remaining 75% of the solution was allowed to react further until it was quenched by the addition of methanol after an overall reaction time of 30 min. The polymer was isolated, its yield determined, and the molecular weight of the polymer samples determined by GPC ($\bar{M}$-values of the corresponding polymer samples obtained after 10 min and 30 min reaction time were identical, within the accuracy of the GPC measurement. The averaged values are given in Table 2). These polymerization reactions were carried out at three different temperatures (20 °C, 0 °C, and −20 °C). A typical set of yields and integral activities is given in Table 3 for the reactions performed with a metallocene enolate:$B(C_6F_5)_3$ ratio of 1:4.

Table 2. Molecular weights of the poly(methyl vinyl ketone) samples obtained at the **1a,b**/$B(C_6F_5)_3$ catalyst system.[a]

	T [°C]	**1**:$B(C_6F_5)_3$ ratio	$\bar{M}_w$	$\bar{M}_w$:$\bar{M}_n$
1b	20	1:1	11100	1.50
(M = Zr)	0	1:1	9800	1.43
	−20	1:1	4000	[b]
	20	1:4	31000	1.39
	0	1:4	30100	1.31
	−20	1:4	24700	1.45
1a	20	1:1	6000	1.59
(M = Ti)	0	1:1	3300	1.36
	−20	1:1	2200	[b]
	20	1:4	28700	1.51
	0	1:4	26500	1.58
	−20	1:4	17200	1.44

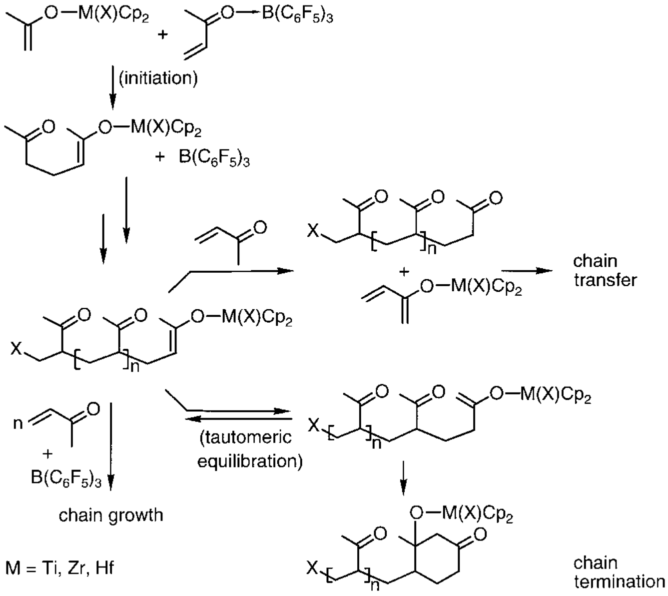
[a] Determined by GPC (silica gel/THF). [b] Not determined.

Table 3. Polymerization of methyl vinyl ketone with the **1a,b**/$B(C_6F_5)_3$ (1:4) catalyst system.[a]

	T [°C]	Polymer yield [%] after 10 min	Polymer yield [%] after 30 min	Catalyst activity[b]
1b	20	61	65	156
(M = Zr)	0	38	42	96
	−20	33	42	85
1a	20	89	c	227
(M = Ti)	0	75	78	192
	−20	31	36	78

[a] In CH_2Cl_2; monomer:catalyst ratio ≈ 600. [b] Integral activity after 10 min, in kg (polymer) per mol **1** per h. [c] Not determined.

The polymerization characteristics (e. g. the molecular weight response to variations in the temperature and Zr,Ti:B ratios as well as the value of the polydispersity) are contraindicative to a coordination polymerization mechanism. We assume that the polymerization mechanism is similar to that proposed for the systems developed by Collins et al. and Soga et al.: it is initiated by nucleophilic attack of the zirconium enolate on the Michael position of the $B(C_6F_5)_3$-activated methyl vinyl ketone monomer (Scheme 4). Chain propagation



Scheme 4. Proposed mechanism for the polymerization of methyl vinyl ketone.

and polymer chain growth then may occur by a further similar nucleophilic attack of the resulting C–C coupled enolate to another $B(C_6F_5)_3$-activated methyl vinyl ketone monomer. From the data presented in Table 2 (and a number of similar values obtained for this polymerization reaction at intermediate **2**:$B(C_6F_5)_3$ ratios) it is evident that this specific polymerization system involves extensive chain transfer. Mechanistically, one could envisage that this probably takes place by means of a proton transfer from a $CH_2{=}CH\text{-}CO\text{-}CH_3$ monomer to the enolate end of the growing polymer chain. The k_{transfer}:$k_{\mathrm{chain\ growth}}$ ratio then would reflect the basic versus nucleophilic properties of the active metal-enolate end of the growing chain under the specific reaction conditions employed. We see from Tables 2 and 3 that decreasing the overall catalyst activities seems to result in the formation of polymers with a lower molecular weight; this is in agreement with an increased transfer of the enolate functionality by proton transfer.

It is also apparent from the initially described experiments (M:B ratio 1:1 to 1:4; monomer to catalyst ratio of 1000) and the data shown in Table 3 (and a number of tentatively similar values obtained at **1**:$B(C_6F_5)_3$ ratios below 1:4) that there is a chain termination reaction effectively competing with the repetitive carbon–carbon coupling which leads to poly(methyl vinyl ketone). The termination becomes very dominant when the overall polymerization reaction is rather slow: either at lower temperatures, or if the amount of the $B(C_6F_5)_3$ activator component is decreased, or if the reaction is almost complete so that the reaction mixture is depleted of the monomeric component. It seems that this competitive situation is responsible for the very pronounced effect of an over-stoichiometric amount of the added $B(C_6F_5)_3$ activator on the polymerization reaction rate. The propagation rate probably profits predominately from an increased concentration of the activated monomer (i.e. the $H_2C{=}CH\text{-}CO[B(C_6F_5)_3]CH_3$ adduct). Increasing its concentration sufficiently seems to create a situation where chain growth becomes predominant over chain transfer and, more importantly, over irreversible chain termination.

We have, as yet, no experimental information on the mechanistic nature of the chain-terminating process. But in view of the ease of formation of an aldol product (i.e. **4**) from a related zirconium-enolate (**2**, see above), it may be possible that there is 1,2-aldol addition to the methyl vinyl ketone monomer[18] or an aldol-type cyclization subsequent to an intramolecular shift of the enolate function (see Scheme 4). Experiments will be carried out in our laboratory to investigate the validity of this speculative interpretation.

Conclusion

We conclude that the metallocene enolates **1** may serve as initiators of an effective polymerization reaction of methyl vinyl ketone in the presence of the strongly Lewis-acidic activator component $B(C_6F_5)_3$. The $[Cp_2M(\text{-}OCMe{=}CH_2)_2]$ nucleophiles (**1**) cleanly add the electrophile $B(C_6F_5)_3$ to yield the complexes **2** and **3**, respectively. Nevertheless, this adduct formation does not lead to an annihilation of the nucleophilic and electrophilic properties of these components. It is apparent that some of their individual properties are retained in the adduct or reconstituted by means of an equilibration process which rapidly takes place upon addition of the methyl vinyl ketone monomer. Thus, the metallocene-enolate/$B(C_6F_5)_3$ combination represents a class of chemical systems in which the combination of a strong nucleophile with a strong electrophile does not result in the formation of an inactive system but rather in a very active and interesting catalyst system. This system effectively makes use of the essential properties of both chemical counterparts to initiate and support, in a concerted mutual effort, a repetitive carbon–carbon coupling process. It is likely that this interesting feature is not limited to the specific combination of nucleophilic and electrophilic reagents employed here, but that a large number of other useful combinations of this type exists. Investigations aimed at detecting more highly reactive catalyst systems of this general type are being carried out in our laboratory.

Experimental Section

Reactions with organometallic compounds were carried out in an inert atmosphere (Ar) in Schlenk-type glassware or in a glovebox. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled under argon prior to use. The following instruments were used for physical characterization of the compounds: Bruker AC200P and Varian Unity Plus (^1H: 600 MHz) NMR spectrometers; Nicolet 5DXC FT-IR spectrometer; elemental analyses were carried out with a Foss–Heraeus CHN-Rapid elemental analyzer; melting points were determined by differential scanning calorimetry (2910 DSC, DuPont/STA Instruments); the molecular weight determinations were carried out by GPC (Polymer Standards) on 10^5 Å–10^2 Å silica gel columns, THF solvent, and polymethylmethacrylate standards; X-ray crystal structure analyses were performed with an Enraf–Nonius MACH3 diffractometer, programs used: data reduction MolEN, structure solution SHELX-86, structure refinement SHELX-93, graphics SCHAKAL-92. $B(C_6F_5)_3$ was prepared according to a literature method.[6] The reagent lithio-2-propenolate was prepared by treatment of 2-propenyltrimethylsilylether with methyllithium.[5a]

Bis(η-cyclopentadienyl)bis(2-propenolato)titanium (**1a**): A 200-mL Schlenk flask was charged with lithio-2-propenolate (400 mg, 6.25 mmol) and titanocene dichloride (750 mg, 3.02 mmol), and THF (70 ml) was added at 0 °C. The mixture was stirred for 30 min at this temperature, then for 24 h at ambient temperature. The solvent was removed in vacuo, the residue taken up in CH_2Cl_2 and filtered. The clear red filtrate was concentrated in vacuo to approximately one third of its volume and cooled. Red-orange crystals of **1a** were obtained at −20 °C, which were collected by filtration. Yield of **1a** : 680 mg (77 %); m.p. 73 °C (decomp. 204 °C); ^1H NMR (200.1 MHz, $CDCl_3$): $\delta = 1.70$ (d, $^4J = 0.8$ Hz, 6H, CH_3), 3.55 (d, $J = 0.8$ Hz, 2H), 3.74 (m, 2H, $H_2C{=}$), 6.26 (s, 10H, Cp); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 23.2$ (CH_3), 85.1 ($H_2C{=}$), 115.2 (Cp), 170.6 ($C{=}C\text{-}CH_3$); IR (KBr): $\tilde{\nu} = 3104$, 2944, 2910, 1712, 1615, 1541, 1438, 1363, 1287, 1267, 1031, 984, 811, 768, 512 cm^{-1}; $C_{16}H_{20}O_2Ti$ (292.2): calcd C 65.76, H 6.92; found C 65.50, H 7.12.

Bis(η-cyclopentadienyl)bis(2-propenolato)zirconium (**1b**): Lithio-2-propenolate (1.00 g, 15.6 mmol) and $[Cp_2ZrCl_2]$ (2.17 g, 7.42 mmol) were dissolved in THF (80 mL) at 0 °C. The mixture was stirred for 30 min at this temperature and for 1.5 h at ambient temperature. The solvent was removed in vacuo, and the residue taken up in pentane and filtered. Removal of the solvent from the filtrate gave **1b** as a white solid. Yield: 2.18 g (88 %); m.p. 75 °C (decomp); ^1H NMR (200.1 MHz, $CDCl_3$): $\delta = 1.69$ (d, $^4J = 0.7$ Hz, 6H, CH_3), 3.66 (d, $J = 0.7$ Hz, 2H, anti), 3.73 (m, 2H, $H_2C{=}$), 6.29 (s, 10H, Cp); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 22.9$ (CH_3), 85.8 ($H_2C{=}$), 112.6 (Cp), 165.5 ($C{=}C\text{-}CH_3$); IR (KBr): $\tilde{\nu} = 3105$, 2963, 2948, 2914, 2850, 1712, 1631, 1366, 1269, 1039, 806, 779, 735 cm^{-1}; $C_{16}H_{20}O_2Zr$ (335.6): calcd C 57.27, H 6.01; found C 56.83, H 6.08.

Bis(η-cyclopentadienyl)bis(2-propenolato)hafnium (1c): In an analogous manner to that described above, the reaction of lithio-2-propenolate (425 mg, 6.64 mmol) with $[Cp_2HfCl_2]$ (1.26 g, 3.32 mmol) in THF (50 mL), followed by workup with dichloromethane gave **1c**. Yield: 1.02 g (86 %); m.p. 83 °C (decomp. 230 °C); ^{1}H NMR (200.1 MHz, C_6D_6): $\delta = 1.73$ (dd, $^4J = 0.8$ Hz, 0.2 Hz, 6H, CH_3), 3.89 (d, $J = 0.8$ Hz, 2H), 3.94 (quint, 2H, $H_2C{=}$), 5.98 (s, 10H, Cp); ^{13}C NMR (50.3 MHz, C_6D_6): $\delta = 23.2$ (CH_3), 86.7 ($H_2C{=}$), 111.5 (Cp), 164.9 ($C{=}C\text{-}CH_3$); IR (KBr): $\tilde{\nu} = 3106$, 2947, 2913, 1708, 1633, 1565, 1439, 1431, 1368, 1292, 1272, 1043, 1016, 989, 878, 813, 779, 512 cm^{-1}; $C_{16}H_{20}O_2Hf \cdot LiCl$ (465.2): calcd C 41.31, H 4.33; found C 42.45, H 4.55.

Reaction of the metallocene enolates with $B(C_6F_5)_3$.

Preparation of 2b from the reaction of 1b with one equivalent of $B(C_6F_5)_3$: An NMR tube was charged with **1b** (20 mg, 0.06 mmol) and $B(C_6F_5)_3$ (31 mg, 0.06 mmol), and the mixture dissolved in [D$_8$]toluene (0.5 mL). The selective formation of **2b** was evident from the NMR spectra at low temperature. At ambient temperature, an averaged set of signals was observed due to a rapid equilibration process. ^{1}H NMR (600 MHz, [D$_8$]toluene, 298 K): $\delta = 1.40$ (broad s, 6H, CH_3), 3.51 (broad s, 4H, $=CH_2$), 5.59 (s, 10H, Cp); ^{1}H NMR (600 MHz, [D$_8$]toluene, 213 K): $\delta = 1.32$ (s, 3H, $C{=}C\text{-}CH_3$), 1.40 (bs, 3H, $O{=}C\text{-}CH_3$), 3.43 (s, 1H, $C{=}CH_2$), 3.53 (bs, 2H, $B\text{-}CH_2\text{-}$), 3.75 (s, 1H, $C{=}CH_2$), 5.43 (s, 10H, Cp); the ^{13}C NMR signals were detected and assigned by means of a C,H-correlated spectrum (GHSQC [20]) at 213 K: ^{13}C NMR (150 MHz, [D$_8$]toluene, 213 K): $\delta = 22.0$ (s, $C{=}C\text{-}CH_3$), 32.3 (s, $O{=}C\text{-}CH_3$), 49.5 (bs, $B\text{-}CH_2\text{-}$), 89.0 (s, $=CH_2$), 114.8 (s, Cp), 137.0 (d, *m*-CF, $^1J(F,C) = 241$ Hz), 139.0 (d, *p*-CF, $^1J(F,C) = 246$ Hz), 148.5 (d, *o*-CF, $^1J(F,C) = 241$ Hz), 164.3 (s, $H_3C\text{-}C{=}CH_2$); signals of the carbonyl carbon and *ipso*-C of C_6F_5 were not detected.

Preparation of 3a from the reaction of 1a with two equivalents of $B(C_6F_5)_3$: $B(C_6F_5)_3$ (70 mg, 0.14 mmol) and **1a** (20 mg, 0.07 mmol) were mixed as solids in an NMR tube. The mixture was then dissolved by adding CD_2Cl_2 (0.5 mL). A dark red, clear solution was obtained from which red crystals appeared after some time at −20 °C. Yield of **3a**: 73 mg (74 %); m.p. 71 °C (decomp 135 °C); the crystals were suitable for X-ray crystal structure analysis (see below); ^{1}H NMR (200.1 MHz, C_6D_6): $\delta = 1.43$ (bs, 6H, CH_3), 3.41 (bs, 4H, CH_2), 5.40 (s, 10H, Cp); ^{13}C NMR (50.3 MHz, C_6D_6): $\delta = 30.8$ (bs, 6H, CH_3), 118.8 (s, Cp), 137.6 (d, *m*-CF, $^1J(F,C) = 249$ Hz), 138.7 (d, *p*-CF, $^1J(F,C) = 251$ Hz), 148.6 (d, *o*-CF, $^1J(F,C) = 245$ Hz); CH_2-carbon atoms adjacent to boron and *ipso*-C of C_6F_5 not detected; IR (KBr): $\tilde{\nu} = 3133$, 2922, 1646, 1588, 1555, 1518, 1464, 1378, 1366, 1322, 1279, 1089, 836, 821, 789, 681 cm^{-1}; $C_{52}H_{20}B_2F_{30}O_2Ti \cdot CD_2Cl_2$ (1403.14): calcd C 45.43, H 1.58; found C 45.37, H 1.78

X-ray crystal structure analysis of 3a: $C_{52}H_{20}B_2O_2F_{30}Ti \cdot CD_2Cl_2$, $M = 1403.14$; crystal dimensions: $0.20 \times 0.10 \times 0.05$ mm; $a = 18.400(2)$, $b = 11.404(2)$, $c = 24.640(3)$ Å, $\beta = 95.87(1)°$, $V = 5143.2(12)$ Å^3, $\rho_{calcd} = 1.809$ g cm^{-3}, $\mu = 4.25$ cm^{-1}, empirical absorption correction by ψ-scan data ($0.973 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $C2/c$ (no. 15), $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 5408 reflections collected ($\pm h$, $\pm k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.50$ Å^{-1}, 2617 independent and 740 observed reflections $[I \geq 2\sigma(I)]$, 190 refined parameters, $R = 0.079$, $wR^2 = 0.165$, max. residual electron density 0.48 (−0.42) e Å^{-3}, hydrogen atoms calculated and riding, disordered CD_2Cl_2 refined with restraints. Due to the small crystal size and poor crystal quality, the structure was only refined isotropically to prove that it is isotypic with the analogous Zr compound. Selected bond lengths [Å] and angles [°] (atom numbering scheme analogous to that used for **3b**, see Figure 1): Ti1–O11 1.999(11), Ti1–C1 2.37(2), Ti1–C2 2.32(2), Ti1–C3 2.37(2), Ti1–C4 2.39(2), Ti1–C5 2.33(2), O11–C12 1.26(2), C12–C13 1.47(2), C12–C14 1.45(2), C13–B1 1.69(3), B1–C21 1.61(3), B1–C31 1.66(3), B1–C41 1.65(3); Ti1-O11-C12 156.9(11), O11-Ti1-O11* 91.4(6), O11-C12-C13 118(2), O11-C12-C14 119(2), C13-C12-C14 122(2), C12-C13-B1 118(2), C13-B1-C21 112(1), C13-B1-C31 112(2), C13-B1-C41 105(1), C21-B1-C31 104(1), C21-B1-C41 112(2), C31-B1-C41 113(1).

Generation of 4a by thermolysis of 3a: A sample of **3a** was freshly prepared in [D$_8$]toluene in an NMR tube, in an analogous manner to that described above. The formation of **3a** was confirmed by spectroscopy. The sample was then kept at 60 °C for about 3 h to give **4a**. ^{1}H NMR (600 MHz, [D$_8$]toluene, 333 K): $\delta = 0.78$ (s, 6H, $\text{-}CH_3$), 2.23 (s, 2H, $CH_2\text{-}C{=}O$), 3.44 (bs, 2H, $B\text{-}CH_2\text{-}$), 5.49 (s, 10H, Cp); ^{13}C NMR (150 MHz, [D$_8$]toluene, 333 K): $\delta = 29.3$ ($^1J(C,H) = 126$ Hz, CH_3), 50.1 (bs, CH_2B), 57.3 (CH_2, $^1J(C,H) = 130$ Hz), 88.6 (s, Me_2C), 116.5 (Cp, $^1J(C,H) = 177$ Hz), 137.7 (d, *m*-$B(C_6F_5)_3$, $^1J(C,F) = 250$ Hz), 148.7 (d, *o*-$B(C_6F_5)_3$, $^1J(C,F) = 243$ Hz), 242.4 (C=O); *p*- and *ipso*-C of C_6F_5 not detected; assignment carried out by 2D-experiments GHSQC and GHMBC.[20]

Preparation of 3b by the reaction of 1b with two equivalents of $B(C_6F_5)_3$: Compound **1b** (40 mg, 0.12 mmol) was treated with $B(C_6F_5)_3$ (122 mg, 0.24 mmol) in dichloromethane (3 mL) at ambient temperature. The mixture was cooled to −40 °C to give white crystals of **3b** which were collected by filtration. Yield: 80 mg (50 %); m.p. 115 °C (decomp); ^{1}H NMR (200.1 MHz, C_6D_6): $\delta = 1.43$ (bs, 6H, CH_3), 3.58 (bs, 4H, CH_2), 5.59 (s, 10H, Cp); ^{13}C NMR (50.3 MHz, C_6D_6): $\delta = 28.1$ (CH_3), 118.8 (Cp), 137.6 (d, *m*-CF, $^1J(F,C) = 249$ Hz), 138.7 (d, *p*-CF, $^1J(F,C) = 251$ Hz), 148.6 (d, *o*-CF, $^1J(F,C) = 245$ Hz), CH_2[B], C=O and *ipso*-C of C_6F_5 not detected; IR (KBr): $\tilde{\nu} = 3118$, 3019, 2933, 1645, 1559, 1536, 1518, 1467, 1280, 1119, 1086, 1019, 976, 821, 787, 745, 680, 546 cm^{-1}; $C_{52}H_{20}B_2F_{30}O_2Zr \cdot CD_2Cl_2$ (1446.46): calcd C 44.07, H 1.54; found C 43.96, H 1.66

X-ray crystal structure analysis of 3b: Single crystals were obtained from a solution in CD_2Cl_2 at −20 °C. $C_{52}H_{20}B_2O_2F_{30}Zr \cdot CD_2Cl_2$, $M = 1446.45$; crystal dimensions: $0.70 \times 0.60 \times 0.15$ mm, $a = 18.538(2)$, $b = 11.455(1)$, $c = 24.753(4)$ Å, $\beta = 95.10(1)°$, $V = 5235.6(11)$ Å^3, $\rho_{calcd} = 1.833$ g cm^{-3}, $\mu = 4.64$ cm^{-1}, empirical absorption correction by ψ-scan data ($0.935 \leq C \leq 0.999$), $Z = 4$, monoclinic, space group $C2/c$ (no. 15); $\lambda = 0.71073$ Å, $T = 223$ K, $\omega/2\theta$ scans, 4755 reflections collected ($-h$, $-k$, $\pm l$), $[(\sin\theta)/\lambda] = 0.59$ Å^{-1}, 4604 independent and 2231 observed reflections $[I \geq 2\sigma(I)]$, 420 refined parameters, $R = 0.055$, $wR^2 = 0.120$, max. residual electron density 0.44 (−0.91) e Å^{-3}, hydrogen atoms calculated and riding, disordered CD_2Cl_2 refined with restraints. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100816. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033, e-mail: deposit@ccdc.cam.ac.uk).

Generation of 4b by the thermolysis of 3b: A sample of **3b** was prepared in [D$_6$]benzene and thermolyzed for 1 h at 60 °C to give **4b**, which was identified by spectroscopy; ^{1}H NMR (600 MHz, C_6D_6, 333 K): $\delta = 0.77$ (s, 6H, $\text{-}CH_3$), 2.17 (s, 2H, $CH_2\text{-}C{=}O$), 3.69 (s, 2H, $B\text{-}CH_2$), 5.65 (s, 10H, Cp); ^{13}C NMR (150 MHz, C_6D_6, 333 K): $\delta = 29.4$ (CH_3, $^1J(C,H) = 126$ Hz), 51.5 (CH_2B, $^1J(C,H) = 128$ Hz), 56.6 (CH_2, $^1J(C,H) = 130$ Hz), 82.4 (Me_2C), 116.5 (Cp, $^1J(C,H) = 175$ Hz), 137.7 (d, *m*-$B(C_6F_5)_3$, $^1J(C,F) = 250$ Hz), 148.7 (d, *o*-$B(C_6F_5)_3$, $^1J(C,F) = 243$ Hz), 242.4 (C=O); *p*- and *ipso*-C of C_6F_5 were not detected; assignment secured by 2D-experiments (GHSQC, GHMBC).[20]

Generation of 3c from 1c and two equivalents of $B(C_6F_5)_3$: In an NMR tube **1c** (30 mg, 0.08 mmol) was treated with $B(C_6F_5)_3$ (81 mg, 0.16 mmol) in [D$_6$]benzene (0.5 mL) to give **3c**. The compound was not isolated from this solution but only characterized by spectroscopy (see below). On a preparative scale complex **3c** was prepared by treatment of **1c** (60 mg, 0.16 mmol) with $B(C_6F_5)_3$ (162 mg, 0.32 mmol) in dichloromethane (3 mL). Crystallization at −40 °C gave white crystals of **3c**. Yield: 70 mg (31 %), m.p. 53 °C (loss of solvent), 85 °C (decomp); ^{1}H NMR (200.1 MHz, C_6D_6): $\delta = 1.43$ (bs, 6H, CH_3), 3.57 (bs, 4H, CH_2), 5.54 (s, 10H, Cp); IR (KBr): $\tilde{\nu} = 3651$, 3638, 2922, 1647, 1519, 1469, 1374, 1285, 1090, 1017, 977, 821, 773, 681 cm^{-1}; $C_{52}H_{20}B_2F_{30}O_2Hf \cdot CH_2Cl_2$ (1531.7): calcd C 41.56, H 1.45; found C 42.02, H 1.46.

General procedure for the polymerization of methyl vinyl ketone: A Schlenk flask was charged with the respective metallocene-enolate complex **1** and $B(C_6F_5)_3$ (1–4 molar equiv). Dichloromethane (usually 3 mL) was then added and the mixture stirred for 3 min at ambient temperature. Methyl vinyl ketone was dried and distilled over $MgSO_4$ and then added to the catalyst solution. The polymerization reaction was usually quite exothermic; thus the mixture had to be cooled to maintain approximately room temperature. The reaction was stopped after a chosen time by adding a small amount of methanol. The mixture was washed with water, dried over magnesium sulfate, and the solvent and remaining volatiles were removed in vacuo to yield the respective polymer sample. ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 1.14$, 1.55, 1.87 (each broad, $\text{-}CH_2\text{-}$), 2.08 (bs, 3H, $C(O)CH_3$), 2.00–2.70 (bs, 1H, CH); ^{13}C NMR (150.3 MHz, $CDCl_3$): $\delta = 29.0$–30.0 (CH_2), 32.0–34.0 (CH_3), 48.2 (CH), 209.0–211.0 (CO); IR (film): $\tilde{\nu} = 3402$, 3019, 2931, 1709, 1425, 1356, 1216, 1164, 1083, 962, 754 cm^{-1}.

A second, larger series of polymerization experiments was carried out with **1a**/$B(C_6F_5)_3$ and **1b**/$B(C_6F_5)_3$ combinations, each in four molar ratios (1:1, 1:2, 1:3, and 1:4). The polymerization reactions were carried out according to the following general scheme: the metallocene bis(enolate) (40 μmol) was mixed with $B(C_6F_5)_3$ (1–4 molar equiv). Dichloromethane (20 mL) was added at 0 °C and the solution stirred for 10 min. The catalyst solution was then brought to the chosen reaction temperature (20 °C, 0 °C, or -20 °C) and methyl vinyl ketone (2 mL, 1.7 g, 24.3 mmol) was added with stirring. A 5 mL sample of the reaction mixture was removed after 10 min by a syringe, quenched, and worked up. The remaining volume was quenched after an additional 20 min and then worked up. The yields were determined and the molecular weights ($\bar{M}_w$, $\bar{M}_n$) of most of the samples determined by GPC (5 μ PSS SDV GPC column, 8×300 mm, 10^5 Å, 10^3 Å, 10^2 Å, consecutively). The molecular weights of equivalent samples obtained after 10 and 30 min were identical, within the accuracy of the method. Therefore, these values were averaged. Characteristic values of a representative variety of experiments are given in Tables 2 and 3 (see above); the additional values can be obtained from the authors on request.

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[12] Complex **4b** readily reacts with methyl vinyl ketone. A complex reaction sequence is initiated that leads to the formation of acetone and a mixture of, as yet, unidentified products. The elucidation of this reaction must await further detailed experimental studies.

[13] A variety of control experiments was carried out. These have revealed that neither complex **1b** nor the borane activator component alone led to any significant polymerization reaction of methyl vinyl ketone under the conditions typically applied in this study. Complex **1b** reacts slowly with methyl vinyl ketone stoichiometrically in an unspecific way giving a mixture of, as yet, unidentified products.

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[18] In an NMR experiment (in [D_6]benzene) it was shown that the related mono-enolate complex $[Cp_2Zr(CH_3)(O\text{-}C(CH_3){=}CH_2)]$[19] reacts slowly with methyl vinyl ketone at ambient temperature by 1,2-carbonyl addition to give a single stoichiometric product of the composition $[Cp_2Zr(CH_3)OC(CH_3)(CH{=}CH_2)CH_2COCH_3]$.

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