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Article

# Catalyst Deactivation Reactions: The Role of Tertiary Amines Revisited

Elena Novarino,[†,‡] Itzel Guerrero Rios,[†,‡] Siebe van der Veer,[†] Auke Meetsma,[†] Bart Hessen,[†] and Marco W. Bouwkamp*[,†]

[†]*Molecular Inorganic Chemistry, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands, and* [‡]*Dutch Polymer Institute, PO Box 902, 5600 AX Eindhoven, The Netherlands*

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Decamethylzirconocene cation $[Cp^*_2ZrMe]^+$ (**2**) decomposes in bromobenzene-$d_5$ solution to generate $\sigma$-aryl species $[Cp^*_2Zr(2\text{-}C_6H_4Br\text{-}\kappa Br,C)][B(C_6F_5)_4]$ (**3**). This $\sigma$-bond metathesis reaction is catalyzed by tertiary amines via a two-step mechanism, in which the amine acts as a proton relay. In benzene-$d_6$ compound **2** decomposes via C−H bond activation of one of the Cp* ligands to generate tucked-in compound $[Cp^*\{\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2)\}Zr]^+$ (**4**). In the presence of $Et_3N$, no formation of tucked-in compound **4** is observed, but instead an overall double C−H bond activation and C−N bond cleavage of the tertiary amine is observed, resulting in $[Cp^*_2Zr\{C(Me)NEt\text{-}\kappa C,N\}]^+$ (**6**). A mechanism is proposed that nominates $[Cp^*_2ZrNEt_2]^+$ as an intermediate, the result of a C−H bond activation of $Et_3N$, followed by $\beta$-amide elimination. Attempted synthesis of this species by treatment of $Cp^*_2Zr(NEt_2)Me$ with $[Ph_3C][B(C_6F_5)_4]$ results, again, in formation of compound $[\mathbf{6}]^+$. The presence of $Et_3N$ also has an effect on the stability of THF adduct $[Cp^*_2ZrMe(THF)]^+$ as the amine performs a nucleophilic THF ring-opening to generate $[Cp^*_2ZrMe\{O(CH_2)_4NEt_3\}]^+$ (**7**). The results show that amine coproducts, often generated in the synthesis of cationic transition-metal complexes, are not necessarily innocent.

## Introduction

In general, the active species in olefin polymerization catalysis using early transition-metal complexes is a cationic metal alkyl.[1] There are a number of methods to prepare these types of species,[2] including the treatment of transition-metal halides with methylaluminoxane[3] and the reaction of the corresponding metal alkyl precursors with Lewis or Brønsted acidic borane or borate reagents.[4] In the case of the frequently applied Brønsted acidic reagents of the type $[R_3NH][BAr_4]$ (R = alkyl, aryl; Ar = Ph, $C_6F_5$), one equivalent of a tertiary amine is generated during the activation process. In general, these amine coproducts are considered innocent, although it is known that these substrates can bind to the metal center, forming a dormant site,[5] and a number of examples are known in which *N*,*N*-dimethylaniline can undergo C−H bond activation reactions at the methyl[6] or the 2-position.[7]

One of the most commonly observed deactivation routes for these Lewis-acidic catalysts for olefin polymerization, not including hydrolysis or oxidation by incorrect handling of these typically highly oxophilic metal complexes, involves

*To whom correspondence should be addressed. E-mail: M.W.Bouwkamp@rug.nl.

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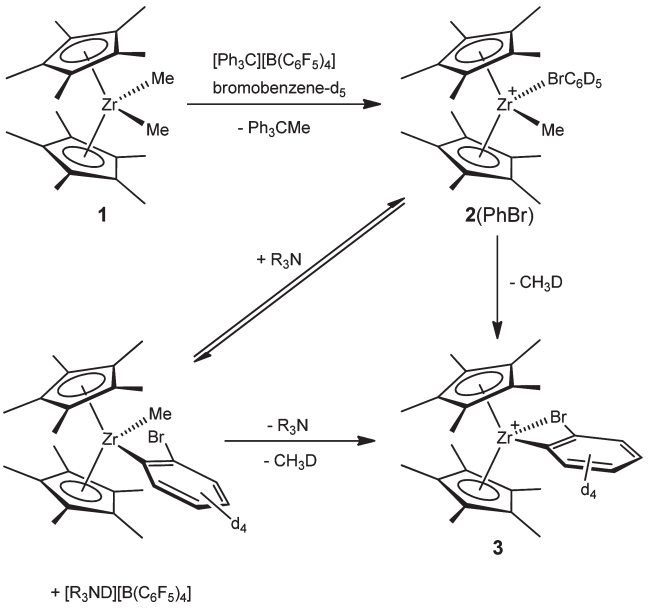


**Figure 1.** C−H bond activation of the bromobenzene to generate [**3**][B($C_6F_5$)$_4$]. Counterions for compounds [**2**(PhBr)][B($C_6F_5$)$_4$] and [**3**][B($C_6F_5$)$_4$] have been omitted for clarity.

C−H bond activation reactions. Among these are cyclometalation reactions of reactive C−H bonds of ancillary ligands,[5e,7c,8] solvents,[9] alkyltris(pentafluorophenyl)borate anions,[10] and α-olefin substrates.[11] Here we report that Brønsted basic coproducts of frequently used activators for olefin polymerization catalysts can have a significant impact on these C−H bond activation processes.

## Results and Discussion

**C−H Activation of Halobenzene Solvents.** Recently we communicated the deactivation of the decamethylzirconocene cation [Cp*$_2$ZrMe]$^+$ (**2**) in bromobenzene solution.[12] As expected, on the basis of the results obtained by Jordan and co-workers using chlorobenzene as a solvent,[9a] we observed C−H activation of the solvent to generate [Cp*$_2$Zr(2-$C_6H_4$Br-$\kappa Br,C$)][B($C_6F_5$)$_4$] ([**3**][B($C_6F_5$)$_4$], Figure 1). What was unexpected, though, was the fact that this reaction is catalyzed by tertiary amines. A computational study revealed a new two-step mechanism, in which the amine acts as a proton relay (Figure 1). After initial coordination of the halobenzene solvent to the metal center,[13] the bromobenzene ligand is deprotonated by the amine base to generate the neutral σ-aryl species Cp*$_2$Zr(2-$C_6H_4$Br)Me and ammonium salt [$R_3$NH][B($C_6F_5$)$_4$]. In a subsequent step, the ammonium reagent thus generated reacts with the Zr−Me bond to afford the observed ion pair [**3**][B($C_6F_5$)$_4$]. These results have been supported by a kinetic study, which reveals that, for $R_3N$ = $PhNMe_2$, the rate of the reaction can be separated into a noncatalyzed reaction and a catalyzed reaction, following the rate depicted in eq 1. Furthermore, there is a qualitative correlation between basicity of the amine and the rate of the C−H bond activation reaction.

$$\text{rate} = -(2.69(8)\times 10^{-6} + 5.52(7)\times 10^{-5}\,[\text{PhNMe}_2])\,[\mathbf{2}] \quad (1)$$

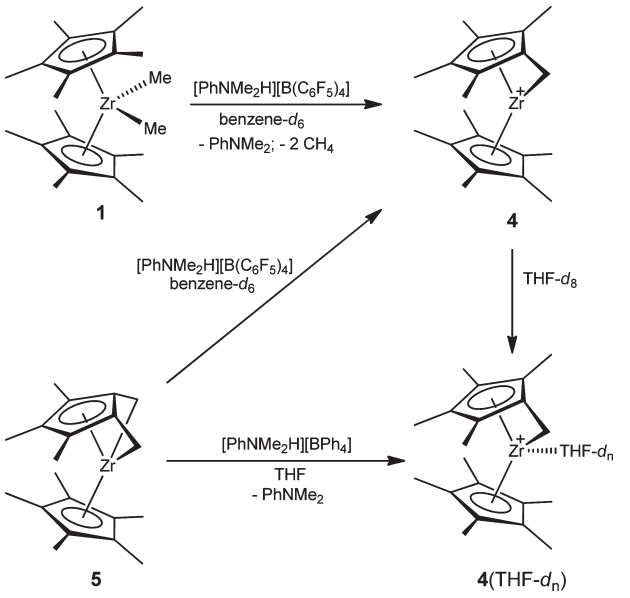


**Figure 2.** C−H bond activation of the Cp* ligand to generate [**4**(THF-$d_n$)][$BAr_4$] (Ar = Ph, $n$ = 0; Ar = $C_6F_5$, $n$ = 8). Counterions of intermediates and [**4**] and [**4**(THF-$d_n$)] have been omitted for clarity.

**C−H Activation of the Pentamethylcyclopentadienyl Ligand.** In the absence of halogenated arene solvents, C−H activation of the pentamethylcyclopentadienyl ligand was observed. Treatment of decamethylzirconocene dimethyl with [$PhNMe_2H$][B($C_6F_5$)$_4$] in benzene-$d_6$ resulted in the overnight formation of an insoluble red oil, identified as [Cp*{$\eta^5$:$\eta^1$-$C_5Me_4(CH_2)$}Zr][B($C_6F_5$)$_4$] by its reaction with THF-$d_8$, which afforded the corresponding THF-$d_8$ adduct ([**4**(THF-$d_8$)][B($C_6F_5$)$_4$], Figure 2). The formation of these types of tucked-in complexes of group 4 metals is a known phenomenon,[14] although this is, to

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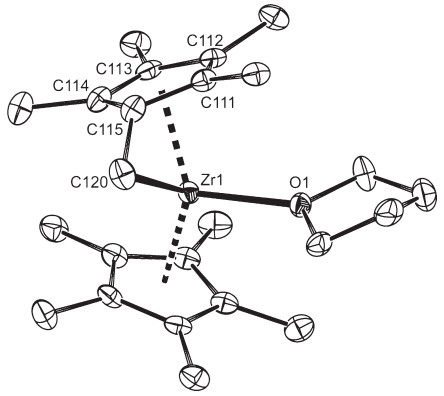


**Figure 3.** ORTEP representation of [**4**(THF)] at the 30% probability level. Hydrogen atoms and [$BPh_4$] counterion are omitted for clarity.

the best of our knowledge, the first time it has been identified as a catalyst decomposition reaction in olefin polymerization catalysis. During the reaction gas evolution was observed, and a Toepler pump experiment revealed that 2 equiv of gas was generated per zirconium (identified by GC analysis as methane). The $^1$H NMR spectrum of a dark purple solution of the compound in THF-$d_8$ reveals two characteristic doublets at 2.45 and 2.13 ppm ($J_{HH}$ = 6.9 Hz) for the methylene group, as well as five singlets for the remaining methyl groups: four for the methyl ligands of the tetramethylfulvene ligand and one with an intensity corresponding to 15 protons for the Cp* ligand. The compound can be prepared independently by treatment of Cp*($\eta^3$:$\eta^4$-$C_5Me_3(CH_2)_2$}Zr[15] with [$PhNMe_2H$][$BAr_4$] (Ar = Ph, $C_6F_5$) in THF or THF-$d_8$ solution (Figure 2).

In the case of [**4**(THF)][$BPh_4$], we were able to crystallize the product from THF/cyclohexane, affording single crystals that were suitable for X-ray analysis. The structure of cation [**4**(THF)] is shown in Figure 3 (see Table 1 for selected bond distances and angles). The geometry of the compound is similar to that of other tetramethylfulvene complexes of zirconium with comparable bond distances and angles.[14d,16] As observed for complexes of this type, the Zr−Fv* distance (2.1507 Å) is shorter compared to the Zr−Cp* distance (2.2055 Å); the Zr−$CH_2$ distance in [**4**(THF)]$^+$ is 2.366(4) Å. As is typical for these types of complexes, the centroids of the Cp* and the Fv* ligands, the metal center, and the THF-oxygen atom are virtually coplanar (sum of the angles around the metal center is 356.34°).

As expected, Cp*-methyl C−H bond activation was also observed when the zirconocene methyl cation was generated using $Cp^*_2ZrMe_2$ and [$Ph_3C$][$B(C_6F_5)_4$]. When monitoring both this reaction and the one where [$PhNMe_2H$][$B(C_6F_5)_4$] was used to generate [$Cp^*_2ZrMe$]$^+$, there is no clear indication, unlike the aforementioned bromobenzene solvent C−H bond activation reaction, that this reaction is catalyzed by tertiary amines. In both activation routes a small amount (~10%) of a side-product was observed. The nature of this species, which shows a resonance, presumably for a Cp* ligand, at $\delta$ 1.40 ppm in the $^1$H NMR spectrum (4:1 benzene-$d_6$/THF-$d_8$ mixture), remains unknown.

**Table 1. Selected Bond Distances (Å) and Angles (deg) of [4(THF)]**

| | |
|---|---|
| Zr1−Cp*[a] | 2.2055 |
| Zr1−Fv* | 2.1507 |
| Zr1−O1 | 2.224(2) |
| Zr1−C120 | 2.366(4) |
| C115−C120 | 1.457(5) |
| C111−C112 | 1.412(5) |
| C111−C115 | 1.446(5) |
| C112−C113 | 1.427(5) |
| C113−C114 | 1.421(5) |
| C114−C115 | 1.448(5) |
| Cp*−Zr1−Fv* | 141.59 |
| Fv*−C115−C120 | 144.3 |
| C120−Zr1−O1 | 105.76(10) |

[a] Cp* is defined as the centroid of C11−C15; Fv* is defined as the centroid of C111−C115.

**C−H Activation of Triethylamine.** Preparation of the decamethylzirconocene cation in benzene-$d_6$ using [$Et_3NH$]-[$B(C_6F_5)_4$] as a reagent again shows unexpected reactivity. Treatment of $Cp^*_2ZrMe_2$ with [$Et_3NH$][$B(C_6F_5)_4$] in benzene-$d_6$ resulted in the formation of a red, oily precipitate, and gas evolution was observed. Recrystallization of the material from THF/cyclohexane resulted in yellow crystals, which were characterized by a single-crystal X-ray diffraction study as the imino-acyl species [$Cp^*_2Zr${C(Me)NEt-$\kappa C,N$}-(THF)][$B(C_6F_5)_4$] ([**6**(THF)][$B(C_6F_5)_4$], Figure 4), resulting from an overall double C−H bond activation and C−N bond cleavage.[17] Refinement was frustrated by disorder in one of the Cp* ligands. From the solution, it was clear that the position of one of the Cp* ligands was highly disordered. A disorder model with two alternative positions of the Cp* ligand with bond restraints was used in the final refinement. The sof of the major fraction of the component of the disorder model refined to a value of 0.555(7). An ORTEP representation of the major fraction of the compound is depicted in Figure 6 (see Table 2 for pertinent bond distances and angles). The zirconocene cation adopts the usual bent-metallocene structure, with a Cp*−Zr−Cp* bent angle of 137.65°. Both the iminoacyl ligand and the THF solvent molecule are located in the plane bisecting the metallocene framework. The iminoacyl ligand is bound to the metal center in the N-inside fashion, which is common for these types of ligands.[18,19] Both the Zr−N and Zr−C bond distances (2.259(5) and 2.207(6) Å, respectively) are similar to other molecules of this type, and the C−N bond distance of 1.258(8) Å[19] is in the range expected for a C−N double bond. Both the carbon and the nitrogen atom of the iminoacyl fragment are planar (sum of the angles is 360.0(9)° and 359.8(8)°).

The $^1$H NMR spectrum of cation [**6**(THF)]$^+$ reveals a singlet at 1.83 ppm for two Cp* ligands, a quartet (3.76 ppm, 2H) and a triplet (1.18 ppm, 3H) for the ethyl moiety, and a singlet (2.63 ppm, 3H) for the iminoacyl-methyl group; $^{13}$C NMR spectroscopy reveals a resonance at 246.3 ppm,

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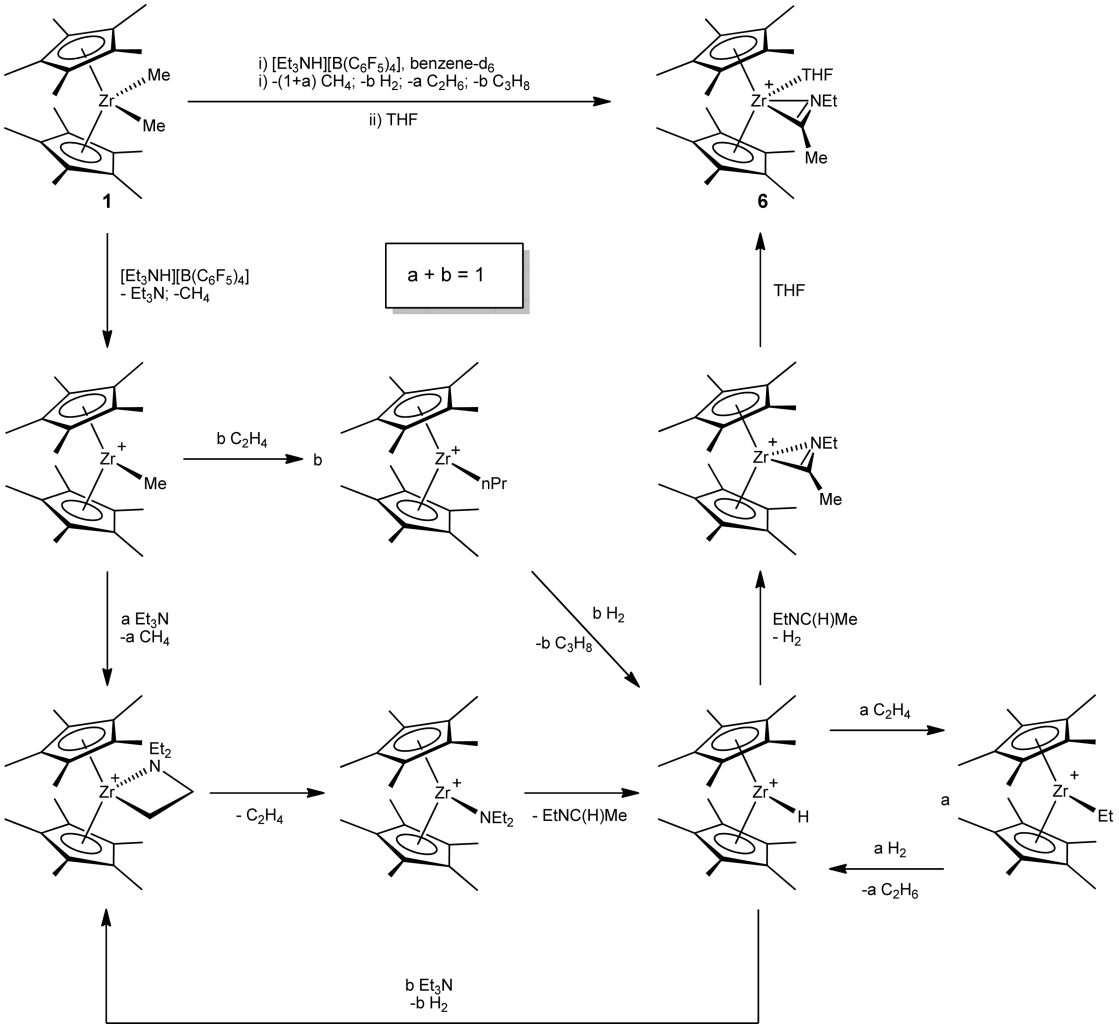


**Figure 4.** Double C−H and C−N bond activation of $Et_3N$ to generate [**6**][$B(C_6F_5)_4$]. Included is a schematic overview of the proposed mechanism. Counterions have been omitted for clarity.

indicative of an $\eta^2$-bound iminoacyl ligand in solution.[20,19a,19c] The iminoacyl compound is further characterized by a $\nu_{CN}$ stretch at 1642 $cm^{-1}$ in the IR spectrum.[20a,b,d]

Intrigued by this overall double C−H bond activation reaction and C−N bond cleavage, we were interested in the mechanism of the formation of cation $[\mathbf{6}]^+$. Generation of [$Cp^*_2ZrMe$][$B(C_6F_5)_4$] using both Lewis and Brønsted acidic borate activators and subsequent addition of one equivalent of triethylamine gave similar results, indicating that the formation of [**6**][$B(C_6F_5)_4$] is the result of the activation of triethylamine by the decamethylzirconocene methyl cation. Depending on the activator, two ([$Ph_3C$][$B(C_6F_5)_4$]) or three ([$Et_3NH$][$B(C_6F_5)_4$]) equivalents of gas per zirconium were generated.[21] GC analysis of the gas reveals a mixture of methane, ethane, and propane, and perhaps molecular hydrogen (we were not able to identify $H_2$ by GC analysis). A meticulous Toepler pump experiment revealed that approximately one ([$Ph_3C$][$B(C_6F_5)_4$]) or two ([$Et_3NH$][$B(C_6F_5)_4$]) equivalents of a mixture of methane and dihydrogen and one equivalent of a mixture of ethane and propane were formed.[22] On the basis of these results, we propose the mechanism as depicted in Figure 4. Although the mechanism for the formation of [**6**][$B(C_6F_5)_4$] is described, the same mechanism can be applied to the reactions where other activators are used and where the triethylamine is added separately. Dimethyl precursor $Cp^*_2ZrMe_2$

**Table 2. Selected Bond Distances (Å) and Angles (deg) of [6(THF)]**

| | |
|---|---|
| Zr1−Cp*1[a] | 2.277 |
| Zr1−Cp*2a[b] | 2.290 |
| Zr1−N1 | 2.259(5) |
| Zr1−O1 | 2.337(4) |
| Zr1−C125 | 2.207(6) |
| N1−C125 | 1.258(8) |
| N1−C127 | 1.456(8) |
| C125−C126 | 1.513(9) |
| Cp*1−Zr1−Cp*2a | 134.85 |
| N1−Zr1−O1 | 82.45(15) |
| N1−Zr1−C125 | 32.68(19) |
| O1−Zr1−C125 | 115.11(17) |

[a] Cp*1 is defined as the centroid of C11−C15. [b] Cp*2a is defined as the centroid of C111a−C115a.

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(21) These amounts are relative to the amount of the iminoacyl species formed.

(22) We were unable to distinguish between propane and propylene using GC analysis, though based on the stoichiometry of the reaction we propose that in this reaction propane is generated.

is converted to the corresponding methyl cation, $[Cp^*_2ZrMe]^+$, followed by C−H bond activation of the concurrently formed triethylamine. The four-membered aza-zirconacyclobutane intermediate thus generated can undergo a $\beta$-diethylamide elimination reaction to generate zirconium-amide cation, $[Cp^*_2ZrNEt_2][B(C_6F_5)_4]$, and one equivalent of ethylene.[23] The amide cation is then converted into the hydride cation $[Cp^*_2ZrH][B(C_6F_5)_4]$,[24] via a $\beta$-hydride elimination,[5h,25] which reacts with the *N*-(ethylidene)ethylamine formed in the $\beta$-hydride elimination to generate the observed iminoacyl species. The ethylene formed in the $\beta$-diethylamide elimination reaction can either be hydrogenated by the $[Cp^*_2ZrH]^+$ to form ethane or alternatively generate propane by insertion into the Zr−Me bond of the initially formed $[Cp^*_2ZrMe]$ cation followed by hydrogenolysis of the Zr−C bond of the resulting cation $[Cp^*_2ZrPr]^+$.

To further investigate the viability of this mechanism, we aimed at the independent synthesis of $[Cp^*_2ZrNEt_2][B(C_6F_5)_4]$ to assess its stability. As a precursor to this species, we prepared the methyl diethylamide compound $Cp^*_2Zr(Me)NEt_2$. The preparation of $Cp^*_2Zr(Me)NEt_2$ from $Cp^*_2Zr(Me)Cl$ and $LiNMe_2$ resulted in low isolated yields. When following the reaction by $^1H$ NMR spectroscopy, the formation of $Cp^*_2ZrMe_2$ was observed. A control experiment in which $Cp^*_2Zr(Me)NEt_2$ was treated with $Cp^*_2Zr(Me)Cl$ in THF-$d_8$ did not show any reactivity, indicating that its formation does not originate from a disproportionation reaction of the product with the starting material. We therefore propose that there is competition between transmetalation of $LiNEt_2$ with the chloride ligand and the methyl ligand of $Cp^*_2Zr(Me)Cl$.[26] This will generate, in addition to $Cp^*_2Zr(Me)NEt_2$ and LiCl, $Cp^*_2Zr(Cl)NEt_2$ and MeLi, the latter of which can react with $Cp^*_2Zr(Me)Cl$ to generate $Cp^*_2ZrMe_2$.

We therefore used a different approach to the synthesis of $Cp^*_2Zr(Me)NEt_2$ in which in situ generated $[Cp^*_2ZrMe(THF)][BPh_4]$ was treated with $LiNEt_2$.[27] Also in this case, the isolated yield is rather low, although NMR spectroscopic studies reveal that on an NMR tube scale this reaction is virtually quantitative. Subsequent treatment of $Cp^*_2Zr(Me)NEt_2$ with $[Ph_3C][B(C_6F_5)_4]$ in benzene-$d_6$ or bromobenzene-$d_5$ did not result in the formation of the corresponding amide cation, $[Cp^*_2ZrNEt_2]^+$. Instead this reaction afforded, upon dissolution in THF-$d_8$, iminoacyl compound $[\mathbf{6}(THF\text{-}d_8)][B(C_6F_5)_4]$ (Figure 5). Unfortunately the reaction is not clean, precluding the performance of a Toepler pump experiment to determine the amount of gas that is produced. One of the secondary products can be identified as $Ph_3CH$. Although small amounts of this coproduct have been observed in previous experiments as well ($< 5\%$), in this case a significant amount of $Ph_3CH$ is formed (**6**:$Ph_3CH \approx 1{:}2$ in benzene-$d_6$ and 1:3 in bromobenzene-$d_5$). We have observed this species only when

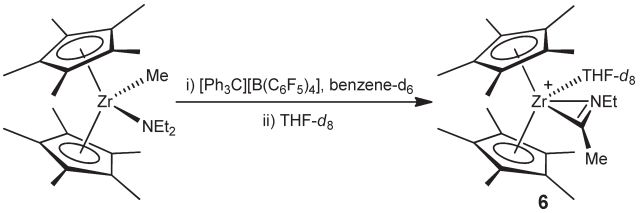


**Figure 5.** Formation of $[\mathbf{6}(THF\text{-}d_8)][B(C_6F_5)_4]$ from $Cp^*_2Zr(NEt_2)Me$ (anion of $[\mathbf{6}(THF\text{-}d_8)][B(C_6F_5)_4]$ omitted for clarity).

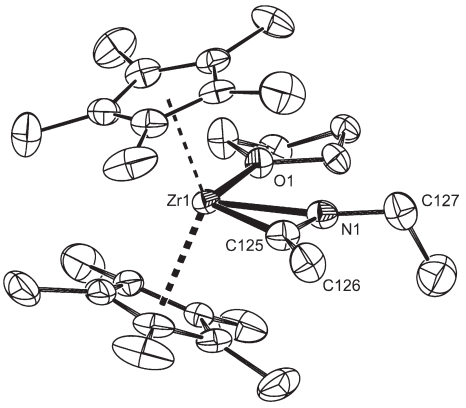


**Figure 6.** ORTEP representation of [**6**(THF)] at the 30% probability level. Hydrogen atoms and counterion are omitted for clarity.

$[Ph_3C][B(C_6F_5)_4]$ is used in combination with amines or transition-metal amides. In a control experiment $[Ph_3C][B(C_6F_5)_4]$ was treated with $Et_3N$ in $C_6D_5Br$. Also in this case the formation of $Ph_3CH$ was observed, showing that these two reagents are not compatible, even in the absence of transition-metal complexes. This is an important observation for the field of cationic transition-metal complexes, as it suggests that trityl reagents may not always be compatible with amine functionalities in ligands or with transition-metal amides. Despite these observations, we are able to conclude that $[Cp^*_2ZrNEt_2]^+$ is a likely intermediate in the formation of the iminoacyl species in the $Et_3N$-mediated deactivation of $[Cp^*_2ZrMe]^+$.

A similar deactivation of a zirconocene diethylamide cation has been reported by Erker and co-workers, in which they prepare the thermally labile zirconocene diethylamide cation, $[Cp_2ZrNEt_2][MeB(C_6F_5)_3]$.[20e] In benzene-$d_6$ the compound decomposes to generate a similar iminoacyl species, $[Cp_2Zr\{C(Me)NEt\text{-}\kappa C,N\}][HB(C_6F_5)_3]$. Although the authors propose a mechanism in which methane is liberated from the initially formed diethylamido ion pair, $[Cp_2ZrNEt_2][MeB(C_6F_5)_3]$, to generate $Cp_2Zr(\eta^2\text{-}EtNCHMe)$, methane, and $B(C_6F_5)_3$, we think that a similar mechanism to the one proposed here is more likely. In that case the diethylamide cation undergoes a $\beta$-H elimination reaction to form a cationic hydride intermediate and *N*-(ethylidene)ethylamine. This compound can undergo isomerization in which the hydride ligand is exchanged for the methyl group that is attached to boron, to account for the observed product with the $[HB(C_6F_5)_3]$ anion, before reacting with the imine to generate the observed product. Addition of the Lewis acidic borane reagent, $B(C_6F_5)_3$, to compound **1** in benzene-$d_6$ in the presence of $Et_3N$ results again in formation of cation [**6**]. It is interesting to note, though, that a mixture of the iminoacyl cation with both the $[MeB(C_6F_5)_3]$ and $[HB(C_6F_5)_3]$

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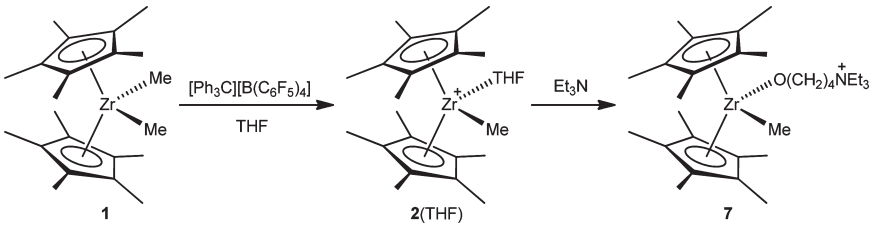


**Figure 7.** Formation of [**7**][$B(C_6F_5)_4$] (anions of [**2**(THF)][$B(C_6F_5)_4$] and [**7**)][$B(C_6F_5)_4$] are omitted for clarity).

anion was observed in a close to 1:1 ratio. We propose that the formation of the species with the [$HB(C_6F_5)_3$] anion is the result of a similar isomerization reaction of [$Cp^*_2ZrH$]-[$MeB(C_6F_5)_3$] as proposed for the parent zirconocene, to form [$Cp^*_2ZrMe$][$HB(C_6F_5)_3$], which can react with *N*-(ethylidene)ethylamine to generate the observed product.

**Ring-Opening of THF.** One method to stabilize highly reactive transition-metal cations is the complexation of a Lewis base such as THF.[28] Treatment of $Cp^*_2ZrMe_2$ with either [$Ph_3C$][$B(C_6F_5)_4$] or [$R_3NH$][$B(C_6F_5)_4$] ($R_3NH$ = $PhNMe_2H$, $Et_3NH$) in THF indeed results in formation of the corresponding THF adduct of the decamethylzirconocene methyl cation, [$Cp^*_2ZrMe(THF)$]$^+$ ([**2**(THF)], Figure 7). In the absence of $Et_3N$, these complexes are stable at room temperature in THF-$d_8$ solution. On the other hand, in the case that $Et_3N$ is present in the reaction mixture, either by treatment of $Cp^*_2ZrMe_2$ with [$Et_3NH$][$B(C_6F_5)_4$] or by addition of $Et_3N$ to a solution of [$Cp^*_2ZrMe(THF)$][$B(C_6F_5)_4$] in THF-$d_8$ solution, ring-opening of the THF solvent molecule to generate [$Cp^*_2ZrMe\{O(CD_2)_4NEt_3\}$][$B(C_6F_5)_4$] ([**7**-$d_8$][$B(C_6F_5)_4$]) is observed. When repeating the reaction in THF, the nondeuterated isotopologue was obtained. The $^1$H NMR spectrum of the compound is characterized by four methylene resonances at 4.06, 3.13, 1.54, and 1.44 ppm for the butylene moiety. An analogous THF ring-opening by nucleophilic attack of the trimethylamine on a THF adduct of zirconocene methyl cation was reported previously by Jordan et al.[29]

## Conclusions

Decamethylzirconocene compound [$Cp^*_2ZrMe$]$^+$ decomposes via C−H bond activation processes. The stability of this species is highly dependent on the presence and nature of tertiary amines in the reaction mixture. In bromobenzene solution, the corresponding bromobenzene adduct [$Cp^*_2ZrMe(BrC_6H_5)$]$^+$ undergoes C−H bond activation of the solvent to generate $\sigma$-aryl species [$Cp^*_2Zr(2\text{-}C_6H_4Br\text{-}\kappa Br,C)$][$B(C_6F_5)_4$]. Results show that this $\sigma$-bond metathesis reaction is accelerated in the presence of tertiary amines, and DFT calculations have revealed a new mechanism for this process, in which the amine acts as a proton relay. In benzene solution, no solvent C−H bond activation has been observed. Instead, when [$Cp^*_2ZrMe$]$^+$ is generated using [$Ph_3C$][$B(C_6F_5)_4$] or [$PhNMe_2H$][$B(C_6F_5)_4$], Cp*-methyl activation was observed, resulting in the formation of tucked-in compound [$Cp^*\{\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2)\}Zr(THF)$]$^+$. In the presence of $Et_3N$, an overall double C−H bond activation and C−N bond cleavage of the amine is observed, to afford [$Cp^*_2Zr\{C(Me)NEt\text{-}\kappa C,N\}(THF)$]$^+$. Also in THF solution, the corresponding THF adduct [$Cp^*_2ZrMe(THF)$]$^+$ reacts with $Et_3N$, resulting in ring-opening of the THF ligand to form [$Cp^*_2ZrMe\{O(CH_2)_4NEt_3\}$]$^+$. These results show that amine coproducts, generated upon activation of transition-metal alkyl complexes with ammonium borate reagents, can have a significant impact on the stability of the corresponding cationic complexes.

## Experimental Section

**General Considerations.** All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk and vacuum line techniques or in an MBraun glovebox. Reagents were purchased from commercial providers and used without further purification, unless stated otherwise. THF and pentane were dried by percolation under nitrogen atmosphere over columns of alumina, molecular sieves, and supported copper oxygen scavenger (BASF R3-11); benzene-$d_n$ ($n$ = 0, 6) and THF-$d_8$ were dried over Na/K alloy; bromobenzene-$d_n$ ($n$ = 0, 5) were dried over $CaH_2$. All solvents were distilled under reduced pressure. $PhNMe_2$ and $Et_3N$ were dried over molecular sieves. $Cp^*_2ZrMe_2$,[30] $Cp^*\{\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_3(CH_2)_2\}Zr$,[15] [$PhNMe_2H$][$BPh_4$],[31] [$Et_3NH$][$B(C_6F_5)_4$],[32] and $B(C_6F_5)_3$[33] were prepared following literature procedures. NMR spectra were recorded on Varian Inova 500, Varian Gemini VXR 400, Varian VXR 300, and Varian Gemini 200 instruments. $^1$H chemical shifts are referenced to residual protons in deuterated solvents and are reported relative to tetramethylsilane. GC analyses were performed on a HP 5890 instrument with a PORAPAK column (2 m length, 0.25 mm i.d.). GC/MS analyses of the reaction products were performed on a HP 5973 mass-selective detector attached to a HP 6890 gas chromatograph equipped with a flame ionization detector and a HP-5MS capillary column (30 m length, 0.25 mm i.d., 0.25 $\mu$m film thickness).

**[$Cp^*\{\eta^5{:}\eta^1\text{-}C_5Me_4(CH_2)\}Zr(THF)$][$BPh_4$].** THF (1 mL) was added to a mixture of $Cp^*\{\eta^5{:}\eta^1{:}\eta^1\text{-}C_5Me_3(CH_2)_2\}Zr$ (58.8 mg, 0.163 mmol) and [$PhNMe_2H$][$BPh_4$] (72.1 mg, 0.163 mmol). After 5 min cyclohexane (3 mL) was cautiously layered on top of the resulting dark purple solution, which, after overnight diffusion of the cyclohexane solvent into the THF solution, resulted in the formation of purple crystals. Decanting of the supernatant and washing with pentane (3 mL) afforded 98.3 mg (0.131 mmol, 80%) of the title compound after evaporation of the residual pentane. $^1$H NMR (400 MHz, THF-$d_8$): $\delta$ 7.24 (br, 8H, o-Ph), 6.82 (t, 7.3 Hz, 8H, m-Ph), 6.68 (t, 7.3 Hz, 4H, p-Ph), 2.45 (d, 6.9 Hz, 1H, $CH_2$), 2.13 (d, 6.9 Hz, 1H, $CH_2$), 2.00 (s, 3H, Me), 1.96 (s, 15H, Cp*), 1.94 (s, 3H, Me), 1.40 (s, 3H, Me), 1.37 (s, 3H, Me) ppm. $^{13}C\{^1H\}$ NMR (125.5 MHz, THF-$d_8$): $\delta$ 165.4 ($BPh_4$-ipso), 137.3 ($BPh_4$), 131.4 ($C_5Me_4CH_2$), 129.3 ($C_5Me_4CH_2$), 127.4 ($C_5Me_4CH_2$), 126.6 ($C_5Me_4CH_2$), 125.9 ($BPh_4$), 124.6 ($C_5Me_4CH_2$), 124.3 ($BPh_4$), 122.1 (Cp*), 74.4

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($C_5Me_4CH_2$), 12.5 ($C_5Me_4CH_2$), 11.7 (Cp*), 11.4 ($C_5Me_4CH_2$), 11.1 ($C_5Me_4CH_2$), 11.0 ($C_5Me_4CH_2$) ppm. Anal. Calcd for $C_{48}H_{47}BOZr$: C 76.66, H 7.64. Found: C 76.61, H 7.72.

**Generation of [Cp*{$\eta^5$:$\eta^1$-$C_5Me_4(CH_2)$}Zr(THF-$d_8$)][$B(C_6F_5)_4$] Starting from Cp*($\eta^5$:$\eta^1$:$\eta^1$-$C_5Me_3(CH_2)_2$}Zr and [$PhNMe_2H$][$B(C_6F_5)_4$].** In an NMR tube, THF-$d_8$ (0.4 mL) was added to a mixture of Cp*($\eta^5$:$\eta^1$:$\eta^1$-$C_5Me_3(CH_2)_2$}Zr (14 mg, 0.040 mmol) and [$PhNMe_2H$][$B(C_6F_5)_4$] (32 mg, 0.040 mmol). An immediate color change to purple was observed. $^1$H NMR spectroscopy revealed the quantitative formation of the title compound, [Cp*{$\eta^5$:$\eta^1$-$C_5Me_4$-$(CH_2)$}Zr(THF-$d_8$)][$B(C_6F_5)_4$].

**Generation of [Cp*{$\eta^5$:$\eta^1$-$C_5Me_4(CH_2)$}Zr(THF-$d_8$)][$B(C_6F_5)_4$] Starting from $Cp^*_2ZrMe_2$ and [$PhNMe_2H$][$B(C_6F_5)_4$].** An NMR tube was charged with $Cp^*_2ZrMe_2$ (7.9 mg, 0.020 mmol) and [$PhNMe_2H$][$B(C_6F_5)_4$] (16.1 mg, 0.0201 mmol) and connected to a vacuum line. Benzene-$d_6$ (0.5 mL) was condensed into the tube in vacuo at −196 °C. The tube was warmed to RT, resulting in the precipitation of a red oil and gas evolution. After 35 h the gas was collected via a series of freeze−pump−thaw cycles into a calibrated volume using a Toepler pump. A total amount of 0.037 mmol of gas was obtained. The $^1$H NMR spectrum of the residue after addition of THF-$d_8$ revealed the formation of the title compound (87% based on integration). The reaction was followed over time by preparing solutions of $Cp^*_2ZrMe_2$ (7.9 mg, 0.020 mmol) and [$PhNMe_2H$]-[$B(C_6F_5)_4$] (16.1 mg, 0.0201 mmol) in benzene-$d_6$ (0.4 mL). After different time intervals (0.5, 1, 2, 3, 17, 24, and 48 h) THF-$d_8$ (0.1 mL) was added to dissolve the species present. These experiments show that after 3 h no more [$Cp^*_2ZrMe(THF)$][$B(C_6F_5)_4$] is present and that the main species observed is the title compound.

**Generation of [Cp*{$\eta^5$:$\eta^1$-$C_5Me_4(CH_2)$}Zr][$B(C_6F_5)_4$] Starting from $Cp^*_2ZrMe_2$ and [$Ph_3C$][$B(C_6F_5)_4$].** The reaction of $Cp^*_2ZrMe_2$ with [$Ph_3C$][$B(C_6F_5)_4$] was followed over time by preparing solutions of $Cp^*_2ZrMe_2$ (7.9 mg, 0.020 mmol) and [$Ph_3C$][$B(C_6F_5)_4$] (18.5 mg, 0.0201 mmol) in benzene-$d_6$ (0.4 mL). After different time intervals (0.5, 1, 2, 3, 17, 24, and 48 h) THF-$d_8$ (0.1 mL) was added to dissolve the species present. These experiments show that after 3 h no more [$Cp^*_2ZrMe$-(THF)][$B(C_6F_5)_4$] is present and that the main species observed is the tucked-in species.

**[$Cp^*_2Zr${C(Me)NEt-$\kappa^2C,N$}(THF)][$B(C_6F_5)_4$].** Benzene (1 mL) was added to a mixture of $Cp^*_2ZrMe_2$ (40.0 mg, 0.102 mmol) and [$Et_3NH$][$B(C_6F_5)_4$] (73.0 mg, 0.102 mmol). Immediately a red oily precipitate was formed. After 20 h at room temperature, the volatiles were removed at reduced pressure. The resulting yellow solid was recyrstallized by slow diffusion of cyclohexane (3 mL) into a THF solution (1 mL) of the compound. Yellow crystals thus obtained were isolated by decanting the supernatant and drying in vacuo. This afforded 67 mg (0.067 mmol, 67%) of the title compound. $^1$H NMR (500 MHz, THF-$d_8$): $\delta$ 3.79 (q, 7.3 Hz, 2H, $NCH_2CH_3$), 2.63 (s, 3H, Me), 1.83 (s, 30H, Cp*), 1.20 (t, 7.3 Hz, $NCH_2CH_3$) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, THF-$d_8$): $\delta$ 150.2 (d, 240 Hz, o-CF), 138.4 (d, 240 Hz, p-CF), 136.4 (d, 241 Hz, m-CF), 125.5 (br, $C_{ipso}$), 120.5 (Cp*), 44.8 ($NCH_2CH_3$), 19.8 (CMe), 15.4 ($NCH_2CH_3$), 11.8 (Cp*) ppm. $^{19}$F NMR (375 MHz, THF-$d_8$): $\delta$ −131.2 (br, 8F, o-F), −163.8 (t, 20 Hz, 4F, p-F), −166.9 (t, 20 Hz, 8F, m-F) ppm. Anal. Calcd for $C_{52}H_{46}BF_{20}NOZr$: C 52.80, H 3.92, N 1.18. Found: C 52.94, H 3.42, N 1.12.

**Generation of [$Cp^*_2Zr${C(Me)NEt-$\kappa^2C,N$}(THF-$d_8$)][$B(C_6F_5)_4$] Starting from $Cp^*_2ZrMe_2$ and [$Et_3NH$][$B(C_6F_5)_4$].** An NMR tube was charged with $Cp^*_2ZrMe_2$ (11.8 mg, 0.030 mmol) and [$Et_3NH$]-[$B(C_6F_5)_4$] (23.5 mg, 0.030 mmol) and connected to a vacuum line. Benzene (0.5 mL) was condensed into the tube in vacuo at −196 °C. The tube was warmed to RT, resulting in the precipitation of a red oil and gas evolution. After 24 h the gas was collected into a calibrated volume using a Toepler pump via a series of freeze−pump−thaw cycles using liquid nitrogen to freeze the sample. A total amount of 0.051 mmol of gas was obtained. The gas was identified by GC analysis as methane. The reaction mixture was subjected to another series of freeze−pump−thaw cycles, using an EtOH/$N_2$ bath at −85 °C to freeze the sample, which resulted in a second batch of gas (0.021 mmol), which was identified by GC analysis as ethane. $^1$H NMR spectroscopy revealed the formation of the title compound (76% based on integration).

**Generation of [$Cp^*_2Zr${C(Me)NEt-$\kappa^2C,N$}(THF-$d_8$)][$B(C_6F_5)_4$] Starting from $Cp^*_2ZrMe_2$, [$Ph_3C$][$B(C_6F_5)_4$], and $Et_3N$.** A Toepler pump experiment analogous to the one described above for the generation of [$Cp^*_2Zr${C(Me)NEt-$\kappa^2C,N$}(THF-$d_8$)][$B(C_6F_5)_4$] starting from $Cp^*_2ZrMe_2$ and [$Et_3NH$][$B(C_6F_5)_4$] was performed using $Cp^*_2ZrMe_2$ (11.8 mg, 0.030 mmol), [$Ph_3C$][$B(C_6F_5)_4$] (27.7 mg, 0.030 mmol), and $NEt_3$ (133 mmHg, 0.0042 mL, 0.030 mmol). This resulted in the observation of 0.027 mmol of methane and hydrogen and 0.026 mmol of ethane and propane. $^1$H NMR spectroscopy revealed the formation of the title compound (81% based on integration).

**Generation of [$Cp^*_2Zr${C(Me)NEt-$\kappa^2C,N$}(THF-$d_8$)][$XB(C_6F_5)_3$] (X = H, Me) Starting from $Cp^*_2ZrMe_2$, $B(C_6F_5)_3$, and $Et_3N$.** A Toepler pump experiment analogous to the one described above for the generation of [$Cp^*_2Zr${C(Me)NEt-$\kappa^2C,N$}(THF-$d_8$)][$B(C_6F_5)_4$] starting from $Cp^*_2ZrMe_2$ and [$Et_3NH$][$B(C_6F_5)_4$] was performed using $Cp^*_2ZrMe_2$ (11.8 mg, 0.030 mmol), $B(C_6F_5)_3$ (0.0153 mg, 0.0299 mmol), and $NEt_3$ (133 mmHg, 0.0042 mL, 0.030 mmol). This resulted in the observation of 0.027 mmol of methane and 0.024 mmol of ethane. $^1$H NMR spectroscopy revealed the formation of the title compound (80% based on integration).

**$Cp^*_2Zr(Me)Cl$.** To a toluene solution (20 mL) of $Cp^*_2ZrMe_2$ (450 mg, 1.14 mmol) was added an equimolar amount of [$PhNMe_2H$]Cl (179.0 mg, 1.14 mmol). The reaction was stirred for 1.5 h at room temperature. Removal of LiCl by filtration followed by evaporation of solvent and volatiles resulted in a white powder. Recrystallization from toluene at −30 °C afforded off-white crystals in 75% yield (472.6 mg, 1.14 mmol). NMR spectroscopy revealed formation of the title compound.[34]

**Synthesis of $Cp^*_2Zr(Me)NEt_2$ from $Cp^*_2Zr(Me)Cl$ and $LiNEt_2$.** To a THF solution (25 mL) of $Cp^*_2ZrMeCl$ (0.2143 g, 0.522 mmol) was added $LiNEt_2$ (83.6 mg, 1.05 mmol). The reaction mixture was stirred overnight at room temperature, resulting in a yellow solution. Solvent and volatiles were removed under reduced pressure. The residue was extracted with 15 mL of toluene. Recrystallization from toluene at −30 °C afforded yellow crystals of the title compound in 25% yield (58.3 mg, 0.137 mmol). $^1$H NMR (200 MHz, $C_6D_6$): $\delta$ 2.98 (q, 6.8 Hz, 4H, $NCH_2CH_3$), 1.86 (s, 30H, Cp*), 0.92 (t, 6.8 Hz, 6H, $NCH_2CH_3$), −0.07 (s, 3H, ZrMe) ppm. $^{13}C\{^1H\}$(125 MHz, $C_6D_6$): $\delta$ 118.06 (Cp*), 44.58 ($NCH_2$), 31.90 (ZrMe), 15.03 ($NCH_2CH_3$), 12.29 (Cp*). Anal. Calcd for $C_{25}H_{43}NZr$: C 66.94, H 9.66, N 3.12. Found: C 67.23, H 9.60, N 2.89. The compound has been further characterized by X-ray analysis (see Supporting Information).

**$Cp^*_2Zr(Me)NEt_2$ from [$Cp^*_2ZrMe(THF)$][$BPh_4$] and $LiNEt_2$.** $Cp^*_2ZrMe_2$ (98.2 mg, 0.25 mmol) and [$PhNMe_2H$][$BPh_4$] (116.2 mg, 0.26 mmol) were dissolved in THF (5 mL). Upon stirring, the mixture immediately turned bright yellow. After 0.5 h $LiNEt_2$ (21.7 mg, 0.275 mmol) was added, and the mixture was stirred overnight, during which the solution turned red. All volatiles were removed in vacuo, after which the tacky yellow solid was suspended in pentane. The product was extracted from the Li[$BPh_4$] residue, and the volatiles were removed. Recrystallization from toluene yielded the title compound (30.5 mg, 0.068 mmol, 27%).

**Generation of [$Cp^*_2Zr${C(Me)NEt-$\kappa^2C,N$}(THF-$d_8$)][$B(C_6F_5)_4$] Starting from $Cp^*_2Zr(Me)NEt_2$ and [$Ph_3C$][$B(C_6F_5)_4$].** In benzene-$d_6$: An NMR tube was loaded with $Cp^*_2Zr(NEt_2)Me$ (9.9 mg, 0.022 mmol), [$Ph_3C$][$B(C_6F_5)_4$] (20.0 mg, 0.0217 mmol), and benzene-$d_6$ (0.4 mL). The yellow solution was stirred overnight, after which a brown oil had precipitated. All volatiles were removed and THF-$d_8$ was added to dissolve all solids. Two major products could be identified by $^1$H NMR spectroscopy: [$Cp^*_2Zr${C(Me)NEt-$\kappa^2$C,N}-(THF-$d_8$)][$B(C_6F_5)_4$] and $Ph_3CH$, 1:2 ratio. In bromobenzene-$d_5$: In an NMR tube $Cp^*_2Zr(NEt_2)Me$ (2.5 mg, 0.0056 mmol) and

(34) Chirik, P. J.; Dalleska, N. F.; Henling, L. M.; Bercaw, J. E. *Organometallics* **2005**, *24*, 2789.

$[Ph_3C][B(C_6F_5)_4]$ (5.0 mg, 0.0054 mmol) were dissolved in bromobenzene-$d_5$ (0.4 mL). After 2.5 h the reaction mixture showed, after addition of THF-$d_8$ to solubilize the reaction mixture, a 1:3 mixture of $[Cp^*_2Zr\{C(Me)NEt\text{-}\kappa^2C,N\}(THF\text{-}d_8)][B(C_6F_5)_4]$ and $Ph_3CH$, as well as a mixture of unidentified species.

**$[Cp^*_2ZrMe\{O(CH_2)_4NEt_3\}][B(C_6F_5)_4]$.** A 10 mL THF solution of $[Cp^*_2ZrMe(THF)][B(C_6F_5)_4]$ (113 mg, 0.100 mmol) was treated with $Et_3N$ (0.014 mL, 0.10 mmol). The reaction mixture was stirred at room temperature for 15 days. Solvent and volatiles were removed under reduced pressure, leaving a pale yellow foam. The solid was washed with pentane and dried under vacuum. The $^1H$ NMR spectrum shows formation of a mixture of the title compound and the starting material. $^1H$ NMR (400 MHz, THF-$d_8$): $\delta$ 4.06 (t, 6.2 Hz, 2H, $OCH_2$), 3.29 (q, 7.2 Hz, 6H, $NCH_2$), 3.13 (m, 2H, $NCH_2$), 1.86 (s, 30H, Cp*), 1.54 (m, 2H, $CH_2$), 1.44 (m, 2H, $CH_2$), 1.29 (t, 6.3 Hz, 9H, $NCH_2CH_3$, 9H), −0.49 (s, 3H, ZrMe) ppm. $^{13}C\{^1H\}$ NMR (75 MHz, THF-$d_8$): $\delta$ 118.1 (Cp*), 71.5 ($OCH_2$), 68.8 ($NCH_2$), 53.6 ($NCH_2$), 31.0 (ZrMe), 26.5 ($CH_2$), 19.6 ($CH_2$), 11.5 (Cp*), 7.6 ($NCH_2CH_3$) ppm.

**Generation of $[Cp^*_2ZrMe\{O(CD_2)_4NEt_3\}][B(C_6F_5)_4]$ from $Cp^*_2ZrMe_2$ and $[Et_3NH][B(C_6F_5)_4]$.** $Cp^*_2ZrMe_2$ (14 mg, 0.040 mmol) was treated with one equivalent of $[Et_3NH][B(C_6F_5)_4]$ (31 mg, 0.040 mmol) in THF-$d_8$ (0.5 mL). Initially formation of $[Cp^*_2ZrMe(THF)][B(C_6F_5)_4]$ was observed. After 14 days at RT, the $^1H$ NMR spectrum of the reaction mixture showed a 1:10 mixture of $[Cp^*_2ZrMe(THF)][B(C_6F_5)_4]$ and $[Cp^*_2ZrMe\{O(CD_2)_4NEt_3\}][B(C_6F_5)_4]$.

**Generation of $[Cp^*_2ZrMe\{O(CD_2)_4NEt_3\}][B(C_6F_5)_4]$ from $[Cp^*_2ZrMe(THF)][B(C_6F_5)_4]$ and $Et_3N$.** A THF-$d_8$ solution of $[Cp^*_2ZrMe(THF)][B(C_6F_5)_4]$ (generated in situ by reaction of $Cp^*_2ZrMe_2$ with one equivalent of trityl borate) was contacted with one equivalent of $Et_3N$ (40 $\mu$mol, 5.5 $\mu$L). After 14 days at room temperature a 1:10 mixture of $[Cp^*_2ZrMe(THF)][B(C_6F_5)_4]$ and $[Cp^*_2ZrMe\{O(CD_2)_4NEt_3\}][B(C_6F_5)_4]$ was obtained.

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**Supporting Information Available:** Crystallographic information files of compounds [**4**(THF)][$BPh_4$], [**6**(THF)][$B(C_6F_5)_4$], and $Cp^*_2Zr(Me)NEt_2$. This material is available free of charge via the Internet at http://pubs.acs.org.