University of Groningen

Amine Catalyzed Solvent C-H Bond Activation as Deactivation Route for Cationic Decamethylzirconocene Olefin Polymerization Catalysts

Rios, Itzel Guerrero; Novarino, Elena; van der Veer, Siebe; Hessen, Bart; Bouwkamp, Marco W.

Published in:
Journal of the American Chemical Society

DOI:
[10.1021/ja908330v](https://doi.org/10.1021/ja908330v)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2009

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Rios, I. G., Novarino, E., van der Veer, S., Hessen, B., & Bouwkamp, M. W. (2009). Amine Catalyzed Solvent C-H Bond Activation as Deactivation Route for Cationic Decamethylzirconocene Olefin Polymerization Catalysts. *Journal of the American Chemical Society*, 131(46), 16658-+. <https://doi.org/10.1021/ja908330v>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

**Amine Catalyzed Solvent C-H Bond Activation as Deactivation Route for Cationic
Decamethylzirconocene Olefin Polymerization Catalysts**

Itzel Guerrero Rios, Elena Novarino, Siebe van der Veer, Bart Hessen and Marco W. Bouwkamp*

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. C_6H_5Br and C_6D_5Br were dried over CaH_2 and distilled under reduced pressure; $PhNMe_2$ and Et_3N were dried over molecular sieves. $Cp^*_2ZrMe_2$ ¹ and $[Et_3NH][B(C_6F_5)_4]$ ² 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. ¹H chemical shifts are referenced to residual protons in deuterated solvents and are reported relative to tetramethylsilane. GC analysis were performed on a HP 5890 instrument with a PORAPAK column (2m 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 μm film thickness).

Generation of $[Cp^*_2ZrMe(BrC_6D_5-\kappa Br)][B(C_6F_5)_4]$. Method A) In an NMR tube $Cp^*_2ZrMe_2$ (7.8 mg, 0.020 mmol) was treated with one equivalent of $[PhNMe_2H][B(C_6F_5)_4]$ (16 mg, 0.020 mmol) in 0.4 mL of C_6D_5Br . After 10 minutes, ¹H and ¹³C NMR spectroscopy revealed the quantitative formation of ionic species $[Cp^*_2ZrMe(BrC_6D_5-\kappa Br)][B(C_6F_5)_4]$ and free $PhNMe_2$. Method B) In an NMR tube $Cp^*_2ZrMe_2$ (7.8 mg, 0.020 mmol) was treated with one equivalent of $[Ph_3C][B(C_6F_5)_4]$ (18.5 mg, 0.020 mmol) in 0.4 mL of C_6D_5Br . After 10 minutes quantitative formation of ionic species $[Cp^*_2ZrMe(BrC_6D_5-\kappa Br)][B(C_6F_5)_4]$ and free Ph_3CCH_3 was observed by ¹H and ¹³C NMR spectroscopy. ¹H NMR (500 MHz, C_6D_5Br , RT) δ 1.63 (s, 30H, C_5Me_5), 0.25 (s, 3H, ZrMe) ppm. ¹³C{¹H} NMR (75 MHz, C_6D_5Br , RT) δ 150.1 (d, J_{CF} = 241 Hz, *o*-CF), 140.0 (d, J_{CF} = 244 Hz, *p*-CF), 138.0 (d, J_{CF} = 241 Hz, *m*-CF), 125.0 (C_5Me_5), 57.9 (ZrMe), 11.2 (s, C_5Me_5) ppm. ¹⁹F NMR (375 MHz, C_6D_5Br , RT) δ -131.9 (br, 8F, *o*-F), -162.0 (t, J = 21 Hz, 4F, *p*-F), -165.9 (t, J = 17 Hz, 8F, *m*-F) ppm.

Generation of $[Cp^*_2Zr(2-BrC_6H_4-\kappa^2 Br, C)][B(C_6F_5)_4]$. In an NMR tube a C_6H_5Br solution (0.5 mL) of $Cp^*_2ZrMe_2$ (16 mg, 0.040 mmol) was added to one equivalent of $[Et_3NH][B(C_6F_5)_4]$ (31 mg, 0.040 mmol). Immediately the reaction mixture turned orange. The solvent and volatiles were removed under reduced pressure and the orange solid was redissolved in 0.5 mL C_6D_5Br for NMR characterization. The product was identified as $[Cp^*_2Zr(2-BrC_6H_4-\kappa^2 Br, C)][B(C_6F_5)_4]$ by NMR spectroscopy. ¹H NMR (400 MHz, C_6D_5Br , RT) δ 7.15 (t, J_{HH} = 7 Hz, 1H, Ar), 7 (m, overlapping with solvent, 2H, Ar), 6.78 (d, J_{HH} = 7 Hz, 1H, Ar), 1.48 (s, 30H, C_5Me_5) ppm. ¹³C{¹H} NMR (75 MHz, C_6D_5Br , RT) δ 180.0 (s, ZrC), 149.7 (d, J_{CF} = 239 Hz, *o*-CF), 139.6 (d, J_{CF} = 245 Hz, *p*-CF), 136.0 (d, J_{CF} = 245 Hz, *m*-CF), 136.6 (s, BrC), 130.0 (s, Ar), 129.5 (s, Ar), 126 (s, C_5Me_5), 125.1 (s, Ar), 123.7 (s, Ar), 10.7 (s, C_5Me_5) ppm. ¹⁹F NMR (375 MHz, C_6D_5Br , RT) δ -132.1 (br, 8F, *o*-F), -162.6 (t, J = 25 Hz, 4F, *p*-F), -166.4 (t, J = 21 Hz, 8F, *m*-F) ppm. In a separate experiment, the amount of methane was quantified using a Toepler pump. An NMR tube charged with $Cp^*_2ZrMe_2$ (16 mg, 0.040 mmol) and one equivalent of $[Et_3NH][B(C_6F_5)_4]$ (31 mg, 0.040 mmol) was connected to a vacuum line and evacuated. C_6H_5Br (0.5 mL) was condensed onto the mixture at -196 °C and the NMR tube was warmed to room temperature. The solution became orange and gas evolution was observed. The amount of gas was determined using a Toepler pump by transferring the volatiles in a series of freeze-thaw cycles through a cold trap (cooled with a liquid nitrogen/ethanol mixture) into a calibrated volume. A total amount of 0.080 mmol of methane was formed (identified by GC).

Decomposition of $[\text{Cp}^*_2\text{ZrMe}(\text{BrC}_6\text{D}_5-\kappa\text{Br})][\text{B}(\text{C}_6\text{F}_5)_4]$ in the absence of amine. In an NMR tube $\text{Cp}^*_2\text{ZrMe}_2$ (12 mg, 0.030 mmol) was treated with one equivalent of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (28 mg, 0.030 mmol) in 0.5 mL of $\text{C}_6\text{D}_5\text{Br}$. After 10 minutes quantitative formation of ionic species $[\text{Cp}^*_2\text{ZrMe}(\text{BrC}_6\text{D}_5-\kappa\text{Br})][\text{B}(\text{C}_6\text{F}_5)_4]$ and free Ph_3CCH_3 was observed by ^1H NMR spectroscopy. After 7d in the dark all $[\text{Cp}^*_2\text{ZrMe}(\text{BrC}_6\text{D}_5-\kappa\text{Br})][\text{B}(\text{C}_6\text{F}_5)_4]$ had reacted, as determined by integration versus Ph_3CCH_3 . Two major products were observed, identified as $[\text{Cp}^*_2\text{Zr}(2-\text{BrC}_6\text{D}_4-\kappa^2\text{Br}, \text{C})][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[(\eta^4:\eta^1-\text{C}_5\text{Me}_5\text{C}_6\text{D}_4)\text{Cp}^*\text{ZrBr}][\text{B}(\text{C}_6\text{F}_5)_4]$. The two species were observed in a 1:1 ratio. With time $[(\eta^4:\eta^1-\text{C}_5\text{Me}_5\text{C}_6\text{D}_4)\text{Cp}^*\text{ZrBr}][\text{B}(\text{C}_6\text{F}_5)_4]$ grew at expenses of $[\text{Cp}^*_2\text{Zr}(2-\text{BrC}_6\text{D}_4-\kappa^2\text{Br}, \text{C})][\text{B}(\text{C}_6\text{F}_5)_4]$ and after 14 days the two compounds were observed in a 1:3 ratio. GC/MS analysis of the quenched sample showed the presence (pentamethyl-cyclopenta-2,4-dienyl)-tetradeuterobenzene ($m/z = 216.20$).

Generation of $[(\eta^4:\eta^1-\text{C}_5\text{Me}_5\text{C}_6\text{H}_4)\text{Cp}^*\text{ZrBr}][\text{B}(\text{C}_6\text{F}_5)_4]$. In an NMR tube a $\text{C}_6\text{H}_5\text{Br}$ solution (0.5 mL) of $\text{Cp}^*_2\text{ZrMe}_2$ (16 mg, 0.040 mmol) was added to one equivalent of $[\text{Et}_3\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$ (31 mg, 0.040 mmol). Immediately the reaction mixture turned orange. The solvent and volatiles were removed at reduced pressure and the orange solid was redissolved in 0.5 mL $\text{C}_6\text{D}_5\text{Br}$, the product was identified as $[\text{Cp}^*_2\text{Zr}(2-\text{BrC}_6\text{H}_4-\kappa^2\text{Br}, \text{C})][\text{B}(\text{C}_6\text{F}_5)_4]$ by ^1H NMR spectroscopy. The tube was kept at room temperature and monitored by ^1H NMR spectroscopy. After 16 days $[\text{Cp}^*_2\text{Zr}(2-\text{BrC}_6\text{H}_4-\kappa^2\text{Br}, \text{C})][\text{B}(\text{C}_6\text{F}_5)_4]$ was converted quantitatively to $[(\eta^4:\eta^1-\text{C}_5\text{Me}_5\text{C}_6\text{H}_4)\text{Cp}^*\text{ZrBr}][\text{B}(\text{C}_6\text{F}_5)_4]$. GC/MS analysis of the quenched sample showed the presence (pentamethyl-cyclopenta-2,4-dienyl)benzene ($m/z = 212$). ^1H NMR (400 MHz, $\text{C}_6\text{D}_5\text{Br}$, RT) δ 7.32 (m, overlapping with solvent, 1H, Ar), 7.20 (m, 2H, Ar), 7.06 (m, overlapping with solvent, 1H, Ar), 1.92 (s, 3H, $\eta^4-\text{C}_5\text{Me}_5$), 1.82 (s, 15H, $\eta^5-\text{C}_5\text{Me}_5$), 1.74 (s, 3H, $\eta^4-\text{C}_5\text{Me}_5$), 1.57 (s, 3H, $\eta^4-\text{C}_5\text{Me}_5$), 1.53 (s, 3H, $\eta^4-\text{C}_5\text{Me}_5$), 1.30 (s, 3H, $\eta^4-\text{C}_5\text{Me}_5$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, $\text{C}_6\text{D}_5\text{Br}$, RT) δ 190.6 (s, ZrC), 166.78, 158.76, 142.56, 138.2, 132.41, 131.31, 129.76, 127.85, 124.49, 118.85 ($\eta^5-\text{C}_5\text{Me}_5$), 61.19 ($\eta^4-\text{C}_5\text{Me}_5$), 26.34 ($\eta^4-\text{C}_5\text{Me}_5$), 15.28 ($\eta^4-\text{C}_5\text{Me}_5$), 12.63 ($\eta^4-\text{C}_5\text{Me}_5$), 12.57 ($\eta^5-\text{C}_5\text{Me}_5$), 12.47 ($\eta^4-\text{C}_5\text{Me}_5$), 12.45 ($\eta^4-\text{C}_5\text{Me}_5$) ppm. ^{19}F NMR (375 MHz, $\text{C}_6\text{D}_5\text{Br}$, RT) δ -132.17 (br, 8F, *o*-F), -162.41 (t, $J = 25$ Hz, 4F, *p*-F), -166.31 (t, $J = 21$ Hz, 8F, *m*-F) ppm.

Decomposition of $[\text{Cp}^*_2\text{ZrMe}(\text{BrC}_6\text{D}_5-\kappa\text{Br})][\text{B}(\text{C}_6\text{F}_5)_4]$ in the presence of anilines. In an NMR tube $\text{Cp}^*_2\text{ZrMe}_2$ (7.8 mg, 0.020 mmol) was treated with one equivalent of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (18.5 mg, 0.020 mmol) in 0.4 mL of $\text{C}_6\text{D}_5\text{Br}$ and after 10 minutes different quantities of PhNMe_2 were added (1.1, 2.6, 3.6, 5.1, 10.6 and 21.1 equiv.). The reactions were followed by ^1H NMR spectroscopy. The concentration of the starting material and the product were determined by integration versus Ph_3CCH_3 . The data thus obtained was fitted to our kinetic model

$$d[\mathbf{1b}]/dt = -(k_{\text{uncat}} + k_{\text{cat}} [\text{PhNMe}_2])[\mathbf{1b}]$$

using a non-linear regression approach with the program SigmaPlot 11.0. Analysis of the data ($R^2 = 0.9828$) resulted in

$$k_{\text{uncat}} = 2.69(8) \cdot 10^{-6} \text{ s}^{-1} \text{ and} \\ k_{\text{cat}} = 5.52(7) \cdot 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}.$$

During these studies we observed the formation of an unknown species which revealed a resonance at 1.75 ppm (presumably for a Cp^* ligand) in the ^1H NMR spectrum. The maximum amount of this species increases upon amine concentration (15% for the reaction with 21.1 equiv. of PhNMe_2). After reaching a maximum, its concentration starts to decrease.

In a similar experiment the C-D bond activation of bromobenzene- d_5 was followed by ^1H NMR spectroscopy in the presence of 1 (*p*- $\text{t-BuC}_6\text{H}_4\text{NMe}_2$ and 2,6-*i-Pr}_2\text{C}_6\text{H}_3\text{NMe}_2) or 5 (*p*- $\text{BrC}_6\text{H}_4\text{NMe}_2$) equiv. of substituted anilines. The concentration versus time was fitted using our kinetic model, using $k_{\text{uncat}} = 2.69(8) \cdot 10^{-6} \text{ s}^{-1}$. This resulted in a k_{cat} for these three anilines of:*

$$k_{\text{cat}} = 6.0(4) \cdot 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1} \text{ for } \text{p-t-BuC}_6\text{H}_4\text{NMe}_2 \text{ (} R^2 = 0.9807 \text{);} \\ k_{\text{cat}} = 1.35(3) \cdot 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1} \text{ for } 2,6\text{-i-Pr}_2\text{C}_6\text{H}_3\text{NMe}_2 \text{ (} R^2 = 0.9980 \text{);} \\ k_{\text{cat}} = 4.0(7) \cdot 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1} \text{ for } \text{p-BrC}_6\text{H}_4\text{NMe}_2 \text{ (} R^2 = 0.9840 \text{).}$$

Decomposition of $[\text{Cp}^*_2\text{ZrMe}(\text{BrC}_6\text{D}_5\text{-}\kappa\text{Br})][\text{B}(\text{C}_6\text{F}_5)_4]$ in the presence of Et_3N . Method A) A $\text{C}_6\text{D}_5\text{Br}$ solution of $\text{Cp}^*_2\text{ZrMe}_2$ (4 mg, 0.01 mmol) was added to $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ (8 mg, 0.01 mmol). After 10 minutes ^1H NMR spectroscopy revealed the clean formation of $[\text{Cp}^*_2\text{ZrMe}(\text{BrC}_6\text{D}_5\text{-}\kappa\text{Br})][\text{B}(\text{C}_6\text{F}_5)_4]$ and Et_3N (1.38 μL , 0.010 mmol) was added resulting in an instantaneous formation of $[\text{Cp}^*_2\text{Zr}(2\text{-BrC}_6\text{D}_4\text{-}\kappa^2\text{Br,C})][\text{B}(\text{C}_6\text{F}_5)_4]$. Method B) The same results were obtained when using $\text{Cp}^*_2\text{ZrMe}_2$ (5 mg, 0.01 mmol) and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (10 μmol , 9 mg). After the initial activation of $\text{Cp}^*_2\text{ZrMe}_2$ (10 minutes), Et_3N (1.38 μL , 0.010 mmol) was added resulting in immediate formation of $[\text{Cp}^*_2\text{Zr}(2\text{-BrC}_6\text{D}_4\text{-}\kappa^2\text{Br,C})][\text{B}(\text{C}_6\text{F}_5)_4]$.

In a separate series of experiments, $[\text{Cp}^*_2\text{ZrMe}(\text{BrC}_6\text{D}_5\text{-}\kappa\text{Br})][\text{B}(\text{C}_6\text{F}_5)_4]$ was generated in $\text{C}_6\text{D}_5\text{Br}$ solution (0.4 mL) using $\text{Cp}^*_2\text{ZrMe}_2$ (5.8 mg, 0.015 mmol) and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ (14 mg, 0.015 mmol). To these solutions, sub-stoichiometric amounts of Et_3N were added using calibrated gas bulb additions. The C-H bond activation reaction was followed qualitatively by ^1H NMR spectroscopy indicating that even in the presence of sub-stoichiometric amounts of Et_3N , the C-H bond activation reaction is accelerated (See Table S1).

Table S1. The effect of (sub-)stoichiometric amounts of Et_3N on the conversion of $[\text{Cp}^*_2\text{ZrMe}(\text{BrC}_6\text{D}_5\text{-}\kappa\text{Br})][\text{B}(\text{C}_6\text{F}_5)_4]$ to $[\text{Cp}^*_2\text{Zr}(2\text{-BrC}_6\text{D}_4\text{-}\kappa\text{Br,C})][\text{B}(\text{C}_6\text{F}_5)_4]$.

	Equiv Et_3N	Time (h)	Conversion (%) ^a
1	0	24	26
2	1	< 0.1	100
3	0.1	< 0.2	100
4	0.08	0.08	80
5	0.08	0.33	100

a) $[\text{Cp}^*_2\text{ZrMe}(\text{BrC}_6\text{D}_5\text{-}\kappa\text{Br})][\text{B}(\text{C}_6\text{F}_5)_4]$ converted to $[\text{Cp}^*_2\text{Zr}(2\text{-BrC}_6\text{D}_4\text{-}\kappa\text{Br,C})][\text{B}(\text{C}_6\text{F}_5)_4]$.

Computational details. All calculations were performed using the Gaussian03 package.³ Geometries for all stationary points and transition states were optimized using the B3LYP level of theory, with the 6-311G basis set for C, H, and N and LANL2DZ for Zr. Each calculation was followed by a single point calculation using 6-311G** (C, H, and N) and LANL2DZ (Zr) to obtain reliable energies, and a vibrational analysis using 6-311G (C, H, and N) and LANL2DZ (Zr) to obtain thermal corrections (enthalpy and entropy); free energies mentioned in the text are for the gas phase, 298.15 K, 1 bar. No attempts were made to correct for solvent effects or for the presence of a counterion. We do not think, however, that these will have an effect on the relative energies of the transition states, although they may have an effect on the ground state energies.

Table S2. Energies of reaction and activation energies in kcal/mol for the overall C-H bond activation reaction at 298 K.

ΔG^0 for the overall reaction		
$[\text{Cp}_2\text{ZrMe}]^+ + \text{C}_6\text{H}_6 \rightarrow [\text{Cp}_2\text{ZrPh}]^+ + \text{CH}_4$		-6.61
ΔG^0 for individual reaction steps		
$[\text{Cp}_2\text{ZrMe}]^+ + \text{C}_6\text{H}_6 \rightarrow [\text{Cp}_2\text{ZrMe}(\text{C}_6\text{H}_6)]^+$		-4.05
$[\text{Cp}_2\text{ZrMe}(\text{C}_6\text{H}_6)]^+ \rightarrow [\text{Cp}_2\text{ZrPh}(\text{CH}_4)]^+$		5.37
$[\text{Cp}_2\text{ZrPh}(\text{CH}_4)]^+ \rightarrow [\text{Cp}_2\text{ZrPh}]^+ + \text{CH}_4$		-7.93
$[\text{Cp}_2\text{ZrMe}(\text{C}_6\text{H}_6)]^+ + \text{NMe}_3 \rightarrow \text{Cp}_2\text{ZrMePh} + [\text{NMe}_3\text{H}]^+$		18.56
$\text{Cp}_2\text{ZrMePh} + [\text{NMe}_3\text{H}]^+ \rightarrow [\text{Cp}_2\text{ZrPh}(\text{CH}_4)]^+ + \text{NMe}_3$		-13.18
$\Delta G^\ddagger$ for individual reaction steps		
$[\text{Cp}_2\text{ZrMe}(\text{C}_6\text{H}_6)]^+ \rightarrow [\text{Cp}_2\text{ZrPh}(\text{CH}_4)]^+$	(TS1)	28.09
$[\text{Cp}_2\text{ZrMe}(\text{C}_6\text{H}_6)]^+ + \text{NMe}_3 \rightarrow \text{Cp}_2\text{ZrMePh} + [\text{NMe}_3\text{H}]^+$	(TS2)	22.47
	(TS4)	22.69
$\text{Cp}_2\text{ZrMePh} + [\text{NMe}_3\text{H}]^+ \rightarrow [\text{Cp}_2\text{ZrPh}(\text{CH}_4)]^+ + \text{NMe}_3$	(TS5)	11.79
	(TS6)	13.48
	(TS3)	2.03
$[\text{Cp}_2\text{ZrPh}(\text{CH}_4)]^+ + \text{NMe}_3 \rightarrow \text{Cp}_2\text{ZrMePh} + [\text{NMe}_3\text{H}]^+$	(TS5)	24.98
	(TS6)	26.66
	(TS3)	15.21
$\text{Cp}_2\text{ZrMePh} + [\text{NMe}_3\text{H}]^+ \rightarrow [\text{Cp}_2\text{ZrMe}(\text{C}_6\text{H}_6)]^+ + \text{NMe}_3$	(TS2)	3.91
	(TS4)	4.13

The ground state structures for the reactants and intermediates, as well as a number of likely transition states for the different reaction pathways have been considered. Included in the manuscript are the transition state for the C-H bond activation in the absence of trimethylamine (**TS1**) and the lowest lying transition states for the deprotonation reaction (**TS2**) and the protonation reaction (**TS3**) in the presence of trimethylamine. For the deprotonation reaction an alternative transition state was found, in which the amine is approaching from the side of the molecule, rather than from in between the methyl and benzene ligand (**TS4**), which is very similar in energy compared to **TS2**. For the protonation reaction two additional transition states can be found which are higher in energy compared to **TS3**. In one of these transition states (**TS5**) the ammonium reagent is approaching from within the methyl and phenyl ligand, whereas in case of the other (**TS6**) the ammonium reagent is approaching from the side of the metallocene. See Figure S1 for a complete overview of the reaction coordinate and Table S2 for Gibbs free energies of the reaction and of activation.

Figure S1. Schematic representation of the reaction coordinate in the overall σ -bond metathesis reaction of $[\text{Cp}_2\text{ZrMe}]^+$ with benzene in the absence (blue) and presence (green) of NMe_3 . Energies at 298K are listed in kcal/mol; hydrogen atoms on the cyclopentadienyl ring have been omitted for clarity.

- 1 Stehling, U. M.; Stein, K. M.; Kesti, M. R.; Waymouth, R. M. *Macromolecules* **1998**, *31*, 2019
- 2 Wang, Q.; Quym, Q. W. R.; Gillis, D. J.; Tudoret, M.-J.; Hunter, D. J. B. K.; Baird, M. C. *Organometallic* **1996**, *15*, 693.
- 3 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, ReVision B.05*; Gaussian, Inc.: Pittsburgh, PA, **2003**.