

Probing the Validity of the $-\text{CH}_2\text{SiMe}_3$ Group as a Model of the Growing Chain in Mechanistic Studies of Olefin Polymerization with Group 4 Catalysts

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Using a DFT approach we investigated the geometry and the stability of cationic bisindenyl zirconocenes paired up with a counterion and of general formula $[\text{rac-Me}_2\text{Si}(\text{1-Ind})_2\text{ZrR}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ and $[\text{rac-Me}_2\text{Si}(\text{1-Ind})_2\text{ZrR}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $\text{R} = -\text{CH}_2\text{SiMe}_3$ or $-\text{CH}_2\text{CHMe}_2$ groups. The two R groups are differently agostic-bonded to the metal. The calculations evidence rather good similarity when systems bearing the two different R groups are compared in terms of geometry, relative energies, and the ion-pair separation energies. They validate to a large extent the $-\text{CH}_2\text{SiMe}_3$ group as a model of the growing chain in catalytic olefin polymerizations. However, they also underline some geometric differences that should be considered when mechanistic schemes are developed from experiments.

Introduction

Group 4 metallocenium cations paired with a weakly coordinating anion are known to be the active species for metallocene-based olefin polymerization. Several kinetic studies have been carried out on these systems in order to get a deeper insight into mechanistic features.^{1–3} Since direct investigation of these systems is not an easy task, model systems that are as close as possible to the real catalytic systems have been often considered. In the search for reliable models of the growing chain, Erker and co-workers proposed the $[\text{Cp}_2\text{Zr}(\mu\text{-butadiene})\text{B}(\text{C}_6\text{F}_5)_3]$ betaine system as a suitable model to derive mechanistic insights into the monomer insertion step.⁴ Other authors investigated the ion-pair structure and dynamics considering zirconocene methyl complexes and derived important mechanistic information.^{5,6} However, as noticed by Bochmann and co-workers, the methyl group is not the ideal model for the growing chain. In fact, the methyl group has less steric demands relative to a polymeryl chain, can form methyl-bridged binuclear complexes, and lacks the possibility of forming β - and γ -agostic interactions with the metal. For these reasons, Bochmann and co-workers proposed recently the $-\text{CH}_2\text{SiMe}_3$ group as a model for the polymeryl chain, considering it is a better model relative to the methyl group, particularly in terms of steric hindrance.^{7,8}

Using this model, they have investigated the structure, dynamics, and reactivity of the $[(\text{SBI})\text{Zr}(\text{CH}_2\text{SiMe}_3)]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ and of the $[(\text{SBI})\text{Zr}(\text{CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ catalysts (SBI = *rac*-coordinated $\text{Me}_2\text{Si}(\text{1-Ind})_2$) and have deter-

mined that the former system exists as an inner-sphere ion-pair (ISIP) whereas the latter is an outer-sphere ion-pair (OSIP). Additionally, on the basis of the ion-pair interaction they derived some mechanistic information on the monomer insertion step.⁷ Their conclusions can be safely extended to the case of the propene polymerization provided that the $-\text{CH}_2\text{SiMe}_3$ group is a valid model for the polypropylenyl growing chain.

To check the validity of this model, we have performed DFT calculations on the systems $[(\text{SBI})\text{ZrR}]^+/\text{X}^-$, with $\text{R} = \text{CH}_2\text{-SiMe}_3$, CH_2CHMe_2 and $\text{X}^- = \text{MeB}(\text{C}_6\text{F}_5)_3^-$, $\text{B}(\text{C}_6\text{F}_5)_4^-$. The isobutyl group has been used to simulate a polypropylene growing chain. We have focused our study on the competition between the different modes of agostic interactions, α , β (when $\text{R} = \text{CH}_2\text{CHMe}_2$) and γ , and the coordination of the counteranion X^- .

Of course, even the isobutyl group cannot be considered representative of a polypropylene growing chain, since it actually corresponds to the growing chain after the first monomer insertion into a Zr-Me bond. However, since the geometries considered here are stabilized by α -, β -, or γ -agostic interactions, we believe the isobutyl group is able to capture almost completely the effects that would occur with a much longer growing chain.

Computational Details

All calculations have been performed with the ADF2004.01 package.⁹ The gradient-corrected BP86 functional has been used.^{10–12} A triple- ζ quality STO basis set was used for Zr atom, while double- ζ were used for H, B, C, F, and Si atoms (TZP and DZP basis sets in ADF, respectively). These basis sets were augmented with one polarization function on each atom: 5p for Zr, 2p for H, 3d for B, C, F, and Si. As it is well known that core electrons almost do not play any role in the chemical properties, the frozen core approximation, up to 3d for Zr, up to 1s for B, C, and F, and up to 2p for Si, was used in order to save calculation time. Geometry

(9) *ADF 2004.01 Users Manual*; Free University of Amsterdam: Amsterdam, The Netherlands.

(10) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(11) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.

(12) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.

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(1) Liu, Z.; Somsok, E.; White, C. B.; Rosaaen, K. A.; Landis, C. R. *J. Am. Chem. Soc.* **2001**, *123*, 11193.

(2) Bochmann, M. *J. Organomet. Chem.* **2004**, *689*, 3982.

(3) Chen, M.-C.; Roberts, J. A. S.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 4605.

(4) Erker, G. *Acc. Chem. Res.* **2001**, *34*, 309.

(5) Beck, S.; Lieber, S.; Schaper, F.; Geyer, A.; Brintzinger, H.-H. *J. Am. Chem. Soc.* **2001**, *123*, 1483.

(6) Zuccaccia, C.; Stahl, N. G.; Macchioni, A.; Chen, M.-C.; Roberts, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **2004**, *126*, 1448.

(7) Song, F.; Lancaster, S. J.; Cannon, R. D.; Schormann, M.; Humphrey, M. B.; Zuccaccia, C.; Macchioni, A.; Bochmann, M. *Organometallics* **2005**, *24*, 1315.

(8) Song, F.; Cannon, R. D.; Bochmann, M. *Chem. Commun.* **2004**, 542.

Table 1. Energies, in kcal/mol, of the Various Agostic Interactions Formed by the $-\text{CH}_2\text{C}(\text{H})\text{Me}_2$ and the $-\text{CH}_2\text{SiMe}_3$ Models of a Growing Chain (the α -agostic geometries are taken as reference at 0 kcal/mol)

interaction	no counterion		$\text{MeB}(\text{C}_6\text{F}_5)_3^-$		$\text{B}(\text{C}_6\text{F}_5)_4^-$	
	CH_2CHMe_2	CH_2SiMe_3	CH_2CHMe_2	CH_2SiMe_3	CH_2CHMe_2	CH_2SiMe_3
α -IS ^a	0	0	0	0	0	0
β -IS ^a			2.8		-5.1	
β -OS ^b	-9.7		<i>d</i>		-3.3	
γ -IS ^a			<i>c</i>	<i>c</i>	0.1	-4.2
γ -OS ^b	-6.6	-15.0	<i>c</i>	6.4	0.9	-5.9

^a IS: inner-sphere coordination of the anion. ^b OS: outer-sphere coordination of the anion. ^c It was not possible to locate a minimum with the γ -agostic interaction in this case, the alkyl chain being pushed away by the anion. ^d It was not possible to locate a minimum corresponding to an OS anion.

optimizations were performed in the gas phase and followed by single-point calculations using the COSMO model of solvation¹³ implemented in ADF¹⁴ for accounting for solvation in toluene ($\epsilon = 2.379$). All the energies have been corrected for the cation-anion basis set superposition error using the Boys-Bernardi counterpoise method on gas-phase structures.¹⁵

Results and Discussion

1. Gas-Phase Cations. These results are displayed in Table 1. As reported in the literature, the bare cations exhibit a marked preference for the β - and γ -agostic interactions rather than for the α interaction.¹⁶ This is due to the strong electrophilic character of the unsaturated cation.

This effect is even larger for $\text{R} = \text{CH}_2\text{SiMe}_3$, in which case the γ -agostic interaction is as much as 15 kcal/mol lower in energy. In fact, in this case, as previously reported by Klooster et al. for the complexes $[(\text{C}_5\text{Me}_5)\text{Y}(\text{OC}_6\text{H}_3^t\text{Bu}_2)\{\text{CH}(\text{SiMe}_3)_2\}]$ and $[(\text{C}_5\text{Me}_5)\text{La}\{\text{CH}(\text{SiMe}_3)_2\}_2]$, the most stable conformer exhibits mainly a β_{SiC} -agostic rather than a γ_{CH} -agostic interaction, even if this interaction is still present.¹⁷ This is indicated by a significant lengthening of the Si-Me bond close to the metal center, by an amount up to 0.11 Å with respect to the other two Si-Me bonds (see Figure 1c), while the lengthening of the C-H bond is only 0.02 Å. However, for consistency with existing literature, this agostic binding mode will still be referred as γ_{CH} or simply γ in the following. An additional stabilizing factor could be geometric: the Si-C bonds being longer than the C-C, the binding of CH_2SiMe_3 in this agostic fashion allows a more efficient "capping" of the metal center.

2. Comparison of Agostic Binding Modes in Ion-Pairs. In the case of ion-pairs, both models for the growing chain behave in the same way for the same anion (Table 1). With $\text{MeB}(\text{C}_6\text{F}_5)_3^-$, the α -agostic interaction and an ISIP geometry are preferred to the β_{CH} - or the γ_{CH} -agostic interaction, as they allow a better coordination of the anion. Differently, with $\text{B}(\text{C}_6\text{F}_5)_4^-$, both β - and γ -agostic interactions are favored due to the weaker coordinating character of the anion. Moreover, in the case of $\text{R} = \text{CH}_2\text{SiMe}_3$ the γ -agostic interaction corresponds to an OSIP geometry. These results are in agreement with Bochmann et al.'s findings. Indeed, on the basis of X-ray and NMR experiments they determined that in $[(\text{SBI})\text{Hf}(\text{CH}_2\text{SiMe}_3)]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ the silyl group adopts a conformation allowing an α_{CH} -agostic interaction and an ISIP geometry, while there is a γ interaction and an OSIP geometry in $[(\text{SBI})\text{Hf}(\text{CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$.⁷

(13) Klamt, A.; Sch  rmann, G. *J. Chem. Soc., Perkin Trans. 2* **1993**, 799.

(14) Pye, C. C.; Ziegler, T. *Theor. Chem. Acc.* **1999**, *101*, 396.

(15) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(16) Lohrenz, J. C. W.; Woo, T. K.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 12793.

(17) Klooster, W. T.; Brammer, L.; Schaverien, C. J.; Budzelaar, P. H. M. *J. Am. Chem. Soc.* **1999**, *121*, 1381.

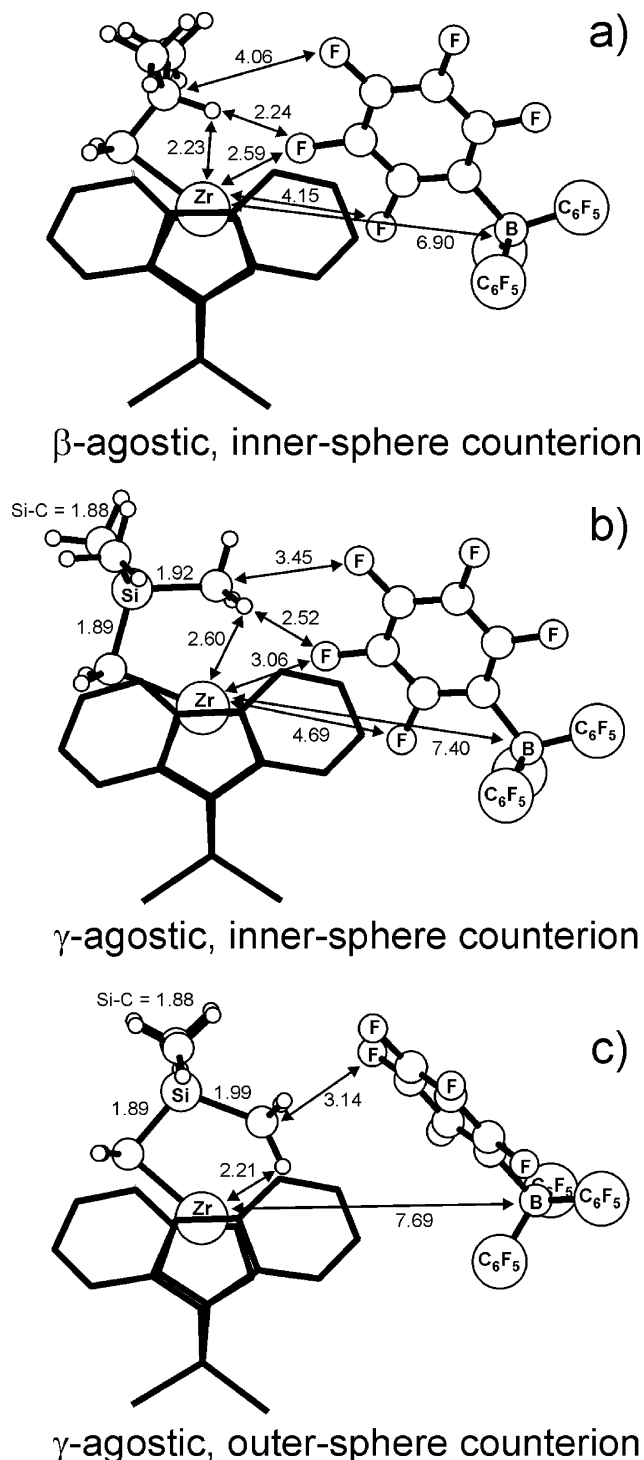


Figure 1. Optimized geometries of some structures discussed in the text. The C_6F_5 groups away from Zr are represented as single spheres.

Table 2. Ion-Pair Binding Energies in kcal/mol^a

interaction	$\text{MeB}(\text{C}_6\text{F}_5)_3^-$		$\text{B}(\text{C}_6\text{F}_5)_4^-$	
	CH_2CHMe_2	CH_2SiMe_3	CH_2CHMe_2	CH_2SiMe_3
α -IS	22.2	18.1	6.1	1.2
β -IS	19.4		11.2	
β -OS			9.4	
γ -IS			6.0	5.4
γ -OS		11.7	5.2	7.1

^a The binding energies are given with respect to separated anion and cation in their most stable conformation (i.e., β_{CH} or γ_{CH}).

Thus, our calculations confirm that CH_2SiMe_3 proves to be a suitable model for the real growing chain if one keeps in mind that this model allows α_{CH} - and γ_{CH} -agostic interactions, while an isobutyl-like growing chain, i.e., with a H atom in β , allows α_{CH} and β_{CH} ones. In fact, for $\text{R} = \text{CH}_2\text{CHMe}_2$ the γ_{CH} interaction seems to play no significant role since it is always significantly higher in energy than either the α or the β . Another dissimilarity is that with $\text{X}^- = \text{MeB}(\text{C}_6\text{F}_5)_3^-$ the energy difference between α and γ geometries with the silyl group is much larger than the difference between the α and β geometries with the isobutyl chain (6.4 vs 2.8 kcal/mol).

Moreover, while $\text{B}(\text{C}_6\text{F}_5)_4^-$ is usually referred to as an outer-sphere anion, we found that it can coordinate to the metal, thus behaving like an inner-sphere anion. In the case of structures bearing an α -agostic interaction this is not very surprising, as the metal has a coordination vacancy. It was less expected to find that the ISIP geometry is the most stable situation for the β -agostic geometry and $\text{R} = \text{CH}_2\text{CHMe}_2$, with the OSIP geometry 1.8 kcal/mol higher in energy. The ISIP geometry is shown in Figure 1a. The relatively compact β -agostic interaction leaves enough space for coordination of one of the meta fluorine atoms. This kind of interaction had already been found by Marks through X-ray diffraction on the $[(\text{Me}_5\text{Cp})_2\text{ThMe}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ complex¹⁸ and by Ziegler's DFT calculations on a zirconocene complex.¹⁹ In both cases, the anion was coordinated by two fluorine atoms. Here, due to the bisindenyl ligand steric hindrance and to a more bulky alkyl group, only one fluorine atom can coordinate to the metal center.

Differently, for the γ -agostic geometry and $\text{R} = \text{CH}_2\text{SiMe}_3$ the ISIP geometry is higher in energy, because anion coordination requires partial displacement of the bulky γ -agostic interaction, whereas in the OSIP geometry an optimal $\text{Zr}-\text{H}$ (agostic) distance occurs (compare Figures 1b and 1c).

3. Ion-Pair Separation Energies. Another point to consider when one wants to study the behavior of an ion-pair is how strongly bound the pair is. The results are shown in Table 2. The binding energies are given with respect to separated anion and cation in their most stable conformation (i.e., β_{CH} or γ_{CH}). When compared to values reported by Ziegler et al., 38 kcal/mol for $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$, our values may appear small, as we obtained 22.2 kcal/mol for $\text{R} = \text{CH}_2\text{CH}$ -

$(\text{CH}_3)_2$ and $\text{X} = \text{MeB}(\text{C}_6\text{F}_5)_3$. However, in this case, the BSSE is as large as 9.9 kcal/mol, leading to an uncorrected value of 32.1 kcal/mol. The remaining difference can be safely attributed to the larger steric demand of the SBI ligand with respect to Cp_2 and to the fact that the isobutyl growing chain is able to form a stabilizing β -agostic interaction with the metal in the naked cation, whereas the methyl group can only form an α -agostic interaction. The rather low binding energy for $\text{X} = \text{B}(\text{C}_6\text{F}_5)_4$ in the presence of α -agostic interactions is a consequence of the fact that binding energies are calculated from a high-energy α -agostic geometry with respect to separated anion and cation in their most stable conformation. Thus, the energy penalty due to separation of the ion-pair is compensated by the energy gain due to formation of the β_{CH} - or γ_{CH} -agostic interaction.

It can be seen that when $\text{R} = \text{CH}_2\text{CH}(\text{CH}_3)_2$, the ion-pair binding energy is significantly larger, by an amount of ca. 4 kcal/mol, than when $\text{R} = \text{CH}_2\text{Si}(\text{CH}_3)_3$. Indeed, the $\text{CH}_2\text{Si}(\text{CH}_3)_3$ group is a stronger coordinating group than $\text{CH}_2\text{CH}(\text{CH}_3)_2$, due to the γ_{CH} - and the β_{SiC} -agostic interactions, which results in a stabilization of the cation and, thus, in a decrease of the ion-pair binding energy. Another factor comes from the larger steric demand of $\text{CH}_2\text{Si}(\text{CH}_3)_3$, which prevents an efficient binding of the cation and also leads to a decrease of the binding energy.

This different behavior could play an important role in any study concerning the displacement of the anion. Indeed the energy difference of ca. 4 kcal/mol is far from being insignificant, as the ion-pair binding energies for the most stable conformers range from 22.2 kcal/mol ($\text{R} = \text{CH}_2\text{CH}(\text{CH}_3)_2$, $\text{X} = \text{MeB}(\text{C}_6\text{F}_5)_3$) to 7.1 kcal/mol ($\text{R} = \text{CH}_2\text{Si}(\text{CH}_3)_3$, $\text{X} = \text{B}(\text{C}_6\text{F}_5)_4$).

Conclusion

Our calculations validate to a large extent the CH_2SiMe_3 group as a model of the growing chain in catalytic olefin polymerizations. This is particularly true when the energetics of the various agostic interactions and of the different counterions are considered. However, they also underline some geometric differences that should be considered when mechanistic schemes are developed from experiments.

About the weaker ion-pair binding energy with $\text{CH}_2\text{Si}(\text{CH}_3)_3$, this could turn to be an advantage rather than a drawback, as a decrease of the binding energy could be expected when the size of the growing chain increases, due to an increased steric hindrance.

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Supporting Information Available: Cartesian coordinates of all the structures reported in the paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(18) Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. *Organometallics* **1997**, *16*, 842.

(19) Vanka, K.; Chan, M. S. W.; Pye, C. C.; Ziegler, T. *Organometallics* **2000**, *19*, 1841.