

Structure–Function–Performance Relationship of Bis(cyclopentadienyl)-Based Group 4 Metallocenes: A DFT Study

Heidrun Gruber-Woelfler

Institute for Process Engineering, Graz University of Technology, 8010 Graz, Austria

Michaela Flock

Institute of Inorganic Chemistry, Graz University of Technology, 8010 Graz, Austria

Jörg Sassmannshausen

Institute of Chemistry and Technology of Organic Materials, Graz University of Technology, 8010 Graz, Austria

Johannes G. Khinast*

Institute for Process Engineering, Graz University of Technology, 8010 Graz, Austria

Received April 29, 2008

In this work a DFT study of the structure–function–performance relationship of bis(cyclopentadienyl)-based (Cp_2 -based) group 4 metallocenes is presented. In particular, the effects of (1) the metal, (2) the *ansa*-bridge, and (3) the π -ligand on steric and electronic parameters, as well as on energetic values, were investigated. In addition, the transition states of the activation reaction of the metallocenes with an alkyllithium compound (i.e., MeLi) were computed. The calculated $\Delta\Delta G$ values confirm that the accessibility of the reaction center and, thus, the reactivity of the metallocenes are generally improved by increasing the $\text{Cp}'\text{--M}$ and M--Cl distances and by decreasing $\text{Cp}'\text{--M--Cp}'$ angles ($\text{M} = \text{Ti, Zr, Hf}$; $\text{Cp}' =$ centroid of the five-membered ring for any Cp-based ligand). Furthermore, the activation process is enhanced when the metallocenes show small gaps between the HOMO of MeLi and the LUMO of the metallocene, as well as high NPA charges on the metal. Additionally, the presented results show that the introduction of an *ansa*-bridge and withdrawing substituents on the Cp ring enhance the activation process of the metallocenes with MeLi. Thus, structural and electronic parameters may serve as guidance for the design of new high-performance metallocenes for hydrogenation and hydrosilylation reactions.

Introduction

Bis(cyclopentadienyl)-based (Cp_2 -based) group 4 metallocenes are an important class of organometallic compounds, the majority being used as catalysts and catalyst precursors, especially for enantioselective reactions, such as hydrogenations,^{1–8} hydrosilylations,^{9–14} and polymerizations.^{15–20} Other catalytic

transformations include the alcoholysis of silanes,²¹ the reaction of silanes with allylic alcohols,²² and other conversions.^{23,24} In all these reactions, the metallocenes need to be activated to yield the active catalytic species. This is usually done by a reaction of the metallocene with organolithium compounds (i.e., MeLi

* Corresponding author. E-mail: khinast@tugraz.at.

(1) Broene, R. D.; Buchwald, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 12569–12570.

(2) Paquette, L. A.; Sivik, M. R.; Bzowej, E. I.; Stanton, K. J. *Organometallics* **1995**, *14*, 4865–4878.

(3) Troutman, M. V.; Appella, D. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 4916–4917.

(4) Vassilyev, O.; Panarello, A.; Khinast, J. G. *Molecules* **2005**, *10*, 587–619.

(5) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 7562–7564.

(6) Willoughby, C. A.; Buchwald, S. L. *J. Org. Chem.* **1993**, *58*, 7627–7629.

(7) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11703–11714.

(8) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8952–8965.

(9) Beagley, P.; Davies, P. J.; Blacker, A. J.; White, C. *Organometallics* **2002**, *21*, 5852–5858.

(10) Carter, M. B.; Schiott, B.; Gutierrez, A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11667–11670.

(11) Halterman, R. L.; Ramsey, T. M.; Chen, Z. *J. Org. Chem.* **1994**, *59*, 2642–2644.

(12) Rahimian, K.; Harrod, J. F. *Inorg. Chim. Acta* **1998**, *270*, 330–336.

(13) Tillack, A.; Lefebvre, C.; Peulecke, N.; Thomas, D.; Rosenthal, U. *Tetrahedron Lett.* **1997**, *38*, 1533–1534.

(14) Yun, J.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 5640–5644.

(15) Togni, A.; Halterman, R. L. *Metallocenes*; Wiley: New York, 1998.

(16) Mohring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1–29.

(17) Kaminsky, W.; Laban, A. *Appl. Catal. A: Gen.* **2001**, *222*, 47–61.

(18) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143–1170.

(19) Kaminsky, W.; Külper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem.* **1985**, *97*, 507.

(20) Kaminsky, W. *Catal. Today* **2000**, *62*, 23–34.

(21) Bedard, T. C.; Corey, J. Y. *J. Organomet. Chem.* **1992**, *428*, 315–333.

(22) Xin, S.; Harrod, J. F. *J. Organomet. Chem.* **1995**, *499*, 181–191.

(23) Corey, J. Y.; Rooney, S. M. *J. Organomet. Chem.* **1996**, *521*, 75–91.

(24) Corey, J. Y.; Zhu, X. H.; Bedard, T. C.; Lange, L. D. *Organometallics* **1991**, *10*, 924–930.

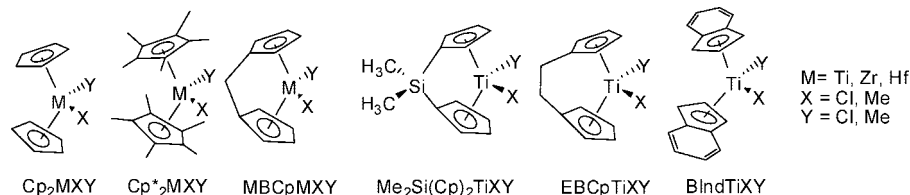


Figure 1. Chemical structures of the bis(cyclopentadienyl)-based metallocenes studied in this work.

and *n*-BuLi) and a silane in case of hydrogenations and hydrosilylations and with MAO (methylalumoxane) and other Lewis acids in the case of polymerization reactions.

In order to optimize existing catalytic systems and to design new catalysts, we aim to understand how certain structural variations influence the reactivity of metallocenes used as precatalysts for hydrogenations and hydrosilylations. For this purpose we conducted extensive simulations of 12 Cp₂-based metallocenes with density functional theory (DFT) methods. The group 4 metallocenes considered in this study are shown in Figure 1:

- L₂TiCl₂, L₂ZrCl₂, and L₂HfCl₂ (L₂ = Cp₂, Cp₂^{*}, and MBCp) were selected to evaluate the influence of the metal;
- Cp₂TiCl₂, Cp₂^{*}TiCl₂, and BlindTiCl₂ were considered to study the influence of the Cp ligand;
- Cp₂TiCl₂, MBCpTiCl₂, EBCpTiCl₂, and Me₂SiCp₂TiCl₂ were chosen to study the impact of the *ansa*-bridge.

Several computational studies of similar compounds have been performed in the past. For example, the dissociation energies of Cp₂MCl₂ and Cp₂^{*}MCl₂ were computed by King et al.²⁵ Recently, simulations of Cp₂MXY (M = Zr, Hf, X = Cl, Me, Y = Cl, Me) were presented by Karttunen et al.²⁶

While these studies focused on the use of metallocenes for polymerization reactions, we concentrate on the application of metallocenes as precatalysts for hydrogenations and hydrosilylations.^{27,28} As described above, for these reactions the metallocenes have to be activated first with an alkyllithium compound and second with a silane to give a catalytically active species. While this catalytically active species was investigated by several research groups^{7,8,12,14,29–31} including our group,²⁸ there is only a limited number of reported experimental studies on the activation kinetics and the determination of the rate-determining step. Since our preliminary results using stopped flow³² experiments indicate that the first step of the activation procedure is kinetically limiting the reaction, this paper concentrates on step 1, i.e., the reaction of the metallocene dichlorides with an alkyllithium compound. (The analysis of the change of UV absorbance at 480 nm shows that the reaction after addition of the silane, i.e., the second activation, is approximately 40 times faster than the first activation step.) As a model case, we analyze the activation of the metallocenes

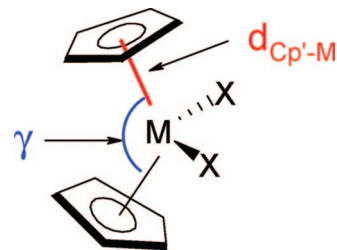


Figure 2. Cp'–M distance $d_{Cp'-M}$ and Cp'–M–Cp' angle γ .

with 2 molar equiv of MeLi. This reaction is also important, e.g., for alcoholysis of silanes,²¹ for the reaction of silanes with allylic alcohols²² and for other conversions,^{23,24} since for these reactions the activation of the metallocenes is carried out only by the addition of an organolithium compound, such as MeLi and *n*-BuLi, to provide the effective catalytic system.

In our study, we first investigated the steric and electronic parameters of the starting materials and the products. The geometrical parameters under consideration include the Cp'–M distances $d_{Cp'-M}$ and the Cp'–M–Cp' angle γ (M = Ti, Zr, Hf; Cp' = centroid of the five-membered ring for any Cp-based ligand; see Figure 2). The accessibility of the reaction center is expected to improve by increasing $d_{Cp'-M}$ and by decreasing γ .^{26,33} Another geometrical parameter we considered is the M–Cl distance d_{M-Cl} , as the elimination of the σ -ligands on the metal plays an important role in the activation of metallocenes. Clearly, the elimination is easier for weaker M–Cl bonds. Shorter bonds are usually stronger; therefore, we expect that a larger d_{M-Cl} leads to a reactivity improvement.

The electronic parameters examined are the energetic level of the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital),³⁴ as well as the NPA³⁵ charges on the metal. We assume that a lower gap between the appropriate molecular orbitals of the metallocene and the reaction partner leads to a higher reactivity. In case of the NPA charges on the metal we expect that a higher (i.e., more positive) charge increases the feasibility of a nucleophilic attack and, thus, the reactivity toward activation. From these results we will draw conclusions regarding the activity of the metallocenes for the reaction with MeLi.

Finally, we will present the calculated Gibbs free energy differences between the reactant and the transition states TS (i.e., the $\Delta\Delta G$ values) to verify our predictions, and we will demonstrate how the *ansa*-bridge, the metal, and the Cp ligand influence the calculated $\Delta\Delta G$ values.

The Reaction Mechanism

It is well known that the reaction of metallocene dichlorides with 2 equiv of MeLi yields dimethyl compounds. (With

(25) King, W. A.; Di Bella, S.; Gulino, A.; Lanza, G.; Fragala, I. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 355–366.

(26) Karttunen, V. A.; Linnolahti, M.; Turunen, A.; Pakkanen, T. A.; Severn, J. R.; Maaranen, J.; Kokko, E.; Pitkanen, P. *J. Organomet. Chem.* **2008**, *693*, 155–163.

(27) Gruber-Woelfler, H. Dissertation, Graz University of Technology, 2007.

(28) Gruber-Woelfler, H.; Flock, M.; Fischer, R. C.; Sassmannshausen, J.; Stanoeva, T.; Gescheidt, G.; Khinast, J. G., submitted to *Organometallics*, 2008.

(29) Woo, H. G.; Tilley, T. D. *J. Am. Chem. Soc.* **1989**, *111*, 8043–8044.

(30) Verdagner, X.; Lange, U. E. W.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **1998**, *37*, 1103–1107.

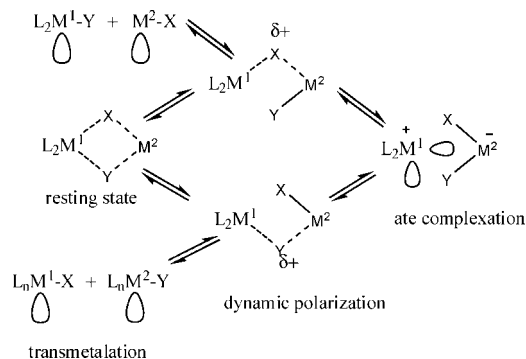
(31) Bareille, L.; Becht, S.; Cui, J. L.; LeGendre, P.; Moise, C. *Organometallics* **2005**, *24*, 5802–5806.

(32) <http://goldbook.iupac.org/S06033.html>, 2008.

(33) Shapiro, P. J. *Coord. Chem. Rev.* **2002**, *231*, 67–81.

(34) DeVasher, R. B.; Spruell, J. M.; Dixon, D. A.; Broker, G. A.; Griffin, S. T.; Rogers, R. D.; Shaughnessy, K. H. *Organometallics* **2005**, *24*, 962–971.

(35) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735–746.

Scheme 1. Mechanism of the Transmetalation Reaction According to Negishi et al.^{39,45,46}


organolithium compounds, the reaction can proceed past dialkylation to produce trialkylated derivatives, which may be accompanied by the replacement of one Cp group.³⁶ However, this reaction will not be considered in this paper.^{22,37,38} This reaction, also called transmetalation, may proceed by a variety of mechanisms. For example, if one metal is significantly more electronegative than the group 4 metallocenes, ate complexation (Scheme 1) may result.³⁹ This complexation represents the extreme form of polarization. More dynamic interactions (dynamic polymerization), in which one or more three-center bonds are formed and cleaved, may also occur. Negishi and Huo³⁹ reported that if M^1L_n corresponds to $ZrCp_2R$, the $^+M^1L_n$ moiety in the ate complex would be a 14-electron d^0+ZrCp_2R species. This has indeed been proposed as active species in alkene polymerization⁴⁰ and in some reactions with carbon electrophiles, such as aldehydes^{41,42} and epoxides.^{43,44}

However, in view of the relatively low electronegativity (= EN) of Ti (EN = 1.5), Zr (EN = 1.4), and Hf (EN = 1.3), Negishi^{39,45} and Takahashi⁴⁶ proposed that with organometallics containing highly electropositive metals, such as Li (EN = 1.0) and Mg (EN = 1.2), transmetalation, including a four-center process requiring the availability of an empty orbital on each metal, is the dominant pathway. This is depicted on the left side of Scheme 1.

In order to support their conjecture, we simulated the reaction of the metallocene dichlorides with MeLi following the four-center mechanism as shown in Scheme 2. The transition states were assumed to follow a σ -metathesis mechanism: the methyl group attacks the metal and at the same time the lithium attacks one of the chlorides (Scheme 2). The effect of the reaction solvent (usually THF) was accounted for by assuming three OMe₂ groups to be coordinated to the lithium atom, i.e., MeLi(OMe₂)₃ instead of MeLi.

Theoretical Methods

All calculations were carried out using Gaussian 03.⁴⁷ The equilibrium geometries were optimized with the hybrid density functional B3LYP^{48,49} in combination with three different basis sets: 3-21G,⁵⁰⁻⁵² LanL2DZ, and a combination of 6-31+G^{53,54} and SDD.^{55,56} The basis set LanL2DZ consists of the Dunning/Huzinaga full double- ζ polarization on first-row elements⁵⁷ and Los Alamos ECP plus double- ζ polarization beyond the first row.⁵⁸⁻⁶⁰ For the combination of 6-31+G and SDD, 6-31+G was used for C, H, Cl, and Si, whereas SDD (D95V up to Ar⁶¹ and Stuttgart/Dresden ECPs on the remainder of the periodic table) was employed for Ti, Zr, and Hf. To confirm that the structures are true minima and for thermochemistry analysis, for all optimized molecules frequency calculations were performed with the same basis sets as for the geometry optimizations. The geometrical parameters were determined using the visualization program ORTEP 3 (Version 1.08).

The results of the computations using the three different basis sets were compared with experimental crystallographic values from the literature,⁶²⁻⁷¹ as presented in the Supporting Information. The results show that the obtained values agree very well with the crystallographic data of the M-Cp' distances and the Cp'-M-Cp' angles (max. deviation 3-21G Cp'-M: -0.09 Å, Cp'-M-Cp' -5.06°; LanL2DZ Cp'-M: 0.066 Å, Cp'-M-Cp' -3.35°; 6-31+G/SDD Cp'-M: -0.089 Å; Cp'-M-Cp' 3.65°). The combination of the B3LYP functional with the LanL2DZ basis set performed best and, thus, was used for further computations.

Results and Discussion

1. Steric and Electronic Parameters of the Starting Materials and Products. In order to understand how certain structural variations influence the reactivity of metallocenes, first

(47) 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.; Bakken, V.; 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. *Gaussian03*; Gaussian Inc., 2004.

(48) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(49) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.

(50) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039-5048.

(51) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797-2803.

(52) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939-947.

(53) Petersson, G. A.; Bennett, A.; Tensfeldt, T. G.; Al Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Phys. Chem.* **1988**, *89*, 2193-2218.

(54) Petersson, G. A.; Al Laham, M. A. *J. Chem. Phys.* **1991**, *94*, 6081-6090.

(55) Cao, X.; Dolg, M. *J. Mol. Struct. (THEOCHEM)* **2002**, *581*, 139-147.

(56) Fuentealba, P.; Preuss, H.; Stoll, H.; Von Szentpaly, L. *Chem. Phys. Lett.* **1982**, *89*, 418-422.

(57) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Plenum: New York, 1976; pp 1-28.

(58) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299-310.

(59) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284-298.

(60) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270-283.

(61) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Plenum: New York, 1976; pp 1-28.

(36) Kondakov, D. Y.; Negishi, E. *Chem. Commun.* **1996**, 963-964.

(37) Smith, J. A.; Brintzinger, H. H. *J. Organomet. Chem.* **1981**, *218*, 159-167.

(38) Grossman, R. B.; Doyle, R. A.; Buchwald, S. L. *Organometallics* **1991**, *10*, 1501-1505.

(39) Negishi, E.; Huo, S. Synthesis and Reactivity of Zirconocene Derivatives. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley VCH, 2002; pp 1-49.

(40) Janiak, C. Metallocene catalysts for Olefin Polymerization. In *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH, 1998; pp 547-623.

(41) Maeta, H.; Hashimoto, T.; Hasegawa, T.; Suzuki, K. *Tetrahedron Lett.* **1992**, *33*, 5965-5968.

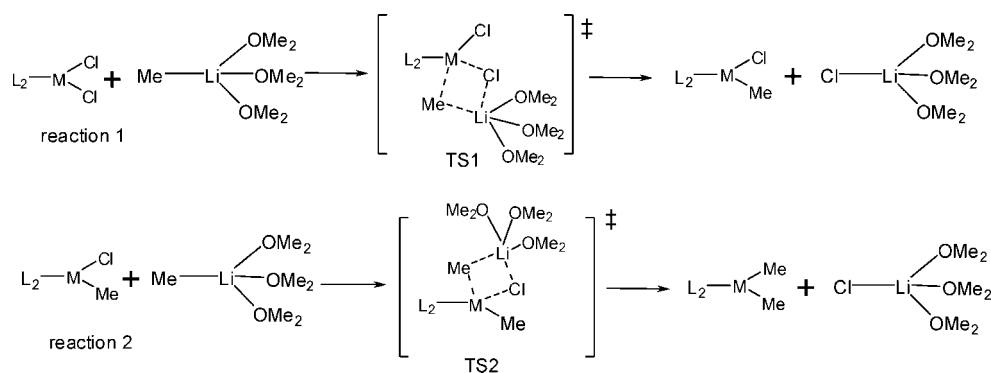
(42) Suzuki, K.; Hasegawa, T.; Imai, T.; Maeta, H.; Ohba, S. *Tetrahedron* **1995**, *51*, 4483-4494.

(43) Wipf, P.; Xu, W. *Tetrahedron* **1995**, *51*, 4551-4562.

(44) Wipf, P.; Xu, W.; Kim, H.; Takahashi, H. *Tetrahedron* **1997**, *53*, 16575-16596.

(45) Negishi, E. *Dalton Trans.* **2005**, 827-848.

(46) Negishi, E.; Takahashi, T. *Aldrichim. Acta* **1985**, *18*, 31-52.

Scheme 2. Reaction of Group 4 Metallocenes (M = Ti, Zr, Hf) with MeLi(OMe)₃Table 1. Steric and Electronic Parameters of L₂MCl₂ (= starting materials for reaction 1 with MeLi)^a

| | Cp'–M [Å] | Cp'–M–Cp' [deg] | Cl–M [Å] | Cl–M–Cl [deg] | gap ^b NPA [eV] | gap ^c [eV] | |
|---|--------------|--------------------|-------------|------------------|------------------------------|--------------------------|-------|
| Cp ₂ TiCl ₂ | 2.073 | 132.57 | 2.362 | 96.06 | 0.309 | 7.047 | 0.163 |
| Cp ₂ ZrCl ₂ | 2.266 | 132.57 | 2.491 | 100.45 | 1.168 | 7.293 | 0.463 |
| Cp ₂ HfCl ₂ | 2.239 | 129.77 | 2.463 | 98.77 | 1.406 | 7.075 | 1.088 |
| Cp* ₂ TiCl ₂ | 2.162 | 138.40 | 2.406 | 92.34 | 0.470 | 6.204 | 0.586 |
| Cp* ₂ ZrCl ₂ | 2.301 | 137.10 | 2.516 | 95.93 | 1.283 | 6.422 | 1.034 |
| Cp* ₂ HfCl ₂ | 2.272 | 137.04 | 2.486 | 94.72 | 1.504 | 6.367 | 1.442 |
| MBCpTiCl ₂ | 2.066 | 121.36 | 2.336 | 97.52 | 0.300 | 6.966 | 0.218 |
| MBCpZrCl ₂ | 2.227 | 115.58 | 2.467 | 104.80 | 1.185 | 7.129 | 0.381 |
| MBCpHfCl ₂ | 2.232 | 115.82 | 2.446 | 101.36 | 1.407 | 7.102 | 0.707 |
| EBCpTiCl ₂ | 2.111 | 128.39 | 2.368 | 96.06 | 0.332 | 6.912 | 0.082 |
| Me ₂ SiCp ₂ TiCl ₂ | 2.087 | 129.03 | 2.351 | 97.37 | 0.314 | 6.884 | 0.109 |
| BIndTiCl ₂ | 2.186 | 130.37 | 2.341 | 98.43 | 0.421 | 6.449 | 0.190 |

^a All calculations were carried out using Gaussian 03 B3LYP/LanL2DZ. All compounds were assumed to be C₂-symmetric. ^b HOMO metallocene–LUMO MeLi(OMe)₃. ^c HOMO MeLi(OMe)₃–LUMO metallocene.

steric and electronic effects of the metallocene dichlorides, the intermediates, and the final products were studied.

Tables 1–3 show the calculated steric and electronic values of L₂MCl₂ (L₂ = Cp₂, Cp₂*, MBCp, EBCp, Me₂SiCp₂, BInd; see Figure 1 and Table 1), L₂MMeCl (Table 2), and L₂MMe₂ (Table 3). L₂MCl₂ and L₂MMe₂ were assumed to be C₂-symmetric. Since the substitution of one chloride through a methyl leads to a loss of the C₂-symmetry, two d_{Cp'–M} distances are presented for L₂MMeCl in Table 2.

For all considered molecules d_{Cp'–M} increases from the dichloride compounds to the L₂MMeCl molecules and to the products L₂MMe₂, reflecting the higher steric demand of the methyl groups in comparison to the chlorides. The same trend was found for the d_{Cl–M} distances and for the Cp'–M–Cp'

Table 2. Steric and Electronic Parameters of L₂MMeCl (= starting materials for reaction 2 and products of reaction 1)^a

| | Cp'–M [Å]* | Cp'–M–Cp' [deg] | Cl–M [Å] | NPA | gap ^b [eV] | gap ^c [eV] |
|--|---------------|--------------------|-------------|-------|--------------------------|--------------------------|
| Cp ₂ TiMeCl | 2.124 (2.124) | 133.54 | 2.371 | 0.461 | 6.803 | 0.571 |
| Cp ₂ ZrMeCl | 2.281 (2.283) | 131.23 | 2.494 | 1.359 | 7.075 | 1.088 |
| Cp ₂ HfMeCl | 2.256 (2.257) | 131.00 | 2.466 | 1.620 | 7.048 | 1.469 |
| Cp* ₂ TiMeCl | 2.180 (2.183) | 138.83 | 2.138 | 0.628 | 5.987 | 1.197 |
| Cp* ₂ ZrMeCl | 2.317 (2.320) | 138.28 | 2.526 | 1.468 | 6.204 | 1.551 |
| Cp* ₂ HfMeCl | 2.292 (2.290) | 137.70 | 2.493 | 1.719 | 6.177 | 1.932 |
| MBCpTiMeCl | 2.106 (2.105) | 121.20 | 2.342 | 0.468 | 6.667 | 0.544 |
| MBCpZrMeCl | 2.276 (2.276) | 114.94 | 2.479 | 1.382 | 6.830 | 1.061 |
| MBCpHfMeCl | 2.248 (2.248) | 115.50 | 2.450 | 1.639 | 6.830 | 1.306 |
| EBCpTiMeCl | 2.128 (2.117) | 127.72 | 2.365 | 0.489 | 6.667 | 0.626 |
| Me ₂ SiCp ₂ TiMeCl | 2.135 (2.135) | 127.98 | 2.359 | 0.474 | 6.640 | 0.544 |
| BIndTiMeCl | 2.206 (2.216) | 131.54 | 2.384 | 0.604 | 6.177 | 0.680 |

^a All calculations were carried out using Gaussian03 B3LYP/LanL2DZ. *Since the L₂MMeCl molecules are not C₂-symmetric two Cp'–M values are listed. ^b HOMO metallocene–LUMO MeLi(OMe)₃. ^c HOMO MeLi(OMe)₃–LUMO metallocene.

Table 3. Steric and Electronic Parameters of L₂MMe₂ (= products of the reaction of L₂MCl₂ with 2 equiv of MeLi)^a

| | Cp'–M [Å] | Cp'–M–Cp' [deg] | Me–M [Å] | Me–M–Me [deg] | HOMO NPA | LUMO [eV] | LUMO [eV] |
|---|--------------|--------------------|-------------|------------------|-------------|--------------|--------------|
| Cp ₂ TiMe ₂ | 2.148 | 134.26 | 2.140 | 92.12 | 0.652 | –6.259 | –1.660 |
| Cp ₂ ZrMe ₂ | 2.301 | 133.36 | 2.273 | 98.70 | 1.585 | –6.504 | –1.279 |
| Cp ₂ HfMe ₂ | 2.280 | 132.58 | 2.343 | 97.02 | 1.869 | –6.504 | –0.898 |
| Cp* ₂ TiMe ₂ | 2.209 | 139.66 | 2.139 | 89.35 | 0.782 | –5.333 | –1.116 |
| Cp* ₂ ZrMe ₂ | 2.342 | 139.55 | 2.280 | 93.53 | 1.677 | –5.497 | –0.871 |
| Cp* ₂ HfMe ₂ | 2.318 | 138.67 | 2.500 | 92.91 | 1.951 | –5.551 | –0.490 |
| MBCpTiMe ₂ | 2.141 | 119.93 | 2.114 | 94.33 | 0.686 | –6.014 | –1.796 |
| MBCpZrMe ₂ | 2.295 | 114.67 | 2.261 | 101.88 | 1.650 | –6.150 | –1.361 |
| MBCpHfMe ₂ | 2.271 | 114.84 | 2.231 | 98.51 | 1.927 | –6.150 | –1.116 |
| EBCpTiMe ₂ | 2.150 | 127.29 | 2.131 | 91.52 | 0.693 | –6.123 | –1.660 |
| Me ₂ SiCp ₂ TiMe ₂ | 2.164 | 127.76 | 2.124 | 91.95 | 0.683 | –6.068 | –1.769 |
| BIndTiMe ₂ | 2.194 | 133.29 | 2.129 | 91.38 | 0.760 | –5.742 | –1.932 |

^a All calculations were carried out using Gaussian 03 B3LYP/LanL2DZ. All compounds were assumed to be C₂-symmetric.

angles γ. Exceptions of this trend are MBCpMX₂, EBCpTiX₂, and Me₂SiCp₂TiX₂, which show a decreasing γ from the dichloride compounds to the products L₂MMe₂. For these molecules our results indicate that due to the tension of the bridging atoms, the bond lengths between the Cp rings and the bridging atoms are increased, while γ is reduced.

Although chloride is more electronegative than the methyl group, the NPA charges on the metal increase from the dichloride compounds to the L₂MMeCl molecules and to the products L₂MMe₂. This lower, i.e., less positive, charge of the L₂MCl₂ and L₂MMeCl compounds can be attributed to a back-donation of the lone pair electrons of the chloride atoms to the metal, as shown by our NBO analysis.

The same as Neghishi and Takahashi,^{45,46} we expect that the methyl group of MeLi(OMe)₃ attacks as Me[–]; that is, the electron-rich HOMO of the methyl group donates into the electron-poor LUMO of the metallocene. Indeed, the gaps between the

(62) Bajgur, C. S.; Tikkanen, W.; Petersen, J. L. *Inorg. Chem.* **1985**, *24*, 2539–2546.

(63) Bryliakov, K. P.; Babushkin, D. E.; Talsi, E. P.; Voskoboynikov, A. Z.; Gritzo, H.; Schroder, L.; Damrau, H. R. H.; Wieser, U.; Schaper, F.; Brintzinger, H. H. *Organometallics* **2005**, *24*, 894–904.

(64) Clearfield, A.; Warner, D.; Saldarriga-Molina, C.; Ropal, R. *Can. J. Chem.* **1975**, *53*, 565.

(65) Collins, S.; Kuntz, B. A.; Taylor, N. J.; Ward, D. G. *J. Organomet. Chem.* **1988**, *342*, 21–29.

(66) Doman, T. N.; Hollis, T. K.; Bosnich, B. *J. Am. Chem. Soc.* **1995**, *117*, 1352–1368.

(67) Linnolahti, M.; Hirva, P.; Pakkanen, T. A. *J. Comput. Chem.* **2001**, *22*, 51.

(68) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr.* **1974**, *B30*, 2290.

(69) Shaltout, R. M.; Corey, J. Y.; Rath, N. P. *J. Organomet. Chem.* **1995**, *503*, 205–212.

(70) Smith, J. A.; von Seyerl, J.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *173*, 175–185.

(71) Zachmanoglou, C. E.; Docrat, A.; Bridgewater, B. M.; Parkin, G.; Brandow, C. G.; Bercau, J. E.; Jardine, C. N.; Lyall, M.; Green, J. C.; Keister, J. B. *J. Am. Chem. Soc.* **2002**, *124*, 9525–9546.

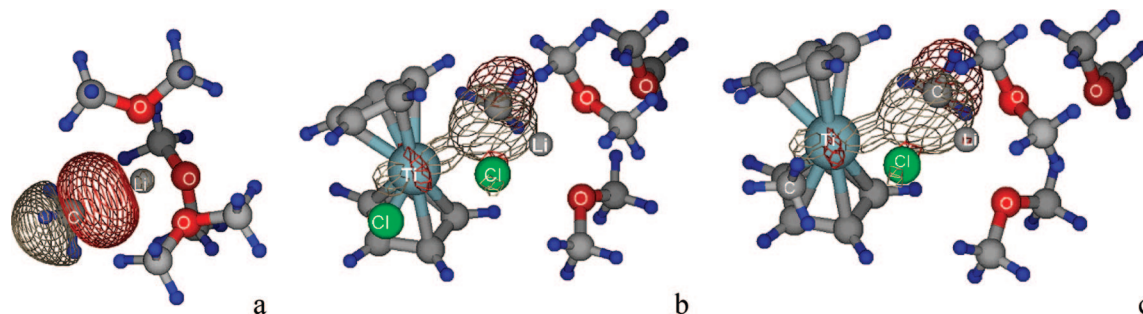


Figure 3. Electron density of the HOMO of (a) MeLi(OMe)₃, (b) the transition state of the reaction of Cp₂TiCl₂ with MeLi(OMe)₃, and (c) the transition state of the reaction of Cp₂TiClMe with MeLi(OMe)₃. Some bonds are omitted for clarity.

HOMO of MeLi(OMe)₃ (−2.912 eV) and the LUMO of the metallocenes, i.e., gap^f in Table 1 and Table 2, are much smaller than the gaps between the LUMO of MeLi(OMe)₃ and the HOMO of the metallocenes (gap^b in Table 1 and Table 2). These findings support the statements by Negishi^{39,45} and Takahashi⁴⁶ that these orbitals (i.e., the HOMO of MeLi(OMe)₃ and the LUMO of the metallocenes) are involved in the reaction. The positions of the HOMOs of MeLi and TS1 and TS2 of the reaction of Cp₂TiCl₂ with MeLi(OMe)₃ confirm this conjecture (Figure 3).

The comparison of the computed geometrical and the electronic parameters shows that MBCpZrXY and MBCpHfXY have large $d_{Cp'-M}$ and d_{M-Cl} and the smallest γ . Thus, these molecules should exhibit the best substrate accessibility. Furthermore, the NPA charges on the metal are high, thus favoring the attack of the nucleophilic methyl group. Although the gaps between the HOMO of MeLi(OMe)₃ and the LUMOs of the metallocenes are large (almost 2 times larger than the gaps of EBCpTiXY and Me₂SiCp₂TiXY), we expect MBCpZrXY and MBCpHfXY to have the smallest $\Delta\Delta G$ values and, thus, the highest reactivity.

2. Correlation between the Geometrical and the Electronic Parameters. For the design of new metallocenes it is important to establish correlations between steric and electronic parameters and to predict their influence on the reactivity of the compound. The steric influence of the ligand framework on the metallocene reactivity was established by three geometrical parameters: $d_{Cp'-M}$, d_{M-Cl} , and γ . Specifically, we expect that (1) the accessibility of the reaction center improves by increasing $d_{Cp'-M}$ and by decreasing γ ³³ and (2) large d_{M-Cl} values lead to a reactivity improvement, since elimination of the σ -ligands is easier for weaker (i.e., longer) M–Cl bonds.

Furthermore, we expect a correlation between the Cp'–M distances and the Cp'–M–Cp' angle; that is, a longer $d_{Cp'-M}$ distance is expected to lead to a smaller γ . In order to verify these trends, we carefully analyzed the correlations of the geometrical parameters. Diagrams of these correlations are presented in the Supporting Information.

Our results indicate that the correlation of the structural parameters is less straightforward than expected: Although we found a linear dependence between d_{M-Cl} and $d_{Cp'-M}$ (see Supporting Information), there is no correlation between $d_{Cp'-M}$ and γ , which might be attributed to simultaneous electronic effects.

Therefore, we studied the correlation between geometrical and electronic parameters. For the considered titanocene dichlorides, the following conclusions can be made: shorter $d_{Cp'-M}$ distances cause more electrons to be donated to the metal by the Cp atoms; that is, the NPA charges decrease with decreasing $d_{Cp'-M}$ distances. In addition, our results show that the NPA

charge on the metal increases (i.e., becomes more positive) with increasing d_{M-Cl} . This can be attributed to the fact that for a longer d_{M-Cl} distance fewer electrons are donated to the metal by the chloride.

In summary, our investigations illustrate that an increase of $d_{Cp'-M}$ and d_{M-Cl} correlates with higher NPA charges. Both effects are expected to lead to an improved reactivity. As shown by the data in Table 1, modifications leading to an increase of $d_{Cp'-M}$ and d_{M-Cl} include the permethylation of the Cp ring or the introduction of an ethylene bridge. The detailed effects of the *ansa*-bridge, the metal, and the π -ligands on the considered parameters and on the reactivity will be discussed in more detail in the following section.

3. Influence of the Structural Variations on the $\Delta\Delta G$ Values. In order to demonstrate how the *ansa*-bridge, the metal, and the Cp ligand influence the reactivity of group 4 metallocenes, we calculated the Gibbs free energy differences between the reactant and the transition states TS (i.e., the $\Delta\Delta G$ values).

Figure 4 summarizes the calculated $\Delta\Delta G$ values for the reactions of L₂MX₂ (X = Y = Cl, reaction 1, and X = Me, Y = Cl, reaction 2) with MeLi(OMe)₃. Typical profiles for the reactions of Cp₂TiCl₂ and Cp₂TiClMe with MeLi(OMe)₃ are presented in Figure 5 and Figure 6, respectively.

To study the influence of the metal, we considered the molecules Cp₂MX₂, Cp₂*MCl₂, and MBCpMCl₂ (M = Ti, Zr, Hf). The steric parameters confirm that the titanocenes have the smallest $d_{Cp'-M}$, which can be attributed to the small dimension of Ti. However, the increasing size of the metal atom is not reflected by an increase in $d_{Cp'-M}$; the hafnocenes have almost the same or sometimes smaller $d_{Cp'-M}$ than the zirconocenes. In the case of EBCpHfCl₂ the distance is even as low as in EBCpTiCl₂. This small Hf ionic radius can be ascribed to the 14f lanthanide contraction, resulting from imperfect shielding of one electron by another in the same 14f subshell.^{72–74}

The γ angles of the various compounds are essentially equal; only the angle of MBCpTiCl₂ is 6° bigger than the angles of MBCpZrCl₂ and MBCpHfCl₂. As expected, MBCpZrCl₂ and MBCpHfCl₂ show small $\Delta\Delta G$ values (29.93 and 30.62 kJ/mol); however, the $\Delta\Delta G$ value of MBCpTiCl₂ is even smaller. This is rather surprising, since this titanocene shows the shortest M–Cl distances and lowest NPA charges on the metal, indicating a low reactivity. However, the MBCpTiCl₂ shows the lowest gap between HOMO MeLi(OMe)₃ and LUMO

(72) Perrin, L.; Maron, L.; Eisenstein, O. *Faraday Discuss.* **2003**, *124*, 25–39.

(73) Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organozirconium and -Hafnium Compounds*; John Wiley and Sons: New York, 1986.

(74) Ewen, J. A.; Haspelsch, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544–6545.

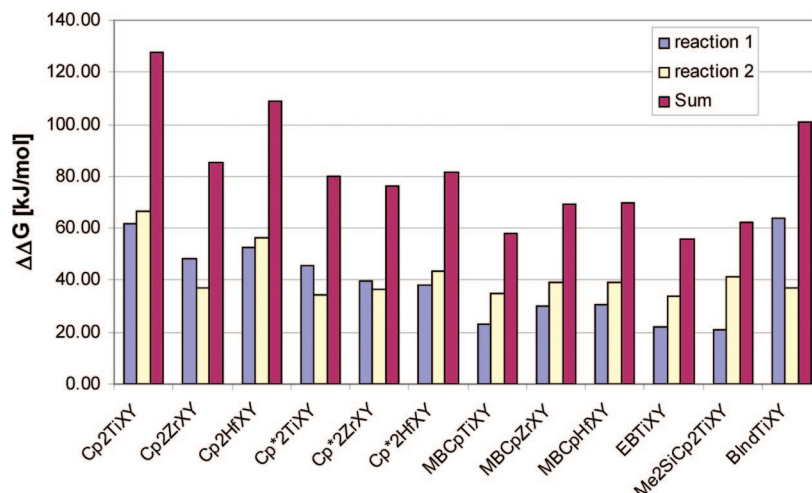


Figure 4. Summary of the calculated $\Delta\Delta G$ values.

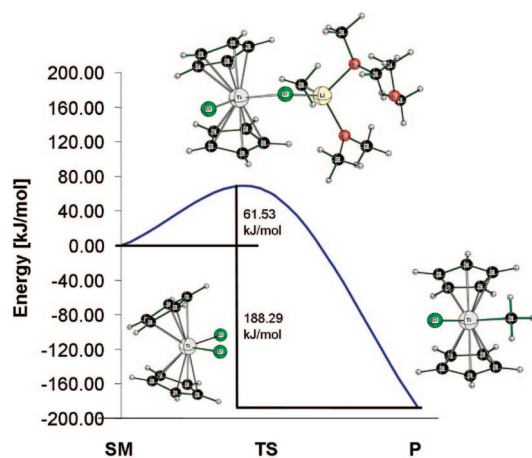


Figure 5. Profile of the reaction of Cp_2TiCl_2 with $\text{MeLi}(\text{OMe})_3$ to Cp_2TiClMe (SM = starting material, TS = transition state, P = product). The molecular structures of the lithium compounds (i.e., $\text{MeLi}(\text{OMe})_3$ and $\text{ClLi}(\text{OMe})_3$) are omitted for clarity.

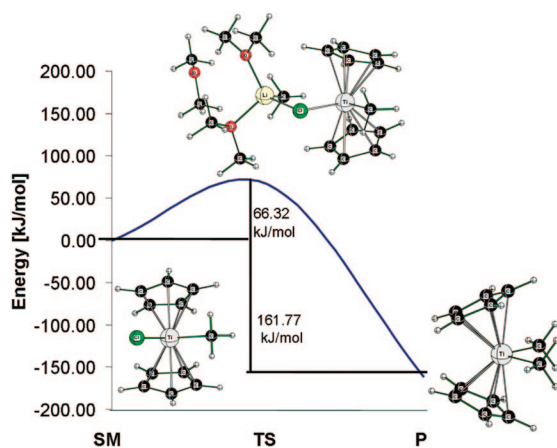


Figure 6. Profile of the reaction of Cp_2TiClMe with $\text{MeLi}(\text{OMe})_3$ to Cp_2TiMe_2 (SM = starting materials, TS = transition state, P = products). The molecular structures of the lithium compounds (i.e., $\text{MeLi}(\text{OMe})_3$ and $\text{ClLi}(\text{OMe})_3$) are omitted for clarity.

metallocene, which may be the reason for the low $\Delta\Delta G$. The largest gaps were found for the hafnocenes. In summary, the combination of all steric and electronic parameters indicates that zirconocenes should exhibit the optimal reactivity.

The calculated $\Delta\Delta G$ values confirm this trend. Among Cp_2MX_2 , $\text{Cp}_2^*\text{MCl}_2$, and MBCpMCl_2 , the titanocenes (except for MBCpTiCl_2 , see above) show the largest $\Delta\Delta G$, followed by the hafnocenes. Thus, our results show that zirconocenes are the most active compounds among the considered molecules. This fact is well known for polymerization experiments and was reported in many publications.^{25,26,75}

In addition, our results show that the *ansa*-metallocenes MBCpMCl_2 , EBCpTiCl_2 , and $\text{Me}_2\text{SiCp}_2\text{TiCl}_2$ have lower $\Delta\Delta G$ values than the nonbridged metallocenes (Cp_2MCl_2 , $\text{Cp}^*_2\text{MCl}_2$, and BindTiCl_2). The calculated geometrical parameters of these compounds indicate that $d_{\text{Cp}'\text{-M}}$ increases for the bridged titanocenes in the following order: $\text{MBCpTiCl}_2 < \text{Me}_2\text{SiCp}_2\text{TiCl}_2 < \text{EBCpTiCl}_2$. As shown before, with increasing $d_{\text{Cp}'\text{-M}}$ the NPA charge on the titanium and $d_{\text{M-C}}$ increase linearly. The increasing $d_{\text{Cp}'\text{-M}}$ distances cause lower electron density to be donated by the Cp atoms to the metal, leading to higher electrophilicity of the metal³³ and, thus, increased reactivity. Furthermore, the introduction of an *ansa*-bridge influences most notably γ , which enforces a bent-sandwich geometry between the rings and leads to an increased access of substrates to the equatorial wedge of the complex.³³ Thus, the high $\Delta\Delta G$ value of Cp_2TiCl_2 to achieve TS1 and TS2 can be attributed to a reduced substrate accessibility due to the small $d_{\text{Cp}'\text{-M}}$ and the large γ . The low activity of Cp_2TiCl_2 was also proven experimentally: Smith and Brintzinger³⁷ investigated the catalytic hydrogenation of cyclohexene after activation of Cp_2TiCl_2 , MBCpTiCl_2 , and EBCpTiCl_2 with MeLi. The authors showed that the highest activity was obtained with the ethylene-bridged compound, with about 3 times the maximum specific reaction rate and twice the total H_2 uptake compared to the analogous Cp_2TiCl_2 reaction. MBCpTiCl_2 also showed better results than Cp_2TiCl_2 but was found to be less reactive than EBCpTiCl_2 .

The introduction of Si in the bridge has an effect on $d_{\text{Cp}'\text{-Ti}}$ as well as on γ . As silicon is larger than carbon (1.11 vs 0.77 Å covalent radius), $d_{\text{Cp}'\text{-M}}$ and γ increase and are similar to the ethylene-bridged titanocene. The NPA charge on the metal and gap^c of $\text{Me}_2\text{SiCp}_2\text{TiCl}_2$ are between the values of MBCpTiCl_2 and EBCpTiCl_2 . Therefore, we believe that the reactivity of $\text{Me}_2\text{SiCp}_2\text{TiCl}_2$ is similar to the reactivity of the carbon-bridged titanocenes. The computed $\Delta\Delta G$ values confirm the computed structural and electronic parameters: The $\Delta\Delta G_1$ values of MBCpTiCl_2 , $\text{Me}_2\text{SiCp}_2\text{TiCl}_2$, and EBCpTiCl_2 differ only by

~1.8 kJ/mol. This confirms that the Si bridge has no significant impact on the $\Delta\Delta G$ values and, thus, on the reactivity.

The influence of the Cp ring was studied considering Cp_2TiCl_2 , $\text{Cp}_2^*\text{TiCl}_2$ (permethylated Cp ring), and BIndTiCl_2 (indenyl ligand). The results of the geometrical and electronic parameters indicate that the permethylation of the Cp ring has the most significant influence on the properties of the titanocenes; it leads to larger $d_{\text{Cp}'-\text{M}}$, $d_{\text{M}-\text{Cl}}$, and γ . The strongest influence was found for the charges and for the energetic levels of the HOMO and the LUMO (increase of up to 24% for the LUMO of $\text{Cp}_2^*\text{TiCl}_2$). The increase of the NPA charges for $\text{Cp}_2^*\text{TiCl}_2$ in comparison to Cp_2TiCl_2 is unexpected, since methyl groups are electron-donating functionalities, which is also shown by our computations of the partial charges on the methyl groups (NPA charges of the methyl group C atoms: -0.645 to -0.661 ; NPA charges of the Cp-ring C atoms -0.032 to -0.011). However, since the introduction of the methyl groups leads to an increase of $d_{\text{Cp}'-\text{M}}$, fewer electrons can be donated to the metal, thus explaining the increase of the NPA charge on the metal. The large γ , the big HOMO–LUMO gap, and the high steric demand of the permethylated Cp ring indicate that Cp_2^*TiXY should have the largest $\Delta\Delta G$ values. However, our results show that $\text{Cp}_2^*\text{TiCl}_2$ has the smallest $\Delta\Delta G$ value of the three considered molecules. Apparently, the increased $d_{\text{Cp}'-\text{M}}$ and the increased NPA charge on the titanium facilitate the reaction with $\text{MeLi}(\text{OMe})_3$, and these factors dominate the effects of the other parameters, illustrating the need to verify predictions based on structural and electronic arguments. The limited number of reported experimental studies involving titanocenes at identical conditions complicates the comparison between the experiment and the theoretical work. However, several research groups^{16,26,75,76} working on experimental polymerization using zirconocenes reported that electron-donating groups generally lead to an increase in catalytic activity. Thus, addition of methyl substituents on the Cp ring should result in enhanced activity,²⁶ which is also indicated by our TS computations.

Summary and Conclusions

In this work a set of 12 different bis(cyclopentadienyl) (= Cp_2)-based metallocenes was studied using computational methods with the aim to improve our understanding of structure–function–performance relationships of group 4 metallocenes for hydrogenations and hydrosilylations.

As a model reaction we chose the activation of 12 Cp_2 -based metallocenes with an alkyllithium compound (MeLi) and computed the structures and energies of the reactants, products, and transition states. Based on the B3LYP/LanL2DZ level of theory, the effects of (1) the *ansa*-bridge, (2) the metal, and (3) the π -ligand on steric and electronic parameters, as well as on the $\Delta\Delta G$ of the transition states, were investigated.

Our work yielded the following results:

- Among the compounds considered, the titanocenes had the highest $\Delta\Delta G$ values, followed by the hafnocenes. These results

are in agreement with multiple experimental studies showing that zirconocenes are the most active compounds.

- The introduction of an *ansa*-bridge leads to a significant reduction of the $\Delta\Delta G$ values. This can be attributed to steric modifications, which are favorable for the reaction with $\text{MeLi}(\text{OMe})_3$: bridged titanocenes show larger $\text{Cp}'-\text{M}$ and $\text{Cl}-\text{M}$ distances as well as smaller $\text{Cp}'-\text{M}-\text{Cp}'$ angles than the Cp_2TiCl_2 compound.

- Comparing Cp_2TiCl_2 , $\text{Cp}_2^*\text{TiCl}_2$, and BIndTiCl_2 , we found that the permethylated metallocenes show the lowest $\Delta\Delta G$ values. Thus, these results confirm experimental findings showing that electron-donating substituents on the Cp ring (e.g., methyl groups) enhance the activation process.

In summary, the calculated $\Delta\Delta G$ values for the first activation step of metallocenes confirm our conjectures based on electronic and steric arguments: the accessibility of the reaction center is generally improved by increasing $\text{Cp}'-\text{M}$ and $\text{M}-\text{Cl}$ distances and by decreasing $\text{Cp}'-\text{M}-\text{Cp}'$ angles. Furthermore, the activation process with $\text{MeLi}(\text{OMe})_3$ is enhanced when the metallocenes show small gaps between the HOMO of MeLi and the LUMO of the metallocene as well as high NPA charges on the metal.

A detailed analysis of the second activation step, as planned for future work,²⁸ will be useful in order to study the influence of the silane and to tailor the structure of the catalytically active species by the choice of the silane. Nevertheless, we expect that for the actual catalytic active species the same trends can be expected as for the metallocene substrate: the accessibility of the reaction center is improved by increasing $\text{Cp}'-\text{M}$ distances and by decreasing $\text{Cp}'-\text{M}-\text{Cp}'$ angles. Additionally, a lower gap between the appropriate molecular orbitals of the catalytically active species and the substrate leads to a higher reactivity.

In summary, structural and electronic parameters may serve as guidance for the design of new high-performance metallocenes for hydrogenation and hydrosilylation reactions. Nevertheless, in some cases detailed computations are required to predict the outcome of the reaction.

Acknowledgment. We kindly acknowledge the financial support by the Austrian Science Fund (Project No. 19410).

Supporting Information Available: Comparison of the calculated $\text{Cp}'-\text{M}$ distances and $\text{Cp}'-\text{M}-\text{Cp}'$ angles with crystallographic data, overview of the sum of electronic and thermal free energies, Cartesian coordinates of the optimized geometries, and diagrams illustrating the correlations of the geometrical parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM800374N

(76) Lee, I. M.; Gauthier, W. J.; Ball, J. M.; Iyengar, B.; Collins, S. *Organometallics* **1992**, *11*, 2115–2122.