

Models for Solvation of Zirconocene Cations: Synthesis, Reactivity, and Computational Studies of Phenylsilyl-Substituted Cationic and Dicationic Zirconocene Compounds

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The reactions of the zirconocene compounds $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_5)\text{ZrMe}_2]$ (**1**) and $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_4\text{Me})_2\text{ZrMe}_2]$ (**2**) with either $\text{B}(\text{C}_6\text{F}_5)_3$ or the trityl salt $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in CD_2Cl_2 were monitored by NMR spectroscopy. In the case of the cationic products $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_5)\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ (**4a**) and $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_4\text{Me})_2\text{ZrMe}]^+ \text{X}^-$ (**5a**, $\text{X} = [\text{MeB}(\text{C}_6\text{F}_5)_3]^-$; **5b**, $\text{X} = [\text{B}(\text{C}_6\text{F}_5)_4]^-$), coordination of the arene, bonded through Si to the cyclopentadienyl ring, to the cationic zirconium was observed. However, this coordination is rather weak, and stronger Lewis donors such as the anion or the starting material replace the coordinated arene moiety. The solid-state structures of **1** and **2** were determined by X-ray crystallography. Density functional computations (B3LYP/ECP1 and B3LYP/II level) have revealed that the phenyl groups in $[(\eta^5\text{-C}_5\text{H}_5)(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_5)\text{ZrMe}]^+$ (**10**), $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_4\text{Me})_2\text{Zr}]^{2+}$ (**11**), and $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_5)_2\text{Zr}]^{2+}$ (**12**) are coordinated via one of the arene carbon atoms. The structural assignments are supported by the good agreement between the experimental NMR shifts and the computed (GIAO-B3LYP/II level) shifts in the case of the cationic compound (**10**). The structure of the dicationic compound **11** differs significantly from that of **12**, indicating a strong influence of the para substituent of the arene ring. Compounds **1** and **2** validate previously suggested models for solvent (arene) adducts in Kaminsky-type polymerization.

Introduction

Group 4 metallocene compounds play an important role as catalyst precursors for the hydrogenation,¹ hydrosilylation, and polymerization of olefins.^{2–11} In particular, for alkene polymerization, these precursors need to be activated by a *cationic generating compound* (CGA) to form what is believed to be the active species $[(\eta^5\text{-Cp})_2\text{MR}]^+$ (Cp = (substituted) cyclopentadienyl, M = Ti, Zr, Hf). Obviously, this rather “naked” ion does not exist by itself in solution; rather, it is paired with the weakly coordinating ligand $[(\eta^5\text{-Cp})_2\text{MR}^+\cdots\text{D}]$ (D = X^- (anion), monomer, solvent). Whereas much effort has gone into elucidating the role of the anion and the coordination of the monomer,^{2,3,5,8,10,12–16} the role of the solvent acting as a ligand

has, to the best of our knowledge, been less actively pursued, probably due to a lack of suitable model systems. In the case of monocyclopentadienyltitanium catalysts, the influence of coordinated arene on ethene trimerization has been studied in detail by Hessen.¹⁷ To this end, we reported some time ago cationic and *dicationic* zirconocene compounds with coordinated phenyl groups.^{18–20} These compounds can be considered as models for the influence of solvent on the cationic zirconocene compound. Earlier studies revealed the dramatic influence of the bridging CR_2 moiety of $[(\eta^5\text{-C}_5\text{H}_4\text{CR}_2\text{Ph})_2\text{ZrMe}]^+$: Whereas in the case $\text{R} = \text{H}$ we observed the formation of the expected zwitterionic compound $[(\eta^5\text{-C}_5\text{H}_4\text{CR}_2\text{Ph})_2\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$ as well as some $[(\eta^5\text{-C}_5\text{H}_4\text{CR}_2\text{Ph})_2\text{ZrMe}]^+$ using low-temperature NMR studies,²¹ in the case of $\text{R} = \text{Me}$ we obtained clear-cut evidence for the formation of $[(\eta^5\text{-C}_5\text{H}_4\text{CR}_2\text{Ph})_2\text{ZrMe}]^+$ under otherwise identical reaction conditions.^{19,20} Furthermore, the formation of the *dicationic* compound of $[(\eta^5\text{-C}_5\text{H}_4\text{CR}_2\text{Ph})_2\text{Zr}]^{2+}$ was only observed in the case $\text{R} = \text{Me}$. This observation led to the conclusion that the coordination of the

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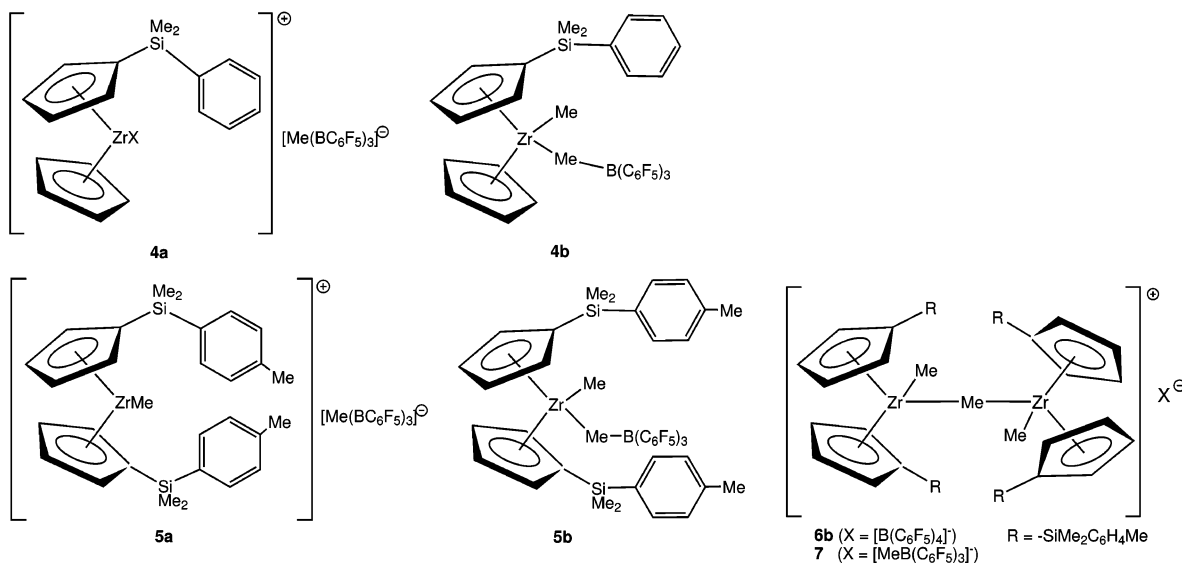
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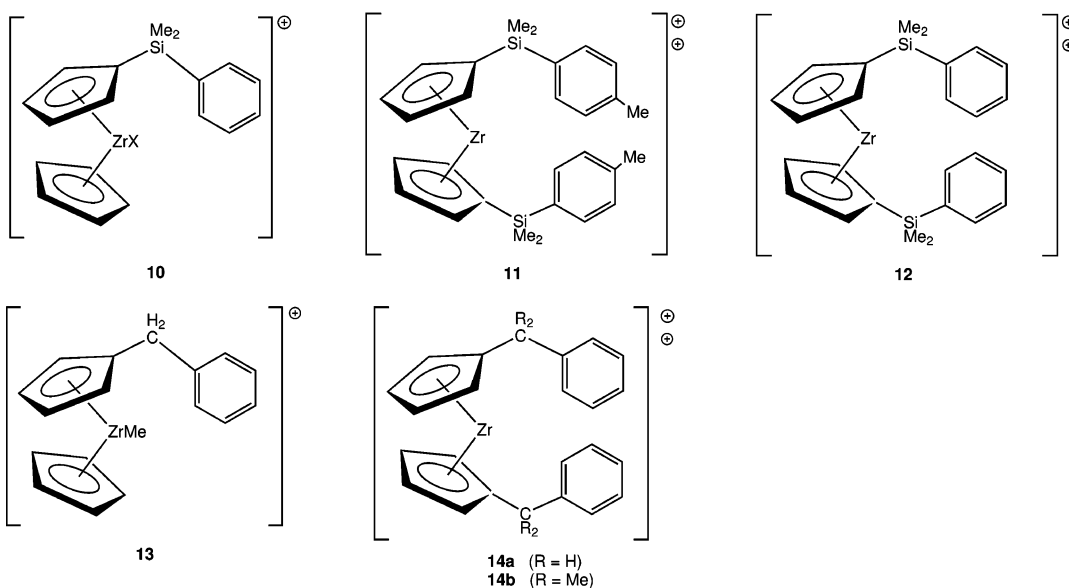
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Chart 1. Diagrams of Compounds Discussed in This Paper

Experimental Compounds



Calculated Compounds



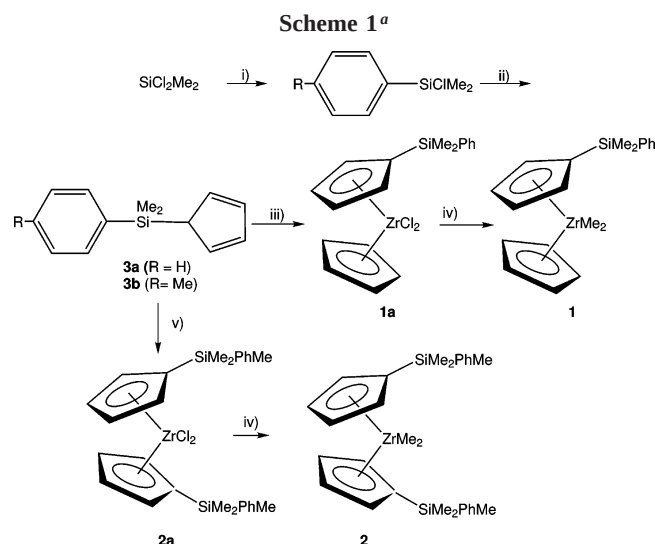
arene moiety is very susceptible to its steric environment: a more crowded environment (R = Me) enhances the coordination, whereas a more open environment (R = H) shows less propensity for arene coordination. Here we extend our studies on these solvent model systems and report the outcome of detailed NMR and DFT investigations of mono- and disubstituted zirconocene compounds of the general type $[(\eta^5\text{-Cp})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Ph})\text{ZrX}]^+$ and $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_4\text{R}')_2\text{Zr}]^{2+}$ (R = H, Me; X = Cl, Me). This combination of NMR and DFT investigations has proven to be very successful in the past¹⁸ and enables investigation of otherwise unobservable reactive intermediates. The paper is organized as following: in part I of the Results and Discussion, the reactions of the compounds $[(\eta^5\text{-Cp})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Ph})\text{ZrMe}_2]$ (**1**) and $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_4\text{Me})_2\text{ZrMe}_2]$ (**2**) with either B(C₆F₅)₃ or the trityl salt $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in CD₂Cl₂, investigated by NMR spectroscopy, are discussed. Part II reports the DFT investigations of $[(\eta^5\text{-Cp})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Ph})\text{ZrX}]^+$, $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_4\text{Me})_2\text{Zr}]^{2+}$, and $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Ph})_2\text{Zr}]^{2+}$ (X =

Cl, Me), respectively. An overview of all discussed cationic and dicationic zirconocenes is given in Chart 1.

Results and Discussion

I. Experimental Investigations. (a) Preparation of the Metallocenes 1 and 2. The compounds **1** and **2** were synthesized according to a modified literature procedure.²² Thus, phenyllithium, freshly prepared from iodobenzene and butyllithium, was reacted with excess dichlorodimethylsilane (cf. Scheme 1). The resulting crude product was further reacted with cyclopentadienyllithium to obtain the ligand **3a** (R = H) in good yields. The ligand **3b** was prepared in a similar manner, phenyllithium being replaced with the Grignard reagent MeC₄H₅MgBr. Both ligands were used as obtained; no attempts of further purification were made, because the NMR spectra

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^a Legend: (i) PhLi or Me₂C₆H₄MgBr; (ii) LiCp; (iii) CpZrCl₃·dme; (iv) LiMe; (v) ZrCl₄(thf)₂.

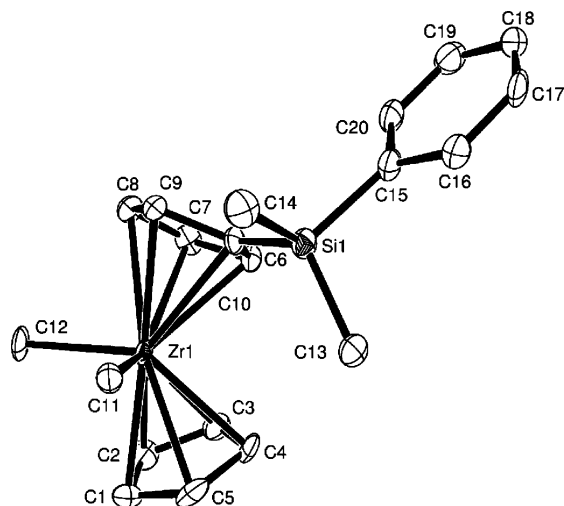


Figure 1. Solid-state structure of **1**.

indicated a pure product. Deprotonation of **3a** and **3b** with butyllithium and quenching with [(η^5 -Cp)ZrCl₃(dme)] and [ZrCl₄(thf)₂], respectively, yielded compounds **1a** and **2a**. Compounds **1a** and **1b** were considered as interim products and used as obtained, the NMR spectra being satisfactory. Methylation with methylolithium furnished the compounds **1** and **2** in good yields.

Crystals suitable for X-ray analysis were obtained by slow cooling of saturated solutions of **1** and **2** in pentane to -30°C , respectively. Compound **1** crystallizes with two independent molecules in the unit cell; only one is shown in Figure 1. The phenyl group is pointing away from the zirconium in an arrangement similar to the previously published solid-state structure of [(η^5 -Cp)(η^5 -C₅H₄CM₂tol)ZrMe₂] (**8**).¹⁹ The Cp_{centr}–Zr–Cp_{centr} angle of 131.93° is close to the reported value of 131.87° for **8**. The C(11)–Zr–C(12) angle of 96.0° is more open, compared to 93.6° for **8**, and the Cp_{centr}–Zr distances of 2.226 and 2.214 Å are comparable to 2.239 and 2.230 Å for **8**, indicating a similar structure. Selected bond distances and angles are given in Table 1; full details are given in the Supporting Information (Table S1). The tolyl groups of **2** (Figure 2) are pointing away from the zirconium, and there is no evidence for intramolecular interactions. The Cp_{centr}–Zr–Cp_{centr} angle (131.49°), Cp_{centr}–Zr distances (2.226, 2.224 Å),

Table 1. Selected Angles (deg) and Distances (Å) of **1** and **2**

	1	2
Cp _{centr} –Zr–Cp _{centr}	131.93	Cp _{centr} –Zr–Cp _{centr} 131.49
C(11)–Zr–C(12)	96.02(14)	C(1)–Zr–C(2) 95.8(2)
Cp _{centr} –C(10)–Si(1)	173.74	Cp _{centr} –C(4)–Si(1) 168.66
Cp _{centr} –Zr	2.226	Cp _{centr} –C(17)–Si(2) 170.34
Cp _{centr} –Zr	2.214	Cp _{centr} –Zr 2.226
C(11)–Zr	2.276(4)	Cp _{centr} –Zr 2.224
C(12)–Zr	2.276(4)	C(1)–Zr 2.296(6)
C(10)–Si(1)	1.862(4)	C(2)–Zr 2.282(5)
		C(17)–Si(2) 1.870(5)
		C(4)–Si(1) 1.854(5)

Table 2. Crystallographic Data for **1**

empirical formula	C ₂₀ H ₂₆ SiZr
formula wt	385.72
temp	100(2) K
wavelength	0.71073 Å
cryst syst, space group	monoclinic, <i>P</i> 2 ₁ / <i>n</i>
unit cell dims	
<i>a</i>	7.6987(15) Å
<i>b</i>	19.594(4) Å
<i>c</i>	12.156(2) Å
α	90
β	92.04(3)
γ	90
<i>V</i>	1832.5(6) Å ³
<i>Z</i> , calcd density	4, 1.398 Mg/m ³
abs coeff	0.661 mm ⁻¹
<i>F</i> (000)	800
crystal size	0.55 × 0.35 × 0.18 mm
θ range for data collection	1.97–26.37°
limiting indices	$-9 \leq h \leq 9$, $-24 \leq k \leq 23$, $-14 \leq l \leq 15$
no. of rflns collected/unique	14 429/3728 (<i>R</i> (int) = 0.0692)
completeness to $\theta = 26.37^\circ$	99.6%
abs cor	SADABS
max and min transmissn	0.8904 and 0.7127
refinement method	full-matrix least squares on <i>F</i> ²
no. of data/restraints/params	3728/0/203
goodness of fit on <i>F</i> ²	1.039
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1 = 0.0467, <i>wR</i> 2 = 0.1118
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0667, <i>wR</i> 2 = 0.1200
largest diff peak and hole	1.280 and -1.360 e Å^{-3}

C(2)–Zr–C(2) angle (95.83°) and C(1)–Zr/C(2)–Zr distances (2.296, 2.282 Å) are in good agreement with those of the reported compound [(η^5 -C₅H₄CM₂Ph)₂ZrMe₂] (**9**).¹⁹ Selected bond distances (Å) and angles (deg) are given in Table 1. Full details are given in the Supporting Information (Table S2).

(b) Low-Temperature NMR Spectroscopy Reaction Studies. All spectroscopic data for these studies are summarized in Table 4, together with detailed assignments. An overview of all discussed cationic and dicationic compounds is given in Chart 1.

The reaction of **1** with B(C₆F₅)₃ in CD₂Cl₂ was monitored by NMR spectroscopy. Unlike the reported compound [(η^5 -Cp)(η^5 -C₅H₄CM₂Ph)ZrMe₂], which reacted cleanly at -60°C to form the ion pair^{14–16} [(η^5 -Cp)(η^5 -C₅H₄CM₂Ph)ZrMe]⁺[MeB(C₆F₅)₃][–] as the sole product,¹⁹ the observed reaction between **1** and B(C₆F₅)₃ yields a mixture of two products: the anticipated ion pair [(η^5 -Cp)(η^5 -C₅H₄SiMe₂Ph)ZrMe]⁺[MeB(C₆F₅)₃][–] (**4a**) as well as the zwitterionic species [(η^5 -Cp)(η^5 -C₅H₄SiMe₂Ph)–Zr(Me)(μ -Me)B(C₆F₅)₃] (**4b**). Evidence for the formation of **4a** could be obtained by the downfield shifts of three protons, a significant high-field shift of the proton in close proximity to the metal, and a marginal high-field shift of the remaining proton of the coordinated²⁸ phenyl group. These results have been

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(24) Selected spectra are available in the Supporting Information.

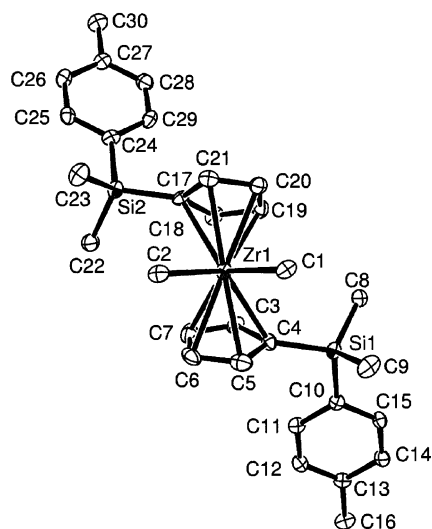


Figure 2. Solid-state structure of 2.

Table 3. Crystallographic Data for 2

empirical formula	C ₃₀ H ₄₀ Si ₂ Zr
formula wt	548.02
temp	100(2) K
wavelength	0.710 73 Å
cryst syst, space group	monoclinic, <i>P</i> ₂ /n
unit cell dims	
<i>a</i>	12.581(3) Å
<i>b</i>	16.726(3) Å
<i>c</i>	13.714(3) Å
α	90
β	99.90(3)
γ	90
<i>V</i>	2842.9(10) Å ³
<i>Z</i> , calcd density	4, 1.280 Mg/m ³
abs coeff	0.487 mm ⁻¹
<i>F</i> (000)	1152
crystal size	0.44 × 0.28 × 0.20 mm
θ range for data collection	1.94–25.00°
limiting indices	–14 ≤ <i>h</i> ≤ 14, –19 ≤ <i>k</i> ≤ 19, –16 ≤ <i>l</i> ≤ 16
no. of rflns collected/unique	20 045/4993 (<i>R</i> (int) = 0.1065)
completeness to θ = 26.37°	99.9%
abs cor	SADABS
max and min transmissn	0.9089 and 0.8143
refinement method	full-matrix least squares on <i>F</i> ²
no. of data/restraints/params	4993/0/306
goodness of fit on <i>F</i> ²	1.258
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0769, <i>wR</i> 2 = 0.1713
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0871, <i>wR</i> 2 = 0.1770
largest diff peak and hole	1.997 and –0.861 e Å ⁻³

observed before and clearly indicate the coordination of one ortho carbon of the phenyl group to the cationic zirconium.¹⁹ The existence of a second, distinguished zirconocene compound is corroborated by the two different anions: the separated anion [MeB(C₆F₅)₃][–] has a chemical shift of δ 0.45 ppm for the CH₃B group and the zwitterionic, bridging μ-CH₃–B group has a chemical shift of δ 0.06 ppm. This finding is further corroborated by ¹⁹F NMR spectroscopy. The chemical shift differences Δδ(m,p) of the aryl fluorines of 4.8 ppm indicates a bridging μ-CH₃–B moiety, whereas the Δδ(m,p) value of 2.7 ppm indicates a separated anion. Similar values have been found before^{19,23} and are in good agreement with the observed ¹H and

¹⁹F NMR data. Both species are interchanging with each other, rendering the NMR spectrum rather complicated. Complete assignment of the spectra was possible due to use of 2D (multinuclear) NMR spectroscopy, in particular NOESY/EXSY spectroscopy.²⁴ Lowering the temperature from –60 to –80 °C sharpens the peaks assigned to **4a**, slowing down the exchange process between **4a** and **4b** and furthermore slowing down site exchange in **4a**. The site exchange of various zirconocene compounds has been studied in detail by Marks.^{25–27} Evidence for the exchange between **4a** and **4b** can be readily obtained by EXSY spectroscopy: exchange peaks are clearly visible between the coordinated and free phenyl moieties (Figure 3), and thus the anion can reversibly replace the coordinated phenyl moiety. Obviously, due to the larger atomic radius of silicon (1.17 Å vs 0.77 Å for carbon), the environment around the metal is less crowded and the phenyl moiety is therefore less prone to bind to the cationic zirconium center, rendering the coordination more labile. Similar observations were made before in the case of the [(η⁵-C₅H₄CR₂Ph)₂ZrMe]⁺ cation (R = H).²¹ In that case the main product was the zwitterionic [(η⁵-C₅H₄CH₂Ph)₂ZrMe(μ-Me)B(C₆F₅)₃], clear-cut evidence for the formation of the ion pair product [(η⁵-C₅H₄CR₂Ph)₂ZrMe]⁺ [MeB(C₆F₅)₃][–] could not be obtained.

The reaction of **2** with 1 equiv of B(C₆F₅)₃ in CD₂Cl₂ was monitored by NMR spectroscopy. At –60 °C, evidence for the formation of the expected ion pair compound [(η⁵-C₅H₄SiMe₂tol)₂ZrMe]⁺ [MeB(C₆F₅)₃][–] (**5a**) was obtained. As in the case of **1**, the zwitterionic compound [(η⁵-C₅H₄SiMe₂tol)₂Zr(Me)-(μ-Me)B(C₆F₅)₃] (**5b**) was observed as a byproduct. Again, this is in contrast with the previously investigated reaction of [(η⁵-C₅H₄CMe₂tol)₂ZrMe₂], which gave the ion pair compound [(η⁵-C₅H₄CMe₂tol)₂ZrMe]⁺ [MeB(C₆F₅)₃][–] as the sole product.¹⁹ Assignment of the NMR spectra was possible due to NOESY/EXSY spectroscopy. Similar to the reaction of **1**, the two products are evidently in equilibrium with each other, as lowering the temperature to –80 °C significantly sharpens the peaks for **5a** and enabled complete assignment.

The reaction of **2** with 1 equiv of the trityl salt [Ph₃C]⁺ [B(C₆F₅)₄][–] in CD₂Cl₂ was monitored by NMR spectroscopy. At –60 °C, evidence for the formation of the expected ion pair [(η⁵-C₅H₄SiMe₂tol)₂ZrMe]⁺ [B(C₆F₅)₄][–] (**6a**) and the homodinuclear compound [(η⁵-C₅H₄SiMe₂tol)₂ZrMe]⁺ [(η⁵-C₅H₄SiMe₂tol)₂ZrMe][–] (**6b**) was obtained. This is in contrast to the previously investigated reaction of [(η⁵-C₅H₄CMe₂tol)₂ZrMe₂] with trityl salt, which exclusively yielded the ion pair product.¹⁹ Again, lowering the temperature to –80 °C sharpened the peaks assigned to **6a** significantly.

The cation [(η⁵-C₅H₄SiMe₂tol)₂ZrMe]⁺ [(η⁵-C₅H₄SiMe₂tol)₂ZrMe][–] has been independently synthesized by reacting 2 equiv of **2** with 1 equiv of B(C₆F₅)₃ in CD₂Cl₂ at –60 °C. The sole product of this reaction was [(η⁵-C₅H₄SiMe₂tol)₂ZrMe]⁺ [(η⁵-C₅H₄SiMe₂tol)₂ZrMe][–] (**7**), as monitored by NMR spectroscopy. Similar observations have been made before by Brintzinger²⁹ using B(C₆F₅)₃ and by Bochmann³⁰ using trityl salt as an activator. Both authors reported the formation of homodinuclear cationic zirconocene compounds in the presence of excess starting material.

We have previously reported the formation of zirconocene dications by reaction of either [(η⁵-C₅H₄CMe₂Ph)₂ZrMe₂] or [(η⁵-C₅H₄CMe₂tol)₂ZrMe₂] with excess B(C₆F₅)₃ in CD₂Cl₂ at –60 °C.²⁰ To ascertain the possibility of a similar reaction, we

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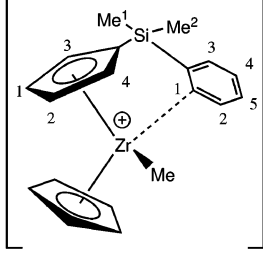
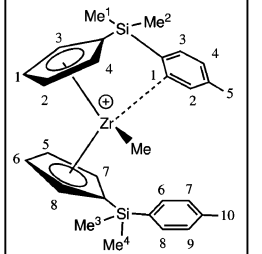
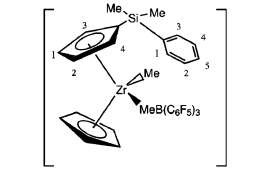
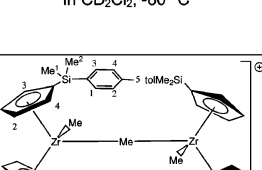
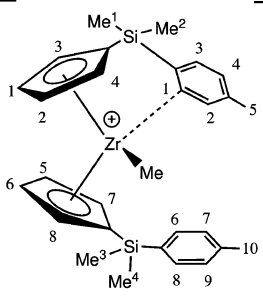
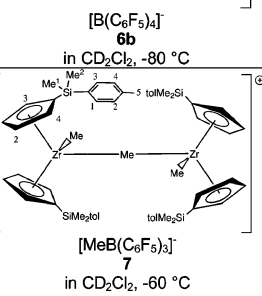
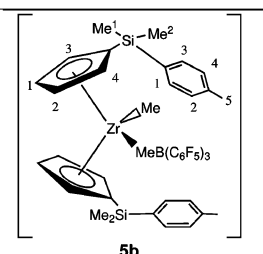
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Table 4. ^1H and ^{13}C NMR Data of the Cationic Complexes 4–7

compound	^1H NMR (ppm) ^a	assgnt	^{13}C NMR (ppm) ^b	assgnt	compound	^1H NMR (ppm) ^a	assgnt	^{13}C NMR (ppm) ^b	assgnt
 4a in CD_2Cl_2 , -60°C	0.76 0.36 0.45 0.48 5.70 6.03 6.20 6.45 6.76 6.85 7.24 7.80 7.95 8.05	ZrMe SiMe ² MeB SiMe ¹ CpH ⁴ CpH CpH ² CpH ¹ CpH ³ PhH ¹ PhH ³ PhH ⁵ PhH ² PhH ⁴	-3.5 -3.4 46.4 113.6 113.8 118.2 120.2 121.2	SiMe ¹ SiMe ² ZrMe CpC ⁴ CpC ² CpC ³ CpC ¹	 6a in CD_2Cl_2 , -80°C	0.37 0.46 0.49 0.74 0.62 2.30 2.54 4.51 5.41 5.62 5.76 6.04 6.70 (d) 7.10 7.12 7.53 (d) 7.58 (d) 7.81 (d)	SiMe ² SiMe ³ SiMe ⁴ ZrMe SiMe ¹ PhMe ¹⁰ PhMe ⁵ CpH ³ CpH ¹ CpH ² CpH ⁴ CpH ⁸ PhH ¹ CpH ⁵ CpH ⁶ PhH ² PhH ³ PhH ⁴	-7.6 -4.0 -2.0 -1.6 21.1 21.1 46.4 109.5 112.8 115.0 118.1 120.9 121.2 123.8 138.6 141.5 142.3	SiMe ¹ SiMe ³ SiMe ⁴ SiMe ² PhMe ⁵ ZrMe CpC ⁸ CpC ² CpC ¹ CpC ⁴ PhC ¹ CpC ⁶ CpC ¹ PhC ⁴ PhC ² PhC ³
 4b in CD_2Cl_2 , -60°C	0.06 0.43 0.56 6.38 6.76 ~7.3 ~7.4 ~7.4	$\mu\text{-Me-B}$ SiMe ² ZrMe CpH ^{3,4} CpH ^{1,2} PhH ^{1,3} PhH ^{2,4} PhH ⁵	21.9 39.8 115.2 122.8 127.6 129.4 132.8	$\mu\text{-Me-B}$ ZrMe CpC ^{3,4} CpC ^{1,2} PhC ^{1,3} PhC ⁵ PhC ^{2,4}	 6b in CD_2Cl_2 , -80°C	-1.17 0.36 0.39 0.49 2.35 5.81 5.85 6.10 6.35	$\mu\text{-Me-Zr}$ SiMe ¹ SiMe ² ZrMe PhMe CpH ³ CpH ⁴ CpH ¹ CpH ²	-3.2 -1.8 21.1 24.5 40.8 116.4 116.6 119.9 124.4	SiMe ² SiMe ¹ PhMe $\mu\text{-Me-Zr}$ CpC ³ CpC ¹ CpC ⁴ CpC ²
 5a in CD_2Cl_2 , -80°C	0.34 0.43 0.45 0.60 0.73 2.30 2.54 4.54 5.41 5.62 5.79 6.06 6.31 6.67 (d) 7.01 7.06 7.10-7.16 7.52 (d) 7.56 (d) 7.83 (d)	SiMe ² SiMe ^{3,4} MeB SiMe ¹ ZrMe PhMe ¹⁰ PhMe ⁵ CpH ³ CpH ¹ CpH ² CpH ⁴ CpH ⁷ CpH ⁸ PhH ¹ CpH ⁵ CpH ⁶ PhH ⁶⁻⁹ PhH ² PhH ³ PhH ⁴	-7.6 -3.9 -1.6 9.3 21.0 21.2 109.4 112.9 115.0 116.7 120.9 121.2 123.2 124.3 127.5 138.5 141.4 142.3	SiMe ¹ SiMe ^{3,4} SiMe ² $\mu\text{-Me-B}$ PhMe ¹⁰ PhMe ⁵ CpC ⁷ CpC ² CpC ¹ CpC ⁴ PhC ¹ CpC ⁶ CpC ³ CpC ⁸ CpC ⁵ PhC ⁴ PhC ² PhC ³	 7 in CD_2Cl_2 , -60°C	-1.17 0.16 0.36 0.39 0.52 2.39 5.81 5.85 6.15 6.35 7.32 7.40	$\mu\text{-Me-Zr}$ ZrMe SiMe ¹ SiMe ² MeB PhMe CpH ³ CpH ⁴ CpH ¹ CpH ² PhH ^{1,3} PhH ^{2,4}	-2.9 -1.6 ~10 21.3 24.2 38.8 117.1 118.2 119.4 120.3 122.4 125.1 129.0 133.5 140.4	SiMe ² SiMe ¹ MeB PhMe $\mu\text{-Me-Zr}$ ZrMe CpC ¹ CpC ³ CpC ⁴ <i>i</i> -C-Cp CpC ² <i>i</i> -C-Ph PhC ^{1,3} PhC ^{2,4} <i>i</i> -C-Ph
 5b in CD_2Cl_2 , -80°C	-0.08 0.22 0.29 0.47 2.34 5.91 6.10 6.37 7.25 (d) 7.33 (d)	$\mu\text{-Me-B}$ SiMe ¹ SiMe ² ZrMe PhMe CpH ^{3,4} CpH ¹ CpH ² PhH ^{2,4} PhH ^{1,3}	-3.2 -2.6 21.1 ~24 (br) 39.7 118.1 118.5 120.7 124.8 128.9 133.2	SiMe ² SiMe ¹ PhMe $\mu\text{-Me-B}$ ZrMe CpC ³ CpC ¹ CpC ⁴ CpC ² PhC ^{2,4} PhC ^{1,3}	 7 in CD_2Cl_2 , -60°C				

^a 500 MHz. ^b 125.7 MHz. ^c 470 MHz. CpHⁿ ($n = 1-4$) denotes hydrogens of the C₅ ring, coupled to CpCⁿ (connectivity determined by CH correlation). PhHⁿ ($n = 1-5$) denotes hydrogens of the C₆ ring, coupled to PhCⁿ (connectivity determined by CH correlation).

treated **2** with excess $\text{B}(\text{C}_6\text{F}_5)_3$ in CD_2Cl_2 at -60°C and monitored the reaction by NMR spectroscopy. However, no clean-cut evidence for such a dication could be obtained; the NMR spectrum is rather crowded and probably consists of a mixture of **5a**, **5b**, and some unknown compound. To model structures for the arene-coordinated cationic products reported here, DFT calculations were performed and are reported in part II.

II. DFT Calculations. An initial optimization of cation **4** from a starting structure similar to the previously described cationic compound $[(\eta^5\text{-Cp})(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{C}_6\text{H}_5)\text{ZrMe}]^+$ (**13**)¹⁸ gave structure **10a** (Figure 4). Resembling **13**, structure **10a** has a close contact between the Zr and one of the ortho carbons of the phenyl ring (Figure 4). The Zr–C² distance of 2.73 Å is somewhat longer than the corresponding distance in **13** (Zr–C² = 2.629 Å) but is in excellent agreement with the recently published values from Ziegler et al.³¹ They reported

the structure of the solvent-separated ion pair $[(\eta^5\text{-1,2-Me}_2\text{C}_5\text{H}_3)_2\text{ZrMe}]^+[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ in toluene and obtained Zr–C distances of 2.60 and 2.74 Å, respectively, for the η^2 -bonded toluene. The hydrogen attached to C² in **10a** is bent away from the Zr, by 8.5° out of the phenyl plane (**13**: ca. 15°). Both values indicate a weaker η^1 coordination of the phenyl ring to the cationic zirconium, in comparison with **13**. All other Zr–C(Ph) distances are significantly larger than 3 Å, corroborating the η^1 coordination mode (cf. Figure 4) rather than an agostic bonding mode.¹⁸

Further exploration of the potential energy surface revealed the presence of at least one other minimum wherein the zirconium is in close proximity to an ortho carbon (**10b**, Zr–C⁶ = 2.71 Å) with the attached hydrogen bent out of the Ph plane

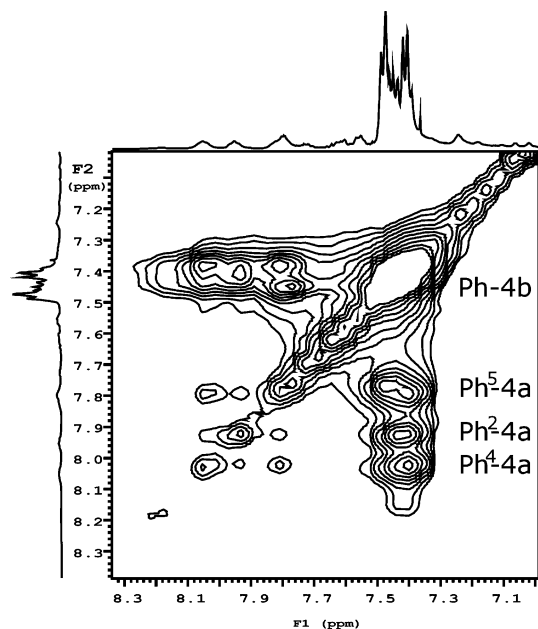


Figure 3. EXSY spectrum of the phenyl region of **4a/4b**.

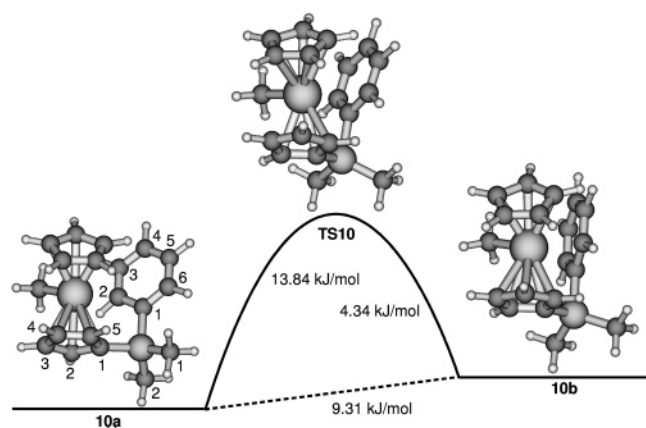


Figure 4. Stationary points and schematic potential energy surface for the phenyl rotation of cation **10**, with relative energies at the B3LYP/ECP1 level.

by 9.6° (Figure 4). This second minimum is slightly higher in energy (9.31 kJ/mol) than **10a**. The transition state **TS10**, connecting these two minima, was located with a loose η^3 coordination of the phenyl ring. The distances between zirconium and C¹, C², and C⁶ are 2.94, 3.65, and 2.69 Å, respectively (**TS13**: 2.840, 2.995, and 3.246 Å, respectively). The smaller value of Zr–C⁶ indicates that **TS10** is closer to the structure of **10b**, rather than to the structure of **10a**, which is probably due to steric reasons. As the resulting barrier is only 13.8 kJ/mol and is lower than the corresponding barrier for **TS13** (19 kJ/mol), rapid scrambling between **10a** and **10b** can be expected on the NMR time scale.

To ascertain any possible steric or electronic effects of the Zr–Me group, we replaced the methyl moiety with a chlorine atom. The structural features of **10a-cl** and of **10b-cl** are similar to those of the parent compounds **10a** and **10b** (Figure 5). The Zr–C² distance of **10a-cl** is 2.74 Å; the hydrogen is bent by 10.6° out of the Ph plane. The Zr–C⁶ distance of **10b-cl** is 2.72 Å; the hydrogen is bent by 10.8° out of the Ph plane. In the transition state **TS10-cl**, similar to **TS10**, the corresponding distances between zirconium and C¹, C², and C⁶ are 2.90, 3.67, and 2.81 Å, respectively. Overall, the chloride derivative **10cl** is structurally very similar to the parent compound **10**. However,

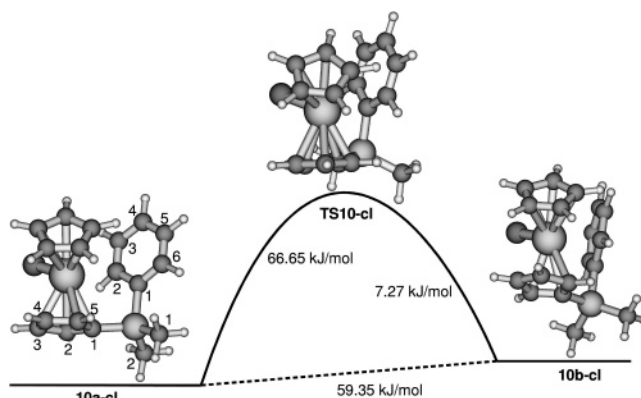


Figure 5. Stationary points and schematic potential energy surface for the phenyl rotation of cation **10-cl**, with relative energies at the B3LYP/ECP1 level.

whereas the barrier for the interconversion of **10a** and **10b** is rather low, the barrier for the interconversion between **10a-cl** and **10b-cl** is significantly higher, namely 66.65 kJ/mol, and thus even higher than the barrier for **TS13**. This may be explained by the greater electronegativity of chlorine and consequent increased bond strength between Zr and C².

Whereas the optimized structures suggest that **10a** is probably the dominant species at low temperature, the energies of the two species are so close that further evidence was sought by comparison between the measured and calculated NMR spectra (Table 5). In general, the IGLO II basis set gives more comparable data with less deviation between the benzene and TMS references. These data are also in good agreement with the calculated shifts using the EPC1 basis set and benzene as a reference. The largest deviation was found using EPC1 and TMS as a reference.

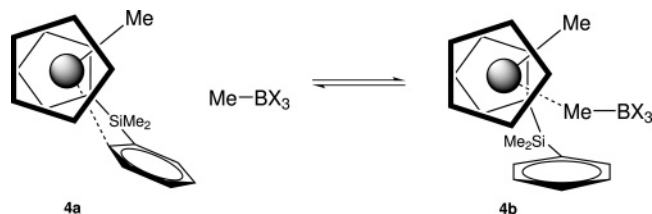
Careful comparison between the calculated values for **10a** and **10b** and the experimental values suggest a marginally closer agreement with structure **10b**. It is probable that **10a** and **10b** are in rapid exchange. However, exchange between **4a** and **4b** has been established experimentally. This exchange is corroborated by the strong EXSY cross-peaks in the phenyl region of the spectrum (Figure 3). The rapid exchange between **4a** and **4b** on the NMR time scale is likely to leave the anion in close proximity to the cation, probably with the methyl group pointing toward the cationic zirconium and thus fitting nicely in the pocket of **10b**. Such a positioning of the anion may inhibit rotation of the phenyl ring and the formation of **10a**. It is tempting to speculate that such rapid exchange between **4a** and **4b** can occur by simply moving the anion to and fro on a Zr–Me–BX₃ axis with a minor rotation of the phenyl ring (Scheme 2) and that the previously observed “overturning” of the anion is unlikely.¹⁶ This translation would not change much of the remaining geometry of the molecule and thus results in observed chemical shifts, which, in consequence, are closer to structure **10b** than to structure **10a**.³²

Whereas the reaction of $[(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_6\text{H}_5)_2\text{ZrMe}_2]$ and $[(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{Me})_2\text{ZrMe}_2]$ with 2 equiv of B(C₆F₅)₃ in CD₂Cl₂ at -60°C yields the dicationic compounds $[(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_6\text{H}_5)_2\text{Zr}]^{2+}$ (**14**) and $[(\eta^5\text{-C}_5\text{H}_4\text{CMe}_2\text{C}_6\text{H}_4\text{Me})_2\text{Zr}]^{2+}$,²⁰ the similar reaction of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_4\text{Me})_2\text{ZrMe}_2]$ and B(C₆F₅)₃ did not yield the dicationic compound $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_4\text{Me})_2\text{Zr}]^{2+}$ (**11**). In light of the above observations, this is probably not too surprising, given the propensity

(32) This exchange is currently under investigation and will be subject to a separate publication.

Table 5. GIAO-B3LYP Calculated and Experimental Chemical Shifts (ppm) of **10a** and **10b**

	ECP1/ TMS	IGLO II/ TMS	ECP1/ C ₆ H ₆	IGLO II/ C ₆ H ₆	exptl
Compound 10a					
CpC	103.7	117.1	116.7	115.5	113.8
CpC ¹	107.7	122.4	121.0	121.1	117.3
CpC ²	111.1	124.5	124.5	123.2	120.2
CpC ³	112.6	125.9	126.0	126.0	113.6
CpC ⁴	103.2	116.0	116.6	114.7	114.7
CpC ⁵	98.3	110.9	111.6	108.77	118.2
PhC ¹	115.6	130.3	129.0	129.0	n.d.
PhC ²	105.7	119.5	199.1	118.2	n.d.
PhC ³	128.0	143.2	141.4	141.9	n.d.
PhC ⁴	120.7	134.4	134.0	133.1	n.d.
PhC ⁵	127.6	142.4	141.0	141.1	n.d.
PhC ⁶	127.4	142.1	140.8	140.8	n.d.
CpH	5.41	5.71	5.53	5.60	6.03
CpH ²	6.75	6.93	7.05	7.00	6.76
CpH ³	6.56	6.70	6.87	6.77	5.70
CpH ⁴	5.91	6.10	6.22	6.17	6.45
CpH ⁵	5.69	5.91	5.99	5.98	6.20
SiC ¹	-11.6	-11.1	1.8	-12.4	-3.4
SiC ²	-6.6	-5.5	6.7	-6.7	-3.5
ZrCH ₃	42.3	52.2	55.7	51.0	46.4
SiCH ¹	0.46	0.76	0.51	0.58	0.36
SiCH ²	0.45	0.75	0.45	0.52	0.48
ZrCH ₃	1.01	1.32	1.26	1.33	0.75
Compound 10b					
CpC	104.0	117.4	117.0	115.8	113.8
CpC ¹	105.6	119.9	118.9	118.6	117.3
CpC ²	118.6	132.5	131.9	131.2	120.2
CpC ³	103.6	116.5	116.9	115.3	113.6
CpC ⁴	106.1	118.4	119.4	117.1	121.2
CpC ⁵	102.5	115.5	115.9	114.3	118.2
PhC ¹	128.9	144.7	142.2	143.5	n.d.
PhC ²	122.1	136.0	135.5	134.7	n.d.
PhC ³	130.3	145.3	143.7	144.1	n.d.
PhC ⁴	118.3	131.8	131.6	131.8	n.d.
PhC ⁵	125.9	140.8	139.2	139.6	n.d.
PhC ⁶	107.35	121.27	120.7	120.0	n.d.
CpH	6.06	6.37	6.24	6.31	6.03
CpH ²	6.91	7.09	7.22	7.16	6.76
CpH ³	5.53	5.74	5.83	5.81	5.70
CpH ⁴	6.19	6.26	6.50	6.33	6.45
CpH ⁵	5.76	5.94	6.07	6.01	6.20
SiC ¹	-7.6	-6.7	5.8	-7.9	-3.4
SiC ²	-11.0	-10.4	2.4	-11.6	-3.5
ZrCH ₃	42.0	53.4	55.4	52.1	46.4
SiCH ¹	0.34	0.64	0.33	0.40	0.36
SiCH ²	0.69	1.00	0.77	0.84	0.48
ZrCH ₃	-0.06	0.24	0.15	0.22	0.76

Scheme 2. Proposed Exchange Mechanism between **4a** and **4b**

of the monocation to coordinate the anion. Thus, the propensity of the hypothetical dication to coordinate the anion would be much higher. DFT calculations of **11** revealed at least three minima on the potential energy surface (Figure 6). The lowest energy was found for structure **11a**, which is stabilized by coordination of the two ortho carbons of the arene ring. The Zr–C² distance of 2.68 Å is similar to the previously reported value of 2.60 Å for **14a**.¹⁸ Similar values can be found for the Zr–C¹ distances: 3.09 Å for **11a** and 3.05 Å for **14a**. Again, the hydrogen bonded to the coordinated carbon is bent out of

the phenyl plane, away from the zirconium by 12.3° (**14a**: 14.5°). Thus, the structural features of **11a** and **14a** are very similar, and this cannot explain the differences in their reactivity. However, the energy difference between **11a** and **11c** of 40.5 kJ/mol is substantially higher than the corresponding energy difference of **14a** and **14c** (18.9 kJ/mol). Again, the structural features of both compounds are similar: the Zr–C⁶ distances of 2.70 and 2.65 Å in **11c**, respectively, are somewhat longer than the reported distance of 2.57 Å for **14c**. It should be noted, however, that **14c** was calculated with symmetry restriction, whereas **11c** was calculated without any restriction. The third located minimum **11b**, which somehow interconnects **11a** and **11c**, is only 12.5 kJ/mol higher in energy than **11a**. It can be assumed that both **11a** and **11b** are exchanging rapidly even at low temperature on the NMR time scale. The most likely explanation for the failure to obtain the *dicationic* compound **11** is a weaker bond between the zirconium and the coordinated carbon of the arene ring, leaving the zirconium more vulnerable to attack by other Lewis bases such as the anion.

Indeed, DFT calculations of the *dicationic* compound **12** indicate this. Whereas in the case of **11** the symmetrical compound **11a** was found to be the most stable compound, in the case of **12** the most stable compound was determined to be the *unsymmetrical* compound **12a**, which is similar to **11b** (Figure 7). The Zr–C² distance of 2.67 Å and Zr–C^{2'} of 2.69 Å for **12a** is similar to the corresponding distances of **11b** (2.66 and 2.70 Å). Again, the hydrogen bonded to the coordinated carbon atom is bent out of the arene plane (11.0 and 14.5° for **12a**; 10.4 and 14.6° for **12b**). Thus, the structural features of **11b** and **12a** are very similar, but with **12a** being lower in energy than **12b**, a situation which is quite unexpected. Furthermore, the energy difference between **12a** and **12b** is significantly larger than the difference between **11a** and **11b**: 50.48 kJ/mol vs 12.54 kJ/mol. The transition state **TS12-1** is, at 74.40 kJ/mol, significantly higher than the corresponding transition state **TS11-1** (23.97 kJ/mol). Similar observations may be made about the energy difference between **12b** and **12c**, compared with **11b** and **11c**. It can be assumed that the calculated structure **12a** would be the only observable structure in low-temperature NMR studies. It can be concluded that the introduction of a methyl group in the para position disturbs the energy balances between the different structures significantly enough to render the stabilizing effect of the arene rings weaker. Therefore, the presence of the anion, although it is claimed to be “noncoordinating”, could perturb this energy balance significantly to render the observation of **11** very difficult.

Conclusion

The reactions of zirconocene compounds bearing one or two dimethylphenylsilyl substituents on one or two cyclopentadienyl moieties with either B(C₆F₅)₃ or trityl salt have been studied. Low-temperature (–60 to –80 °C) multinuclear NMR studies of **1** provide evidence for the formation of the ion pair product **4a** with a Zr-coordinated phenyl group. This product is in equilibrium with the zwitterionic compound **4b**, as observed by EXSY spectroscopy. This reaction pattern is in strong contrast to the previously observed reactions of arene-substituted zirconocene compounds with a carbon bridging atom instead of a silicon bridging atom, where the ion pair product with phenyl coordination was the sole product. Similar observations of the reaction of **2** with either B(C₆F₅)₃ or trityl salt were made. Again, evidence for the formation of the ion pair product **5a** with a coordinated phenyl group was obtained, which is in equilibrium with the zwitterionic product **5b**. It is apparent that

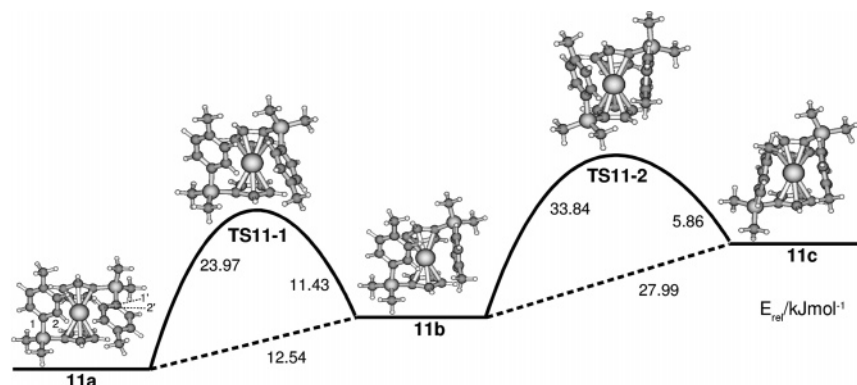


Figure 6. Stationary points and schematic potential energy surface for the phenyl rotation of dication **11**, with relative energies at the B3LYP/ECP1 level.

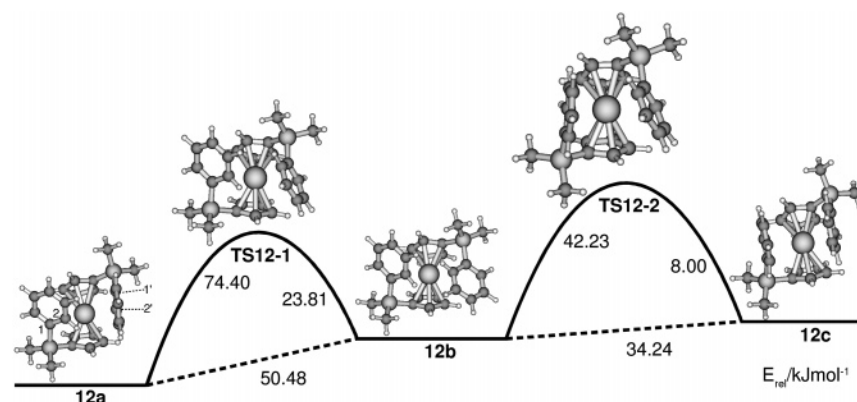


Figure 7. Stationary points and schematic potential energy surface for the phenyl rotation of dication **12**, with relative energies at the B3LYP/ECP1 level.

the larger atomic radius of silicon (1.17 vs 0.77 Å for carbon) moves the arene moiety further away from the cationic metal center, thus making coordination less likely to occur.

The DFT calculations of the observed cationic compound **4** support the inferences drawn from the experimental results. The phenyl moiety is further away from the cationic metal center compared with the carbon-bridged compound **13**. Hence, the stabilization effect of the phenyl moiety is less pronounced. Similar to the case for **13**, the hydrogen attached to the coordinated carbon is bent out of the phenyl plane, away from the zirconium. The structural features of **10** are similar to those of **13**, supporting the results. The calculated NMR chemical shifts, however, indicate a more complex scenario than in **13**: close inspection reveals that **10b** is in better agreement with the experimental values than **10a**. This can be explained by taking into consideration the experimental observed exchange between **4a** and **4b**. Indeed, the calculated structure **10b** is more prone to accommodate the methyl group of the anion by simple rotation of the phenyl group, whereas **10a** has to undergo a more complex rearrangement.

On the basis of the calculated structures of **11**, no clear explanation for the failure to observe the *dicationic* compound in the NMR could be drawn. However, comparison with the calculated structure of **12** indicates that the stabilization of the arene is weaker in the case of the silicon-bridged compound in comparison to the carbon-bridged compound **14**. This is in concert with the results of both experimental and DFT investigations of **4a**. This is strong support for these compounds as models for arene (solvent) adducts in Kaminsky-type polymerization: the likelihood of arene coordination decreases as the arene moves further away from the cationic metal center, and thus by comparison stronger Lewis bases such as the anion or

the starting material are more likely to bind to the cationic metal center, a situation which has been observed and documented before.

Experimental Section

All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were dried over sodium (toluene, low in sulfur), sodium/potassium alloy (diethyl ether, light petroleum, bp 40–60 °C, pentane), potassium (thf), and calcium hydride (dichloromethane). NMR solvents were dried over activated molecular sieves, freeze–thawed, and stored in Young's-Tap-sealed ampules.

NMR spectra were recorded on a Varian Gemini 200, a Varian UnityPlus 500, or a Bruker AM300 spectrometer and referenced to the residual protio solvent peak for ¹H. Chemical shifts are quoted in ppm relative to tetramethylsilane. ¹³C NMR spectra were referenced with the solvent peak relative to TMS and were proton-decoupled using a WALTZ sequence. CH coupling constants were measured by coupled pfg-ghsqc spectroscopy. ¹⁹F NMR spectra were referenced to external C₆F₆ (δ –163.0 ppm).

For X-ray structure analyses the crystals were mounted onto the tip of glass fibers, and data collection was performed with a Bruker-AXS SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation (0.710 73 Å). The data were reduced to *F*_o² and corrected for absorption effects with SAINT³³ and SADABS,^{34,35} respectively. The structures were solved by direct methods and refined by full-matrix least-squares methods (SHELXL97).³⁶ If not noted otherwise, all non-hydrogen atoms

(33) SAINTPLUS: *Software Reference Manual*, Version 6.45; Bruker-AXS: Madison, WI, 1997–2003.

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(35) SADABS: Version 2.1; Bruker AXS, Madison, WI, 1998.

were refined with anisotropic displacement parameters. All hydrogen atoms were located in calculated positions to correspond to standard bond lengths and angles. All diagrams were drawn with 30% probability thermal ellipsoids, and all hydrogen atoms were omitted for clarity. Crystallographic data (excluding structure factors) for the structures of compounds **1** and **2** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication Nos. CCDC-278805 (**1**) and CCDC-278806 (**2**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (internat.) +44-1223/336-033; e-mail, deposit@chemcrs.cam.ac.uk).

Computational Details. Density functional theory calculations were carried out using the GAUSSIAN03³⁷ program package, running on a Mandrake Linux Dual-Opteron or a Dual-Xeon system, respectively. Geometries have fully been optimized without symmetry constraints, involving the functional combinations according to Becke³⁸ (hybrid) and Lee, Yang, and Parr³⁹ (denoted B3LYP), with the corresponding valence basis set for Zr (Stuttgart-Dresden, keyword SDD in GAUSSIAN) and standard 6-31G* basis set⁴⁰ for C, H, Cl, and Si (denoted as ECP1). The stationary points and transition states were characterized as minima by analytical harmonic frequency (zero or one imaginary frequency, respectively), which were used without scaling for zero-point and thermal corrections.

Magnetic shieldings σ have been evaluated for the B3LYP/ECP1 geometries using a recent implementation of the GIAO (gauge-included atomic orbitals)-DFT method,⁴¹ involving the same B3LYP level of theory, together with the recommended IGLO-basis II⁴² on C, H, and Si or with the ECP1 basis set for comparison. The former approach with this particular combination of functionals and basis sets has proven to be quite effective for chemical shift computations for transition-metal complexes.¹⁸ ¹H and ¹³C chemical shifts have been calculated relative to benzene as a primary reference and TMS for comparison, with absolute shieldings for benzene $\sigma(^1\text{H}) = 24.54$ and $\sigma(^{13}\text{C}) = 47.83$ and for TMS $\sigma(^1\text{H}) = 31.73$ and $\sigma(^{13}\text{C}) = 177.59$ with the IGLO II basis set. For the ECP1 basis set, the absolute shieldings for benzene were calculated to be $\sigma(^1\text{H}) = 24.96$ and $\sigma(^{13}\text{C}) = 68.62$, and for TMS $\sigma(^1\text{H}) = 31.92$ and $\sigma(^{13}\text{C}) = 183.77$, respectively. The values for benzene were converted into the TMS scale using the experimental δ values of benzene (7.26 and 128.5, respectively). Tables of Cartesian coordinates of all calculated structures are available as Supporting Information in x, y, z format.

Preparation of Compounds 1 and 2. The compound $[(\eta^5\text{-Cp})\text{-ZrCl}_3(\text{dme})]$ was prepared as described in the literature.⁴³ The

zirconocene dichlorides **1a** and **2a** were characterized by NMR spectroscopy and were methylated without further purification due to the NMR spectra being satisfactory.

(a) Preparation of $[(\eta^5\text{-Cp})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Ph})\text{ZrCl}_2]$ (1a**).** The compound *n*-butyllithium (20 mL, $c = 2.5$ mol/L, 50 mmol) was added dropwise to a solution of freshly distilled cyclopentadiene (3.33 g, 50 mmol) in 120 mL of thf at -78°C . After complete addition, the reaction mixture was warmed to room temperature and slowly added to a solution of 10.2 g of chlorodimethylphenylsilane (60 mmol) in 20 mL of thf. After the addition was completed, the pale yellow solution was stirred for 2 h at room temperature. The reaction mixture was poured onto ice/water, and the aqueous phase was extracted two times with 80 mL of pentane. The combined organic phases were washed with 40 mL of brine, dried over Na_2SO_4 , and filtered and the volatiles removed under reduced pressure, yielding a pale yellow oil. The product was used without further purification. Yield: 6.00 g (30 mmol, 60%).

The ligand obtained above (3.00 g, 15 mmol) was diluted with 80 mL of thf and cooled to -78°C . The compound *n*-butyllithium (6 mL, $c = 2.5$ mol/L, 15 mmol) was added via syringe. After the addition was completed, the reaction mixture was warmed to room temperature and stirred for 30 min to ensure complete reaction. After the mixture was recooled to -78°C , $[(\eta\text{-Cp})\text{ZrCl}_3(\text{dme})]$ (5.29 g, 15 mmol) was added in small portions. The dark yellow solution was warmed to room temperature and stirred overnight.

The volatiles were removed under reduced pressure, and the resultant dark solid was extracted into 20 mL of toluene. The extract was stored at -30°C to yield the desired compound as a off-white solid. Yield: 2.45 g (5.9 mmol, 40%). ¹H NMR (CDCl_3 , 200 MHz, 20°C): δ (ppm) 0.63 (s, 6H, SiCH_3); 6.27 (s, 5H, Cp); 6.57 (t, 2H, Cp'); 6.75 (t, 2H, Cp'); 7.38–7.42 (m, 3H, Ph); 7.55 (d, 2H, Ph). ¹³C NMR (CDCl_3 , 50 MHz, 20°C): δ (ppm) -1.8 (SiCH_3); 116.0 (Cp); 118.2 (Cp'); 125.2 (Cp'); 128.0 (*m*-C, Ph); 129.5 (*p*-C, Ph); 134.0 (*o*-C, Ph).

(b) Preparation of $[(\eta^5\text{-Cp})(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{Ph})\text{ZrMe}_2]$ (1**).** A suspension of **1a** (2.45 g, 5.7 mmol) in 100 mL of diethyl ether at -78°C was treated with 8.4 mL of MeLi (11.8 mmol, $c = 1.6$ mol/L in diethyl ether) in a dropwise manner. The reaction mixture was slowly warmed to room temperature and stirred for 1 h. The volatiles were removed under reduced pressure to yield a light tan solid, which was extracted into 150 mL of light petroleum. The volatiles were removed under reduced pressure to yield a white solid. Yield: 1.6 g (4.2 mmol, 72.7%). Anal. Found: C, 61.8; H, 6.5. Calcd for $\text{C}_{20}\text{H}_{26}\text{SiZr}$: C, 62.2; H, 6.7. ¹H NMR (CDCl_3 , 200 MHz, 20°C): δ (ppm) -0.39 (ZrCH_3); 0.49 (s, 6H, SiCH_3); 5.94 (s, 5H, Cp); 6.28 (dd, 4H, Cp'); 7.35–7.39 (m, 2H, Ph); 7.48–7.52 (m, 2H, Ph). ¹³C NMR (CDCl_3 , 50 MHz, 20°C): δ (ppm) -1.5 (SiCH_3); 30.1 (ZrCH_3); 110.5 (Cp); 114.6 (Cp'); 117.5 (Cp'); 127.8 (*m*-C Ph); 129.2 (*p*-C Ph); 133.8 (*o*-C Ph); 147.3 (*i*-C Ph); 178.4 (*i*-C Ph).

(c) Preparation of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_2\text{C}_6\text{H}_4\text{Me})_2\text{ZrCl}_2]$ (2a**).** The compound 4-bromotoluene (34.2 g, 200 mmol) was added to a suspension of 4.9 g of magnesium turnings (210 mmol) in 400 mL of diethyl ether at 0°C and stirred at this temperature for 2 h. The reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was slowly filtered into a solution of dichlorodimethylsilane (29.7 g, 230 mmol) in 100 mL of diethyl ether at -30°C and was slowly warmed to room temperature. After the mixture was stirred overnight, the volatiles were removed under reduced pressure, yielding a yellow oil and a white precipitate. The oil was extracted into 90 mL of light petroleum and three times into 80 mL of dichloromethane. The volatiles of the combined extracts were removed under reduced pressure, yielding a yellow oil. Yield: 29.26 g (158.9 mmol, 64.57%). ¹H NMR (CDCl_3 , 500

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MHz, 20 °C): δ (ppm) 0.85 (s, 3H, SiCH₃); 1.00 (s, 3H, SiCH₃); 2.54 (s, 3H, PhCH₃); 7.40 (d, 2H, Ph); 7.71 (d, 2H, Ph). ¹³C NMR (CDCl₃, 125 MHz, 20 °C): δ (ppm) 2.1 (SiCH₃); 2.9 (SiCH₃); 21.5 (PhCH₃); 128.9 (*m*-C Ph); 132.3 (*i*-C Ph); 133.1 (*o*-C Ph); 140.4 (*i*-C Ph).

To the compound ClSiMe₂C₆H₄Me thus prepared (29.26 g, 158.9 mmol) in 100 mL of diethyl ether was slowly added a solution of sodium cyclopentadienyl, freshly prepared from NaH (6.35 g, *w* = 60% in mineral oil, 158.9 mmol) and freshly distilled cyclopentadiene (10.5 g, 158.9 mmol), in 300 mL of thf at 0 °C. After the addition was completed, the reaction mixture was stirred overnight. The reaction mixture was quenched by pouring it onto a mixture of ice and water and ammonium chloride. The phases were separated, and the aqueous phase was extracted twice into 100 mL of petroleum ether. The combined organic phases were washed with brine, dried over magnesium sulfate, and filtered. The volatiles were removed under reduced pressure, yielding a yellow oil. Yield: 28.07 g (130.9 mmol, 82.7%). ¹H NMR (CDCl₃, 500 MHz, 20 °C): δ (ppm) 0.36 (s, 6H, SiCH₃); 2.55 (s, 3H, PhCH₃); 6.70 (br, 2H, Cp'); 6.81 (br, 2H, Cp'); 7.38 (d, 2H, Ph); 7.65 (d, 2H, Ph). ¹³C NMR (CDCl₃, 125 MHz, 20 °C): δ (ppm) -4.4 (SiCH₃); 21.4 (PhCH₃); 128.5 (*m*-C Ph); 130.5 (Cp'), 133.3 (Cp'); 133.5 (*o*-C Ph); 133.8 (*i*-C Ph); 139.1 (*i*-C Ph).

The ligand obtained above (12.9 g, 60 mmol) was diluted with 250 mL of petroleum ether, and the compound *n*-butyllithium (24 mL, *c* = 2.5 mol/L, 60 mmol) was slowly added. The white suspension was stirred for 2 h. The supernatant yellow solution was filtered off, and the white precipitate was washed twice with 80 mL of light petroleum and dried at reduced pressure. The product was dissolved in 200 mL of thf and the red solution cooled to -78 °C. The compound ZrCl₄(thf)₂ (11.3 g, 30 mmol) was slowly added, and the reaction mixture was stirred for 1 h at -78 °C, slowly warmed to room temperature, and stirred for an additional 3 h. The volatiles were removed under reduced pressure, yielding a yellow, sticky solid, which was extracted into 180 mL of dichloromethane.

The volatiles of the extract were removed under reduced pressure, yielding a yellow oil, which crystallized after 2 days. Yield: 2.76 g (5.22 mmol, 17.4%). ¹H NMR (CDCl₃, 300 MHz, 20 °C): δ (ppm) 0.57 (s, 12H, SiCH₃); 2.36 (s, 6H, PhCH₃); 6.28 (t, 4H, Cp'); 6.58 (t, 4H, Cp'); 7.21 (d, 4H, Ph); 7.41 (d, 4H, Ph). ¹³C NMR (CDCl₃, 75 MHz, 20 °C): δ (ppm) -1.7 (SiCH₃); 21.5 (PhCH₃); 117.1 (Cp'); 123.9 (*i*-C Ph); 126.6 (Cp'); 128.7 (*m*-C Ph); 134.1 (*o*-C Ph); 139.3 (*i*-C Ph).

(d) Preparation of [(η⁵-C₅H₄SiMe₂C₆H₄Me)₂ZrMe₂] (2). A suspension of **2a** (2.76 g, 5.22 mmol) in 150 mL of diethyl ether at -78 °C was treated with 7.0 mL of MeLi (10.4 mmol, *c* = 1.5 mol/L in diethyl ether) in a dropwise manner. The reaction mixture was slowly warmed to room temperature and stirred for 2 h. The volatiles were removed under reduced pressure to yield an off-white solid, which was extracted into 150 mL of light petroleum. The extract was concentrated and cooled to -30 °C to yield light tan crystals. Crystals suitable for X-ray analysis were grown by slowly cooling a solution in light petroleum to -30 °C. Yield: 1.63 g (3.3 mmol, 63.2%). Anal. Found: C, 65.0; H, 7.3. Calcd for C₃₀H₄₀Si₂Zr: C, 65.8; H, 7.3. ¹H NMR (CDCl₃, 300 MHz, 20 °C): δ (ppm) -0.44 (s, 6H, ZrCH₃); 0.44 (s, 12H, SiCH₃); 2.36 (s, 6H, PhCH₃); 6.06 (t, 4H, Cp'); 6.15 (t, 4H, Cp'); 7.19 (d, 4H, Ph); 7.38 (d, 4H, Ph). ¹³C NMR (CDCl₃, 125 MHz, 20 °C): δ (ppm) -1.4 (SiCH₃); 21.5 (PhCH₃); 30.2 (ZrCH₃); 114.2 (Cp'); 116.6 (*i*-C Ph); 118.3 (Cp'); 128.6 (*m*-C Ph); 133.9 (*o*-C Ph); 135.1 (*i*-C-Cp') 139.0 (*i*-C Ph).

Supporting Information Available: Tables and figures giving crystal data and additional views of **1** and **2**, figures giving ¹H, ¹³C, ³¹F, and EXSY NMR spectra for **4a/4b**, and tables giving Cartesian coordinates for all compounds calculated in this paper. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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