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Displacement of $H_3CB(C_6F_5)_3^-$ Anions from Zirconocene Methyl Cations by Neutral Ligand Molecules: Equilibria, Kinetics, and Mechanisms

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The displacement of the $MeB(C_6F_5)_3^-$ anion from seven different zirconocene methyl cations by neutral Lewis bases, such as dimethylaniline, benzyldimethylamine, and di^{n}butyl ether, was investigated by 1D and 2D NMR spectroscopy. Equilibrium constants for reactions with di^{n}butyl ether change by factors of less than 5 between the zirconocene contact ion pairs studied, despite substantial steric differences. Rate constants of this displacement reaction, however, change by a factor of more than 10^5 between $Me_2Si(C_5H_4)_2ZrMe^+MeB(C_6F_5)_3^-$, the most "open" complex, and *rac*-$Me_2Si(2\text{-}Me\text{-}BzInd)_2ZrMe^+MeB(C_6F_5)_3^-$, the most highly substituted species studied. Kinetic and stereochemical data indicate that Lewis base−anion exchange proceeds by way of an associative mechanism, which occurs without side change of the zirconium-bound methyl group. DFT calculations support an associative substitution mechanism and propose five-coordinated reaction intermediates with the Lewis base coordinated to the central coordination site.

Introduction

The reaction paths through which active species arise when zirconocene precatalyst complexes are combined with suitable activators are still incompletely understood. Particularly unsatisfactory, despite recent advances,[1−3] is our understanding of the elementary reaction steps induced by methylalumoxane (MAO) as an activator. For reaction systems generated from zirconocene dimethyl complexes by perfluorophenyl borane or borate activators,[4,5] well-defined ion pairs have been shown to contain metallocene alkyl cations in contact with $H_3CB(C_6F_5)_3^-$, $B(C_6F_5)_4^-$, or other related anions.[6]

Even here it is not clear, however, which course of events generates the catalyst proper: Dissociation of the weakly coordinating anion is frequently assumed to release a zirconocene alkyl cation,[7] which would then enter into a catalytic cycle by repeated olefin uptake and insertion. The active catalyst is seen here as a solvated alkyl zirconocene cation, while the nature of the anion determines only the actual concentration of this active species. In line with this view, molecular modeling studies of olefin insertion, chain termination, and isomerization mechanisms have mainly dealt with naked cationic intermediates in the gas phase.[8]

In a recent study on the side exchange of borate anions in *ansa*-zirconocene methyl cations, we have obtained evidence that this process occurs through associative mechanisms, probably via ion quadruples or higher ion aggregates present in these systems,[9] and that anion-free, solvated zirconocene methyl cations are unlikely to be relevant intermediates for this exchange process. Formation of an olefin-containing reaction complex might thus likewise occur by way of an associative displacement of the anion rather than via olefin coordination to a solvated cation.

A number of recent density functional or ab initio calculations have dealt with reactions between ethene and alkylmetallocene contact ion pairs.[10−14] So far, however, a consistent picture has emerged neither for

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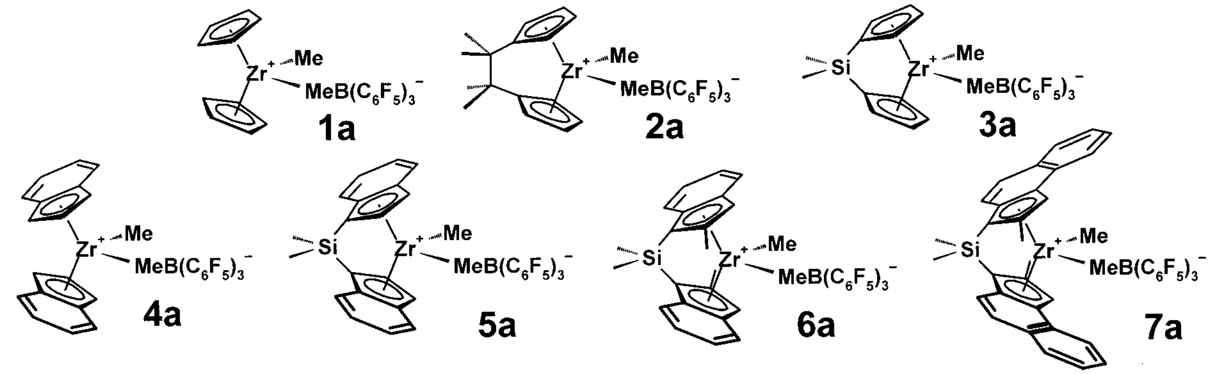
Scheme 1



the course of this reaction, i.e., the position of olefin attack, nor for its energetics.[12−14]

Direct evidence in this regard is hard to come by: Even for zirconocene cations carrying intramolecularly tethered olefin ligands,[15−17] no observations on anion−olefin exchange mechanisms have been reported so far. Intermolecular olefin−anion exchange in zirconocene alkyl cations, on the other hand, is even less likely to become directly observable, due to the high reactivity expected for olefin-containing zirconocene alkyl cations. We have thus set out to study the characteristics of this type of reaction by using an inert Lewis base instead of an olefin substrate.

Strong Lewis bases have been used in several instances to stabilize cationic zirconocene complexes.[18−21] Our aim in this study, however, was to find more weakly coordinating Lewis bases, which would allow us to determine equilibria and kinetics of anion displacement reactions for a series of different zirconocene complexes. It has been reported, for example, that dimethylaniline (DMA) is partially coordinated to zirconocene methyl cations when dimethylanilinium borate salts are reacted with zirconocene dimethyl complexes.[22] We have thus chosen to study the reactions of weakly binding ligand molecules such as DMA with zirconocene contact ion pairs, generated in situ from the appropriate dimethyl complex by reaction with tris(pentafluorophenyl) borane. Thermodynamics and mechanisms of these ligand substitutions were characterized for various zirconocene complexes (**1a**−**7a**, Scheme 1) with the aim to extrapolate useful information concerning the uptake of olefin substrates by these ion pairs.

Experimental Part

$(C_5H_5)_2ZrCl_2$,[23] $Me_4C_2(C_5H_4)_2ZrCl_2$,[24] $Me_2Si(C_5H_4)_2ZrCl_2$,[25] $(C_9H_7)_2ZrCl_2$,[26] *rac*-$Me_2Si(C_9H_6)_2ZrCl_2$,[27] and $B(C_6F_5)_3$[28] were synthesized as described in the literature. *rac*-$Me_2Si(2\text{-}Me\text{-}C_9H_5)_2ZrCl_2$ and *rac*-$Me_2Si(2\text{-}Me\text{-}C_{13}H_7)_2ZrCl_2$ were donated by BASF AG, Ludwigshafen. The dimethyl complexes were obtained by reaction of the corresponding dichloride complexes with methylmagnesium chloride as described in ref 29. All operations were carried out using drybox or Schlenk techniques. Solvents were distilled from sodium; Lewis bases were distilled from sodium or passed through a column of molecular sieve (4 Å). NMR solvents were dried and stored over molecular sieves under nitrogen atmosphere. 1D NMR spectra were recorded at 250 MHz in benzene-d_6 at 300 K with C_6D_5H as internal standard ($\delta = 7.15$ ppm). 2D NMR spectra were recorded at 600 MHz. The temperatures in NMR experiments were determined using methanol or ethylene glycol standards as chemical thermometers.

General Procedure for the NMR Experiments. Stock solutions of the corresponding dimethyl complexes, of $B(C_6F_5)_3$, and of the respective Lewis base in C_6D_6 were prepared and stored over molecular sieves (4 Å) under nitrogen atmosphere. Borane (1.05−1.1 equiv) was added to the zirconocene dimethyl complex and the slightly yellow solution diluted to the desired concentration, in most cases 2 mM. The desired amount of Lewis base was added. In general coordination to the metal center was accompanied by decolorization of the solution. ^1H NMR data of the Lewis-base adducts obtained are given in the Supporting Information.

Computational Details. Semiempirical calculations were carried out with the program Spartan 4.1.[30] For DFT calcula-

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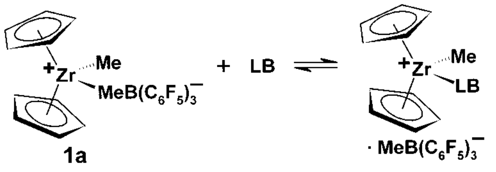
tions, TURBOMOLE[31] was used for the calculation of energies and gradients and OPTIMIZE[32] for geometry relaxation. In all cases the gradient-corrected nonlocal functionals of Becke[33] and Perdew[34] (BP86) were used. These had been found to yield reaction energies for ethene insertion into a Ti−Me bond close to those obtained by CCSD(T) methods.[35] For structure determinations, SVP (split valence with polarization) basis sets were used, while final energies were obtained with TZVP (triple-ζ split valence with polarization) basis sets for all atoms except zirconium,[36] to which the ecp-28-mwbopt basis set was applied in both cases.[37] Reaction energies obtained with a TZVP basis are more positive by 0−15 kJ/mol than those obtained with a SVP basis in most cases; only for $B(C_6F_5)_4^-$ anions were reaction energies more negative by approximately 10 kJ/mol with the bigger basis set (see Supporting Information). Corresponding auxiliary basis sets were used for the J_{ij} Coulombic term.[38] For $MeB(CF_3)_3^-$ anions all stationary points were checked by frequency calculations for the absence of negative eigenvalues and the presence of only one for transition states. For both anions, $MeB(C_6F_5)_3^-$ or $B(C_6F_5)_4^-$, geometry optimizations were carried out until the internal gradient was well below 3×10^{-4} au. Reaction energies in toluene solution were calculated from single-point energies using the conductor-like screening model (COSMO)[39] for the gas-phase optimized geometries, with $\epsilon = 2.4$ CV^{-1} m^{-1}, $r_H = 1.3$, $r_C = 2.0$, $r_B = 1.08$, $r_F = 1.72$, $r_O = 1.72$, $r_{Si} = 2.52$, and $r_{Zr} = 2.28$ Å. The use of gas-phase-optimized geometries, instead of geometries optimized by use of COSMO, was shown for several examples to have only minor effects (1−6 kJ/mol) on the absolute energies.

Results and Discussion

1. Anion Displacement Equilibria. In a series of NMR experiments, dimethylaniline was reacted with the contact ion pairs **1a**−**7a**, which were obtained by addition of 1.1 equiv of $B(C_6F_5)_3$ to the appropriate zirconocene dimethyl complex in 1−10 mM solutions in benzene-d_6.[40] The bridged and unbridged cyclopentadienyl complexes **1a**−**3a** react partially with DMA to yield the DMA adducts **1b**−**3b**. At constant [DMA]:[Zr] ratios, formation of the DMA adducts is favored at higher zirconocene concentrations. This concentration dependence, which is in accord with the equilibrium relation represented in eq 1, indicates that the displaced anion remains associated with the DMA-containing cation in the form of some outer-sphere complex in the nonpolar benzene solutions and that formation of separated, solvated ions does not occur to any significant extent (Scheme 2).[41] The formation of associated ion pairs, rather than separately solvated ions, has previously been reported for anion displacement from $(C_5H_5)_2Zr(CH_3)^+\cdots H_3CB(C_6F_5)_3^-$ by trialkylphosphines.[21]

Scheme 2



1a **1b-d**

LB = $Me_2N(C_6H_5)$ (DMA) : **1b - 7b**
= $(C_4H_9)_2O$ (DBE) : **1c - 7c**
= $Me_2N(CH_2C_6H_5)$ (BDMA) : **1d - 7d**

Table 1. Equilibrium Constants and Thermodynamic Parameter for the Displacement of $MeB(C_6F_5)_3^-$ from Complexes 1a−3a by DMA[a]

contact ion pair	K [L·mol^{-1}][b]	$\Delta H^{ø}$ [kJ·mol^{-1}]	$\Delta S^{ø}$ [J·mol^{-1}·K^{-1}]
1a	70	−53(3)[c]	−148(9)[c]
2a	160	−47(4)[d]	−120(13)[d]
3a	270		

$$K = \frac{[\mathrm{ZrMe(Lb)}^+\mathrm{A}^-]}{[\mathrm{ZrMe}^+\ \mathrm{A}^-]\cdot[\mathrm{Lb}]} \qquad (1)$$

$$\mathrm{ZrMe}^+\mathrm{A}^- = \mathbf{1a}-\mathbf{7a},\ \mathrm{Lb} = \text{Lewis base}$$

Equilibrium constants and thermodynamic parameters of these reactions are shown in Table 1. Values of $\Delta S^{\ominus} = -150$ and -120 J·(mol·K)$^{-1}$ support the view that the anion remains bound—presumably electrostatically—to the DMA-containing cation in **1b**−**3b**, even though it is no longer coordinated to the Zr center. The ring-bridged DMA complexes **2b** and **3b** have somewhat higher stabilities than the parent complex **1b**. This appears to be due to entropic contributions, as indicated by the less negative values of both $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ for the formation of **2b**. Since cyclopentadienyl rotation is equally quenched in **2a** as in **2b** by the Me_4C_2 bridging unit, the $\Delta S^{\ominus}$ value of -120 J·(mol·K)$^{-1}$ for the formation of **2b** is likely to reflect just the associative character of this process. Rotation of the cyclopentadienyl rings, on the other hand, is probably more strongly hindered in **1b** than in **1a**; this appears to contribute additional -30 J·(mol·K)$^{-1}$ to $\Delta S^{\ominus}$ for the formation of **1b**.

For the indenyl complexes **4a**−**7a** no reaction was observed even with a 10−20-fold excess of DMA. To investigate the effects of bridging, substitution, and annelation of the cyclopentadienyl rings on these anion displacement reactions, we have searched for Lewis bases other than DMA, which allow a comparison of all the zirconocene complexes in the series **1a**−**7a**. These contact ion pairs were thus reacted with a number of aliphatic and aromatic, cyclic and noncyclic ethers, thioethers, phosphines, and amines.

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[41] Slight changes of the equilibrium constants according to eq 1 with the overall zirconocene concentration, indicated by the experimental data, would require an exponent for [ZrMe$^+$A$^-$] greater than that for [ZrMe(Lb)$^+$A$^-$] by ca. 0.2. This is in line with the experimentally observed increased tendency of outer-sphere complexes to form ion quadruples or higher aggregates (see refs 9b, 29). Since these effects are small compared to the experimental error and are not distinguishable from ionic strength effects, no quantitative analysis was performed.

Table 2. Reactions of the Contact Ion Pairs 1a−7a with Different Lewis Bases[a]

Lewis base	reactions with **1a**−**3a**[b]	reactions with **4a**−**7a**[b]
$(C_6H_5)_3P{=}CH_2$	complete coordination, unidentified side products, stable Lewis base boran adduct[c]	
$(CH_2)_5C{=}CH_2$	no coordination[d]	
NMe_3	complete coordination	complete coordination
$Me_2N(CH_2C_6H_5)$	complete, fast coordination	nearly complete, slow coordination
$NMe_2(SiMe_3)$	partial coordination, $K \approx 30-100$ L·mol^{-1}, unidentified side products	
$NMe_2(C_6H_5)$	partial coordination, CH-activation of NMe as a side reaction	no coordination[d]
1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)	complete coordination, some side products	partial coordination, overlapping peaks prevent quantitative evaluation
2-Me-1-pyrroline	complete coordination	complete coordination
2,6-lutidine	fast CH-activation reaction[e]	fast CH-activation reaction[e]
pyridazine	complete coordination	
$(C_2H_5)_2O$	complete coordination	
$(C_4H_9)_2O$	partial coordination	partial coordination
$(CH_2)_5O$	complete coordination	complete coordination
$(CH_2)_3(CH)_2O$	broadened peaks prevent quantitative evaluation	broadened peaks prevent quantitative evaluation
$(CH_2)_2(CH)_2O$	broadened peaks prevent quantitative evaluation	
$(CH)_4O$	no coordination[d]	
$P(OMe_3)$	unidentified side products	
$Me_2P(C_6H_5)$	complete coordination	partial coordination
$P(CH_2C_6H_5)_3$	complete coordination	partial coordination
$(CH_2)_4S$	very low solubility and broadened peaks prevent quantitative evaluation[f]	
$(CH)_4S$	no coordination[d]	

[a] Typical conditions: in benzene-d_6 at 300 K, [Zr] = 1−5 mM, [Zr]:[Lewis base] = 2:1−1:20. [b] Not all combinations were investigated (see Supporting Information). [c] Cf. Döring, S.; Erker, G.; Fröhlich, R.; Meyer, O.; Bergander, K. *Organometallics* **1998**, *17*, 2183. [d] At 20-fold excess of Lewis base. [e] Cf. ref 18g. [f] Cf. ref 20a.

Table 3. Estimates for Equilibrium Constants for the Coordination of Different Lewis Bases to Complexes 1a−7a

Lewis base	$K = [ZrMe(Lb)^+A^-]/[ZrMe^+A^-]\cdot[Lb]$
PMe_3, NMe_3, Et_2O, C_4H_8S, C_4H_8O	$K \gg 1$ mM^{-1}
$PMe_2(C_6H_5)$, PBn_3, Me_2NBn	$K > 1$ mM^{-1}
$^nBu_2O$	$K \approx 1$ mM^{-1}
$Me_2N(C_6H_5)$, $Me_2N(SiMe_3)$	$K < 1$ mM^{-1}
C_4H_4O, C_4H_4S, olefin[a]	$K \ll 1$ mM^{-1}

[a] Estimated from DFT calculations.

For most of the Lewis bases studied, determination of equilibrium constants for the whole range of complexes **1a**−**7a** was prevented either by complete lack of reactivity or by fast, quantitative reactions, accompanied in some cases by side reactions (Table 2). Partial coordination is achieved by increasing the steric bulk of the Lewis base. Substituted phosphines such as tribenzylphosphine or dimethylphenylphosphine gave the desired equilibrium with the indenyl complexes **4a**−**7a**, but coordinated completely to the unsubstituted cyclopentadienyl complexes **1a**−**3a**.

Qualitative estimates of coordination constants for different Lewis bases *vis à vis* zirconocene contact ion pairs **1a**−**7a** are given in Table 3. As expected, the coordination ability decreases with increasing steric bulk and decreasing basicity of the Lewis base. Of the Lewis bases studied here, only di^{n}butyl ether (DBE) was found to react with cyclopentadienyl complexes **1a**−**3a** as well as with the indenyl complexes **4a**−**7a** under partial formation of complexes which are reasonably stable against side reactions at room temperature. This ligand was therefore chosen for a comparative study of anion displacement from complexes **1a**−**7a**.

Table 4. Equilibrium and Rate Constants for the Displacement of $MeB(C_6F_5)_3^-$ from Complexes 1a and 3a−7a by Dibutyl Ether

	1a[a]	**3a**[a]	**4a**[b]	**5a**[c]	**6a**[b]	**7a**[b]
K [L·mol^{-1}]	2800	4900	2000	1500	800	1100
$\Delta G^{\varnothing}_{300\,K}$[d]	−20	−21	−19	−18	−17	−17
k [L·mol^{-1}·s^{-1}]	270	4000	2	8	0.1	0.03
$\Delta G^{\ddagger}_{300\,K}$[d,e]	60	53	72	68	79[f]	82

[a] At 300 K in benzene-d_6 solution. k determined from 2D EXSY spectra. [b] k determined from conventional ^1H spectra. [c] k estimated from rate constants at higher and lower temperatures. [d] In kJ/mol. [e] Determined from the Eyring equation $\Delta G^{\ddagger} = -RT \ln(hk/(c^{\ominus}k_BT))$. [f] $\Delta H^{\ddagger} = 36(2)$ kJ/mol, $\Delta S^{\ddagger} = -142(7)$ J/(mol·K).

The unsubstituted dimethylsilyl-bridged complex **3a** has the highest tendency to coordinate this Lewis base, followed by the parent zirconocene **1a** (Table 4, Figure 1). Annelation of an aromatic ring reduces the coordination constant by a factor of 2−3. Bridging of the indenyl ligands has surprisingly small effects on the stability of the DBE adducts **4c** and **5c**. A methyl group in the 2-position of the indenyl ring diminishes the coordination constant by a factor of ca. 2, while annelation of another benzene ring has only minimal effects on the equilibrium constant. In the series **1a**−**7a**, equilibrium constants differ only by factors less than 5, corresponding to $\Delta\Delta G^{\ominus} \leq 4$ kJ/mol, despite substantial steric differences among these complexes.

2. Kinetics of the Anion Displacement Reaction. Reaction of benzyldimethylamine (BDMA) with the bridged 2-methylindenyl complexes **6a** and **7a** was essentially quantitative but slow enough to be monitored via standard ^1H NMR spectroscopy. Rate constants were determined under pseudo-first-order conditions with a relatively large excess of the amine. Alternatively, the amine was used in approximately

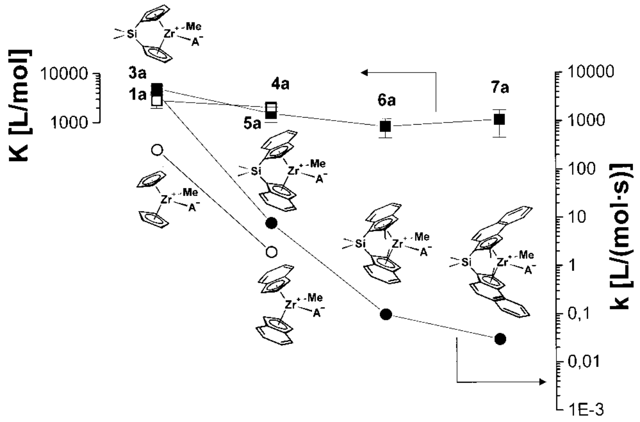

Figure 1. Equilibrium (□,■) and rate constants (○,●) for the substitution of $MeB(C_6F_5)_3^-$ by dibutyl ether (DBE) from unbridged complexes **1a** and **4a** (open symbols) and from Me_2Si-bridged complexes **3a**, **5a**−**7a** (filled symbols).

Table 5. Rate Constants and Activation Parameters for the Displacement of $MeB(C_6F_5)_3^-$ from 6a and 7a by BDMA in Benzene-d_6

complex	T [K]	k [L·(mol·s)$^{-1}$]	ΔH‡ [kJ·mol^{-1}]	ΔS‡ [J·mol^{-1}·K^{-1}]
6a	300	0.094		
6a	328	1.2	64(4)	−50(11)
6a	340	2.1		
7a	300	0.059		
7a	327	0.065	67(2)	−43(7)
7a	348	2.9		

stoichiometric amounts, and the resulting concentration profiles were analyzed with a second-order rate law. In either case, the data obtained are in excellent agreement with the rate law expressed in eq 2, i.e., with a reaction first-order in the concentration of zirconocene as well as of Lewis base.

$$v = k[\mathrm{Zr}][\mathrm{BDMA}] \qquad (2)$$

Annelation of a further ring to the indenyl moiety causes only minor changes of reaction rates from **6a** to **7a** (Table 5). Complexes **1a**−**4a**, on the other hand, reacted with approximately stoichiometric amounts of BDMA quantitatively in less than 5 min at room temperature.[42] Determination of rate constants for these reactions was thus not possible under the conditions used.[43]

With DMA as a Lewis base, displacement of the methylborate anion from the cyclopentadienyl complexes **2a** and **3a** was observable by means of 2D NOESY NMR spectra at 0 °C in toluene-d_8 solution.[44] Exchange signals were detected and integrated for the cyclopentadienyl protons as well as for the Zr- and Si-bound methyl groups (Figure 2). In this manner, pseudo-first-order rate constants were obtained by the method described by Perrin and Dwyer (see Supporting Information).[45] The reaction rate was found to depend linearly on the concentrations of zirconocene and of Lewis base (Table 6), in agreement with the rate law found for the anion substitution by benzyldimethylamine. Similar rate constants of 30 and 22 L/(mol·s) are found for the bridged cyclopentadienyl complexes **2a** and **3a**, respectively. Due to the lack of reaction of DMA with complexes **4a**−**7a**, determination of anion displacement kinetics was not possible for these indenyl complexes.

Table 6. Rate Constants for the Displacement of $MeB(C_6F_5)_3^-$ by DMA[a]

contact ion pair	Zr:DMA	k [L·mol^{-1}·s^{-1}]
$Me_4C_2(C_5H_4)_2ZrMe^+ \cdot MeB(C_6F_5)_3^-$, **2a**[b]	1:1	30 ± 6
$Me_2Si(C_5H_4)_2ZrMe^+ \cdot MeB(C_6F_5)_3^-$, **3a**[c]	1:1	21 ± 4
$Me_2Si(C_5H_4)_2ZrMe^+ \cdot MeB(C_6F_5)_3^-$, **3a**[c]	1:7	22 ± 3

[a] Determined from 2D-EXSY spectra in toluene-d_8 at 0 °C with an overall zirconocene concentration of 1 mmol/L. Errors are determined from exchange rates observed for different proton pairs. [b] Mixing time 500 or 800 ms. [c] Mixing time 500 ms.

Displacement of the anion by di^{n}butyl ether (DBE) from complexes **1a** and **3a** was studied by 2D NMR spectroscopy at 300 K. Rate constants in benzene-d_6 were determined from 2D NOESY spectra and analyzed according to the rate law in eq 2 (Table 4). For the indenyl complexes **4a**, **6a**, and **7a**, anion−base exchange was too slow to be measured by 2D exchange spectroscopy. In these cases it was possible, however, to monitor the reactions with DBE by conventional one-dimensional NMR spectroscopy at 300 K. Again, a first-order dependence on the concentrations of the zirconocene complex and of the Lewis base was found in all cases. The reaction of DBE with **5a** at room temperature was too slow for 2D NMR spectroscopy, but too fast for conventional 1D NMR measurements. To estimate the rate constant of this reaction at 300 K, the exchange rate at 320 K was determined via EXSY spectroscopy (partial decomposition of the complex already occurred at this temperature) and at lower temperatures (240−250 K) in toluene solution by use of 1D NMR techniques.

The rate constants at 300 K (estimated in the case of **5a**) are displayed in Figure 1 and Table 4. Annelation of a benzene ring to **3a** decreases the rate constant for complex **5a** by a factor of about 500. Introduction of a methyl group in the 2-position slows the reaction down by another 2 orders of magnitude. The anion displacement reaction thus appears to be particularly sensitive toward substituents in α-position of a bridged cyclopentadienyl ring, more so than toward substituents in the β-position. Further annelation of a benzene ring to the indenyl moiety has only minor effects on the reaction rates of **7a** vs **6a**, in accordance with the results obtained with benzyldimethylamine as Lewis base. The Me_2Si-bridged complexes **3a** and **5a** react faster by approximately 1 order of magnitude than their unbridged analogues **1a** and **4a**. This is most likely due to the more open ligand framework in the bridged complexes and possibly also to a hindrance of ring rotation in the unbridged complexes upon formation of a crowded

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[42] No coordination of BDMA was observed for the sterically crowded permethyl complex $(C_5Me_5)_2ZrMe^+MeB(C_6F_5)_3^-$.

[43] Complexes **1a**−**7a** and especially their base adducts tend to form aggregated species at elevated zirconocene concentrations (see ref 29). To avoid this in our kinetic experiments, zirconocene concentrations were limited to ca. 1−4 mmol/L at room temperature. Cooling was found to enhance the formation of the more aggregated forms, and at concentrations low enough to avoid this problem it was not possible to integrate NMR spectra with reasonable accuracy.

[44] DMA adducts **1b**−**3b** undergo CH activation of *N*-methyl groups within a period of 0.5−2 h at room temperature to yield a mixture of two products, probably either with the anion or the nitrogen donor coordinated to the metal. Similar CH activations have been reported by Jordan and co-workers for other Lewis bases (see ref 18 g). To avoid these side reactions, 2D NMR spectra were recorded at 0 °C. At this temperature, a mixing time of 500 μs was necessary to observe the anion displacement.

[45] Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935.

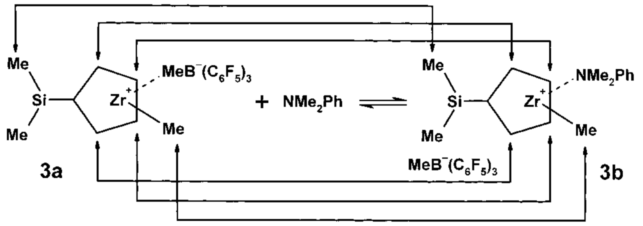

Figure 2. Exchange processes observed in 2D NOESY spectra for anion–DMA exchange in a reaction mixture containing **3a**, **3b**, and dimethylaniline (DMA).

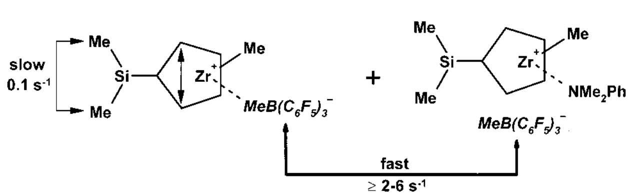

Figure 3. Exchange signals for anion exchange between **3a** and **3b** and for side migration of the Zr-methyl group in **3a** in 2D NOESY spectra of a reaction mixture as described in Figure 3.

transition state. Activation parameters of $\Delta H^{\ddagger} = 36(2)$ kJ/mol and $\Delta S^{\ddagger} = -142(7)$ J/(mol·K) were determined for the reaction of **6a** with DBE in the temperature range 300–340 K. The significantly higher activation entropy compared to the reaction with BDMA indicates that entropic effects, most likely a decrease in the rotational freedom of the *n*-butyl chains, might cause the relatively slow reaction with DBE.

While the equilibrium constants for Lewis-base adduct formation are affected by factors of 5 or less by any modification of the metallocene ligand framework, the rates of the anion displacement vary by more than 5 orders of magnitude: Complex **3a** reacts 120 000 times faster with DBE than complex **7a**. Possible origins of these unexpected rate differences, which correspond to activation energy differences of $\Delta\Delta G^{\ddagger} \approx 30$ kJ/mol, will be discussed below.

3. Stereochemistry of the Anion Displacement Reaction. Assignment of the proton positions in contact ion pairs **2a** and **3a** and in their DMA adducts **2b** and **3b** by use of NOE techniques shows that the anion displacement reaction is stereospecific in the sense that incoming DMA occupies the same coordination site that the anion has left. We are unable to detect any exchange signals, e.g., between protons on the methyl side of **3a** and protons on the DMA side of **3b**, which would indicate that the methyl group moves from one side of the complex to the other during the substitution process (Figure 2).

Another process observed in these reaction systems is the exchange of the anions of complexes **2a** and **3a** with the anions of their respective Lewis-base adducts **2b** and **3b** (Figure 3). Under the conditions applied, this exchange was nearly saturated. We can thus estimate only a lower boundary of the observed rate constant, $k_{\mathrm{obs}} > 2-6$ s^{-1}. This corresponds to rate constants of $k > 5000$ L·(mol·s)$^{-1}$ if we assume that the reaction is first-order both in the contact ion pair and the DMA-containing ion pair. Much lower pseudo-first-order rate constants of $k_{\mathrm{obs}} \approx 0.1$ s^{-1} for site migration of the methyl group[9a,46,47] are indicated by small exchange signals between the methyl and the anion sides of **2a**, **2b**, **3a**, or **3b**. Exchange of a coordinated anion against one bound in an outer-sphere complex thus proceeds with the same stereospecifity as that of a coordinated anion against a Lewis base. The same observations concerning anion–Lewis base and anion–anion exchange were made, when a reaction mixture of **3a**, DBE, and **3c** was studied by 2D NMR. This stereoselectivity provides further clues with regard to the mechanism of the anion displacement reaction, to be discussed below.

4. Mechanism of the Anion Substitution Reaction. The rate law represented in eq 2, which holds for all of the anion displacement reactions studied here, can arise in principle from either one of two mechanisms: (i) Either the anion is simply substituted by the Lewis base by way of an S_N2-type, associative mechanism involving a transition state with a five-coordinated Zr center, or (ii) the anion becomes reversibly detached from the Zr center to form an outer-sphere ion pair. In this case, coordination of the Lewis base to the vacant coordination site would have to be rate-determining (Scheme 3). The latter alternative is quite unlikely, however: Ab initio calculations have indicated that even the uptake of a weakly basic olefin ligand by a methyl zirconocene cation is free of any significant enthalpic barriers.[8a−c]

Rather than by a reversible anion dissociation, the anion substitution reactions studied here are thus most likely initiated by an associative attack of the Lewis base at the Zr center. This is supported by negative activation entropies of $\Delta S^{\ddagger} = -50$ to -40 J·mol^{-1}·K^{-1}, obtained for the reactions of **6a** and **7a** with BDMA at temperatures of 300–350 K (Table 5). The stereochemical course of the anion displacement process indicates, furthermore, that the five-coordinated zirconocene species, which functions as a transition state or intermediate in this process, retains the methyl ligand in its initial coordination site and has the anion and the incoming ligand—either Lewis base or excess anion—in adjacent coordination sites.

To check, at least qualitatively, on the accessibility of such a species, we have modeled the reaction of a somewhat simplified species $H_2Si(C_5H_4)_2ZrMe^{+}\cdot Me(C_6F_5)_3^{-}$ (**8a**) with trimethylamine by a semiempirical method (PM3-tm). Along the reaction path, five-coordinated Zr centers are indeed found as intermediates (**8d**–**8f,** Figure 4). Each of these is lower in energy by 200–250 kJ/mol than an outer-sphere ion pair with a vacant coordination site (**8g**) plus free NMe_3. This significant value supports—despite the low accuracy level of the method used—an associative mechanism of the ligand exchange process studied.

Among the five-coordinated intermediates, **8d** is more stable by approximately 40 kJ/mol than **8e** or **8f**. This energy ordering agrees with the observed stereochemistry of the ligand exchange: The intermediate of lowest energy carries the incoming Lewis base in the middle position such that ligand exchange occurs with retention

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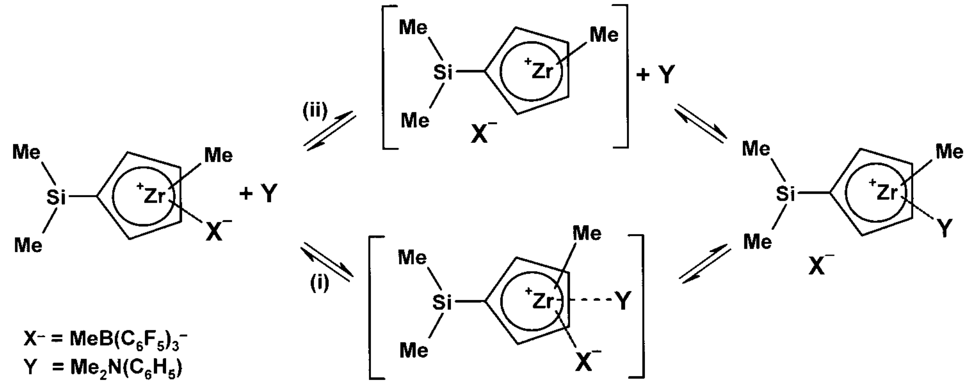
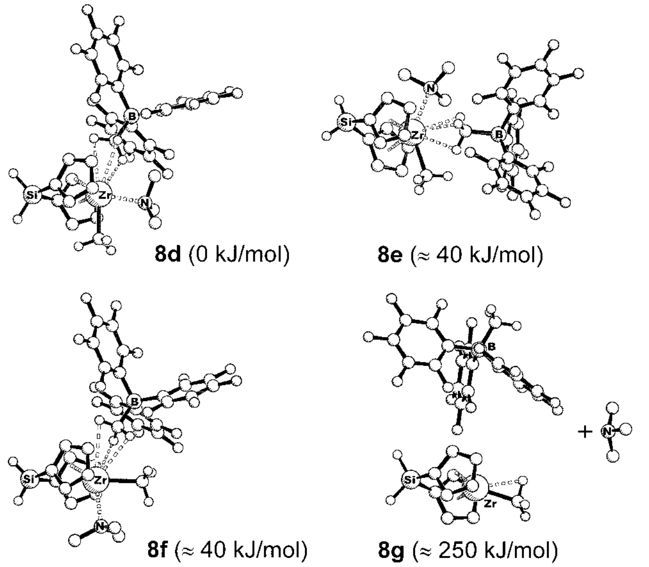
(46) Siedle, A. R. *Proc. Met. Con. 1993*; Catalyst Consultants Inc.: Spring House, PA, 1993; p 351. Siedle, A. R.; Newmark, R. A. *J. Organomet. Chem.* **1995**, *497*, 119.

(47) Deck, P. A.; Marks, T. J. *J. Am. Chem. Soc.* **1995**, *117*, 6128. Chen, Y. X.; Stern, C. L.; Yang, S. T.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451.

Scheme 3





8d (0 kJ/mol) **8e** (≈ 40 kJ/mol)

8f (≈ 40 kJ/mol) **8g** (≈ 250 kJ/mol)

Figure 4. Geometries and energies (relative to **8d**) calculated for intermediates in the substitution of the anion from **8a** by NMe_3, calculated by semiempirical methods (PM3-tm). Hydrogen atoms are omitted for clarity (with the exception of Zr-bound methyl groups).

of stereochemistry at the metal center. Due to the uncertain accuracy of the semiempirical method employed, we abstain from detailed characterizations of probable transition states.[48] The geometries and energies of these can nevertheless be assumed to resemble those of the intermediates discussed above.

5. DFT Calculations on Anion Displacement by Olefins. To extrapolate the insights gained with regard to anion displacement reactions by Lewis bases also toward corresponding reactions with an olefin substrate, the course of these reactions was further investigated by means of DFT calculations.

To limit the CPU time required for this more accurate method,[49] complex structures were simplified as follows: For the zirconocene contact ion pair, structure **9a** was used, which corresponds to the experimentally studied complex **3a**, with Me_2Si replaced by H_2Si and $MeB(C_6F_5)_3^-$ by $MeB(CF_3)_3^-$. For contact ion pairs $H_2Si(C_5H_4)_2ZrMe^+MeB(C_6F_5)_3^-$, **8a**, and $H_2Si(C_5H_4)_2ZrMe^+MeB(CF_3)_3^-$, **9a**, closely similar coordination geometries are calculated by DFT methods (Table 7): Zr−C distances differ by less than 2 pm, coordination angles by less than 2 deg.[50] Energy profiles for elongation of the Zr−(μ-Me) distance (anion dissociation) for both complexes are similar within deviations of less than 10% (see Supporting Information).

Anion displacement was first modeled with dimethyl ether as a Lewis base. For reaction of **9a** with Me_2O, an energy minimum is found for a five-coordinated intermediate $H_2Si(C_5H_4)_2ZrMe(OMe_2)^+MeB(CF_3)_3^-$, **9b**, with the Lewis base positioned between the methyl ligand and the anion (Figure 5), while lateral attack of the Lewis base does not yield stable intermediates.[51] Zr−C and Zr−O distances in **9b**, which are similar to experimental values reported for tetracoordinated cationic zirconocene-alkyl-ether complexes,[18a,b,52] confirm the strong interaction between the cationic zirconium center and the Lewis base in the five-coordinated intermediate. The ether ligand is oriented perpendicular to the equatorial Me−Zr−O plane. Similar coordination of THF to $(C_5H_5)_2ZrMe^+$ was found by diffractometry and explained by participation of oxygen p-orbitals in the zirconium−oxygen bond.[18a]

Dissociation of the anion leads to the outer-sphere ion pair **9c**, where the ether ligand is now rotated into the equatorial plane. The anion is without bonding contact to the Zr center.[53] Accordingly, the latter adopts a tetrahedral coordination geometry, with Zr−C and Zr−O distances slightly shorter than those in intermediate **9b**.

Formation of the five-coordinated intermediate **9b** from **9a** and free dimethyl ether is found to be exothermic with a coordination energy of −21 kJ/mol. Subse-

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(48) Børve, K. J.; Jensen, V. R.; Karlsen, T.; Støvneng, J. A.; Swang, O. *J. Mol. Model.* **1997**, *3*, 193.

(49) Ziegler, T. *Chem. Rev.* **1991**, *91*, 651.

(50) Different orientations are found for the ligands in the equatorial plane. While the methyl groups of **8a** are symmetrically coordinated in the equatorial plane with comparable C−Zr−Si angles, the Zr(Me)(anion) fragment in **9a** is rotated in the equatorial plane by ca. 15° relative to the Me_2Si bridge. (cf. Burger, P.; Diebold, J.; Gutmann, S.; Hund, H.-U.; Brintzinger, H. H. *Organometallics* **1992**, *11*, 1319. Brintzinger, H. H.; Prosenc, M.-H.; Schaper, F.; Weeber, A.; Wieser, U. *J. Mol. Struct.* **1999**, *485−486*, 409.)

(51) When the Zr−O distance is fixed to 2.6 Å, Lewis base attack from the methyl side or the anion side leads to structures that are 40 and 20 kJ/mol, respectively, higher in energy than the corresponding five-coordinated complex with the Lewis base in the middle position.

(52) (a) Alelyunas, Y. W.; Baenziger, N. C.; Bradley, P. K.; Jordan, R. F. *Organometallics* **1994**, *13*, 148. (b) Bijpost, E. A.; Zuideveld, M. A.; Meetsma, A.; Teuben, J. H. *J. Organomet. Chem.* **1998**, *551*, 159. (c) Amorose, D. M.; Lee, R. A.; Petersen, J. L. *Organometallics* **1991**, *10*, 2191.

(53) One fluorine atom of the anion is found at a distance of 3.5 Å from the metal center; this is presumably responsible for the relatively large Me−Zr−O angle of 108°, compared to other tetrahedral oxygen-coordinated cations and to the anion-free complex **9d**.

Table 7. Selected Bond Distances[a] (Å) and Angles (deg) Calculated for Complexes 8a and 9a−d

	8a	**9a**	**9b**	**9c**	**9d**[c]
$Zr-C_{term}$[b]	2.26	2.27	2.29	2.26	2.26
$Zr-C_{\mu}$ (Zr−H)[b]	2.45 (2.25)	2.45 (2.19)	3.70 (2.77)	4.80	
Zr−B	4.12	4.06	5.04	5.89	
$Zr-Z_{Cp}$	2.24, 2.25	2.23, 2.23	2.24, 2.25	2.23, 2.26	2.23, 2.23
Zr−O			2.28	2.24	2.28
$C_{term}-Zr-C_{\mu}$[b]	96	97	152	65	
$Z_{Cp}-Zr-Z_{Cp}$[b]	126	127	125	126	126
$C_{term}-Zr-O$[b]			83	108	99

[a] In Å. [b] C_{term}: methyl ligand bonded to Zr, C_{μ}: bridging methyl or trifluormethyl group bonded to B. [c] Anion-free cationic complex.

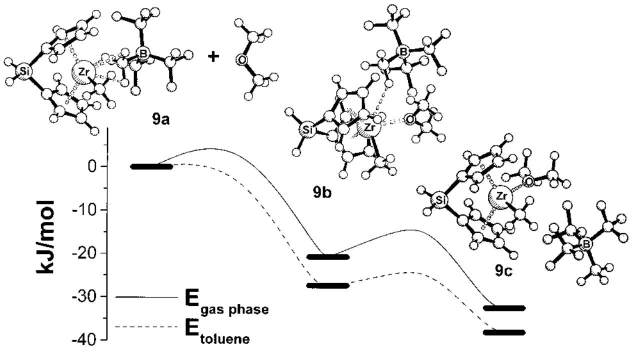

Figure 5. Geometries and energies of the five-coordinated intermediate and the outer-sphere reaction product of anion substitution from **9a** by Me_2O calculated by DFT methods.

Table 8. Relative Energies[a] Calculated for the Five-Coordinated Intermediates 8b−12b and for Outer-Sphere Reaction Products 8c−12c Occuring in the Reactions of 8a, 9a, or 12a with Dimethyl Ether or Olefins

			intermediates 8−12b		products 8−12c	
	Lewis base	anion	$E_{toluene}$	$E_{gas\ phase}$	$E_{toluene}$	$E_{gas\ phase}$
9	Me_2O	$MeB(CF_3)_3^-$	−27	−21	−38	−32
11	C_3H_7	$MeB(CF_3)_3^-$	23	30	11	21
10	C_2H_4	$MeB(CF_3)_3^-$	22	29	19	28
8	C_2H_4	$MeB(C_6F_5)_3^-$	40	39	52	58
12	C_2H_4	$B(C_6F_5)_4^-$	5	18	11	18

[a] In kJ/mol, relative to noninteracting **8**−**12a** + Lewis base.

quent reorganization to the outer-sphere complex **9c** is further downhill by −11 kJ/mol (Table 8, Figure 5). When single-point energies of complexes **9a**−**9c** are calculated in toluene solvent rather than in vacuo, complexes **9b** and **9c** are found to be stabilized by 6 kJ/mol relative to the situation in the gas phase. Formation of the outer-sphere ion pair is expected to be further favored by entropy contributions. Reaction entropies calculated from the harmonic frequencies at 298 K in the gas phase are less negative by ca. 60 J/(mol·K) for the formation of **9c** than for **9b**. Accordingly, outer-sphere ion pairs of type **9c** are expected to be the dominant products in solution.

For anion substitution by ethene or propene, five-coordinated intermediates with the olefin in the middle position (**10b** and **11b**) are again found to arise from **9a** (Figure 6). Bond distances and angles at the zirconium center are similar to those obtained for **9b** (Table 9). The ethene and propene ligands are coordinated perpendicular to the equatorial Si−Zr−Me plane of the complex with unequal Zr−C distances.[54] In the tetracoordinated outer-sphere ion pairs, **10c** and **11c**, the olefin is rotated into the equatorial plane and the asymmetry in the olefin bonding becomes more pronounced, especially for propene, most likely due to a buildup of positive charge on the β-C atom.

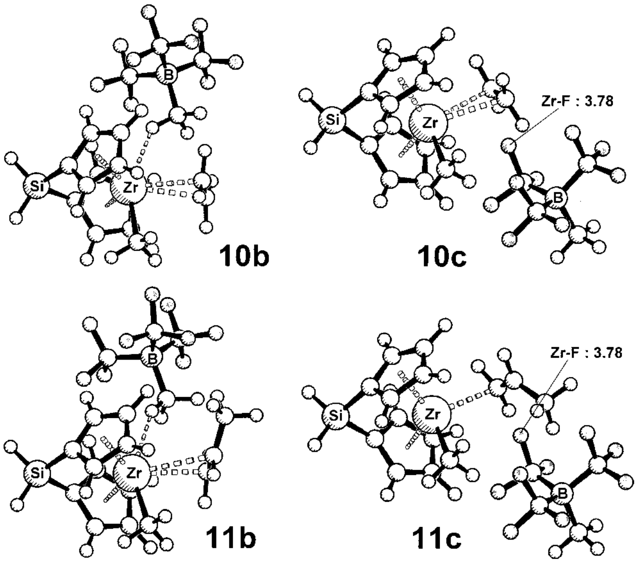

Figure 6. Geometries of intermediates and products of anion substitution from **9a** by ethene (**10b**,**c**) or propene (**11b**,**c**) calculated by DFT methods.

For the propene-coordinated outer-sphere ion pair **11c**, it was possible to calculate the geometry without any restraints. In the case of the ethene complex **10c**, however, the distance between the metal center and the nearest fluorine atom of the anion has to be fixed to the value obtained for **11c**.[55] As expected, olefins act as much weaker Lewis bases than Me_2O. Starting from the contact ion pair **9a** and ethene, formation of an outer-sphere ion pair with Zr-bound ethene is calculated to require 19 kJ/mol; this is more endothermic by 57 kJ/mol than for the analogous reaction with Me_2O (Table 8). The reaction energy for formation of the outer-sphere ion pair **11c** from **9a** and propene is 11 kJ/mol. A higher Lewis basicity of propene, presumably by stabilization of positive charge on the β-C atom by the methyl substituent, is in agreement with coordination energies quoted by other authors, which are more exothermic for propene by ca. 10 kJ/mol.[8e]

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(54) Bonding distances calculated for coordinated propene in **11b** ($Zr-C_1$ = 2.67 Å and $Zr-C_2$ = 3.04 Å) are comparable to those observed in crystal structures of tetrahedral zirconocene complexes containing a chelated $O-CHMe-(CH_2)_2-CH=CH_2$ ligand (see ref 15b). As reported in these cases as well as in previous calculations on cationic alkyl zirconocene complexes (see refs 8a,b,d), the olefin is found to be unsymmetrically bound.

(55) Without restraints, coordination of a trifluoromethyl group of the hypothetical $MeB(CF_3)_3^-$ anion to the metal center is followed by dissociation of the olefin ligand or by its insertion into the zirconium−methyl bond; finally fluoride is abstracted from the anion.

Table 9. Selected Bond Distances[a] (Å) and Angles (deg) Calculated for Olefin Complexes with Structures 10b–e and 11b–c

	10b	**10c**	**10e**	**11b**	**11c**
Zr–C_{term}[b]	2.31	2.24	2.34	2.30	2.25
Zr–C_μ (Zr–H)[b]	3.41 (2.40)	7.4	2.90 (2.32)	3.65 (2.66)	7.4
Zr–B	4.72	5.91	4.43	4.90	5.95
Zr–Z_{Cp}	2.23, 2.23	2.22, 2.24	2.24, 2.24	2.23, 2.23	2.22, 2.25
Zr–olefin[b]	2.81, 2.83	2.79, 2.82	3.01, 3.01	2.67, 3.04	2.57, 3.11
C_{term}–Zr–C_μ[b]	141		140	145	
Z_{Cp}–Zr–Z_{Cp}[b]	126	126	126	126	126
Si–Zr–C_1(olefin)	177	139	163	173	150

[a] In Å. [b] C_{term}: methyl ligand bonded to Zr, C_μ: bridging methyl group bonded to B, carbon atoms of the olefin given in the order C_1, C_2.

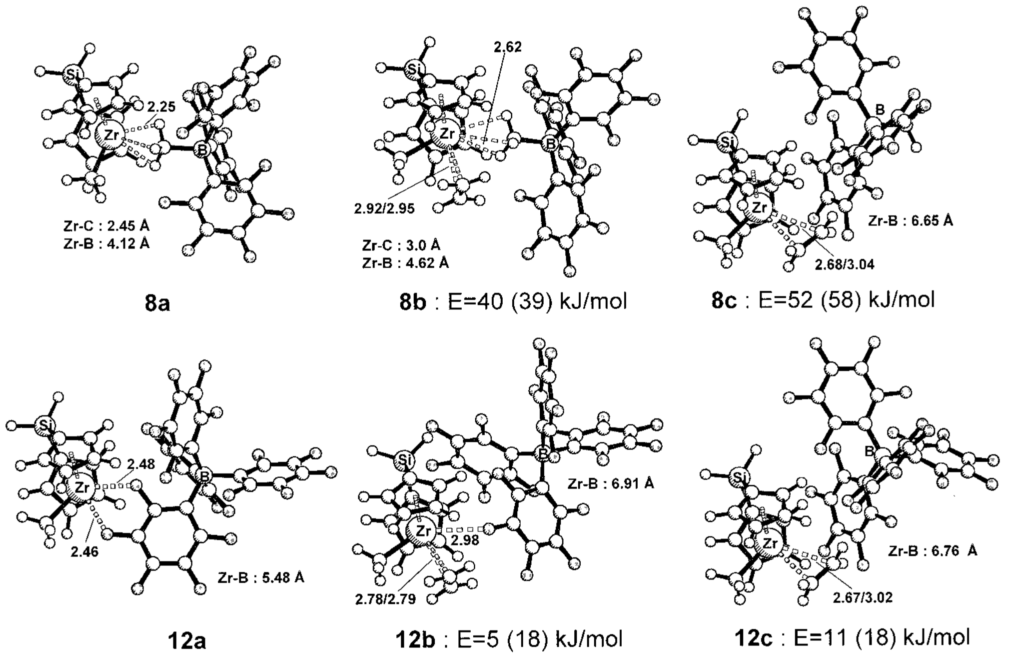

Figure 7. Geometries of intermediates and products of anion substitution from **8a** and **12a** by ethene calculated by DFT methods.

Formation of the five-coordinated complexes **10b** and **11b**, on the other hand, requires 22–23 kJ/mol, both for ethene and propene. This similarity between the two olefins is unexpected in view of their different Lewis basicity. The more symmetrical bonding of the olefins in these five-coordinated complexes would indicate a less pronounced buildup of positive charge on the β-carbon. In addition, steric interactions, which are more unfavorable in the case of propene, might counteract its electronic advantages. The transition state, **10e**, for the formation of the five-coordinated ethene complex **10b** has a geometry that is rather similar to that of the latter (see Table 9). It is located at an energy of 32 kJ/mol above that of **9a** and free ethene, i.e., 10 kJ/mol above that of **10b**.

To study the influence that the anion might have on the substitution process, five-coordinated intermediates and outer-sphere reaction products were calculated for the reactions of ethene with the methyltris(pentafluorophenyl)borate ion pair $H_2Si(C_5H_4)_2ZrMe^+MeB(C_6F_5)_3^-$, **8a**, and with the tetrakis(pentafluorophenyl)borate complex $H_2Si(C_5H_4)_2ZrMe^+B(C_6F_5)_4^-$, **12a** (Figure 7).[56] Rearrangement of the five-coordinated intermediates to the outer-sphere ion pairs, i.e., from **8b** to **8c** and **12b** to **12c**, is calculated to be endothermic with reaction energies of 12 and 6 kJ/mol, respectively (Table 8). While these reaction energies would indicate that five-coordinated intermediates occur in notable concentrations, formation of outer-sphere ion pairs is likely to be favored again by reaction entropies (vide supra). Formation of the five-coordinated intermediate and of the outer-sphere complex requires 35–41 kJ/mol less for $B(C_6F_5)_4^-$ than for $MeB(C_6F_5)_3^-$ as the counterion.[57] This is in agreement with results from NMR experiments: While DBE reacts with *rac*-$Me_2Si(2\text{-}Me\text{-}BenzInd)_2ZrMe^+$-$MeB(C_6F_5)_3^-$, **7a**, only partly within about 1 h, an immediate and complete reaction was observed when $B(C_6F_5)_4^-$ instead of $MeB(C_6F_5)_3^-$ was displaced by DBE. The increased rate and extent of $B(C_6F_5)_4^-$ displacement might explain the generally higher polymerization activity of zirconocene ion pairs with the tetrakis(pentafluorophenyl)borate anion.

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(56) $B(C_6F_5)_4^-$ coordination is possible either through two fluorine atoms in the ortho and meta or in the meta and para posititions of the phenyl ring. Since the latter results in an increased zirconium–boron distance, the resulting structures are higher in energy by 47 kJ/mol. In both cases, coordination with the $B(C_6F_5)_3$ fragment pointing to the outside of the complex, i.e., with the ortho-fluorine in the lateral or the para-fluorine in the central coordination site, is more stable by 1–2 kJ/mol (see Supporting Information).

(57) In accord with this energy difference, we find that coordination of the $MeB(C_6F_5)_3^-$ anion in the contact ion pair **8a** via the methyl group is more stable by 31 kJ/mol than coordination via two of the fluorine atoms (see Supporting Information).

Table 10. Reaction Energies[a] (in kJ/mol) Calculated for the Displacement of $MeB(C_6F_5)_3^-$ and $B(C_6F_5)_4^-$ Anions by Ethene

	$H_2Si(C_5H_4)_2ZrMe^+$	Cp_2ZrMe^+		Cp_2ZrEt^+	Cp_2ZrBu^+	$(Me_2C_5H_3)_2ZrMe^+$			
	this work	ref 21	ref 13b	ref 14	ref 13a	ref 13d	this work		
anion	nonlocal[b]	nonlocal [b]	local [b]	nonlocal [b]	local[b]	local [b]	local [b,c]	nonlocal[b,d]	nonlocal[d,e]
$MeB(C_6F_5)_3^-$	52 (58)	(44)	34	(9/−4)[f]	(38)	59	71 (91)		
$B(C_6F_5)_4^-$	11 (18)			(−19/−40) [f]		−65	−59 (−41)	10 (31)	9 (32)

[a] Single-point energies in toluene solution with gas-phase-optimized geometries (energies in gas phase are denoted with parentheses). [b]Functional used for determination of the molecular geometry. [c]Geometries taken from ref 13d. [d]Geometries taken from ref 13d and reoptimized with the gradient-corrected BP functional. [e]Alternative geometry for the contact ion pair. [f]Olefin complex without/with β-agostic interaction of the ethyl group.

In any case, we find that anion displacement proceeds by way of a five-coordinated intermediate with ethene or propene in the central coordination position. While alternative reaction pathways have been proposed in several recent DFT studies,[12,13] our results are fully in agreement with a thorough study by Nifant'ev et al.,[14] in which transition states for various pathways of anion substitution were compared for the first time.

Reaction energies obtained here for exchange of $MeB(C_6F_5)_3^-$ by ethene in the gas phase and in toluene solution (52 and 58 kJ/mol, respectively) agree well with values of 34−59 kJ/mol previously calculated[13] or obtained by combining DFT methods and NMR results (Table 10).[21] Much more negative reaction energies were obtained by Vanka et al. for exchange of $B(C_6F_5)_4^-$ by ethene.[13c,d] Reoptimization of the reported molecular geometries[13c,d] with a nonlocal functional, however, lead to substantial changes in the geometry of the contact ion pair and to more endothermic reaction energies for the formation of the outer-sphere complex, which are in close agreement with our results.

For anion substitution in $Cp_2ZrEt^+A^-$, exothermic reaction energies have been calculated by Nifant'ev et al. from geometries obtained with nonlocal functionals (Table 10).[14] Activation and reaction energies obtained by these authors for the formation of five-coordinated intermediates are also lower by 20−30 kJ/mol than the values obtained here. These differences can be attributed at least in part to the stabilization of the electron-deficient olefin complex by a β-agostic interaction of the ethyl group. Our values of 11 and 52 kJ/mol calculated for the displacement of $B(C_6F_5)_4^-$ or $MeB(C_6F_5)_3^-$ from $H_2Si(C_5H_4)_2ZrMe^+A^-$ by ethene are thus likely to represent an upper limit for the respective reaction energies.

In summary, our DFT calculations support the picture of the anion displacement by a Lewis base derived from experimental data, most notably the associative character of this ligand exchange reaction as well as its stereochemistry. With olefin as a Lewis base, the reaction follows the same patterns. Although our results lead us to assume that anion displacement by ethene or propene is likely to be slower than that by Me_2O, we refrain from quantitative estimates of the rates with which these olefins might displace the anion from alkyl zirconocene ion pairs, due to the ill-defined effects of reaction entropies and solvent interactions. Nevertheless, it is to be expected that the relative rates of anion displacement by an olefin follow a pattern similar to that observed for DBE in the series **1a**−**7a**.[58]

Conclusions

From the experimental and theoretical results obtained above, we can derive the following conclusions concerning elementary reactions in zirconocene-based catalyst systems for the polymerization of olefins.

The unexpectedly small rate constants found for the substitution of the methylborate anion by Lewis bases, e.g., in the case of complex **7a**, indicate that the initial displacement of the anion from the metal centers will result in observable induction periods in polymerization experiments, especially for propene in conjunction with demanding zirconocene substituents, for which unfavorable steric interactions are likely to interfere with the formation of five-coordinated intermediates. Stopped-flow experiments at 40 °C with the catalyst *rac*-Me_2Si-(2-Me-4-Ph-Ind)$_2$$ZrCl_2$/MAO have indeed revealed an induction period of about 0.3 s for the growth of polymer chains with propene as monomer, while none was observed for ethene.[59]

In the outer-sphere ion pair arising from the initial substitution reaction, subsequent olefin insertions are likely to proceed by way of a chain migratory insertion mechanism analogous to that calculated for "free" alkyl zirconocene cations.[8] Coordination of an olefin and chain growth are then in constant competition with re-coordination of the anion. The rate with which the model ligand DBE is substituted by the methylborate anion, $k_{-1} = k/K$, can be obtained from the experimental data in Table 4 to be in the range 3×10^{-5} to 0.8 s^{-1} for complexes **1a**−**7a**. Even though olefins, as weaker Lewis bases,[60] are probably replaced more rapidly than dibutyl ether, it appears unlikely that substitution of the olefin by the methylborate anion (and even more so by less coordinating cocatalyst anions such as $B(C_6F_5)_4^-$ or X-MAO^-) can compete with the insertion reaction, for which rates of approximately 10−100 s^{-1} can be estimated from overall polymerization activities.

It might be argued that re-coordination of the anion would occur to a coordinatively unsaturated insertion product after each insertion step, instead of by an olefin displacement. Such a scenario would require that the anion be displaced again by an olefin before the next

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[58] From molecular mechanics calculations it can be estimated that displacement of $MeB(C_6F_5)_3^-$ follows a similar trend with regard to steric interactions in the series **1a**−**7a** for DBE as well as for ethene and propene (see Supporting Information).

[59] Busico, V.; Cipullo, R.; Esposito, V. *Macromol. Rapid Commun.* **1999**, *20*, 116.

[60] Catalyst activity in MAO-activated polymerizations using the dichloride analogue of **7a** is completely quenched by addition of DBE in concentrations of 10^{-4}−10^{-3} mol/L, i.e., lower by several orders of magnitude than that of propene (Schaper, F.; Kirsten, R.; Brintzinger, H. H. Unpublished results).

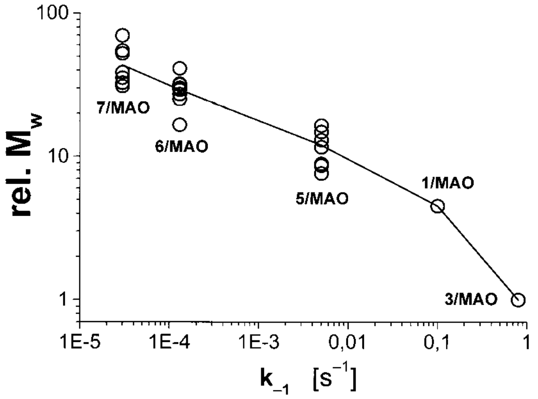

Figure 8. Correlation of estimated relative molecular weights in propene and ethene polymerizations catalyzed by the dichloride analogues of **1a**−**7a**/MAO relative to **3a**/MAO with the rate constant of anion re-coordination, estimated for the substitution of dibutyl ether (DBE) by $MeB(C_6F_5)_3^-$.

insertion can occur. Our results indicate, however, that such an anion displacement would be much too slow in comparison with average rates of polymer chain growth, at least for more highly substituted complexes such as **6a** and **7a**. This allows us to conclude that coordination of an olefin to the coordinatively unsaturated insertion product is faster than coordination of the anion by reorganization of the outer-sphere ion pair.

Lifetimes of approximately 100 s, however, for which a polymer chain remains attached to a zirconium center, might be long enough for re-coordination of the anion to occur. A possible consequence of the formation of a zirconocene polymer contact ion pair is the termination of chain growth. Such an anion-initiated chain termination might explain shorter chain lengths found in some polymerizations using the methylborate anion $MeB(C_6F_5)_3^-$ compared to the less coordinating $B(C_6F_5)_4^-$ anion[29,47b] and relative molecular weights obtained in MAO-activated ethene and propene polymerizations using the dichloride analogues of **1a**−**7a**.[61] Chain lengths in these polymerizations differ by a factor of ca. 100 and correlate qualitatively with the estimated rate constants of anion re-coordination (Figure 8).

These considerations make it likely that practically important polymer properties are connected with relative rates of ligand substitution in metallocene catalyst systems. It would therefore appear highly desirable to gain more direct access, by improved experimental or theoretical methods, to the rates with which olefins displace different anions or—in the case of MAO-activated catalysts—trimethylaluminum units from coordinative contact with the Zr centers of different catalysts.[1,2,62]

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Supporting Information Available: Tables of proton ^1H NMR data for reactions of **1a**−**7a** with Lewis bases. DFT calculations regarding effects of the ligand framework. Molecular mechanics calculations of the substitution reaction. Details on the determination of kinetic constants in the 2D NMR experiments and on the determination of relative molecular weights. Energy profiles of anion dissociation from complexes **8a** and **9a**. Tables of absolute energies and of atomic coordinates for complexes calculated by DFT methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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(61) (a) Karol, F. J.; Kao, S.-C.; Wasserman, E. P.; Brady, R. C. *New J. Chem.* **1997**, *21*, 797. (b) Suhm, J.; Schneider, M. J.; Mülhaupt, R. *J. Mol. Catal. A: Chem.* **1998**, *128*, 215. (c) Spaleck, W.; Kuber, F.; Winter, A.; Rohrmann, J.; Bachmann, B.; Antberg, M.; Dolle, V.; Paulus, E. P. *Organometallics* **1994**, *13*, 954. (d) Stehling, U.; Diebold, J.; Kirsten, R.; Röll, W.; Brintzinger, H. H.; Jüngling, S.; Mülhaupt, R.; Langhauser, F. *Organometallics* **1994**, *13*, 964. (e) Herfert, N. Dissertation, MPI Mülheim, Universität Düsseldorf, 1992.

(62) Bochmann, M.; Lancaster, S. J. *Angew. Chem.* **1994**, *106*, 1715.