

Diffusion coefficients of zirconocene–borate ion pairs studied by pulsed field-gradient NMR—evidence for ion quadruples in benzene solutions

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Diffusion coefficients for ion pairs containing zirconocene cations and fluorinated tetraphenyl- or methyltriphenylborate anions in benzene solutions are substantially smaller than those expected for monomeric species and indicate that ion quadruples are present in these solutions.

Electron deficient metallocene alkyl cations of group 4 metals, in combination with weakly coordinating anions are considered to be reactive species in homogeneous olefin polymerization catalysis.¹ Particularly well defined in this regard, in several instances even by solid-state structures,^{2,3a} are zirconocene ion pairs which contain the fluorinated borate anions $B(C_6F_5)_4^-$ or $MeB(C_6F_5)_3^-$; these are obtained by reaction of a dimethyl zirconocene complex with a triorganylammonium or triphenylcarbenium salt of $B(C_6F_5)_4^-$ or with $B(C_6F_5)_3$, respectively.⁴ The binding of the anion to the cationic center in these contact-ion pairs is of importance for the activity of a catalyst system, since the anion A^- has to be displaced by the olefin substrate to initiate the catalytic cycle. Exchange of these anions between zirconocene coordination sites as well as their displacement by entities such as a Lewis base, $AlMe_3$ or another dimethyl zirconocene complex have been studied in considerable detail.^{1–3} Rather little is known, however, about the structures of these ion pairs in solution, especially with regard to the extent to which they form dissociated, associated or aggregated ion pairs in the non-polar solvents commonly used for homogeneous olefin polymerizations. In order to clarify this point, we have determined the size of these catalytically active species in solution by measuring their translational diffusion coefficients D_t by NMR methods.

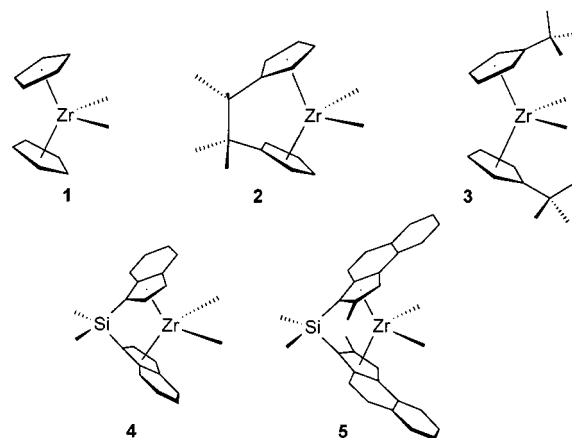
The LED (longitudinal eddy current delay) experiment measures the intensity of a spin-echo amplitude as a consequence of the change in spatial position of a molecule during the time interval between two pulsed field gradients.⁵ The changing signal intensity (I) with incremented gradient strength G is related to the translational diffusion coefficient D_t by the Stejskal–Tanner equation $I = I_0 \exp\{-(\gamma\delta G)^2 [\Delta - (\delta/3)] D_t\}$,⁶ where γ is the gyromagnetic ratio, δ the gradient duration and Δ the interval between the pulsed field gradients. The method works also for complexes and salts.⁷ For approximately spherical particles which are significantly larger than the solvent molecules, the Stokes–Einstein equation $D_t = kT/(6\pi\eta r)$, where k = Boltzmann constant, T = absolute temperature and η = viscosity of the solvent, is used to relate the translational self-diffusion coefficient D_t to the radius r of the dissolved particle. For molecules with van der Waals radii $r_W < 5 \text{ \AA}$, the Stokes–Einstein factor of 6 has to be changed to a value of 4.⁸ We find this so-called perfect slip condition to hold for dilute benzene solutions of the bis(cyclopentadienyl) dimethylzirconium compounds shown in Scheme 1 (Table 1). The diffusion coefficients of these neutral, monomeric zirconocene complexes decrease linearly with increasing molecular size: The inverse diffusion coefficients of these species correlate with their calculated van der Waal's radii r_W with deviations of <10% (Fig. 1).

Rather unexpected results, however, pertain to a number of ion pairs derived from compounds **1** and **5**: While the D_t value obtained for the methylborate ion pair **5A** deviates only slightly from the calibration provided by compounds **1–5**, the experimentally determined D_t value of ion pair **1A** amounts to only ca. 80% of the expected value. These deviations from expectation are even more pronounced for the ion pairs **1B** and **5B**, which contain the more weakly coordinating $B(C_6F_5)_4^-$ anion and are, hence, presumably more polar. The D_t value obtained for ion pair **1B** in particular ($5.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$), yields an apparent particle volume of 1260 \AA^3 , which corresponds to just twice the expected volume of this ion pair.

Even though a number of caveats have to be heeded—a pronounced anisotropic molecular shape, a change from perfect slip (SE factor 4) to perfect stick conditions (SE factor 6) or an increased solvent shell might contribute to the observed decrease of D_t —we propose that ion pair **1B** is present in these solutions predominantly in form of its dimer, *i.e.* of an ion quadruple (Scheme 2). This contention is supported by the observation that **1B** has practically the same diffusion coefficient as the related ion pair $[(C_5H_5)_2ZrMe(\mu-Me)Me-Zr(C_5H_5)_2]^+ B(C_6F_5)_4^-$ **1C**, for which a binuclear structure has been independently established.^{3a,9}

From the theory of ion solutions in organic solvents it is indeed to be expected that ion quadruples are present in benzene solutions of ion pairs such as **1B** at the concentrations considered here,¹⁰ which are close to the limiting concentrations at which these ion pairs begin to form separate phases. In accord with these theoretical considerations, the degrees of ion quadruple formation, indicated by the deviations of D_t from the values expected for monomeric species, are higher for the more polar ion pairs **1B** and **5B** than for the presumably partly covalent ion pairs **1A** and **5A** and higher for ion pairs **1A** and **1B**, which contain the rather small $(C_5H_5)_2ZrMe^+$ cation, than for their more voluminous analogues **5A** and **5B**, respectively.

More detailed data on degrees of aggregation and their dependence on the nature of the zirconocene cation and its counter anion will clearly be needed for a full description of



Scheme 1

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Table 1 Diffusion coefficients D_t , measured for the neutral dimethyl zirconocene compounds **1–5** and for the ion pairs **1A–C** and **5A, B** in C_6D_6 solution at 300 K, and van der Waals radii r_W and molecular volumes V_W of these zirconocene complexes

Zirconocene complex ^a	$10^{10} D_t^b/m^2 s^{-1}$	$r_W^c/\text{Å}$	$V_W^c/\text{Å}^3$
1 $(C_5H_5)_2ZrMe_2$	14.9	3.6	196
2 $Me_4C_2(C_5H_4)_2ZrMe_2$	13.4	4.1	290
3 $(C_5H_4Bu^t)_2ZrMe_2$	12.0	4.3	335
4 $rac\text{-}Me_2Si(ind)_2ZrMe_2$	11.5	4.4	354
5 $rac\text{-}Me_2Si(2\text{-}Me\text{-}benz[e]ind)_2ZrMe_2$	10.1	4.9	481
1A $[(C_5H_5)_2ZrMe^+\cdots MeB(C_6F_5)_3^-]$	8.1	5.0	513
1B $[(C_5H_5)_2ZrMe^+\cdots B(C_6F_5)_4^-]$	5.1	5.2	593
1C $\{[(C_5H_5)_2ZrMe]_2(\mu\text{-}Me)^+\} B(C_6F_5)_4^-$	4.9	5.7	789
5A $[rac\text{-}Me_2Si(2\text{-}Me\text{-}benz[e]ind)_2ZrMe^+\cdots MeB(C_6F_5)_3^-]$	8.2	5.7	797
5B $[rac\text{-}Me_2Si(2\text{-}Me\text{-}benz[e]ind)_2ZrMe^+\cdots B(C_6F_5)_4^-]$	6.1	5.9	877

^a Zirconocene concentrations ($mmol\ dm^{-3}$): **1**, 1–20; **2–5**, 1; **1A**, 4.7; **1B**, 1.6; **1C**, 2; **5A**, 4; **5B**, 2. ^b Measured on a Bruker DRX 600 spectrometer with a BGU II gradient unit using ten different gradient strengths ($5\text{--}50\ G\ cm^{-1}$) of 1 ms duration, with diffusion times Δ of 0.5 s (32 scans) and relaxation delays of 20 s. Integrals and peak intensities were quantified with the Bruker T1/T2 software package. Independent D_t values, determined for individual NMR signals of each complex, gave the average values listed with mean deviations of $< 5\%$. ^c Calculated from molecular hard-sphere volume increments: D. Ben-Amotz and K. G. Willis, *J. Phys. Chem.*, 1993, **97**, 7736.

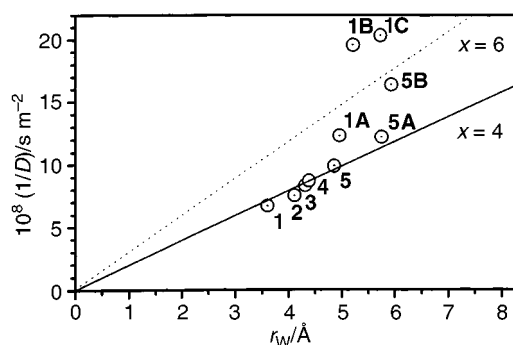
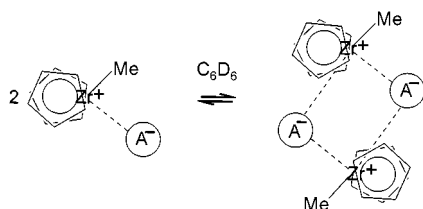


Fig. 1 Reciprocal diffusion coefficients, $1/D_t$, and van der Waals radii, r_W , for the neutral zirconocene complexes **1–5**, for the ion pairs $[(C_5H_5)_2ZrMe^+\cdots MeB(C_6F_5)_3^-]$ **1A**, $[(C_5H_5)_2ZrMe^+\cdots B(C_6F_5)_4^-]$ **1B**, $[rac\text{-}Me_2Si(2\text{-}Me\text{-}benz[e]ind)_2ZrMe^+\cdots MeB(C_6F_5)_3^-]$ **5A** and $[rac\text{-}Me_2Si(2\text{-}Me\text{-}benz[e]ind)_2ZrMe^+\cdots B(C_6F_5)_4^-]$ **5B**, and for the dinuclear complex $\{[(C_5H_5)_2ZrMe]_2(\mu\text{-}Me)^+\} B(C_6F_5)_4^-$ **1C**.



Scheme 2

reaction systems of this type. From the data presented here it is already clear, however, that the hitherto entirely neglected formation of ion quadruples will have to be taken into account for an analysis of exchange reactions between anions and other ligands in zirconocene-based catalyst systems.

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Notes and references

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