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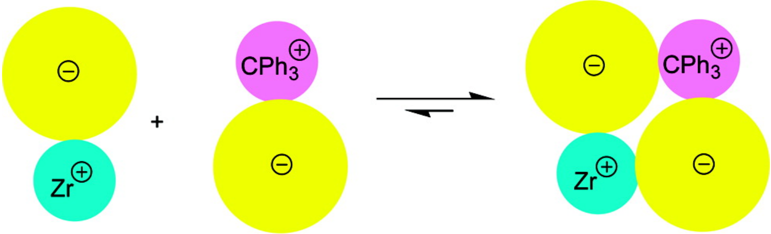

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Evidence for Mixed-Ion Clusters in Metallocene Catalysts: Influence on Ligand Exchange Dynamics and Catalyst Activity

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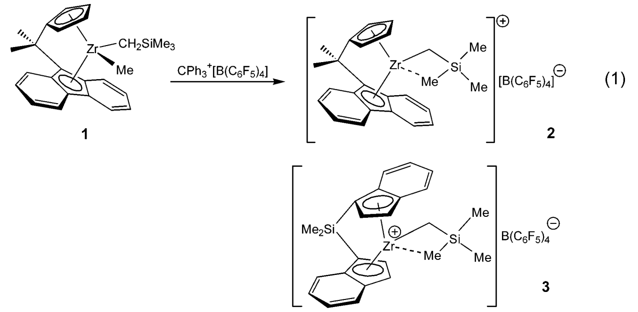
Ionic metallocene alkyl complexes $[L_2M{-}R^+\cdots X^-]$ (M = Ti, Zr, or Hf) are well-known as highly active olefin polymerization catalysts.[1,2] The solution structure of these catalysts in typical hydrocarbon solvents is, however, complicated by their tendency to form ion aggregates $[L_2M{-}R^+\cdots X^-]_n$ (n = 2, 3, or higher).[3−5] These ion aggregates show enhanced dynamic behavior; that is, the rates of "chain swinging" or site epimerization, k_{ex}, increase with increasing ion pair concentration. Since alkyl ligand migration is a key step in polymer chain growth, such an enhancement in ligand mobility may have important implications for catalytic activity.

We have recently used the $Zr{-}CH_2SiMe_3$ complexes as a model for the metal-bound polymeryl chain in order to determine solution structures and dynamics of metallocene catalysts.[5,6] It was shown that the *ansa*-metallocene $[(SBI)Zr{-}CH_2SiMe_3{}^+\cdots B(C_6F_5)_4{}^-]$ (SBI = *rac*-$Me_2Si(1\text{-indenyl})_2$) exists as an outer-sphere ion pair where agostic interactions with the alkyl ligand are preferred over anion binding.[5] Catalysts of this type are generated by activating metallocene dialkyls with $[Ph_3C][B(C_6F_5)_4]$, and we found earlier that, surprisingly, the addition of $[Ph_3C][B(C_6F_5)_4]$ to metallocenes over and above the 1:1 stoichiometry required to generate the cationic metallocenium species can lead to very substantial increases in catalytic activity, by an order of magnitude in some cases ("trityl effect"), while no such enhancement was found for others.[7] We have therefore explored the role of trityl activator in these systems in more detail. Two catalyst systems were chosen for comparison, $[(SBI)Zr\text{-}R^+\cdots B(C_6F_5)_4{}^-]$ and $[(IPCF)Zr{-}R^+\cdots B(C_6F_5)_4{}^-]$ [IPCF = $Me_2C(C_5H_4)$(9-fluorenyl)]. These complexes differ mainly in the position of one annulated C_6 ring; however, whereas the SBI catalyst shows a strong trityl effect, the IPCF system does not. The results have provided the first evidence for the formation of mixed-ion aggregates in solutions of metallocene catalysts.

The ion pairs $[(L)Zr{-}R^+\cdots B(C_6F_5)_4{}^-]$ (**2**, L = IPCF; **3**, L = SBI) were prepared as shown in eq 1 for the new IPCF compound **2**.



1 **2** (1)

3

Table 1. Translational Diffusion Coefficient (D_t, 10^{-10} m^2 s^{-1}), Hydrodynamic Volumes (V_H, Å^3), and Aggregation Numbers (N) for $[(L)Zr(CH_2SiMe_3)][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$ Ion Pairs as a Function of the Total Ion Pair Concentration

entry	[Zr] (mM)	$[Ph_3C][B(C_6F_5)_4]$ (mM)	D_t^+	D_t^-	D_t^{CPh3+}	V_H^+	V_H^-	V_H^{CPh3+}	N^+	N^-
1	**2** (7)	−	5.24	5.17		1766	1823		1.8	1.9
2	**2** (7)	14	4.87	4.83		1941	1979		2.0	
3	**2** (7)	28	4.43	4.51		2208	2115		2.3	
4	**3** (7)	−	5.32	5.31		1689	1697		1.8	1.8
5	**3** (7)	28	4.50	4.53	4.74	2135	2092	1867	2.2	
6		0.9		6.83	6.87		922	909	1.1	1.1
7		8		5.81	5.78		1346	1354	1.6	1.6
8		39		4.72	4.74		1938	1924	2.3	2.3

^1H and ^{19}F pulsed field-gradient spin−echo (PGSE) NMR experiments were carried out for ion pairs **2** and **3** in toluene-d_8/1,2-$F_2C_6H_4$ (8:2 v/v) in the presence of variable amounts of $[Ph_3C][B(C_6F_5)_4]$, using 1,2-$F_2C_6H_4$ as internal standard. Solutions of $[Ph_3C][B(C_6F_5)_4]$ were also investigated over a concentration range of 0.9−39 mM. PGSE measurements allowed the translational self-diffusion coefficients (D_t) for both cationic (D_t^+) and anionic (D_t^-) moieties to be determined (Table 1). From the measured self-diffusion coefficients (D_t), the average hydrodynamic radius (r_H) of the diffusing particles was derived, taking advantage of the Stokes−Einstein eq 2:

$$D_t = \frac{kT}{c\pi\eta r_H} \qquad (2)$$

where k is the Boltzman constant, T is the temperature, c is a numerical factor and η is the solution viscosity. D_t data were treated taking all the methodological precautions described in a recent paper.[8] From r_H, the average hydrodynamic volumes ($V_H^+$and V_H^-) of the aggregates were obtained on the assumption that they had a spherical shape. The ratio between V_H and the hydrodynamic volume of a single ion pair (V_H^{IP0}),[9] determined as described in the Supporting Information, afforded the aggregation number N. In agreement with previous findings,[4c,5] both **2** ($N^+ = 1.8$, $N^- = 1.9$, Table 1, entry 1) and **3** ($N^+ = N^- = 1.8$, entry 4) lead to a predominance of ion quadrupoles[3a,4,5,10] at a concentration of 7 mM and exhibit the same tendency to self-aggregate.

Addition of a 4-fold excess of $[Ph_3C][B(C_6F_5)_4]$ resulted in a further and similar increase of the aggregation of the two ion pairs, with aggregation numbers that passed from 1.8−1.9 to 2.2−2.3 (cf. entries 1 and 3 for **2** and 4 and 5 for **3**). The observed increment reflects the formation of *mixed-ion* aggregates between the metallocenium ion pairs and $[Ph_3C][B(C_6F_5)_4]$, of the type $[\{LZrR^+\}_n\{CPh_3{}^+\}_m\{X^-\}_{(n+m)}]$.

Further support for the formation of mixed aggregates could be derived from the determination of V_H^+ for the CPh_3^+ cation, which is expected to increase when mixed aggregates are formed.

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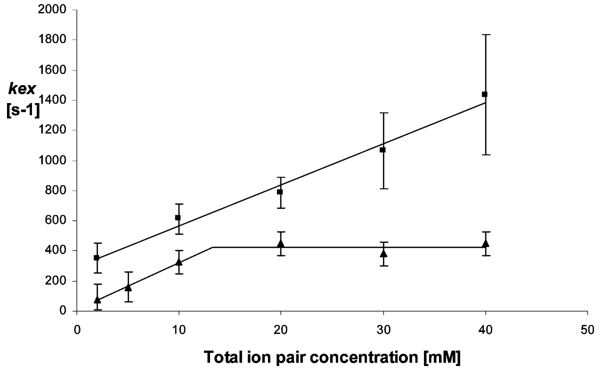

Figure 1. Site epimerization rate constants k_{ex} as a function of the ion pair concentration at 20 °C. (■) (SBI)ZrMe(CH_2SiMe_3)/$[Ph_3C]^+[B(C_6F_5)_4]^-$, (▲) (IPCF)ZrMe(CH_2SiMe_3)/$[Ph_3C]^+[B(C_6F_5)_4]^-$.

Unfortunately, two complications made this test difficult to carry out: (1) in some cases, the proton resonances of CPh_3^+ proved difficult to observe (Table 1, entries 2 and 3); (2) $[Ph_3C][B(C_6F_5)_4]$ alone self-aggregates, forming adducts of a dimension similar to those expected for mixed aggregates (Table 1, entries 6−8). Therefore, the strongest support for the formation of metallocenium/$[Ph_3C][B(C_6F_5)_4]$ mixed aggregates is the increase of N^+ observed for the former when the concentration of $[Ph_3C][B(C_6F_5)_4]$ is increased. While the effects of an excess of $[Ph_3C][B(C_6F_5)_4]$ on catalytic activity and site epimerization rate could be also explained assuming that an enhancement of the relative permittivity of the solution, due to the dissolution of a rather large amount of salt, leads to a weakening of the metallocenium ion pair, this is in conflict with the observed increase in the volume of the aggregates. Thus PGSE NMR results afford the crucial information to support an associative process between metallocenium ion pairs and $[Ph_3C]$-$[B(C_6F_5)_4]$.

The ion pair symmetrization rate constants ("anion exchange" rates k_{ex}) in ion pairs **2** and **3** in the absence of olefin were followed by variable-temperature ^{1}H NMR spectroscopy and calculated with the help of simulated spectra. The trends in k_{ex} are shown in Figure 1.

The site epimerization rates of **3** increase linearly with increasing ion concentration over the observed range of $[A^+X^-] = 2-50$ mM; as previously established, this increase is paralleled by the formation of larger ion aggregates; for example, at $[Zr] = 10$ mM, ion hextuplets are significantly present.[5] The rate increase is understandable assuming that in an ion cluster the attraction of a given ion to a particular counterion is weakened by the presence of other ions in the immediate vicinity. Thus an ion quadruple $[A^+X^-]_2$ can dissociate into $A^+\cdots[X^-A^+X^-]$, where $[X^-A^+X^-]$ represents a "super anion" of reduced nucleophilicity. This pathway is not open to a simple ion pair $[A^+X^-]$.[11]

Up to a site epimerization rate $k_{ex} \approx 400$ s^{-1}, the increase in rate for the IPCF ion pair **2** parallels the trend observed for the SBI analogue; that is, both systems respond equally to the presence of other ion pairs in the system. However, whereas in the case of **3** the rate acceleration with increasing ion pair concentration continues over the observed concentration range from 2 to 50 mM, up to $k_{ex} \approx 1400$ s^{-1} at 20 °C, there is no such rate increase for the IPCF system **2**, and the exchange rate plateaus. Since both systems show no differences in the ion aggregation behavior, the most probable explanation for the limit imposed on the mobility of the alkyl ligand in the case of **2** is steric factors: catalysts that show no such barrier can be accelerated by excess ionic activator, while others such as **2** are unable to show such a response. The results demonstrate that ion concentration induced rate acceleration can be used to probe previously inaccessible kinetic barriers to ligand mobility.

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Supporting Information Available: Synthesis of **1** and **2**, PGSE and VT NMR measurements This material is available free of charge via the Internet at http://pubs.acs.org.

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