Cation–Anion Interactions

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Weakly Coordinating Cations as Alternatives to Weakly Coordinating Anions**

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The ongoing pursuit of weakly coordinating anions[1] (WCAs) has allowed the synthesis, isolation, and catalytic utilization of highly electrophilic transition-metal[2] and main-group[3] species. The combined strategies of charge delocalization and kinetic stabilization have yielded classic WCAs such as $[B(C_6F_5)_4]^-$ and exotic dinuclear WCAs like $[(C_6F_5)_3Al(imidazolyl)Al(C_6F_5)_3]^-$.[4,5] While a truly non-coordinating anion has not been identified, there is little doubt that this class of anion has been a wellspring of both fundamental insights and industrial applications.[6]

During our studies of sterically expanded single-site catalysts for olefin polymerization,[7] we observed consistent trends indicating that increased steric bulk around the electrophilic transition metal yielded increased catalytic activity, for both metallocene catalysts (Figure 1) and constrained-geometry catalysts (CGCs).[8] These observations are reminiscent of the increased activities observed with increasingly non-coordinating anions, but they must have a different root cause, as the same methylaluminoxane (MAO)-derived counteranion was common among these polymerizations.

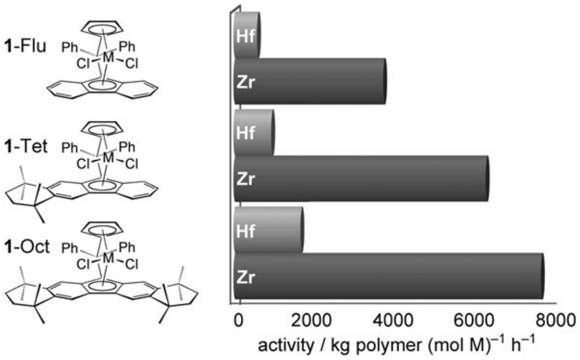

Figure 1. Catalyst steric bulk increases the activities of MAO-co-catalyzed propylene polymerizations ($T_p = 20$ °C).

We postulated that the increased activity was a result of steric shielding effected by the expanded ancillary ligands; this steric sheath diminished the ability of the encased electrophilic metal center to accept the larger counteranion, but it still allowed access to the relatively small monomers. Figure 2 illustrates how steric bulk might retard the accepting ability of such electrophiles, resulting in what should be weakly coordinating cations (WCCs).[9] We then sought additional evidence to test this supposition and turned our attention to UV/Vis spectroscopy.[10]

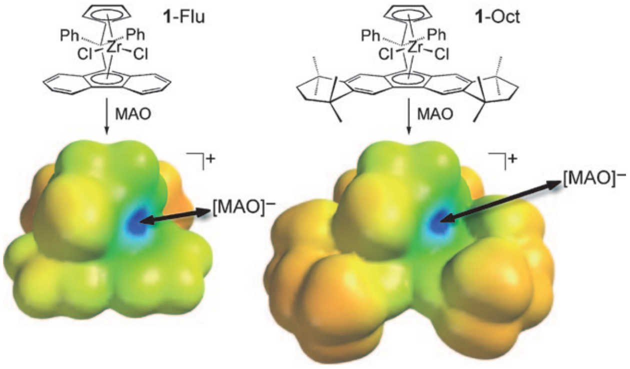

Figure 2. Steric encapsulation of the electrophilic metal center results in a more weakly coordinating cation. (Potential energy surface for $[\{Ph_2C(C_5H_4)(C_xH_y)\}ZrCH_3]^+$ depicted.)

Upon activation with MAO (5000 equiv), zirconocene $[\{Ph_2C(C_5H_4)(C_{13}H_8)\}ZrCl_2]$ (**1**-Flu) undergoes an immediate red shift of its visible absorption maximum λ_{max} from 499 to 557 nm ($\Delta E = -5.97$ kcal mol^{-1} = -25.0 kJ mol^{-1}). Zirconocene $[\{Ph_2C(C_5H_4)(C_{29}H_{36})\}ZrCl_2]$ (**1**-Oct) also undergoes a rapid red shift, but of significantly greater magnitude: 521 to 622 nm ($\Delta E = -8.91$ kcal mol^{-1} = -37.3 kJ mol^{-1}). For these species, λ_{max} corresponds to a ligand-to-metal charge transfer (LMCT),[10a,11] and the change in λ_{max} upon MAO activation is a direct measure of the resultant electron density at the zirconium center, because the LMCT is correspondingly more facile for more electron-deficient metals. Thus, the zirconocenium ion pair generated from **1**-Oct features a more electron-deficient metal center, and a plausible explanation for this electron deficiency is a greater average cation–anion separation caused by steric shielding (Figure 2).

Over the course of 3 h, the λ_{max} of activated **1**-Oct relaxes back to 590 nm, while the λ_{max} of activated **1**-Flu remains unchanged at 557 nm. Figure 3 plots this dynamic process and

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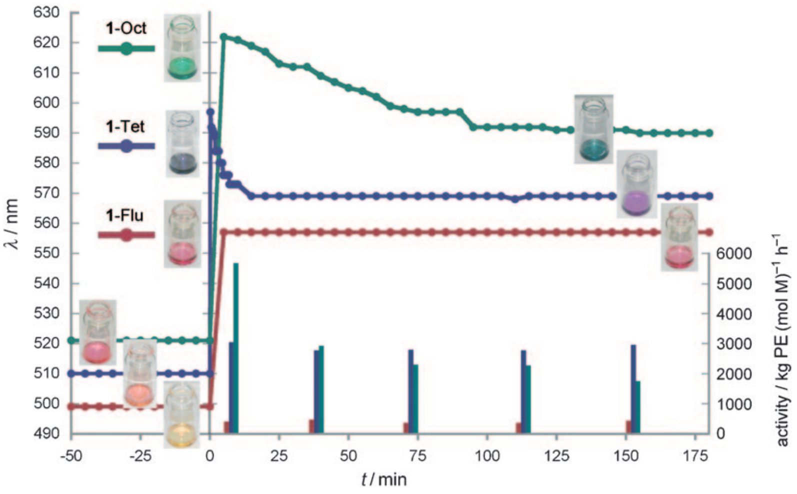

Figure 3. The addition of 5000 equivalents of MAO to **1**-Flu, **1**-Tet, or **1**-Oct effects a red shift in λ_{max} proportional to the size of the metallocene and a subsequent temporal blue shift in λ_{max} that is particularly slow for **1**-Oct, thus indicating that it initially is a weak acceptor of the MAO counteranion.

also includes the temporal dependence of **1**-Tet ([{Ph_2C-(C_5H_4)($C_{21}H_{22}$)}$ZrCl_2$]), which exhibits an initial red shift of intermediate energy (510 to 597 nm; $\Delta E = -8.17$ kcal mol^{-1} = -34.2 kJ mol^{-1}), blue shifts much faster than **1**-Oct (ca. 15 min), and is intermediate in steric size. The half-life ($t_{1/2}$) for **1**-Oct is calculated to be 32 min, while that for **1**-Tet is shorter by an order of magnitude (2.9 min). Repetition of these experiments yielded similar half-lives of 29 and 2.2 min, respectively. Our explanation of this behavior is that the initially formed MAO counteranion assumes a structure that readily approaches the **1**-Flu cation but is farther from the **1**-Oct cation because of steric shielding. Over time, the MAO counteranion reorganizes to a sterically compatible structure that is more capable of interacting with the lowest unoccupied molecular orbital (LUMO) of the **1**-Oct cation; this interaction increases the electron density at the metal and blue shifts λ_{max}. Indeed, isosbestic points appear in the time-dependent UV/Vis spectra of both **1**-Oct (415, 483, and 609 nm) and **1**-Tet (469 and 579 nm), thus indicating the transformation of one structure into another and further supporting our argument that the MAO counterion reorganizes from a species that poorly associates with the metallocene to one that more strongly associates. These reorganization events are inconsequential to activated **1**-Flu and its λ_{max}, because the lack of steric shielding allows both the initial and reorganized counteranions to approach with equal facility, meaning that the effective positive charge and color of this compound are static over time.

Fittingly, the ethylene polymerization activity is proportional to the red shift of λ_{max} (Figure 3). For **1**-Oct, an increase in the metallocene/MAO aging period ($t = 5$, 35, 70, 110, or 150 min before monomer introduction) results in a progressive attenuation of polymerization activity, with the lowest activity matching the longest aging period and the smallest net red shift. For **1**-Flu, the activity is considerably less (6 % that of **1**-Oct for $t = 5$ min) and is essentially independent of the catalyst aging period, just like its λ_{max}. These observations complete the phenomenological connections between the metal's electron density, the λ_{max} of the LMCT, the average cation–anion distance, and the catalytic activity. Indeed, it appears that a sterically protected cation can be a relatively weak acceptor of the MAO counteranion.

Although MAO and its corresponding anions are complex molecules that adopt a variety of structures,[1,6] the dynamic phenomena caused by MAO (Figure 3) would generally not be expected from boron-based co-catalysts. Indeed, when the dimethyl zirconocenes **1**-Flu-Me_2 and **1**-Oct-Me_2 (in which the chlorido ligands of **1**-Flu and **1**-Oct are replaced by methyl groups) are activated by 1.0 equivalent $B(C_6F_5)_3$ in toluene, initial red shifts are observed in the λ_{max}, but there is no subsequent change in this absorption. This result is consistent with the presumed static structure of the $[MeB(C_6F_5)_3]^-$ counteranion. The initial red-shift energetics indicate a greater cation–anion distance for the activated **1**-Oct-Me_2 species (470 to 541 nm, $\Delta E = -7.98$ kcal mol^{-1} = -33.4 kJ mol^{-1}) than for **1**-Flu-Me_2 (452 to 502 nm, $\Delta E = -6.30$ kcal mol^{-1} = -26.4 kJ mol^{-1}).

Preliminary ^{19}F NMR spectroscopy provides a corroborating comparative distance assessment. Combining **1**-Flu-Me_2 with 1.0 equivalent $B(C_6F_5)_3$ in C_6D_6 (with C_6H_5F as internal reference) gives peaks in the ^{19}F NMR spectrum for *ortho*, *meta*, and *para* fluorine substituents of $\delta = -132.3$, -167.0, and -164.3 ppm, respectively, while the same experiment with **1**-Oct-Me_2 affords peaks at $\delta = -132.1$, -164.6, and -167.1 ppm. The observed deviations (from $\delta = -128.2$, -160.3, and -141.9 ppm in $B(C_6F_5)_3$ alone) upon introduction of a dimethyl metallocene are commonly interpreted as a measure of sp^3 character at the boron atom and thus of the ionic separation.[15] The *para* position is particularly sensitive, and the *para*-F peak deviations upon introduction of $B(C_6F_5)_3$ to **1**-Flu-Me_2 and **1**-Oct-Me_2 are $\Delta\delta = -22.4$ and -25.2 ppm, respectively. This latter change in chemical shift is surprisingly large and is apparently an unprecedented case in which the *para*-F chemical shift actually inverts with that of the *meta*-F atom. Even for the very weakly associated ion pair [NBu_3-(CH_2Ph)][$MeB(C_6F_5)_3$], the order does not invert (*o*, *m*, *p* at $\delta = -133.1$, -167.8, -165.0 ppm), although this assessment was made in the polar solvent CD_2Cl_2.[16] In the polar solvent C_6D_5Br, both **1**-Flu-Me_2 and **1**-Oct-Me_2 combine with $B(C_6F_5)_3$ to yield essentially the same ^{19}F NMR spectrum (*o*, *m*, *p* at $\delta = (-133.7 \pm 0.1)$, (-167.4 ± 0.1), (-164.8 ± 0.1) ppm). This stark contrast with the above results in C_6D_6 suggests that a specific interaction exists between the *para*-F atom and the transition metal in the nonpolar solvent. Specific *ortho*-F–metal interactions are known to result in drastic upfield shifts (to $\delta = -208.9$ ppm),[17] and perhaps the upfield *para*-F chemical shift in **1**-Oct-Me_2/$B(C_6F_5)_3$ indicates a preferential approach of the perfluoroaryl rings over the less extended borate methyl group into the sterically expanded metallocenium cation. In any case, the extreme behavior of **1**-Oct-Me_2/$B(C_6F_5)_3$, as evidenced by ^{19}F NMR spectroscopy, further illustrates the high degree of ion separation and matches the collective data from UV/Vis spectroscopy.

Upon activation of metallocenes **1**-Flu and **1**-Oct with increasing quantities of MAO, we noted that the ultimate color change was achieved with only 1000 equivalents for **1**-Oct, whereas 3000 equivalents were required for **1**-Flu. Interestingly, these same proportions of MAO, respectively, were found to give the maximum ethylene polymerization activities for these catalysts (Figure 4). This correlation further supports our idea that sterically expanded catalysts more weakly interact with counteranions and promulgates the economic advantages of employing less MAO co-catalyst with bulky single-site catalysts akin to **1**-Oct.

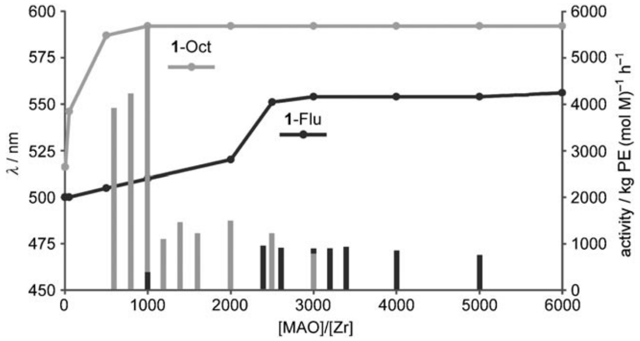

Figure 4. The [MAO]/[Zr] ratio required to effect the ultimate color change is the same as the ratio that maximizes the ethylene polymerization activity.

In summary, the addition of steric bulk to zirconocenium polymerization catalysts results in weakly coordinating cations that represent a complementary strategy to weakly coordinating anions for diminishing cation–anion interactions. In the present case, this decreased interaction resulted in a more electron-deficient metal, a weaker LMCT absorption in the UV/Vis spectrum, a greater cation–anion separation, and increased polymerization activity. Just as weakly coordinating anions have been extensively engineered to regulate catalyst behavior,[12] future modifications of weakly coordinating cations should offer improved control of catalytic performance.

Experimental Section

The *ansa*-metallocene dichlorides (**1**-Flu, **1**-Tet, and **1**-Oct) were synthesized according to previously reported methods.[7,13] (Oct = octamethyloctahydrodibenzofluorenyl; Tet = tetramethyltetrahydrobenzofluorenyl, and Flu = fluorenyl.)

Synthesis of the dimethyl zirconocenes[14] (**1**-Flu-Me$_2$ and **1**-Oct-Me$_2$) is as follows: In the glovebox, the appropriate zirconocene dichloride was added to a 50 mL recovery flask and dissolved in diethyl ether (ca. 20 mL). Methylmagnesium chloride (0.43 mL of a 22 wt % solution in THF, 2.2 equiv) was added by syringe, and a swivel frit apparatus was attached. The reaction was stirred at room temperature for three days, during which time a white precipitate formed. The swivel frit was rotated, and the reaction was filtered to remove the insoluble salt. The filtrate was concentrated to approximately 5 mL, cooled to 0 °C, and the frit was rotated again to isolate the product by filtration and in vacuo drying.

For all $t = 0$ min UV/Vis spectroscopy measurements, a stock solution of the appropriate metallocene (2.0 mM in toluene, 1.0 mL) was added to an air-tight cuvette apparatus inside the glovebox, and toluene (7.0 mL) was added. The apparatus was sealed with a teflon valve and brought out of the glovebox. A background spectrum was recorded using toluene in a matched cuvette, and the $t = 0$ min spectrum was recorded.

Inside the glovebox, the round-bottom portion of the air-tight cuvette apparatus was charged with the appropriate amount of a toluene stock solution of the chosen activator (MAO or $B(C_6F_5)_3$), enough toluene to bring the volume to 7.0 mL, and a stock solution (2.0 mM in toluene, 1.0 mL) of the chosen metallocene (**1**-Flu, **1**-Tet, **1**-Oct, **1**-Flu-Me$_2$, or **1**-Oct-Me$_2$). The apparatus was sealed with a teflon valve and brought out of the glovebox. A background spectrum was recorded using toluene in a matched cuvette. The apparatus was tipped to allow the activated catalyst solution to flow into the cuvette portion, and UV/Vis spectra were recorded every 5 min for 180 min (every 15 seconds for 15 min, then every 5 min for the next 165 min for **1**-Tet).

All polymerizations should be carried out in a fume hood and behind a blast shield. Polymerizations were carried out in an 85 mL glass Lab-Crest (Andrews Glass Company) cylindrical polymerization reactor equipped with a 5 cm octagonal stir bar able to provide ample surface agitation while stirring. In the glovebox, the vessel was charged with the appropriate amount of a 1.0 M MAO stock solution, enough toluene to bring the total volume in the reactor to 24.0 mL, and the appropriate precatalyst (0.5 mM in toluene, 1.0 mL). The addition of the precatalyst represents $t = 0$ min. The reactor was assembled, and the reaction mixture was allowed to stir inside the glovebox until 5 min before the polymerization run was to begin. In the case of the polymerization runs beginning at $t = 5$ min, the reactor was brought out of the glovebox immediately. After removal from the glovebox, the reactor was placed in a water bath held at 25 °C by a thermostat, and rapid stirring was begun. At the appropriate time, the reactor was pressurized to 40 psi with a continuous supply of ethylene. After the appropriate time (5 min for **1**-Flu, 3 min for **1**-Tet, and 1 min for **1**-Oct), the reaction was quenched by slowly venting the vessel and adding approximately 8 mL of an acidic methanol solution (methanol plus 10 % aqueous concentrated HCl). The insoluble polymer was collected by vacuum filtration and dried under reduced pressure.

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