Weak Interactions in Polymerization

Observation of Intramolecular C–H···F–C Contacts in Non-Metallocene Polyolefin Catalysts: Model for Weak Attractive Interactions between Polymer Chain and Noninnocent Ligand**

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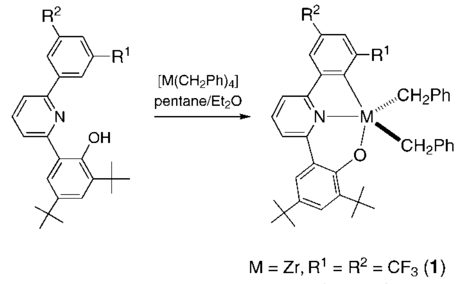
The mechanisms of stereoselectivity for the polymerization of prochiral α-olefins by Group 4 metallocene catalysts are well understood and are principally derived from steric effects (i.e. repulsive nonbonded interactions).[1] By comparison, the study of attractive interactions between the ancillary ligand and the polymer chain remains uncharted. In this context, multidentate ligands with mixed functionalities ("hemilabile" ligands) in which the labile moiety is employed to stabilize the metal center have been extensively utilized in late transition-metal catalysts[2] and more recently in metallocene-type derivatives.[3,4]

The application of attractive interactions between the ligand and growing alkyl chain to manipulate the reactivity of polyolefin catalysts becomes viable only if such interactions are weak and reversible, so that the intrinsic polymerization process is not disrupted. Significantly, the Fujita and Coates groups have recently described a novel class of fluorinated phenoxyimine titanium polyolefin catalysts. Fujita et al. reported that these catalysts can mediate living polyethylene formation at remarkably elevated temperatures[5] as well as highly syndiotactic living polymerization of propylene,[6a] and elucidated that propylene insertions occur with predominant 2,1 regiochemistry,[6b] which is exceedingly rare for Group 4 catalysts. Coates and co-workers observed virtually exclusive 2,1 regiochemistry for these Ti^{IV} fluorine-rich catalysts in ethylene/propylene copolymerization and cyclopolymerization processes.[7] Based on DFT calculations,[5b] Fujita and co-workers proposed that a fluorine atom adjacent to the imine nitrogen atom, which interacts with the polymer chain to curtail β-hydrogen-transfer pathways, is required for a living process. We now report the first direct observation of weak intramolecular C–H···F–C contacts in neutral and cationic Group 4 polyolefin procatalysts. The CH···FC interaction is amongst the weakest hydrogen bond to be proposed and apparent consensus regarding its validity has only just been reached.[8] Herein, the potential importance of such weak attractive interactions between the ligand and polymer chain in olefin polymerization processes will be emphasized.

We have targeted unsymmetric tridentate ligand sets that can support active olefin polymerization catalysts. In particular, we are evaluating the suitability of aromatic σ-carbanions, because the resultant metal–carbon bond should be more inert than aliphatic analogues and its relative covalency is expected to yield a highly electrophilic catalytic center. Metalation of 2-(2′-phenol)-6-arylpyridine substrates containing acidic protons ensues upon reaction with the basic metal precursors $[M(CH_2Ph)_4]$ (M = Zr, Ti) and is accompanied by elimination of toluene to afford complexes **1**–**3** as orange to red crystalline solids (Scheme 1). The cyclometalation process



M = Zr, $R^1 = R^2 = CF_3$ (**1**)
$R^1 = H$, $R^2 = CF_3$ (**2**)
M = Ti, $R^1 = R^2 = CF_3$ (**3**)

Scheme 1. Synthesis of **1**–**3**.

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readily proceeds at room temperature and appears highly regioselective; for complex **2**, in which two cyclometalation sites are available, only the pictured compound (where R^1 is less bulky) has been isolated or detected. We note that endeavors to synthesize Zr derivatives where $R^1 = R^2 =$ *tert*-butyl groups yielded intractable mixtures, characterization of which (by ^1H NMR spectroscopy) signified non-cyclometalation.

Characterization of complexes **1** and **3** by NMR spectroscopy was highly informative (also see Supporting Information). The ^1H NMR spectrum (C_6D_6) of **1** is typical for η^2-coordinated benzyl groups,[9] except that one of the two expected doublets for the diastereotopic methylene hydrogen atoms, at $\delta = 3.09$ ppm, appears as an overlapping doublet of quartets (Figure 1). Furthermore, the $^{13}C\{^1H\}$ NMR spectrum displays a quartet signal at $\delta = 70.50$ ppm ($J = 5.9$ Hz) for the methylene groups. The magnitudes of the coupling constants are clearly not consistent with formal six- or five-bond coupling. Subsequent ^{19}F decoupling of the ^1H NMR spectrum demonstrates coupling between one of the two CH_2 protons and three equivalent ^{19}F nuclei. Similarly, while the coupling in the $^{19}F[^1H]$ NMR spectrum is not clearly resolved, the $^{19}F\{^1H\}$ NMR spectrum undergoes significant narrowing for the downfield signal at $\delta = -58.09$ ppm only (Figure 1). A ^{19}F–^1H 2D correlation experiment (see Supporting Information) also revealed a cross-peak between the upfield ^1H multiplet and the downfield ^{19}F signal only. These observations thus strongly implicate the existence of intramolecular "through-space" coupling through C–H···F–C hydrogen bonds.[10] The effects of solvent polarity upon this coupling have been probed, and $^{1h}J_{H,F}$ values of 3.3 and 3.1 Hz in C_6D_6 and CD_2Cl_2, respectively, have been obtained, whereas in $[D_8]$THF this coupling is unresolved yet still apparent (Figure 1). The decreases in the $^{1h}J_{H,F}$ value correspond to the increasing hydrogen-bonding capabilities of the solvents. The persistence of CH···FC coupling in $[D_8]$THF is surprising and can be attributed to the "locked" conformation of the rigid molecular framework.

The proposed hydrogen-bonding interaction and the environment around the CF_3 moieties in complex **1** were further investigated by $^1H/^{19}F$ NOE difference experiments (see Supporting Information). When the signal for the proximal CF_3 group was selectively irradiated, strong enhancement was apparent for the multiplet exhibiting ^{19}F coupling at $\delta = 3.09$ ppm only, and no response was perceived for the doublet at $\delta = 3.26$ ppm. Intriguingly, we also observed moderate enhancement for the *ortho*-benzyl protons. Irradiation of the distal CF_3 substituent resulted in enrichment for the two adjacent aromatic proton signals only as anticipated. An illustration of the weak hydrogen bonding involving one of the methylene hydrogen atoms and the rapidly rotating trifluoromethyl unit is depicted in Figure 1. A virtually identical intramolecular CH···FC interaction in complex **3** is indicated by analogous NMR experiments, although the

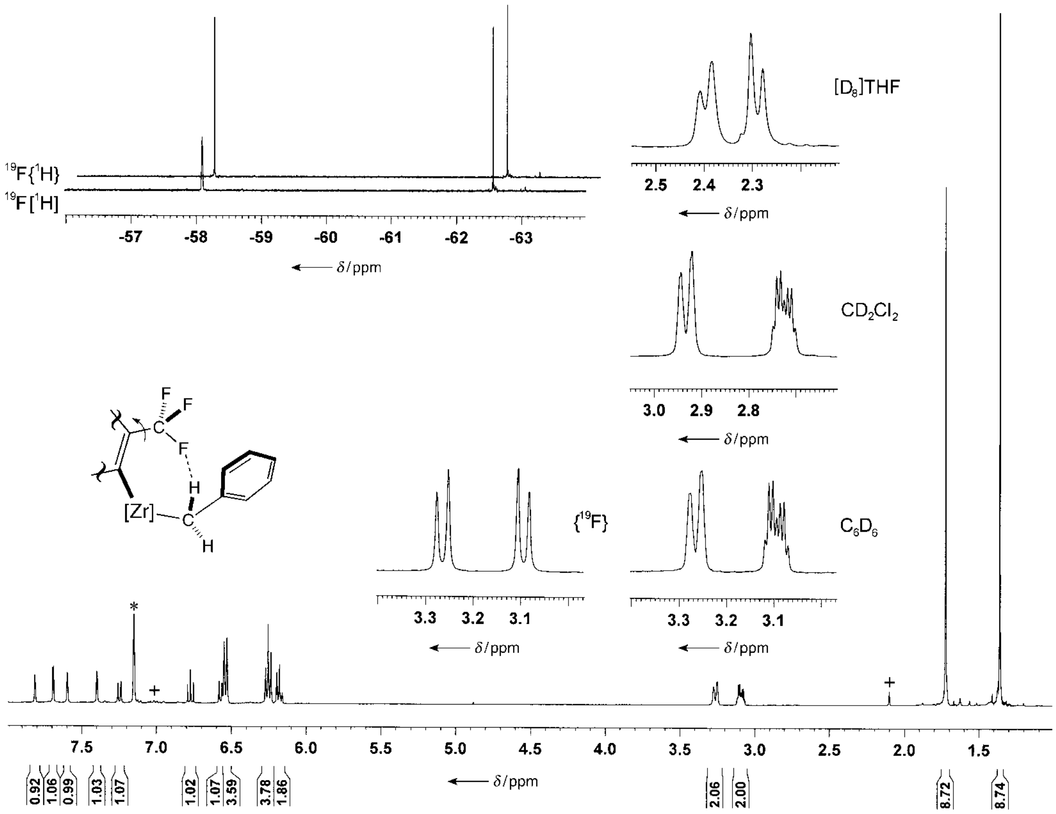

Figure 1. ^1H (400 MHz) and ^{19}F (376 MHz, CF_3 region) NMR spectra (C_6D_6, 300 K) of **1**, demonstrating the effects of ^{19}F and ^1H decoupling (ppm axis displaced for clarity), respectively, and of solvent polarity upon the diastereotopic methylene hydrogen atoms (* = C_6D_6, + = residual toluene).

through-space coupling is slightly weaker (in C_6D_6: ${}^{1h}J_{H,F} \approx$ 2 Hz, ${}^{2h}J_{C,F} = 5.3$ Hz).

We have also attempted to characterize the corresponding benzyl cationic species. The reaction of complex **1** with $B(C_6F_5)_3$ in CD_2Cl_2 yielded a complicated mixture of products. However, in the presence of a few drops of $[D_8]$THF, the transformation resulted in the clean generation of an η^2-CH_2Ph cation that is presumably stabilized by the OC_4D_8 ligand (Figure 2; see Supporting Information for ^1H–^1H COSY spectrum). Saliently, the broad upfield ^1H doublet peak for one of the methylene protons and the downfield ^{19}F signal for the proximal CF_3 group are both partially sharpened upon decoupling of the ^{19}F and ^1H nuclei, respectively. Moreover, the $^{13}C\{^1H\}$ NMR spectrum reveals a rather broad but partially resolved quartet signal at $\delta = 76.9$ ppm (${}^{2h}J_{C,F} \approx$ 4 Hz) for the $ZrCH_2$ group. These observations imply the presence of weak C–H···F–C contacts between the ancillary ligand and an alkyl fragment in a Group 4 metal cation.

The molecular structures of complexes **1** (Figure 3) and **2** have been determined by X-ray crystallography.[11] The zirconium center in both structures is chelated by a phenolate–pyridine–carbanion [O,N,C] ligand in a distorted trigonal-bipyramidal geometry, with axial O,C atoms and equatorial N and C(benzyl) groups. The most striking difference between **1** and **2** is the orientation of the benzyl moieties, which exist in the "*anti,anti*" and "*syn,anti*" configurations, respectively (see below). Nevertheless, like in their solution structures, the benzyl units can participate in η^2 coordination to the electrophilic metal core,[12] although this interaction appears fractionally weaker in **1**. While there are no close Zr···F contacts[4] (shortest Zr···F distance 2.940(2) Å) in the crystal lattice of **1**, the structural parameters concerning the C–H···F–C fragment are consistent with a weak hydrogen bond[8] (e.g. H···F 2.47 and 2.59 Å, C–H···F 114°). The unusual *anti,anti* benzyl arrangement in **1** may be attributed to a combination of the stabilizing effect from the CH···FC interactions and the congested environment around the equatorial central cleft (see space-filling diagram in Supporting Information), although crystal packing effects cannot be disregarded. Interestingly, the N-Zr-C-C_{ipso} dihedral angles for the *anti* benzyl ligands (which wrap around the pyridyl ring) are 8.4 and 26.5° (the corresponding angle in **2** is 2.8°), hence the CH_2Ph units appear to incline *towards* the more crowded surroundings of the CF_3 moiety (Figure 3b). We note the position of the *ortho*-phenyl hydrogen atoms H34 and H41 relative to the CF_3 group.

The intramolecular CH···FC contacts depicted in this work, demonstrated in the solution state and supported by X-ray structural determinations, represent unique models of weak attractive interactions between a functionalized ligand and a polymer chain at an active catalytic center.[13] Our results provide substantiating evidence for the proposition derived by Fujita et al. from DFT calculations regarding ligand–polymer interactions originating from (sp^2)C–F moieties.[5b]

In conclusion, this study highlights the potential of weak attractive interactions between the ligand and polymer chain as a new paradigm in olefin polymerization reactions. Fragile

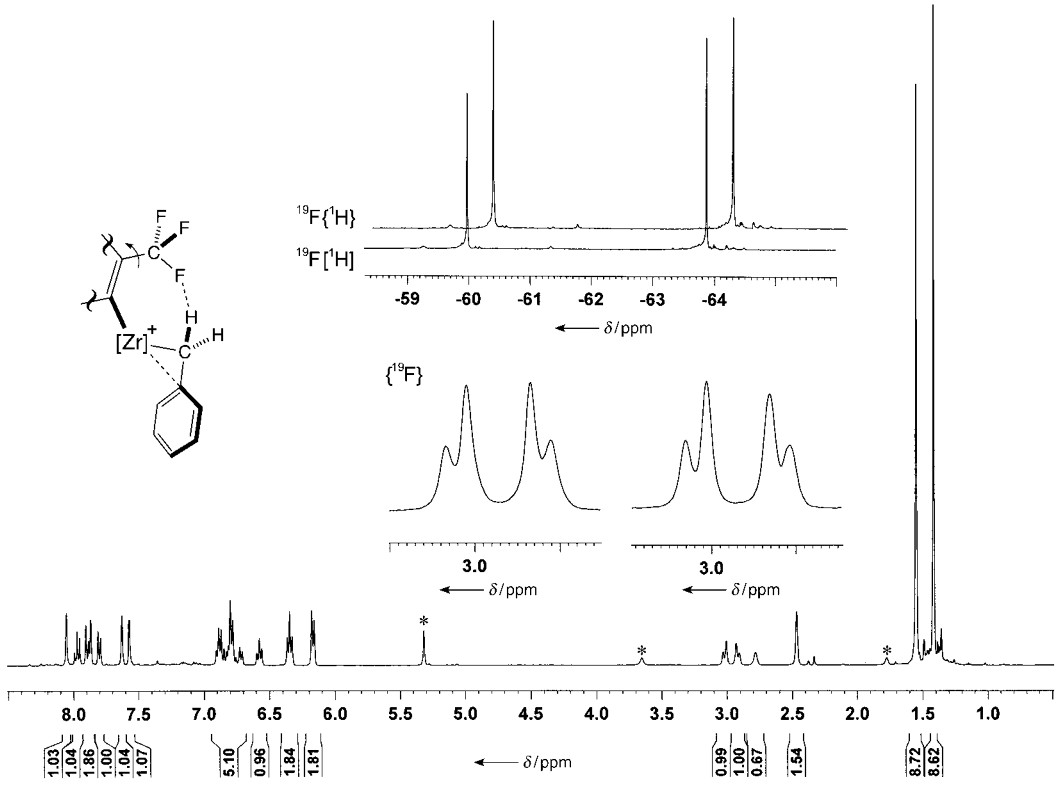

Figure 2. ^1H (400 MHz) and ^{19}F (376 MHz, CF_3 region) NMR spectra (CD_2Cl_2 + $[D_8]$THF, 300 K) for the η^2-CH_2Ph cation derived from the reaction of **1** with $B(C_6F_5)_3$, demonstrating the effects of ^{19}F and ^1H decoupling (ppm axis displaced for clarity), respectively (* = deuterated solvents).

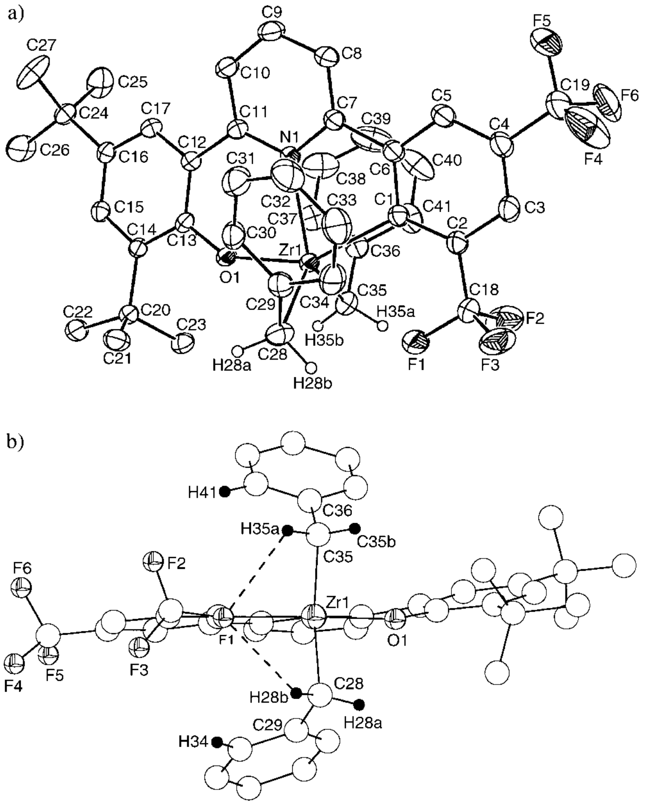

Figure 3. a) Structure of **1** (30% probability ellipsoids, only methylene hydrogen atoms are shown for clarity). Selected bond lengths [Å] and angles [°]: Zr1-C1 2.330(3), Zr1-N1 2.391(2), Zr1-O1 1.952(2), Zr1-C28 2.276(3), Zr1···C29 2.729(3), Zr1-C35 2.267(3), Zr1···C36 2.765(3); C13-O1-Zr1 147.3(2), C29-C28-Zr1 90.7(2), C36-C35-Zr1 92.8(2). b) View along the Zr1–N1 vector in **1**, depicting the short CH···FC contacts (F1···H28b 2.471, F1···C28 2.996(3), F1···H35a 2.592, F1···C35 3.115(3) Å; F1···H28b-C28 113.8, F1···H35a-C35 114.0°) and the apparent "tilt" of the CH$_2$Ph planes towards the CF$_3$ moiety.

noncovalent contacts such as hydrogen bonds are ideal for this role, and their diverse nature paves the way for molecular recognition possibilities. These weak interactions may potentially be exploited for the stabilization of hitherto unstable intermediates and new polymer architectures.

Experimental Section

Synthetic procedure: The 2-(2′-phenol)-6-arylpyridine substrate in pentane/diethyl ether (5:1) was slowly added to a stirred solution of [M(CH$_2$Ph)$_4$] in pentane/diethyl ether (5:1) at −78°C. The reaction mixture was allowed to warm up to room temperature and stirred for 12 h. The resultant solution was filtered, concentrated to about 10 mL and stored at −15°C to afford a crystalline solid. Analytically pure products were obtained by recrystallization from pentane (see Supporting Information for detailed characterization data and labeling schemes).

1: red crystals; yield: 0.19 g, 62%; elemental analysis calcd (%) for $C_{41}H_{39}F_6NOZr$ (766.98): C 64.21, H 5.13, N 1.83; found: C 63.99, H 5.57, N 1.89; selected NMR data (C_6D_6, 300 K): ^{1}H NMR (400 MHz): $\delta = 1.36$ (s, 9H; 5-*t*Bu), 1.72 (s, 9H; 3-*t*Bu), 3.09 (dq, $J = 9.6$ Hz, $^{1h}J_{H,F} = 3.3$ Hz, 2H; ZrCH$_2$), 3.26 (d, $J = 9.4$ Hz, 2H; ZrCH$_2$), 6.18 (t, $J = 7.3$ Hz, 2H; *p*-Ph), 6.25 (t, $J = 7.7$ Hz, 4H; *m*-Ph), 6.54 (d, $J = 7.4$ Hz, 4H; *o*-Ph), 6.57 (d, $J = 7.9$ Hz, 1H; H^{10}), 6.77 (t, $J = 8.0$ Hz, 1H; H^9), 7.25 (d, $J = 8.0$ Hz, 1H; H^8), 7.40 (d, $J = 2.3$ Hz, 1H; H^6), 7.60 (s, 1H; H^{13}), 7.69 (d, $J = 2.4$ Hz, 1H; H^4), 7.81 ppm (s, 1H; H^{15}); ^{19}F NMR (376 MHz): $\delta = -58.09$ (CF$_3$ at R^1), −62.56 ppm (CF$_3$ at R^2); ^{13}C NMR (126 MHz): $\delta = 70.50$ ppm (q, $^{2h}J_{C,F} = 5.9$ Hz ($J_{CH} = 133.3$ Hz); ZrCH$_2$).

2: orange-red crystals; yield: 0.23 g, 60%; elemental analysis calcd (%) for $C_{40}H_{40}F_3NOZr$ (698.98): C 68.73, H 5.77, N 2.00; found: C 68.21, H 5.68, N 2.02; selected NMR data (C_6D_6, 300 K): ^{1}H NMR (500 MHz): $\delta = 1.36$ (s, 9H; 5-*t*Bu), 1.58 (s, 9H; 3-*t*Bu), 2.27 (d, $J = 9.3$ Hz, 2H; ZrCH$_2$), 2.49 (d, $J = 9.3$ Hz, 2H; ZrCH$_2$), 6.64 (t, $J = 7.3$ Hz, 2H; *p*-Ph), 6.71 (d, $J = 7.2$, 4H; *o*-Ph), 6.80 (m, 5H; *m*-Ph and H^{10}), 6.86 (t, $J = 7.9$ Hz, 1H; H^9), 7.20 (d, $J = 7.4$ Hz, 1H; H^8), 7.39 (d, $J = 2.3$ Hz, 1H; H^6), 7.41 (d, $J = 7.3$ Hz, 1H; H^{15}), 7.63 (d, $J = 2.4$ Hz, 1H; H^4), 7.70 (s, 1H; H^{13}), 7.79 ppm (d, $J = 7.3$ Hz, 1H; H^{16}); ^{19}F NMR (376 MHz): $\delta = -62.27$ ppm; ^{13}C NMR (126 MHz): $\delta = 66.33$ ppm ($J_{C,H} = 135.0$ Hz; ZrCH$_2$).

3: dark red crystals; yield: 0.18 g, 57%; elemental analysis calcd (%) for $C_{41}H_{39}F_6NOTi$ (723.66): C 68.05, H 5.43, N 1.93; found: C 68.08, H 5.58, N 2.09; selected NMR data (C_6D_6, 300 K): ^{1}H NMR (500 MHz): $\delta = 1.34$ (s, 9H; 5-*t*Bu), 1.77 (s, 9H; 3-*t*Bu), 4.00 (dq, $J = 8.4$ Hz, $^{1h}J_{H,F} = 1.2$ Hz, 2H; TiCH$_2$), 4.04 (d, $J = 8.3$ Hz, 2H; TiCH$_2$), 6.25 (t, $J = 7.2$ Hz, 2H; *p*-Ph), 6.32 (t, $J = 7.1$ Hz, 4H; *m*-Ph), 6.42 (d, $J = 8.3$ Hz, 1H; H^{10}), 6.44 (d, $J = 7.3$ Hz, 4H; *o*-Ph), 6.66 (t, $J = 8.0$ Hz, 1H; H^9), 7.21 (d, $J = 8.0$ Hz, 1H; H^8), 7.40 (d, $J = 2.1$ Hz, 1H; H^6), 7.60 (s, 1H; H^{13}), 7.70 (d, $J = 2.3$ Hz, 1H; H^4), 8.12 ppm (s, 1H; H^{15}); ^{19}F (376 MHz): $\delta = -56.45$ (CF$_3$ at R^1), −62.60 ppm (CF$_3$ at R^2); ^{13}C (126 MHz): $\delta = 96.19$ ppm (q, $^{2h}J_{C,F} = 5.3$ Hz ($J_{CH} = 138.9$ Hz); TiCH$_2$).

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[10] The fact that only one of the two methylene hydrogen atoms exhibits ^{19}F coupling eliminates the possibility of the involvement of Zr···F interactions (and more generally of the coupling occurring “through-bond” through the methylene carbon atom).

[11] For **1**: $C_{41}H_{39}F_6NOZr$, $M_r = 766.98$, triclinic, $P\bar{1}$ (no. 2), $a = 9.613(2)$, $b = 11.860(2)$, $c = 16.928(3)$ Å, $\alpha = 109.37(3)$, $\beta = 90.88(3)$, $\gamma = 97.88(3)°$, $V = 1799.7(6)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.415$ g cm^{-3}, $\mu(\mathrm{Mo}_{K\alpha}) = 0.370$ mm^{-1}, $F(000) = 788$, $T = 253(2)$ K, $2\theta_{max} = 50.9°$, 5448 independent reflections ($R_{int} = 0.0252$), 479 variable parameters, $R_1 = 0.032$ ($I > 2\sigma(I)$), $wR_2 = 0.081$, GOF(F^2) = 0.976, largest diff. peak/hole = 0.41/−0.39 e Å^{-3}. For **2**: $C_{43}H_{47}F_3NOZr$, $M_w = 742.07$, triclinic, $P\bar{1}$ (no. 2), $a = 10.948(2)$, $b = 13.354(3)$, $c = 13.922(3)$ Å, $\alpha = 73.36(3)$, $\beta = 82.38(3)$, $\gamma = 82.56(3)°$, $V = 1923.9(7)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.281$ g cm^{-3}, $\mu(\mathrm{Mo}_{K\alpha}) = 0.333$ mm^{-1}, $F(000) = 774$, $T = 301(2)$ K, $2\theta_{max} = 50.7°$, 6262 independent reflections ($R_{int} = 0.0273$), 436 variable parameters, $R_1 = 0.045$ ($I > 2\sigma(I)$), $wR_2 = 0.118$, GOF(F^2) = 1.007, largest diff. peak/hole = 0.63/−0.60 e Å^{-3}. CCDC-190342 (**1**) and CCDC-190343 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[13] Preliminary ethylene polymerization data revealed that complex **1** is an efficient catalyst (ca. 800 g(PE) (mmol catalyst)$^{-1}$ h^{-1} atm^{-1}; 2000 equiv MAO) at 25 °C, while the activity of **2** under identical conditions is low (< 10 g mmol^{-1} h^{-1} atm^{-1}). We note that this difference in activity may also be attributed to other factors, such as the electron-withdrawing effect of multiple CF_3 groups (see ref. [5c]). We thank the reviewers for helpful comments, and we are indebted to Dr. Wa-Hung Leung (HKUST) for assistance in variable-temperature NMR experiments.