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Chelating σ-Aryl Post-Metallocenes: Probing Intramolecular [C−H···F−C] Interactions and Unusual Reaction Pathways

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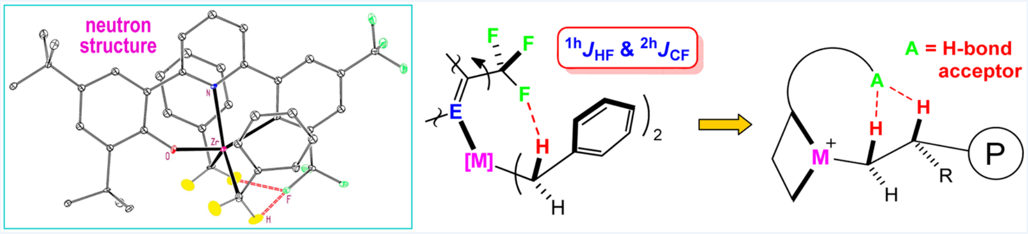

CONSPECTUS: Our interest in chelating σ-aryl ancillary ligands was motivated by their potential to impart unusual reactivity, since we envisioned that σ-donors with minimal π-donation would create a catalytic center with enhanced electrophilicity. We developed a family of Group 4 post-metallocene catalysts supported by pyridine-2-phenolate-6-(σ-aryl) [O,N,C] ligands bearing a fluorinated moiety in the vicinity of the metal. Notable features of these meta-substituted tris(hetero)aryl frameworks include their coordination geometry and inherent rigidity. For the first time, the elusive C−H···F−C interaction was manifested as NMR-discernible ^{1}H−^{19}F coupling in solution and characterized by a neutron diffraction study. Their existence carries implications for catalyst design and in the context of weak attractive ligand−polymer interactions (WALPI), since they substantiate the practical viability of the ortho-F···H(β) ligand−polymer interactions proposed for living Group 4 fluorinated bis(phenoxyimine) catalysts. In metal-catalyzed olefin polymerization reactions, the notion of noncovalent interactions between an active ancillary ligand and the growing polymer chain is new. These interactions must be fragile and transient in nature, otherwise the intrinsic chain propagation process would be disrupted, and inherently tunable attractive forces such as hydrogen bonds are ideally suited to this role. The nature, relevance, and usability of extremely weak hydrogen bonds such as C−H···F−C has been a topical yet controversial area of research.

We subsequently prepared a series of Group 4 complexes supported by fluorinated (σ-aryl)-2-phenolate-6-pyridyl [O,C,N] ligands. [^{1}H,^{19}F]-HMBC NMR experiments were conducted to probe the observed ^{1}H−^{19}F coupling, and specifically separate contributions from scalar (J) coupling and cross-correlation (CR) interference. For the first time, a significant scalar component was confirmed for the ^{1}H−^{19}F coupling in Ti-[O,C,N] and [O,N,C] complexes, which occurs with chemical connectivity across intramolecular C−H···F−C interactions. This result is important because the applicability of weak attractive ligand−polymer interactions in catalysis is feasible only if the observed coupling and hence the noncovalent interaction is genuine. The verified intramolecular C−H···F−C contacts in these complexes can therefore be considered as synthetic models for ligand−polymer interactions in olefin polymerization processes. Significantly, reports concerning late transition metal systems have appeared that hint at the generality of the WALPI concept for modulating polymerization reactions.

We evaluated the olefin polymerization reactivity of Ti-[O,N,C] catalysts through judicious substitution. DFT calculations, which revealed diverse kinetically competitive reaction pathways and active sites (including unusual ethylene-assimilated species) in addition to normal chain propagation, were also employed to rationalize polymerization efficiencies. Further developments in catalytic applications of multidentate σ-aryl ligand systems and novel reactivity of the corresponding complexes can be envisaged.

■ INTRODUCTION

Our interest in (σ-aryl)-chelating ancillary ligands stemmed from our initial attempts to develop the pyridine-2,6-bis(phenolate) [O,N,O] system as suitable tridentate auxiliaries for efficient Group 4 olefin polymerization catalysts.[1] The conformationally rigid and chemically robust aromatic [O,N,O] framework provides meridional (rather than facial) coordination, while strong binding by the central pyridine unit is deemed to give lower olefin insertion barriers,[2] leading to high activities for Zr(IV) catalysts.[3] Thereafter, instigated by our experience of the prevalence of facile cyclometalation processes for late transition metal complexes,[4] we became attracted to the development of pyridine-2-phenolate-6-(σ-aryl) [O,N,C] ligands (Figure 1).

We reasoned that (i) since the σ-aryl moiety is established as a pure σ-donor with minimal π-donation (in contrast to strong π-donors such as Cp), the resultant metal center would exhibit enhanced electrophilicity, an important criterion for catalytic efficiency; (ii) the R^{1} substituent, at the ortho position from the M−C(σ-aryl) linkage, would be in close proximity to the metal/active site but nevertheless "tethered" back (due to intrinsic

Received: January 8, 2015
Published: May 20, 2015

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DOI: 10.1021/acs.accounts.5b00008
Acc. Chem. Res. 2015, 48, 1580−1590

complex	R^1	R^2	R^3	M
1	CF_3	CF_3	H	Ti
2	CF_3	CF_3	H	Zr
3	CF_3	H	F	Ti
4	CF_3	H	F	Zr
5	F	CF_3	H	Ti
6	H	CF_3	H	Zr
7	CH_3	H	CH_3	Ti
8	Cl	H	Cl	Ti
9	Br	Br	H	Ti

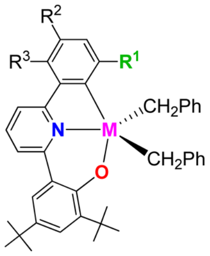


Figure 1. Pyridine-2-phenolate-6-(σ-aryl) [O,N,C] complexes **1**–**9**.

ligand rigidity) to preclude interaction with the metal; (iii) the possibility of competitive olefin insertion into the M–C(sp^3 of alkyl/polymer chain) and M–C(sp^2 of σ-aryl) bonds during polymerization should be considered.

Prior to our undertakings, (σ-aryl)-chelating Group 4 complexes supported by Cp ligands were known in the literature.[5,6] With regards to amine-based relatives,[7] it is pertinent to note that facile olefin insertion into the M–C(sp^2) bond of a chelating σ-aryl moiety was observed spectroscopically for a cationic titanium complex bearing bidentate (σ-aryl)amine and bis(phenolate) ligands (Chart 1, **I**),[8] while zirconocene complexes (Chart 1, **II**) also undergo analogous insertion chemistry.[9] During the course of our work, Hessen and co-workers described the employment of zirconium complexes with tridentate amine-bis(σ-aryl) ligands (Chart 1, **III**) as propylene polymerization catalysts.[10] The reported low efficiencies and broad molecular weight distributions caught our attention, since it correlated with our concurrent results for pyridine-2,6-bis(σ-aryl) [C,N,C]-Ti and -Zr complexes, which were highly unstable (^1H NMR spectroscopy indicated facile decomposition via demetalation) and displayed poor catalytic activities.

■ INTRAMOLECULAR [C–H···F–C] INTERACTIONS IN [O,N,C] COMPLEXES

NMR Characterization and Neutron Diffraction Study

Our original underlying aim, of developing efficient Group 4 [O,N,C] catalysts for olefin polymerization, rapidly evolved following some unexpected preliminary NMR spectroscopic observations.[11] Consequently, the effects of σ-aryl substituents displaying different steric and electronic characteristics upon spectroscopic and polymerization properties were examined.[12] In particular, the principal objective was to position fluorine-containing groups in the vicinity of (but not interacting with) the metal core, so that the resultant complexes could potentially engage in intramolecular contacts reminiscent of "weak attractive ligand–polymer interactions" (see below).

The synthesis of [O,N,C] bis(benzyl) complexes typically entails metalation of 2-(2′-phenol)-6-arylpyridine containing acidic protons with basic $M(CH_2Ph)_4$ precursors to yield dark red (Ti), yellow (Zr), and pale yellow (Hf) crystalline solids in moderate yields. As an illustrative example of the abnormal spectroscopic features for selected complexes, the following observations relate to **2** (in C_6D_6 at 300 K): (i) regarding the ^1H NMR resonances for the diastereotopic methylene hydrogens (customarily a doublet of doublets in *AB* pattern), while the downfield doublet at 3.26 ppm for H^b is normal (J = 9.4 Hz), the upfield resonance at 3.09 ppm for H^a appears as an overlapping

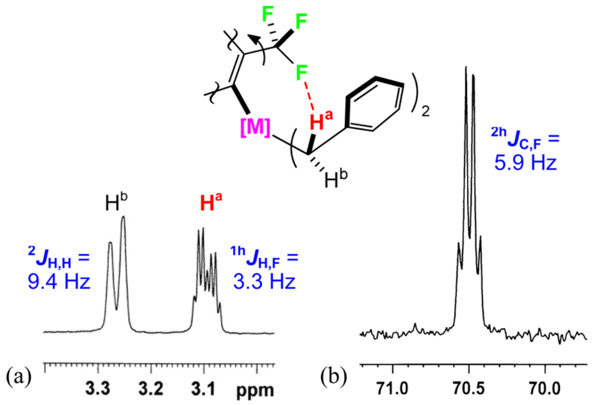
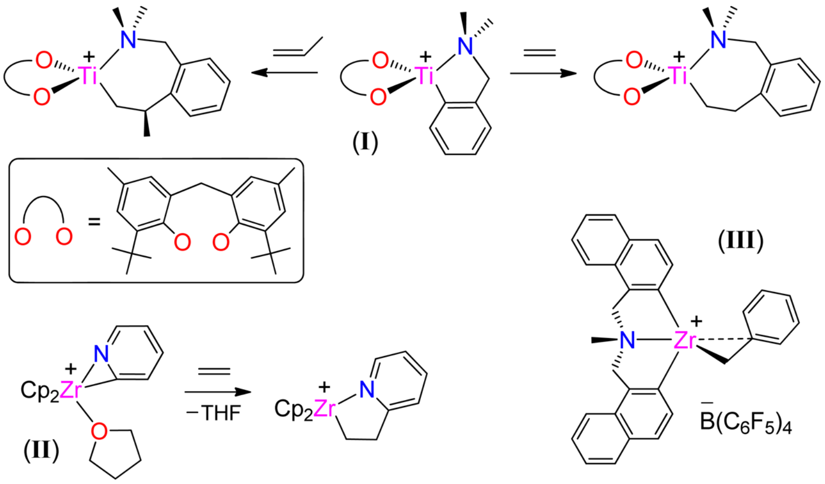


Figure 2. ^1H (a; 400 MHz) and $^{13}C\{^1H\}$ (b; 101 MHz) NMR spectra (C_6D_6, 300 K) for the methylene hydrogen (diastereotopic) and carbon atoms in complex **2** (M = Zr; benzyl groups are related by symmetry), with proposed mechanism for apparent ^1H–^{19}F and ^{13}C–^{19}F coupling in [O,N,C] complexes (^{nh}J refers to n-bond J-coupling occurring through a hydrogen bond; see discussion on [^1H,^{19}F]-HMBC experiments for confirmation regarding origin of ^{19}F-coupling).

Chart 1. Amine-Based (I and III) and Zirconocene (II) Chelating σ-Aryl Relatives



doublet of quartets (J = 9.4 and 3.3 Hz; Figure 2a); (ii) the $^{13}C\{^1H\}$ NMR spectrum unexpectedly exhibits a quartet signal at 70.50 ppm (J = 5.9 Hz; Figure 2b) for the methylene groups; (iii) although coupling in the $^{19}F[^1H]$ NMR spectrum is not resolved, the $^{19}F\{^1H\}$ NMR spectrum undergoes obvious narrowing for the downfield resonance at −58.09 ppm only; similarly, the dq ^1H resonance for H^a reverts back to a normal doublet upon ^{19}F-decoupling; (iv) a strong $[^1H,^{19}F]$-HMQC crosspeak is evident between the downfield ^{19}F signal and the upfield dq ^1H resonance only; (v) for the dq ^1H resonance, a decrease in the magnitude of the abnormal coupling for solvents with increasing hydrogen-bonding capabilities was evident (3.3 and 3.1 Hz in C_6D_6 and CD_2Cl_2, respectively; unresolved in $[D_8]THF$).[11]

The magnitudes of the coupling constants, which are apparently J-coupling (for confirmation, see subsection "Scalar Coupling across [C−H···F−C] Interactions"), are clearly not indicative of formal 6- or 5-bond coupling. Hence, we concluded that these observations are consistent with coupling of one of the CH_2 protons (and the carbon atom) on each benzyl ligand with three equivalent ^{19}F nuclei of a rotating CF_3 group through intramolecular C−H···F−C interactions (Figure 2, top). Importantly, the fact that only one of the two methylene resonances (for H^a) exhibits obvious ^{19}F-coupling indicate that M···F interactions are absent, and more generally that the coupling does not occur through the methylene carbon atom (otherwise both resonances would display ^{19}F-coupling; such a scenario is evident below for Zr- and Hf-[O,C,N] complexes). Multinuclear NMR findings that closely resemble those for **2** have been recorded for all [O,N,C-R^1] derivatives where R^1 = CF_3 (Figure 1), while comparable albeit less pronounced results were obtained for the corresponding benzyl cation derived from the reaction of **2** with $B(C_6F_5)_3$.[11] These NMR observations imply the presence of C−H···F−C interactions in solution between the ancillary ligand and an alkyl fragment in cationic as well as neutral Group 4 complexes. By comparison, the methylene ^1H NMR resonances for complex **5** (R^1 = F), as well as all congeners with a nonfluorinated substituent at R^1, appear as normal *AB*-type doublet of doublets.

In addition to spectroscopic evidence, we endeavored to probe the existence and nature of C−H···F−C interactions by structural elucidations. Saliently, this was conducted for complex **2** using a neutron diffraction study,[13] thus enabling the location of hydrogen atoms to be accurately determined (Figure 3). Indeed, this constituted the first time that the topical yet controversial C−H···F−C interaction had been characterized by a neutron diffraction study. The H···F distances and C−H···F angles observed in **2** are entirely consistent with the C−H···F−C contacts described in previously reported X-ray crystal structures.[14,15] Although controversy regarding weak dispersion-dominated C−H···F−C interactions has ensued,[16,17] there is a growing body of evidence concerning their existence and consequences in areas as diverse as crystal engineering,[18] advanced spectroscopy[19,20] and biomolecular design.[21,22]

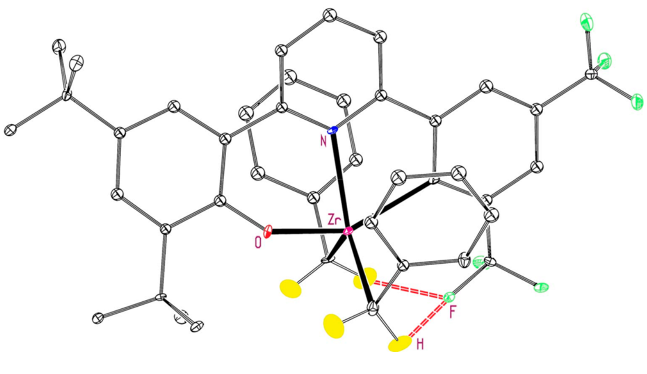


Figure 3. Perspective view of **2** from neutron diffraction study (50% probability ellipsoids), showing methylene hydrogen atoms; H···F distances of 2.572(6) and 2.607(5) Å, and C−H···F angles of 103.3(4) and 108.2(3)° are observed.

Examination of the crystallographically determined[11,13] (X-ray, plus neutron diffraction for **2**) molecular structures of Ti- and Zr-[O,N,C-R^1] (R^1 = CF_3) bis(benzyl) complexes reveal two additional features, which provide key insights into the spectroscopic results and coupling mechanism. (1) The shortest M···F distances are around or in excess of 3 Å, which clearly exceed the range attributable to a M···F−C interaction (M = Ti, Zr).[23,24] This underlines the tethered nature of the R^1 group, and further advocates that the ^{19}F-coupling across C−H···F−C interactions occurs without contribution from M···F interactions. (2) In all structures, the two benzyl units extend toward the pyridyl ring in an unusual "anti,anti" configuration, in contrast to the "syn,anti" arrangement typically found in tridentate post-metallocene derivatives and observed for analogues where R^1 = H (e.g., complex **6**).[13] Consequently, as signified by $^1H-^1H$ ROESY experiments, we concluded that rotation of the M−C(methylene) bonds in CF_3-substituted complexes is severely hindered, and the resultant conformational preference for the intramolecular C−H···F−C interactions may thus facilitate their detection by NMR spectroscopy.

Synthetic Models of Weak Attractive Ligand−Polymer Interactions

Aside from their elusiveness, the significance of the intramolecular C−H···F−C contacts in the [O,N,C] complexes lie in their evocation of the ortho-F···H(β) ligand−(polymer chain) interactions postulated[25,26] (based on DFT calculations) to account for the remarkable living olefin polymerization capabilities[27,28] of fluorine-rich bis(phenoxyimine) Group 4 catalysts, as pioneered by Fujita and coworkers. We thus recognized that the exploitation of noncovalent interactions between a functionalized ligand (i.e., bearing a hydrogen-bond acceptor group) and the growing polymer chain in olefin polymerization was a new direction for such well-established reactions,[29] and may offer the intriguing possibility of controlling or manipulating reactivity at the polymer chain, which would potentially lead to novel catalytic behavior and polymer properties. More generally, such an approach may be applicable to any organometallic catalyst bearing a β-hydrogen atom, the elimination of which is often facile and difficult to control, for inhibiting β-H elimination/transfer termination pathways. The unexplored WALPI concept could therefore establish a bridge between catalysis science and supramolecular chemistry. Interestingly, Mikami and co-workers invoked the influence of C−H···F−C interactions to rationalize the observation of enhanced enantioselectivity for the catalytic hydrogenation of acyclic perfluoroalkyl ketimines.[30]

■ FROM [O,N,C] TO [O,C,N] COMPLEXES

Scalar Coupling across [C−H···F−C] Interactions

Although the Ti-[O,N,C] complexes can function as efficient olefin polymerization catalysts, characterization of the resultant polymers often signified high M_w/M_n indicative of multisite behavior, arising (as elaborated below) from competitive olefin insertion[8,9] into the Ti−C(σ-aryl) bond. This stimulated us to modify our ligand design and devise new (σ-aryl)-2-phenolate-6-pyridyl [O,C,N] auxiliaries: (i) olefin insertion into the M−C(σ-aryl) bond would yield 8-membered metallacycles and should be disfavored; (ii) more versatile (including Pd-catalyzed) synthetic routes become accessible; (iii) one may anticipate the [O,C,N] and [O,N,C] complexes to be structurally analogous. In particular, Group 4 bis(benzyl) complexes supported by [O,C,N-R^{1}] ligands bearing a fluorinated R^{1} group (CF_3 or F) have been synthesized (Figure 4).[31]

complex	R^{1}	M
10	CF_3	Ti
11	CF_3	Zr
12	CF_3	Hf
13	F	Ti

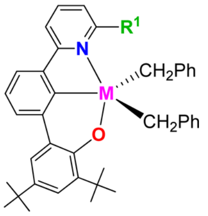


Figure 4. (σ-Aryl)-2-phenolate-6-pyridyl [O,C,N] complexes **10**−**13**.

To our surprise, while the NMR spectroscopic properties for the Ti-[O,C,N-CF_3] complex **10** was directly comparable to its [O,N,C] congener **1**, the spectral patterns for **11** and **12** were found to be different from that of the Zr-[O,N,C] analogue **2**: (i) the ^{1}H NMR resonances for the CH_2 hydrogens are observed as two sets of nonidentical doublets of quartets (collapsing to two normal *AB* doublets upon ^{19}F-decoupling), indicating non-equivalent coupling between each CH_2 proton and the three ^{19}F nuclei, and (ii) in the [^{1}H,^{19}F]-HMQC spectrum, strong crosspeaks are evident for both dq resonances. This additional ^{19}F-coupling for **11** and **12** may conceivably occur according to **A** (invoking the aforementioned C−H···F−C interactions, assuming (albeit unlikely) that $^{1h}J_{H,F}$ and $^{3h}J_{H,F}$ values are comparable) or **B** ($^{3}J_{H,F}$ via M···F contacts, to afford comparable $^{3}J_{H,F}$ values for all CH_2) in Figure 5. Pertinently, evidence in support of mechanism **B** was provided by the X-ray crystal structure of the Hf derivative **12**, which revealed a close Hf···F contact of 2.677(3) Å. It should be noted that the ^{1}H NMR resonances for the diastereotopic methylene hydrogens in Ti-, Zr- and Hf-[O,C,N] congeners bearing a methyl substituent at R^{1} appear as two normal *AB* doublets (unpublished result).

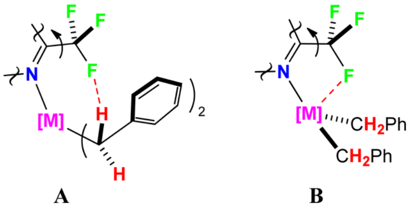


Figure 5. ^{19}F-coupling schemes A ($^{1h}J_{H,F} \gg {}^{3h}J_{H,F}$; M = Ti) and B ($^{3}J_{H,F}$ via M···F; M = Zr, Hf) to rationalize NMR resonances for the methylene hydrogens in [O,C,N] complexes **10**−**12**.

Although the observed coupling within the C−*H*···*F*−C fragments may formally be referred to as $^{1h}J_{H,F}$, we realized at this juncture that clarification was necessary, since apparent ^{1}H−^{19}F scalar coupling (*J*, with chemical connectivity) through non-covalent contacts can contain interference from cross-correlation (CR) interactions, which occur through space without bonding.[32,33] Hence, a series of highly sensitive [^{1}H,^{19}F]-HMBC experiments were performed to separately evaluate contributions from *J* coupling and CR interference.[31] Bearing in mind the emerging importance of fluorinated substituents, it is clearly desirable to develop new spectroscopic techniques to probe fluorine atoms and elucidate their surrounding environment and connectivity.

As an illustrative example, the ^{1}H NMR and [^{1}H,^{19}F]-HMBC spectra of complex **13** (R^{1} = F) is shown in Figure 6: (i) importantly, the [^{1}H,^{19}F]-HMBC (*J*) spectrum (Figure 6c) demonstrates that the ^{19}F-coupling for the methylene resonances contains a significant scalar component; (ii) regarding the diastereotopic methylene hydrogens, while the downfield doublet at 4.00 ppm for H^{b} is normal (thus implying no Ti···F interaction), the upfield resonance at 3.26 ppm for H^{a} appears as an overlapping doublet of doublets ($^{1h}J_{H,F}$ = 3.5 Hz). By extension, the doublet signal for the methylene groups at 83.20 ppm in the ^{13}C{^{1}H} NMR spectrum can be ascribed to $^{2h}J_{C,F}$ (6.3 Hz). Taken together, these observations signify the occurrence of scalar coupling across C−H···F−C interactions with a single ^{19}F nuclei. Similar results have been obtained in [^{1}H,^{19}F]-HMBC (*J*) experiments for the [O,C,N-CF_3] complexes **10**−**12**. Furthermore, selective [^{1}H,^{19}F]-HMBC experiments were performed for [O,N,C] derivatives bearing multiple ^{19}F resonances such as **4**, which gave comparable findings upon excitation of the ^{19}F resonance corresponding to R^{1}. By analogy, this confirms that the abnormal ^{1}H and ^{13}C NMR coupling for the methylene resonances in complex **2** (Figure 2) can be assigned as $^{1h}J_{H,F}$ and $^{2h}J_{C,F}$ respectively.

Our assumption that the [O,C,N] and [O,N,C] systems are structurally analogous requires revision, because subtle differences have been translated into dissimilar spectroscopic features for the CH_2 moiety (e.g., normal doublet plus dd for Ti-[O,C,N−F] complex **13**, compared with conventional *AB* doublet of doublets for [O,N,C] congener **5**; two nonidentical dq for Zr-[O,C,N-CF_3] complex **11**, compared with normal doublet plus dq for [O,N,C] congener **2**). These results indicate that the R^{1} moiety in [O,C,N-R^{1}] complexes lies in closer proximity to the methylene group and metal.

In summary, the single dq ^{1}H NMR peak for one of the CH_2 hydrogens in **10** and the [O,N,C] analogues **1**−**4**, plus the corresponding dd peak (for H^{a}) in **13**, can confidently be assigned to intramolecular $^{1h}J_{H,F}$ scalar coupling across C−H···F−C interactions, because (i) a significant scalar contribution was confirmed by [^{1}H,^{19}F]-HMBC (*J*) experiments, (ii) in all cases the resonance for the other CH_2 hydrogen (*H^{b}*−C−H···F−C) appears as a "normal" doublet seemingly without ^{19}F-coupling (i.e., $^{1h}J_{H,F} \gg {}^{3h}J_{H,F}$), and (iii) the available crystal structures of Ti and Zr derivatives show that M···F−C contacts are absent. This was an imperative result from our viewpoint, because the potential applicability of C−H···F−C contacts in olefin polymerization catalysis is only feasible if the observed coupling contains a *J* component, and the noncovalent interaction is therefore genuine.

■ COMPARISONS AND DISCUSSION

Applicability of [C−H···F−C] Interactions in Catalysis

Significantly, recent reports regarding late transition metal catalyst systems point to the potential and generality of the WALPI concept for modulating olefin polymerization reactions. Delferro and Marks have examined the ethylene polymerization properties of CF_3- and Me-substituted terphenylphenoxyimine-Ni(II) (plus bimetallic[34]) catalysts, and found that the former afforded enhanced activities and polymers with higher M_w and lower degrees of branching.[35] The suppressed β-H elimination

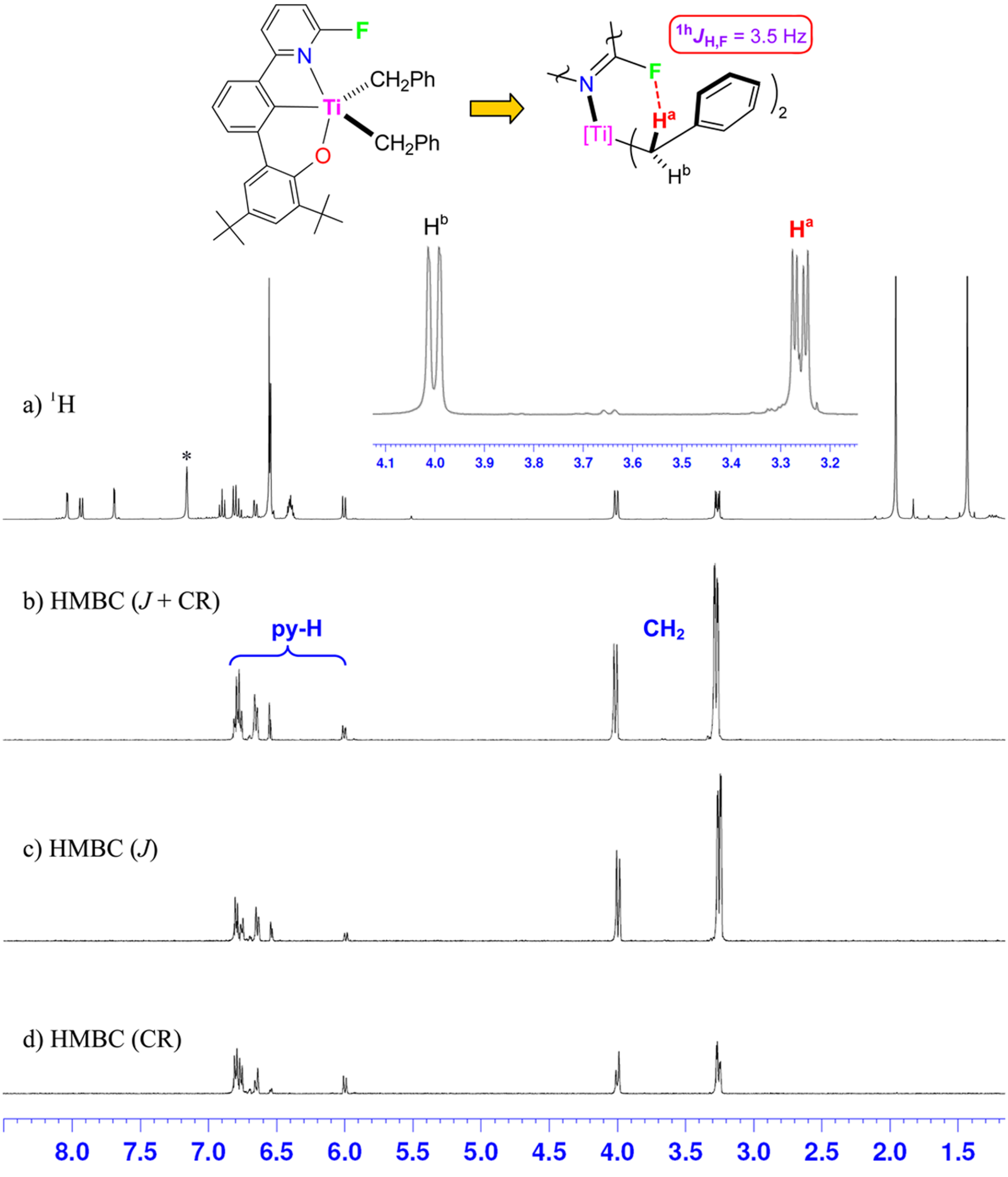


Figure 6. ^{1}H NMR spectrum (400 MHz, C_6D_6*, 298 K) for complex **13** (a; with expanded methylene region), and 1D [^{1}H,^{19}F]-HMBC NMR spectra showing signals arising from (b) both ^{1}H−^{19}F scalar (*J*) and cross correlation (CR) interactions; (c) exclusively from scalar couplings (*J*); and (d) exclusively from dipolar cross correlation (CR).

for the fluorinated catalysts was ascribed to stabilization afforded by the existence of $C_\beta-H_\beta\cdots F-C$ interactions, based on the appearance of ^{1}H···^{19}F dipolar interactions from [^{1}H,^{19}F]-HOESY NMR experiments for a model ethyl complex (Chart 2, **IV**), in addition to molecular modeling studies. For related Ni(II) catalysts, Mecking previously ascribed the unexpected influence of remote substituents (particularly C_8F_{17} and CF_3) upon polymerization behavior to an electronic effect, although a mechanism involving ligand−polymer interactions may also be relevant.[36] The improved performance of Ni(II) and Pd(II)

Chart 2. Literature Examples of Compounds Displaying Intramolecular $^{1}H-^{19}F$ (and $^{13}C-^{19}F$) Coupling (or $^{1}H\cdots^{19}F$ Dipolar Interactions for IV), Occurring via C−H···F−C or M···F−C Interactions (refer to text and Table 1 for details)

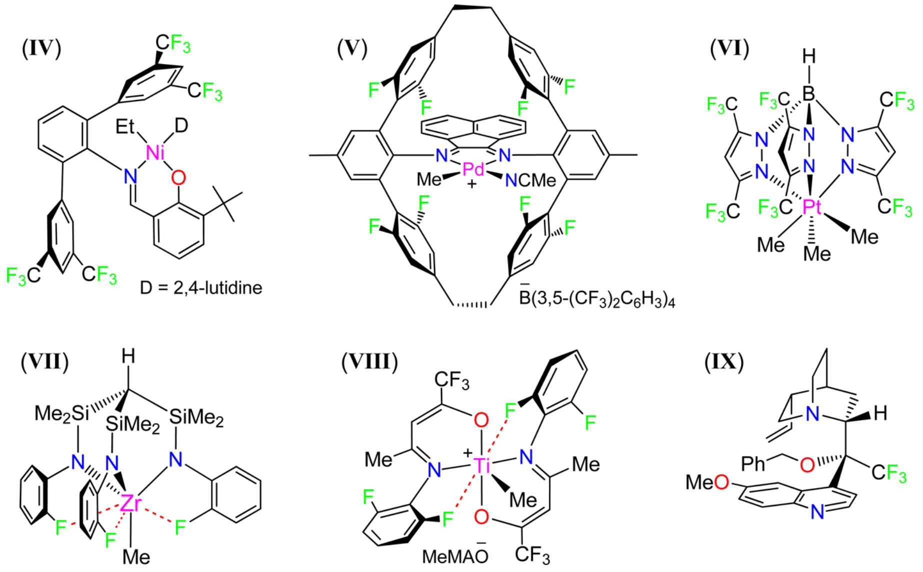


Table 1. Comparison of Selected NMR Spectroscopic Data[a] Involving C−H···F−C interactions ($^{1h}J_{H,F}$/$^{2h}J_{C,F}$; analogous to Figure 2) or Coupling via M···F ($^{3}J_{H,F}$/$^{2}J_{C,F}$; analogous to Scheme B in Figure 5), and Associated Structural Parameters[b]

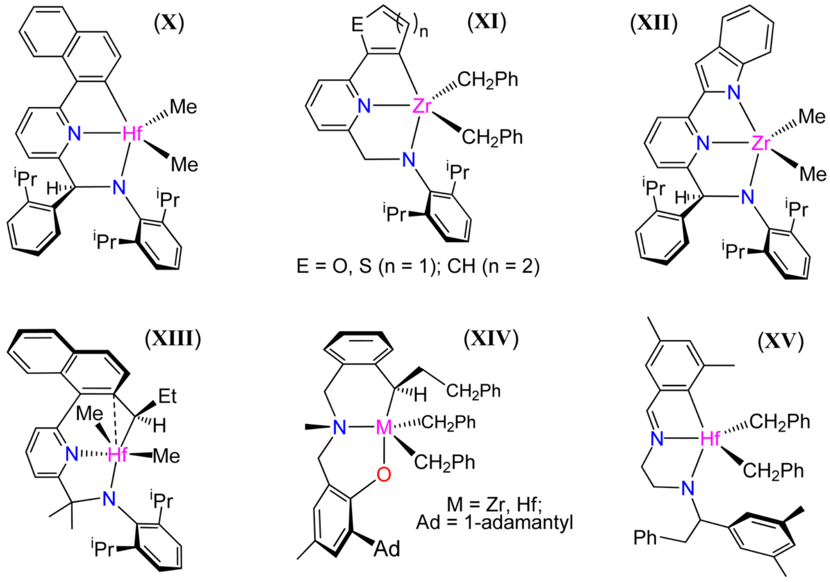
	^{1}H (ppm)	$^{1h}J_{H,F}$ or $^{3}J_{H,F}$ (Hz)	$^{13}C\{^{1}H\}$ (ppm)	$^{2h}J_{C,F}$ or $^{2}J_{C,F}$ (Hz)	$J_{C,F}/J_{H,F}$	^{19}F (ppm)	M···F (Å)	mean H···F (Å)	mean C−H···F (deg)
2 (Zr)	3.09 (dq)	3.3	70.5 (q)	5.9	1.8	−58.1	2.959(4)	2.589(6)	105.8(4)
4 (Zr)	3.09 (dq)	3.6	70.6 (q)	6.5	1.8	−56.3			
10 (Ti)[c]	3.07 (dq)	3.5	80.5 (q)	6.5	1.9	−61.6			
11 (Zr)[c]	2.68 (dq)	3.8 (via Zr···F)	63.8 (q)	6.4 (via Zr···F)	1.7; 2.7	−62.8			
	2.96 (dq)	2.4 (via Zr···F)							
12 (Hf)[c]	2.40 (dq)	3.9 (via Hf···F)	72.3 (q)	7.3 (via Hf···F)	1.9; 2.7	−63.4	2.677(3)	2.51	106
	2.73 (dq)	2.7 (via Hf···F)							
13 (Ti)	3.26 (dd)	3.5	83.3 (d)	6.3	1.8	−66.1			
14 (Ti)	3.98 (dq)	2	101.3 (q)	5.4	2.7	−56.5			
$Tp^{(CF_3)_2}PtMe_3$, **VI**[d,e]	1.58 (sept)	1.8	−4.9 (sept)	3.9	2.2	−57.0	n.o.	2.63	
$(F-N_3)ZrMe$, **VII**[d,f]	0.65 (q)	8.4 (via Zr···F)	47.3 (q)	17.6 (via Zr···F)	2.1	−121.3	[2.535(5)][j]		
$[(F_8-Cyc)PdMe(NCMe)]^+$, **V**[c,g]	0.80 (t)	4.5 (via Pd···F)	8.0 (t)	10.6 (via Pd···F)	2.4	−107.5			
$[(EI^F)_2TiMe][Me\text{-}MAO]$, **VIII**[h]	2.80 (s)	n.o.	126.6 (t)	7 (via Ti···F)		−120.0			
CF_3-benzyl-cinchona alkaloid, **IX**[i]	4.77 (dq)	1.4	68.8 (q)	2.2	1.6	−60.0	[no M]	2.54	

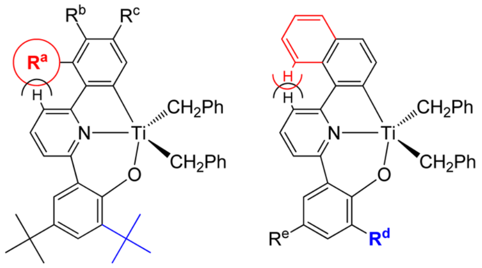
[a] At 400 (^{1}H) and 101 (^{13}C) and 376 (^{19}F) MHz in C_6D_6 at 25 °C unless otherwise stated; n.o. = not observed. [b] From X-ray crystallography, except **2** (neutron diffraction). [c] At 500 (^{1}H) and 126 (^{13}C) MHz. [d] At 200 (^{1}H), 63 (^{13}C), and 188 (^{19}F) MHz. [e] Reference 38; in acetone-d_6. [f] Reference 39; in CD_2Cl_2. [g] Reference 37; in CD_2Cl_2. [h] Reference 40; in toluene-d_8/1,2-difluorobenzene at −25 °C. [i] Reference 41; *O*-benzyl-9-dehydro-9-trifluoromethyl-9-epiquinidine; in $CDCl_3$. [j] X-ray data for chloro-bridged analogue.

olefin polymerization catalysts supported by an octafluorinated cyclophane-based α-diimine (F_8−Cyc) ligand, relative to the nonfluorinated congener, was attributed by Guan to stabilization of the reactive intermediate by M···F−C interactions; we wish to highlight the feasibility of C−H···F−C interactions in these species bearing in mind the close proximity between the polymer chain and multiple F atoms, and it is notable that $^{1}H-^{19}F$ coupling for the Pd-methyl moiety was detected in cations such as $[(F_8-Cyc)PdMe(NCMe)]^+$ (Chart 2, **V**).[37]

It should be emphasized that literature reports of spectroscopically discernible C−H···F−C interactions accompanied by structural authentication are rare, and the examples in our work provide an opportunity to probe the nature of these weak contacts. Comparisons can be drawn with organometallic complexes exhibiting intramolecular $^{1}H-^{19}F$ and $^{13}C-^{19}F$ coupling (Table 1), assigned to C−*H*···*F*−C interactions [such as $Tp^{(CF_3)_2}PtMe_3$ ($Tp^{(CF_3)_2}$ = HB{3,5-bis(trifluoromethyl)-pyrazolyl}$_3$; Chart 2, **VI**)],[38] or *H*−C−M···*F*−C contacts [$(F-N_3)ZrMe$ ($F-N_3$ = HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$; Chart 2, **VII**),[39] $[(F_8-Cyc)PdMe(NCMe)]^+$ (Chart 2, **V**)[37]]. In this connection, Möller and Bryliakov ascribed $^{13}C-^{19}F$ coupling for the Ti-methyl signal in $[(EI^F)_2TiMe][Me\text{-}MAO]$ (EI^F = *o*-F-substituted enolatoimine; Chart 2, **VIII**) to the presence of Ti···F−C interactions [i.e., $^{2}J(C-Ti\cdots F)$], although $^{1}H-^{19}F$ coupling ($^{3}J_{H,F}$) is not detected.[40] It is instructive to note that an approximate relationship of $J_{C,F} \approx n\, J_{H,F}$ (n = 1.7−2.7) is invariably observed, and this relationship is preserved for both $^{2h}J_{C,F}$ (for C−H···*F*−C) and $^{2}J_{C,F}$ (for H−C−M···*F*−C) values across a range of 3.9−17.6 Hz. By comparison, in organic systems such as fluorinated cinchona alkaloid derivatives (Chart 2, **IX**),[41]

Chart 3. Development of Amide-Based Chelating σ-Aryl and Related C(sp^3)-Chelating Catalysts (see text for details; only one diastereoisomer shown for X and XII–XIV)





complex	R^a	R^b	R^c	R^d	R^e	activity	M_n (×10^6)	M_w/M_n
15	F	H	H	^{t}Bu	^{t}Bu	1.1	1.72	2.8
16	F	H	F	^{t}Bu	^{t}Bu	1.0	0.87	4.9
17	CF_3	H	H	^{t}Bu	^{t}Bu	1.6	0.82	7.5
18	benzo (C_4H_4)		H	^{t}Bu	^{t}Bu	2.3	0.41	8.1
19	benzo (C_4H_4)		H	CF_3	H	1.7	0.57	10.8
20	benzo (C_4H_4)		H	CMe_2Ph	Me	2.7	3.99	2.5
21	benzo (C_4H_4)		H	CPh_2Me	H	4.1	0.83	7.6

Figure 7. Ethylene polymerization results for [O,N,C] complexes **15–21**. Conditions: 5 mL of toluene, 0.3 μmol of catalyst, ^{i}Bu$_3$Al/[Ph$_3$C][B(C$_6$F$_5$)$_4$]/catalyst (50/2/1 equiv, respectively), 7 atm of ethylene pressure (maintained by continuous supply), 20 min reaction time at 50 °C; activity in kg(polymer) (mmol catalyst)$^{-1}$ h^{-1} (±10%).

the $J_{C,F} \approx 2\ J_{H,F}$ relationship for "long-range through-space" coupling is well-established.[42]

The appeal and versatility of chelating σ-aryl catalysts have gained greater prominence. Concurrent with our initial publications, researchers at Symyx and Dow developed a high-performance class of pyridylamido [N,N,C]-Hf isotactic propylene polymerization catalysts (which are amide congeners of our [O,N,C] system) through the use of high-throughput screening,[43] and described their employment in combination with Zr bis(phenoxyimine) catalysts for production of multiblock polyolefin materials via a novel chain shuttling mechanism.[44] Mechanistic studies probing the active species for these[45] and related[46,47] Zr catalysts (Chart 3, **X–XII** respectively) have been undertaken. Coates et al. reported that metalation of vinyl-appended pyridylamido[48] and phenolate-amine[49] ligands with Group 4 alkyl derivatives was found to afford C(sp^3)-chelating complexes (Chart 3, **XIII** and **XIV**), which catalyzed the living isoselective polymerization of α-olefins. The application of chelating (σ-aryl)-imine-amido Hf complexes (Chart 3, **XV**) to mediate the oxidant-free coupling of internal alkynes and 2-alkylpyridine was recently described by Mashima and co-workers.[50]

■ CATALYTIC REACTIVITY AND INSIGHTS

With regard to Group 4 [O,N,C] catalysts, the Ti derivatives consistently display superior performance for olefin polymerization. For example, catalyst **5** gave reasonably high ethylene polymerization efficiencies and comonomer incorporation (40

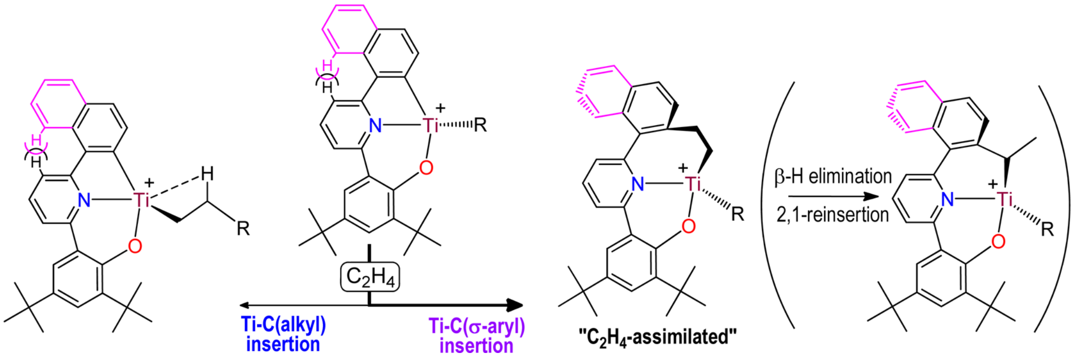


Figure 8. Kinetically competitive reaction pathways generated by ethylene insertion into [O,N,C(σ-naphthyl)]TiR^+ species.

mol % for propylene; 20 mol % for norbornene) with narrow polydispersity (M_w/M_n = 1.5 for ethylene-norbornene copolymerization using $[Ph_3C][B(C_6F_5)_4]$).[13] In order to create a F-dominated catalytic environment, the *tert*-butyl phenolate substituent in complex **1** was replaced with a CF_3 moiety to give the tris-CF_3 derivative **14**, for which further enhancement in electrophilicity and its ability to counteract the effects of ion-pairing (with fluorinated cocatalysts) were expected.[51] Compared with **1**, the ethylene polymerization activities for **14** with $[Ph_3C][B(C_6F_5)_4]$ at 50 °C were substantially higher and improvements in polymer properties were achieved [polymerization conditions: identical to those described in Figure 7; results for **14** (**1** in parentheses): activity =1.41 (0.23) kg $mmol^{-1}$ h^{-1}; 10^{-5} M_n = 5.36 (0.29)].

Investigations into the effects of σ-aryl substituents upon olefin homo- and copolymerizations by Ti-[O,N,C] catalysts, in conjunction with MAO[12] and trityl borate,[52] revealed (i) superior activities for derivatives bearing a σ-aryl substituent [especially benzo (C_4H_4), forming σ-naphthyl] in an ortho position directly adjacent to the pyridyl ring (i.e., "py-adjacent"), and (ii) protection of the active site by a substituent adjacent to the metal center is not necessary (and may be detrimental to efficiency). However, it became apparent that these catalysts suffer from the production of high M_w/M_n (and occasionally multimodal) polymers, implying multisite behavior. We postulated, based on a crystal structure showing repulsion between a py-adjacent chloro substituent and a pyridyl proton,[52] that the py-adjacent substituent may impact upon the Ti-[O,N,C] chelation by introducing strain at the Ti−C(σ-aryl) linkage, thereby facilitating olefin insertion into this bond to afford supplementary "olefin-assimilated" active species (this refers to a modified $[M-C_2H_3R-aryl]$ species arising from olefin insertion into the M−C(sp^2) bond of a chelating σ-aryl ligand), analogous to that reported for the [N,N,C]-Hf system.[45,53] Evidently, this scenario would explain the absence of commendable polymer properties (corresponding to suppressed β-H elimination) for F-containing catalysts such as **1** and **14**, since the olefin assimilation process would displace the fluorinated moiety from the catalytic center and preclude any potential weak attractive ligand−polymer interactions.

We recently employed a systematic approach for studying the impact of both py-adjacent (R^a) and phenolate (R^d) substituents upon ethylene polymerization behavior (Figure 7).[54] The polymerization results using $[Ph_3C][B(C_6F_5)_4]$ showed that the σ-naphthyl moiety was able to confer enhanced activities, while suitable steric protection afforded by the phenolate substituent can improve catalyst integrity and afford high-M_w polymers. The cumyl-phenolate σ-naphthyl catalyst (**20**) at 50 °C displayed elevated activity (2.7 kg $mmol^{-1}$ h^{-1}) and produced polyethylene with high M_n (4 × 10^6) and an M_w/M_n value (2.5) approaching single-site character, but multisite behavior was prevalent for other catalysts.

Hence, DFT calculations were performed to probe the initial ethylene insertion and propagation steps, the role of the py-adjacent substituent, as well as rationalize the superior efficiencies of σ-naphthyl catalysts. Significantly, these studies revealed several kinetically competitive reaction pathways and active sites (Figure 8). In particular, ethylene assimilation (insertion into Ti−C(σ-aryl) bond) was found to be faster than conventional Ti−C(alkyl) insertion for all py-adjacent substituents (**15**−**18**), and chain propagation for the resultant ethylene-assimilated species also proceeded along a lower-energy pathway. Interestingly, the activation barrier for ethylene insertion/propagation was calculated to be the lowest for σ-naphthyl (**18**), which was ascribed to its ability to facilitate formation of the initial $[Ti-CH_2CH_2-aryl]$ species through thermodynamic means (by alleviating steric repulsion), as well as lower the activation barrier for successive ethylene insertion (by weakening the η^2-benzyl coordination). Furthermore, subsequent isomerization via β-H elimination and 2,1-reinsertion to give a benzylic-type [Ti−CH(Me)−aryl] species was determined to be another viable pathway. Hence, the considerable complexity of this system became apparent from these investigations, and the likelihood of multiple catalytic species (each with potentially different chain propagation and termination rates) is thus consistent with the multisite character during polymerization.[54]

With regards to the [O,C,N] system, the M···F interaction evident in **12** (and implicated for **11**) is generally accepted to be detrimental to catalytic efficiency, and it follows that **11** and **12** are inactive for ethylene polymerization. While appreciable activities were observed for the Ti catalysts **10** and **14**, they remain inferior to their [O,N,C] counterparts. New strategies to improve the performance of [O,C,N] catalysts will be reported in due course.

■ CONCLUSIONS AND PROSPECTS

In this Account, we have presented the development, characterization, and applications of Group 4 organometallic complexes supported by [O,N,C] and [O,C,N] chelating σ-aryl ligands. In these derivatives, the elusive C−H···F−C interaction has been investigated using multinuclear NMR spectroscopy and structural determinations, including for the first time a neutron diffraction study. Hence, the molecular structures may be considered as structural references for intramolecular C−H···F−C interactions that are spectroscopically discernible in solution. We contend that the conformational rigidity of these meta-substituted tris(hetero)aryl systems plays a fundamental role, by imposing "locked" conformations for the benzyl moieties and averting M···F interactions (at least for Ti derivatives). Our endeavors to probe the ^{1}H−^{19}F coupling using [^{1}H,^{19}F]-HMBC NMR experiments confirmed the existence of significant scalar (*J*) coupling across C−H···F−C interactions in M-[O,N,C−CF$_3$] (M = Ti, Zr) and Ti-[O,C,N−R^1] (R^1 = CF$_3$, F) complexes.

Inspired by the ortho-F···H(*β*) ligand−polymer interactions proposed for the living bis(phenoxyimine) Group 4 catalysts, we have demonstrated that such interactions are experimentally viable. These complexes therefore constitute synthetic models of weak attractive ligand−polymer interactions (WALPI), a novel strategy that offers the capability to manipulate the reactivity of the polymer chain during catalysis. For example, these interactions may be harnessed to stabilize hitherto unstable intermediates as well as impede unwanted processes, and may pave the way toward new polymerization reactions. In this context, literature reports have appeared which point to the applicability and generality of the WALPI concept derived from C−H···F−C interactions. In future developments, we intend to expand the range of [C−H···A] (A = hydrogen-bond acceptor) interactions and investigate their influence upon polymerization behavior.

With reference to recent success stories concerning multidentate *σ*-aryl auxiliaries, notable advances for these and related anionic carbon-based chelating ligands, as well as their employment in novel catalytic reactions, are keenly anticipated. The multisite behavior of Ti-[O,N,C] catalysts have been rationalized with the aid of DFT calculations, revealing several kinetically competitive reaction pathways and active sites (including ethylene-assimilated species) in addition to conventional chain propagation. Our current focus is directed toward controlling the multisite characteristics and the development of well-defined catalysts.

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Notes

The authors declare no competing financial interest.

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Cham-Chuen Liu was born in Hong Kong in 1987. He received his B.Sc. in chemistry in 2010 from City University of Hong Kong, where he is currently undertaking his Ph.D. studies under the supervision of Dr. Michael Chan. His research interests focus on the reactivity and catalytic applications of (carbon-based)-chelating postmetallocene complexes, and multinuclear NMR spectroscopy.

Michael Chan was born in Hong Kong and emigrated to England in 1978. He received his B.Sc. (1992) and Ph.D. (1995) from Durham University (supervisor: Prof. Vernon C. Gibson) and conducted postdoctoral research with Prof. Chi-Ming Che at the University of Hong Kong, where he was appointed Research Assistant Professor (1998), before joining City University of Hong Kong in 2004. Underpinned by employment of supramolecular strategies, his research focuses on design of novel catalyst systems for polymerization reactions and development of weak attractive ligand−polymer interactions in catalysis, and shape-persistent luminescent molecular architectures and materials.

ACKNOWLEDGMENTS

I am enormously indebted to my students, group members and collaborators, especially Dr. Jacqueline M. Cole (Cambridge) for the neutron structure elucidation, Dr. Kong-Hung Sze (University of Hong Kong) for [^{1}H,^{19}F]-HMBC experiments, Dr. Kai-Chung Lau (City University of Hong Kong) for DFT calculations, Drs. Nianyong Zhu (University of Hong Kong) and Shek-Man Yiu (City University of Hong Kong) for X-ray structural determinations, and Drs. Terunori Fujita and Haruyuki Makio (Mitsui Chemicals Inc.) for assistance in polymerization studies. The work described in this Account was supported by the Research Grants Council of the Hong Kong SAR, China (CityU 100313 and 100409).

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