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Weak Attractive Ligand–Polymer and Related Interactions in Catalysis and Reactivity: Impact, Applications, and Modeling

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Abstract: The notion of weak attractive ligand–polymer interactions is introduced, and its potential application, importance, and conceptual links with “cooperative” ligand–substrate interactions are discussed. Synthetic models of weak attractive ligand–polymer interactions are described, in which intramolecular weak C–H···F–C interactions (the existence of which remains contentious) have been detected by NMR spectroscopy and neutron and X-ray diffraction experiments. These C–H···F–C interactions carry important implications for the design of catalysts for olefin polymerization, because they provide support for the practical feasibility of *ortho*-F···H_{β} ligand–polymer contacts proposed for living Group 4 fluorinated phenoxyimine catalysts. The notion of weak attractive noncovalent interactions between an “active” ligand and the growing polymer chain is a novel concept in polyolefin catalysis.

Keywords: catalysis • hydrogen bonds • ligand–polymer interactions • neighboring-group effects • polymerization

1. Introduction

What are weak attractive ligand–polymer interactions? In the realm of metal-catalyzed olefin-polymerization reactions, the concept of noncovalent interactions between a “non-innocent” ancillary ligand and the growing polymer chain is new. The β-H-elimination step for a conventional cationic metal–(alkyl chain) catalytic species is facile, difficult to control, and often leads to undesirable chain transfer or termination reactions (Scheme 1 a). On the other hand, if one integrates a substituent that can interact with the polymer chain (such as a hydrogen-bond acceptor A; Scheme 1 b) into the ligand, then such interactions could potentially stabilize against or suppress β-elimination and chain-termination pathways. It is proposed that these interactions must be weak and dynamic in nature, otherwise the intrinsic chain-insertion/propagation process would be disrupted. Fragile attractive forces such as hydrogen bonding are ideally suited to this role because, in contrast to “hard” steric repulsions, they offer diversity and inherent tunability in a rational manner.

The concept of weak attractive ligand–polymer interactions in olefin polymerization is appealing and potentially influential because 1) it may pave the way towards an unprecedented ability to *control and manipulate the reactivity at the polymer chain* and 2) the stabilization of reactive intermediates and the generation of novel or unknown polymeric microstructures and materials may become possible.

2. Background and Context

As stated above, the viability of weak attractive ligand–polymer interactions depends on reversible intramolecular noncovalent contacts that constitute the fundamental (intermolecular) building blocks in supramolecular chemistry, whereas their proposed adaptability evokes the elementary ideas behind molecular recognition. Indeed, the development of weak ligand–polymer interactions necessitates the union of catalyst design and facets of supramolecular chemistry, and to fully exploit this novel approach, it is a prerequisite that the principles of supramolecular chemistry[1] and supramolecular synthons[2] are diligently applied. At this juncture, it is appropriate to present a brief overview of a conceptually related body of research concerned with the impact of secondary or “cooperative” ligand–substrate contacts through hydrogen bonds and associated noncovalent “supramolecular” interactions upon organic/organometallic catalysis and reactivity.[3,4] However, the contrast between these contacts and weak attractive ligand–polymer interactions should be noted; the former are predominantly employed for activation and/or directing purposes, whereas stabilizing effects are intended for the latter.

2.1. Cooperative Ligand–Substrate Interactions in Biomimetic and Multifunctional Catalysts

Nature is, in the form of enzymes, the supreme designer of catalytic reactions that involve multiple substrate interactions to enhance efficiency and selectivity. Considerable

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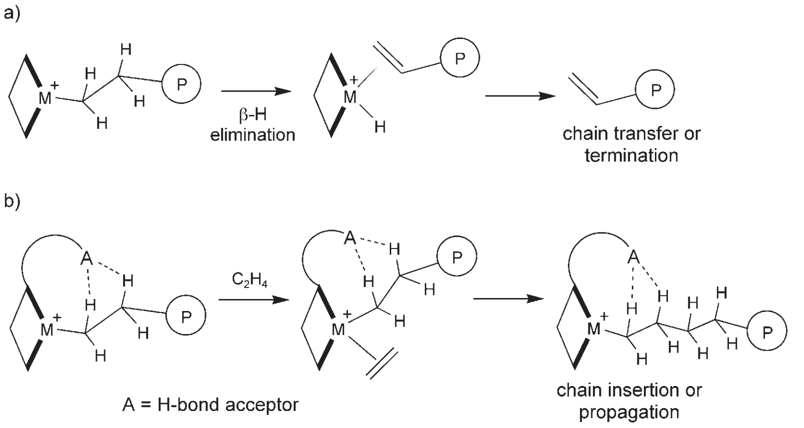


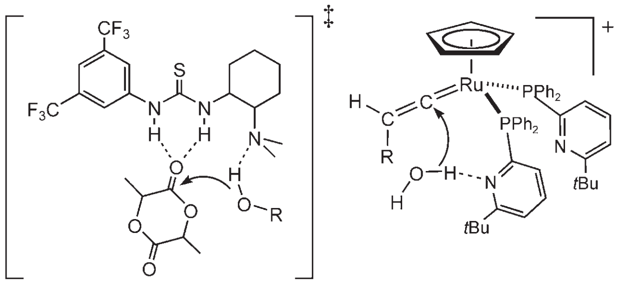
Scheme 1. Metal-catalyzed olefin-polymerization reactions. a) Conventional catalyst. b) Potential advantages of weak ligand–polymer interactions.

effort has been devoted to emulating this exceptional reactivity by the development of synthetic “cooperative” organo- and metallocatalysts featuring hydrogen-bonding moieties in proximity to the active site that can affect the catalytic cycle and alter product profiles.[5] Several classes of structurally diverse multifunctional metal-based catalysts have been described, wherein weak “secondary” noncovalent interactions with substrates were indicated or demonstrated.[6–8]

For example, a prolific and versatile family of bifunctional organocatalysts that employ urea/thiourea H-bond donors with an additional H-bond acceptor for substrate activation (Scheme 2) was recently developed for a wide variety of organic transformations,[9] and detailed mechanistic studies revealed the unequivocal impact of the hydrogen-bonding interactions and especially the Brønsted basic H-bond acceptor group (e.g., amine or imine).[10] Moreover, reports that bifunctional organoruthenium catalysts that bear pendant imidazolyl- and pyridylphosphine ligands can mediate the anti-Markovnikov hydration of terminal alkynes[11] further exemplify the ability of peripheral hydrogen-bonding substituents to activate substrates towards unusual and unprecedented reactivity.

2.2. Impact of Noncovalent Interactions upon Organic and Organometallic Reactivity

It is interesting to highlight selected instances of neighboring-group effects that are noncatalytic but nevertheless of relevance to this discussion. The atypical insertion chemistry of hydroxy-substituted aryl–palladium complexes with unsaturated nitrile substrates has been attributed to the involvement of the *ortho*-OH moiety, which “assists” the reaction by hydrogen bonding/transfer to the nitrile N atom.[12] The preferential *ortho* iodination of β- and γ-aryl alkylamine compounds that bear a trifluoroacetamide group was recently reported, and the unexpected selectivity was ascribed to a mechanism featuring “intramolecular electrophile delivery” by the CF_3 substituent through C−F···I−X interactions.[13] Significantly,



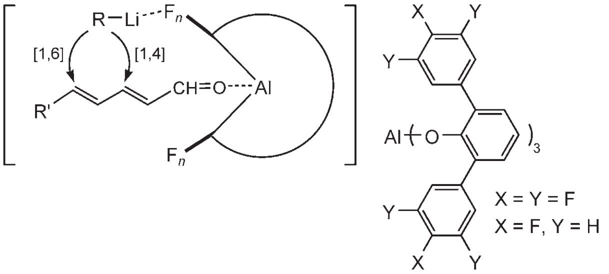
Scheme 2. Examples of bifunctional organocatalysts (left: proposed hydrogen-bonded transition state in ring-opening polymerization of lactide[10d]) and transition-metal catalysts (right: Brønsted base activated anti-Markovnikov hydration of terminal alkynes[11]).

Abstract in Chinese:

作者提出了配體和聚合物的微弱相互吸引力概念、以及討論了其潛在應用性和重要性，概念亦引申至配體和附體的相互吸引力。藉由核磁共振光譜、中子和 X 光衍射實驗觀察到分子內的微弱 C–H···F–C 相互吸引力（這存在性仍然是爭論中），作者描繪出配體和聚合物微弱相互吸引的虛擬模型；因為從理論計算學得知第四組金屬元素觸媒劑的氟化苯氧基亞胺配體與聚合物的接觸 ortho-F···H_β有實在的可能性，C–H···F–C 相互吸引力為聚合作用觸媒劑的設計帶來新的啟示。在有機化合物聚烯烴觸媒劑的研究中，利用「活潑的」配體和聚合物的微弱非共價相互吸引力是一個新穎的概念。

Michael Chan *received his PhD in 1995 from Durham Univ. under Prof. Vernon C. Gibson (Imperial College, London) in catalyst design and polymerization technology. He continued his studies as a postdoctoral fellow with Prof. Chi-Ming Che in light-emitting materials at the Univ. of Hong Kong, where he was appointed Research Assist. Prof. in 1998. He joined City Univ. of Hong Kong as an Assist. Prof. in 2004. His research focuses on the development of novel catalyst systems and metal-mediated polymerizations, as well as functional materials for sensory and environmental applications, with an emphasis on supramolecular strategies.*

the protruding aromatic C−F moieties at the "lip" of the Lewis acidic substrate-binding site in Al(OAr)$_3$ were proposed to coordinate and activate RLi (R = alkyl, allyl) reagents through C−F···Li$^{\delta+}$−R$^{\delta-}$ contacts, so that the nucleophilic attack is directed at preferred positions of the unsaturated aldehyde substrates (Scheme 3).[14] The unique reactivity and selectivity observed in these transformations are accomplished through the weakly attractive metal–fluorine contacts and the increased depth of the receptor site due to the peripheral F atoms.

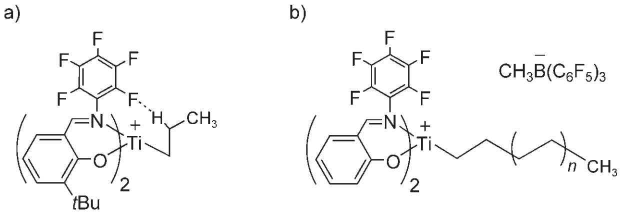


Scheme 3. Directing and activating effects of C−F groups in Lewis acidic Al(OAr)$_3$ receptors.[14]

2.3. Fluorinated Group 4 Phenoxyimine Catalysts: Living Olefin Polymerization and Weak Attractive Ligand–Polymer Interactions

The notion of weak ligand–polymer interactions was evoked by Fujita and co-workers for a novel class of Group 4 olefin-polymerization catalysts that bear fluorine-rich bis(phenoxyimine) auxiliaries.[15] These catalysts have generated tremendous interest because, besides their outstanding activities and versatility, the observation of the exceedingly rare 2,1-insertion of olefins, as well as diverse applications in the synthesis of multiblock copolymers and chain-end functionalized polyolefins, Ti^{IV} derivatives with (perfluorinated aryl)imine substituents have been shown to mediate the living polymerization of ethylene and propylene (with high syndiotacticity) at remarkably elevated temperatures of up to 70 °C.[16] Notably, the living propagating species[17] generated from the corresponding methyl cation and a slight excess of ethylene was explicitly observed in solution at room temperature by ^{1}H NMR spectroscopy (Scheme 4).[18] Furthermore, the Coates[19] and Pellecchia[20] groups have employed these phenoxyimine catalysts for the production of stereoregular polymers, and theoretical studies of the catalytic species and reaction mechanism have been undertaken.[21]

To elucidate the vital function of the fluorine groups in living-polymerization processes, Fujita and co-workers performed DFT calculations on the probable active species, which indicated that a β-hydrogen atom of the polymer chain and a C(sp^2)−F moiety *ortho* to the imine N atom are



Scheme 4. Fluorinated bis(phenoxyimine)–Ti catalyst for living olefin polymerization a) DFT-calculated[15] active species. b) Living propagating species observed by ^{1}H NMR spectroscopy.[18a]

engaged in a weak noncovalent C−H···F−C interaction (Scheme 4).[15] The *ortho*-F···H$_\beta$ interaction was proposed to mitigate the formation of a β-H agostic interaction (see Section 2.5.1) and, hence, hinder the reactivity of the β-hydrogen atom towards the metal and/or a coordinated olefin, thus resulting in the prevention of termination (β-H-elimination/transfer) processes. However, this interaction was not observed or verified. The use of the C−F unit as a hydrogen-bond acceptor in weak attractive ligand–polymer interactions is reasonable because it displays good robustness and can be tolerated by a catalytic center. Nevertheless, the postulated interaction with the low-polarity C−H bonds of the polymeryl chain (rather than O−H or N−H) may prompt reservations, and a hypothesized explanation based on C−H···F−C interactions is undoubtedly controversial.

2.4. C−H···F−C Hydrogen Bonds

At first glance, the manifestation of C−H···F−C contacts as weak ligand–polymer interactions is surprising because they are one of the weakest[22] hydrogen bonds to be proposed, and their existence, importance, and applicability remain controversial.[23] Notwithstanding this, the plethora of evidence espousing C−H···F−C contacts, based on structural determinations,[24] rotational spectroscopy,[25] and theoretical studies,[26] continues to accumulate conspicuously. The solid-state characteristics and (self-)assembly of richly fluorinated organic conjugated materials, with potential relevance in optoelectronics and nanotechnology, have been accredited to the influence of C−H···F−C interactions,[27] and sensing applications derived from these weak reversible contacts have been developed.[28] In biomolecular recognition, the incorporation of fluorinated motifs and the generation of fluorine-rich environments at nucleotide bases[29] and the active sites of peptides and enzymes[30] have been advocated, and beneficial effects from the resultant C−H···F−C contacts, such as enhanced affinity and selectivity, have been realized. Incidentally, the spectroscopic and structural observation of the more polar N−H···F−C interaction in weakly coordinating amine-based borane and diborate cocatalysts was recently described,[31] whereas "cooperative" noncovalent Si···F−C contacts were invoked to rationalize the optical activity of fluorinated poly(alkylsilane) materials.[32]

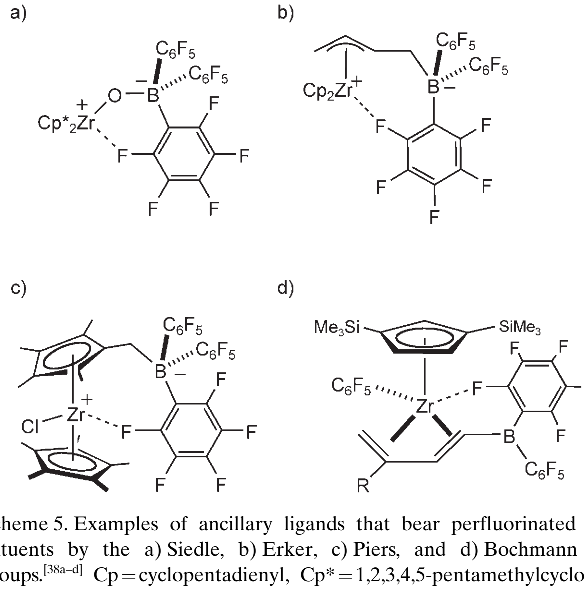
2.5. Weak Interactions in Olefin Polymerization and Related Processes

2.5.1. Agostic Interactions

It is universally acknowledged that weak attractive noncovalent interactions play multiple critical roles during the catalytic cycle of olefin polymerization. The existence and mechanistic impact of agostic interactions between the α- and β-hydrogen atoms of the polymer chain and the metal center have been established.[33,34] The involvement of analogous α-Si–H···M interactions in Ti-catalyzed silane-dehydrocoupling reactions was recently suggested.[35]

2.5.2. Noncovalent M···F–C Contacts and Hemilabile Ligands

The propensity for organofluorine moieties, in the form of supposed "noninteracting" perfluorinated cocatalysts[36] and fluorinated ligand fragments,[37] to coordinate metal centers through weak C–F···M contacts (compare Section 2.2[14]) has attracted particular attention because it can block or saturate the catalytic site and cause deactivation. Conversely, several studies have exploited such interactions for the stabilization of extremely electrophilic, unsaturated catalytic centers by elegantly assembling ancillary ligands appended with perfluorinated substituents (Scheme 5).[38] Schrock et al. indicated the possible participation of C–X···M (X = F, Cl) interactions to rationalize the 1-hexene-polymerization behavior and organometallic reactivity of multidentate amido/donor-ligated complexes that bear *ortho*-halide substituents.[39] Intriguingly, Grubbs and co-workers attributed the enhanced efficiency of olefin metathesis of a ruthenium catalyst supported by a fluorinated N-heterocyclic carbene ligand to the effects of a C–F···Ru interaction.[40]



Scheme 5. Examples of ancillary ligands that bear perfluorinated substituents by the a) Siedle, b) Erker, c) Piers, and d) Bochmann and groups.[38a–d] Cp = cyclopentadienyl, Cp* = 1,2,3,4,5-pentamethylcyclopentadienyl.

The conceptually related strategy of developing polydentate hemilabile ligands[41] that bear a flexible pendant donor group, whereby the substitutionally labile donor can be displaced from and yet remain available for recoordination to the catalytic site in a reversible fashion, has also been undertaken in the search for new catalysts for olefin polymerization.[42] In this context, it is appropriate to highlight the difference between weak attractive ligand–polymer interactions and the approaches described in this section, because in the latter, the fluorine or pendant donor group interacts directly with the metal center. Indeed, it is interesting to note the design relationship between biomimetic/multifunctional catalysts, in which the secondary or cooperative interaction involves coordination to the metal-based active site (see Section 2.1), and those supported by hemilabile ligands.

2.5.3. Repulsive Ligand–Polymer Interactions

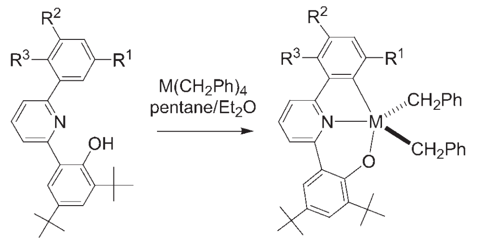
Tremendous advances have been achieved in the development of Group 4 metallocene-catalyzed stereoselective α-olefin polymerizations.[34,43] The mechanism of stereocontrol has largely been elucidated and originate from steric effects or repulsive nonbonding interactions between the approaching prochiral olefin and Cp ligands that bear a variety of bulky substituents. Significantly, unlike attractive interactions, such "hard" contacts cannot be rationally modulated.

3. Modeling Weak Attractive Ligand–Polymer Interactions

3.1. Spectroscopic Observation of Intramolecular C–H···F–C Contacts in Post-Metallocene Complexes

We communicated the first spectroscopic and X-ray crystallographic evidence for the existence of weak C–H···F–C interactions, which are reminiscent of the *ortho*-F···H_β contacts proposed for the living Ti–bis(phenoxyimine) catalysts by Fujita and co-workers,[15] in Group 4 complexes that bear fluorinated pyridine-2-aryloxide-6-(σ-aryl) [O,N,C] auxiliaries.[44] The complexes impose a fluorinated substituent in the direct vicinity of the catalytic site (R^1 in Scheme 6), but the R^1 group is crucially "tethered back" due to the rigidity of the ligand to avert unwanted C–F···M contacts. In this regard, literature reports of fluorine-rich ancillary ligands are scarce and portray nonliving olefin-polymerization processes.[39a,45]

Our interest in developing [O,N,C] ligands to support olefin-polymerization catalysts stems from the following: 1) aryloxide-type chelates have been successfully applied to post-metallocene catalyst design for many years;[46] 2) although the σ-aryl moiety is seldom used,[47] it is principally a σ donor with minimal π donation and is thus anticipated to enhance the electrophilicity of the metal center; 3) the resultant metal–C(σ-aryl) linkage should be more inert relative to the metal–C(alkyl) counterparts. We recently designed and synthesized a series of Group 4 complexes supported by [O,N,C] ligands (important examples are shown in Scheme 6).[48,49]



R^1	R^2	R^3	M
CF_3	CF_3	H	Zr (**1**), Ti (**7**)
CF_3	H	F	Zr (**2**), Ti (**8**)
CH_3	H	CH_3	Zr (**3**), Ti (**9**)
F	CF_3	H	Zr (**4**), Ti (**10**)
Cl	H	Cl	Zr (**5**), Ti (**11**)
Br	Br	H	Zr (**6**), Ti (**12**)

Scheme 6. Synthesis of Group 4 catalysts that bear pyridine-2-phenolate-6-(σ-aryl) [O,N,C] ligands.

Multinuclear NMR spectroscopic characterization of complex **1** produced unexpected but revealing results: 1) the upfield resonance of the diastereotopic benzyl CH_2 hydrogen atoms, which typically appear as a doublet of doublets in the ^1H NMR spectrum, was observed as a complicated multiplet (overlapping doublet of quartets) that collapsed to the expected doublet upon ^{19}F decoupling and was also affected by solvent polarity (Figure 1; formal $^{1h}J_{H,F}=3.3$ and 3.1 Hz in C_6D_6 and CD_2Cl_2 respectively); 2) correspondingly, the more downfield of the two resonances in the ^{19}F NMR spectrum was relatively broad but underwent discernible sharpening upon ^1H decoupling; 3) the $^{13}C\{^1H\}$ NMR signal for the methylene carbon atom appeared as an unusual but distinctive quartet (formal $^{2h}J_{C,F}=5.9$ Hz in C_6D_6); 4) the ^{19}F–^1H 2D correlation experiment for the CH_2 region revealed a cross-peak between the upfield ^1H multiplet and the broadened downfield ^{19}F resonance only. Virtually identical spectroscopic features were observed for **2**, **7**, and **8**, and can be persuasively ascribed to intramolecular C−H···F−C coupling between one methylene hydrogen atom on each benzyl ligand and the three equivalent ^{19}F nuclei of the rapidly rotating CF_3 group.[44]

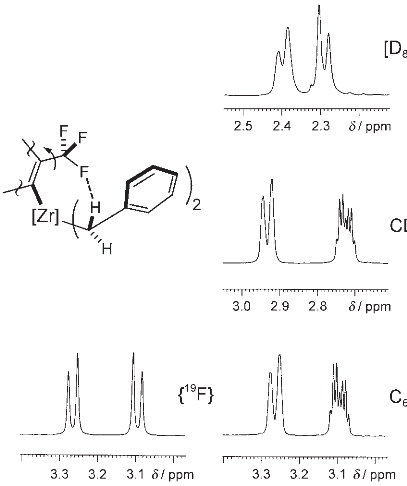


Figure 1. ^1H NMR spectra (400 MHz, 300 K) of the diastereotopic methylene hydrogen atoms in **1**, demonstrating the effects of ^{19}F decoupling and solvent polarity.

$^1H/^{19}F$ NOE difference experiments,[50] in which the ^1H NMR spectrum is observed as ^{19}F nuclei are selectively irradiated, were performed to elucidate the proton environments around the CF_3 groups in **1**. Importantly, irradiation of the proximal (adjacent) CF_3 moiety yielded enhancement of the upfield multiplet but not the downfield doublet of the CH_2 hydrogen atoms. This demonstrates the immediacy of only one methylene hydrogen atom on each benzyl group to this CF_3 unit, consistent with the proposed model (Figure 1), and implies that the M–C(benzyl) bonds cannot rotate freely (see Section 3.2). For **2** and **8**, additional intraligand H···F coupling was detected between a pyridyl H atom and the peripheral F atom at R^3, whereas C−H···F−C coupling with the sole F atom at R^1 in **4** and **10** is absent because of the excessive F···H(methylene) separation. Last but not least, NMR spectroscopic characterization of the alkyl cation generated from the interaction of **1** with $B(C_6F_5)_3$ also implied weak interactions between the CF_3 and benzyl substituents. Therefore, the intramolecular C−H···F−C contacts detected spectroscopically in solution serve as unique models of weak attractive ligand–polymer interactions at a catalytic center for olefin polymerization.

3.2. Structural Characterization: The First Neutron Diffraction Study of C−H···F−C Interactions

Neutron diffraction is ideal for the investigation of hydrogen bonds in crystal lattices, because unlike X-ray crystallography, the position of H atoms can be accurately located and refined. We reported[48] the neutron diffraction structure of the fluorinated Zr complex **1** (Figure 2), which represents the first characterization of the controversial and elusive C−H···F−C interaction by a neutron diffraction study. Saliently, one of the methylene hydrogen atoms on each benzyl ligand

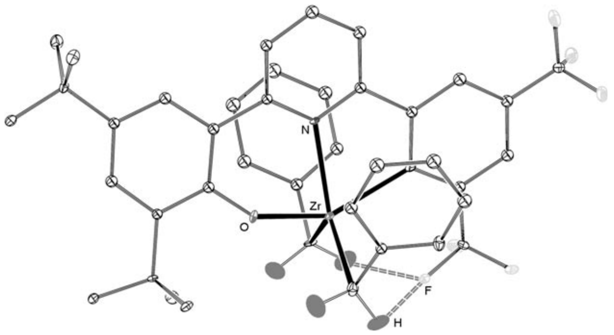


Figure 2. Perspective view of **1** from the neutron diffraction study, showing selected hydrogen atoms. Ellipsoids are drawn at the 50 % probability level.

points toward the CF_3 moiety, and the observed H···F distances (2.572(6) and 2.607(5) Å) and C–H···F angles (103.3(4) and 108.2(3)°) are entirely consistent with the C–H···F–C interactions previously determined from X-ray diffraction studies.[24,27,28]

The X-ray crystal structures of several bis(benzyl) complexes, including **7**, **8**, and **10**, were determined. As expected, the corresponding H···F (or C···F) distances and C–H···F angles in **7** and **8** similarly reflect the presence of intramolecular C–H···F–C interactions, albeit based on calculated hydrogen positions. Notably, all M···F separations (>2.95 Å for Zr, >3.15 Å for Ti) far exceed the expected or previously reported values for M···F–C interactions.[36,38] All structures exhibit close M···C_{ipso}(benzyl) distances and acute M–C–C_{ipso}(benzyl) angles, which signifies η^2 coordination to the metal.

The unusual but recurring *anti*,*anti* orientation of the benzyl groups, which protrude towards the pyridyl moiety in **1**, **7**, **8**, and **10**, contrasts starkly with the conventional *syn*, *anti* arrangement observed for analogues in which R^1 = H[44] and for related post-metallocene complexes.[46] The *anti*,*anti* conformation is ascribed to the severe steric congestion at the metal cleft, which cannot support η^2-benzyl coordination in the equatorial plane between the *tert*-butyl and fluorinated substituents; as a consequence, rotation of the M–C(benzyl) bonds is greatly hindered. Therein lies the uniqueness of the molecular structure of **1**: the overall [O,N,C] and benzyl ligands are rigid and are expected to remain relatively static in solution, so that the benzyl CH_2 and CF_3 units become "locked" in position and primed for intramolecular C–H···F–C interactions. In other words, it may not have been possible to observe the spectroscopic H···F coupling if complex **1** had exhibited a more flexible and dynamic molecular structure.

3.3. Discussion and Evaluation

It is instructive to compare the NMR spectroscopic data showing intramolecular C–H···F–C coupling, as well as associated structural parameters, with those of related organometallic complexes in the literature. Van Eldik, Goldberg, and co-workers[51] studied the spectroscopic and structural properties of $Tp^{(CF_3)_2}PtMe_3$ ($Tp^{(CF_3)_2}$ = HB[3,5-bis(trifluoromethyl)pyrazolyl]$_3$) and tentatively indicated the presence of weak C–H···F–C coupling (formal $^{1h}J_{H,F}$ and $^{2h}J_{C,F}$ values of 1.8 and 3.9 Hz, respectively, in [D_6]acetone) between the methyl ligands and CF_3 substituents, as supported by the observation of close H···F (or C···F) contacts in the X-ray crystal structure. Clark and Manzer[52] attributed the detected H–F coupling ($J_{H,F}$ = 2–3 Hz in $CDCl_3$) between the methyl protons (and H^3 of Tp) and F atoms in a series of TpPtMe(F_n-olefin) complexes to a "through-space" mechanism. In contrast, Gade and co-workers[53] proposed that the noticeably larger $J_{H,F}$ and $J_{C,F}$ coupling constants for the tripodal amido-ligated methylzirconium derivative (FN_3)ZrMe (FN_3 = HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$) arise from weak Zr···F coordination, as signified by a close Zr···F contact (2.535(5) Å) in the crystal structure of a chloro-bridged congener, and were accordingly assigned as ^3J(H–C–Zr···F) and ^2J(C–Zr···F) (8.4 and 17.6 Hz, respectively, in C_6D_6). Crabtree and co-workers reported that the intramolecular (six-membered) N–H···F–Ir hydrogen bonding in [(2-NH$_2$py)IrF(H)$_2$(PPh$_3$)$_2$] (py = pyridyl) and the cyclometalated 2-amino-7,8-benzoquinoline congener afford noticeably larger $J_{H,F}$ values of 63 and 52 Hz at 253 and 183 K, respectively.[54] Besides, there is a comprehensive history of long-range or through-space C–H···F–C coupling in fluorinated organic molecules.[55]

Overall, the spectroscopic and structural data in the present work[44,48] evidently bear closer (relative to the amido system) resemblance to the Pt–tris(pyrazolyl)borate systems described above. Undisputably, the M···F separations observed for the [O,N,C] derivatives are too long to be considered even as weak interactions. This supports the conclusion that the spectroscopically detected ^1H–^{19}F coupling occurs through C–H···F–C interactions and not by an M···F coordination mechanism. This hypothesis carries great importance because 1) in complexes whereby fluorinated substituents can undergo M···F–C contacts that are stronger than C–H···F–C interactions, the latter will apparently be preempted, and 2) it is known that such M···F contacts can cause crowding of the active site, impede approach of olefin substrates, and lead to suppressed catalytic activity (see Section 2.5.2). Moreover, DFT calculations[48] on the alkyl cationic complex derived from **1** (alkyl = *n*-propyl as model for polymer chain) revealed the presence of a weak interaction (2.606 Å) between one of the F atoms and a β-hydrogen atom of the propyl chain, which resembles the corresponding calculated structures of the fluorinated bis(phenoxyimine) Group 4 alkyl cations.[15]

4. Outlook

Future studies to elucidate the strength of the C–H···F–C interaction in this class of compounds and in general is required. It is anticipated that further applications of weak ligand–polymer interactions based on "supramolecular" principles can be developed. Indeed, this research direction promises a bright and unprecedented future for tailor-made catalysts and precise control of polymer synthesis derived from noncovalent interactions. Interestingly, Mecking and co-workers recently noted the effects of remote substituents on the activity and olefin-polymerization behavior of Ni–Schiff base derivatives, although the mechanism is currently unclear.[56]

The prospects for ancillary ligands that bear a σ-aryl moiety appear highly promising[57] on the basis of the excellent propylene-polymerization characteristics displayed by Hf–[N,N,C] (cyclometalated pyridylamido) catalysts[58] and their successful application, in tandem with Zr–bis(phenoxyimine) catalysts, in the commercial-scale production of attractive multiblock polyolefin materials by a remarkable "chain-shuttling" polymerization process.[59]

5. Summary

The foremost intention of this article is to stimulate interest and discussion in weak attractive ligand–polymer interactions. A relationship between the well-established strategy of cooperative or secondary ligand–substrate interactions and the new concept of weak attractive ligand–polymer interactions has emerged, and this link is underpinned by the reliance of both approaches on hydrogen bonding and analogous noncovalent or supramolecular interactions that must be weak, dynamic, and allow selectivity and molecular recognition.

A family of Group 4 post-metallocene catalysts, supported by F-functionalized tridentate ligands bearing the fluorine group adjacent to the metal/active site, has been designed and synthesized as models of weak attractive ligand–polymer interactions. Studies to elucidate the nature of the intramolecular C—H···F—C interactions in these complexes in solution (by multinuclear NMR spectroscopy) and the solid state (with neutron diffraction and X-ray crystallography) have been undertaken, and the evidence gathered signifies that the hydrogen-fluorine coupling occurs through C—H···F—C contacts rather than by an M···F coordination mechanism. Significantly, this work contains an authenticated example of a neutron diffraction structure that exhibits weak intramolecular C—H···F—C interactions, the geometric parameters of which are manifested as NMR-discernible H–F coupling in solution. Furthermore, these results substantiate the *ortho*-F···H_{β} ligand–polymer contacts proposed by Fujita and co-workers and demonstrate that such interactions are experimentally feasible.

In 1996, Crabtree et al.[3] were prescient in their view that "It may be possible to use intra- and intermolecular H-bonds to influence structure, equilibria, and reactivity in transition-metal complexation and catalysis, in molecular recognition, and in designing catalysts for such reactions as asymmetric hydrogenation. After all, nature uses hydrogen bonds very successfully in enzymes, so we might benefit by introducing them into our synthetic catalysts." We believe that this statement is now applicable to metal-catalyzed olefin-polymerization reactions. As opposed to conventional agostic and M···X contacts, attractive noncovalent interactions between the growing polymer chain and a judiciously designed "active" ligand is an innovative concept in olefin polymerization, and new guidelines for the design of polymerization catalysts can be envisaged.

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