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New C_1-Symmetric Ph_2C-Bridged Multisubstituted *ansa*-Zirconocenes for Highly Isospecific Propylene Polymerization: Synthetic Approach via Activated Fulvenes†

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The synthesis of multisubstituted diphenylmethylene-bridged fluorenyl−cyclopentadienyl proligands $Ph_2C(3,6\text{-}tBu_2FluH)(3\text{-}R^1\text{-}5\text{-}R^2C_5H_3)$ (Flu = fluorenyl; R^1 = *tert*-butyl, R^2 = H (**2a**); R^1 = *tert*-butyl, R^2 = Me (**2b**); R^1 = cumyl, R^2 = Me (**2c**)) was developed using a nucleophilic addition protocol based on regular and activated fulvenes. Two highly congested proligands (**2b**,**c**) were prepared in a two-step procedure, starting first by addition of $[3,6\text{-}tBu_2Flu]^+Li^-$ onto 6,6′-bis(*p*-chlorophenyl)fulvenes, followed by a Pd-catalyzed reductive dechlorination. The X-ray crystal structures of **2a** and $\mathbf{2b}\cdot CH_2Cl_2$ were determined. These revealed a preorganized sandwichlike positioning of the fluorenyl and cyclopentadienyl plane fragments, similar to that observed in the metallocenes. The corresponding dichlorozirconium complexes $\{Ph_2C(3,6\text{-}tBu_2Flu)(3\text{-}R^1\text{-}5\text{-}R^2\text{-}C_5H_2)\}ZrCl_2$ (R^1 = *tert*-butyl, R^2 = H (**3a**); R^1 = *tert*-butyl, R^2 = Me (**3b**); R^1 = cumyl, R^2 = Me (**3c**)) were prepared by salt metathesis and characterized by elemental analysis, NMR spectroscopy, and X-ray crystallography (for **3a**,**c**). These C_1-symmetric zirconocenes exist as racemic mixtures of two enantiomers, arising from planar chirality at the Cp ring. When activated with MAO, **3a**,**b** showed high activity in the polymerization of propylene (5020 and 3580 kg of iPP mol^{-1} h^{-1}, respectively; toluene solution, 60 °C), affording highly isotactic ($[m]^4$ 94.0%) polymers with molecular weights in the range M_w = 30 000−175 000, which are similar to those obtained with the corresponding CMe_2-bridged catalysts. No activity was observed with the **3c**/MAO system, which was proposed to be due to a deactivation involving a cumyl phenyl ring. This was supported by DFT computations on the cationic species $[\{Ph_2C(3,6\text{-}tBu_2Flu)(3\text{-cumyl-5-Me-}C_5H_2)\}ZrMe]^+$, which revealed facile coordination of the phenyl ring to the metal center, followed by C−H(phenyl) activation at the ortho position with concomitant elimination of methane; propylene insertion into the resulting ortho-metalated species was found to be thermodynamically unfavorable.

Introduction

Among the great number of industrially relevant metallocene-based polymerization catalysts, group 4 *ansa*-metallocenes supported by fluorenyl−cyclopentadienyl ligands hold a unique position. Their highly tunable ligand platform allows the introduction of various substituents at different positions of the cyclopentadienyl (Cp), fluorenyl (Flu), and bridge moieties and, therefore, access to a class of catalysts that features high catalytic activity, excellent control, and remarkable stereospecificity in olefin (co)polymerization.[1] For instance, in the series of single-carbon-bridged systems, C_s-symmetric precatalysts (Scheme 1; **I**), highly syndiotactic polypropylene is commonly produced ($[r]^4$ 75−91%; liquid propylene, MAO, T_{polym} = 40−80 °C).[2] Simple modification of the ligand skeleton in the precatalyst, namely, installation of a bulky substituent (*t*Bu group) at the 3-Cp position that imposes an overall C_1 symmetry of the molecule (Scheme 1; **II** and **III**), results in highly isospecific systems for polymerization of propylene ($[m]^4$ 79−98%; liquid propylene, MAO, T_{polym} = 40−80 °C).[2b,3,4] All these stereoselective polymerization catalyst systems operate via an enantiomorphic-site control mechanism.

† Part of the Dietmar Seyferth Festschrift. Dedicated to Prof. Dietmar Seyferth in warm appreciation of his decades of valuable service to the organometallic community.

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(2) For leading references, see: (a) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255. (b) Razavi, A.; Bellia, V.; De Brauwer, Y.; Hortmann, K.; Peters, L.; Sirol, S.; Van Belle, S.; Thewalt, U. *Macromol. Chem. Phys.* **2004**, *205*, 347.

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(4) (a) Wondimagegn, T.; Wang, D.; Razavi, A.; Ziegler, T. *Organometallics* **2009**, *28*, 1383. (b) Tomasi, S.; Razavi, A.; Ziegler, T. *Organometallics* **2009**, *28*, 2609.

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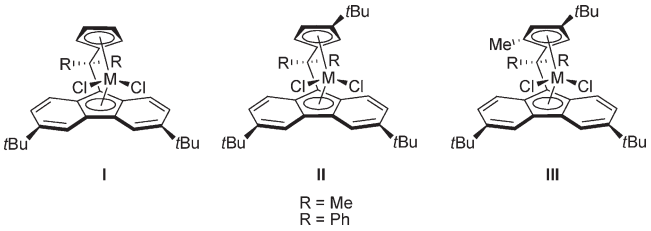
Scheme 1



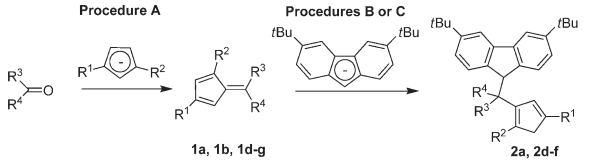
Another interesting feature of this class of catalysts is the influence of the distal substituents R in the R_2C bridge on the catalytic activity and the molecular weight of the resulting iPP. Thus, replacement of methyl groups with phenyl groups in the R_2C bridge enabled a ca. 4-fold increase of the molecular weight of polypropylene obtained with the syndiospecific system **I**; the same observation was made for the nonsubstituted fluorenyl system.[5] For those syndiospecific systems, it was proposed that such a replacement would result in an increase of hapticity (from η^1/η^3 to η^5) of the fluorenyl moiety and a concomitant decrease of electrophilicity of the metal center.[6] Some Ph_2C-bridged variations of the 3-substituted-Cp system **II** have been reported by Bercaw et al. (2-adamantyl or norbornyl instead of *t*Bu: hemiisotactic PP, $[m]^4$ 14−28%; liquid propylene, MAO, T_{polym} = 0−20 °C).[7] In this case, a similar 4-fold increase of molecular weights was observed upon going from Me_2C- to Ph_2C-bridged systems. On the other hand, metallocene systems of type **III** (i.e., 3,5-disubstituted Cp[8]) bearing such Ph_2C bridges, and their performance in propylene polymerization (anticipated to not only be highly isospecific but also offer high-molecular-weight polymers), have not been documented thus far.

Accordingly, we set out to synthesize Ph_2C-bridged proligands of the type **III** and *ansa*-zirconocene complexes derived therefrom and assess the influence of the phenyl groups on the production of iPP. As detailed here, the catalytic performances of the zirconium complexes were, after their activation, investigated in homogeneous polymerizations of propylene and compared to those of the classic system based on $\{Me_2C(3,6\text{-}tBu_2Flu)(3\text{-}tBu\text{-}5\text{-}MeC_5H_2)\}ZrCl_2$ (**III-Me$_2$**). Interestingly, the syntheses of the highly sterically hindered proligands and corresponding metallocenes proved to be quite challenging, regarding significant modifications of protocols used for analogous Me_2C-bridged systems.

Results and Discussion

Syntheses of Proligands. Nucleophilic addition of cyclopentadienyl-type anions to fulvenes has proven to be the most versatile and efficient route for the synthesis of the monocarbon-bridged bis(cyclopentadienyl) ligands.[9] A variety of such fluorenyl−cyclopentadienyl type ligands have been prepared via this economical procedure using the appropriate fulvene and fluorenyl anion. It appears, however, that the success of this reaction strongly depends on the nature of the substituents on the five-membered fulvene ring and, even more importantly, of the terminal substituents at the exomethylene group. For instance, 6,6′-undecamethylene- and 6,6′-tetradecamethylenefulvenes do not react with $[Flu]^-Li^+$ ($Flu^- = C_{13}H_9^-$ = fluorenyl anion), even in the presence of HMPA.[10] Indene-derived 6,6′-diphenylbenzofulvene showed no reactivity toward $[Flu]^-Li^+$, as well.[11] Also, 6,6′-diphenyl-2,5-dimethylfulvene and $[Flu]^-Li^+$ were found intact, whereas 6-phenyl-2,5-dimethylfulvene readily reacts with $[Flu]^-Li^+$ to give (after hydrolytic workup) the desired product Ph(H)C(FluH)(2,5-$Me_2C_5H_3$).[12] Nonetheless, the successful synthesis of several sterically hindered $Ph_2C(Flu^{\#}H)$(3-RCpH) proligands ($Flu^{\#}$ = fluorenyl, 2,7-di-*tert*-butylfluorenyl, octamethyloctahydrodibenzofluorene and R = H, 2-adamantyl) was reported by Bercaw.[7,13]

Scheme 2. Synthesis of Fulvenes and Flu/Cp Ligands



Procedures: **A:** (i) THF or Et_2O, RT, 1-2 h; (ii) HCl or NH_4Cl, 12 h
B: (i) Et_2O, 90 °C, 50-70 h; (ii) H^+
C: (i) THF, RT, 4 h; (ii) H^+

R	Proc.	Fulvene	Yield (%)	Proc.	Ligand	Yield (%)
R^1 = *t*Bu, R^2 = H R^3 = R^4 = Ph	**A**	**1a**	50	**B**	**2a**	21
R^1 = *t*Bu, R^2 = Me R^3 = R^4 = Ph	**A**	**1b**	60	**B, C** **D**	**2b** *	<2 50
R^1 = CMe_2Ph, R^2 = Me R^3 = R^4 = Ph				**D**	**2c**	74
R^1 = *t*Bu, R^2 = Me R^3 = R^4 = 4-Cl-Ph	**A**	**1d**	60	**B**	**2d**	60
R^1 = CMe_2Ph, R^2 = Me R^3 = R^4 = 4-Cl-Ph	**A**	**1e**	51	**B**	**2e**	80
R^1 = *t*Bu, R^2 = Me R^3 = R^4 = 4-F-Ph	**A**	**1f**	15	**B**	**2f**	7
R^1 = *t*Bu, R^2 = Me R^3 = R^4 = (3,5-CF_3)$_2$-Ph	**A**	**1g**	19	**B, C**	–**	

* these products were unavailable by routes **B** and **C** and were obtained from the parent chlorophenyl ligands **2d,e** by reductive dehalogenation (route **D**; Scheme 3)
** this reaction gave complex mixture of unidentified materials

In the present investigation, a variety of fulvenes (**1a**[14] and **1b**−**g**) were synthesized in good yields using an inexpensive and efficient methodology (Scheme 2).[15] To prepare the target proligands $Ph_2C(3,6\text{-}tBu_2FluH)(3\text{-}R^1\text{-}5\text{-}R^2C_5H_3)$, these fulvenes were subsequently reacted with the $[3,6\text{-}tBu_2Flu]^-$ anion (Scheme 2). It turned out that the relatively less crowded fulvene **1a**, which does not bear a methyl substituent at the 5-position, reacts with $[3,6\text{-}tBu_2Flu]^-Li^+$ exclusively in Et_2O at 90 °C (in an autoclave) over several days. The corresponding proligand was subsequently isolated in low yield (21%).[16] In striking contrast, the more sterically encumbered fulvene **1b** did not undergo nucleophilic addition of the fluorenyl anion under a variety of

(5) Razavi, A.; Peters, L.; Nafpliotis, L. *J. Mol. Catal. A* **1997**, *115*, 129.
(6) Razavi, A.; Atwood, J. L. *J. Organomet. Chem.* **1993**, *459*, 117.
(7) Miller, A.; Bercaw, J. E. *Organometallics* **2002**, *21*, 934.
(8) Those systems should be officially referred to as (1),2,4-trisubstituted. However, the (1),3,5 method of numbering the Cp ring in this publication is adapted for historical reasons (researchers first prepared the 3-*tert*-butyl-substituted complex and then complexes having an additional substituent at the "5" position).
(9) Day, J. H. *Chem. Rev.* **1953**, *53*, 167.
(10) Alt, H.; Jung, M. *J. Organomet. Chem.* **1998**, *568*, 87.
(11) Alt, H.; Jung, M.; Kehr, J. *J. Organomet. Chem.* **1998**, *562*, 153.
(12) Won, Y. C.; Kwon, H. Y.; Lee, B. Y.; Park, Y.-W. *J. Organomet. Chem.* **2003**, *677*, 133.
(13) Miller, S. A.; Bercaw, J. E. *Organometallics* **2004**, *23*, 1777.
(14) Miller, S. A.; Bercaw, J. E. *Organometallics* **2006**, *25*, 3576.
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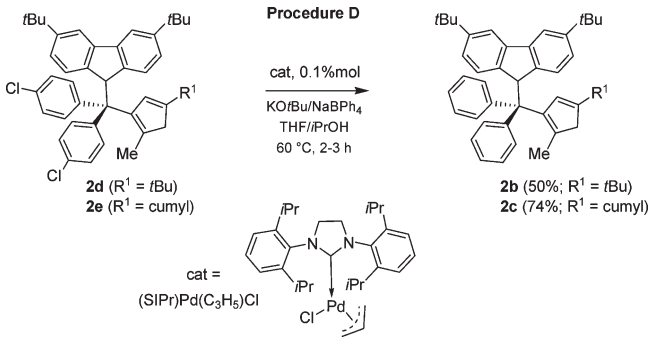
Scheme 3. Palladium-Catalyzed Reductive Dechlorination of 2d,e



conditions, some of them quite severe (solvents refluxing THF, Et_2O, nBu_2O, toluene; addition of HMPA).[17]

These observations prompted us to strive for an indirect approach, employing more reactive starting compounds. Thus, the reaction of [3,6-tBu$_2$Flu]$^-$Li$^+$ with "activated" fulvenes **1d**,**e**, which have slightly electron-withdrawing *p*-chloro substituents on both phenyl rings, allowed access to the corresponding ligand precursors **2d**,**e** in good yields (60 and 80%, respectively). The latter compounds were further subjected to a Pd-catalyzed reductive dechlorination using a 2:1 KOtBu/NaBPh$_4$ mixture as the reducing agent[18] and Nolan's catalyst (SIPr)Pd(C_3H_5)Cl[19] to afford selectively the desired compounds **2b**,**c** (Scheme 3). The analogous reaction of [3,6-tBu$_2$Flu]$^-$Li$^+$ with the bis(*p*-fluorophenyl)fulvene **1f** afforded adduct **2f** in significantly lower yield (7%).[20] However, a similar reaction of [3,6-tBu$_2$Flu]$^-$Li$^+$ with fulvene **1g**, which has two trifluoromethyl meta substituents on each phenyl ring, gave a complex mixture of unidentified products. Therefore, the use of chloro activating groups appears crucial to achieve selective nucleophilic addition of the fluorenyl anion and allow their subsequent selective removal, to eventually yield the diphenylmethylene-bridged proligand.

All the proligands prepared were stable at room temperature in solution and in the solid state, and the structures were authenticated by NMR spectroscopy, FAB-MS, and elemental analysis. The steric congestion of **2a**−**f** was evidenced by NMR spectroscopy in $CDCl_3$ or THF, which showed

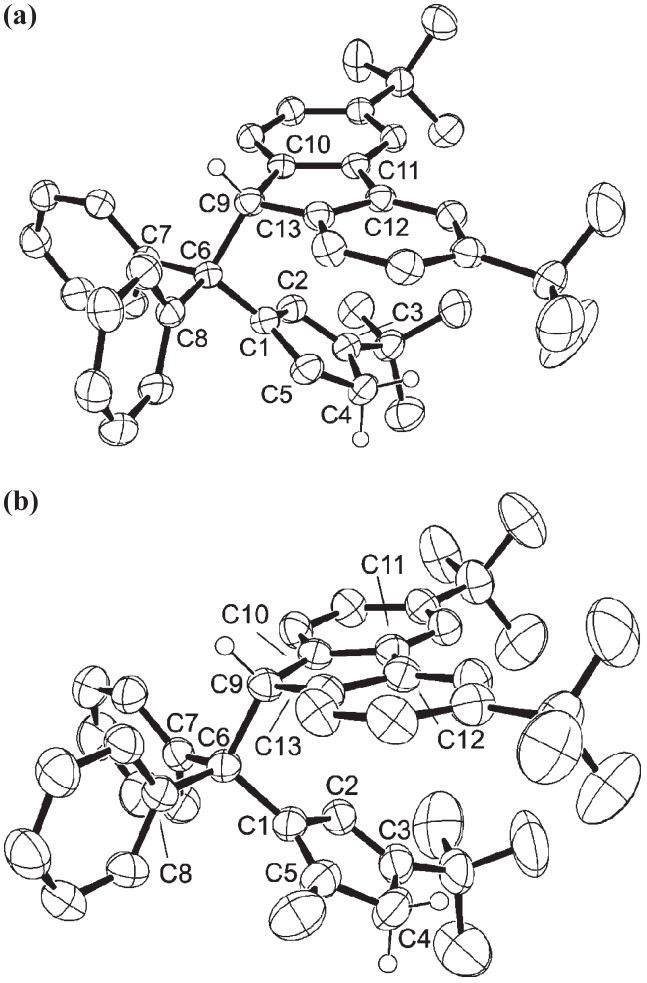


Figure 1. Crystal structures of compounds **2a** (a) and **2b**·CH_2Cl_2 (b). H atoms, except some of the five-membered rings, and solvates are omitted for clarity; ellipsoids are drawn at the 50% probability level.

fluxional behavior that was attributed to hindered rotation of all substituents around the bridging quaternary carbon atom (and possibly isomerization of C=C bonds within the CpH ring as well). In fact, the ^{1}H NMR spectra of these compounds were remarkably broadened at ambient temperature. On the NMR time scale, sharp resonances are observed at −40 °C. However, the complexity of these spectra, arising from the presence of several isomers and/or conformers (and the consequent overlapping of resonances), made them hardly informative (see the Supporting Information). Also, the fast exchange regime could not be reached, as these compounds decompose at 90−100 °C in $C_2D_2Cl_4$, giving thus far unidentified materials (most likely arising from C−C bond cleavage at the quaternary carbon atom).

To further characterize these constrained molecules, single-crystal X-ray diffraction analyses were performed for two of them, **2a** and **2b** (as the **2b**·CH_2Cl_2 solvate) (Figure 1). Interestingly, in the solid state, both molecules were preorganized in a sandwich-type structure with the Cp′H and Flu′H groups arranged in a fashion similar to that expected after coordination to a metal center. Furthermore, the conformers exhibit planar chirality, although both enantiomers are found in the two unit cells. Striking consequences of the sterically demanding substituents at the quaternary carbon atoms in **2a** and **2b**·CH_2Cl_2 are the C(1)−C(6)−C(9) and

(16) The solvent has a pronounced influence upon this reaction. For example, when THF was used, no addition of the fluorenyl anion to fulvene **1a** took place, even at elevated temperatures and in the presence of HMPA. When Et_2O was used, the reaction proceeded; however, significant heating was required (autoclave conditions).

(17) The preparation of proligand **2b** in 71% yield by the direct addition of [3,6-tBu$_2$Flu]$^-$Li$^+$ to the nonactivated fulvene **1b** has been claimed following extended reaction times (refluxing diethyl ether, 13 days); however, several attempts to reproduce this experiment failed in our hands. See: Ikenaga, S.; Okada, K.; Takayasu, H.; Inoue, N.; Hirota, N.; Kaneyoshi, H.; Funaya, M.; Kawai, K.; Kawahara, N.; Kojoh, S.; Kashiwa, N.; Mori, R. (Mitsui Chemicals Inc.) Eur. Pat. Appl. 1614699, 2006; *Chem. Abstr.* **2006**, *141*, 332634.

(18) Considerably poorer results were obtained when KOtBu alone was used as the reducing agent; in this case, many side products formed.

(19) Navarro, O.; Marion, N.; Oonishi, Y.; Kelly, R. A., III; Nolan, S. P. *J. Org. Chem.* **2006**, *71*, 685.

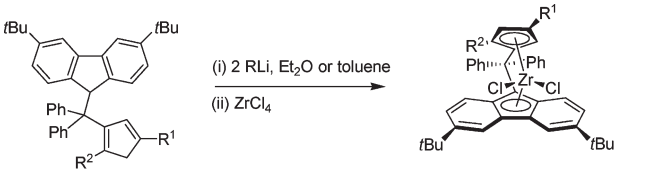
(20) The observation that 6,6′-bis(arene)fulvenes can be "activated" toward nucleophilic addition by introducing electron-withdrawing groups X in the para positions of the arenes is in line with the effect of such substituents described by their Hammett σ_p values. For example, ligands **2b**,**c** could not be prepared by the classical way starting from **1b**,**c** (X = H, σ_p = 0.00), even under forcing reaction conditions. At the same time, **2d**,**e** were obtained in rather good yields (X = Cl, σ_p = 0.23), whereas the yield of the fluorinated congener **2f** was much lower (X = F, σ_p = 0.06).

Table 1. Selected Bond Distances (Å) and Angles (deg) for Proligands 2a and 2b·CH_2Cl_2, Complexes 3a,c, and Reference Molecule III-Me_2[1c]

	2a	2b·CH_2Cl_2	3a	3c	III-Me_2
Zr−Cl			2.425(2)	2.4227(10)	2.8020(6)
			2.427(2)	2.4283(10)	2.6390(11)[a]
Zr−C(1)			2.440(7)	2.442(4)	2.427(3)
Zr−C(2)			2.470(8)	2.492(3)	2.464(3)
Zr−C(3)			2.602(7)	2.630(4)	2.611(4)
Zr−C(4)			2.571(7)	2.547(4)	2.549(4)
Zr−C(5)			2.468(8)	2.457(4)	2.461(4)
$Zr-Cp_{Cent}$			2.201(7)	2.204(4)	
Zr−C(9)			2.422(7)	2.426(3)	2.432(4)
Zr−C(10)			2.545(7)	2.497(4)	2.512(4)
Zr−C(11)			2.704(7)	2.666(4)	2.653(4)
Zr−C(12)			2.670(7)	2.712(4)	2.688(4)
Zr−C(13)			2.515(7)	2.588(4)	2.611(4)
$Zr-Flu_{Cent}$			2.257(7)	2.269(4)	
$Cp_{Cent}-Zr-Flu_{Cent}$			118.07(5)	118.03(4)	118.5(3)
C(1)−C(6)−C(9)	104.03(17)	105.48(12)	98.9(5)	98.60(3)	100.2(3)
C(7)−C(6)−C(8)	103.28(17)	103.03(13)	103.1(6)	104.00(4)	105.3(3)

[a] The crystal structure reported in ref 1c is for a mixed chloro−iodo zirconocene, and the Zr−Cl bond distances must therefore be interpreted with caution.

Scheme 4. Synthesis of *ansa*-Zirconocenes 3a−c



2a (R^1 = *t*Bu, R^2 = H)
2b (R^1 = *t*Bu, R^2 = Me)
2c (R^1 = cumyl, R^2 = Me)

3a (46%; R^1 = *t*Bu, R^2 = H)
3b (93%; R^1 = *t*Bu, R^2 = Me)
3c (71%; R^1 = cumyl, R^2 = Me)

C(7)−C(6)−C(8) bond angles (104.03(17), 103.28(17)° and 105.48(12), 103.03(13)°, respectively). Note, however, that the C(1)−C(6)−C(9) bond angles remain expectedly much larger (6−7°) than those observed in the corresponding metallocenes (vide infra, Table 1).

Synthesis and Structure of Zirconocenes. In order to prepare zirconocene dichlorides, standard salt metathesis reactions between $ZrCl_4$ and ligand dianions, generated in situ in Et_2O, were attempted (Scheme 4). Thus, zirconium complex **3a** was isolated in good yield as a characteristically pink, microcrystalline material. Unexpectedly, similar one-pot synthetic protocols to coordinate proligands **2b**,**c** appeared to fail. Instead, unidentified brownish amorphous solids were obtained after in situ metalation of these proligands and subsequent treatment with $ZrCl_4$ in Et_2O, followed by the usual workup. In striking contrast to **2a**, the more sterically hindered molecules **2b**,**c**, which incorporate an additional methyl group at the 5-position of the Cp ligand, do not undergo deprotonation at the sp^3 carbon of the fluorenyl moiety upon addition of MeLi or *n*BuLi (in Et_2O or pentane).[21] Pure crystalline **3c** was finally obtained from the reaction conducted in toluene, using the more strongly basic *sec*-BuLi as the deprotonating reagent. A similar approach afforded **3b** as a reddish pink solid. However, this complex was not entirely pure, as reflected by a few minor broadened ^1H NMR signals in addition to those expected for **3b** (see the Supporting Information).[22] All attempts to further purify the material were unsuccessful. Nonetheless, the formulations of all zirconium complexes were supported by microanalyses (see the Experimental Section).

Selective deprotonation of compounds **2d**,**e** by *n*BuLi, *sec*-BuLi, *t*BuLi, and MeLi failed; rather, metalation/alkylation sequences involving the chlorinated phenyl groups appeared to occur.[23] Also, when *n*BuLi/TMEDA, KO*t*Bu/*n*BuLi in Et_2O, *t*BuLi in pentane, or LDA in refluxing THF were used, only unidentified brownish solids were isolated after subsequent addition of $ZrCl_4$. Attempts to isolate and characterize dianionic derivatives of these ligands failed as well, apparently reflecting their high instability.

Single crystals of **3a**,**c** suitable for X-ray diffraction studies were grown from CH_2Cl_2/hexane (1:1 v/v) solutions at room temperature. Their solid-state structures are depicted in Figure 2, and selected geometrical parameters are given in Table 1. The unit cells of both C_1-symmetric complexes are composed of pairs of enantiomers. These molecules exhibit geometrical parameters essentially similar to those of zirconocene dichlorides incorporating isopropylidene- and diphenylmethylene-bridged {Cp/Flu} ligands.[1c,7,13,24] In both complexes, the coordination mode of the central five-membered ring of the fluorenyl ligand deviates slightly from η^5 toward η^3, as evidenced by the significant differences in the M−C(ring) distances (ca. 0.3 Å between the shortest and the longest bond lengths). The $Cp_{cent}-Zr-Flu_{cent}$ bite angles in **3a**,**c** are almost identical (118.07(5) and 118.03(4)°, respectively) and compare well with the corresponding value in the isopropylidene-bridged metallocene **III-Me_2** (118.5(3)°). One must keep in mind, however, that such Cp-Flu *ansa*-zirconocenes may have very similar structural features in the solid state but quite different chemical behavior (i.e., catalytic performance in propylene polymerization, propensity of adjacent

(21) This tentative conclusion stems from the fact that, when $ZrCl_4$ was added after the deprotonation step, the products isolated after workup all featured ^1H NMR spectra consistent with the formulation {Ph_2C(FluH)(Cp)}Zr(R)Cl_2 (R = Me, Bu).

(22) Attempted syntheses of zirconocenes by reacting protio ligands **2b**,**c** with $Zr(CH_2Ph)_4$ or $Zr(NMe_2)_4$ gave only products with Cp-coordinated ligands but pendant FluH groups, i.e. {Ph_2C(FluH)-(Cp′)}ZrX_3 with X = CH_2Ph, NMe_2, as revealed by NMR monitoring. Similar alkane or amine elimination reactions conducted at elevated temperatures resulted in substantial decomposition of the aforementioned intermediates.

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(24) Razavi, A.; Thewalt, U. *J. Organomet. Chem.* **2001**, *621*, 267 and references cited therein.

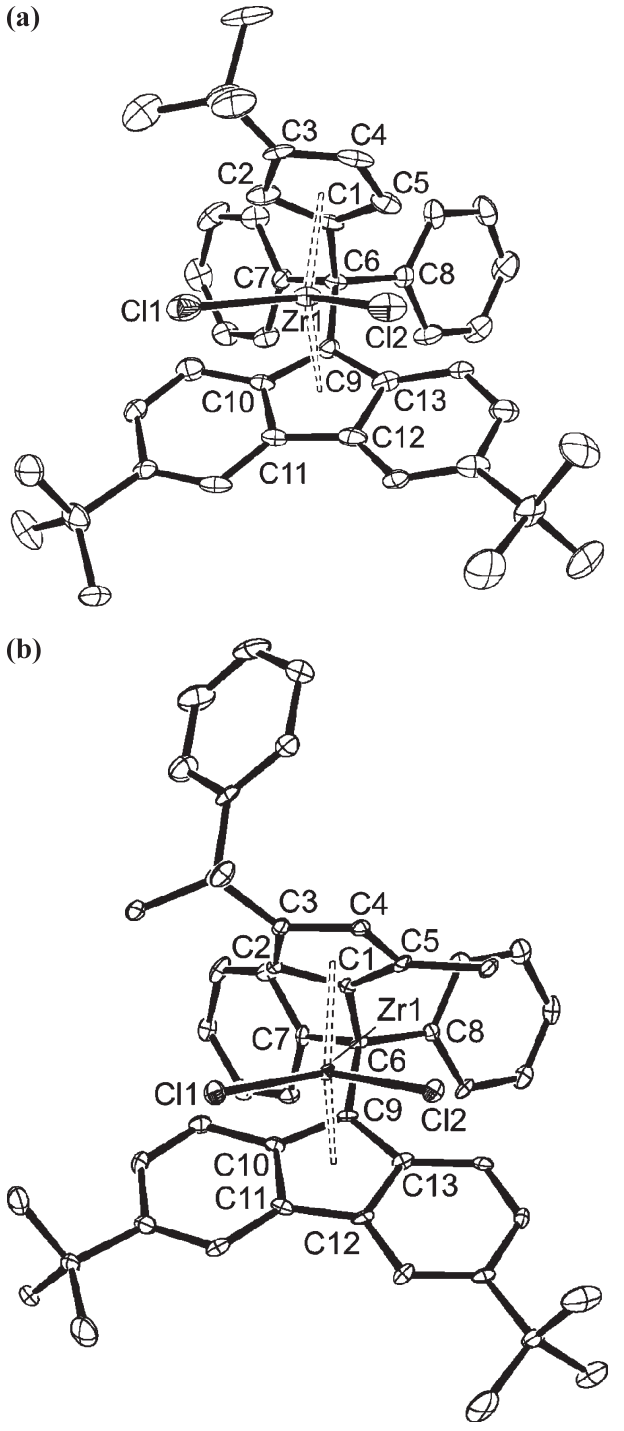


Figure 2. Crystal structures of complexes **3a** (a) and **3c** (b). H atoms are omitted for clarity; ellipsoids are drawn at the 50% probability level.

C6 rings of the fluorenyl moiety to be hydrogenated or not[25]) in solution.

The ^{1}H and ^{13}C NMR spectra of **3a**−**c** show a single set of resonances, consistent with the C_1 symmetry of these species. Accurate assignment of the ^{1}H and ^{13}C NMR resonances (see the Experimental Section) was made by 2D (COSY, HETCOR) experiments. Analysis of the ^{1}H and ^{13}C NMR chemical shifts, in particular that of the C9-fluorenyl carbon, which could be unambiguously assigned in the case of **3a**, was not conclusive regarding the actual hapticity of the fluorenyl moiety in solution.[26]

Propylene Polymerization Catalysis. Metallocenes **3a**−**c**, in combination with MAO, were evaluated in the homogeneous polymerization of propylene (toluene, 5 bar of constant pressure, 60 °C). Each polymerization experiment was repeated independently three times under the same conditions, revealing good reproducibility in terms of activity (gas uptake) and productivity (polymer yield), as well as physicochemical properties (M_w, M_n, T_m, isotacticity) of the isolated polymer. For comparison purposes, the catalytic performance of the system based on the reference metallocene precatalyst **III-Me$_2$** under these conditions was determined as well. Selected polymerization results are summarized in Table 2.

Analysis of these results reveals that systems based on metallocenes **3a**,**b** feature, under our experimental conditions, superior activities (5020 and 3580 kg of iPP mol^{-1} h^{-1}, respectively; entries 2 and 3) as compared to the already high activity of the reference metallocene precatalyst **III-Me$_2$** (1710 kg of iPP mol^{-1} h^{-1}; entry 1).[27]

Regarding the molecular weights of the polypropylenes produced, systems based on **III-Me$_2$** and **3b** (= **III-Ph$_2$**) yielded very similar products (compare entries 1 and 3). These results are in contrast to the increased molecular weights commonly observed when a Me_2C bridge is replaced by a Ph_2C bridge. On the other hand, the molecular weight of the polypropylene obtained from **3a** is significantly lower, about 20% of those obtained from **III-Me$_2$** and **3b** (entry 2). This trend is not unexpected and can be accounted for by the absence of the 5-methyl substituent on the Cp ring of **3a**, which is known to be responsible for destabilizing a transition state leading to chain transfer to monomer or β-H elimination.[2b,3,4]

The regioselectivities for primary insertion of the monomer are nearly perfect for all metallocene precursors (99.8−99.9%). In terms of stereocontrol, the new metallocenes **3a**,**b** also afforded polypropylenes featuring high pentad $[m]^4$ values, as determined by ^{13}C NMR spectroscopy. This also confirmed an operative enantiomorphic-site stereocontrol mechanism (see the Supporting Information). These isotacticities were quite similar to that for the polymer obtained with the reference precatalyst **III-Me$_2$**. This is also reflected by the identical T_m values determined for these polymers.

Remarkably, the system **3c**/MAO appeared to be completely inactive under the conditions used (entry 4). The latter observation may be accounted for by a deactivation involving the phenyl ring of the cumyl group. Indeed, a similar catalytic inactivity has been documented for the metallocene precursor {Me_2C(Flu)(3-(2-Ph-2-adamantyl)-Cp)}$ZrCl_2$.[28]

DFT Computations of a Possible Deactivation Pathway. To gain a better insight into this deactivation phenomenon, DFT computations were conducted starting from the putative

(25) For instance, the benzenoid rings of the fluorenyl ligand in {Ph_2C(Cp)(Flu)}$ZrCl_2$ readily undergo hydrogenation while the isostructural Me_2C-bridged analogue does not, even under forcing conditions. This behavior has been rationalized by the η^5 coordination mode in the former case, while in the latter case, the prevalent coordination mode is η^3, with dynamic hapticity toward η^1.[6]

(26) (a) Irwin, L. J.; Reibenspies, J. H.; Miller, S. A. *Polyhedron* **2005**, *24*, 1314. (b) Drago, D.; Pregosin, P. S.; Razavi, A. *Organometallics* **2000**, *19*, 1802.

(27) As a consequence, polymerizations with such systems must be operated at very low metallocene concentration (10 μmol·L^{-1}) in order to control the high exothermicity.

Table 2. Propylene Polymerization[a]

entry	precatalyst	C_{cat} (μmol L^{-1})	amt of MAO (equiv)	time (min)	m_p (g)	productivity (g/g of prectatalyst)	activity (kg mol^{-1} h^{-1})	T_m (°C)[b]	$10^3 M_w$[c]	M_w/M_n[c]	[*m*][4] [d] (%)	1,2-insertion[d] (%)
1	**III-Me$_2$**	10	5000	30	1.39	1390	1710	152	166	2.4	95.2	>99.9
2	**3a**	10	5000	30	3.46	3460	5020	152	30	2.1	93.9	99.8
3	**3b**	10	5000	30	2.42	2420	3580	152	175	2.3	94.0	99.9
4	**3c**	200	1000	30	0	0	0					

[a] Polymerization conditions: 300 mL high pressure glass reactor; solvent toluene, 150 mL; *P*(propylene) = 5 bar; T_{pol} = 60 °C. [b] Determined by DSC. [c] Determined by GPC. [d] Determined by ^{13}C NMR.

cationic methyl−zirconocene species obtained upon activation with MAO, namely [{Ph$_2$C(3,6-*t*Bu$_2$Flu)(3-cumyl-5-Me-C$_5$H$_2$)}ZrMe]$^+$ (**A**; Scheme 5) (BP86 level, see the Supporting Information for details). The objectives of these nonexhaustive computations were to assess the energy profiles for two possible concurrent processes: i.e., (a) classical coordination/insertion of propylene into the Zr−Me bond of species **A** to afford the corresponding insertion product **C** versus (b) intramolecular C−H activation in the pendant phenyl group by the cationic metal center to form *o*-phenyl-metalated species **D** (vide infra) and further reaction of the latter species with propylene to yield species **E**. Although metallocene species with all real substituents on the Cp and fluorenyl rings were considered, a series of simplifications/assumptions was made to reduce the calculation costs: (i) the influence of the MAO counteranion was neglected and only single cationic species in gas phase were computed;[29,30] (ii) the methyl group (polymeryl chain) is located opposite to the bulky cumyl substituent. In addition, when reactions with propylene were envisioned, it was considered that (iii) propylene insertion proceeds in a primary fashion and (iv) propylene coordinates to zirconium with its methyl group positioned "head down" into the free space in the central region of the fluorenyl ligand and the methylene directed toward the less crowded quadrant (opposite to the methyl group/polymeryl chain), as usually considered for isospecific propylene polymerization mediated by C_1-symmetric cyclopentadienyl−fluorenyl metallocene catalysts.

The propagation pathway was evaluated at the first insertion stage: that is, conversion of π-complex **A-*si*-C$_3$H$_6$** (Scheme 5) to isobutyl product **C**. This process appeared favorable on both kinetic and thermodynamic grounds, with a low calculated activation barrier of 6.9 kcal mol^{-1} for insertion[31] and was significantly exergonic, −8.1 kcal mol^{-1}.

On the other hand, coordination of the cumyl phenyl ring to the zirconium center of the three-coordinated species **A** to form eventually **B-I** (in which the hydrogen bound to the interacting C(phenyl) points opposite to the Zr−Me group) and related species **B-II** (in which the hydrogen bound to the interacting C(phenyl) points toward the Zr−Me group) was found to be significantly exergonic ($\Delta E_{\mathbf{A}\rightarrow\mathbf{B}}$ = −10.2 and −7.7 kcal.mol^{-1}, respectively). There are precedents in the literature for π coordination of pendant arene groups to cationic group 4 metal centers (η^1−η^3 coordination mode observed both in the solid state and in solution)[32−34] similar to that in computed species **B-I**/**B-II** (η^1 coordination mode). Exchange of the π-coordinated phenyl ring in **B-I** for a propylene unit (leading to **A-*si*-C$_3$H$_6$**) is only slightly thermodynamically unfavorable ($\Delta E_{\mathbf{A\text{-}si\text{-}C_3H_6}\rightarrow\mathbf{B\text{-}I}}$ = +3.8 kcal mol^{-1}), and that with **B-II** is even more accessible. The low energy differences associated with these reversible processes (**B-I** ↔ **A-*si*-C$_3$H$_6$** ↔ **B-II**) are unlikely to account for the observed complete inactivity toward propylene.

We therefore investigated subsequent chemical events. In this respect, a likely phenomenon, mentioned above and previously suggested by Bercaw et al.,[28] is metalation (C−H activation) of the cumyl phenyl ring at the ortho position and concomitant alkane (methane) elimination. This chemical event, which requires proximal C−H and Zr−Me groups as found in **B-II** (and not in **B-I**), is computed to occur through an accessible transition state ($E^{\ddagger}_{\mathbf{B\text{-}II}\rightarrow\mathbf{D}}$ = 13.9 kcal mol^{-1}).[35] If this reaction takes place in the absence of propylene, the overall energy balance appears quite unfavorable ($\Delta E_{\mathbf{B\text{-}II}\rightarrow\mathbf{D}}$ = +6.4 kcal mol^{-1}); however, in the presence of propylene, a significant stabilization is calculated ($\Delta E_{\mathbf{B\text{-}II}\rightarrow\mathbf{D}\ \textit{si}\text{-}\mathbf{C_3H_6}}$ = −9.6 kcal mol^{-1}), associated with the formation of the new π complex **D-*re*-C$_3$H$_6$**.

Further propylene insertion in the resulting ortho-metalated species **D-*re*-C$_3$H$_6$** (to give species **E**) is computed to be thermodynamically disfavored by 8.4 kcal mol^{-1}. We also checked that the product resulting from a second propylene insertion is just further stabilized by only 2−3 kcal mol^{-1}. These results indicate that the formation of an ortho-metalated species such as **D-*re*-C$_3$H$_6$** is a likely process and

(28) No direct experimental evidence has thus far been obtained to support this hypothesis. Attempts to generate cationic species starting from the dimethylated version of **3c** and [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$ led to unidentified compounds, probably arising from rapid decomposition. On the other hand, similar catalytic inactivity has been documented for the metallocene precursor {Me$_2$C(Flu)(3-(2-Ph-2-adamantyl)-Cp)}ZrCl$_2$.[14]

(29) Previous QM/MM studies by Ziegler et al. on the polymerization reactions have been conducted using the large size ion pair [metallocenium]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ as a model for the active species: (a) Wang, D.; Tomasi, S.; Razavi, A.; Ziegler, T. *Organometallics* **2008**, *27*, 2861. (b) Wondimaggen, T.; Wang, D.; Razavi, A.; Ziegler, T. *Organometallics* **2008**, *27*, 6434. See also ref 4.

(30) Theoretical investigations dealing with possible structures of oligomeric MAO have been reported; see: Zurek, E.; Ziegler, T. *Prog. Polym. Sci.* **2004**, *29*, 107.

(31) A 6.7 kcal mol^{-1} barrier for the (second) insertion of propylene into the Zr−C bond was calculated for [{Me$_2$C(3,6-*t*Bu$_2$Flu)(3-*t*Bu-5-Me-C$_5$H$_2$)}Zr(Polymeryl)]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$.[4a]

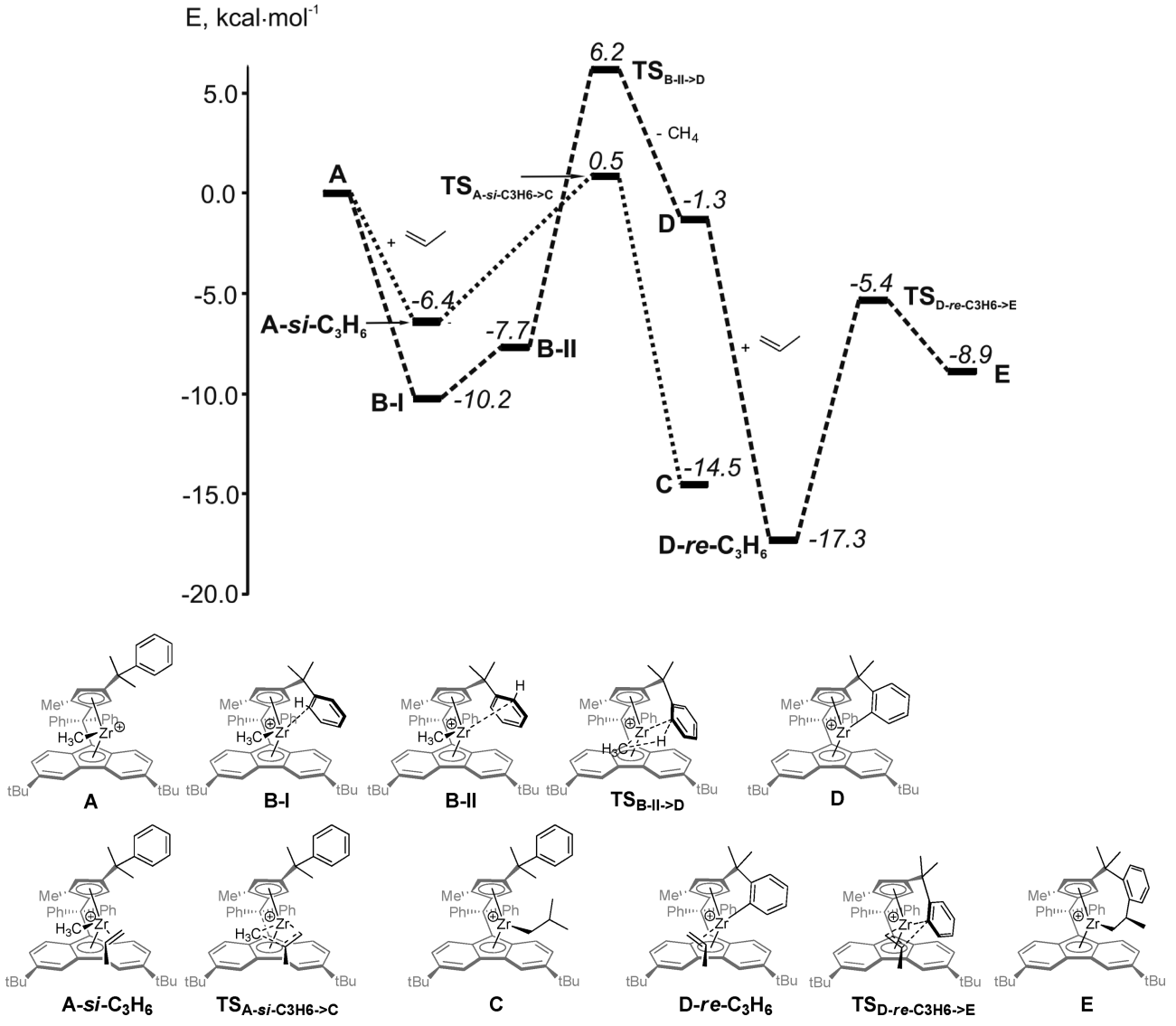
(32) Upon activation with [Ph$_3$C]$^+$[B(C$_6$F$_5$)$_4$]$^-$, {PhMe$_2$SiC$_5$H$_4$}-TiMe$_3$ undergoes coordination of the pendant phenyl ring onto the cationic titanium center: (a) Deckers, P. J. W.; Van der Linden, A. J.; Meetsma, A.; Hessen, B. *Eur. J. Inorg. Chem.* **2000**, 929. (b) Deckers, P. J. W.; Hessen, B.; Teuben, J. H. *Angew. Chem., Int. Ed.* **2001**, *40*, 2516. (c) Deckers, P. J. W.; Hessen, B.; Teuben, J. H. *Organometallics* **2002**, *21*, 5122.

(33) For computational studies of this process, see: (a) Blok, A. N. J.; Budzelaar, P. H. M.; Gal, A. W. *Organometallics* **2003**, *22*, 2564. (b) De Bruin, T. J. M.; Magna, L.; Raybaud, P.; Toulhoat, H. *Organometallics* **2003**, *22*, 3404. (c) Tobisch, S.; Ziegler, T. *Organometallics* **2003**, *22*, 5392.

(34) Experimental and theoretical studies on intramolecular C−H activation involving the pendant tolyl group in the cationic titanocene [(Cp)(CpCMe$_2$C$_6$H$_4$Me)TiMe]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ were reported; see: Sassmannshausen, J.; Baumgartner, J. *Organometallics* **2008**, *27*, 1996.

(35) DFT computations of the similar intramolecular C−H activation reaction of [(Cp)(CpCMe$_2$C$_6$H$_4$Me)TiMe]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$, yielding [(Cp)(CpCMe$_2$(σ-*o*-C$_6$H$_3$Me))Ti]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ and methane, gave the following parameters: $\Delta G^{\ddagger}$ = 23.5 kcal mol^{-1} and ΔG = 3.1 kcal·mol^{-1}.[34]

Scheme 5. Energy Profiles Computed at the BP86 Level for Propylene Coordination/Insertion and Possible Decomposition Pathways for Active Species Derived from 3c[a]



[a] Energies are given in kcal mol^{-1} relative to **A**.

that the latter species is stable, which is nonreactive toward propylene.

Conclusions

We have developed an effective synthetic approach toward sterically encumbered Ph_2C-bridged cyclopentadienyl−fluorenyl-based ligand systems. A new series of C_1-symmetric metallocenes was synthesized and successfully applied to the highly isospecific polymerization of propylene. Precursors **3a**,**b** afford 2−3-fold more active systems than the reference precatalyst {Me_2C(3,6-*t*Bu_2Flu)(3-*t*Bu-5-MeC_5H_2)}-$ZrCl_2$ (**III-Me$_2$**) for the polymerization of propylene in toluene. On the other hand, in striking contrast to both systems **I** and **II** (Scheme 1), replacement of the bridge methyl groups by phenyl groups in the isospecific precursor **III** does not affect substantially the molecular weight of iPP. The complete inactivity of the **3c**/MAO system in propylene polymerization could be rationalized by DFT calculations, which indicate a concurrent decomposition pathway involving intramolecular C−H activation in the cumyl phenyl ring. Other structural modifications of this class of metallocenes to further improve catalytic performance and control over iPP properties are underway and will be reported in due course.

Experimental Section

General Considerations. All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were distilled from Na/benzophenone (THF, Et_2O) and Na/K alloy (toluene, pentane) under nitrogen, degassed thoroughly, and stored under nitrogen prior to use. Deuterated solvents (benzene-d_6, toluene-d_8, THF-d_8; >99.5% D, Deutero GmbH and Euroisotop) were vacuum-transferred from Na/K alloy into storage tubes. $CDCl_3$, CD_2Cl_2, and $C_2D_2Cl_4$ were kept over calcium hydride and vacuum-transferred before use. The ligand precursors 3,6-di-*tert*-butylfluorene and 6,6′-diphenyl-3-*tert*-butyl-5-methylfulvene (**1b**) were generously provided by Total Petrochemicals. The precursors 3,6,6′-trimethylfulvene, 1-*tert*-butyl-3-methylcyclopentadiene (mixture of isomers), and (1-methyl-3-*tert*-butylcyclopentadienyl)lithium were prepared according to literature protocols[36] and

characterized by ^{1}H NMR spectroscopy. 1-*tert*-butylcyclopentadiene (mixture of isomers) was prepared according to the published procedure.[37] The reference metallocene {Me_2C(3,6-tBu$_2$-Flu)(3-tBu-5-MeC_5H_2)}$ZrCl_2$ (**III-Me$_2$**) was synthesized as described in the patent literature.[36] The catalyst (SIPr)Pd(C_3H_5)Cl was synthesized as reported.[19] Other starting materials were purchased from Acros, Strem, and Aldrich and used as received. MAO (30 wt % solution in toluene, Albermale; contains ca. 10 wt % of free $AlMe_3$) was used as received.

NMR spectra of complexes were recorded on Bruker AC-200, AC-300, AM-400, and AM-500 spectrometers in Teflon-valved NMR tubes at 25 °C, unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported in ppm vs $SiMe_4$ (0.00), as determined by reference to the residual solvent peaks. ^{19}F chemical shifts were determined by external reference to an aqueous solution of $NaBF_4$. The resonances of organometallic complexes were assigned from 2D ^{1}H−^{13}C HMQC and HMBC NMR experiments. Coupling constants are given in hertz. Elemental analyses (C, H, N) were performed using a Flash EA1112 CHNS Thermo Electron apparatus and are the average of two independent determinations. FAB-HRMS spectra were recorded on a Micromass ZABSpecTOF high-resolution MS/MS spectrometer. DSC measurements were performed on a SETARAM Instrumentation DSC 131 differential scanning calorimeter at a heating rate of 10 °C/min; first and second runs were recorded after cooling to 30 °C, and the melting temperatures reported in tables correspond to the second run. GPC analyses of iPP samples were carried out in 1,2,4-trichlorobenzene at 135 °C in the research center of Total Petrochemicals in Feluy, Belgium, using polystyrene standards for universal calibration. ^{13}C NMR analyses of iPP samples were run in the research center of Total Petrochemicals in Feluy, Belgium, on a AM-500 Bruker spectrometer using the following conditions: solutions of ca. 200 mg of PP polymer in a trichlorobenzene/C_6D_6 mixture at 135 °C in 10 mm tubes, inverse gated experiment, pulse angle 90°, delay 11 s, acquisition time 1.25 s, number of scans 6000.

1-Cumyl-3-methylcyclopentadiene (Mixture of Isomers). To a solution of 3,6,6′-trimethylfulvene (27.70 g, 230.5 mmol) in THF (500 mL) was added phenyllithium (120.0 mL of a 2.0 M solution in dibutyl ether, 240.0 mmol) at 0 °C with stirring. After 20 h, the reaction mixture was hydrolyzed with a concentrated solution of NH_4Cl (150 mL). This mixture was stirred overnight. The organic layer was separated, dried over $MgSO_4$, and evaporated. The crude product was distilled under vacuum (80−84 °C/0.1 Torr) to give 1-cumyl-3-methylcyclopentadiene as a mixture of isomers (40.63 g, 205.1 mmol, 89%). Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 91.13; H, 10.01.

6,6′-Diphenyl-3-*tert*-butylfulvene (1a). To a solution of *tert*-butylcyclopentadiene (1.47 g, 12.0 mmol; mixture of isomers) in diethyl ether (50 mL) was added *n*-butyllithium (4.8 mL of a 2.5 M solution in hexane, 12.0 mmol) at 0 °C with stirring. After 2 h, a solution of benzophenone (2.20 g, 12.0 mmol) in diethyl ether (30 mL) was added dropwise. The reaction mixture turned orange. After 2 h, aqueous HCl (50 mL of a 20% solution) was added slowly. The mixture was stirred overnight. The organic layer was separated, washed with water and $NaHCO_3$ solution, and dried over $MgSO_4$, and all the volatiles were removed in vacuo. The orange residue was recrystallized from methanol at −30 °C to give **1a** (1.72 g, 6.00 mmol, 50%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.34 (m, 10H, Ph), 6.63 (dd, J = 2.3, J = 7.3, 1H, C*H*), 6.27 (dd, 2.3, J = 7.3, 1H, C*H*), 5.93 (t, J = 2.3, 1H, C*H*), 1.18 (s, 9H, CCH_3). Anal. Calcd for $C_{22}H_{22}$: C, 92.26; H, 7.74. Found: C, 92.84; H, 7.88.

6,6′-Bis(4-chlorophenyl)-3-*tert*-butyl-5-methylfulvene (1d). To a solution of 1-methyl-3-*tert*-butylcyclopentadiene (2.27 g, 16.7 mmol; mixture of isomers) in THF (150 mL) was added *n*-butyllithium (6.67 mL of a 2.5 M solution in hexane, 16.7 mmol) at 0 °C with stirring. After 2 h, a solution of 4,4′-dichlorobenzophenone (4.18 g, 16.66 mmol) in THF (50 mL) was added dropwise with stirring. The mixture turned orange. After 4 h, concentrated aqueous NH_4Cl (50 mL) was added slowly. This mixture was stirred overnight. The organic layer was separated and dried over $MgSO_4$, and all the volatiles were removed in vacuo. The deep red residue was recrystallized from hot methanol to give **1d** (3.7 g, 10.02 mmol, 60%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.32 (m, 4H, Ph), 7.18 (m, 4H, Ph), 6.37 (s, 1H, C*H*), 5.66 (s, 1H, C*H*), 1.53 (s, 3H, CH_3), 1.17 (s, 9H, CCH_3). Anal. Calcd for $C_{23}H_{22}Cl_2$: C, 74.80; H, 7.00. Found: C, 74.85; H, 7.10.

6,6′-Bis(4-chlorophenyl)-3-cumyl-5-methylfulvene (1e). Using a protocol similar to that described above for **1d**, compound **1e** was obtained from 1-methyl-3-cumylcyclopentadiene (5.60 g, 28.3 mmol; mixture of isomers), *n*-butyllithium (11.30 mL of a 2.5 M solution in hexane, 28.3 mmol), and dichlorobenzophenone (6.00 g, 23.9 mmol). The crude product was recrystallized from hot methanol to give deep red crystals of **1e** (6.20 g, 14.4 mmol, 51%). ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ 7.41−7.10 (m, 8H, Ph), 6.02 (br m, 1H, C*H*), 5.85 (br m, 1H, C*H*), 1.55 (s, 6H, CCH_3), 1.46 (s, 3H, CH_3). Anal. Calcd for $C_{23}H_{22}Cl_2$: C, 77.96; H, 5.61. Found: C, 78.11; H, 6.01.

6,6′-Bis(4-fluorophenyl)-3-*tert*-butyl-5-methylfulvene (1f). Using a protocol similar to that described above for **1d**, compound **1f** was obtained from 1-methyl-3-*tert*-butylcyclopentadiene (2.29 g, 16.8 mmol; mixture of isomers), *n*-butyllithium (6.72 mL of a 2.5 M solution in hexane, 16.8 mmol), and 4,4′-difluorobenzophenone (3.30 g, 15.1 mmol). The red residue was recrystallized from hot methanol at 25 °C to give **1f** (0.74 g, 2.22 mmol, 15%). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.17 (m, 4H, Ph), 7.03 (m, 4H, Ph), 6.32 (s, 1H, Cp), 5.63 (s, 1H, Cp), 1.47 (s, 3H, CH_3), 1.13 (s, 9H, CCH_3). ^{19}F{^{1}H} NMR ($CDCl_3$, 282 MHz, 25 °C): δ −112.9 (s). Anal. Calcd for $C_{23}H_{22}F_2$: C, 82.11; H, 6.59. Found: C, 83.03; H, 7.34 (these data do not indicate analytical purity but are provided to illustrate the best result obtained).

6,6′-Bis(3,5-bis(trifluoromethyl)phenyl)-3-*tert*-butyl-5-methylfulvene (1g). Using a protocol similar to that described above for **1d**, compound **1g** was obtained from 1-methyl-3-*tert*-butylcyclopentadiene (1.30 g, 9.54 mmol; mixture of isomers), *n*-butyllithium (3.90 mL of a 2.5 M solution in hexane, 9.54 mmol), and 3,3′,5,5′-tetrakis(trifluoromethyl)benzophenone (5.00 g, 9.57 mmol). The red residue was recrystallized from hot methanol at 25 °C to give **1g** (1.05 g, 1.83 mmol, 19%). ^{1}H NMR ($CDCl_3$, 300 MHz, 25 °C): δ 7.90 (d, 2H, Ph), 7.68 (d, 4H, Ph), 6.38 (s, 1H, Cp), 5.43 (s, 1H, Cp), 1.37 (s, 3H, CH_3), 1.11 (s, 9H, CCH_3). ^{19}F{^{1}H} NMR ($CDCl_3$, 282 MHz, 25 °C): δ −62.51 (s, 6F), −62.56 (s, 6F). Anal. Calcd for $C_{27}H_{22}F_{12}$: C, 56.45; H, 3.86. Found: C, 56.88; H, 4.08.

3,6-Di-*tert*-butyl-9-[(3-*tert*-butylcyclopenta-1,4-dien-1-yl)diphenylmethyl]-9*H*-fluorene (2a). To a solution of **1a** (1.68 g, 5.87 mmol) in Et_2O (20 mL) was added at room temperature a diethyl ether solution of (3,6-di-*tert*-butylfluorenyl)lithium (30 mL) prepared from 3,6-di-*tert*-butylfluorene (1.63 g, 5.85 mmol) and *n*-butyllithium (2.35 mL of a 2.5 M solution in hexane, 5.85 mmol) with stirring. The mixture was refluxed for 7 days, quenched with saturated aqueous NH_4Cl (50 mL), and diluted with diethyl ether (45 mL). The organic layer was separated, washed with water (2 × 150 mL), and dried over $CaCl_2$. The volatiles were removed in vacuo, and the residue was dissolved in hot MeOH. The solution was cooled to −30 °C, and a white precipitate formed. The precipitate was collected by filtration, washed with cold methanol (−30 °C), and dried in vacuo overnight to give **2a** as a white powder (0.70 g, 1.24 mmol, 21%). ^{1}H NMR ($CDCl_3$, 300 MHz, 60 °C): δ 7.6−6.8 (br m, 16H), 5.73 (br s, 1H, C*H*), 5.46 (s, 1H, 9-Flu), 5.40 (br s, 1H, C*H*), 2.59 (br s, 2H, CH_2), 1.33 (s, 18H, CCH_3-Flu), 0.91 (s, 9H, CCH_3-Cp). Anal. Calcd for $C_{43}H_{48}$: C, 91.43; H, 8.57. Found: C, 91.88; H, 8.97.

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3,6-Di-*tert*-butyl-9-{(4-*tert*-butyl-2-methylcyclopenta-1,4-dien-1-yl)[bis(4-chlorophenyl)]methyl}-9*H*-fluorene (2d). To a solution of **1d** (1.33 g, 3.60 mmol) in Et_2O (30 mL) was added at room temperature a diethyl ether solution of (3,6-di-*tert*-butylfluorenyl)lithium (30 mL) prepared from 3,6-di-*tert*-butylfluorene (1.00 g, 3.59 mmol) and *n*-butyllithium (1.44 mL of a 2.5 M solution in hexane, 3.59 mmol) with stirring. The mixture was refluxed for 5 days, quenched with saturated aqueous NH_4Cl (50 mL), and diluted with diethyl ether (50 mL). The organic layer was separated, washed with water (2 × 200 mL), and dried over $CaCl_2$. The volatiles were removed in vacuo. The residue was washed on a filter with MeOH and then with cold pentane (−30 °C) and then dried in vacuo overnight to give **2d** as a white powder (1.40 g, 2.16 mmol, 60%). ^{1}H NMR (THF-d_8, 300 MHz, 90 °C): δ 7.53 (br s, 2H), 7.40−6.80 (br m, 14H), 6.20 (br s, 1H, C*H*), 5.64 (s, 1H, 9-Flu), 2.78 (s, 2H, CH_2, C*H*), 1.36 (s, 3H, CH_3), 1.32 (s, 18H, CCH_3), 1.09 (s, 9H, CCH_3). MS-FAB (*m*-nitrobenzyl alcohol, *m*/*z*): 647.3 ([M − H]$^+$), 369.1 ([(*p*-Cl-$C_6H_4)_2$C(3-C_4H_9-5-CH_3-C_5H_3)]$^+$), 277.3 ([2,6-$(C_4H_9)_2C_{13}H_6$H]$^+$). Anal. Calcd for $C_{44}H_{48}Cl_2$: C, 81.58; H, 7.47. Found: C, 82.04; H, 7.55.

3,6-Di-*tert*-butyl-9-{(4-cumyl-2-methylcyclopenta-1,4-dien-1-yl)[bis(4-chlorophenyl)]methyl}-9*H*-fluorene (2e). Using a protocol similar to that described above for **2d**, compound **2e** was obtained from 3,6-di-*tert*-butylfluorene (4.00 g, 14.4 mmol), *n*-butyllithium (5.80 mL of a 2.5 M solution in hexane, 14.4 mmol), and **1e** (6.20 g, 14.4 mmol). A similar workup gave **2e** as an off-white powder (8.15 g, 11.5 mmol, 80%). ^{1}H NMR (CD_2Cl_2, 200 MHz, 25 °C): δ 8.00−6.30 (br m, 19H), 5.70−5.20 (br m, 2H, C*H* and 9-Flu), 3.00−2.00 (br m, 2H, CH_2), 1.80−0.80 (br m, 27H, CCH_3, CH_3). MS-FAB (*m*-nitrobenzyl alcohol, *m*/*z*): 707.3 ([M − H]$^+$), 431.1 (*p*-Cl-$C_6H_4)_2$C(3-C$(CH_3)_2C_6H_6$-5-CH_3-C_5H_3)]$^+$), 277.3 (([2,6-$(C_4H_9)_2C_{13}H_6$H]$^+$). Anal. Calcd for $C_{49}H_{50}Cl_2$: C, 82.91; H, 7.10. Found: C, 83.01; H, 7.15.

3,6-Di-*tert*-butyl-9-{(4-*tert*-butyl-2-methylcyclopenta-1,4-dien-1-yl)(diphenyl)methyl}-9*H*-fluorene (2b). In a Schlenk flask containing **2d** (2.00 g, 3.09 mmol) dissolved in dry THF (50 mL) were added under an argon stream $NaBPh_4$ (2.30 g, 6.72 mmol), KO*t*Bu (1.50 g, 13.4 mmol), (SIPr)Pd(C_3H_5)Cl (0.018 g, 0.030 mmol), and *i*PrOH (10 mL) with stirring. The mixture was kept at 60 °C for 3 h and then filtered through a silica pad. The filtrate was evaporated, and the residue was recrystallized from CH_2Cl_2/MeOH (ca. 1/1 v/v) to give colorless prisms of **2b**·CH_2Cl_2. The crystals were dissolved in toluene (3 mL). The solution was evaporated and dried under vacuum overnight to yield **2b** (0.89 g, 1.54 mmol, 50%). ^{1}H NMR (500 MHz, CD_2Cl_2, −40 °C; at least three CpH double bond isomers were detected): δ 8.3−6.5 (m, 16H), 6.0−5.0 (m, 2H, C*H* and 9-Flu), 3.3−1.8 (m, 2H, CH_2), 1.3−1.0 (m, 21H, CCH_3 and CH_3), 0.8−0.7 (m, 9H, CCH_3). MS-FAB (*m*-nitrobenzyl alcohol, *m*/*z*): 577.4 ([M − H]$^+$), 301.2 ([$(C_6H_5)_2$C(3-C_4H_9-5-CH_3-C_5H_3)]$^+$), 277.3 ([2,6-$(C_4H_9)_2C_{13}H_6$H]$^+$). Anal. Calcd for $C_{44}H_{50}$: C, 91.28; H, 8.71. Found: C, 91.12; H, 9.23.

3,6-Di-*tert*-butyl-9-{(4-cumyl-2-methylcyclopenta-1,4-dien-1-yl)diphenylmethyl}-9*H*-fluorene (2c). This ligand was prepared using a procedure similar to that described above for **2b**, starting from **2e** (6.30 g, 8.88 mmol), $NaBPh_4$ (6.70 g, 19.6 mmol), KO*t*Bu (4.40 g, 39.2 mmol), (SIPr)Pd(C_3H_5)Cl (0.052 g, 0.090 mmol), THF (100 mL), and *i*PrOH (20 mL). After recrystallization of the crude material from MeOH and drying under vacuo, pure **2e** was isolated as an off-white powder (4.21 g, 6.57 mmol, 74%). ^{1}H NMR (CD_2Cl_2, 200 MHz, 25 °C): δ 8.10−6.40 (br m, 21H), 5.90−4.90 (br m, 2H, C*H* and 9-Flu), 3.00−1.90 (br m, 2H, CH_2), 1.80−0.60 (br m, 27H, CCH_3 and CH_3). MS-FAB (*m*-nitrobenzyl alcohol, *m*/*z*): 639.4 ([M − H]$^+$), 363.2 ($(C_6H_5)_2$C(3-C$(CH_3)_2C_6H_6$-5-CH_3-C_5H_3)]$^+$), 277.3 ([2,6-$(C_4H_9)_2C_{13}H_6$H]$^+$). Anal. Calcd for $C_{49}H_{52}$: C, 91.82; H, 8.18. Found: C, 92.13; H, 8.25.

3,6-Di-*tert*-butyl-9-{(4-*tert*-butyl-2-methylcyclopenta-1,4-dien-1-yl)[bis(4-fluorophenyl)]methyl}-9*H*-fluorene (2f). To a solution of **1f** (0.74 g, 2.22 mmol) in Et_2O (30 mL) was added at room temperature a diethyl ether solution of (3,6-di-*tert*-butylfluorenyl)lithium (30 mL) prepared from 3,6-di-*tert*-butylfluorene (0.62 g, 2.23 mmol) and *n*-butyllithium (0.89 mL of a 2.5 M solution in hexane, 2.23 mmol) with stirring. The mixture was refluxed for 6 days, quenched with saturated aqueous NH_4Cl (50 mL), and diluted with diethyl ether (50 mL). The organic layer was separated, washed with water (2 × 200 mL), and dried over $CaCl_2$. The volatiles were removed in vacuo. The residue was washed with MeOH and then with cold pentane (−30 °C) on a filter and dried in vacuo overnight to give **2f** as a white powder (0.10 g, 0.16 mmol, 7%). The ^{1}H NMR spectrum of this compound (90 °C, $CDCl_3$, Teflon-valved J. Young NMR tube) featured extremely broadened resonances and was not informative. ^{19}F{^{1}H} NMR ($CDCl_3$, 282 MHz, 90 °C): δ −117.3 (br s). MS-FAB (*m*-nitrobenzyl alcohol, *m*/*z*): 614.3 ([M − H]$^+$), 337.2 ([$(p$-F-$C_6H_4)_2$C(3-C_4H_9-5-CH_3-C_5H_3)]$^+$), 277.3 ([2,6-$(C_4H_9)_2$-$C_{13}H_6$H]$^+$). Anal. Calcd for $C_{44}H_{48}F_2$: C, 85.95; H, 7.87. Found: C, 86.09; H, 8.25.

{Ph$_2$C(3,6-*t*Bu$_2$-Flu)(3-*t*Bu-C$_5$H$_3$)}ZrCl$_2$ (3a). To a solution of **2a** (0.80 g, 1.42 mmol) in Et_2O (30 mL) was added *n*-butyllithium (1.10 mL of a 2.5 M solution in hexane, 2.84 mmol) at 0 °C with stirring. After 12 h, anhydrous $ZrCl_4$ (0.33 g, 1.43 mmol) was added to the reaction flask in the glovebox. This resulting pink solution was stirred at room temperature overnight. Then the volatiles were evaporated in vacuo and hexane (ca. 40 mL) was vacuum-transferred under reduced pressure. The mixture was filtered and the solvent was removed from the filtrate to give a pink powder. Hexane (5 mL) was added to the pink powder. After 1 month at room temperature, a red microcrystalline powder had formed, which was filtered and dried under vacuum to give **3a** (0.47 g, 0.65 mmol, 46%). ^{1}H NMR (CD_2Cl_2, 300 MHz, 25 °C): δ 8.16 (m, 2H, Flu), 7.99 (m, 2H, Ph), 7.89 (m, 2H, Ph), 7.47 (m, 2H, Ph), 7.34 (m, 2H, Ph), 7.07 (m, 2H, Flu), 6.35 (m, 2H, Flu), 6.19 (t, J = 2.6, 1H, Cp), 5.74 (t, J = 2.6, 1H, Cp), 5.58 (t, J = 2.6, 1H, Cp), 1.44 (s, 9H, CCH_3-Flu), 1.43 (s, 9H, CCH_3-Flu), 1.19 (s, 9H, CCH_3-Flu). ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C): δ 150.9, 146.1, 145.8, 145.7, 129.9, 129.6, 129.5, 129.4, 127.9, 127.8, 127.7, 127.6, 127.4, 127.2, 124.0, 123.5, 123.4, 120.7, 120.4, 120.0, 119.9, 115.4, 109.52, 105.84, 101.6, 77.9 (C9-Flu), 58.4 (Ph$_2$*C*(Cp)(Flu)), 35.6 (*C*CH$_3$), 33.6 (*C*CH$_3$), 32.2 (C*C*H$_3$), 32.1 (C*C*H$_3$), 30.4 (C*C*H$_3$). Anal. Calcd for $C_{43}H_{46}Cl_2Zr$: C, 71.24; H, 6.40. Found: C, 70.55; H, 7.18.

{Ph$_2$C(3,6-*t*Bu$_2$-Flu)(3-*t*Bu-5-Me-C$_5$H$_2$)}ZrCl$_2$ (3b). To a solution of **2b** (0.84 g, 14.5 mmol) in toluene (50 mL) was added *sec*-butyllithium (2.22 mL of a 1.3 M solution in hexane, 14.5 mmol) at −30 °C with stirring. The mixture was warmed to room temperature. After 12 h, the flask was transferred to a glovebox, and anhydrous $ZrCl_4$ (0.34 g, 14.51 mmol) was added. The deep red mixture was stirred at room temperature overnight. The volatiles were evaporated in vacuo, and hexane (ca. 40 mL) was vacuum-transferred in under reduced pressure. The mixture was filtered, and the solvent was removed form the filtrate to give the crude **3b** as a reddish pink powder (0.99 g, 13.4 mmol, 93%). Attempts to further purify this solid by recrystallization failed. ^{1}H NMR (CD_2Cl_2, 300 MHz, 25 °C; crude product): δ 8.10 (m, 2H), 7.89 (m, 3H), 7.70 (m, 1H), 7.45−6.88 (m, 9H), 6.25 (d, J = 9.2, 1H), 6.14 (d, J = 3.0, 1H, Cp), 5.58 (d, J = 3.0, 1H, Cp), 1.88 (s, 3H, CH_3), 1.42 (s, 18H, CCH_3), 1.09 (s, 9H, CCH_3). Anal. Calcd for $C_{44}H_{48}Cl_2Zr$: C, 71.51; H, 6.55. Found: C, 72.15; H, 7.09.

{Ph$_2$C(3,6-*t*Bu$_2$-Flu)(3-PhCMe$_2$-5-Me-C$_5$H$_2$)}ZrCl$_2$ (3c). Using a protocol similar to that described above for **2b**, compound **2d** was obtained from **2c** (0.35 g, 0.55 mmol), *sec*-butyllithium (0.84 mL of a 1.3 M solution in hexane, 1.10 mmol), and $ZrCl_4$ (0.13 g, 0.55 mmol). This crude product was recrystallized from hexane (3 mL) to give pure **3c** as a pink powder (0.31 g, 0.39 mmol, 71%). ^{1}H NMR (CD_2Cl_2, 300 MHz, 25 °C): δ 8.16 (d, J = 8.4, 2H), 8.04 (m, 2H), 7.99 (d, J = 7.7, 1H), 7.88 (d, J = 7.7, 1H), 7.60−7.27 (m, 8H), 7.25−7.12 (m, 4H), 7.11−7.00 (m, 2H), 6.28 (d, J = 9.2, 1H),

Table 3. Summary of Crystal and Refinement Data for Compounds 2a, 2b·CH_2Cl_2, and 3a,c

	2a	2b·CH_2Cl_2	3a	3c
empirical formula	$C_{43}H_{48}$	$C_{45}H_{52}Cl_2$	$C_{43}H_{46}Cl_2Zr$	$C_{49}H_{50}Cl_2Zr$
formula wt	564.81	663.77	724.92	801.01
temp, K	173(2)	293(2)	173(2)	100(2)
wavelength, Å	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	triclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	Cc
a, Å	11.9603(3)	12.2450(6)	12.6849(8)	22.104(4)
b, Å	15.9036(7)	12.8780(6)	20.6181(15)	10.2250(16)
c, Å	18.0774(7)	15.5643(8)	21.5412(16)	35.465(6)
β, deg	94.048(2)	73.819(3)	77.198(5)	92.746(9)
V, Å^3	3430.0(2)	2048.59(17)	5480.9(7)	8006(2)
Z	4	2	6	8
density (calcd), Mg/m^3	1.094	1.076	1.318	1.329
abs coeff, mm^{-1}	0.061	0.186	0.476	0.442
cryst size, mm^3	0.10 × 0.10 × 0.10	0.45 × 0.18 × 0.14	0.15 × 0.10 × 0.10	0.4 × 0.18 × 0.09
no. of rflns collected	13 897	40 262	95 753	58 396
no. of indep rflns	7679 (R(int) = 0.0424)	9355 (R(int) = 0.0316)	21 489 (R(int) = 0.2234)	18 178 (R(int) = 0.0612)
max and min transmissn	0.9939 and 0.9939	0.974 and 0.920	0.9539 and 0.9320	0.961 and 0.830
no. of data/restraints/ params	7679/0/388	9355/0/452	21 489/0/1243	18 178/2/956
final R indices ($I > 2\sigma(I)$)	R1 = 0.0707, wR2 = 0.1859	R1 = 0.0648, wR2 = 0.2102	R1 = 0.0808, wR2 = 0.1818	R1 = 0.0490, wR2 = 0.0903
R indices (all data)	R1 = 0.1313, wR2 = 0.2157	R1 = 0.0927, wR2 = 0.2273	R1 = 0.1890, wR2 = 0.2275	R1 = 0.0545, wR2 = 0.0926
goodness of fit on F^2	1.175	1.119	1.063	1.13
largest diff peak, e Å^{-3}	0.906 and −0.344	0.353 and −0.507	1.499 and −1.209	0.603 and −1.088

6.19 (d, J = 2.8, 1H, Cp), 5.90 (d, J = 2.8, 1H, Cp), 1.92 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 1.48 (s, 18H, CCH_3), 1.35 (s, 3H, CH_3). ^{13}C NMR (CD_2Cl_2, 75 MHz, 25 °C; many signals in the aromatic region overlapped; resonances from quaternary carbons were not observed): δ 150.5, 149.7, 142.8, 128.7, 128.0, 126.9, 125.6, 124.0, 123.0, 122.7, 120.6, 120.5, 119.3, 119.2, 105.0, 104.3, 40.0 (Ph*C*(CH$_3$)$_2$), 34.9 (*C*CH$_3$), 32.8 (*C*CH$_3$), 31.6 (C*C*H$_3$), 31.5 (C*C*H$_3$), 25.9 (PhC(*C*H$_3$)$_2$), 25.8 (PhC(*C*H$_3$)$_2$), 20.2 (*C*H$_3$Cp). Anal. Calcd for $C_{49}H_{50}Cl_2Zr$: C, 73.47; H, 6.29. Found: C, 73.68; H, 6.11.

Propylene Polymerization. Polymerizations were performed in a 300 mL high-pressure glass reactor equipped with a mechanical stirrer (Pelton turbine) and externally heated with a double mantle with a circulating water bath. The reactor was filled with toluene (80 to 150 mL) and MAO (1.5 mL of a 30 wt-% solution in toluene) and pressurized at 5 atm of propylene (Air Liquide, 99.99%). The reactor was thermally equilibrated at the desired temperature for 30 min, the propylene pressure was decreased to 1 atm, and a solution of the catalyst precursor in toluene (ca. 2 mL) was added by syringe. The propylene pressure was immediately increased to 5 atm (kept constant with a back regulator) and the solution was stirred for the desired time (typically 30 min). The temperature inside the reactor was monitored using a thermocouple. The polymerization was stopped by venting the vessel and quenching with a 10% HCl solution in methanol (ca. 3 mL). The polymer was precipitated in methanol (ca. 200 mL), and 35% aqueous HCl (ca. 1 mL) was added to dissolve possible catalyst residues. The polymer was collected by filtration, washed with methanol (ca. 200 mL), and dried under vacuum overnight.

Crystal Structure Determination of 2a,b and 3a,c. Diffraction data were collected at 100 K using a Bruker APEX CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A combination of ω and ϕ scans was carried out to obtain at least a unique data set. The crystal structures were solved by direct methods; the remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F^2 (programs SIR97 and SHELXL-97).[38] Many hydrogen atoms could be found from the Fourier difference analysis. Carbon-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystals of **2b** were found to contain lattice disordered solvent molecules, which could not be sufficiently modeled in the refinement cycles. These molecules were removed using the SQUEEZE procedure[39] implemented in the PLATON package.[40] The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance. Crystal data and details of data collection and structure refinement for the different compounds are given in Table 3. The principal crystallographic data (excluding structure factors) are available as Supporting Information, as CIF files.

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Supporting Information Available: Figures giving representative ^{1}H and ^{13}C NMR spectra, CIF files giving crystallographic data for **2a**,**b** and **3a**,**c**, and text and tables giving computational details, including Cartesian coordinates of computed structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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