Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Molecular Catalysis A: Chemical 214 (2004) 187–198
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Synthesis of unsymmetrical *ansa*-fluorenyl metallocenes

A.R. Siedle*, Richard A. Newmark, Brook F. Duerr, Peter C. Leung[1]

3M Corporate Research Laboratories, St. Paul, MN 55144-1000, USA

Received 3 March 2003; received in revised form 22 April 2003; accepted 14 July 2003

Abstract

General syntheses of unsymmetrical *ansa*-fluorenyl (flu)-containing ligands of the type flu-bridge-flu' (bridge: C_2H_4, CH_2-$SiMe_2$, $SiMe_2$, $SiPh_2$) and of the corresponding [flu-bridge-flu']$ZrCl_2$ metallocenes are described. Substituent effects in [2,7-R_2-flu-C_2H_4-flu]$ZrCl_2$ (R: H, *t*-Bu, F, Cl) on rates of 1-octene polymerization are described.

Keywords: Bridged fluorenyl metallocenes; Catalysts; Olefin polymerization

1. Introduction

Cyclopentadienyl-containing compounds have played an important role in the development of organometallic chemistry as a discrete intellectual endeavor and of the first "single site", homogeneous olefin polymerization catalysts exemplified by combinations of Cp_2ZrCl_2, $(ind)_2MX_2$ or $(flu)_2MX_2$ (Cp: cyclopentadienyl; ind: indenyl; flu: 9-fluorenyl; X = halogen) with organoaluminum co-catalysts such as methylaluminoxane $(MeAlO)_x$ [1,2]. Organic chemists early developed routes to symmetrical bridging ligands such as $Me_2Si(ind)_2$ [3], 1,2-$(ind)_2C_2H_4$ [4], $Ph_2Si(flu)_2$, [5] and 1,2-$(flu)_2C_2H_4$ [6]. *ansa*-Derivatives of the type [$(ind)_2$-bridge]MX_2 (bridge = C_2H_4 and R_2Si; M = Ti, Zr, Hf; X = Cl, Br), in which the carbocyclic ligands are connected by a bridging group, were then found to be very active catalysts and useful for the synthesis of atactic or isotactic polypropylene, depending on whether the *meso* or *rac* isomers were employed [7,8]. The compound [Cp-CMe_2-flu]$ZrCl_2$ was one of the first highly syndiospecific polymerization catalysts [9,10], a development which stimulated investigation of other fluorenyl-containing metallocenes [11]. Ewen observed that, for polypropylene, polymer molecular weights increased about 10-fold for every C_6 aromatic ring fused to the C_5 ring [12] and we have made similar observations for polyhexene [13]. This paper describes bridged metallocene catalysts containing two fluorenyl ligands and focuses in particular on unsymmetrical compounds that contain two different fluorenyl moieties. We have recently reported that introduction of substituents at C(4,5) in one of the fluorenyl rings in *ansa*-fluorenyl metallocenes provides a rational means to sculpt catalyst shapes and thereby influence their stereoregulating abilities [14]. C_s metallocenes substituted in this way are useful for synthesis of a novel class of nanocrystalline polypropylenes [15]. Efficient syntheses of the starting ligands (and hence the derived metallocenes) have not previously been available. They are the subjects of this paper.

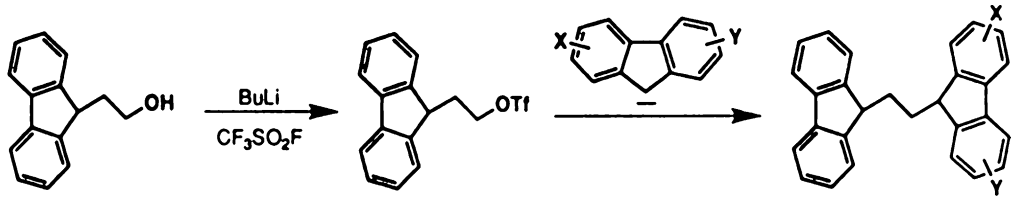
2. Results and discussion

2.1. Ligand syntheses

The problems in synthesizing asymmetrical difluorenyl ligands are illustrated by the difficulties in obtaining the symmetrical compound 1,2-di(9-fluorenyl)ethane (**1**), in good yield. Originally, reaction of Na(flu) with 1,2-$Br_2C_2H_4$ gave flu-C_2H_4-Br which, when treated with more Na(flu), produced flu-C_2H_4-flu [6,16]. Problems arise when Li(flu), readily obtained from fluorene and BuLi, is used instead. Li(flu) can react with 1,2-$Br_2C_2H_4$ to produce the intermediate flu-C_2H_4-Br. Subsequent reaction with a second equivalent of Li(flu) can proceed by nucleophilic attack at the *C*H_2Br carbon to produce the desired product. Alternatively, deprotonation at the C(9) position in the fluorene ring can occur and it is followed by intramolecular

* Corresponding author. Tel.: +1-651-736-1994; fax: +1-651-737-2590.
E-mail address: arsiedle@mmm.com (A.R. Siedle).
[1] Deceased.

1381-1169/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2003.07.020



Scheme 1.

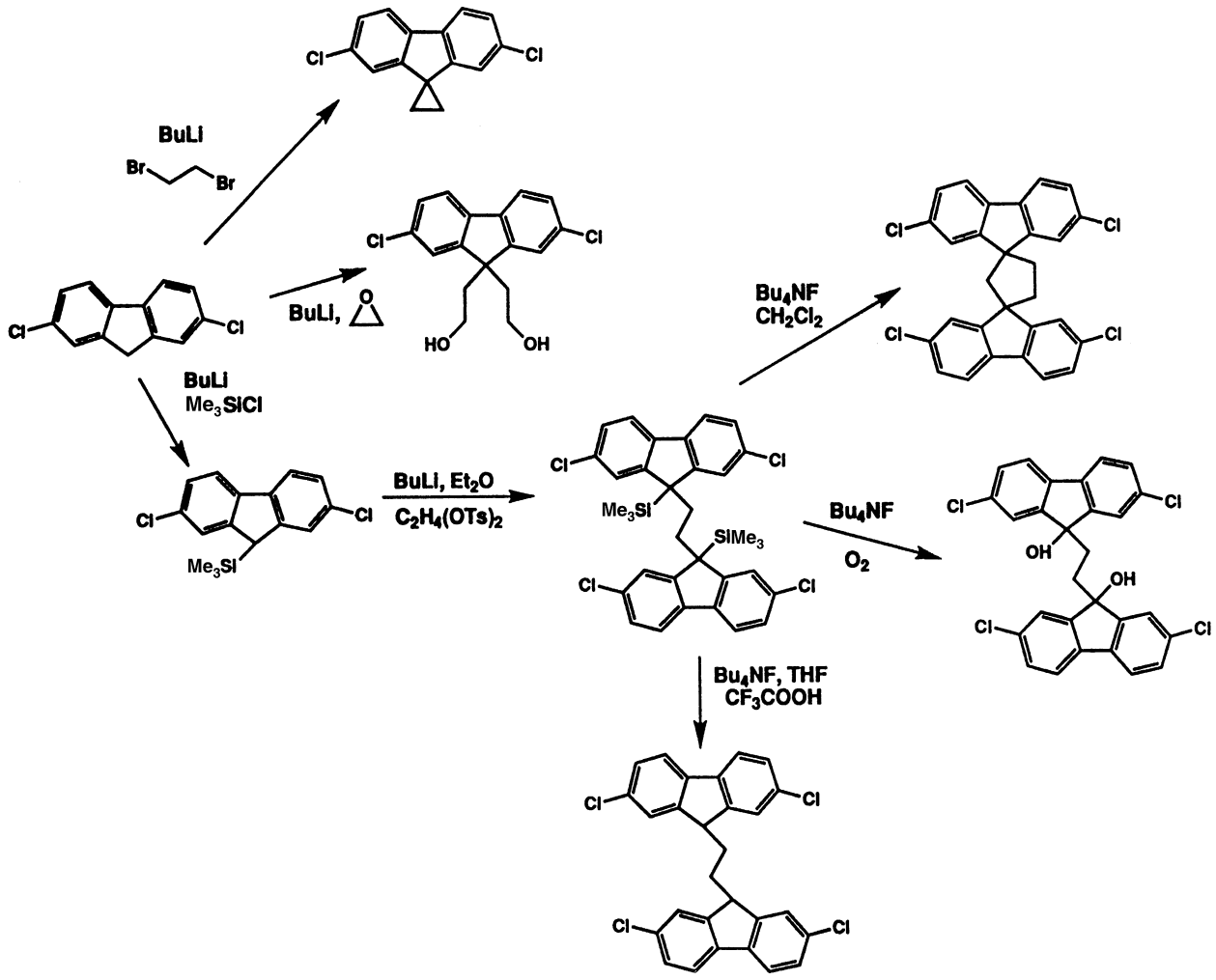
cyclization to produce *spiro*-cyclopropane-9-fluorene. This compound is difficult to separate from **1** and it is easily recognized by the characteristic ^{1}H NMR peak from the *spiro*-cyclopropane ring at 1.74 ppm. Which of the two pathways is followed depends critically on reaction conditions. We find that the best yield of **1** is obtained by adding $Br_2C_2H_4$ to Li(flu) in THF at low temperature. Yields are much lower at 25° and repeated recrystallization is required in order to obtain pure **1**. Addition of tetramethylethylenediamine (TMEDA) or use instead of ethylene glycol ditosylate did little to improve yields. Our approach to the synthesis of unsymmetrical ethylene-bridged difluorenyl ligands of the type fluorenyl-C_2H_4-R_n-fluorenyl required as an intermediate a compound fluorenyl-CH_2-CH_2X in which nucleophilic attack at carbon with displacement of X^- would be much faster than deprotonation followed by intramolecular ring closure. Proton loss from carbon-centered acids, although thermodynamically favorable, is kinetically slow [17]. Triflate, $CF_3SO_3^-$, is known to be a very good leaving group. Therefore, we set out to prepare fluorenyl-C_2H_4-OSO_2CF_3 (**2**). Because **2** was expected to be very sensitive to nucleophilic attack, it was generated in an apolar solvent so that no potentially nucleophilic by-products were formed. Thus, treatment of flu-C_2H_4-OH in toluene with one equivalent of BuLi afforded flu-C_2H_4-OLi (**3**). The stoichiometry of this reaction was easily followed by observation of color for **3** is colorless but removal of an additional proton from C(9) forms an orange dianion. Treatment of **3** with CF_3SO_3F then yielded **2** and inert LiF. The compound CF_3SO_3F is a gas at room temperature and any excess employed was easily removed by pumping. After filtration to remove LiF and evaporation of solvent, **2** was obtained as a colorless oil, stable, either under nitrogen or when redissolved in toluene, for at least several days at room temperature [18].

In preparative experiments, **2** was not isolated. Subsequent addition to the crude reaction mixture of Li^+ salts in ethereal solvents of cyclopentaphenanthrene (CPA), 4,5-dihydrocyclopentaphenanthrene (H_2CPA), 4,5-dimethylfluorene, 2,7-Cl_2-fluorene, 2,7-F_2-fluorene, 4-Mefluorene, 4-*i*-Prfluorene, 2,7-(*p*-tolyl)$_2$-fluorene, 2,7-*t*-Bu_2-fluorene, 9-Me-benzo[c]fluorene, and 2,7-*t*-Bu_2-4-Npflu (Np ≡ α−naphthyl) afforded the ligands flu-C_2H_4-CPA (**4**), flu-C_2H_4-H_2CPA (**5**), flu-C_2H_4-4,5-Me_2-flu (**6**), flu-C_2H_4-2,7-Cl_2-flu (**7**), flu-C_2H_4-2,7-F_2-flu (**8**), flu-C_2H_4-4-Meflu (**9**), flu-C_2H_4-4-*i*-Prflu (**10**), flu-C_2H_4-2,7-(*p*-tolyl)$_2$-flu (**11**), flu-C_2H_4-2,7-(*t*-Bu)$_2$-flu (**12**), flu-C_2H_4-9-Me-2,3-benzoflu (**13**), and flu-C_2H_4-2,7-*t*-Bu_2-4-α-Npflu (**14**), respectively, as indicated in Scheme 1. Dimethoxyethane or diethyl ether are solvents preferred to THF so as to avoid complications from triflate-catalyzed oligomerization of THF.

For synthesis of compounds of the type flu-C_2H_4-X, triflate (X = CF_3SO_3) was the best leaving group found. Other leaving groups failed to give the desired products or led to unexpected results. For example, treatment of a toluene solution of flu-C_2H_4-OLi with Me_2NSO_2Cl and then with Li[2,7-F_2-flu] in ether produced a coupling product, 9,9′-(2,7-F_2-flu)$_2$ (**15**) in 40% yield. A similar reaction using $(CF_3CO)_2O$ and Li[2,7-Br_2-flu] led to the ketone 9-CF_3CO-2,7-Br_2-flu (**16**), in 60% yield.

Even symmetrical derivatives of 2,7-dichlorofluorene (**17**), are difficult to obtain because reaction of its lithium salt with ethylene oxide forms the diol 2,7-Cl_2-flu-9,9-$(C_2H_4OH)_2$ [19]. One of the C(9) positions must be protected. Thus, treatment of the Li^+ salt of 2,7-Cl_2-flu with Me_3SiCl afforded 2,7-Cl_2-9-Me_3Si-flu (**18**). Deprotonation with BuLi and reaction with ethylene glycol ditosylate afforded the protected intermediate 1,2-(2,7-Cl_2-9-Me_3Siflu)$_2C_2H_4$ (**19**). Removal of the Me_3Si group was achieved with $[Bu_4N]F$ in THF under N_2 followed by quenching of the resulting carbanion with CF_3CO_2H to afford 1,2-(2,7-Cl_2-flu)$_2C_2H_4$ (**20**). Choice of reaction conditions was important. Run in air, the deprotection reaction produced 1,2-(2,7-Cl_2-9-HOflu)$_2C_2H_4$ (**21**). If the acid quench were omitted and workup with dichloromethane started, reaction of the intermediate anion with this solvent occurred to give *spiro*-2,2″,7,7″-tetrachlorodi(fluorene-9,1′-cyclopentane-3′,9″-fluorene) (**22**), as shown in Scheme 2.

A ligand having an unsymmetrical bridge, flu-$SiMe_2$-CH_2-flu (**23**) was also prepared. Reaction of Li(flu) with $ClSiMe_2$-CH_2Br afforded flu-$SiMe_2$-CH_2Br, **24**. To enhance reactivity at the methylene carbon (**24**) was converted to flu-$SiMe_2$-CH_2I (**25**) by metathesis with NaI in acetone. Compound **25** was quite reactive towards both acids (protiodesilation, cf. Section 2.5) and bases. The latter caused elimination of HI and formation of a silacyclopropane. Silacyclopropanes undergo nucleophilic ring opening far more readily than cyclopropanes. The ring opening by fluorenyl carbanions is not regiospecific. Thus, treatment of **25** with two equivalents of K(2,7-*t*-Bu_2-flu) produced an inseparable mixture of the isomers flu-$SiMe_2$-CH_2-(2,7-*t*-Bu_2-flu),



Scheme 2.

26, and flu-CH_2-$SiMe_2$-(2,7-*t*-Bu_2-flu), **27**. These two compounds correspond to two possible pathways for C–Si bond cleavage by a second equivalent of 2,7-*t*-Bu_2-flu produced by the second equivalent of this base. Therefore, this synthetic method is *usually* an inefficient route to compounds of the type flu(1)-$SiMe_2$-CH_2-flu(2) where the two fluorenyl ligands, 1 and 2, are different. In general, the Mg–C bond in organomagnesium compounds is considered to be more covalent than those in alkali metal compounds and, therefore, the former are anticipated to be weaker bases [20]. Accordingly, reaction of **25** with one half equivalent of flu_2Mg produced pure **23** and no fluorene. Similarly, reaction of **24** with Li [2,7-Cl_2-flu] in 1,2-dimethoxyethane-hexane produced flu-$SiMe_2$-CH_2-(2,7-Cl_2-flu), **28**, in modest (19%) yield.

Unsymmetrical ligands of the type flu-SiR_2-flu', containing a R_2Si bridge, were prepared from flu-SiR_2Cl (R= Me, Ph) and Li[flu']. In this way, CPA-$SiMe_2$-flu, **29**, H_2CPA-$SiMe_2$-flu, **30**, and H_2CPA-$SiPh_2$-flu, **31** were obtained.

The new ligands described above could be converted to the corresponding metallocenes by treatment in ether or THF with two equivalents of BuLi followed by removal of the ethereal solvent and reaction with metal salts such as $ZrCl_4$ or $HfCl_4$ as described in Section 2.18. Solvents used in the metal insertion step were CH_2Cl_2 (at −78 °C) or toluene at room temperature. The latter was preferred and probably safer. In this way, the ligands **4**–**14**, **20**, **23**, **29**–**31** were converted to the metallocenes [flu-C_2H_4-CPA]$ZrCl_2$ (**32**), [flu-C_2H_4-H_2CPA]$ZrCl_2$ (**33**), [flu-C_2H_4-4,5-Me_2-flu]$ZrCl_2$ (**34**), [flu-C_2H_4-2,7-Cl_2-flu]$ZrCl_2$ (**35**), [flu-C_2H_4-2,7-F_2-flu]$ZrCl_2$ (**36**), [flu-C_2H_4-4-Meflu]$ZrCl_2$ (**37**), [flu-C_2H_4-4-*i*-Prflu]$ZrCl_2$ (**38**), [flu-C_2H_4-2,7-(*p*-tolyl)$_2$-flu]$ZrCl_2$ (**39**), [flu-C_2H_4-2,7-*t*-Bu_2-flu]$ZrCl_2$ (**40**), [flu-C_2H_4-9-Mebenzo[c]flu]$ZrCl_2$ (**41**), [flu-C_2H_4-2,7-*t*-Bu_2-4-(α-Np) flu]ZrC_2 (**42**), [Cl_2-flu-C_2H_4-Cl_2-flu]$ZrCl_2$ (**43**), [flu-$SiMe_2$-CH_2-flu]$ZrCl_2$ (**44**), [flu-$SiMe_2$-CPA]$ZrCl_2$ (**45**), [flu-$SiMe_2$-H_2CPA]$ZrCl_2$ (**46**), and [flu-$SiPh_2$-H_2CPA]$ZrCl_2$ (**47**). The new fluorenyl-containing metallocenes separated as finely divided, bright red luminescent solids that were most conveniently isolated by centrifugation. Those containing a C_2H_4 bridge were sufficiently hydrolytically stable that by-product LiCl and other salts could be removed by rapid washing with absolute ethanol. Metallocenes contain-

ing a Me_2Si bridge were quickly decomposed by ethanol and were purified by recrystallization from CH_2Cl_2, one of the few suitable, non-reactive solvents. They are extremely moisture sensitive in solution and rigorously dried solvent is required. Solubility of most of the *ansa*-bridged fluorenyl metallocenes in CH_2Cl_2 is low, on the order of several hundred mg l^{-1}, which makes obtention of good NMR spectra difficult. However, it is possible to use the metallocenes in other settings without removal of the lithium salts. We have used these compounds to polymerize propylene and their stereoregulating properties have been described elsewhere [14,15]. Here, we focus on some electronic effects in metallocene-catalyzed olefin polymerization.

2.2. Substituent effects in olefin polymerization

The relative rates of 1-octene polymerization by [2,7-R_2-flu-C_2H_4-flu]$ZrCl_2$ (R = H, R: Cl, **35**; F, **36**; and *t*-Bu, **40**) at 30 °C in the presence of methylaluminoxane as co-catalyst were examined. Octene is a convenient substrate because it is a liquid at room temperature and so reactions can be carried out in glass jars at atmospheric pressure.

Results are collected in Table 1 along with GPC data for the product polymers. The electron-withdrawing substituents Cl and F are associated with 1.7- and 1.9-fold increases, respectively, in conversion efficiencies with a slight increase in polyoctene molecular weight. The effect of two *t*-butyl groups in the 2,7 positions of one fluorenyl ring on conversion efficiency is striking—a 17-fold reduction. There is only a slight decrease in the polymer molecular weight. Incorporation of *t*-butyl groups into the second fluorenyl ring, i.e. [2,7-*t*-Bu_2-flu-C_2H_4-2,7-*t*-Bu_2-flu]$ZrCl_2$ (**48**) reduces the polymerization rate and polymer molecular weight even further.

2.3. Discussion of substituent effects

Our results above appear to be inconsistent with some earlier studies. Although substituent effects in metallocene catalysts have been incisively reviewed [21], we believe that a complete and comprehensive theory of these effects has yet to be put forward. Two problems lie at the core of the analysis: (1) the initiating metallocenium species are (often) ion pairs and the degree of ion pairing, and hence reactivity can depend on the structure (i.e. number and type of carbocyclic ligands) of the ions; (2) the overall rate observed is a convolution of rates of several elementary steps including initiation, propagation, chain transfer, chain termination and catalyst deactivation. All of these rates are, in principle, influenced by the steric and electronic effects exerted by a substituent.

Table 1
1-Octene polymerization data

Metallocene	Conversion efficiency (kg polyoctene h^{-1} $(g\ Zr)^{-1}$	M_w, M_n ($\times 10^{-5}$; g mol^{-1})
(flu-C_2H_4-flu)$ZrCl_2$	59	2.2, 1.0
(Cl_2-flu-C_2H_4-flu)$ZrCl_2$ (**35**)	100	2.7, 1.3
(F_2-flu-C_2H_4-flu)$ZrCl_2$ (**36**)	113	2.7, 1.3
(*t*-Bu_2-flu-C_2H_4-flu)$ZrCl_2$ (**40**)	3.4	2.1, 1.1
(*t*-Bu_2-flu-C_2H_4-*t*-Bu_2-flu)$ZrCl_2$ (**48**)	0.6	1.5, 0.6

Conditions: run in neat octene, [Zr] = 2 ppm, [Al]/[Zr] = 2400.

Thus, in the indenyl metallocenes (5,6-$X_2C_9H_5)_2ZrCl_2$ and the ethylene-bridged analogues [1,2-(5,6-$X_2C_9H_4)_2C_2H_4$]$ZrCl_2$, the empirical rate of ethylene polymerization was decreased (relative to X = H) when X was Cl or OMe. However, the effect of the methoxy group was obscured by a competing catalyst deactivation reaction [22]. In the metallocenes [2,7-X_2-flu-CMe_2-Cp]$ZrCl_2$, relative rates for propylene polymerization were in the order X = H > t−Bu > F ≫ Cl [23]. A study of the unbridged metallocenes (4,7-R_2-indenyl)$_2ZrCl_2$ indicated that electron-withdrawing substituents (Cl, F) decreased both catalyst molecular weights and polypropylene molecular weights; and that electron-releasing substituents such as Me affected neither [24].

A study of the constrained-geometry catalysts (XC_9H_5)-($SiMe_2$-*t*-Bu)$TiMe_2$, activated with $(C_6F_5)_3B$, revealed an increase in activity for ethylene-octene copolymerization and in polymer molecular weight for X = 2-OMe; and a dramatic increase for the 3-*N*-pyrrolidine compound X = c-C_4H_8N [25]. In contrast, the activity of *rac*-[2-$Me_2NC_9H_6)_2SiMe_2$]$ZrCl_2$ was lower than that of the unsubstituted compound. Additionally, the Me_2N-substituted *ansa*-indenyl metallocene exhibited an unusually long induction period. The dominant chain termination process was exchange of Me and polymer chains between Al centers of the $(MeAlO)_x$ co-catalyst and Zr in the metallocene [26].

It is difficult to distill a consensus from these results. Indeed, it might seem reasonable to suspect that even the sign of a substituent effect can depend on the structure of the metallocene molecule. Here, the accelerating effect on polymerization rate of Cl and F in (2,7-X_2-flu-C_2H_4-flu)$ZrCl_2$ is regarded as electronic in nature, a consequence of the electron-withdrawing properties of these halogen substituents. In a study of the rates of activation of *ansa*-bridged fluorenyl metallocenes by $(MeAlO)_x$, we found that F and Cl substituents also accelerate this reaction, which transforms (flu-C_2H_4-flu)$ZrCl_2$ into the resting state of the catalyst, (flu-C_2H_4-flu)Zr(μ-Me_2)$AlMe_2^+$ [27]. So they appear to have the same effect on rates of octene polymerization. However, these trends run counter to those described above for halogen substituents. We surmise that electron-withdrawing substituents should accelerate olefin polymerization because they render the metal center in the catalyst more nucleophilic. On the other hand, a more nucleophilic metal center should have enhanced interactions with the "non-coordinating" counterion associated with the metallocenium ion initiator, leading, in turn, to slower

initiation and propagation. Which situation predominates depends on the structure of the metallocene. If the metal center is incompletely shielded by the steric bulk of the ligands, then the effect of tighter ion pairing should prevail. If, on the other hand, the metal is well protected by bulky fluorenyl groups, as is the case here with (2,7-X_2-flu-C_2H_4-flu)$ZrCl_2$ metallocenes, tighter ion pairing is disfavored and, instead, increased metal nucleophilicity results in enhanced interactions with an olefin substrate.

It is tempting to think that the effect of *t*-Bu substituents in **40** and **48** is of steric origin. We determined the solid state structure of **48** in an effort to find ground state structural differences in this metallocene that would account for the much slower rate of octene polymerization. However, the molecular structure appears not to differ significantly from that reported for [flu-C_2H_4-flu]$ZrCl_2$ [28]. At this point, we are faced with a conundrum because the problem is under-determined. It is possible that the steric effects of the *t*-Bu groups are manifested in one of the intermediates in the polymerization reaction rather than in the ground state structure of the precursor metallocene. Alternatively, they may be due to the electron-releasing properties of *t*-Bu groups. The data are insufficient to make a distinction.

2.4. Structure of [2,7-t-Bu_2-flu-C_2H_4-2,7-t-Bu_2-flu]$ZrCl_2$ (48)

Compound **48** crystallized from chloroform as a 1:1 solvate whose structure was determined by X-ray crystallography. Selected bond distances are given in Table 2. Because the structure is similar to that of [flu-C_2H_4-flu]$ZrCl_2$, only key differences in the Zr–C distances will be highlighted. Zirconium is bonded to all five carbon atoms in the η^5-fluorenyl rings. It is, however, displaced toward the unique, bridgehead carbon atoms and these participate in the shortest Zr–C bonds, $d(Zr–C)_{av} = 2.147(5)$ Å. The bonds to the pairs of carbon atoms α and β to this carbon atom, 2.571(5) and 2.682(5) Å, respectively, are progressively longer. Bonding is therefore distorted from a η^5 arrangement towards η^3. In [flu-C_2H_4-flu]$ZrCl_2$, the corresponding Zr–C distances are 2.426(5), 2.550(5) and 2.670(5) Å.

Table 2
Selected bond distances (Å) and angles (°) in **48**·$CHCl_3$

Zr-C212	2.414(5)
Zr-C112	2.421(5)
Zr-C113	2.563(5)
Zr-C213	2.565(5)
Zr-C211	2.574(5)
Zr-C111	2.583(5)
Zr-C15	2.670(5)
Zr-C26	2.673(6)
Zr-C25	2.689(6)
Zr-C16	2.694(6)
Zr-C11	2.410(2)
Zr-C12	2.411(2)
Cl1-Zr-C12	100.07(6)

2.5. Experimental

Reactions were conducted under an atmosphere of dry nitrogen unless otherwise indicated. Fluorenyl ligands were isolated and purified in air in which they are stable. Dichlorozirconium and hafnium metallocenes are stable to oxygen but are moisture sensitive to varying degrees. They were isolated and stored under dry nitrogen. THF, diethyl ether and toluene were distilled under N_2 from Na-benzophenone; CH_2Cl_2 was distilled from CaH_2. NMR spectra were obtained on Varian XL-400 or Unity 500 instruments. Chemical shifts are referenced to internal Me_4Si (^1H, ^{13}C, ^{29}Si) and $CFCl_3$ (^{19}F) with positive shifts, in ppm, being downfield of the references. Coupling constants are given in Hz. Physical properties of new compounds and some starting materials are collected in Table 3. The compounds 2,7-di-(*p*-tolyl)fluorene, 2,7-di-*t*-Butylfluorene [29], 9-Mebenzo[c]fluorene [30], 2,7-Cl_2-fluorene [31], 7-F_2-fluorene [32], 4,5-Me_2-fluorene [33], flu-$SiMe_2Cl$ [34], flu-$SiPh_2Cl$ [35] and flu-C_2H_4OH[2] were prepared by literature methods. CF_3SO_2F was a 3 M product. The compound flu-C_2H_4-OH was kept under N_2 for long term storage for it very gradually became gummy in air. Similar deterioration was observed for flu-C_2H_4Br which, over 10 months, there accrued 15 mol% of an impurity whose NMR spectra were consistent with 9-HOO-9-(BrC_2H_4)flu. *n*-BuLi refers to a 2.5 M solution in hexane. Mass spectra were obtained in electron impact mode using 70 eV electron beam energy. Thermal desorption was used for neutral ligands; laser desorption was more successful for metallocenes.

2.6. 1-Octene polymerization

Methylaluminoxane was obtained from Albemarle Corp. as a solution in toluene that contained 26 wt.% $(MeAlO)_x$ and 5.2 wt.% Me_3Al. It was diluted with toluene (vacuum transferred from *i*-Bu_3Al) to give a solution having an aluminum concentration (determined by ICP analysis) of 1.7 M. In a drybox, metallocenes and this $(MeAlO)_x$ solution were combined in toluene to give [Zr] = 2 ppm and [Al]/[Zr] = 2400 after dilution with monomer. After stirring for 30 min, the catalyst was added to neat octene that had been vacuum transferred from NaK alloy. Reactions were run for 1 h, quenched with deoxygenated methanol and removed from the drybox. The precipitated polymer was separated and dried in a vacuum oven at 75 °C. GPC analyses were performed on toluene solu-

[2] cf. [18]. Successful reaction of the Li^+ salt of a fluorenide with ethylene oxide appears to be very sensitive to reaction conditions. The procedure, applied to 2,7-Cl_2-fluorene, yields 9,9-$(HOC_2H_4)_2$-2,7-Cl_2-flu [19]. Applied to cyclopentaphenanthrene, a mixture of 9,9-$(HOC_2H_4)_2$CPA (**51**) and 9-HOC_2H_4CPA (**52**) was obtained. Despite repeated recrystallization, the latter was never obtained in more than 85 mol% purity.

Table 3
Characterization data for ligands and metallocenes[a]

Flu-C_2H_4-flu (**1**): ^{1}H NMR ($CDCl_3$): 7.75 (d, 8), 7.37 (td, 8, 2), 7.30–7.29 (m), 3.83 (H_9), 1.73 (CH_2). ^{13}C NMR: 146.7, 141.2 (C_{ipso}), 126.8, 126.7, 124.0, 119.6, 46.9 (C_9), 26.5 (CH_2). Mass spectrum: *m/z* 358 (M^+), 191 ($C_{13}H_{11}^+$), 178 ($C_{14}H_{10}^+$), mp 222–223 °C (xylenes), 36%.

Flu-C_2H_4-OSO_2CF_3 (**2**): ^{1}H NMR ($CDCl_3$): 7.81 (d,7, $H_{4,5}$), 7.54 (dd, 8, 1, $H_{1,8}$), 7.45 (t, 7, $H_{3,6}$), 7.39 (td, 8, 1, $H_{2,7}$), 4.41 (t, 7, CH_2OSO_2), 4.18 (t, 6, H_9), 2.62 (td, 7, 6 $CH_2CH_2OSO_2$). ^{13}C NMR: 144.6, 140.8, 127.6, 127.2, 123.9, 120.1, 74.4 (CH_2OSO_2), 43.4 (C_9), 32.1 ($CH_2CH_2OSO_2$). ^{19}F NMR: −78.8.

Flu-C_2H_4-CPA (**4**): ^{1}H NMR ($CDCl_3$): 7.81 (s, $H_{4*,5*}$), 7.80 (d, $H_{3*,6*}$), 7.74 (dt, 7, 1, $H_{4,5}$), 7.61 (dd, 8, 7, $H_{2*,7*}$), 7.51 (d, 7, $H_{1*,8*}$), 7.37 (dd, 7, 1, $H_{1,8}$), 7.35 (tm, 7, $H_{3,6}$), 7.28 (td, 7, 1, $H_{2,7}$), 4.39 (t, 6, H_{9*}), 3.91 (t, 5, H_9), 2.01 (m, CPA-CH_2), 1.91 (m, Flu-CH_2). ^{13}C NMR: 146.7, 145.4, 141.2, 137.4, 127.7, 127.2, 126.9, 126.8, 125.2, 125.1, 122.8, 120.6, 119.7, 49.5 (C_9), 47.0 (C_{9*}), 28.4 (CPA-CH_2), 27.0 (flu-CH_2). Mass spectrum: *m/z* 382 (M^+), 203 ($C_{16}H_{11}^+$). mp 225–227 °C (heptane–toluene), 51%. *Anal*. C, 94.2 (94.1); H, 5.8 (5.9).

Flu-C_2H_4-H_2CPA (**5**): ^{1}H NMR ($CDCl_3$): 7.73 (dt, 7, 1, $H_{4,5}$), 7.39 (dq, 7, 1, $H_{1,8}$), 7.35 (tdd, 7, 1, 0.6, $H_{3,6}$), 7.28 (td, 8, 1, $H_{2,7}$), 7.16 (m, 4H, H_2CPA), 7.08 (m, 2H, H_2CPA), 3.92 and 3.91 (overlapping t, 2H, $H_{9,9*}$), 3.12 (m, 4H, H_2CPA-$H_{4,5}$), 2.01 (m, 2H, H_2CPA-CH_2), 1.72 (m, 2H, flu-CH_2). ^{13}C NMR: 146.8, 144.1, 141.2, 138.5, 130.2, 127.2, 126.83, 126.79, 124.83, 124.16, 122.0, 119.7, 49.3 and 47.1 ($H_{9,9*}$), 28.6 (CH_2), 27.1 (CH_2), 26.0 (H_2CPA CH_2). Mass spectrum: *m/z* 384.1813 (M^+, calcd. 384.1827), 206 ($M^+ - C_{14}H_{10}$). mp 189–190 °C (CH_2Cl_2–acetone), 65%. *Anal*. C, 93.8 (93.7); H, 6.2 (6.2).

Flu-C_2H_4-4,5-Me_2-flu (**6**): ^{1}H NMR ($CDCl_3$): 7.66 (d, 8, $H_{4,5}$), 7.28 (m, $H_{3,6}$), 7.21–7.19 (m, $H_{2,7}$, $H_{1,8}$), 7.12 (t, 7, $H_{2*,7*}$), 7.08 (d, 7, $H_{1*,8*}$ or $H_{3*,6*}$), 7.02 (d, 7, $H_{3*,6*}$ or $H_{1*,8*}$), 3.71 and 3.67 (t, 5, H_9 and H_{9*}), 2.67 (s, CH_3), 1.61 (m, CH_2), 1.50 (m, CH_2). ^{13}C NMR: 148.0, 146.8, 141.19, 141.16, 131.8, 130.6, 126.77, 126.74, 126.56, 124.1, 121.3, 119.6, 46.86 and 46.45 ($C_{9,9*}$), 26.9 and 25.6 (CH_2), 25.3 (CH_3). Mass spectrum: *m/z* 386.2036 (M^+, calcd. 386.2029). mp 173–175 °C (heptane), 57%. *Anal*. C, 92.8 (92.9); H, 7.2 (7.0).

Flu-C_2H_4-2,7-Cl_2-flu (**7**): ^{1}H NMR ($CDCl_3$): 7.74 (d, 7, $H_{4,5}$), 7.58 (d, 8, $H_{4*,5*}$), 7.37 (t, 7, $H_{3,6}$), 7.32 (m, $H_{2,7}$ and $H_{3*,6*}$), 7.27 (d, 8, $H_{1,8}$), 7.19 (m, $H_{1*,8*}$), 3.83 and 3.75 (H_9 and H_{9*}), 1.64 and 1.58 (CH_2). ^{13}C NMR: 148.2, 146.2, 141.3, 138.8, 132.9, 127.4, 127.0, 126.9, 124.5, 124.0, 120.6, 119.7, 46.8 and 46.6 ($C_{9,9*}$), 25.9 and 25.7 (CH_2). Mass spectrum: *m/z* 426.0964 (M^+, calcd. 426.0937). mp 206–208 °C (toluene), 45%. *Anal*. C, 78.7 (78.4); H, 4.7 (4.8).

Flu-C_2H_4-2,7-F_2-flu (**8**): ^{1}H NMR ($CDCl_3$): 7.76 (d, 8, $H_{4,5}$), 7.60 (dd, 8, 5 [$^4J_{HF}$], $H_{4*,5*}$), 7.39 (td, 8, 2, $H_{3,6}$), 7.32 (td, $H_{2,7}$) overlapping 7.29 (m, $H_{1,8}$), 7.06 (t, $^3J_{HH}$ and $^3J_{HF} = 9$, m, $H_{3*,6*}$), 6.94 (dd, $^3J_{HH} = 9$, $^4J_{HH} = 2$, $H_{1*,8*}$), 3.88 (m, H_{9*}), 3.78 (m, H_9), 1.67 and 1.54 (m, CH_2). ^{13}C NMR: 162.2 (d, $^1J_{CF} = 245$, $H_{2*,7*}$), 148.6 (d, $^3J_{CF} = 10$, $H_{1*,8*}$), 146.2 ($C_{1a,8a}$), 141.2 ($C_{4a,5a}$), 136.4 (d, $^4J_{CF} = 2$, $C_{4a*,5a*}$), 126.9, 126.8, 123.9, 120.2 (d, $^3J_{CF} = 10$, $H_{4*,5*}$), 119.7, 114.1 (d, $^2J_{CF} = 23$, $C_{1*,8*}$ or $C_{3*,6*}$), 111.4 (d, $^2J_{CF} = 23$, $C_{3*,6*}$ or $C_{1*,8*}$), 49.93 and 49.60 (C_9 and C_{9*}), 25.95 and 25.90 (CH_2). ^{19}F NMR: −116.2 (td, 9, 5). Mass spectrum: *m/z* 394.1472 (M^+, calcd. 394.1526), 201 ($C_{13}H_7F_2^+$), 180 ($C_{14}H_{12}^+$). mp 207–208 °C (toluene–hexane), (50%). *Anal*. C, 85.3 (85.5); H, 5.1 (5.3).

Flu-C_2H_4-4-Meflu (**9**): ^{1}H NMR ($CDCl_3$): 7.90 (d, 8, H_{5*}), 7.76 (d, 7, $H_{4,5}$), 7.40–7.36 (m, 3H), 7.34–7.30 (m, 6H), 7.21 (t, 7, H_{2*}), 7.16 (t, 8, $H_{2,7}$), 3.83 (2H, br, $H_{9,9*}$), 1.75–1.70 (m, 4H, CH_2). ^{13}C NMR: 147.07, 147.03, 146.69, 142.2, 141.2, 139.2, 132.8, 129.1, 126.78, 126.73, 126.70, 126.42, 126.05, 124.1, 123.9, 122.9, 121.5, 119.6, 46.89 and 46.65 ($C_{9,9*}$), 26.55 and 26.17 (CH_2), 21.0 (CH_3). Mass spectrum: *m/z* 372.1892 (M^+, calcd. 372.1873), 192 ($C_{15}H_{12}^+$), 178 ($C_{14}H_{10}^+$), 165 ($C_{13}H_9^+$). mp 194–195 °C (CH_2Cl_2–EtOH), 69%. *Anal*. C, 93.(93.4); H, 6.5 (6.8).

Flu-C_2H_4-4-*i*-Prflu (**10**): ^{1}H NMR ($CDCl_3$): 7.92 (d, 8, H_{5*}), 7.71 (d, 8, $H_{4,5}$), 7.36–7.25 (m, 11H), 7.12 (d, 7, H_{3*}), 3.78 (m, $H_{9,9*}$ and $CHCH_3$), 1.67 (m, CH_2), 1.43, (d, 7, CH_3), 1.37 (d, 7, CH_3). ^{13}C NMR: 147.34, 147.32, 146.7, 144.1, 141.57, 141.17, 141.16, 138.0, 126.77, 126.75, 126.71, 126.0, 124.06, 124.04, 123.9, 123.36, 123.15, 121.4, 119.6, 46.9 and 46.5 ($C_{9,9*}$), 29.4 ($CHCH_3$), 26.61 and 26.16 (CH_2), 22.92 and 22.57 (CH_3). Mass spectrum: *m/z* 400 (M^+), 357 ($M^+ - C_3H_7$). mp 115–117 °C (heptane), 65%. *Anal*. C, 93.0 (92.9); H, 7.0 (7.0).

Flu-C_2H_4-2,7-(*p*-tolyl)$_2$-flu (**11**): ^{1}H NMR ($CDCl_3$): 7.80 (d, 8, H_{4*5*}), 7.76 (d, 7, $H_{4,5}$), 7.62 (dd, 8, 2, H_{3*6*}), 7.56 (AA′XX′ pattern, d, 8, H_{tolyl} *meta* to CH_3), 7.50 (s, $H_{1*,8*}$), 7.35 (t, 7, $H_{3,6}$), 7.30 (AA′XX′ pattern, d, 8, H_{tolyl} *ortho* to CH_3), 7.28 (d, 8, $H_{1,8}$), 7.20 (td, 8, 1, $H_{2,7}$), 3.92 and 3.84 (m, $H_{9,9*}$), 2.45 (s, CH_3), 1.76 (m, CH_2). ^{13}C NMR: 147.5, 146.6, 141.2, 139.96, 139.66, 138.4, 136.8, 129.4, 126.87, 126.78, 126.77, 125.9, 124.1, 122.5, 119.89, 119.65, 46.91 and 46.78 ($C_{9,9*}$), 26.0 and 25.9 (CH_2), 21.1 (CH_3). Mass spectrum: *m/z* 538.2640 (M^+, calcd. 538.2655). mp 242–243 °C (toluene), 70%. *Anal*. C, 93.7 (93.6); H, 6.3 (6.4).

Flu-C_2H_4-2,7-*t*-Bu_2-flu (**12**): ^{1}H NMR ($CDCl_3$): 7.80 (d, 8, $H_{4,5}$), 7.66 (d, 8, H_{4*5*}), 7.41 (d, 7, $H_{3*,6*}$), 7.40 (tm, 7, $H_{3,6}$), 7.35 (s, H_{1*8*}), 7.33 (t, 7, $H_{2,7}$), 7.30 (d, 7, $H_{1,8}$), 3.84 and 3.83 (t, H_9 and H_{9*}), 1.67 (m, CH_2), 1.41 (s, CH_3). ^{13}C NMR: 149.6, 146.86, 146.70, 141.3, 138.7, 126.79, 126.78, 123.76, 123.72, 120.8, 119.7, 118.9, 46.65 and 46.61 ($C_{9,9*}$), 34.8 (CCH_3), 31.6 (CH_3), 25.4 and 24.1 (CH_2). Mass spectrum: *m/z* 470.2896 (M^+, calcd. 470.2968), 413 ($M^+ - C_4H_9$), 357 (*m/z* 413-C_4H_8). mp 227–228 °C (heptane), 70%. *Anal*. C, 91.9 (91.9); H, 8.1 (8.0).

Flu-C_2H_4-9-Mebenzo[c]flu (**13**): ^{1}H NMR ($CDCl_3$): 8.76 (d, 8, H_{1*}), 8.26 (d, 8, H_{11*}), 7.98 (d, 8, H_{4*}), 7.81 (d, 8, H_{5*}), 7.78 (d, 7, $H_{4,5}$), 7.65 (ddd, 8, 7, 1, H_{2*}), 7.54 (td, 7, 1, H_{3*}), 7.46 (d, 8, H_{6*}), 7.40 (t, 7, $H_{3,6}$), 7.34–7.24 (m, $H_{2,7}$, $H_{1,8}$ and H_{10*}), 7.18 (s, H_{8*}), 3.88 (t, 5, H_{7*}), 3.80 (t, 5, H_9), 2.50 (s, CH_3), 1.75–1.65 (m, CH_2 next to benzoflu), 1.53 (m, CH_2 next to flu). ^{13}C NMR: 147.9, 146.6, 145.2, 141.25, 141.21, 139.7, 135.83, 135.62, 133.4, 129.20, 129.01, 127.76, 127.24, 126.80, 126.76, 126.64, 126.25, 124.87, 124.67, 124.07, 123.7, 122.35, 122.13, 119.6, 46.87 and 46.82 ($CHCH_2$), 25.65 and 25.62 (CH_2), 21.48 (CH_3). Mass spectrum: *m/z* 422 (M^+), 229 ($C_{15}H_{13}^+$), 257 ($M^+ - C_{13}H_9$). mp 154.5–156 °C (CH_2Cl_2–EtOH), 62%. *Anal*. C, 93.8 (93.6); H, 6.2 (6.3).

Flu-C_2H_4-2,7-*t*-Bu_2-4-(α-Np)flu (**14**): ^{1}H NMR ($CDCl_3$): 7.98 (m, 2H), 7.82 (m, 2H), 7.64–7.20 (m), 6.87 (dm, 8, 1, 1H), 6.13 (t, 9, 1H), 3.90 (m, $H_{9,9*}$), 1.8–1.7 (m, CH_2), 1.44 (s, CH_3), 1.28 (s, CH_3). ^{13}C NMR: Over 43 peaks between 149.1 and 119.7 ppm, 46.77 and 46.69 ($C_{9,9*}$), 34.81 and 34.58 (CCH_3), 31.60 and 31.43 (CH_3), 25.85, 25.49, 25.32 and 25.17 (CH_2). Mass spectrum: *m/z* 596.3513 (M^+, calcd. 596.3438), 483, 305, 291. Mp 115 °C (MeOH), 45%. *Anal*. C, 92.6 (92.4); H, 7.4 (7.4).

9,9′-(2,7-F_2-flu)$_2$ (**15**): ^{1}H NMR (CD_2Cl_2): 7.53 (dd, 8, 5 [$^4J_{HF}$], $H_{4,5}$), 7.00 (td, 9 ($^3J_{HH}$ and $^3J_{HF}$), 2 ($^4J_{HH}$), $H_{3,6}$), 6.61 (br, $H_{1,8}$), 4.66 (s, H_9). ^{13}C NMR: 161.8 (d, 246 ($^1J_{CF}$), $C_{2,7}$), 145.7 (d, 8 ($^3J_{CF}$), $C_{1a,8a}$), 136.6 (s, $C_{4a,5a}$), 120.5 (d, 9 ($^3J_{CF}$), $C_{4,5}$), 114.9 (d, 23 ($^2J_{CF}$), $C_{1,8}$ or $C_{3,6}$), 111.3 (d, 23 ($^2J_{CF}$), $C_{3,6}$ or $C_{1,8}$), 49.5 (C_9). ^{19}F NMR: −115.3 (br). Mass spectrum: *m/z* 402 (M^+), 201 ($C_{13}H_7F_2^+$). mp 233–234 °C (heptane), 40%. *Anal*. C, 77.6 (77.9); H, 3.5 (3.6).

Table 3 (*Continued*)

9-CF_3CO-2,7-Br_2-flu (**16**): ^{1}H NMR ($CDCl_3$): 7.64–7.60 (m, 6H), 5.21 (s, H_9). ^{13}C NMR: 188.1 (q, $^2J_{CF} = 36$, *C*O), 139.99, 139.92, 132.3, 128.3, 121.78, 121.76, 115.3 (q, 293, $^1J_{CF} = 293$, *C*F_3), 55.7 (C_9). Mass spectrum: *m/z* 418 (M^+), 321 ($M^+ - COCF_3$). IR: 1770 cm^{-1} (Nujol). mp 125.5–126 °C (heptane), 60%. *Anal*. C, 42.9 (43.3); H, 1.7 (1.9).

2,7-Cl_2-9-Me_3Siflu (**18**): ^{1}H NMR ($CDCl_3$): 7.70 (d, 8, $H_{4,5}$), 7.44 (d, 2, $H_{1,8}$), 7.32 (dt, 8, 2, $H_{3,6}$), 3.82 (H_9), −0.37 (CH_3). ^{13}C NMR: 147.1, 137.7, 131.9 (*C*Cl), 125.7, 123.9, 120.7, 42.9 (C_9), −2.8 (*C*H_3). Mass spectrum: *m/z* 306.0400 (M^+, calcd. 306.0393), 291 ($M^+ - CH_3$), 233 ($M^+ -$ $SiMe_3$); self-CIMS *m/z* 309, 307 ($M^+ + H$). mp 127.5–128 °C (hexane), 47%. *Anal*. C, 62.5 (62.5); H, 5.2 (5.3).

1,2-(2,7-Cl_2-9-Me_3Siflu)$_2C_2H_4$ (**19**): ^{1}H NMR ($CDCl_3$): 7.73 (d, 8 $H_{4,5}$), 7.36 (dd, 8, 2, $H_{3,6}$), 7.10 (d, 2, $H_{1,8}$), 1.60 (CH_2), −0.47 (CH_3). ^{13}C NMR: 149.4, 137.7, 132.4, 126.1, 122.8, 120.8, 49.9 (C_9), 24.6 (*C*H_2), 4.32 (*C*H_3). Mass spectrum: *m/z* 638.0896 (M^+, calcd. 638.0948), 550 ($M^+ -$ $SiMe_3$). mp >260° (CH_2Cl_2–heptane), 86%. *Anal*. C, 63.8 (64.2); H, 5.3 (5.2); Cl, 22.2 (22.1).

1,2-(2,7-Cl_2-flu)$_2C_2H_4$ (**20**): ^{1}H NMR ($CDCl_3$): 7.62 (d, 8, $H_{4,5}$), 7.36 (dd, 2, 8, $H_{3,6}$), 7.27 (m, $H_{1,8}$), 3.83 (C_9), 1.67 (CH_2). ^{13}C NMR: 147.8 ($C_{4a,5a}$), 138.7 ($C_{1a,8a}$), 133.1 ($C_{2,7}$), 127.6 ($H_{3,6}$), 124.4 ($C_{1,8}$), 120.7 ($C_{4,5}$), 46.7 (C_9), 26.2 (*C*H_2). Mass spectrum: *m/z* 494.0157 (M^+, calcd. 494.0242), 459 (M^+ − Cl). mp 240–241 °C (toluene), 66%. *Anal*. C, 67.7 (67.4); H, 3.6 (3.8).

1,2-(2,7-Cl_2-9-HOflu)$_2C_2H_4$ (**21**): ^{1}H NMR ($CDCl_3$): 7.50 (d, 8, $H_{4,5}$), 7.36 (dd, 8, 1, $H_{3,6}$), 7.23 (d, 2, $H_{1,8}$), 1.64 (s, CH_2). ^{13}C NMR: 149.1 ($C_{4a,5a}$), 137.0 ($C_{1a,8a}$), 134.2 (*C*Cl), 129.5 ($C_{3,6}$), 123.9 ($C_{1,8}$), 121.1 ($C_{4,5}$), 81.6 (C_9), 33.0 (*C*H_2). IR (Nujol): 3524 cm^{-1}. Mass spectrum: *m/z* 526 (M^+), 249 ($C_{13}H_7OCl_2^+$), 37%. *Anal*. C, 73.5 (73.7); H, 3.9 (3.8).

***spiro*-1,3-(2,7-$Cl_2C_{13}H_6$)$_2C_3H_2$** (**22**): ^{1}H NMR ($CDCl_3$): 7.79 (d, 2, $H_{1,8}$), 7.61 (d, 8, $H_{4,5}$), 7.38 (dd, 8, 2, $H_{3,6}$), 2.76 (CH_2), 2.65 (CH_2CH_2). ^{13}C NMR: 154.9, 137.0, 133.7, 127.7, 123.4, 120.8, 58.7 ($C_{9,9*}$), 50.5 (*C*H_2), 42.0 (*CH*$_2$*C*H_2). Mass spectrum: *m/z* 506 (M^+), 260 ($C_{15}H_{10}Cl_2^+$), 246 ($C_{14}H_8Cl_2^+$). mp >260 °C (CH_2Cl_2–hexane), 6%. *Anal*. C, 68.5 (68.4); H, 3.5 (3.5); Cl, 28.0 (28.2).

Flu-$SiMe_2$-CH_2-flu (**23**): ^{1}H NMR ($CDCl_3$): 7.91(8, 2, $H_{4*,5*}$), 7.70 (d, 8, $H_{4,5}$), 7.40 (d, 7, $H_{1*,8*}$), 7.39 (t, 7, $H_{3*,6*}$), 7.32 (t, 8, $H_{3,6}$), 7.31 (td, 8, 1, $H_{2*,7*}$), 7.21 (td, 7, 1, $H_{2,7}$), 7.11 (dd, 8, 1, $H_{1,8}$), 3.92 (t, 6, H_9), 3.68 (s, H_{9*}), 0.98 (d, 6, CH_2), −0.47 (s, CH_3). ^{13}C NMR: 148.2, 145.4, 140.46, 140.32 126.73, 126.64, 125.90, 125.13, 124.30, 124.00, 119.76, 119.53, 43.2 and 42.9 ($C_{9,9*}$), 14.1 (*C*H_2), −2.34 (*C*H_3). ^{29}Si NMR: 5.8 (s). Mass spectrum: *m/z* 237 ($M^+ - C_{13}H_9$), 165 ($C_{13}H_9^+$); M^+ not observed. mp 145–147 °C (heptane), 63%. *Anal*. C, 86.6 (86.3), H, 6.5 (6.7).

Flu-$SiMe_2$-CH_2Br (**24**): ^{1}H NMR ($CDCl_3$): 7.90 (d, 8, $H_{4,5}$), 7.56 (d, 8, $H_{1,8}$), 7.41 (t, 8, $H_{3,6}$), 7.35 (t, 8, $H_{2,7}$), 4.16 (s, H_9), 2.47 (s, CH_2), 0.03 (s, CH_3). ^{13}C NMR: 144.3, 140.4, 126.2, 125.5, 123.8, 120.0, 40.2 (C_9), 15.8 (*C*H_2), 5.50 (*C*H_3). ^{29}Si NMR: 5.9 (s). Mass spectrum: *m/z* 316.0295 (M^+, calcd. 316.0277), 236 (M^+ − HBr), 221 (*m*/z 236 − CH_4), 179 ($C_{14}H_{11}^+$), 178 ($C_{14}H_{10}^+$), 165 ($C_{13}H_9^+$), 151 ($Me_2SiCH_2Br^+$), 123 ($SiCH_2Br^+$). mp 77–79 °C (heptane), 61%. *Anal*. C, 60.6 (60.4); H, 5.4 (5.5).

Flu-$SiMe_2$-CH_2I (**25**): ^{1}H NMR ($CDCl_3$): 7.87 (d, 8, $H_{4,5}$), 7.53 (d, 8, $H_{1,8}$), 7.38 (t, 7, $H_{3,6}$), 7.32 (td, 8, 1, $H_{2,7}$), 4.13 (s, H_9), 1.94 (s, CH_2), 0.03 (s, CH_3). ^{13}C NMR: 144.5, 140.4, 126.2, 125.5, 123.8, 120.0, 40.8 (C_9), −4.5 (*C*H_3), −14.7 (*C*H_2). ^{29}Si NMR: 7.2 (s). Mass spectrum: *m/z* 364.0190 (M^+, calcd. 364.0139), 237 (M^+ − I), 199 $C_3H_8SiI^+$), 171 (CH_4SiI^+), 165 ($C_{13}H_9^+$). mp 86–87 °C (heptane), 66%. *Anal*. C, 52.7 (53.1), H, 4.7 (4.8).

Flu-$SiMe_2$-CH_2-2,7-Cl_2-flu (**28**): ^{1}H NMR ($CDCl_3$): 7.93 (d, 8, $H_{4,5}$), 7.53 (d, 8, $H_{4*,5*}$), 7.43 (t, 8, $H_{3,6}$), 7.41 (d, 7, $H_{1,8}$), 7.36 (t, 7, $H_{2,7}$), 7.29 (dd, 8, 2, $H_{3*,6*}$), 6.98 (bd, $H_{1*,8*}$), 3.74 (t, 6, H_{9*}), 3.71 (s, H_9), 0.77 (d, 6, CH_2), −0.34 (CH_3). ^{13}C NMR: 149.8, 144.9, 140.3, 137.9, 132.7, 127.3, 126.1, 125.4, 124.7, 123.9, 120.5, 119.8, 43.1 and 42.6 ($C_{9,9*}$), 13.3 (*C*H_2), −2.0 (*C*H_3). ^{29}Si NMR: 6.4 (s). Mass spectrum: *m/z* 470.0999 (M^+, calcd. 470.1019), 305 ($M^+ - C_{13}H_9$), 165 ($C_{13}H_9^+$). mp 157–158.5 °C (heptane), 19%. *Anal*. C, 73.9 (74.2); H, 5.1 (5.1).

Flu-$SiMe_2$-CPA (**29**): ^{1}H NMR ($CDCl_3$): 7.90 (s, $H_{4*,5*}$), 7.90 (d, 8, $H_{4,5}$), 7.85 (d, 7, $H_{3*,6*}$), 7.68 (d, 7, $H_{1*,8*}$), 7.65 (t, 7, $H_{2*,7*}$), 7.58 (d, 8, $H_{1,8}$), 7.38 (t, 7, $H_{3,6}$), 7.30 (td, 7, 1, $H_{2,7}$), 4.65 (s, H_{9*}), 4.38 (s, H_9), −0.46 (s, CH_3). ^{13}C NMR: 144.7, 143.5, 140.7, 137.3, 128.1, 126.84, 126.15, 125.52, 125.45, 124.1, 121.5, 120.37, 120.06, 41.2 and 40.6 ($C_{9,9*}$), −6.8 (*C*H_3). Mass spectrum: *m/z* 412.1654 (M^+, calcd. 412.1642). mp 153–154 °C (CH_2Cl_2–heptane), 47%. *Anal*. C, 87.4 (87.2); H, 5.8 (5.9).

Flu-$SiMe_2$-H_2CPA (**30**): ^{1}H NMR ($CDCl_3$): 7.89 (d, 8, $H_{4,5}$), 7.56 (d, 8, $H_{1,8}$), 7.37 (t, 8, $H_{2,7}$), 7.33 (d, 8, $H_{1*,8*}$), 7.29 (td, 8, 1, $H_{3,6}$), 7.19 (t, 8, $H_{2*,7*}$), 7.12 (d, 7, $H_{3*,6*}$), 4.28 (s, H_9), 4.21 (H_{9*}), 3.20 (m, CH_2), −0.46 (CH_3). ^{13}C NMR: 144.9, 142.1, 140.7, 138.6, 130.8, 126.88, 126.14, 125.5, 124.2, 123.5, 121.9, 120.0, 41.1 and 40.6 ($C_{9,9*}$), 26.4 (*C*H_2), −6.8 (*C*H_3). Mass spectrum: *m/z* 414.1740 (M^+, calcd. 414.1798), 249 ($C_{17}H_{17}Si^+$), 221 ($C_{15}H_{13}Si^+$). mp 155–156 °C (CH_2Cl_2–acetone), 58%. *Anal*. C, 87.0 (87.1); H, 6.3 (6.3).

Flu-$SiPh_2$-H_2CPA (**31**): ^{1}H NMR ($CDCl_3$): 7.65 (br d, 8, $H_{1*,8*}$), 7.53 (d, 7, $H_{4,5}$), 7.38 (br d, 8, $H_{3*,6*}$), 7.24 (t, 7, $H_{2,7}$ or $H_{3,6}$), 7.20 (td, 7, 1, $H_{3,6}$ or $H_{2,7}$), 7.12 (tt, 8, 1, Ph H_{para}), 7.10 (t, 8, $H_{2*,7*}$), 6.96 (d, 7, $H_{1,8}$), 6.86 (t,7, Ph H_{meta}), 6.70 (d, 7, Ph H_{ortho}), 4.98 and 4.96 (s, $H_{9,9*}$), 2.94 and 2.71 (AA′XX′ pattern, CH_2). ^{13}C NMR: 143.6, 140.99, 140.63, 138.8, 134.94, 130.6, 128.94, 128.78, 126.58, 126.18, 125.90, 125.35, 124.5, 123.2, 122.3, 119.6, 39.0 and 38.2 ($C_{9,9*}$), 26.1 (*C*H_2). Mass spectrum: *m/z* 538.2160 (M^+, calcd. 538.2111), 373 ($M^+ - C_{13}H_9$). mp 220–221 °C (heptane–toluene), 47%. *Anal*. C, 89.2 (89.0); H, 5.5 (5.5).

[Flu-C_2H_4-CPA]ZrCl_2 (**32**): Mass spectrum (laser desorption) *m/z* 562.9804 (Na·M^+, calcd. 562.9881), 528 (M^+ − Cl), 493 (M^+ − 2Cl), 362 ($M^+ -$ $C_{14}H_{10}$), 338 ($C_{14}H_9Cl_2Zr^+$). 27% (CH_2Cl_2). *Anal*. C, 66.4 (66.2); H, 3.7 (3.9); Cl, 13.1 (13.5).

[Flu-C_2H_4-H_2CPA]ZrCl_2 (**33**): Mass spectrum: *m/z* 542.0184 (M^+, calcd. 542.0140). 53% (CH_2Cl_2). *Anal*. C, 66.2 (61.9); H, 4.0 (4.2); Cl, 13.1 (13.3).

[Flu-C_2H_4-4,5-Me_2-flu]ZrCl_2 (**34**): Mass spectrum: *m/z* 544.0305 (M^+, calcd. 544.0297). 38% (CH_2Cl_2). *Anal*. C, 65.9 (65.5); H, 4.4 (4.5); Cl, 13.0 (13.1).

[Flu-C_2H_4-2,7-Cl_2-flu]ZrCl_2 (**35**): ^{1}H NMR (CD_2Cl_2): 7.82 (dt, 9, 1, $H_{4,5}$), 7.80 (dd, 2, 1, $H_{1*,8*}$), 7.79 (dt, 9, 1, $H_{1,8}$), 7.64 (dd, 9, 1, $H_{4*,5*}$), 7.36 (ddd, 8, 7, 1, $H_{2,7}$), 7.25 (ddd, 9, 7, 1, $H_{3,6}$), 7.24 (dd, 9, 2, $H_{3*,6*}$), 4.45 and 4.39 (AA′BB′ pattern, CH_2). Assignments for [$H_{4,5}$ and $H_{1,8}$] and for [$H_{2,7}$ and $H_{3,6}$] may be reversed. Laser desorption mass spectrum: *m/z* 584 (M^+), 549 (M^+ − Cl), 514 (M^+ − 2Cl), 24% (CH_2Cl_2). *Anal*. C, 57.2 (56.9); H, 3.1 (3.2); Cl, 24.2 (24.4).

Table 3 (*Continued*)

[**Flu-C_2H_4-2,7-F_2-flu]$ZrCl_2$** (**36**): ^{1}H NMR (CD_2Cl_2): 7.80 (dm, 9, $H_{4,5}$), 7.78 (dm, 9, $H_{1,8}$), 7.69 (dd, 9, 5, $H_{4*,5*}$), 7.39 (dd, 9, 2, $H_{1*,8*}$), 7.35 (ddd, 9, 7, 1, $H_{2,7}$), 7.23 (ddd, 9, 7, 1, $H_{3,6}$), 7.08 (td, 9, 2, $H_{3*,6*}$), 4.42 and 4.36 (AA′BB′ pattern, CH_2). ^{19}F NMR: −114.9 (td, 9, 5). Mass spectrum: *m/z* 551.9730 (M^+, calcd. 551.9735), 338 ($M^+ - C_{14}H_8F_2$), 214 ($C_{14}H_8F_2{}^+$). 23% (CH_2Cl_2). *Anal*. C, 60.7 (60.2); H, 3.2 (3.4); Cl, 12.8 (12.9).

[**Flu-C_2H_4-4-Meflu]$ZrCl_2$** (**37**): Mass spectrum: *m/z* 530.0131 (M^+, calcd. 530.0140), 495 ($M^+ - Cl$), 352 $C_{15}H_{12}Cl_2Zr^+$). 33% (CH_2Cl_2). *Anal*. C, 65.4 (65.0); H, 4.1 (4.2); Cl, 13.4 (13.6).

[Flu-C_2H_4-4-*i*-Prflu]$ZrCl_2$ (**38**): Laser desorption mass spectrum: *m/z* 558 (M^+), 523 ($M^+ - Cl$). 52% (CH_2Cl_2). *Anal*. C, 66.4 (66.0); H, 4.6 (4.8); Cl, 16.3 (15.9).

[Flu-C_2H_4-2,7-(*p*-tolyl)$_2$-flu]$ZrCl_2$ (**39**): ^{1}H NMR (CD_2Cl_2): 7.95 (s, $H_{1*,8*}$), 7.88 (d, 9, $H_{4,5}$), 7.79 (d, 9, $H_{4*,5*}$), 7.76 (d, 8, $H_{1,8}$), 7.53 (dd, 8, 2, $H_{3*,6*}$), 7.52 (d, AA′XX′ pattern, d, 8, *p*-tolyl H_{meta} to CH_3), 7.35 (d, AA′XX′ pattern, d, 8, *p*-tolyl H_{ortho} to CH_3), 7.28 (tm, 8, $H_{3,6}$), 7.14 (t, 8, $H_{2,7}$), 4.54 (s, CH_2), 2.44 (s, CH_3). Laser desorption mass spectrum: *m/z* 696 (M^+), 661 ($M^+ - Cl$). 35% (CH_2Cl_2). *Anal*. C, 72.2 (71.9); H, 4.6 (4.4); Cl, 10.2 (9.9).

[Flu-C_2H_4-2,7-*t*-Bu_2-flu]$ZrCl_2$ (**40**): ^{1}H NMR (CD_2Cl_2): 7.84 (dt, 8, 1, $H_{4,5}$), 7.73 (dt, 8, 1, $H_{1,8}$), 7.69 (dd, 2, 1, $H_{1*,8*}$), 7.61 (dd, 9, 1, H_{4*5*}), 7.38 (dd, 9, 2, $H_{3*,6*}$), 7.28 (ddd, 9, 7, 1, $H_{3,6}$), 7.15 (ddd, 9, 7, 1, $H_{2,7}$), 4.47 (s, CH_2), 1.37 (s, CH_3). ^{13}C NMR: 150.7, 127.86, 127.81, 127.31, 124.84, 124.74, 124.69, 124.22, 122.8, 121.9, 119.8, 117.5, 105.3 ($C_{9,9*}$), 34.8 (*C*CH_3), 30.7 (C*C*H_3), 25.36 and 25.14 (*C*H_2). Laser desorption mass spectrum: *m/z* 628 (M^+), 593 ($M^+ - Cl$). 60% (toluene–hexane). *Anal*. C, 68.6 (67.6); H, 5.7 (6.0); Cl, 13.4 (13.7).

[Flu-C_2H_4-9-Mebenzo[c]flu]$ZrCl_2$ (**41**): Mass spectrum: *m/z* 580.0386 (M^+, calcd. 580.0297), 545 ($M^+ - Cl$), 510 ($M^+ - 2Cl$). 62% (CH_2Cl_2). *Anal*. C, 68.0 (67.7); H, 4.1 (4.2); Cl, 12.2 (12.4).

[**Flu-C_2H_4-2,7-*t*-Bu_2-4-(α-Np)flu]$ZrCl_2$** (**42**): ^{1}H NMR ($CDCl_3$): 7.87 (dt, 9, 1, H_4), 7.78 (dm, 8, Np H_5), 7.77 (dm, 8, Np H_4), 7.73 (dt, 9, 1, H_5), 7.67 (dt, 8, 1, H_1), 7.641 (dd, 7, 1, Np H_2), 7.636 (dt, 9, 1, H_8), 7.60 (m, $H_{1*,8*}$), 7.37 (dd, 8, 7, Np H_3), 7.30 (ddd, 8, 7, 1, Np H_6), 7.27 (ddd, 8, 7, 1, H_6), 7.190 (dm, 9, Np H_8), 7.174 (d, 2, H_{3*}), 7.166 (ddd, 8, 7, 1, H_2), 7.139 (ddd, 9, 7, 1, H_3), 7.087 (ddd, 8, 7, 1, Np H_7), 7.00 (ddd, 9, 7, 1, H_7), 6.76 (dd, 9, 2, H_{6*}), 6.04 (dd, 9, 1, H_{5*}), 4.53 and 4.36 (m, CH_2), 1.27 and 1.15 (s, CH_3). ^{13}C NMR: 150.2, 149.8, 137.4, 136.6, 133.3, 131.7, 128.19, 128.06, 127.60, 127.48, 127.40, 127.33, 127.08, 126.73, 126.67, 125.99, 125.70, 125.39, 125.28, 124.82, 124.77, 124.62, 124.45, 124.19, 122.53, 123.38, 122.19, 120.0, 118.9, 104.64 and 104.49 (C_9 and C_{9*}), 35.1 and 34.9 (*C*CH_3), 30.71 and 30.53 (*C*H_3), 29.65 and 29.49 (*C*H_2). Mass spectrum: *m/z* 754.1570 (M^+, calcd. 754.1505), 576.0921 ($M^+ - C_{14}H_{10}$). 45% (hexane). *Anal* C, 73.0 (72.5); H, 5.6 (5.5); Cl, 9.4 (9.7).

[(2,7-Cl_2-flu)$_2$$C_2H_4$]$ZrCl_2$ (**43**): Laser desorption mass spectrum: *m/z* 652 (M^+), 617 ($M^+ - Cl$), 582 ($M^+ - 2Cl$). 20% (CH_2Cl_2–hexane). *Anal*. C, 51.2 (50.7); H, 2.4 (2.5); Cl, 32.5 (32.8).

[Flu-$SiMe_2$-CH_2-flu]$ZrCl_2$ (**44**): Mass spectrum: *m/z* 560.0017 (M^+, calcd. 560.0066), 382 ($M^+ - C_{14}H_{10}$), 237 ($C_{13}H_9SiMe_2CH_2{}^+$). 30% (CH_2Cl_2–toluene). *Anal*. C, 61.9 (61.5); H, 4.3 (4.5); Cl, 12.6 (12.9).

[Flu-$SiMe_2$-CPA]$ZrCl_2$ (**45**): Mass spectrum: *m/z* 569.9994 (M^+, calcd. 569.9909) 247 ($C_{17}H_{15}Si^+$), 223 ($C_{15}H_{15}Si^+$). 21% (CH_2Cl_2). *Anal*. C, 62.9 (62.4); H, 3.8 (3.9); Cl, 12.4 (12.6).

[Flu-$SiMe_2$-H_2CPA]$ZrCl_2$ (**46**): Laser desorption mass spectrum: *m/z* 572 (M^+). 38% (CH_2Cl_2). *Anal*. C, 62.7 (62.2); H, 4.2 (4.3); Cl, 12.4 (12.7).

[Flu-$SiPh_2$-H_2CPA]$ZrCl_2$ (**47**): Mass spectrum: *m/z* 696.0329 (M^+, calcd. 696.0379). 62% (CH_2Cl_2). *Anal*. C, 68.8 (68.5); H, 4.0 (4.1); Cl, 10.7 (10.9).

[(2,7-*t*-Bu_2-flu)$_2$$C_2H_4$]$ZrCl_2$ (**48**): ^{1}H NMR ($CDCl_3$): 7.59 (d, 9 $H_{4,5}$), 7.46 (br d $H_{1,8}$), 7.26 (dd, 9, 2, $H_{3,6}$), 4.32 (s, CH_2), 1.26 (s, CH_3). ^{13}C NMR: 150.3, 128.8, 124.6, 124.2, 120.3, 116.1, 105.3 (C_9), 35.2 (*C*CH_3), 30.9 (*C*H_3), 29.4 (*C*H_2). Laser desorption mass spectrum: *m/z* 740 (M^+), 705 ($M^+ - Cl$). 70% (toluene–hexane). *Anal*. C, 71.2 (70.4); H, 7.0 (7.2); Cl, 9.6 (9.4).

(2,7-*t*-Bu_2-flu)$_2$$C_2H_4$ (**49**): ^{1}H NMR ($CDCl_3$): 7.61 (d, 9, $H_{4,5}$), 7.46 (br d, $H_{1,8}$), 7.36 (dd, 8, 2, $H_{3,6}$), 3.84 (m, H_9), 2.04 (m, CH_2), 1.38 (s, CH_3). ^{13}C NMR: 149.5, 147.3, 138.4, 124.0, 121.0, 118.9, 47.4 (C_9), 34.8 (*C*Me_3), 31.6 C*C*H_3), 30.3 (*C*H_2). Mass spectrum: *m/z* 582.4211 (M^+, calcd. 582.4220), 525 ($M^+ - C_4H_9$), 469 ($M^+ - C_4H_9 - C_4H_8$). mp 271.5–273 °C (heptane), 47%. *Anal.* C, 90.7 (90.4); H, 9.3 (9.3).

9-**HOC_2H_4-CPA** (**51**): ^{1}H NMR ($CDCl_3$): 7.85 (s, $H_{4,5}$), 7.68 (d, 7, $H_{3,6}$ and $H_{1,8}$), 7.64 (t, 7, $H_{2,7}$), 4.67 (H_9), 3.88 (CH_2OH), 2.38 (CH_2CH_2). GC/MS: *m/z* 234 (M^+).

[a] In listings of NMR chemical shifts, asterisk (*) refers to positions in the substituted fluorenyl ring. Peak multiplicities, coupling constants and assignments are given in parentheses. Melting points are followed by solvent(s) used for recrystallization and yield. Combustion analytical data are given as calcd. (found).

tions and molecular weights determined using polystyrene standards.

2.7. 4-Methylfluorene

Reduction of 4-CO_2H-fluorene (Lancaster Synthesis Co.) with BH_3·THF [36] afforded 4-$HOCH_2$-fluorene, mp 122–123 °C, ν_{OH} (Nujol) 3300, 3200 cm^{-1}. Hydrogenation using 10% Pd/C catalyst [37] produced crude 4-Me-fluorene. Purification was by vacuum sublimation at 60° with the small amount of oily material that sublimed first being discarded. After recrystallization from hexane, colorless crystals, mp 69–70 °C (93%), were obtained.

2.8. 4-i-Pr-fluorene

Treatment of 4-COCl-9-fluoreneone (Aldrich) with one equivalent of pyridine in excess MeOH produced 4-CO_2Me-fluoreneone, mp 130.5–131.5 °C. Hydrogenation under 20 psi (above atmospheric) H_2 using 10% Pd/C catalyst produced 4-CO_2Me-fluorene, mp 71–74 °C after recrystallization from MeOH-H_2O. Reaction of this ester with 5 eq.

of Me_3Al in refluxing toluene gave 4-$Me_2C(OH)$-fluorene, mp 99–105 °C, ν_{OH} 3310 cm^{-1} (Nujol) as colorless plates after recrystallization from heptane. Reduction of this alcohol was carried out using Et_3SiH and CF_3CO_2H in CH_2Cl_2 [38]. NMR analysis of the crude product disclosed a 1:3 mixture of 4-*i*-Pr-fluorene and 4-isopropenylfluorene. The latter was converted to the former when the mixture was hydrogenated (10% Pd/C, 6 psi H_2) in 1:4 toluene–heptane. GC analysis of the colorless liquid product indicated that it was >98% pure 4-*i*-Pr-fluorene (56%).

2.9. Dihydrocyclopentaphenanthrene

A mixture of 2 g cyclopentaphenanthrene (Aldrich), 0.2 g 10% Pd/C and 50 ml toluene was stirred under 10 psi (above atmospheric) H_2. The reaction was monitored by GC. When the reaction was nearly complete, catalyst was removed by filtration and the filtrate evaporated. The crude product weighed 1.97 g and was contaminated with a small amount of octahydrocyclopentaphenanthrene, **49**, in which one of the benzene rings had also been reduced. Recrystallization from hexane gave 1.8 g (90%) colorless plates, mp 136–137 °C, of >98% purity by GC analysis. Mass spectrum: *m/z* 192.0934 (M^+, calcd. 192.0936). Repeated recrystallization from hexane of the material remaining in the mother liquor gave **49** of 83 mol% purity.

2.10. 1,2-di(9-Fluorenyl)ethane (*1*)

A solution of 41.5 g (0.25 mol) fluorene in 500 ml THF was cooled, with efficient magnetic stirring, in a dry ice-acetone bath until the mixture became very thick due to the fluorene that had crystallized. BuLi, 100 ml of a 2.5 M solution in hexane, was added by canula in one portion. The cooling bath was removed and the reaction mixture warmed to room temperature. The butane evolved was swept with nitrogen into a hood. The reaction mixture was again cooled with dry ice. As the Li(flu) crystallized, it became very thick. Then, 23.5 g (0.125 mol) 1,2-$Br_2C_2H_4$ was added in one portion. The reaction mixture was allowed to warm to room temperature overnight. Solvents were removed under vacuum. The residue was washed with 250 ml 50% aqueous ethanol then recrystallized from boiling xylenes from which the product separated as colorless blades, 24 g (54%), mp 222–223 °C. Further concentration of the mother liquor gave mixtures of fluorene, **1** and *spiro*-cyclopropane-9-fluorene.

2.11. 2-(9-Fluorenyl)ethyl triflate (*2*)

A 2.5 M solution of BuLi in hexane was added with stirring to 5 g (23.8 mmol) 2-(9-fluorenyl)ethanol in 90 ml toluene. Addition was terminated when the reaction mixture developed a persistent, very pale orange color (due to deprotonation at carbon); about 10 ml was required. The resulting solution of **3** was cooled in a dry ice-acetone bath and 3.8 g CF_3SO_2F added by vacuum transfer. After warming to room temperature and stirring overnight, the reaction mixture was passed through a Schlenk filter. Solvents and any unreacted CF_3SO_2F were removed under vacuum. There remained 7.7 g (95%) of product as a colorless oil.

2.12. Fluorenyl-C_2H_4-cyclopentaphenanthrenyl (*4*)

2-(9-Fluorenyl)ethanol, 5 g, was converted to the triflate as described above. Unreacted CF_3SO_2F was removed by pumping but it was not necessary to remove LiF. A slurry of the Li^+ salt of cyclopentaphenanthrene, prepared by addition of 23.8 mmol of *n*-BuLi in hexane to 4.52 g (23.8 mmol) cyclopentaphenanthrene in 1:1 toluene–ether, was added to the triflate solution in portions by means of a wide bore canula. After stirring overnight, solvents were removed under reduced pressure and the residue recrystallized from toluene–heptane to give 5.7 g (51%) colorless microcrystals.

2.13. 2,7-Cl_2-9-Me_3Si-fluorene (*18*)

n-BuLi, 34 ml of a 2.5 M solution in hexane, was added dropwise to a solution of 20.0 g (85 mmol) 2,7-Cl_2-fluorene in 75 ml toluene. After stirring overnight, 9.23 g (85 mmol) Me_3SiCl was added with stirring. Twenty hours later, the reaction mixture was filtered through celite and evaporated to dryness. The residue was dissolved in 150 ml boiling hexane and filtered. On cooling to room temperature, the filtrate deposited 12.3 g (47 %) of product as long, colorless needles.

2.14. 1,2-(2,7-Cl_2-9-$SiMe_3$-fluorenyl)$_2C_2H_4$ (*19*)

To a solution of 12.4 g (40 mmol) **15** in 125 ml ether was added with stirring 40 mmol *n*-BuLi in hexane. This was then added dropwise to a suspension of 7.4 g (20 mmol) ethylene glycol ditosylate (Aldrich) in 75 ml ether. After stirring for 10 h, the reaction mixture was filtered. The solid phase was washed with 20% aqueous ethanol then absolute ethanol. After air drying, 8.82 g (69 %) **16** was obtained as a white powder.

2.15. 1,2-(2,7-Cl_2-fluorenyl)$_2C_2H_4$ (*20*)

$[Bu_4N]F$, 28 ml of a 1 M solution in THF (Aldrich), was deoxygenated by sparging with N_2 then added to a solution of 8.72 g (13.7 mmol) **15** in 90 ml THF. After 30 min, the deep red solution was quenched by adding 3.2 g (28 mmol) CF_3CO_2H by syringe. Solvent was removed under reduced pressure and the residue washed with saturated aqueous $NaHCO_3$, water and then ethanol. The residue was vacuum dried to afford 6.6 g (97%) of product.

In a similar reaction, the acid quench was omitted and workup was carried out in air. THF was removed under reduced pressure. The residue was taken up in CH_2Cl_2 and passed through a short column of neutral alumina. Ethanol was added and the solution slowly concentrated on a rotary evaporator. Compound **22** (7%) separated as colorless

microcrystals. The filtrate was treated with aqueous HCl to give a gum that was recrystallized from toluene–heptane to afford **21** in 42% yield.

2.16. Fluorenyl-SiMe$_2$-CH$_2$I (25)

A solution of 43.8 g (0.26 mol) fluorene in 500 ml ether was cooled with a dry ice bath and treated with an equimolar quantity of *n*-BuLi in hexane. The solution of Li[flu] was warmed to room temperature and added dropwise to 50 g 0.26 mol) ClSiMe$_2$-CH$_2$Br (Petrarch) in 100 ml toluene. After 8 h, the reaction mixture was evaporated. The residue was twice recrystallized from heptane to afford 50 g (61%) of fluorenyl-SiMe$_2$-CH$_2$Br (**24**). 6.3 g **24** was added to a solution of 4 g NaI in 100 ml acetone. After stirring overnight, the reaction mixture was filtered and the filtrate evaporated under reduced pressure. The residue was extracted with 30 ml boiling heptane. On cooling of this extract to −5 °C, 4.9 g (66%) **25** separated as beige nodules.

2.17. Flu-SiMe$_2$-CH$_2$-flu (23)

Di(fluorenyl)magnesium, flu$_2$Mg, was synthesized by refluxing and vigorously stirring for 8 h a mixture of 6 ml 1 M Bu$_2$Mg in heptane (Alfa), 1.66 g (10 mmol) fluorene and 10 ml heptane. The organomagnesium reagent separated as a yellow powder. The air- and water-sensitive product was isolated by filtration at room temperature, washed with 25 ml heptane then vacuum dried; the yield was 1.4 g (76%).

THF, 20 ml, was added to a mixture of 0.71 g (2 mmol) flu$_2$Mg and 1.46 g (4 mmol) **25**. After stirring for 8 h, the reaction mixture was quenched with 5 ml MeOH. Solvents were removed under reduced pressure and the residue extracted with 50 ml CH$_2$Cl$_2$. The filtered extract was concentrated on a rotary evaporator until crystals appeared and then cooled to −78 °C. Pale yellow crystals were collected on a filter; the yield was 1.01 g (63%).

2.18. [(2,7-t-Bu$_2$-flu)$_2$C$_2$H$_4$]ZrCl$_2$ (48)

A solution of 16.7 g (60 mmol) 2,7-*t*-Bu$_2$-fluorene in 150 ml THF was cooled in a dry ice bath and treated with 60 mmol BuLi. After warming to room temperature, the solution was added with stirring to 11.1 (30 mmol) ethylene glycol ditosylate (Aldrich) in 100 ml THF. After 12 h, the reaction mixture was quenched with 6 ml 70% aqueous CF$_3$CO$_2$H. Solvents were removed under reduced pressure. Washing the residue with ethanol afforded 14 g crude product. This was recrystallized from hot heptane–toluene to give 8.2 g (47%) of 1,2-(2,7-*t*-Bu$_2$-flu)$_2$C$_2$H$_4$ (**50**). Concentration of the mother liquor afforded a mixture of **50** and *spiro*-cyclopropane-9-(2,7-*t*-Bu$_2$-fluorene).

To 2.3 g (4 mmol) **50** in 50 ml ether was added 8 mmol BuLi. An ice water bath was used to moderate the exotherm. After 3 h, volatiles were removed on a vacuum line. The residue was subjected to pumping for 4 h. Toluene, 90 ml, and 0.93 g (4 mmol) ZrCl$_4$ were added. The reaction mixture was stirred vigorously for 10 h then filtered through celite. The filtrate was evaporated and the residue washed with 10 ml hexane. There remained 2.1 g red, microcrystalline product (70%). Slow evaporation of a CHCl$_3$–hexane solution of **48** produced crystals of **48**·CHCl$_3$ that could be freed of solvent by heating under vacuum. This metallocene has high solubility in hydrocarbon solvents.

2.19. Crystal structure determination

An orange needle of **48**·CHCl$_3$ was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed on an Enraf-Nonius CAD4 computer-controlled kappa axis diffractometer having a graphite crystal, incident beam monochromator.

Cell constants and an orientation matrix were obtained from least-squares refinement using the setting angles of 25 reflections between 11 and 21° measured by the computer controlled diagonal slit method of centering. As a check on crystal quality, ω scans of several intense reflections were measured; the width at half height was 0.65° with a take-off angle of 3°, indicating moderate crystal quality. The systematic absences $h\,0\,l$ ($l = 2n$) and $0\,k\,0$ ($k = 2n$) and subsequent least-squares refinement revealed the space group to be $P2_1/c$ (#14).

Lorentz and polarization corrections were applied to the data. The structure was solved using the Patterson heavy-atom method that disclosed the position of the Zr atom. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the

Table 4
Crystal data and structure refinement for **48**·CHCl$_3$

Formula	$C_{45}H_{53}Cl_5Zr$
Formula weight	862.41
Crystal size (mm)	0.72 × 0.22 × 0.19
Crystal system	Monoclinic
Space group	$P2_1/c$
T (K)	295
Unit cell dimensions	$a = 11.378(2)$ Å, $\beta = 93.229(15)°$ $b = 19.178(4)$Å $c = 20.227(3)$Å
V (Å^3)	4406(2)
Z	4
$\rho_{calcd.}$ (gm cm^{-3})	1.300
λ (Å)	0.71073
μ (mm^{-1})	0.579
2θ range for data collection (°)	5.26–45.12
Reflections collected	6331
Independent reflections	5765 [R(int) = 0.032]
Minimum, maximum transmission factors	0.64, 1.00
GOF on F^2	1.068
$R(F_0)$	0.048
$R_w(F_0^2)$	0.112
Largest difference peak and hole (e Å^{-3})	0.60 and –0.60

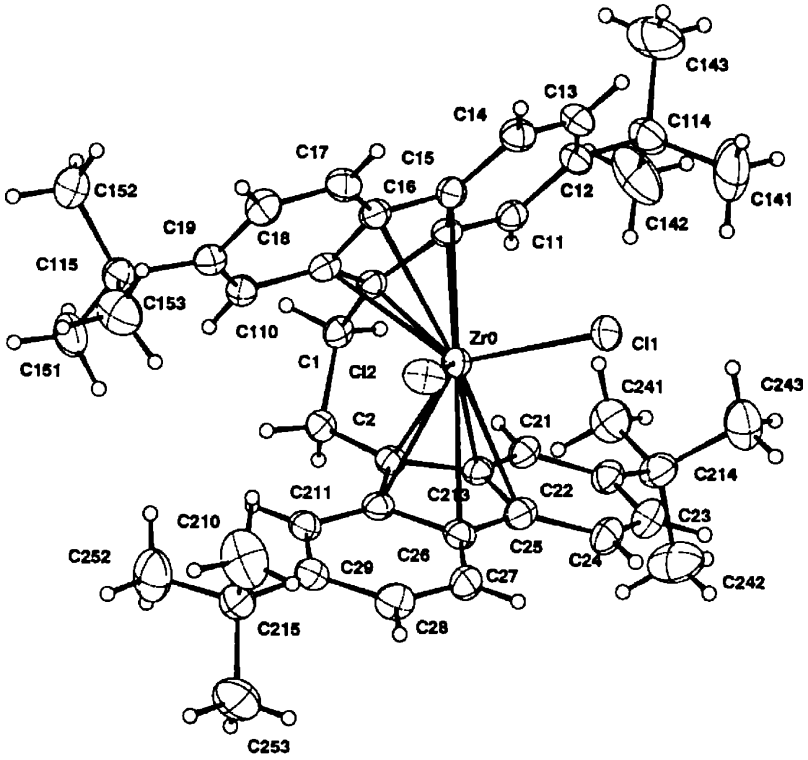


Fig. 1. ORTEP drawing of [*t*-Bu_2-flu-C_2H_4-*t*-Bu_2-flu]$ZrCl_2$ (**48**).

refinement but constrained to ride on the atoms to which they are bonded. Crystallographic data are given in Table 4. An ORTEP drawing showing the numbering scheme is shown in Fig. 1. Selected bond distances and angles are given in Table 2. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 230530. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

References

[1] (a) Selected recent reviews: W. Kaminsky, Adv. Catal. 46 (2001) 89;
(b) J.-N. Pédeutour, H. Radhakrishnan, A. Cramail, A. Deffieux, Macromol. Rapid Commun. 22 (2001) 1095;
(c) G. Hlatky, Coord. Chem. Rev. 199 (2000) 235;
(d) G.W. Coates, J. Chem. Soc., Dalton Trans. (2002) 467;
(e) L. Resconi, L. Cavallo, W. Fait, Chem. Rev. 100 (2000) 1253;
(f) G.W. Coates, Chem. Rev. 100 (2000) 1223;
(g) Y.X. Chen, T.J. Marks, Chem. Rev. 100 (2000) 1391;
(h) G. Hlatky, Chem. Rev. 100 (2000) 8019.

[2] (a) H.H. Brintzinger, D. Fischer, R. Mullhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. Int. Ed. 34 (1995) 1143;
(b) M. Bochman, J. Chem. Soc., Dalton Trans. (1996) 255;
(c) W. Kaminsky, J. Chem. Soc., Dalton Trans. (1998) 1413;
(d) W. Kaminsky, Macromol. Chem. Phys. 197 (1996) 3907;
(e) K. Soga, T. Shiono, Prog. Polym. Sci. 22 (1997) 1503;
(f) W. Kaminsky, M. Arndt, Adv. Polym. Sci. 127 (1997) 143.

[3] L.H. Sommer, N.S. Marans, J. Am. Chem. Soc. 73 (1951) 5135.

[4] E. Marechal, A. Lepert, Bull. Soc. Chim. Fr. (1967) 2954.

[5] H. Gilman, J.J. Goodman, J. Org. Chem. 22 (1957) 45.

[6] E.J. Greenhow, D. McNeil, J. Chem. Soc. (1956) 3204. The dilithium salt was first reported by B. Becker, V. Enkelmann, K. Mullen, Angew. Chem. Int. Ed. 29 (1989) 458.

[7] (a) F.W.R.P. Wild, L. Zsolnai, G. Huttner, H.H. Brintzinger, J. Organometal. Chem. 232 (1982) 233;
(b) F.W.R.P. Wild, M. Wasiucionek, G. Huttner, H.H. Brintzinger, J. Organometal. Chem. 288 (1985) 263;
(c) J.A. Ewen, L. Haspeslagh, J.L. Atwood, H. Zhang, J. Am. Chem. Soc. 109 (1987) 6544;
(d) E. Hoel, US Patent 4,871,705;
(e) J.A. Ewen, US Patent 4,794,096.

[8] (a) V. Dolle, H.F. Herrman, A. Winter, European Patent Application 480,390;
(b) M. Antberg, W. Spalek, J. Rohrman, V. Dolle, European Patent Application 485,820;
(c) M. Antberg, W. Spalek, J. Rohrman, V. Dolle, European Patent Application 485,821.

[9] The first report of olefin polymerization by ring-substituted indenyl- and fluorenyl metallocenes appeared in British Patent 934,282, 1963.

[10] J.A. Ewen, R.L. Jones, A. Razavi, J.D. Ferrara, J. Am. Chem. Soc. 110 (1988) 6255.

[11] (a)Fluorenyl metallocenes have been reviewed by H.G. Alt, E. Samuel, Chem. Soc. Rev. 27 (1998) 323;
(b) H.G. Alt, A. Köppl, Chem. Rev. 100 (2000) 1205.

[12] J.A. Ewen, M.J. Elder, R.L. Jones, S. Curtis, H.N. Cheng, in: T. Keii, K. Soga (Eds.), Catalytic Olefin Polymerization, Elsevier, 1990.

[13] (a) A.R. Siedle, W.M. Lamanna, J.M. Olofson, B.A. Nerad, R.A. Newmark, ACS Symp. Ser. 517 (1993) 156;
(b) N.G. Alameddin, M.F. Ryan, J.R. Eyler, A.R. Siedle, D.E. Richardson, Organometallics 14 (1995) 5005.

[14] A.R. Siedle, K.M. Theissen, J. Stevens, J. Mol. Catal. A: Chem. 191 (2003) 167.
[15] (a) A.R. Siedle, D.K. Misemer, V.V. Kolpe, B.F. Duerr, US Patent 6,265,512;
(b) A.R. Siedle, D.K. Misemer, V.V. Kolpe, B.F. Duerr, US Patent 6,323,151;
(c) A.R. Siedle, D.K. Misemer, V.V. Kolpe, B.F. Duerr, US Patent 6,429,274;
(d) A.R. Siedle, D.K. Misemer, V.V. Kolpe, B.F. Duerr, U.S. Pat 6,448,358.
[16] An alternate synthesis, starting with fluorene, ethylene glycol and KOH, has been reported by H.E. Fritz, D.W. Peck, M.A. Eccles, K.E. Atkins, J. Org. Chem. 30 (1965) 2542. We have been unable to reproduce this result.
[17] K.W. Kramarz, J.R. Norton, Prog. Inorg. Chem. 42 (1994) 1.
[18] B. Rieger, G. Jany, R. Fawzi, M. Steimann, Organometallics 13 (1994) 647. These workers prepared **2** from Flu-C_2H_4OH, $(CF_3SO_2)_2O$ and pyridine in CH_2Cl_2. They reported that it decomposed above 0 °C.
[19] J. Perumattam, C. Shao, W.L. Confer, Synthesis (1994) 1181.
[20] A.W. Duff, P.B. Hitchcock, M.F. Lappert, R.G. Taylor, J.A. Segal, J. Organometal. Chem. 293 (1985) 271.
[21] Substituent effects in metallocene catalysts have been reviewed by P.C. Mohring, N. Coville, J. Organometal. Chem. 479 (1994) 1.
[22] I.-M. Lee, W.J. Gauthier, J.M. Ball, B. Iyengar, S. Collins, Organometallics 11 (1992) 2115.
[23] J.A. Ewen, Macromol. Symp. 89 (1995) 181.
[24] N. Piccolrovazzi, P. Pino, G. Consiglio, A. Sironi, M. Moret, Organometallics 9 (1990) 309.
[25] J. Klosin, W.J. Kruper Jr., P.N. Nickias, G.R. Roof, P. DeWaele, K. Abboud, Organometallics 20 (2001) 2663.
[26] E. Barsties, S. Schaible, M.-H. Prosenc, U. Reif, W. Röll, O. Weyand, B. Doer, H.-H. Brintzinger, J. Organometal. Chem. 520 (1996) 63.
[27] A.R. Siedle, K.M. Theissen, submitted for publication.
[28] H.G. Alt, W. Milius, S.J. Palackal, J. Organometal. Chem. 472 (1994) 113.
[29] S. Kajigaeshi, T. Kadowaki, A. Nishida, S. Fujisaki, Bull. Chem. Soc. Jpn. 59 (1986) 97.
[30] M.E. Gross, H.P. Lankelma, J. Am. Chem. Soc. 73 (1951) 3439.
[31] L.A. Carpino, H.G. Chao, J.-H. Tien, J. Org. Chem. 45 (1980) 4250.
[32] H.-L. Pan, T.L. Fletcher, J. Med. Chem. 8 (1965) 491.
[33] T.P.C. Mulholland, G. Ward, J. Chem. Soc. (1956) 2415.
[34] J.A.M. Canich, US Patent 5,026,798.
[35] K. Patsidis, S.J. Palackal, H.G. Alt, US Patent 5,393,911.
[36] N.M. Yoon, C.S. Pak, H.C. Brown, S. Krishnamurthy, T.P. Stocky, J. Org. Chem. 38 (1973) 2786.
[37] K. Patsidis, S.J. Palackal, H.G. Alt, US Patent 5,191,132.
[38] J. Pataki, R.G. Harvey, J. Org. Chem. 52 (1987) 2226.