Synthesis and structural characterization of Group 14 complexes containing two {9-[2-(dimethylamino)ethyl]fluorenyl-} ligands and a unique coupling product

Richard A. Kemp [a],*, Linfeng Chen [a], Ilia Guzei [b], Arnold L. Rheingold [b]

[a] *Union Carbide Corporation, 3333 Highway 6 South, Houston, TX 77082, USA*
[b] *Department of Chemistry, University of Delaware, Newark, DE 19716, USA*

Respectfully dedicated to Professor F.A. Cotton on the occasion of his 70th birthday with gratitude for his numerous contributions to inorganic and organometallic chemistry.

Abstract

Reaction of two equivalents of {9-[2-(dimethylamino)ethyl]fluorenyl}lithium (Fl^NLi) with either Me_2GeCl_2 or Me_2SnCl_2 leads cleanly to the new compounds $(Fl^N)_2MMe_2$, where M = Ge, Sn. These new complexes are the first compounds that contain multiple Fl^N ligands which have been characterized by X-ray diffraction. Attempts to prepare the analogous Pb compound using Et_2PbCl_2 were not successful, yielding instead a product where the two Fl^N ligands have coupled. Structural characterization of the coupled product is presented. Neither of the main-group complexes showed significant activity for the polymerization of propylene using either MAO or BARF salts as activators. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Main group compounds; Olefin polymerization; Germanium; Tin; Coupling reaction

1. Introduction

Organic ligands that possess the ability to bond to metal centers to create controlled environments have been a hallmark of synthetic organometallic chemistry for years. More specifically, there has been significant interest in preparing transition-metal and lanthanide complexes using chelating ligands capable of intramolecular base stabilization via pendant arms [1]. However, the use of ligands such as **1** or **2** towards main-group elements has been more limited [2]. Recently, the groups of van Koten [3] and Cowley [4] in particular have been actively pioneering the expanded use of these ligands into main-group chemistry by preparing numerous main-group compounds with unusual bonding modes and stabilities. Culp and Cowley have structurally characterized two lithium salts of the substituted fluorenyl ligand 9-[2-(dimethylamino)ethyl]fluorenyl (Fl^N, **3**) [5] and have

also shown the first example of the coordination chemistry of this ligand towards Group 13 elements [6], including a $(Fl^N)_2$GaCl complex which could not be characterized by X-ray diffraction.
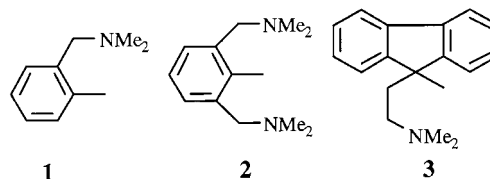
Very recently, the initial example of ligative behavior of (Fl^N)Li to transition metals was demonstrated in a patent issued to DSM N.V. in which (Fl^N)TiCl$_2$ was prepared and used as a homogeneous olefin polymerization catalyst [7]. Common to both Fl^N ligand studies [6,7] is the use of a single Fl^N ligand per metal atom in the structurally characterized compounds. We were interested in preparing and characterizing complexes of Group 14 elements that contained two Fl^N ligands per main-group metal. Two principal interests drove our curiosity about these new complexes. First, we were interested in whether the pendant arms on the Fl^N ligands

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* Corresponding author. Fax: +1-281-560-1670.
 E-mail address: kempra@ucarb.com (R.A. Kemp)

would intramolecularly coordinate to the central Group 14 atom to form a compound having approximate C_2 symmetry. Secondly, we were interested in whether these main-group complexes could polymerize 1-olefins upon activation with methylaluminoxane (MAO) or other weakly coordinating anions, much as Jordan has observed with aluminum amidinates [8].

2. Results and discussion

Since our interests were mainly in the eventual preparation of cationic main-group alkyls to evaluate as olefin polymerization catalysts, we chose to focus on the heavier Group 14 elements — germanium, tin, and lead. Additionally, we were interested in preparing dialkyl derivatives of the main-group elements in order to allow catalyst activation by normal procedures. Removal of an alkyl group by reaction with either MAO or weakly coordinating perfluorinated boron anions, such as $B(C_6F_5)_3$, $[Ph_3C]^+[B(C_6F_5)_4]^-$, or $[PhN(H)Me_2]^+[B-(C_6F_5)_4]^-$, is the standard method of activating transition-metal single-site catalysts [9]. The starting Fl^NLi salt was conveniently prepared by the method of Culp and Cowley [5]. Reaction of two equivalents of Fl^NLi with either Me_2GeCl_2 or Me_2SnCl_2 in toluene led in $\sim 90\%$ yield to provide $[Fl^N]_2GeMe_2$ (4) and $[Fl^N]_2SnMe_2$ (5), respectively (Fig. 1). Recrystallization of each compound from pentane afforded colorless X-ray quality crystals. Initial characterization of 4 and 5 was by proton NMR. The number of peaks along with the integration ratios in the spectrum of each compound was consistent with the addition of two Fl^N ligands onto the dimethyl-metal core (see Section 3). Although the proton NMR spectra of the two new compounds are similar, the spectrum of 5 exhibits satellite peaks due to $^{119}Sn-^1H$ coupling to the Sn-bound methyls. The ^{13}C spectra were also consistent with the addition of two Fl^N ligands. However, it is not possible from the NMR data to determine whether the pendant arms of the Fl^N ligand are intramolecularly coordinated to the central Ge or Sn atoms. In order to establish the solid-state structure we performed X-ray crystal-structure determinations on 4 and 5.

Both 4 and 5 crystallize in the monoclinic space group $P2_1/c$. In each case, there are two independent molecules in the unit cell which are almost identical structurally.

The molecular structures of the Ge (4) and Sn (5) complexes are shown in Fig. 2 and Fig. 3, respectively, along with important structural data. Crystallographic data are listed in Table 1. The structure of 4 shows the four-coordinate nature of Ge and the σ-bonded nature of the interaction between Ge and the Fl^N ligands. The Ge atom is slightly distorted from tetrahedral, with the angle formed by the two Fl^N ligand carbons and Ge being opened to 116.3°. The Ge–C(Fl^N) bonds are on average 0.08 Å longer than the Ge–C bonds in the Ge–Me groups, thus accommodating the sterically larger Fl^N ligand. There is no evidence of any π-bonding between Ge and the Fl^N ligand as was seen in the previously characterized Fl^NLi complexes [5], but rather the interaction between the Fl^N ligand and Ge more closely resembles the σ-bonding found in $(Fl^N)GaCl_2$ [6]. This lack of π-bonding is likely due to the covalent nature of the Ge–Fl^N bond rather than the more ionic interaction found in the Fl^N–Li complex, described thoroughly by Culp and Cowley [5]. The structure also shows a lack of any intra- or intermolecular coordination of the pendant arms of Fl^N to the Ge center. The reduced Lewis acidity of the tetrahedral Ge atom is likely the reason for the lack of coordination of the pendant arms. The Sn analog 5 reveals similar features in the X-ray structure to 4 with a minor difference in that N(2′) is disordered over two positions in 5. As with 4, 5 exhibits no π-bonding between the Fl^N ligands and Sn, nor is any intra- or intermolecular bonding of the pendent ligand arm to the Sn center present. Due to the larger size of the Sn atom, there is a significant increase of ~ 0.22 Å in the metal–C(Fl^N) bond length in 5 versus 4. It is thus somewhat surprising that despite this increased accessibility and the higher Lewis acidity of Sn versus Ge there is still no tendency for the pendent arms to intramolecularly bond to Sn, despite the fact that five- or six-coordinate complexes of Sn are quite common [10].

The attempt to prepare the Pb analog of 4 and 5 via reaction of Et_2PbCl_2 with two equivalents of Fl^NLi in toluene led to a quite different reaction product. Rather than starting with the more volatile and toxic Me_2PbCl_2, we chose to use the more readily available Et_2PbCl_2 as the starting main-group material. After removal of a black solid and isolation of pale yellow crystals, proton NMR analysis revealed that the ethyl groups were no longer present in the yellow crystals,
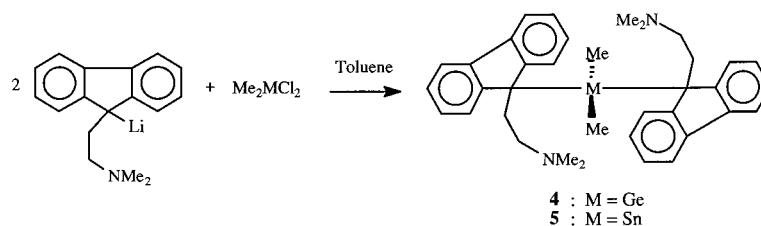

Fig. 1. Reaction scheme for preparation of of $(Fl^N)_2MMe_2$ (M = Ge, Sn).
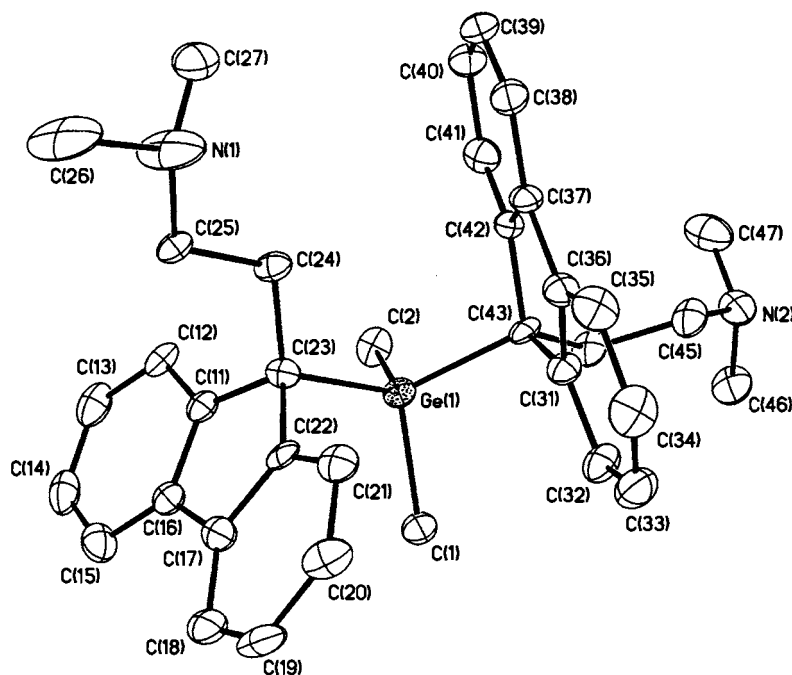
Fig. 2. Molecular structure showing one of the two independent molecules of $[Fl^N]_2GeMe_2$ (**4**). Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ge(1)–C(1) 1.945(5), Ge(1)–C(2) 1.952(4), Ge(1)–C(23) 2.025(4), Ge(1)–C(43) 2.024(4), C(1)–Ge(1)–C(2) 108.5(2), C(23)–Ge(1)–C(43) 116.3(2), C(1)–Ge(1)–C(23) 106.6(2), C(1)–Ge(1)–C(43) 108.2(2), Ge(1)–C(23)–C(24) 113.2(3).
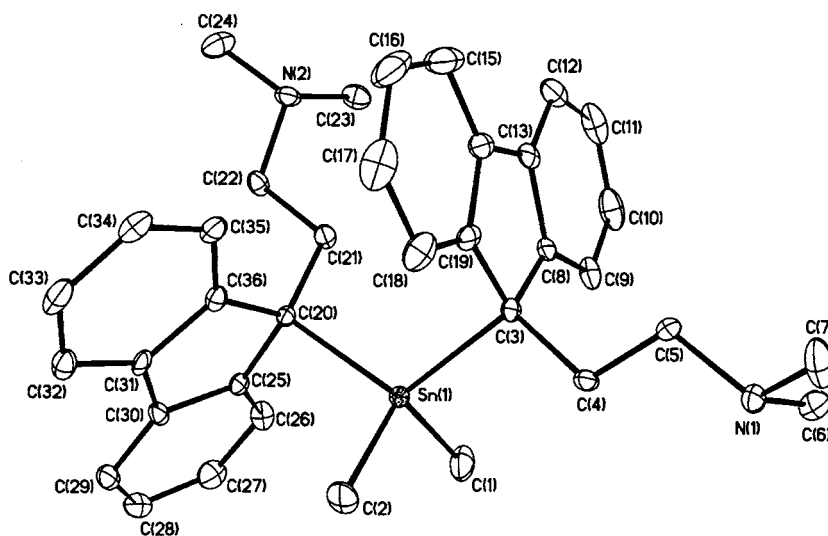

Fig. 3. Molecular structure showing one of the two independent molecules of $[Fl^N]_2SnMe_2$ (**5**). Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Sn(1)–C(1) 2.159(7), Sn(1)–C(2) 2.157(6), Sn(1)–C(3) 2.253(5), Sn(1)–C(20) 2.262(5), C(1)–Sn(1)–C(2) 111.0(3), C(3)–Sn(1)–C(20) 113.9(2), C(1)–Sn(1)–C(3) 105.6(2), C(1)–Sn(1)–C(20) 109.3(3), C(2)–Sn(1)–C(20) 108.3(2), C(2)–Sn(1)–C(3) 108.8(3), Sn(1)–C(20)–C(21) 108.9(3), Sn(1)–C(3)–C(4) 106.2(3).

and further analysis of the proton NMR spectrum indicated the product was consistent with a coupled structure, $[Fl^N]_2$ (**6**). Coupling reactions of fluorene compounds to form 9,9′-bifluorenyls have been investigated previously by Olah et al. [11]; however, we are unaware of any reported metal-mediated coupling of Fl^N ligands to form compounds such as **6**.
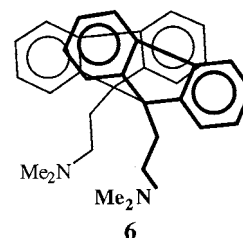

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Table 1
Crystallographic data for **4** and **5** and **6**

	4	5	6
Formula	$C_{36}H_{42}GeN_2$	$C_{36}H_{42}N_2Sn$	$C_{34}H_{36}N_2$
Formula weight	575.31	621.41	472.65
Space group	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
a (Å)	16.0909(2)	16.3496(5)	9.9445(2)
b (Å)	21.6370(3)	22.0168(3)	15.2690(3)
c (Å)	18.7607(2)	19.1784(6)	17.8586(3)
β (°)	111.7936(2)	111.684(2)	–
V (Å^3)	6064.85(14)	6415.0(3)	2711.70(8)
Z	8	8	4
Crystal color, habit	Colorless, plate	Colorless, block	Colorless, needle
D_{calc} (g cm^{-3})	1.260	1.287	1.158
μ(Mo–K$_\alpha$) (cm^{-1})	10.37	8.22	0.67
Temperature (K)	218(2)	173(2)	213(2)
Independent reflections	8677	12530	3456
Goodness-of-fit on F^2	0.963	0.993	1.051
Diffractometer		Siemens P4/CCD	
Radiation		Mo–K$_\alpha$ ($\lambda = 0.71073$ Å)	
$R(F)$ (%)[a]	5.17	6.01	5.82
$R(wF^2)$ (%)[a]	10.23	13.62	15.09

[a] Quantity minimized $= R(wF^2) = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[(wF_o^2)^2]^{1/2}$; $R = \Sigma \Delta/\Sigma(F_o)$, $\Delta = |(F_o - F_c)|$.

The identity of **6** was established unambiguously by elemental analysis, proton NMR, and X-ray diffraction (Table 1). In addition, we synthesized **6** independently via the direct oxidation of Fl^{N}Li·Et$_2$O with bromine or iodine [12]. The structure of **6** is shown in Fig. 4 along with important structural data. Similarly to Olah et al. [11], we see the two rings arranged in a *gauche* conformation, with the C(14)–C(1)–C(18)–C(31) torsion angle being 59.1(5)°. This conformation allows for the greatest relief of steric strain in the coupled product. The most interesting feature of the structure is the notable lengthening of the central C(1)–C(18) bond joining the two rings relative to the model 9,9′-bifluorenyls prepared by Olah et al. In **6** the C–C bond has now lengthened to 1.622(5) Å, significantly longer than the 1.542–1.585 Å range mentioned by Olah et al. for two bifluorenyls — the parent 9,9′-bifluorene and 9-*tert*-butyl-9,9′-bifluorenyl [11]. This indicates that the attachment of the –CH$_2$CH$_2$NMe$_2$ arm onto the fluorene is adding a surprisingly large degree of steric bulk to the fluorene ring.

The mechanism by which **6** forms is not known with certainty. However, previous work in lead chemistry has shown that tetraethyllead or related organolead compounds oxidize quite easily either by thermolysis or phototolysis in a multiple series of reactions [13,14]. The initial step in the thermolysis of tetraethyllead is believed to be homolysis of a Pb–C bond to generate Et$_3$Pb$^\bullet$ and Et$^\bullet$ radicals, which then causes a complex mixture of radical reactions to occur, generating a complex variety of products. In the absence of oxygen, elemental Pb can be generated in the decomposition of tetraalkyllead compounds [13]. Thus, we speculate that
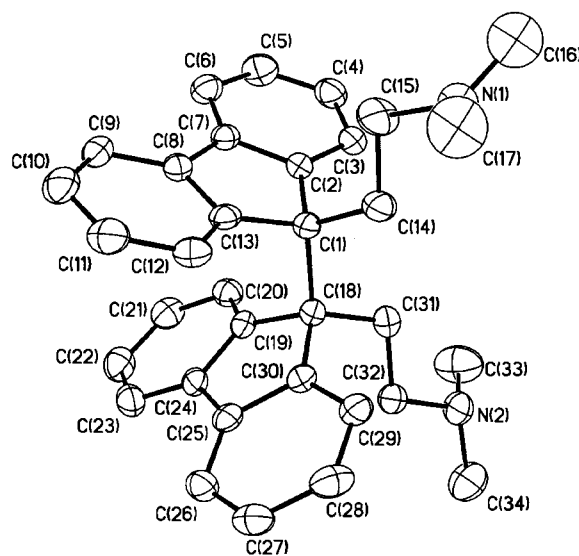

Fig. 4. Molecular structure of [Fl^N]$_2$ (**6**). Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å), angles (°), and torsions (°): C(1)–C(18) 1.622(5), C(1)–C(14) 1.548(5), C(18)–C(31) 1.543(5), C(13)–C(1)–C(18) 108.4(3), C(14)–C(1)–C(18) 112.0(3), C(1)–C(18)–C(31) 111.7(3), C(13)–C(1)–C(18)–C(30) 57.4(5), C(14)–C(1)–C(18)–C(31) 59.1(5).

initially the desired compound, $[Fl^N]_2PbEt_2$, is formed, similarly to the Ge and Sn cases. The sterically demanding Fl^N ligand likely destabilizes the lead compound and accelerates the decomposition via Pb–C bond scission. Relatively stable {Fl^N} radicals could be generated and cause formation of **6** by dimerization. Black solid, presumably lead metal, is also formed in the reaction to generate **6**.

In order to assess the possibility of **4** or **5** acting as main-group polymerization catalysts for propylene, we attempted to prepare polypropylene resins using these complexes. However, prior to performing the polymerization runs we needed to assess that there was indeed reaction between the main group dialkyls and the activators. We contacted **4** and **5** separately with traditional metallocene activation co-catalysts outside of the autoclave. Combining **4** or **5** with either MAO, $B(C_6F_5)_3$, $[Ph_3C]^+[B(C_6F_5)_4]^-$, or $[PhN(H)Me_2]^+[B(C_6F_5)_4]^-$ at room temperature in toluene showed obvious reactions between the main-group complexes and the activators by color changes in the resulting solutions. We next evaluated **4** and **5** (0.25 mmol) activated with 400–1000 equivalents of MAO as possible polymerization catalysts in typical stainless steel autoclaves using liquid propylene as both solvent and monomer source. In each case, after a 1 h reaction period, a very small amount of polymer (approximately 1–5 g) was formed upon removal of the excess propylene monomer. This very small amount of polymer is also formed in reactions in the absence of any main group compound, thus indicating the main group cationic complexes, if formed, have *at best* extremely low activities. We speculate that the very small amount of polypropylene formed in these runs is the by-product of trace quantities of transition metal impurities activated by either MAO or the small amount of aluminum alkyl used as a scavenger. Using the borate anions as activators rather than MAO for **4** and **5** led to essentially no polymer formation. In order to further evaluate the possibility of transition metal impurities confounding the autoclave results, **4** and **5** were re-tested in glass-lined reactors, thus eliminating the possibility of transition metal impurities. In these experiments, no polymer was formed in any case regardless of the nature of the activating agent. This lack of activity indicates further the strong possibility that small levels of transition metal impurities are present in the stainless steel autoclaves which lead to small amounts of polymer and the main group cations, if formed, are not highly active.

3. Experimental

3.1. General considerations

All reactions were carried out under an atmosphere of dry argon or nitrogen. Air-sensitive products and re-agents were handled by standard Schlenk techniques or in a drybox. Starting materials Me_2GeCl_2, Me_2SnCl_2, and Et_2PbCl_2 were purchased from Alfa. MAO, $B(C_6F_5)_3$, $[Ph_3C]^+[B(C_6F_5)_4]^-$, and $[PhN(H)Me_2]^+$-$[B(C_6F_5)_4]^-$ were kindly provided by Albermarle Corporation. $Fl^NLi \cdot Et_2O$ was prepared according to the reported procedure [5]. ^{1}H- and ^{13}C-NMR spectra were recorded on a Brüker AM-360 MHz spectrometer. Elemental analyses were performed by Desert Microanalytics, Tucson, AZ.

3.2. Preparation of $[Fl^N]_2GeMe_2$ (**4**)

Me_2GeCl_2 (274 mg, 1.58 mmol) was added to $Fl^NLi \cdot Et_2O$ (1.00 g, 3.15 mmol) in toluene (40 ml). The color changed instantaneously from orange to colorless with formation of a white precipitate. The reaction mixture was stirred at room temperature (r.t.) for 2 h. After the solid was removed via filtration, the solution was evaporated under vacuum to give a white powder. The white powder was redissolved in pentane (10 ml) and upon gradual removal of the solvent yielded colorless crystals of **4** (810 mg, 89%). ^{1}H-NMR (in C_6D_6, ppm): 7.62 (d, $^3J_{H-H} = 7.0$ Hz, Fl, 4H), 7.18 (t, $^3J_{H-H} = 6.8$ Hz, Fl, 4H), 7.01 (t, $^3J_{H-H} = 6.8$ Hz, Fl, 4H), 6.84 (d, $^3J_{H-H} = 6.7$ Hz, Fl, 4H), 2.02 (t, $^3J_{H-H} = 5.8$ Hz, (Fl)CH_2CH$_2$, 4H), 1.69 (s, NMe_2, 12H), 1.36 (t, $^3J_{H-H} = 5.6$ Hz, (Fl)CH$_2$CH_2, 4H), 0.3 (s, GeMe_2, 6H). MS: $MH^+ = 577$. Anal. (Calc.): C, 75.75 (75.15); H, 7.52 (7.36), N, 4.22 (3.99).

3.3. Preparation of $[Fl^N]_2SnMe_2$ (**5**)

Me_2SnCl_2 (347 mg, 1.58 mmol) was added to a suspension of $Fl^NLi \cdot Et_2O$ (1.00g, 3.15 mmol) in toluene (40 ml). The orange color $Fl^NLi \cdot Et_2O$ disappeared gradually. After stirring at r.t. for 2 h, the white solid formed (LiCl) was filtered off, and the yellowish solution was evaporated under vacuum to give a yellow viscous material. This yellow material was redissolved in pentane (10 ml). Slow evaporation resulted in the formation of very pale yellow to colorless crystals (910 mg, 93%). ^{1}H-NMR (in C_6D_6, ppm): 7.74 (d, $^3J_{H-H} = 6.8$ Hz, Fl, 4H), 7.18 (t, $^3J_{H-H} = 6.6$ Hz, Fl, 4H), 7.11 (t, $^3J_{H-H} = 6.7$ Hz, Fl, 4H), 6.96 (d, $^3J_{H-H} = 6.8$ Hz, Fl, 4H), 2.21 (t, $^3J_{H-H} = 5.7$ Hz, (Fl)CH_2CH$_2$, 4H), 1.75 (s, NMe_2, 12H), 1.43 (t, $^3J_{H-H} = 5.6$ Hz, (Fl)CH$_2$C$H2$, 4H), −1.28 (t, $^2J_{Sn-H} = 28.8$ Hz, SnMe_2, 6H). ^{13}C-NMR (in C_6D_6, ppm): 147.5 (Fl, 4C), 138.0 (Fl, 4C), 127.2 (Fl, 4C), 125.1 (Fl, 4C), 122.5 (Fl, 4C), 120.6 (Fl, 4C), 54.5 (Fl, 2C), 53.8 ((Fl)CH_2CH$_2$, 2C), 45.1 (NMe_2, 6C), 30.0 ((Fl)CH$_2$$CH_2$, 2C), −11.3 (Sn$Me_2$, 2C). Anal. (Calc.): C, 70.02 (69.58); H, 6.94 (6.81), N, 4.22 (4.51).

3.4. Attempted preparation of $[Fl^N]_2PbEt_2$: synthesis of $[Fl^N]_2$ (6)

The reaction procedure was similar to the syntheses of compounds **4** and **5**. Black solid was formed and removed by filtration. Evaporation of the solvent under vacuum afforded the isolation of colorless crystals. ^{1}H-NMR showed there was no Et group in the product. An X-ray single-crystal structure analysis revealed that the product is $[Fl^N]_2$ (**6**), resulting from the coupling of two Fl^N ligands. The yield is $\sim 55\%$ based on Fl^N. ^{1}H-NMR (in C_6D_6, ppm): 7.34 (d, $^3J_{H-H} = 6.8$ Hz, Fl, 4H), 7.08 (t, $^3J_{H-H} = 6.9$ Hz, Fl, 4H), 6.96 (t, $^3J_{H-H} = 6.8$ Hz, Fl, 4H), 6.88 (br, Fl, 4H), 3.16 (t, $^3J_{H-H} = 5.6$ Hz, (Fl)CH_2CH$_2$, 4H), 1.95 (s, NMe_2, 12H), 1.62 (t, $^3J_{H-H} = 5.6$ Hz, (Fl)CH$_2$CH_2, 4H). Anal. (Calc.): C, 85.88 (86.40); H, 7.84 (7.68), N, 5.63 (5.93).

3.5. Direct synthesis of $[Fl^N]_2$ (6)

A solution of I_2 (231 mg, 0.91 mmol) in toluene (10 ml) was added dropwise to a suspension of $[Fl^N]$Li·Et$_2$O (0.50 g, 1.57 mmol) in toluene (50 ml). The reaction mixture was stirred at r.t. for 14 h. The solid was removed by filtration, and the solvent was evaporated under vacuum to yield **6** (325 mg, 88%) as a yellow powder. **6** can also be synthesized with a similar yield using Br$_2$ in place of the I$_2$. Spectral and analytical data are identical to that reported above. X-ray quality crystals were obtained by slow evaporation of a MeOH solution of **6** held at r.t.

3.6. Autoclave propylene polymerization procedure

The main-group complexes were tested for catalytic behavior according to the following procedure. Liquid propylene (2.7 l) was added to a cooled 4 l autoclave that had been dried under a stream of nitrogen at greater than 90°C. To the stirred autoclave at 62°C were added 0.25 mmol of the main-group complex, 1.5 l of hydrogen, 2.0 ml of 5.0% by weight tri-isobutyl-aluminum solution in heptane to act as scavenger, and either MAO or the BARF salts. The materials were allowed to react for 60 min at 67°C. At the end of this time, the excess propylene was flashed off and any resulting polymer recovered. Drying of the resin formed was accomplished by allowing the polymer to sit overnight in a vented hood.

3.7. Crystal-structure determination

Crystal, data collection, and refinement parameters for **4**, **5**, and **6** are given in Table 1. The systematic absences in the diffraction data were uniquely consistent for the assigned space groups. **4** and **5** are isomorphous. The structures were solved using direct methods, completed by subsequent difference Fourier syntheses and refined by full-matrix least-squares procedures. There are two chemically equivalent but crystallographically independent molecules per asymmetric unit for compounds **4** and **5**. In the case of **4**, atom N(2′) is disordered 50:50 over two positions. For **5**, the dimethylamido group containing N(1) is disordered 55:45 over two positions. All non-disordered non-hydrogen atoms were refined with anisotropic displacement coefficients and all hydrogen atoms were treated as idealized contributions. The absolute structure of **6** could not be determined.

All software and sources of the scattering factors are contained in the SHELXTL (version 5.03) program library (G. Sheldrick, Bruker XRD, Madison, WI).

4. Supplementary material

Anisotropic thermal parameters, hydrogen atom coordinates, and structure factor tables for **4**, **5**, and **6** may be obtained from the author. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 133361 for compound **4**, CCDC no. 133362 for compound **5**, and CCDC no. 133363 for compound **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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