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Aminofluorenyl−Pentamethylcyclopentadienyl and Bis(aminofluorenyl) Derivatives of Group 4 Metals

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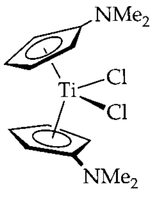
New group 4 compounds containing a 9-(dialkylamino)fluorenyl ligand have been prepared, and their properties and reactivities have been briefly investigated. Single-crystal X-ray analysis of {9-(*N*,*N*-dimethylamino)fluorenyl}$_2$ZrCl$_2$ (**4**) reveals strong zirconium−nitrogen dative bonds. The asymmetric unit contains two molecules with an unusual coordination of aminofluorenyl ligands, best described as comprised of a strong Zr−N dative interaction and essentially an η^1-fluorenyl coordination, supplemented by a weak additional C=C dative interaction of one double bond of one of the benzo units. The barrier to rotation around the C−N bond of {9-(*N*,*N*-diisopropylamino)fluorenyl}(pentamethylcyclopentadienyl)ZrCl$_2$ (**9**) has been determined: $\Delta G^{\ddagger}(-25\ ^\circ\mathrm{C}) = 11.1$ kcal·mol^{-1}. Unlike related aminoborollide complexes, aminofluorenyl complexes resist quaternization by alkyl halides. Several aminofluorenyl complexes have been tested for propylene polymerization behavior in the presence of methylaluminoxane (MAO); atactic polypropylene is obtained with very low activities. The syntheses of 9-(dialkylamino)fluorene compounds are described, as are the syntheses of group 4 compounds via the corresponding 9-(dialkylamino)fluorenide lithium salts.

Introduction

Group 4 metallocenes bearing amine groups directly appended to the cyclopentadienyl rings[1−4] have long been synthetic targets and have recently been shown to be of catalytic interest.[5] For example, (*N*,*N*-dimethylaminocyclopentadienyl)$_2$TiCl$_2$ (**1**)[2] and *rac*-Me$_2$Si(2-(*N*,*N*-dimethylamino)indenyl)$_2$ZrCl$_2$ (**2**)[5] can be prepared from the corresponding lithium salts and TiCl$_4$ or ZrCl$_4$. In conjunction with methylaluminoxane (MAO), **2** forms an active propylene polymerization catalyst.[5]



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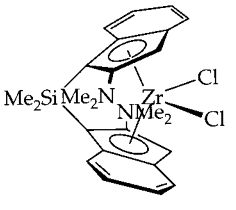
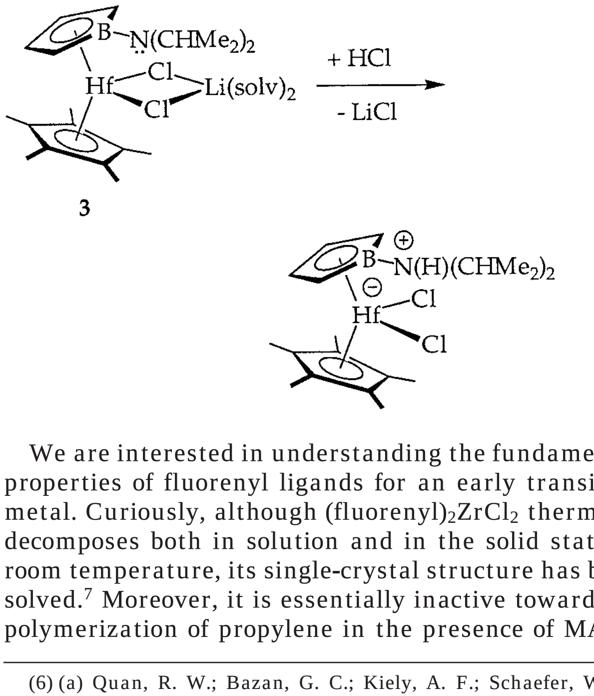


2

Several group 4 compounds containing the dianionic aminoborollide ligand have been prepared and characterized.[6] Compound **3** contains a diisopropylamino group directly bound to the boron atom of the borole ligand. Such amphoteric complexes show Lewis acidic and basic reactivity and effect heterolytic cleavage of various bonds. For example, **3** reacts with hydrogen chloride to give the zwitterionic compound shown in eq 1.



3

(1)

We are interested in understanding the fundamental properties of fluorenyl ligands for an early transition metal. Curiously, although (fluorenyl)$_2$ZrCl$_2$ thermally decomposes both in solution and in the solid state at room temperature, its single-crystal structure has been solved.[7] Moreover, it is essentially inactive toward the polymerization of propylene in the presence of MAO.[8]

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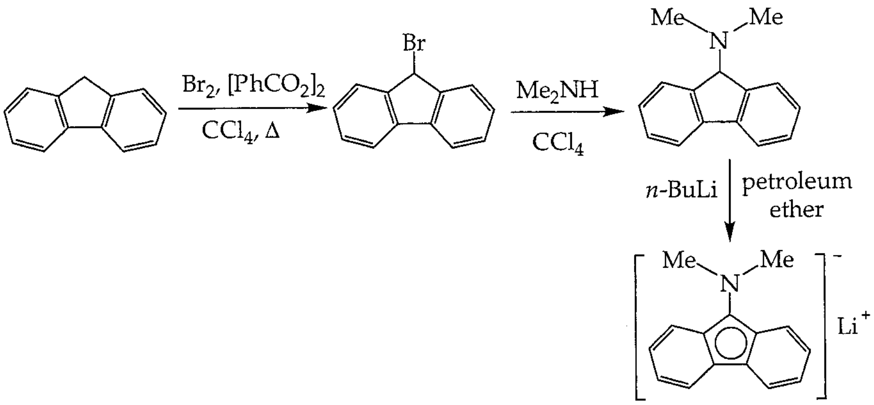
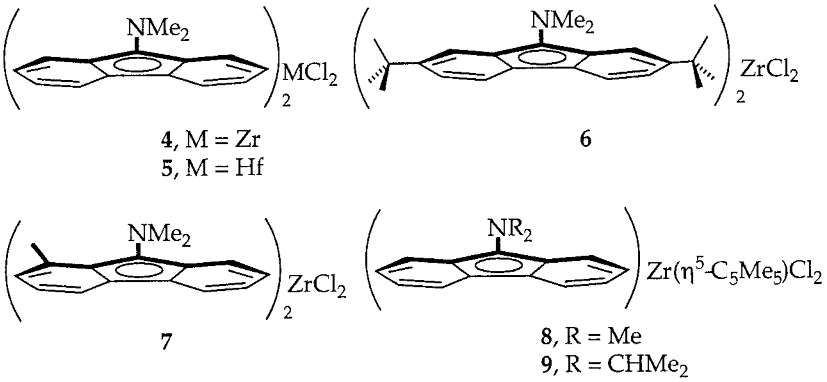
10.1021/om000723r CCC: $19.00

Scheme 1



Scheme 2



4, M = Zr
5, M = Hf

6

7

8, R = Me
9, R = $CHMe_2$

Various modifications of the fluorenyl ligand, including the placement of alkyl groups in the 9 and 1–8 benzo positions, afford stability to such metallocene dichloride complexes. It was proposed that placement of dialkylamino groups in the 9 positions of the fluorenyl moieties would not only provide a more robust compound but create one having interesting structural features, possibly amphoteric reactivity, on account of its Lewis basic and acidic sites, and polymerization activity.

Results and Discussion

Ligand Synthesis. The syntheses of several 9-(*N*,*N*-dialkylamino)fluorenes are known.[9,10] Synthetic methods for aminofluorenes are much simpler and allow for greater substituent variation than those for aminocyclopentadiene and aminoindene compounds. The reasons are twofold: the availability of 9-bromofluorene, which is subject to nucleophilic attack by various nonhindered secondary amines to afford 9-(*N*,*N*-dialkylamino)fluorenes, and the thermal stability of the aminofluorene products (compare *N*,*N*-dimethylaminocyclopentadiene, which decomposes above −30 °C).[1]

A more general route was sought, however, that was amenable to the amination of benzo-functionalized fluorenes, since several of these are available by other synthetic routes, including Friedel–Crafts acylations and alkylations. Hence, a general, two-pot synthesis of 9-(*N*,*N*-dimethylamino)fluorenyllithium in gram quantities from inexpensive starting materials was devised (Scheme 1). This bromination/amination sequence was successfully applied to fluorene, 1-methylfluorene, and 2,7-di-*tert*-butylfluorene.

Metallocene Synthesis. Reaction of 2 equiv of the corresponding aminofluorenide lithium salt with $ZrCl_4$ (or $HfCl_4$) in diethyl ether provided metallocenes **4**–**7** (Scheme 2). Reaction with Cp^*ZrCl_3 ($Cp^* = (\eta^5-C_5Me_5)$) in diethyl ether provided mixed ring metallocenes **8** and **9**. Compound **7** was obtained as a 61:39 mixture of diastereomers. Attempts to prepare metallocenes bearing two dialkylaminofluorenyl ligands with bulky alkyl groups (e.g., 9-(*N*,*N*-diisopropylamino)fluorenyl, 9-(*N*-piperidine)fluorenyl, or 9-(*N*-methyl-*N*-phenyl)fluorenyl) were unsuccessful and resulted in decomposition.

The metallocene dichlorides have been characterized by ^1H NMR (Experimental Section). The solution ^1H NMR spectra of **4**, **5**, and **6** are consistent with structures of C_{2v} symmetry; **8** and **9** display C_s symmetry; and one diastereomer of **7** is consistent with C_2 symmetry, while the other is of C_s symmetry. In solution, all molecules undergo rapid fluxional rearrangements that equalize the benzo moieties of the aminofluorenyl ligands (vide infra).

Compound **9** was subjected to variable-temperature ^1H NMR in order to establish the barrier to rotation around the C–N bond of the aminofluorenyl ligand (eq 2).[11] The ^1H NMR (400 MHz) spectra (in toluene-d_8) were monitored between 65 and −65 °C at 5 °C incre-

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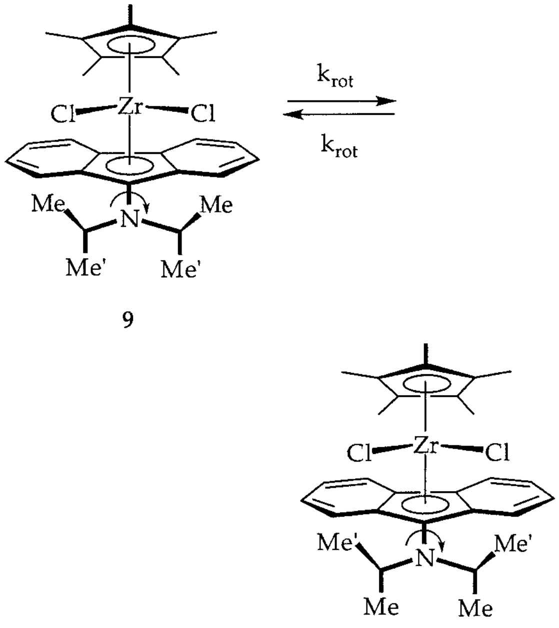
ments. At the high-temperature limit, the methyl protons of the isopropyl groups give rise to a doublet centered at 1.19 δ. At the low-temperature limit, two doublets, separated by 358 Hz, are observed: one at 0.79 δ and the other at 1.69 δ. The coalescence temperature is approximately −25 °C; hence $\Delta G^{\ddagger}(-25\ °C) = 11.1$ kcal·mol^{-1}.



9

9

(2)

{9-(*N*,*N*-Dimethylamino)fluorenyl}$_2$ZrCl$_2$ (**4**) has been characterized by X-ray crystallography.[12] For both of the independent molecules in the asymmetric unit (Figure 1), there is a novel coordination geometry for the dimethylaminofluorenyl ligand. Each may be described as bis(η^4-aminofluorenyl), where, in addition to η^3 coordination to fluorenyl, Zr is also bound to the amine nitrogen (*d*((ZrA)-N(1A)) = 2.379(6) Å; *d*((ZrA)−N(21A)) = 2.330(5) Å; *d*((ZrB)−N(1B)) = 2.357(6) Å; *d*((ZrB)−N(21B)) = 2.373(5) Å). The coordination to the fluorenyl unit is quite asymmetric, however, with short Zr−C distances to that carbon bearing the dimethylamino group (*d*((ZrA)−C(1A)) = 2.394(7) Å; *d*((ZrA)−C(21A)) = 2.337(7) Å; *d*((ZrB)−C(1B)) = 2.384(7) Å; *d*((ZrB)−C(21B)) = 2.326(7) Å) and relatively long Zr−C distances associated with the coordinated C═C of the benzo moieties of the fluorenyl (2.516(7), 2.633(7), 2.731(7), 2.939(8), 2.605(6), 2.736(7), 2.614(7), and 2.834(7) Å). Indeed, the very long distances to one of the carbons of the aminofluorenyl for each independent molecule (C(23A) and C(32B); 2.939(8) and 2.834(7) Å) brings into question whether there is a true zirconium−carbon bonding interaction, especially when one compares the significantly shorter Zr−C bonds of 2.50 ± 0.05 Å for the zirconium cyclopentadienyl ring carbons of Cp*{η^5-C$_5$H$_3$(CHMe$_2$)$_2$}ZrCl$_2$[13] and the shorter Hf−C bonds of 2.55 ± 0.10 Å for the fluorenyl ring carbons for {Me$_2$C-(fluorenyl)(η^5-C$_5$H$_5$)}HfCl$_2$.[14] This coordination geometry also contrasts that seen for *N*,*N*-dimethylaminocyclopentadienyl,[2] 2-(*N*,*N*-dimethylamino)indenyl,[4,5] and *N*,*N*-diisopropylaminoborollide,[6] for which there is essentially no metal−nitrogen bonding observed in the solid state. The C−N bond lengths determined for **4** are 1.454(8),

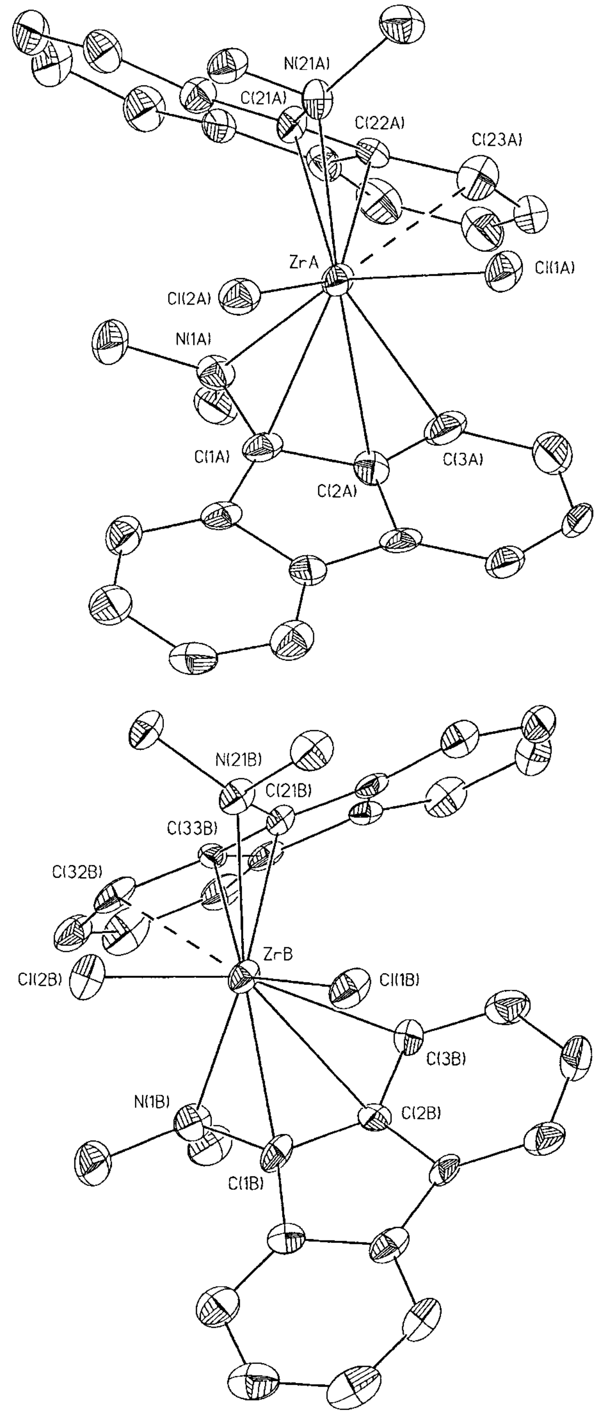


Figure 1. Single-crystal X-ray structure of **4**, depicted with 50% probability ellipsoids.

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[11] Although the (η^5-aminofluroenyl) coordination is indicated in eq 2, the fluxional (N, η^1-, η^3-aminofluorenyl) mode found for **4** in the solid state, might also be favored for **9**.

[12] (9-(*N*,*N*-Dimethylamino)fluorenyl)$_2$ZrCl$_2$ (**4**, crystallized from dichloromethane) is monoclinic, $P2_1/n$ (No. 14), $a = 18.781(3)$ Å, $b = 30.088(9)$ Å, $c = 8.994(8)$ Å, $\beta = 99.17(3)°$, $V = 5017(3)$ Å^3, $Z = 8$, $T = 160$ K. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number 100582.

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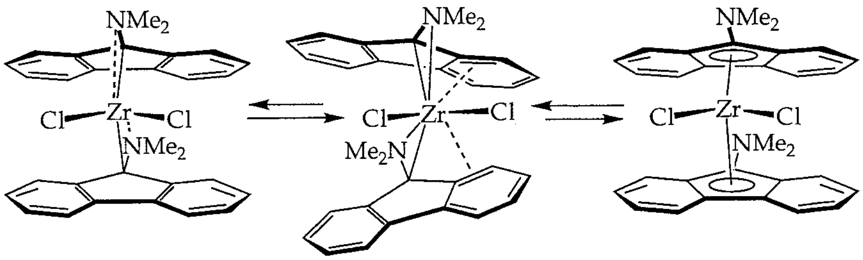
Scheme 3



1.444(8), 1.436(8), and 1.448(8) Å, whereas those determined for **1** and **2** are 1.347(5) and 1.354(7) Å, respectively. While there is significant C−N double-bond character in complexes **1** and **2**, such double-bond character in **4** has been sacrificed to form a metal−nitrogen bond. Thus, the zirconium−aminofluorenyl bonding for **4** may be viewed as comprised of a strong Zr−N dative interaction and essentially an η^1-fluorenyl coordination, supplemented by a weak additional C=C dative interaction of one double bond of one of the benzo units.

The ^{1}H NMR data suggest the solution structure has NMR time-averaged higher symmetry than that for **4** in the solid state. More symmetric (N, η^1-, C, η^1-) or (η^5-aminofluorenyl) isomeric structures must therefore be close in energy, such that the interchange of the two sides of the fluorenyl ligands is rapid on the NMR time scale (Scheme 3).

Electronic Spectroscopy. The UV−visible electronic spectra of the zirconium complex **4** and the hafnium complex **5** were obtained (in toluene). The deep red zirconium complex shows an absorption band at 420 nm ($\epsilon = 6400$ M^{-1} cm^{-1}). The corresponding absorption band for the orange-yellow hafnium complex is blue shifted and lies at 402 nm ($\epsilon = 5800$ M^{-1} cm^{-1}). This blue shift of the absorption band on going from zirconium to hafnium is consistent with a LMCT arising from excitation of a Zr(IV) or Hf(IV) ground state d^0 complex and argues against other ground state resonance descriptions, such as Zr(II) or Hf(II), for which a MLCT band would presumably red shift for hafnium relative to zirconium.[6b]

Reactivity of Aminofluorenyl Metallocenes. In contrast with the reactivity observed with group 4 complexes containing the aminoborollide ligand (e.g., **3**), zirconium and hafnium compounds containing a dialkylaminofluorenyl ligand are relatively unreactive toward methyl iodide. Complexes **4**, **5**, and **8** show no reactivity toward an excess of methyl iodide over 24 h at room temperature, as starting material persists (solvent = CH_2Cl_2; **4** and **5**: slight decomposition, 80% starting material retained; **8**: no reaction, 100% starting material retained). This reactivity difference is likely associated with the metal−nitrogen bond present in **4**, **5**, and **8**, but absent in **3**.

Polymerization Results. Propylene polymerizations with **2**/MAO suffer from long induction periods (2−3 h) and relatively low activity.[5] The metallocene dichlorides **4**, **5**, **8**, and **9**, when combined with MAO, polymerize propylene, but are likewise plagued with low activities (Table 1). Moreover, the integrity of the starting organometallic complex during catalysis is questionable, since all complexes bleach upon exposure to MAO. The species responsible for polymerization has likely lost its dialkylaminofluorenyl ligands. The polymerization runs are generally irreproducible and afford only small quantities of amorphous, atactic polypropylene.

Table 1. Propylene Polymerization Results with 4, 5, 8, and 9/MAO[a]

metallocene (mg)	propylene (mL)	MAO (equiv)	temp (°C)	time (h)	yield (g)
4 (10)	25	500	20	16	2.00
4 (11)	25	500	0	2	0.02
5 (12)	25	500	20	16	0.02
8 (9)	25	500	20	7.5	0.03
9 (10)	25	500	20	7.5	0.02

[a] Propylene is condensed into a 3 oz Lab Crest glass pressure reactor containing MAO at 0 °C. A solution of metallocene in 2.0 mL of toluene is injected via a septum. The reaction is vented and quenched with MeOH/HCl, and the polymers are precipitated with MeOH.

Conclusions

Bromination of fluorene, followed by nucleophilic substitution by a secondary amine, provides access to large quantities of a variety of 9-(*N*,*N*-dialkylamino)fluorenes. Several group 4 metallocene dichloride complexes containing the 9-(*N*,*N*-dialkylamino)fluorenyl ligand have been prepared and characterized, including mixed fluorenyl/pentamethylcyclopentadienyl metallocene dichlorides. The complex {9-(*N*,*N*-dimethylamino)fluorenyl}$_2$ZrCl$_2$ displays novel modes of aminofluorenyl binding, which includes a zirconium−nitrogen dative interaction. The observed blue shift of the visible absorption on changing from zirconium to hafnium for the bis(aminofluorenyl) dichloride derivatives is consistent with a d^0 ground state and a ligand-to-metal charge transfer transition. In contrast with the reactivity observed with group 4 complexes containing the aminoborollide ligand, zirconium and hafnium compounds containing a 9-(*N*,*N*-dialkylamino)fluorenyl ligand are relatively unreactive toward methyl iodide. Group 4 metallocenes bearing the 9-(*N*,*N*-dialkylamino)fluorenyl ligand are capable of promoting propylene polymerization in the presence of MAO, although such systems suffer from low overall catalytic activity and poor reproducibility.

Experimental Section

General Methods. High-vacuum line or standard Schlenk line techniques were employed in the synthesis and manipulation of all air-sensitive compounds. Solvents were distilled from sodium, sodium benzophenone ketyl, or calcium hydride. 9-Bromofluorene is synthesized by the thermal bromination of fluorene[15] or by the reduction of 9-fluorenone by sodium borohydride followed by the reaction of the isolated 9-fluorenol with phosphorus tribromide.[16] 9-Bromofluorene was also used as received from TCI America. Methylaluminoxane (Ethyl Corporation) was used as the dry solid obtained by removal of all volatiles from the toluene solution. Crystalline $LiCH_2Si(CH_3)_3$ (Aldrich, solution in pentane) is obtained by concentrating the pentane solution. All other commercial materials were used as received: fluorene (Aldrich, 98%); *n*-butyllithium (Aldrich, 1.4 M in hexanes); dimethylamine (Aldrich, 40% in H_2O); $ZrCl_4$ (Aldrich, 99.5+%); $HfCl_4$ (Cerac, 99%); dibenzoylperoxide (Aldrich); Cp^*ZrCl_3 (Strem, 99%); and diisopropylamine (Aldrich, 99%).

Instrumentation. NMR spectra were recorded on a JEOL GX-400 (^{1}H, 399.78 MHz; ^{13}C, 100.53 MHz) spectrometer interfaced with the Delta software package. GC−MS were acquired with a Hewlett-Packard 5890 Series II gas chromatograph connected to a Hewlett-Packard 5989A mass spectrometer. The GC was equipped with a column of dimensions 7.1 m × 0.1 μm having an HP-1 phase (cross-linked methyl silicone gum).

9-(*N*,*N*-Dimethylamino)fluorene. Bromine (17.5 mL, 340 mmol) in 200 mL of carbon tetrachloride was added dropwise via an addition funnel to a refluxing solution of fluorene (50.00 g, 300.8 mmol) and dibenzoylperoxide (3.00 g, 12.4 mmol) in 500 mL of carbon tetrachloride in a 2 L flask over a period of 8 h. After 1 additional hour of refluxing, the pH neutral solution (which showed 95.9% conversion of fluorene to bromofluorene, by GC) was cooled, and 100 mL of dimethylamine solution (40% in H_2O, 797 mmol) was syringed in. The sealed vessel was stirred at room temperature for 58 h before H_2O/HCl (50 mL H_2O/50 mL concentrated aqueous HCl) was added gradually. The aqueous layer was isolated, and the organic layer was extracted with H_2O/HCl (90 mL H_2O/10 mL concentrated aqueous HCl) and H_2O (2 × 100 mL). The aqueous layers were made basic with 100 mL of 10% aqueous NaOH. This was extracted with diethyl ether (1 × 200 mL and 2 × 100 mL), and the combined organic layers were dried over $MgSO_4$ and pushed through a column of alumina, which was rinsed with another 150 mL of ether. Rotavap removal of solvent gave a viscous yellow oil, which crystallized upon cooling. In vacuo drying afforded 51.30 g (81.5%) of 9-(*N*,*N*-dimethylamino)fluorene. MS (GC−MS): *m*/*z* 209.3 (M^+). ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 6H, CH_3), 4.85 (s, 1H, 9-*H*-Flu), 7.29, 7.38 (t, $^3J_{HH}$ = 7.7, 7.3 Hz, 4H, Flu-*H*), 7.64, 7.70 (d, $^3J_{HH}$ = 7.7, 7.3 Hz, 4H, Flu-*H*). Anal. Calcd for $C_{15}H_{15}N_1$: C, 86.08; H, 7.22; N, 6.69. Found: C, 85.45, 85.57; H, 6.92, 6.76; N, 6.46, 6.39.

9-(*N*,*N*-Dimethylamino)fluorenyllithium. A large swivel frit apparatus was charged with 20.092 g of 9-(*N*,*N*-dimethylamino)fluorene (96.00 mmol) before evacuation, backfilling with argon, and addition of 150 mL of petroleum ether to dissolve the solid. A 60.0 mL portion of 1.6 M *n*-butyllithium solution in hexanes (96.0 mmol) was added dropwise at room temperature over 15 min. The red precipitate was collected by filtration after 4 h of stirring. In vacuo drying afforded 19.89 g (96.7%) of the desired product as a red powder. Anal. Calcd for $C_{15}H_{14}N_1Li_1$: C, 83.71; H, 6.56; N, 6.51. Found: C, 83.13, 83.27; H, 7.21, 6.74; N, 6.43, 6.73.

{9-(*N*,*N*-Dimethylamino)fluorenyl}$_2$ZrCl$_2$ (4). A swivel frit apparatus is charged with 6.000 g of 9-(*N*,*N*-dimethylamino)fluorenyllithium (27.88 mmol) and 3.248 g of sublimed $ZrCl_4$ (13.94 mmol). A 60 mL sample of diethyl ether was condensed in at −78 °C, and the cold bath subsequently removed. After 22 h of stirring, solvent was removed and 60 mL of methylene chloride was condensed in. The product was not fully soluble in this amount of solvent, but continuous extraction by refluxing for several hours left only the insoluble LiCl on the frit. The volume was reduced to 20 mL and the precipitate collected at 0 °C. In vacuo drying gave 6.08 g (75.3%) of the desired product. ^{1}H NMR (CD_2Cl_2): δ 2.97 (s, 12H, C*H*$_3$), 6.89 (d, $^3J_{HH}$ = 7.7 Hz, 4H, Flu-*H*), 7.00 (t, $^3J_{HH}$ = 7.3 Hz, 4H, Flu-*H*), 7.17 (t, $^3J_{HH}$ = 7.4 Hz, 4H, Flu-*H*), 7.91 (d, $^3J_{HH}$ = 7.7 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 46.58 (*C*H$_3$), 115.28, 121.54, 122.82, 127.32 (Flu-*C*H$_1$), 132.66, 133.02 (Flu-*C*$_0$), 9-Flu-*C*, not determined. Anal. Calcd for $C_{30}H_{28}N_2Zr_1Cl_2$: C, 62.27; H, 4.88; N, 4.84. Found: C, 61.09, 60.65; H, 4.96, 4.90; N, 5.08, 4.81.

{9-(*N*,*N*-Dimethylamino)fluorenyl}$_2$HfCl$_2$ (5). The procedure for **4** was employed except 3.000 g of 9-(*N*,*N*-dimethylamino)fluorenyllithium (13.94 mmol) and 2.232 g of $HfCl_4$ (6.97 mmol) were used; the reaction duration was 9 h; in vacuo drying gave 2.78 g (59.9%) of the desired product. ^{1}H NMR (CD_2Cl_2): δ 3.03 (s, 12H, C*H*$_3$), 6.93 (d, $^3J_{HH}$ = 8.1 Hz, 4H, Flu-*H*), 7.01 (t, $^3J_{HH}$ = 7.7 Hz, 4H, Flu-*H*), 7.09 (t, $^3J_{HH}$ = 7.0 Hz, 4H, Flu-*H*), 7.88 (d, $^3J_{HH}$ = 7.4 Hz, 4H, Flu-*H*). ^{13}C NMR (CD_2Cl_2): δ 47.05 (*C*H$_3$), 118.15, 120.78, 122.85, 126.20 (Flu-*C*H$_1$), 133.91, 134.05 (Flu-*C*$_0$), 9-Flu-*C*, not determined. Anal. Calcd for $C_{30}H_{28}N_2Hf_1Cl_2$: C, 54.11; H, 4.24; N, 4.21. Found: C, 53.45, 53.45; H, 4.36, 4.07; N, 4.43, 4.41.

9-(*N*,*N*-Dimethylamino)-2,7-di-*tert*-butylfluorene. Bromine (2.1 mL, 40.8 mmol) in 25 mL of carbon tetrachloride was added dropwise via an addition funnel to a refluxing solution of 2,7-di-*tert*-butylfluorene[17] (10.00 g, 35.91 mmol) and dibenzoylperoxide (0.36 g, 1.5 mmol) in 100 mL of carbon tetrachloride in a 500 mL flask over a period of 75 min. After 1 additional hour of refluxing, the pH neutral solution was cooled, and 20 mL of dimethylamine solution (40% in H_2O, 147 mmol) was syringed in. The sealed vessel was stirred at 55 °C for 24 h before H_2O/HCl (50 mL H_2O/25 mL concentrated aqueous HCl) was added gradually. A 400 mL portion of H_2O and 200 mL of hexane were added, and the precipitate was collected by filtration and washed with 100 mL of hexane (9.61 g, 74.7%). The salt was combined with 200 mL of H_2O, 50 mL of 10% aqueous NaOH, and 200 mL of diethyl ether. The organic layer was isolated and the aqueous layer extracted with diethyl ether (3 × 50 mL). The organic layers were dried over $MgSO_4$, pushed through a column of alumina, which was rinsed with 150 mL of diethyl ether, rotavapped, and dried in vacuo to provide 8.48 g (73.5%) of product. MS (GC−MS): *m*/*z* 321.5 (M^+). ^{1}H NMR ($CDCl_3$): δ 1.36 (s, 18H, C(C*H*$_3$)$_3$), 2.33 (s, 6H, N-(C*H*$_3$)$_2$), 4.81 (s, 1H, 9-Flu-*H*), 7.37, 7.56 (d, $^3J_{HH}$ = 8.0, 8.1 Hz, 4H, 3- and 4-Flu-*H*), 7.62 (s, 2H, 1-Flu-*H*). Anal. Calcd for $C_{23}H_{31}N_1$: C, 85.93; H, 9.72; N, 4.36. Found: C, 85.50; H, 9.67; N, 4.32.

{9-(*N*,*N*-Dimethylamino)-2,7-di-*tert*-butylfluorenyl}$_2$ZrCl$_2$ (6). A swivel frit apparatus was charged with 9-(*N*,*N*-dimethylamino)-2,7-di-*tert*-butylfluorene (2.00 g, 6.22 mmol) and $LiCH_2Si(CH_3)_3$ (0.586 g, 6.22 mmol). Tetrahydrofuran (40 mL) was condensed in, and the reaction was stirred at room temperature for 30 min before solvent was removed and $ZrCl_4$ (0.725 g, 3.11 mmol) was added. Diethyl ether (50 mL) was condensed in, and the reaction was stirred at room temperature for 12 h before it was filtered. The volume was reduced to 10 mL, and 5 mL of petroleum ether was condensed in. The chilled solution (−20 °C) gave a precipitate, which was collected and dried in vacuo: 0.589 g (23.6%) of **6** as an orange powder. ^{1}H NMR (C_6D_6): δ 1.37 (s, 36H, C(C*H*$_3$)$_3$), 2.72 (s, 12H, C*H*$_3$), 7.16 (d, $^3J_{HH}$ = 8.1 Hz, 4H, Flu-*H*), 7.35 (s, 4H, Flu-*H*), 7.61 (d, $^3J_{HH}$ = 8.1 Hz, 4H, Flu-*H*). Anal. Calcd for $C_{46}H_{60}N_2Zr_1Cl_2$: C, 68.80; H, 7.53; N, 3.49. Found: C, 63.91, 63.98; H, 7.84, 7.57; N, 2.88, 2.83.

9-(*N*,*N*-Dimethylamino)-1-methylfluorene. A solution of 1-methylfluorene (4.87 g, 27.0 mmol) and dibenzoylperoxide in carbon tetrachloride was brought to reflux before a solution of bromine (1.6 mL, 31 mmol) in 25 mL of carbon tetrachloride was added dropwise over 1 h. After refluxing an additional 1.5 h, the vessel was allowed to cool before dimethylamine

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(40% in H_2O, 20 mL, 146 mmol) was added. This was heated at 55 °C for 50 h and cooled. The reaction was stirred open overnight to remove excess dimethylamine, and then gaseous HCl was bubbled through. The entire reaction was pumped to dryness via rotavap. Diethyl ether (200 mL) and hexane (100 mL) were added, and the organic layer was extracted with dilute aqueous HCl (2 × 100 mL). The aqueous layer, in turn, was extracted with diethyl ether (3 × 50 mL) before being made basic with aqueous NaOH. The aqueous layer was then extracted with diethyl ether (3 × 75 mL), and the organic layer was dried over $MgSO_4$, pushed through a column of alumina, and rotavapped to provide the product as a light yellow oil, which crystallized upon standing (3.66 g, 60.7%). MS (GC−MS): m/z 223.3 (M^+). ^1H NMR ($CDCl_3$): δ 2.25 (s, 6H, N-(CH_3)$_2$) 2.52 (s, 3H, 1-Flu-CH_3), 4.85 (s, 1H, 9-Flu-H), 7.06, 7.48, 7.60, 7.68 (d, $^3J_{HH}$ = 7.3, 7.3, 7.3, 7.7 Hz, 4H, 2-, 4-, 5- and 8-Flu-H), 7.23, 7.26, 7.35 (t, $^3J_{HH}$ = 7.3, 7.7, 7.3 Hz, 3H, 3-, 6-, and 7-Flu-H). Anal. Calcd for $C_{16}H_{17}N_1$: C, 86.06; H, 7.67; N, 6.27. Found: C, 84.61, 84.56; H, 7.16, 7.21; N, 6.24, 6.22.

{9-(*N,N*-Dimethylamino)-1-methylfluorenyl}$_2$ZrCl$_2$ (7). The procedure for **6** was followed with 9-(*N,N*-dimethylamino)-1-methylfluorene (1.00 g, 4.48 mmol), $LiCH_2Si(CH_3)_3$ (0.422 g, 4.48 mmol), and $ZrCl_4$ (0.522 g, 2.24 mmol). The first crop was collected from a saturated diethyl ether solution as a red solid: 0.080 g. A second crop was obtained (0.903 g) for a total yield of 72.4%. ^1H NMR (C_6D_6, 50 °C): minor diastereomer (39%): δ 2.47 (s, 6H), 2.87 (s 12H), 6.69 (t, 2H), 6.91 (t, 2H), 7.05, (t, 2H), 7.28 (d, 2H), 7.43 (d, 2H), 7.50 (d, 2H), 7.54 (d, 2H); major diastereomer (61%): δ 2.58 (s, 6H), 2.87 (s 12H), 6.75 (t, 2H), 6.78 (t, 2H), 6.95, (t, 2H), 7.28 (d, 2H), 7.43 (d, 2H), 7.50 (d, 2H), 7.54 (d, 2H). Anal. Calcd for $C_{32}H_{32}N_2Zr_1Cl_2$: C, 63.35; H, 5.32; N, 4.62. Found: C, 58.59, 58.75; H, 5.61, 5.85; N, 4.38, 4.81.

{9-(*N,N*-Dimethylamino)fluorenyl)(pentamethylcyclopentadienyl}ZrCl$_2$ (8). A swivel frit apparatus was charged with 0.485 g of 9-(*N,N*-dimethylamino)fluorenyllithium (2.254 mmol) and 0.750 g of Cp*$ZrCl_3$ (2.254 mmol). A 30 mL sample of diethyl ether was condensed in at −78 °C, and the reaction was allowed to warm slowly. After 9 h, the reaction was filtered and the yellow solid extracted with refluxing diethyl ether. Condensation of the filtrate led to isolation of 0.729 g (64.0%) of **8** in two crops as a yellow crystalline solid. ^1H NMR (C_6D_6): δ 1.45 (s, 15H, Cp*-H), 2.98 (s, 6H, CH_3), 7.04 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 7.12 (t, $^3J_{HH}$ = 7.3 Hz, 2H), 7.24 (d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.73 (d, $^3J_{HH}$ = 7.7 Hz, 2H). Anal. Calcd for $C_{25}H_{29}N_1Zr_1Cl_2$: C, 59.39; H, 5.78; N, 2.77. Found: C, 58.82, 58.76, 58.73, 58.72; H, 5.91, 5.89, 6.00, 6.26; N, 2.86, 2.84, 2.96, 2.97.

9-(*N,N*-Diisopropylamino)fluorene. A flask was charged with 5.12 g of 9-bromofluorene (20.9 mmol), 50 mL of diisopropylamine, and 60 mL of acetonitrile. The reaction was refluxed for 11 days, and all volatiles were removed by rotary evaporation. A solution of 50 mL of concentrated aqueous HCl/150 mL water was added to the white solid. This was extracted with diethyl ether (2 × 50 mL). The remaining aqueous layer was made basic by addition of 200 mL of 10% aqueous NaOH. This was extracted with diethyl ether (3 × 50 mL) and dried over $MgSO_4$. Filtration, rotary evaporation, and in vacuo drying gave 4.258 g of product (76.8%). Recrystallization of the crude material from 50 mL of EtOH gave the product as white crystals: 2.933 g (52.9%). MS (GC−MS): m/z 265.3 (M^+). ^1H NMR (C_6D_6): δ 1.09 (d, $^3J_{HH}$ = 6.2 Hz, 12H, CH_3), 2.90 (m (br), 1H, CHMe$_2$), 4.96 (s, 1H, 9-H-Flu), 7.28, 7.35 (t, $^3J_{HH}$ = 7.3, 7.3 Hz, 4H, Flu-H), 7.60, 7.69 (d, $^3J_{HH}$ = 7.0, 7.7 Hz, 4H, Flu-H). Anal. Calcd for $C_{19}H_{23}N_1$: C, 85.99; H, 8.73; N, 5.28. Found: C, 85.48, 86.70; H, 8.21, 8.25; N, 5.11, 5.08.

{9-(*N,N*-Diisopropylamino)fluorenyl}(pentamethylcyclopentadienyl)ZrCl$_2$ (9). A swivel frit apparatus was charged with 0.598 g of 9-(*N,N*-diisopropylamino)fluorene (2.253 mmol) and 0.212 g of $LiCH_2Si(CH_3)_3$ (2.251 mmol). Tetrahydrofuran (20 mL) was condensed in at −78 °C and the solution allowed to warm slowly. After 30 min, the solvent was removed and 0.750 g of Cp*$ZrCl_3$ (2.254 mmol) was added. Diethyl ether (30 mL) was condensed in and the reaction stirred at room temperature for 12 h. The solution was filtered and the orange material extracted with refluxing ether. The volume of the filtrate was reduced, and the product **9** was collected in two crops (the second crop from CH_2Cl_2) as an orange crystalline solid: 0.758 g (59.9%). ^1H NMR (C_6D_6, 50 °C): δ 1.22 (d, $^3J_{HH}$ = 6.6 Hz, 12H, CH_3), 1.59 (s, 15H, Cp*-H), 2.04 (b, 2H, Me$_2$CH), 6.87 (b, 2H), 6.99 (b, 2H), 7.70 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 8.01 (d, $^3J_{HH}$ = 8.4 Hz, 2H). Anal. Calcd for $C_{29}H_{37}N_1Zr_1Cl_2$: C, 62.01; H, 6.64; N, 2.49. Found: C, 57.37, 58.17, 61.40, 61.70; H, 6.21, 6.89, 6.99, 6.51; N, 2.21, 2.22, 2.62, 2.56.

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Supporting Information Available: Details of the structure determination for **4**, including listings of final atomic coordinates, thermal parameters, and selected bond distances and angles; ^1H NMR data employed to calculate the barrier to rotation around the C−N bond of **9**; UV−visible spectra of **4** and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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