Synthesis and Characterization of Zirconium Complexes Containing a Linked Amido–Fluorenyl Ligand[†]

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Zirconium complexes containing an amido-fluorenyl ligand bridged by a dimethylsilylene group, $C_{13}H_8SiMe_2NCMe_3$, have been synthesized. The dichloro complexes $Zr(\eta^5:\eta^1-C_{13}H_8 SiMe_2NCMe_3)Cl_2(L)$ (L = THF, Et_2O) were prepared by reacting $ZrCl_4L_2$ with $Li_2[C_{13}H_8-C_{1$ SiMe₂NCMe₃] and characterized as labile mono(solvent) adducts. Reaction with MeMgCl gives the thermally sensitive dimethyl complex $Zr(\eta^5:\eta^1-C_{13}H_8SiMe_2NCMe_3)Me_2(THF)$. whereas solvent-free dialkyl derivatives $Zr(\eta^5; \eta^1-C_{13}H_8SiMe_2NCMe_3)Ph_2$ and $Zr(\eta^5; \eta^1-C_{13}H_8-C_{13}$ SiMe₂NCMe₃)(CH₂SiMe₃)₂, all under preservation of the chelate structure, are obtained with PhMgCl and Me₃SiCH₂MgCl, respectively. Variable-temperature ¹H NMR spectroscopic data reveal a sterically congested ligand sphere around the zirconium atom which is confirmed by a single-crystal X-ray diffraction study in the case of the bis(trimethylsilylmethyl) derivative. The substituted fluorenyl ligand is pentahapto-bonded with some variation of the zirconium-ring carbon bond lengths. The amido nitrogen is trigonal planar as a result of significant π -donation to the zirconium. The two (trimethylsilyl)methyl groups do not appear to be strongly distorted despite being bound to a 12-electron d⁰ center but give rise to a conformation in which the repulsion between the trimethylsilyl and the tert-butyl groups is minimized. This compound crystallizes from pentane in the monoclinic space group $P2_1/n$ with a = 9.326(3), b = 16.806(5), and c = 19.638(6) Å, $\beta = 93.23(2)^\circ$, V = 3073(2) Å³, Z = 4, $R = 0.0308, wR_2 = 0.079.$

Introduction

Since the report that ansa-metallocenes of zirconium and hafnium containing linked fluorenyl-cyclopentadienyl ligand systems such as $Zr(\eta^5:\eta^5-C_{13}H_8CMe_2C_5H_5)$ - Cl_2 act as components for syndiospecific α -olefin polymerization catalysts,¹ there has been renewed interest in fluorenyl ligands in group 4 metal coordination chemistry.² These C_s -symmetric zirconocene and hafnocene catalysts lead to the formation of racemic sequences during the polymerization of α -olefins. While mechanistic details responsible for the syndiospecificity remain unclear, the presence of two differently sized rings around the metal center seems to regulate the alternating attack of the α -olefin in the lateral sector of the metallocene by influencing the conformation of the growing polymer chain.³ Consequently, a number of studies have focussed on fluorenyl ligands bridged to the cyclopentadienyl ligand via an alkylidene bridge.⁴

Recently, Bercaw and Shapiro showed that replacing a cyclopentadienyl moiety of a linked bis(cyclopentadienyl) ligand by the 3-electron-donating *tert*-butylamido group results in a ligand system⁵ that forms *ansa*metallocene-like complexes of scandium with higher Lewis acidity, *i.e.* increased reactivity toward α -olefin substrates. In order to examine the detailed complexation behavior of this novel chelating ligand type⁶ also for potentially syndiospecific metallocene catalysts, we carried out the synthesis and characterization of zirconium complexes containing a amido-fluorenyl ligand linked by a dimethylsilylene bridge.⁷

 $^{^{\}rm t}$ Dedicated to Professor Hans H. Brintzinger, with all best wishes, on the occasion of his 60th birthday.

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Results and Discussion

When crude 9-(chlorodimethylsilyl)fluorene⁸ is treated with lithium tert-butylamide in pentane, 9-{(tertbutylamino)dimethylsilyl}fluorene is obtained as a moisture-sensitive colorless oil that can be purified by careful Kugelrohr or short-path vacuum distillation (Scheme 1). Double deprotonation with 2 equiv of *n*-butyllithium in ether/hexane,⁹ followed by reaction with ZrCl₄(THF)₂ in THF at low temperatures, gives the mono(tetrahydrofuran) adduct $Zr(\eta^5:\eta^1-C_{13}H_8SiMe_2NCMe_3)Cl_2(THF)$ (1a), in about 60% yield as dark yellow microcrystalline material. The presence of one molecule of THF per zirconium in samples obtained by crystallization from toluene/THF/pentane is indicated by both ¹H and ¹³C spectroscopy.¹⁰ The chemical shifts of the THF protons are strongly temperature dependent: both α - and β -CH₂ protons undergo substantial high-field shifts upon cooling (Figure 1), although decoalescence of the signals could not be detected. The high-field shift can be explained by the coordinated THF molecule being shielded by the fluorenyl ligand's ring current. The presence of THF in excess of 1 equiv in the solution of 1a results in low-field shift of the THF signals, approaching the values for free THF. Addition of excess



Figure 1. Temperature dependence of the chemical shift for the α - and β -CH₂ protons of the coordinated THF molecule in Zr(η^5 : η^1 -C₁₃H₈SiMe₂NCMe₃)Cl₂(THF) (1a).

THF- d_8 results in instantaneous exchange of all coordinated THF. These observations are in accordance with the existence of a dissociation equilibrium between monomeric 1 and the THF adduct 1a which is fast both on the chemical and NMR time scales.¹¹ Solutions of 1a slowly form a fine powdery precipitate over a period of days. Once precipitated from toluene, this compound does not dissolve even in hot THF. Upon heating 1a above 100 °C, the coordinated THF is also lost irreversibly, forming an insoluble pale yellow solid of what we believe to be di- or oligomeric dichloride 1.

By following the analogous procedure, the even more labile mono(diethyl ether) adduct $Zr(\eta^5:\eta^{1}-C_{13}H_8SiMe_2-NCMe_3)Cl_2(Et_2O)$ (1b) is formed. The ether molecule in 1b can be easily displaced by 1 equiv of THF to form 1a. According to NMR spectroscopic results, other Lewis bases such as PMe₃, pyridine, triethylamine, HMPTA, dmpe, or DME appear to substitute the ether ligand in 1a and 1b. However, no stable adducts could be isolated, most notably, even in the case of the

⁽⁷⁾ Recent patents disclose that $Zr(\eta^5:\eta^1-C_{13}H_3SiMe_2NCMe_3)Cl_2$ in conjunction with methylalumoxane cocatalyst forms isotactic, whereas $[Zr(\eta^5:\eta^1-C_{13}H_3SiMe_2NCMe_3)Me][B(C_6F_5)_4]$ gives syndiotactic polypropylene: (a) Canich, J. A. M. U.S. Patent 5,026,798 to Exxon Chemical; *Chem. Abstr.* **1993**, *118*, 60284; Canich, J. A. M. U.S. Patent 5,055,438 to Exxon Chemical; *Chem. Abstr.* **1993**, *118*, 60283. (b) Turner, H. W.; Hlatky, G. G.; Canich, J. A. M. PCT Int. Appl. WO 9319103; *Chem. Abstr.* **1994**, *120*, 271442.

⁽⁸⁾ Lithium fluorenide reacts with dichlorodimethylsilane in ether to give a mixture of 9-(chlorodimethylsilyl)fluorene and di(9-fluorenyl)dimethylsilane which is extremely difficult to separate. Due to the high nucleophilicity of lithium fluorenide, the formation of the latter could not be completely suppressed in our hands.

⁽⁹⁾ Attempts to obtain single crystals have failed so far. The benzene-soluble THF adduct of dilithium 9-((tert-butylamino)dimethylsilyl)fluorenide show inequivalent signals for the enantiotopic SiMe₂ signals, implying a rather complex structure in solution (cf. ref 5d). For examples of structurally characterized main group element fluorenides, see: (a) Brooks, J. J.; Rhine, W.; Stucky, G. D. J. Am. Chem. Soc. **1972**, 94, 7339. (b) Zerger, R.; Rhine, W.; Stucky, G. D. J. Am. Chem. Soc. **1974**, 96, 5441. (c) Corbelin, S.; Kopf, J.; Weiss, E. Chem. Ber. **1991**, 124, 2417. (d) Janiak, C. Chem. Ber. **1993**, 126, 1603. (e) Mösges, G.; Hampel, F.; Schleyer, P. v. R. Organometallics **1992**, 11, 1769. (f) Neumüller, B. Chem. Ber. **1993**, 126, 11.

⁽¹⁰⁾ In samples crystallized over a prolonged period of time from pentane/THF, two molecules of THF are present. However, the loss of the second solvent molecule is very facile. We suspect that this THF molecule might not be coordinated to the zirconium but acts as lattice solvent.

⁽¹¹⁾ Assuming that the observed chemical shift for the THF protons δ_{obs} is the weighted mean of the values for free and complexed THF ($\delta_{obs} = N \delta_{free} + N \delta_{comp}, N =$ mole fraction), the equilibrium constant at 25 °C was estimated as $K_{eq} = 0.02$ M. Slejiko, F. L.; Drago, R. S.; Brown, D. G. J. Am. Chem. Soc. **1972**, 94, 9210.



bidentate ligands dmpe and DME. Again, insoluble dichloride is rapidly precipitated from these reaction mixtures.

Despite much effort, no single crystal of either 1a or 1b could be obtained so far. A plausible structure is that of a four-legged piano stool, the sterically demanding fluorenyl occupying an apical site. Because of the strong π -donation of the amido ligand, the most probable coordination site of L will be cis to the amido ligand. We conclude that the tetravalent zirconium center in $Zr(\eta^5:\eta^1-C_{13}H_8SiMe_2NCMe_3)Cl_2$ is sufficiently electrophilic to bind a THF or ether molecule. The 14-electron zirconium atom (counting the fluorenyl as a five- and amido as three-electron ligand according to the neutral ligand formalism) on the other hand is not capable of expanding its coordination number to more than five.¹² We ascribe this feature at least partly to the steric encumbrance of the rather rigid chelating ligand system $\eta^5:\eta^1-C_{13}H_8SiMe_2NCMe_3.$

Reaction of 1a with methylmagnesium chloride in THF affords yellow, extremely light and thermally sensitive crystals of the dimethyl derivative 2, which also contains one molecule of THF, in 60% yield (Scheme 2). The synthesis of 2 requires very careful control of the reaction temperature by slowly warming the reaction mixture from -78 to -15 °C and working up below 0 °C. Above this temperature immediate and complete decomposition takes place. Furthermore, the use of the Grignard reagent is mandatory, since methyllithium leads to an intractable mixture even at temperatures as low as -110 °C. The resonance for the two equivalent methyl groups is detected in the ¹H NMR spectrum at δ 0.32 and in the ¹³C NMR spectrum at 40.6 ppm as a quartet with $J_{CH} = 114$ Hz. This value excludes the presence of any strong agostic interaction.¹³ The coordinated THF molecule displays the same feature as in the dichloride 1a.

The reaction of **1a** with benzylmagnesium chloride gives only inseparable materials of what appears to be

Table 1. Crystallographic Data for $Zr(\eta^5:\eta^1-C_{13}H_8SiMe_2NCMe_3)(CH_2SiMe_3)_2$ (4)

Crystal Data					
chem formula	C ₂₇ H ₄₅ NSi ₃ Zr				
fw	559.14				
cryst color	orange yellow				
cryst dimensions, mm	$0.5 \times 0.3 \times 0.15$				
cryst system	monoclinic				
space group	$P2_1/n$				
a, Å	9.326(3)				
b, Å	16.806(5)				
c, Å	19.638(6)				
β (deg)	93.23(2)				
<i>V</i> , Å ³	3073(2)				
Z	4				
$D_{\rm calc}, {\rm g}~{\rm cm}^{-3}$	1.209				
abs. coeff., mm ⁻¹	0.489				
F(000)	1184				
Data Colle	ection				
radiation	Mo Ka ($\lambda = 0.71073$ Å)				
Т, К	293				
2θ range	2.08° to 22.50°				
rflns measd	h, -1 to +10; $k, -1$ to +18, l .				
	-21 to $+21$				
Refinement					
no. of rflns measd	5252				
no, of indep rflns	$3987 (R_{int} = 0.0218)$				
no, of obsd rflns	$3241 (I \ge 2\sigma(I))$				
GOF	1.060				
R	0.0308				
wR_2 (all F^2)	0.0397				
largest e-max, e-min, e Å ⁻³	+0.284, -0.283				
	,				

mixtures of the dibenzyl, mono(benzyl)chloro complex and bibenzyl. On the other hand, treatment of **1a** with phenylmagnesium chloride at low temperatures affords the diphenyl complex 3 in moderate yield as pale yellow powder. Analytical and NMR spectroscopic data of 3 reveal the absence of any coordinated THF molecule. In the ¹H NMR spectrum the resonance for the ten phenyl protons appear as two broad signals which sharpen upon heating to 80 °C. Due to overlapping in the aromatic region, a conclusive variable-temperature NMR spectroscopic study could not be performed. It is obvious, however, that the free rotation of the phenyl ligands about the zirconium-ipso carbon is hindered.

Alkylation of 1a with ((trimethylsilyl)methyl)magnesium chloride in THF cleanly yields pentane-soluble, yellow bis((trimethylsilyl)methyl) complex 4 in high yields. 4 is significantly less thermally and light sensitive than the dimethyl complex 2. Like the phenyl derivative 3, 4 does not contain any coordinated THF nor does it tend to bind THF, as can be deduced from NMR spectroscopic data. The signals for the pairwise diastereotopic protons of the two equivalent (trimethylsilyl)methyl groups are detected at unusually high fields of δ -0.49 and -1.26 as an AB spin system. The geminal coupling constant is ${}^{2}J_{HH} = 10.5$ Hz, in agreement with values found for diastereotopic Zr-CH₂SiMe₃ resonances such as $Cp*Zr(\eta^6-C_5Me_4CH_2)CH_2SiMe_3^{14}$ and similar molybdenum and tungsten complexes of the type $(\eta^5 - C_5 R_5) M(NO) (CH_2 Si Me_3)_2$.¹⁵ In contrast, the electronically analogous complex $Zr(\eta^5:\eta^1-C_5H_4CH_2CH_2-$ CH₂NMe)(CH₂SiMe₃)₂, reported by Teuben et al., displays a value of only 2.1 Hz, suggesting an agostic interaction.^{6b} The high-field shifts of the signals are again due to the shielding effect of the fluorenyl

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Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for 4

Zr(1) - N(1)	2.061(2)	Zr(1) - C(20)	2.232(3)
Zr(1) - C(30)	2.248(3)	Zr(1) - C(1)	2.400(3)
Zr(1) - C(2)	2.538(3)	Zr(1) - C(13)	2.548(3)
Zr(1) - C(7)	2.695(3)	Zr(1)-C(8)	2.708(3)
C(1) - C(2)	1.454(4)	C(2)-C(7)	1.426(4)
C(7) - C(8)	1.442(4)	C(8)-C(13)	1.431(4)
C(1) - Si(1)	1.866(3)	Si(1) - N(1)	1.738(2)
C(20)-Si(2)	1.852(3)	C(30)-Si(3)	1.848(3)
N(1) - Zr(1) - C(20)	113.0(1)	N(1) - Zr(1) - C(30)	110.5(1)
C(20) - Zr(1) - C(30)	103.8(1)	N(2) - Si(1) - C(1)	95.1(1)
C(14) - Si(1) - C(15)	106.5(2)	C(40) - N(1) - Si(1)	126.3(2)
C(40) = N(1) = Zr(1)	130.1(2)	Si(1) = N(1) = Zr(1)	103.4(1)
Si(2) - C(20) - Zr(1)	136.1(2)	Si(3) - C(30) - Zr(1)	123.8(2)

Table 3. Fractional Coordinates and Equivalent Isotropic Temperature Factors (Å²) for 4^a

atom	x	у	z	$U_{ m eq}$
Zr (1)	0.98252(3)	0.20993(2)	0.08611(1)	0.02517(11)
C(1)	0.0295(3)	0.0718(2)	0.07670(15)	0.0319(7)
C(2)	0.1248(3)	0.0810(2)	0.0214(2)	0.0308(7)
C(3)	0.2690(3)	0.0573(2)	0.0149(2)	0.0403(8)
C(4)	0.3350(4)	0.0760(2)	-0.0434(2)	0.0513(10)
C(5)	0.2669(4)	0.1204(2)	-0.0958(2)	0.0536(10)
C(6)	0.1298(4)	0.1461(2)	-0.0913(2)	0.0455(9)
C(7)	0.0569(3)	0.1280(2)	-0.03158(15)	0.0319(7)
C(8)	-0.0867(3)	0.1458(2)	-0.01245(15)	0.0313(7)
C(9)	-0.2012(4)	0.1874(2)	-0.0458(2)	0.0444(9)
C(10)	-0.3284(4)	0.1935(2)	-0.0156(2)	0.0521(10)
C(11)	-0.3462(4)	0.1586(2)	0.0475(2)	0.0523(10)
C(12)	-0.2386(4)	0.1185(2)	0.0829(2)	0.0411(8)
C(13)	-0.1029(3)	0.1091(2)	0.0524(2)	0.0326(8)
Si(1)	0.09729(11)	0.05941(5)	0.16728(5)	0.0407(3)
C(14)	0.2324(5)	-0.0216(2)	0.1785(2)	0.0738(13)
C(15)	-0.0506(5)	0.0349(2)	0.2250(2)	0.0709(13)
N(1)	0.1640(3)	0.15567(14)	0.17582(12)	0.0314(6)
C(40)	0.2583(4)	0.1866(2)	0.2334(2)	0.0384(8)
C(41)	0.2126(4)	0.1534(2)	0.3010(2)	0.0621(11)
C(42)	0.4144(4)	0.1632(2)	0.2239(2)	0.0590(11)
C(43)	0.2468(4)	0.2774(2)	0.2349(2)	0.0546(10)
C(20)	-0.0656(4)	0.3070(2)	0.1017(2)	0.0424(8)
Si(2)	-0.17724(10)	0.33960(6)	0.17159(5)	0.0440(3)
C(21)	-0.2027(4)	0.2590(2)	0.2351(2)	0.0669(12)
C(22)	-0.0925(4)	0.4276(2)	0.2154(2)	0.0612(11)
C(23)	-0.3602(4)	0.3694(3)	0.1372(2)	0.0804(14)
C(30)	0.2746(3)	0.2721(2)	0.0379(2)	0.0337(7)
Si(3)	0.25578(11)	0.36774(6)	-0.00813(5)	0.0483(3)
C(31)	0.0905(5)	0.3694(3)	-0.0667(2)	0.0787(14)
C(32)	0.4132(5)	0.3840(3)	-0.0624(2)	0.092(2)
C(33)	0.2489(5)	0.4523(2)	0.0522(2)	0.0804(14)

ligand.^{15b} In the ${}^{13}C$ NMR spectrum of 4, the ZrCH₂ resonance appears at δ 57.1 with ${}^{1}J_{CH} = 104$ Hz.

One set of the aromatic protons, most probably those at the carbon atoms 4 and 5, exhibits temperaturedependent chemical shifts. This finding can be ascribed to the possibility that upon performing a full rotation about the zirconium-carbon bond the Me₃SiCH₂ groups sense the close proximity to the periphery of the fluorenyl ring.

A single-crystal X-ray diffraction analysis of 4 was performed to elucidate the details of the molecule. Crystal data are listed in Table 1. Selected bond lengths and angles are given in Table 2 and atomic parameters in Table 3. The compound adopts a three-legged piano stool configuration with a pseudotetrahedral arrangement of the four ligands (Figure 2). The fluorenyl ligand is bonded in a fashion which is between pentahapto and trihapto, as judged by the zirconium ring-carbon distances ranging from 2.400(3) to 2.708(3) Å. This distorted bonding with the bridgehead fluorenyl carbon bonded closest to the zirconium is a consequence of the molecular orbital structure of the fluorenyl anion.¹⁶ Unlike the mostly pentahapto-bound cyclopentadienyl and indenyl ligands in transition metal complexes, the



Figure 2. ORTEP view of $Zr(\eta^5:\eta^1-C_{13}H_8SiMe_2NCMe_3)(CH_2 SiMe_{3}_{2}(4)$, with thermal ellipsoids at the 50% probability level. Hydrogen atoms of methyl groups have been omitted for the sake of clarity.

fluorenyl ligand is found to be coordinated at a transition metal center in a variety of bonding modes. For zirconium complexes the η^5 -,^{1,2} η^3 -,^{2a} and η^3 -benzallyl^{4b} bonding was structurally verified. The zirconiumnitrogen bond length of 2.061(2) Å is in the typical range for an amido ligand bound to a d⁰ zirconium center with strong π -bonding: Cp*Zr(NHCMe₃)₃ 2.00(1), 2.02(1);¹⁷ MeZr[NHSi(CMe₃)₃)]₃ 2.039(7);¹⁸ [Zr(η^5 : η^1 -C₅H₄CH₂CH₂- $CH_2NMe)Cl(CH_2Ph)]_2 1.988(2);^{6b} Zr(\eta^5:\eta^1-C_5Me_4SiMe_2-NCMe_3)Cl_2 2.056(6) Å.^{19}$ In agreement with the implication of a three-electron ligand, the nitrogen atom is trigonal planar, the sum of the angles at the nitrogen atom amounting to 360°. The zirconium-carbon bond lengths of the (trimethylsilyl)methyl groups of 2.232(3) and 2.248(3) Å are in the expected region for $Zr-C(sp^3)$ bond distances and are only slightly shorter than those in $Cp_2Zr(CH_2SiMe_3)_2$ (2.278(4) and 2.281(4) Å)²⁰ or similar to that in $[Cp*_2Zr(CH_2SiMe_3)(THF)]^+$ (2.238(6) Å).21

The somewhat unexpected orientation of the two (trimethylsilyl)methyl groups is such that both the bulky (trimethylsilyl)methyl groups are turned to the same side away from the zirconium center (Figure 3). The angles at the chemically equivalent methylene carbons are 123.8(2) and $136.1(2)^{\circ}$. Thus, the angles for the two alkyl groups are significantly different. This feature cannot be implied to reflect any agostic distortion. Rather, this conformation may reflect the steric influence of the rigid $\eta^5:\eta^1-C_{13}H_8SiMe_2NCMe_3$ ligand system that forces the two (trimethylsilyl)methyl groups away form the tert-butyl group at the amido group. The "wedge" in the present ligand system therefore is more open as compared to the familiar Cp_2Zr fragment, but in a different way. From inspection of models, it is evident that completely free and independent rotation

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Figure 3. View of $Zr(\eta^5:\eta^1-C_{13}H_8SiMe_2NCMe_3)(CH_2SiMe_3)_2$ (4) perpendicular to the fluorenyl ligand.

of both the (trimethylsilyl)methyl groups about the zirconium-carbon bond is not viable. Consequently, the methyl groups at the silicon atoms come close to the sixmembered aromatic rings, in particular to the two ring protons at the carbon atoms C(6) and C(9), as was implied by ¹H NMR spectroscopic studies (vide supra). If one regards the bulky (trimethylsilyl)methyl group as a crude surrogate for a growing polypropylene chain $CH_2CH(Me)R$, it is quite evident that upon occupying the lateral site in fluorenvl-based ansa-zirconocenes. both the methyl and the polymer chain R will interfere with the ring. These steric repulsions lead to the preference of one favored conformation which allow the next incoming propylene to approach the metal only with the opposite topicity (methyl group directed away from the fluorenyl ligand), provided that the alkyl group can "swing" from one lateral site to the other.^{3d}

No thermal decomposition of 4 was observed by heating to 110 °C over 24 h. Despite being 14-electron species, the alkyl complexes 2-4 are fairly unreactive toward olefins, even activated ones such as methyl methacrylate and acrylonitrile. Hydrogenolysis as well as alkyl group abstraction to give alkyl cations is being investigated. It seems that a 12-electron metal center is required for olefin polymerization.^{5c}

Conclusion

In summary, the linked amido-fluorenyl ligand system exhibits coordination behavior at the zirconium(IV) center which differs somewhat from that of the linked fluorenyl-cyclopentadienyl ligand. The expected higher Lewis acidity results in the accessibility of pentacoordination.²² However, steric saturation of the electrondeficient (14-electron) d⁰ center is very facile, as illustrated by the solvent-free dialkyl 3 and 4. The complexes described above therefore are best considered as analogs Organometallics, Vol. 14, No. 2, 1995 793

of mono(cyclopentadienyl)zirconium complexes²³ rather than as ansa-zirconocene complexes. It is noteworthy that to the best of our knowledge, there seems to be no mono(fluorenyl) complexes of group 4 metals known. The complexes described above also constitute the first members of this class of half-sandwich complexes which we believe owe their synthetic accessibility to the chelate effect of the ancillary ligand. Finally, the molecular structure of the dialkyl 4 has revealed intramolecular steric repulsions within the $Zr(n^5:n^1-C_{13}H_8)$ SiMe₂NCMe₃) fragment that may be relevant in the context of mechanistic discussion on syndiospecific polymerization of a-olefins by fluorene-based ansametallocenes.⁷

Experimental Section

General Consideration. All operations were performed under an inert atmosphere of nitrogen using standard Schlenkline or glovebox techniques. THF and diethyl ether were distilled from sodium benzophenone ketyl. Pentane and hexane were purified by distillation from sodium/triglyme benzophenone ketyl. Dichlorodimethylsilane was distilled over copper turnings. tert-Butylamine was distilled from CaH2 and stored over molecular sieves. ZrCl₄(THF)₂²⁴ was synthesized as described in the literature. All other chemicals were commercially available and used as received. ¹H NMR and ¹³C NMR spectra were recorded in C_6D_6 at 25 °C, unless otherwise stated, on a Varian GX 400 spectrometer. The numbering scheme for the hydrogen and carbon atoms of the fluorenyl ring corresponds to that commonly used in the literature.9f Elemental analyses were performed by Oneida Research Services, Inc. and the Microanalytical Laboratory of this department.

(tert-Butylamino)dimethyl(9-fluorenyl)silane. To a solution of fluorene (16.62 g, 100 mmol) in diethyl ether (90 mL) was added at 0 °C a solution of n-butyllithium (40 mL, 100 mmol, 2.5 M in hexane) within 60 min. After stirring for 3 h at room temperature, the resulting orange solution was transferred to an addition funnel and added dropwise at 0 °C within 75 min to a solution of dichlorodimethylsilane (200 mL) in diethyl ether (200 mL). The resulting suspension was stirred for 30 min at room temperature, and the solvent and excess dichlorodimethylsilane were removed under vacuum. After precipitating lithium chloride with methylene chloride and filtering, followed by removal of the solvent, 21.75 g (84.0%) of an off-white solid was obtained. According to the ¹H NMR spectrum, the product is contaminated by 8% of bis-(9-fluorenyl)dimethylsilane. ¹H NMR (CDCl₃): δ 7.89 (dd, 2H, 1-, 8-H), 7.70 (dd, 2H, 4-, 5-H), 7.43 (dt, 2H, 2-, 7-H), 7.37 (dt, 2H, 3-, 6-H), 4.13 (s, 1H, 9-H), 0.21 (s, 6H, SiCH₃).

To a solution of this crude 9-(chlorodimethylsilyl)fluorene (21.75 g, contaminated with 8% bis(9-fluorenyl)dimethylsilane) in diethyl ether (140 mL) was added solid lithium tertbutylamide (6.05 g, 76.5 mmol) at 0 °C over a period of 1 h. Stirring overnight at room temperature gave a yellow suspension. After removal of all of the volatiles under vacuum, lithium chloride was precipitated with methylene chloride and filtered off. Removal of the solvent and distillation under vacuum (bp 108-110 °C) gave a colorless oil that crystallizes at -20 °C: yield 15.93 g (70.5%). ¹H NMR (CDCl₃): δ 7.90 $(dd, 2H, J_{HH} = 7.1, 1.5 Hz, 1-, 8-H), 7.69 (dd, 2H, J_{HH} = 7.0,$ 1.1 Hz, 4-, 5-H), 7.37 (m, 4H, 2-, 7-, 3-, 6-H), 3.97 (s, 1H, 9-H), 1.26 (s, 9H, NCCH₃), 0.72 (br s, 1H, NH), -0.03 (s, 6H, SiCH₃).

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 $^{13}\mathrm{C}$ NMR (CDCl₃): δ 145.8 (C-10, -13), 140.7 (C-11, -12), 125.9, 125.1, 124.5 (C-1, -2, -3, -6, -7, -8), 119.8 (C-4, -5), 49.7 (NCCH₃), 45.0 (C-9), 33.9 (NCCH₃), -0.8 (SiCH₃). GC MS: m/z 294 (M⁺). Anal. Calcd for C₁₉H₂₄NSi: C, 77.49; H, 8.21; N, 4.76. Found: C, 77.00; H, 8.10; N, 4.50.

[tert-Butyl(dimethylfluorenylsilyl)amido](tetrahydrofuran)dilithium. To a solution of (tert-butylamino)dimethylfluorenylsilane (0.61 g, 2.06 mmol) in 20 mL of pentane was added at -78 °C n-butyllithium (1.7 mL of a 2.5 M solution in hexane, 4.25 mmol) via syringe within 15 min. After the solution was warmed up to room temperature and stirred overnight, a precipitate formed. After filtration the yellow powder was washed with pentane and dried under vacuum. The yield is almost quantitative. Because of the insolubility in hydrocarbons and extreme air sensitivity, it was characterized by ¹H NMR spectroscopy as the tris(THF) adduct. ¹H NMR (C₆D₆): δ 8.39 (br d, 2H, 1-, 8-H), 7.96 (m, 2H, 4-, 5-H), 7.29 (br t, 2H, 2-, 7-H), 7.07 (t, 2H, 3-, 6-H), 2.79 (t, 12H, OCH₂), 1.40 (s, 9H, NCCH₃), 1.09 (m, 12H, OCH₂CH₂), 0.87 (br s, 6H, SiCH₃). ¹H NMR (C₆D₆, 70 °C): δ 8.19 (d, 2H, $J_{\rm HH} = 7.5$ Hz, 1-, 8-H), 7.91 (d, 2H, $J_{\rm HH} = 8.7$ Hz, 4-, 5-H), 7.27 (t, 2H, $J_{\text{HH}} = 8.0, 7.1 \text{ Hz}, 2., 7.\text{H}$), 6.99 (t, 2H, $J_{\text{HH}} = 7.6$ Hz, 3-, 7-H), 3.01 (m, 12H, OCH₂), 1.24 (s, 9H, NCCH₃), 1.24 (m, 12H, OCH₂CH₂), 0.87 (br s, 6H, SiCH₃).

 $[\eta^1:\eta^5$ -tert-Butyl(dimethylfluorenylsilyl)amido]dichloro-(tetrahydrofuran)zirconium (1a). A solution of (tert-butylamino)dimethylfluorenylsilane (4.79 g, 16.2 mmol) in diethyl ether (180 mL) was treated at -78 °C with *n*-butyllithium in hexane (13.0 mL of a 2.5 M solution, 32.4 mmol) within 20 min. After the solution was stirred for 2 h at -78 °C and 2 h at room temperature, the solvent was removed and the resulting orange residue redissolved in THF. $ZrCl_4(THF)_2$ was added as a solid at -78 °C over a period of 40 min, and after the solution was stirred for 2 h at -78 °C, it was gradually warmed up to room temperature. After overnight stirring, all volatiles were removed under vacuum and LiCl was precipitated with toluene and filtered off. The filtrate was concentrated to ca. 5 mL and, after addition of pentane, was cooled to -30 °C to afford a yellow microcrystalline precipitate. Concentration of the filtrate and precipitation with pentane yielded a second crop: total yield 4.80 g (56.1%). ¹H NMR $(C_6D_5CD_3)$: δ 7.92 (d, 2H, $J_{HH} = 7.9$ Hz, 1-, 8-H), 7.76 (d, 2H, $J_{\rm HH}$ = 7.7 Hz, 4-, 5-H), 7.31 (dt, 2H, $J_{\rm HH}$ = 7.9, 7.2 Hz, 2-, 7-H), 7.14 (dt, 2H, $J_{\rm HH}$ = 7.3, 7.7 Hz, 3-, 6-H), 2.43 (br t, 4H, OCH₂), 1.64 (s, 9H, NCCH₃), 0.75 (br t, 4H, OCH₂CH₂), 0.52 (s, 6H, SiCH₃). ¹³C{¹H} NMR (C₆D₅CD₃): δ 140.5 (C-10, -13), 137.3 (C-11, -12), 126.5 (C-3, -6), 122.8 (C-1, -8), 120.9 (C-4, -5), 120.4 (C-2, -7), 95.8 (C-9), 73.6 (OCH₂), 59.9 (NCCH₃), 33.7 (NCCH₃), 25.0 (OCH₂CH₂), 1.6 (SiCH₃). Anal. Calcd for $C_{27}H_{39}Cl_2NO_2SiZr:\ C,\ 54.06;\ H,\ 6.55;\ N,\ 2.34.\ Found:\ C,$ 54.57; H, 6.33; N, 2.57.

[η¹:η⁵-tert-Butyl(dimethylfluorenylsilyl)amidoldichloro-(diethyl ether)zirconium (1b). This compound was synthesized from ZrCl₄(Et₂O)₂ in a manner analogous to that described for the preparation of 1a and isolated as yellow microcrystals: yield 50%. ¹H NMR (C₆D₆): δ 7.99 (d, 2H, J_{HH} = 7.8 Hz, 1-, 8-H), 7.78 (d, 2H, J_{HH} = 7.7 Hz, 4-, 5-H), 7.34 (dt, 2H, J_{HH} = 7.9, 7.2 Hz, 2-, 7-H), 7.15 (dt, 2H, J_{HH} = 7.3, 7.7 Hz, 3-, 6-H), 2.60 (br, 4H, OCH₂), 1.67 (s, 9H, NCCH₃), 0.74 (br, 6H, OCH₂CH₃), 0.54 (s, 6H, SiCH₃). ¹³C{¹H} NMR (C₆D₆): δ 140.6 (C-10, -13), 137.4 (C-11, -12), 126.6 (C-3, -6), 122.9 (C-1, -8), 120.4 (C-4, -5), 120.5 (C-2, -7), 96.0 (C-9), 73.0 (OCH₂), 60.0 (NCCH₃), 33.8 (NCCH₃), 25.1 (OCH₂CH₃), 1.6 (SiCH₃).

 $[\eta^1:\eta^5$ -tert-Butyl(dimethylfluorenylsilyl)amido]dimethyl(tetrahydrofuran)zirconium (2). Methylmagnesium chloride in THF (1.45 mL, 4.35 mmol, 2.5 M) was added to a solution of zirconium dichloro complex 1a (1.13 g, 2.14 mmol) in THF (60 mL) at -78 °C within 15 min. After stirring for 1 h at -78 °C, the reaction mixture was gradually warmed up to -20 °C and stirred for an additional hour below -15 °C. The solvent was removed under vacuum, keeping the temperature below -15 °C. Warming up of the reaction mixture above 0 °C led to almost spontaneous darkening and complete decomposition. Extraction of the residue with a 1:1 mixture of pentane and toluene (60 mL) gave, after evaporating all volatiles, a thermally and light-sensitive yellow powder: yield 0.60 g (59.0%). ¹H NMR (C₆D₆): δ 7.92 (d, 2H, J_{HH} = 7.8 Hz, 1-, 8-H), 7.79 (d, 2H, $J_{\rm HH}$ = 7.8 Hz, 4-, 5-H), 7.30 (dt, 2H, $J_{\rm HH}$ = 8.1, 7.8, 1.2 Hz, 2-, 7-H), 7.19 (dt, 2H, $J_{\rm HH}$ = 8.1, 7.8, 1.2 Hz, 3-, 6-H), 2.32 (br m, 4H, OCH₂), 1.60 (s, 9H, NCCH₃), 0.82 (br m, 4H, OCH₂CH₂), 0.62 (s, 6H, SiCH₃), 0.32 (s, 6H, ZrCH₃). ¹³C NMR (C₆D₆): δ 140.9 (C-10, -13), 134.2 (C-11, -12), 125.6 (C-3, -6), 121.3 (C-1, -8), 120.9 (C-4, -5), 120.8 (C-2, -7), 86.2 (C-9), 71.2 (OCH₂), 57.3 (NCCH₃), 40.6 (q, $J_{CH} = 114$ Hz, ZrCH₃), 34.8 (NCCH₃), 25.0 (OCH₂CH₂), 3.8 (SiCH₃). Anal. Calcd for C₂₅H₃₇NOSiZr: C, 61.67; H, 7.66; N, 2.80. Found: C, 60.51; H, 7.47; N, 2.61.

[n¹:n⁵-tert-Butyl(dimethylfluorenylsilyl)amido]diphenylzirconium (3). Phenylmagnesium chloride (0.93 mL, 1.86 mmol, 2.0 M in THF) was added via syringe to a solution of the dichloro complex 1a (0.49 g, 0.93 mmol) in diethyl ether (50 mL) at -78 °C. The reaction mixture was allowed to warm up to -15 °C and stirred for 2.5 h below -10 °C. The solvent was removed under vacuum, keeping the temperature below 0 °C. When the reaction mixture warmed up to room temperature, extensive decomposition occurred, as observed by darkening of the mixture. Extraction of the residue with a 1:1 mixture of pentane and toluene (60 mL), followed by filtration and evaporating of all volatiles, gave the product as a yellow powder in 40% yield. ¹H NMR ($C_6D_5CD_3$): δ 7.82 (d, 2H, $J_{\rm HH} = 8.3$ Hz, 1-, 8-H), 7.79 (d, 2H, $J_{\rm HH} = 8.6$ Hz, 4-, 5-H), 7.29 (br, 4H, C₆H₅), 6.99 (br m, 6H, C₆H₅); 6.89 (t, 2H, $J_{HH} =$ 7.7, 7.0 Hz, 2-, 7-H); 6.66 (t, 2H, $J_{\rm HH}$ = 7.7, 7.0 Hz, 3-, 6-H), 1.22 (s, 9H, NCCH_3), 0.86 (s, 6H, SiCH_3). $^{13}\mathrm{C}$ NMR (C_6D_6): δ 188.5 (p-C_6H_5), 136.3 (C-10, -13), 135.3 (C-11, -12), 135.1 (p-C_6H_5), 135.1 (p-C C₆H₅), 128.0 (C-3, -6), 126.4 (C-1, -8), 124.5 (C-4, -5), 123.9 (C-2, -7), 68.1 (C-9), 57.2 (NCCH₃), 34.0 (NCCH₃), 6.5 (SiCH₃). Anal. Calcd for C25H37NOSiZr: C, 69.10; H, 6.17; N, 2.60. Found: C, 69.18; H, 6.37; N, 2.39.

 $[\eta^1:\eta^5$ -tert-Butyl(dimethylfluorenylsilyl)amido{bis-(trimethylsilyl)methyl}zirconium (4). A solution of ((trimethylsilyl)methyl)magnesium chloride (6 mL, 1.0 M solution in ether, 6 mmol) was added via syringe to a solution of the zirconium dichloro complex 1a (1.14 g, 2.16 mmol) in 70 mL of diethyl ether at -78 °C within 15 min. After the addition was complete, the reaction mixture was warmed up to 0 °C and left stirring for 4 h. The solvent was removed under vacuum, leaving a yellow powder. Extraction of the residue with pentane (60 mL), filtration, concentration, and crystallization at 0 $^{\circ}C$ afforded 1.10 g (91.0%) of yellow needles. ^{1}H NMR (C₆D₆): δ 7.84 (d, 2H, J_{HH} = 7.1 Hz, 1-, 8-H), 7.80 (d, 2H, $J_{\rm HH}$ = 7.9 Hz, 4-, 5-H), 7.13 (dt, 2H, $J_{\rm HH}$ = 8.1, 7.7, 1.0 Hz, 2-, 7-H); 7.19 (dt, 2H, $J_{\rm HH}$ = 8.1, 7.0, 1.2 Hz, 3-, 6-H), 1.33 (s, 9H, NCCH₃), 0.77 (s, 6H, SiCH₃), 0.09 (s, 9H, CH₂SiCH₃), -0.49 (d, $J_{\text{HH}} = 10.5$, ZrCH_2), -1.26 (d, $J_{\text{HH}} = 10.5$, ZrCH_2). ¹³C NMR (C₆D₅CD₃): δ 135.7 (C-10, -13), 128.3 (C-3, -6), 126.2 $(C\text{-}1, \text{-}8), 123.8 \, (C\text{-}4, \text{-}5), 123.6 \, (C\text{-}2, \text{-}7), 120.2 \, (C\text{-}11, \text{-}12), 74.3$ (C-9), 57.2 (t, $ZrCH_2$), $J_{CH} = 104$ Hz), 56.1 (NCCH₃), 34.2 $(NCCH_3)$, 6.5 $(SiCH_3)$, 3.6 (CH_2SiCH_3) . Anal. Calcd for C₂₇H₄₅NSi₃Zr: C, 58.00; H, 8.11; N, 2.51. Found: C, 57.49; H, 7.92; N, 2.30.

X-ray Structure Determination. Crystal data for **4** are summarized in Table 1. The compound, obtained as yellow crystals by slow cooling of an *n*-pentane solution, crystallizes in the monoclinic space group $P2_1/n$. Data collection in the range $2^{\circ} < \theta < 22.5^{\circ}$ was performed using ω -scans on an Siemens P4 diffractometer with graphite-monochromated Mo K α radiation. From 5252 measured reflections, all 3987 independent reflections were used and 289 parameters were refined by full-matrix least-squares on F_0^2 data (SHELXL-

Linked Amido-Fluorenyl Ligand in Zr Complexes

93).²⁵ The structure was solved using direct methods (SHELXS-86)²⁶ and difference Fourier syntheses and refined with anisotropic thermal parameters for the non-hydrogen atoms. All hydrogen atoms were located and refined isotropically. Refinements converged with residuals of $wR_2 = 0.079$ for all F_0^2 data corresponding to R = 0.0308 for 3241 observed reflections with $F_0^2 > 46(F)$.

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(26) Sheldrick, G. M. SHELXS-86, Program for the Solution of Fonds der Chemischen Industrie, General Electric Co., and the donors of the Petroleum Research Fund, administered by the American Chemical Society. Part of this work was performed at the State University of New York at Albany. We are indebted to Professor J. E. Bercaw for helpful discussions and communicating unpublished results.

Supplementary Material Available: Listings of all crystal data and refinement parameters, atomic parameters including hydrogen atoms, thermal parameters, and bond lengths and angles for 4 (8 pages). Ordering information is given on any current masthead page.

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