Tripodal Amido Ligands Containing an "Active" Ligand Periphery

Harald Memmler, Kevin Walsh, and Lutz H. Gade*

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

Joseph W. Lauher

Department of Chemistry, State University of New York, Stony Brook, New York 11794

Received February 15, 1995[⊗]

The trifunctional trisilylmethane-derived amine $HC\{SiMe_2NH(2\text{-}FC_6H_4)\}_3$ (**1**) has been prepared which contains fluorine atoms in the ligand periphery which may act as additional donor functions in its amido complex derivatives. Lithiation with *n*-BuLi and reaction with YCl_3 yields the seven-coordinate yttrium complex $HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3Y(OEt_2)$ (**3**) which has been structurally characterized by X-ray crystallography: triclinic, $P\bar{1}$ (No. 2), $a = 9.4244(2)$ Å, $b = 10.5951(3)$ Å, $c = 16.6929$ Å, $\alpha = 93.280(8)°$, $\beta = 91.918(7)°$, $\gamma = 93.465(8)°$, $Z = 2$, $V = 1659.9(1)$ Å^3, and $R = 0.062$. All three fluorine donor atoms are coordinated to the yttrium center ($^1J(^{89}Y-^{19}F) = 5.3$ Hz at 295 K). Rapid dynamic processes in solution which cannot be frozen out at 180 K confer an effective 3-fold symmetry upon the molecule at ambient temperature. Reaction of lithiated **1** with $ZrCl_4$ in diethyl ether yields the $(\mu\text{-}Cl)_2$-bridged complex $HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3ZrCl_2Li(OEt_2)_2$ (**4**) which has one peripheral F-atom weakly coordinated to the Zr-center as established analytically and by an X-ray structure analysis: monoclinic, $P2_1/a$ (No. 14), $a = 13.4123(2)$ Å, $b = 18.0086(3)$ Å, $c = 17.3750(3)$ Å, $\beta = 90.391(7)°$, $Z = 4$, $V = 4196.6(2)$ Å^3, and $R = 0.048$. Reaction of **4** with MeLi gives the methyl-zirconium compound $HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3ZrCH_3$ (**5**) while upon condensation with $[CpFe(CO)_2]^-$ the dinuclear Zr−Fe-bonded complex $HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3ZrFe(CO)_2Cp$ (**6**) is obtained. The spectroscopic data and structural considerations indicate that in **5** all three F-donors are bonded to Zr whereas in **6** all are uncoordinated, demonstating the coordinative flexibility of the ancillary donor functions in the tripodal amido complexes derived from **1**.

Introduction

The recent introduction of tripodal amido ligands to the coordination chemistry of early transition elements[1−3] has enabled the stabilization of otherwise labile molecular fragments at the metal centers[4] as well as unusual complex geometries[5] and early−late transition heterobimetallics.[6] This stabilizing effect is due to a combination of electronic and steric factors of the ligands. The σ- and π-donor capabilities of the amido-N atoms partially saturate the electronic demands of a high valent highly Lewis acidic metal center, while the *ligand framework* and *ligand periphery* shield most of the coordination sphere around the metal. Furthermore, they define the size of the *binding site* offered by the ligand as well as the geometry and size of the *active site* at the metal center in the complexes containing tripod amides (Figure 1).

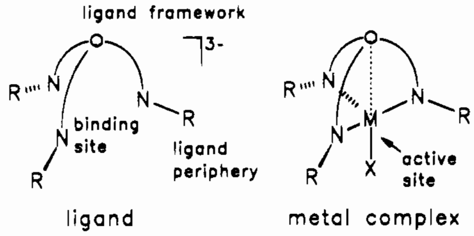


Figure 1. Coordination properties of tripodal amido ligands.

We have recently studied a series of related tripodal amides containing neopentane-,[7,8] trisilylmethane-,[9,10] and trisilylsilane-frameworks[11] which generate more open complex geometries than found in the azatranes investigated by Verkade, Schrock, and others.[1−5] One of the aims of this research effort was the construction of building blocks for stable dinuclear complexes containing an unsupported metal−metal bond between early and late transition elements.[6,12] On the other hand, the less efficient steric protection offered by these systems in comparison to the azatranes, and thus increased chemical reactivity and sensitivity has been a limiting factor in their application to a wider range of metals. We were therefore interested in the development of ligands which combine an efficient shielding of the metal with

---

[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1995.

(1) Verkade, J. G. *Acc. Chem. Res.* **1993,** *26,* 483.

(2) (a) Naiini, A. A.; Menge, W. M. P. B.; Verkade, J. G. *Inorg. Chem.* **1991,** *30,* 5009. (b) Menge, W. M. P. B.; Verkade, J. G. *Inorg. Chem.* **1991,** *30,* 4628. (c) Plass, W.; Verkade, J. G. *J. Am. Chem. Soc.* **1992,** *114,* 2275. (d) Plass, W.; Verkade, J. G. *Inorg. Chem.* **1993,** *32,* 3762.

(3) (a) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Organometallics* **1992,** *11,* 1452. (b) Kol, M.; Schrock, R. R.; Kempe, R.; Davis, W. M. *J. Am. Chem. Soc.* **1994,** *116,* 4382. (c) Schubart, M.; O'Dwyer, L.; Gade, L. H.; Li, W.-S.; McPartlin, M. *Inorg. Chem.* **1994,** *33,* 3893.

(4) (a) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 756. (i) Cristou, V.; Arnold, J. *Angew. Chem., Int. Ed. Engl.* **1993,** *32,* 1450. (j) Cummins, C. C.; Schrock, R. R.; Davis, W. M. *Inorg. Chem.* **1994,** *33,* 1448.

(5) Cummins, C. C.; Lee, J.; Schrock, R. R.; Davis, W. M. *Angew. Chem., Int. Ed. Engl.* **1992,** *31,* 1501.

(6) Friedrich, S.; Memmler, H.; Gade, L. H.; Li, W.-S.; McPartlin, M. *Angew. Chem., Int. Ed. Engl.* **1994,** *33,* 676.

(7) (a) Gade, L. H.; Mahr, N. *J. Chem. Soc., Dalton Trans.* **1993,** 489. (b) Hellmann, K. W.; Gade, L. H.; Li, W.-S.; McPartlin, M. *Inorg. Chem.* **1994,** *33,* 5974.

(8) (a) Friedrich, S.; Gade, L. H.; Edwards, A. J.; McPartlin, M. *Chem. Ber.* **1993,** *126,* 1797. (b) Hellmann, K. W.; Friedrich, S, Gade, L. H.; Li, W. S.; McPartlin, M. *Chem. Ber.* **1995,** *128,* 29.

(9) Gade, L. H.; Becker, C.; Lauher, J. W. *Inorg. Chem.* **1993,** *32,* 2308.

(10) (a) Memmler, H.; Gade, L. H.; Lauher, J. W. *Inorg. Chem.* **1994,** *33,* 3064. (b) Hellmann, K. W.; Steinert, P.; Gade, L. H. *Inorg. Chem.* **1994,** *33,* 3859.

(11) Schubart, M.; Findeis, B.; Gade, L. H.; Li, W.-S.; McPartlin, M. *Chem. Ber.* **1995,** *128,* 329.

(12) Herberhold, M.; Jin, G.-X. *Angew. Chem., Int. Ed. Engl.* **1994,** *33,* 964.

0020-1669/95/1334-4062$09.00/0

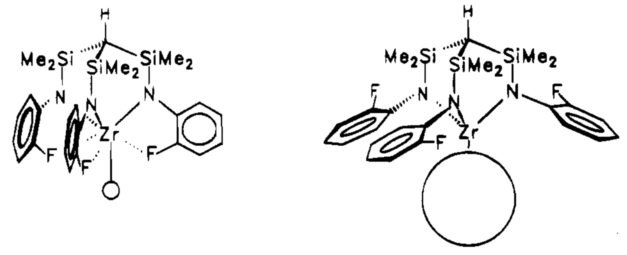


Figure 2. Steric adjustment of the "active" periphery in a 2-fluorophenyl-substituted tris(amidosilyl)methane ligand.

a potentially increased space at the reactive site. In analogy to the application of functionalized phosphines with additional labile donor functionalities in the coordination chemistry of late transition elements,[13] the synthesis of a tripod amide containing such additional donor functions in its ligand periphery (an *active* ligand periphery) was the chosen strategy.

In this paper we present an example of the facile implementation of this concept: the introduction of weak donor functions (fluorine atoms) in the *ortho* position of phenyl-substituted tris(aminosilyl)methanes (Figure 2) and the coordination of the tripodal amine thus obtained as an amido ligand to Y(III) and Zr(IV). While there are a few examples of C−F••M (M = transition metal) bonding in the literature,[14,15] this is the first time that this type of interaction is specifically "built into" a ligand system.

Experimental Section

All manipulations were performed under an inert gas atmosphere of dried argon in standard (Schlenk) glassware which was flame-dried with a Bunsen burner prior to use. Solvents were dried according to standard procedures and saturated with Ar. The deuterated solvents used for the NMR spectroscopic measurements were degassed by three successive "freeze−pump−thaw" cycles and dried over 4-Å molecular sieves.

The ^{1}H-, ^{13}C-, ^{29}Si-, ^{19}F-, and ^{7}Li-NMR spectra were recorded on a Bruker AC 200 spectrometer equipped with a B-VT-2000 variable temperature unit (at 200.13, 50.32, 39.76, and 188.31 MHz, respectively) with tetramethylsilane, $CFCl_3$ and LiI/H_2O (external) as references. Infrared spectra were recorded on Perkin-Elmer 1420 and Bruker IRS 25 FT-spectrometers.

Elemental analyses were carried out in the microanalytical laboratory of the chemistry department at Würzburg. $HC(SiMe_2Br)_3$ was prepared according to the literature procedure.[9,16] *o*-Fluoroaniline employed in the ligand synthesis was distilled before use. All other chemicals used as starting materials were obtained commercially and used without further purification.

Preparation of Compounds. HC{SiMe$_2$NH(2-FC$_6$H$_4$)}$_3$ (1). Over a period of 30 min a solution of $HC(SiMe_2Br)_3$ (4.40 g = 8.50 mmol) in 50 mL of diethyl ether was added to a stirred mixture of 3.44 g (28.0 mmol) of 2-fluoroaniline and triethylamine (5 mL = 3.60 mmol) in 200 mL diethyl ether which was cooled at 0 °C with an ice bath. Subsequently, the reaction mixture was stirred at room temperature for 10 h, the triethyl ammonium bromide removed by filtration through a G3 frit and the solvent of the filtrate evaporated *in vacuo*. The colorless residue was dissolved in 20 mL of diethyl ether and the solution stored at −30 °C to yield **1** as a highly crystalline colorless solid. Yield: 4.36 g (82%). Mp: 101 °C. Anal. Calcd for $C_{25}H_{34}F_3N_3Si_3$: C, 57.99; H, 6.62; N, 8.11. Found: C, 57.59; H, 6.49; N, 7.98. ^{1}H-NMR ($CDCl_3$, 295 K): δ = 0.51 (s, Si(C*H*$_3$)$_2$), 1.02 (s, *H*C(Si...)$_3$), 3.99 (d, $^3J_{FH}$ = 3.4, N*H*), 6.51−7.09 (m, 2-FC$_6$*H*$_4$). {^{1}H}^{13}C-NMR ($CDCl_3$, 295 K): δ = 3.2 (Si(*C*H$_3$)$_2$), 4.4 (H*C*(Si...)$_3$), 115.7 (d, $^2J_{FC}$ = 20.4, C^3), 117.2 (C^5), 118.2 (d, $^3J_{FC}$ = 6.8, C^4), 125.1 (C^6), 135.6 (d, $^2J_{FC}$ = 13.1, C^1), 153.0 (d, $^1J_{FC}$ = 241.1, C^2). {^{1}H}^{29}Si-NMR ($CDCl_3$, 295 K): δ = 2.5. {^{1}H}^{19}F-NMR ($CDCl_3$, 295 K): δ = −119.2. IR (KBr): 3393 (m), 3015 (w), 2948 (w), 2795 (w), 1611 (s), 1587 (w), 1494 (vs), 1457 (w), 1379 (m), 1300 (vs), 1262 (s), 1251 (s), 1235 (s), 1178 (m), 1147 (w), 1091 (m), 1030 (m), 998 (m), 890 (vs), 831 (vs), 792 (s), 768 (s), 739 (s), 682 (m), 641 (w) cm^{-1}.

HC{SiMe$_2$N(Li)(2-FC$_6$H$_4$)}$_3$(OEt$_2$)$_2$ (2). To a solution of **1** (1.0 g = 1.9 mmol) in diethyl ether which was cooled at −78 °C was added dropwise 2.3 mL of a solution of *n*-BuLi (2.5 M in hexanes). The reaction mixture was warmed to room temperature and stirred for another 1 h. After removal of the solvent *in vacuo* the lithium amide **2** was obtained as an extremely air and moisture sensitive colorless microcrystalline solid in quantitative yield. Anal. Calcd for $C_{33}H_{51}F_3N_3Si_3Li_3O_2$: C, 57.92; H, 7.52; N, 6.14. Found: C, 57.78; H, 7.58; N, 6.33. ^{1}H-NMR (C_6D_6, 295 K): δ = −0.73 (s, *H*C(Si...)$_3$), 0.56 (s, Si(C*H*$_3$)$_2$), 0.60 (t, $^3J_{HH}$ = 7.0 Hz, OCH$_2$C*H*$_3$), 2.79 (q, OC*H*$_2$CH$_3$), 6.32−6.99 (m, 2-FC$_6$*H*$_4$). {^{1}H}^{13}C-NMR (C_6D_6, 295 K): δ = 6.4 (Si(*C*H$_3$)$_2$), 9.5 (H*C*(Si...)$_3$), 14.1 (OCH$_2$*C*H$_3$), 64.8 (O*C*H$_2$CH$_3$), 113.4, 123.5, 125.7 (C$^{4-6}$), 113.9 (d, $^2J_{FC}$ = 22.7, C^3), 147.6 (br, C^1), 159.5 (d, $^1J_{FC}$ = 177.8, C^2). {^{1}H}^{19}F-NMR (C_6D_6, 295 K): δ = −141.1.

HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$Y(OEt$_2$) (3). To a solution of **2** prepared as described above by lithiation of 2.0 g (3.9 mmol) of **1** in 40 mL of diethyl ether which was cooled at −78 °C was added 800 mg (4.1 mmol) of solid YCl_3. After warming to ambient temperature over a period of 8 h and addition of 20 mL of pentane (in order to precipitate the LiCl formed), the reaction mixture was filtered through a G3 frit. The filtrate was concentrated to 20 mL and stored at −30 °C to yield **3** as a colorless crystalline solid. Yield: 1.56 g (58%). Mp: 97 °C (dec.). Anal. Calcd for $C_{29}H_{41}F_3N_3Si_3OY$: C, 53.04; H, 5.85; N, 5.99. Found: C, 52.91; H, 5.93; N, 6.17. ^{1}H-NMR (C_6D_6, 295 K): δ = −0.44 (s, *H*C(Si...)$_3$), 0.58 (s, Si(C*H*$_3$)$_2$), 0.69 (t, $^3J_{HH}$ = 7.0 Hz, OCH$_2$C*H*$_3$), 3.19 (q, OC*H*$_2$CH$_3$), 6.33−6.94 (m, 2-FC$_6$*H*$_4$). {^{1}H}^{13}C-NMR (C_6D_6, 295 K): δ = 5.8 (Si(*C*H$_3$)$_2$), 8.3 (H*C*(Si...)$_3$), 13.3 (OCH$_2$*C*H$_3$), 55.6 (O*C*H$_2$CH$_3$), 113.7 (br, C^3), 121.5, 125.0, 125.1 (C$^{4-6}$), 145.0 (br, C^1), 153.0 (d, $^1J_{FC}$ = 241.1, C^2). {^{1}H}^{29}Si-NMR (C_6D_6, 295 K): δ = −4.1. {^{1}H}^{19}F-NMR (C_6D_6, 295 K): δ = −124.4 (d, $^1J_{YF}$ = 5.3). IR (Nujol): 1600 (m), 1496 (m), 1465 (vs), 1310 (m), 1299 (s), 1288 (m), 1275 (m), 1250 (m), 1230 (m), 1075 (m), 1020 (m), 1008 (m), 983 (m), 810 (vs), 762 (w), 729 (m) cm^{-1}.

HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$ZrCl$_2$Li(OEt$_2$)$_2$ (4). To a solution of **2** prepared as described above by lithiation of 1.67 g (3.2 mmol) of **1** in 40 mL diethyl ether which was cooled at −78 °C was added 800 mg (3.4 mmol) of solid $ZrCl_4$. After warming to ambient temperature over a period of 8 h, the reaction solution was decanted from the LiCl formed in the conversion. Upon slow removal of the solvent the colorless product **4** precipitated as single crystals. Yield: 1.33 g (50%). Mp: 88 °C (dec.). Anal. Calcd for $C_{33}H_{51}Cl_2F_3LiN_3Si_3O_2Zr$: C, 47.63; H, 6.18; N, 5.05. Found: C, 47.79; H, 5.86; N, 5.09. ^{1}H-NMR (THF-d_8, 320 K): δ = 0.44 (s, Si(C*H*$_3$)$_2$), 0.54 (s, *H*C(Si...)$_3$), 1.20 (t, $^3J_{HH}$ = 7.0 Hz, OCH$_2$C*H*$_3$), 3.47 (q, OC*H*$_2$CH$_3$), 6.81−7.09 (m, 2-FC$_6$*H*$_4$). {^{1}H}^{13}C-NMR (THF-d_8, 320 K): δ = 5.5 (Si(*C*H$_3$)$_2$), 8.0 (H*C*(Si...)$_3$), 17.0 (OCH$_2$*C*H$_3$), 57.6 (O*C*H$_2$CH$_3$), 116.7 (d, $^2J_{FC}$ = 23.4, C^3), 123.0, 126.1, 128.1 (C$^{4-6}$), 142.9 (br, C^1), 160.2 (d, $^1J_{FC}$ = 235.1, C^2). {^{1}H}^{29}SiNMR (THF-d_8, 295 K): δ = 4.3, 5.8 (int. 1:2). {^{1}H}-^{19}F-NMR (THF-d_8, 295 K): δ = −120.1, −121.6. ^{7}Li-NMR (THF-d_8): δ = 1.4. IR (Nujol): 1615 (m), 1500 (s), 1487 (vs), 1310 (m), 1290 (w), 1258 (s), 1242 (m), 1093 (m), 1029 (m), 977 (w), 920 (w), 859 (m), 828 (vs), 796 (s), 690 (s) cm^{-1}.

HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$ZrCH$_3$ (5). To a stirred solution of **4** (0.5 g = 0.6 mmol) in 20 mL of diethyl ether which was cooled at −78 °C was added 0.4 mL of MeLi (1.7 M in diethyl ether). The reaction mixture was slowly warmed to room temperature over a period of 9 h, and the solution was subsequently decanted from the LiCl. Upon concentration of the solution *in vacuo* the product **5** preciptated in colorless crystals. Yield: 330 mg (88%). Mp: 82 °C (dec.). Anal. Calcd for $C_{26}H_{34}F_3N_3Si_3Zr$: C, 50.28; H, 5.52; N, 6.77. Found: C, 50.11; H, 5.73; N, 6.62. ^{1}H-NMR (C_6D_6, 295 K): δ = −0.46 (s, *H*C-(Si...)$_3$), 0.37 (s, Si(C*H*$_3$)$_2$), 0.65 (q, $^3J_{FH}$ = 8.4, C*H*$_3$-Zr), 6.44 - 6.85 (m, 2-FC$_6$*H*$_4$). {^{1}H}^{13}C-NMR (C_6D_6, 295 K): δ = 4.3 (Si(*C*H$_3$)$_2$), 6.3 (H*C*(Si...)$_3$), 47.3 (q, $^2J_{FC}$ = 17.6, *C*H$_3$-Zr), 114.6 (d, $^2J_{FC}$ = 22.0, C^3),

---

(13) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27.

(14) Siedle, A. R.; Newmark, R. A.; Lamanna, W. M.; Huffman, J. C. *Organometallics* **1993**, *12*, 1491.

(15) Catalá, R.-M.; Cruz-Garritz, D.; Sosa, P.; Terreros, P.; Torrens, H.; Hills, A.; Hughes, D. L.; Richards, R. L. *J. Organomet. Chem.* **1989**, *359*, 219.

(16) Eaborn, C.; Hitchcock, P. B.; Lickiss, P. D. *J. Organomet. Chem.* **1983**, *252*, 281.

Table 1. Crystal Data and Experimental Details for **3** and **4**

	3	**4**
empirical formula	$C_{29}H_{41}F_3N_3OSi_3Y$	$C_{33}H_{51}N_3F_3O_2Si_3Cl_2LiZr$
fw	677.82	832.10
cryst syst	triclinic	monoclinic
cell params		
a (Å)	9.4244(2)	13.4123(2)
b (Å)	10.5951(3)	18.0086(3)
c (Å)	16.6929(3)	17.3750(3)
α (deg)	93.280(8)	-
β (deg)	91.918(7)	90.391(7)
γ (deg)	93.465(8)	-
V (Å$^{3)}$	1659.9(1)	4196.6(2)
Z	2	4
D_{calcd} (g cm^{-3})	1.356	1.317
space group	*P*-1 (no. 2)	$P2_1$/a (no. 14)
F_{000}	704	1728
μ(Mo Kα) (cm^{-1})	19.14	5.12
2θ(max) (deg)	49.9	44.0
no. of observns, $I > 3\sigma(I)^b$	2374	2849
no. of variables^c	333	388
residuals *R*; $R_w{}^d$	0.062; 0.067	0.048; 0.056
goodness of fit	2.07	1.88
data/parameter	7.13	7.34

[a] An empirical absorption correction, using the program DIFABS (Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A,* **1983**, *39*, 158) was applied to all three crystals; the data were corrected for Lorentz and polarization effects. [b] The intensities of three representative reflections were measured every 60 min of X-ray exposure time; they remained constant throughout the data collection indicating in every case crystal and electronic stability (no decay correction was applied). [c] Neutral atom scattering factors were taken from Cromer, D. T.; Waber, J. T. *International Tables of X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974. Anomalous dispersion effects were included in the final F_{calc} (Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.). [d] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2}$.

120.0, 122.0, 125.9 (C^{4-6}), 139.8 (d, $^2J_{FC}$ = 14.0, C^1), 158.7 (d, $^1J_{FC}$ = 224.8, C^2). {^{1}H}^{19}F-NMR (C_6D_6, 295 K): δ = −121.3. IR (Nujol): 1621 (m), 1500 (s), 1476 (vs), 1310 (s), 1285 (s), 1266 (s), 1253 (s), 1246 (s) 1062 (m), 1036 (m), 968 (w), 937 (m), 823 (vs), 739 (s), 727 (m) cm^{-1}.

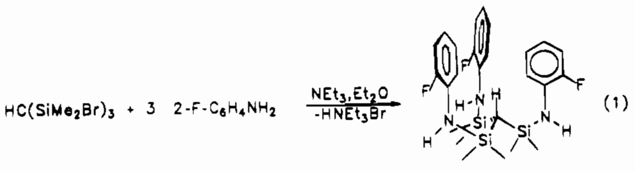
HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$ZrFe(CO)$_2$Cp (6). Solid K[Fe(CO)$_2$Cp] (53 mg = 0.24 mmol) was added to a solution of **4** (200 mg = 0.241 mmol) in toluene (30 mL) cooled at −30 °C, and the reaction mixture was warmed to room temperature over a period of 20 h. Filtration through a G3 frit to remove the alkali metal chlorides yielded an orange solution consisting mainly of the heterobimetallic product and about 5−10% of $[CpFe(CO)_2]_2$. Evaporation of the solvent and washing of the residue with cold toluene gave the reaction product **6** as a yellow microcrystalline solid. Depending upon the amount of $[CpFe(CO)_2]_2$ formed, the products obtained were pale or deep yellow. Recrystallization of the crude product yielded the pure compound as a pale yellow solid. Yield: 63 mg (34%). Due to the extreme air and moisture sensitivity, a satisfactory elemental analysis could not be obtained. ^{1}H-NMR (C_6D_6, 295 K): δ = −0.63 (s, *H*C(Si...)$_3$), 0.39 (s, Si(C*H*$_3$)$_2$), 3.66 (s, C$_5$*H*$_5$), 6.59 - 8.25 (m, 2-FC$_6$*H*$_4$). {^{1}H}^{13}C-NMR (C_6D_6, 295 K): δ = 4.0 (Si(*C*H$_3$)$_2$), 4.3 (H*C*(Si...)$_3$), 83.4 (s, *C*$_5$H$_5$), 116.1 (d, $^2J_{FC}$ = 21.7, C^3), 124.2, 124.8, 129.6 (C^{4-6}), 137.5 (d, $^2J_{FC}$ = 14.3, C^1), 158.2 (d, $^1J_{FC}$ = 240.4, C^2). {^{1}H}^{19}F-NMR (C_6D_6, 295 K): δ = −120.5. {^{1}H}^{29}Si-NMR (C_6D_6, 295 K): δ = 1.6. IR (toluene) ν(CO) = 1967, 1915 cm^{-1}.

X-ray Crystallographic study of 3 and 4. The crystals of both compounds were colorless and had a block shaped prismatic habit. A fragment of a crystal of **3** with the approximate dimensions 0.250 × 0.350 × 0.400 mm was mounted under argon in a Lindemann capillary. An irregular fragment of a crystal of **4** having the approximate dimensions 0.600 × 0.350 × 0.150 mm was mounted in a similar way. The X-ray diffraction data were collected using an Enraf Nonius CAD 4A diffractometer with graphite monochromated Mo-K$_\alpha$ radiation. Unit cell parameters were determined by a least-squares analysis of 25 automatically centered reflections in the range 20° < 2θ < 30°. Data were collected at 22 ± 1 °C using the ω/2θ scan technique with full details presented in Table 1.

The data analysis and refinement was carried out with the programs of the TEXSAN software package. Both structures were solved by using direct methods and the non-hydrogen atoms were refined anisotropically. The ethyl groups in the yttrium-bound diethyl ether molecule in **3** were severely disordered, and the C-positions of one of the ethyl groups could only be refined isotropically while the positions and thermal factors of the other ethyl function were fixed (as found in the difference Fourier map) throughout the refinement. All H-atoms were assigned calculated positions and were included in the final full-matrix refinement.

Results and Discussion

Preparation of HC{SiMe$_2$NH(2-FC$_6$H$_4$)}$_3$ (1) and Its Conversion to the Amide Transfer Reagent HC{SiMe$_2$N-(Li)(2-FC$_6$H$_4$)}$_3$(Et$_2$O)$_2$ (2). The tripodal amine precursor of the amido ligand, HC{SiMe$_2$NH(2-FC$_6$H$_4$)}$_3$ (**1**) has been prepared by condensation of 2-fluoroaniline with HC(SiMe$_2$-Br)$_3$ (eq 1).



Amine **1** is obtained as a colorless, highly crystalline solid which melts without decomposition (mp 101 °C). As previously shown in a comprehensive study of the solid state and solution structures of a series of arylamino-substituted trisilylmethanes, the preferred geometric arrangement in solution is probably "inverted" with respect to a potential adamantoidal geometry as indicated in eq 1. This is inferred from the low field shift of the apical C−H proton (δ = 1.02 in CDCl$_3$) as well as the results of ^{1}H-NOESY spectra (recorded at 295 K and 250 K, t_{mix} = 0.5 s, 1.0 s, 1.5 s) in which the cross peak between the resonance of SiMe$_2$-methyl protons and the CH-signal is barely visible. Upon reaction of **1** with three molar equivalents of *n*-BuLi in diethyl ether, the ether adduct of the corresponding trilithium triamide HC{SiMe$_2$N(Li)(2-FC$_6$H$_4$)}$_3$ (**2**) is formed. Although the compound may be isolated as a colorless microcristalline solid, its extreme air and moisture sensitivity has thus far only allowed its analytical and spectrosopic characterization. The formulation as (deduced from the analytical data) a bis(diethyl ether)-adduct might suggest a similar structure as established by X-ray crystallography for HC{SiMe$_2$N(Li)*t*Bu}$_3$(THF)$_2$[9] and postulated for HC{SiMe$_2$N(Li)Ar}$_3$(OEt$_2$)$_2$ (Ar = Aryl).[10] However, the considerable shift of the ^{19}F-signal in comparison to **1** [**1**; δ(^{19}F) = −119.2; **2**; δ = −141.1] indicates that the fluorine atoms participate in the bonding to Li. It is therefore likely that the structural arrangement in **2** differs from that observed previously. Exchange broadening in the spectra recorded at 200 K (in toluene-d_8) indicates that dynamic processes are operative and responsible for the high effective symmetry of the molecule at ambient temperature. Unfortunately, low temperature limit spectra could not be obtained even below 200 K, and a satisfactory elucidation of the structure will therefore only be obtained in a future X-ray diffraction study of the compound.

Synthesis and Crystal Structure and Solution Dynamics of HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$Y(OEt$_2$) (3). Reaction of *in situ* generated **2** with YCl$_3$ in diethyl ether at −78 °C and subsequent warming to room temperature gives the amido yttrium complex HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$Y(OEt$_2$) (**3**). The presence of coordinated diethyl ether is established analytically and spectroscopically. Even heating of the compound *in vacuo* to below its decomposition point at 97 °C does not lead to a complete loss of the diethyl ether ligand. The ^{1}H-, ^{13}C-, ^{29}Si-, and ^{19}F-NMR

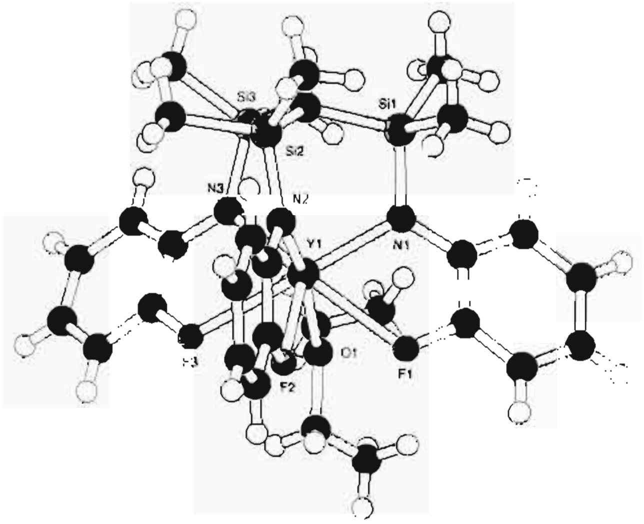


Figure 3. Molecular structure of HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$Y(OEt$_2$) (**3**) in the crystal.

Table 2. Selected Bond Lengths (Å) and Interbond Angles (deg) for **3**

Y(1)−F(1)	2.482(6)	N(3)−C(20)	1.40(1)
Y(1)−F(2)	2.438(7)	Y(1)−F(3)	2.517(7)
Y(1)−O(1)	2.437(8)	Y(1)−N(1)	2.235(9)
Y(1)−N(2)	2.258(9)	Y(1)−N(3)	2.265(9)
SI(1)−N(1)	1.736(9)	SI(1)−C(1)	1.89(1)
SI(1)−C(2)	1.89(1)	SI(1)−C(3)	1.88(1)
SI(2)−N(2)	1.733(9)	SI(2)−C(1)	1.91(1)
SI(2)−C(4)	1.85(1)	SI(2)−C(5)	1.88(1)
SI(3)−N(3)	1.71(1)	SI(3)−C(1)	1.90(1)
SI(3)−C(6)	1.88(1)	SI(3)−C(7)	1.86(1)
F(1)−C(9)	1.43(1)	F(2)−C(15)	1.40(1)
F(3)−C(21)	1.40(1)	O(1)−C(26)	1.43(2)
O(1)−C(28)	1.560(8)	N(1)−C(8)	1.37(1)
N(2)−C(14)	1.36(1)		

F(1)−Y(1)−F(2)	65.2(2)	C(2)−SI(1)−C(3)	103.4(6)
F(1)−Y(1)−F(3)	116.5(2)	N(2)−SI(2)−C(1)	105.6(5)
F(1)−Y(1)−O(1)	73.7(2)	N(2)−SI(2)−C(4)	108.4(5)
F(1)−Y(1)−N(1)	69.4(3)	N(2)−SI(2)−C(5)	115.9(6)
F(1)−Y(1)−N(2)	102.2(3)	C(1)−SI(2)−C(4)	114.9(6)
F(1)−Y(1)−N(3)	159.6(3)	C(1)−SI(2)−C(5)	108.5(5)
F(2)−Y(1)−F(3)	67.3(2)	C(4)−SI(2)−C(5)	103.8(7)
F(2)−Y(1)−O(1)	99.0(3)	N(3)−SI(3)−C(1)	104.6(5)
F(2)−Y(1) −N(1)	128.0(3)	N(3)−SI(3)−C(6)	113.5(6)
F(2)−Y(1)−N(2)	68.6(3)	N3−SI(3)−C(7)	110.2(6)
F(2)−Y(1)−N(3)	130.1(3)	C(1)−SI(3)−C(6)	109.7(6)
F(3)−Y(1)−O(1)	74.7(3)	C(1)−SI(3)−C(7)	112.7(6)
F(3)−Y(1)−N(1)	161.5(3)	C(6) −SI(3)−C(7)	106.3(6)
F(3)−Y(1)−N(2)	97.1(3)	Y(1)−F(1)−C(9)	111.1(7)
F(3)−Y(1) −N(3)	67.7(3)	Y(1)−F(2)−C(15)	115.4(6)
O(1)−Y(1)−N(1)	91.3(3)	Y(1)−F(3)−C(21)	113.1(7)
O(1)−Y(1)−N(2)	167.2(3)	Y(1)−O(1)−C(26)	121.4(8)
O(1)−Y(1)−N(3)	89.1(3)	Y(1)−O(1)−C(28)	121.8(5)
N(1)−Y(1)−N(2)	98.6(3)	C(26)−O(1)−C(28)	114.8(9)
N(1)−Y(1)−N(3)	100.6(3)	Y(1)−N(1)−SI(1)	113.2(5)
N(2)−Y(1)−N(3)	96.8(3)	Y(1)−N(1)−C(8)	119.5(8)
N(1)−SI(1)−C(1)	105.4(5)	SI(1)−N(1)−C(8)	122.4(8)
N(1) SI(1)−C(3)	109.1(5)	Y(1)−N(2)−C(14)	121.7(8)
C(1)−SI(1)−C(2)	109.7(6)	SI(2)−N(2)−C(14)	124.8(8)
C(1)−SI(1)−C(3)	112.4(6)	Y(1)−N(3)−SI(3)	113.2(5)
Y(1)−N(3)−C(20)	118.9(8)	SI(3)−N(3)−C(2)0	127.9(9)
SI(1)−C(1)−SI(2)	115.5(6)	SI(1)−C(1)−SI(3)	116.2

spectra recorded at 295 K are consistent with an effective 3-fold symmetry of the compound. Coupling between the spin $^1/_2$ nuclei ^{83}Y and ^{19}F observed in the ^{19}F-NMR spectrum [$^1J(^{89}\mathrm{Y}-^{89}\mathrm{F}) = 5.3$ Hz ($\delta = -124.4$) at 295 K] may be interpreted as due to direct coordination of all three fluorine atoms to the metal center. However, exchange processes at lower temperatures (*vide infra*) indicate a structure of lower than 3-fold molecular symmetry.

Table 3. Fractional Atomic Coordinates of **3**

atom	*x*	*y*	*z*
Y(1)	0.2263(1)	0.3130(1)	0.78751(8)
Si(1)	−0.0716(4)	0.4238(3)	0.7150(2)
Si(2)	0.2280(4)	0.5406(3)	0.6583(2)
Si(3)	0.1170(4)	0.2602(4)	0.5960(2)
F(1)	0.1550(7)	0.3536(6)	0.9280(4
F(2)	0.4144(7)	0.4104(6)	0.8787(4)
F(3)	0.4607(7)	0.2151(7)	0.7690(4)
O(1)	0.199(1)	0.1067(8)	0.8445(5)
N(1)	−0.008(1)	0.3362(8)	0.7916(6)
N(2)	0.296(1)	0.5092(8)	0.7523(5)
N(3)	0.240(1)	0.2140(9)	0.6644(5)
C(1)	0.069(1)	0.422(1)	0.6371(6)
C(2)	−0.250(1)	0.368(1)	0.6665(8)
C(3)	−0.101(2)	0.588(1)	0.7567(8)
C(4)	0.372(1)	0.529(1)	0.5858(8)
C(5)	0.167(1)	0.705(1)	0.6479(9)
C(6)	0.187(2)	0.272(1)	0.4921(8)
C(7)	−0.039(1)	0.143(1)	0.5861(9)
C(8)	−0.074(1)	0.327(1)	0.8630(8)
C(9)	0.005(1)	0.334(1)	0.9343(8)
C(10)	−0.044(2)	0.329(1)	1.0121(8)
C(11)	−0.183(2)	0.310(1)	1.0208(9)
C(12)	−0.270(2)	0.297(1)	0.953(1)
C(13)	−0.221(1)	0.309(1)	0.8765(8)
C(14)	0.402(1)	0.581(1)	0.7939(7)
C(15)	0.467(1)	0.531(1)	0.8606(8)
C(16)	0.574(1)	0.589(1)	0.9099(7)
C(17)	0.623(1)	0.709(1)	0.8931(9)
C(18)	0.567(2)	0.762(1)	0.827(1)
C(19)	0.459(2)	0.701(1)	0.7797(8)
C(20)	0.341(2)	0.124(1)	0.6527(8)
C(21)	0.457(2)	0.124(1)	0.7050(8)
C(22)	0.564(1)	0.041(1)	0.702(1)
C(23)	0.555(2)	−0.049(2)	0.640(1)
C(24)	0.450(2)	−0.056(2)	0.586(1)
C(25)	0.342(2)	0.025(1)	0.5904(8)
C(26)	0.123(2)	0.001(2)	0.802(1)
C(27)	−0.018(2)	−0.015(2)	0.822(1)
C(28)	0.2946	0.0713	0.9169
C(29)	0.2190	0.0433	0.9633

In order to establish the overall molecular arrangement of the yttrium complex **3** and to assess the degree to which the *ortho*-fluorine atoms participate in the coordination to the yttrium center a single crystal X-ray structure analysis of the compound was carried out. The molecular structure is depicted in Figure 3, selected bond lengths and interbond angles are given in Table 2, and the fractional coordinates are listed in Table 3.

The yttrium complex has a remarkable sevenfold coordination geometry[17] involving the three amido-N atoms and all three fluorine donor atoms of the tripodal amido ligand as well as an oxygen donor atom of a diethyl ether molecule. Whereas the three N-functions adopt an almost undistorted triangular arrangement as in all previously characterized compounds containing this type of amido ligand,[6,10] the three fluorine atoms and the oxygen atom of the ether molecule are arranged in the form of a distorted square. It is difficult to assign a reasonably defined coordination polyhedron to the type of geometry found in this complex.[18] The most closely related "standard" arrangement within the manifold of seven-vertex coordination polyhedra is derived from the triangulated dodecahedron by removal of one of its four-connected vertices (Figure 4; a triangulated dodecahedron has four four-connected and four five-connected vertices) generating the open square face defined by the three fluorine and the oxygen atom.

---

(17) Hart, F. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., McCleverty, J. A., Gilland, R. D., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 3, p 1059.

(18) Kepert, D. L. In *Comprehensive Coordination Chemistry*; Wilkinson, G., McCleverty, J. A., Gillard, R. D., Eds.; Pergamon Press; Oxford, England, **1987**; Vol. 1, p 31. Kepert, D. L. *Prog. Inorg. Chem.* **1979**, *25*, 67; Drew, M. G. B., *Prog. Inorg. Chem.* **1977**, *23*, 67.

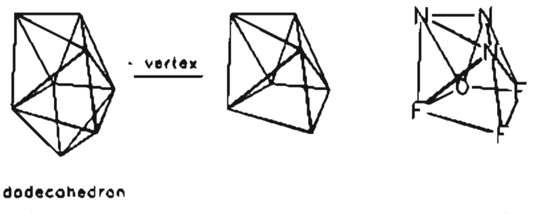


Figure 4. Relation of the coordination polyhedron in **3** to the triangulated dodecahedron by removal of a four-connected vertex.

As previously observed[6,10] and as a consequence of the steric repulsion of the methyl groups at the silicon atoms, the trisilylmethane and tris(amido)yttrium units in the [2.2.2]-bicyclooctane derived ligand cage are slighty twisted relative to each other [average torsion angle 20.2(6)°]. This element of C_3 symmetry in the amido-ligand part of the molecule is incommensurate with the pseudo C_s-symmetrical arrangement of the additional four donor atoms. This leads to considerable distortions particularly at the amido nitrogen N(1). Whereas N(2) and N(3) have a trigonal planar arrangement [$\Sigma(\angle_N)$ = 358.4(8) and 360(1), respectively] N(1) deviates significantly [$\Sigma(\angle_{N1})$ = 355.1(8)] from this standard geometry in transition metal amide chemistry.[19] In addition, the torsional angle of the phenyl group at N(1) relative to the Si(1)-N(1) axis is considerably larger (42°) than for the other two phenyl amido units (13° at N(2) and 19.2° at N(3)).

The average Si−N and Y−N distances of 1.73 and 2.25 Å, respectively, lie within the expected range.[20-23] All other geometrical parameters of the ligand do not deviate significantly from the trisilylmethane-derived tripodal amido complexes studied previously.[6,10]

The lower molecular symmetry of the crystal structure of **3** than the effective symmetry reflected in the NMR spectra at room temperature indicates that dynamic processes must be operative in solution. When the temperature is lowered, exchange broadening is observed. Below 250 K the average ^{89}Y−^{19}F-coupling of the rapid exchange regime breaks down, and coalescence of all signals is observed at 180 K (in toluene-d_8). Although the structure determined for the solid state could thus not be frozen out, it is reasonable to propose a mechanistic pathway for the processes responsible for the room temperature spectra. Rapid exchange of the ether ligand between the three equivalent positions "between" two fluorine atoms in the basal F(1)−F(2)−F(3)−O(1)-set of donor atoms would render the F-ligands (and thus the amido-N atoms) equivalent on the time scale of the experiment and confer overall 3-fold symmetry upon the molecule. Provided that the exchange does not occur dissociatively, which would be consistent with the difficulty encountered in the thermal removal of the ether, a possible intermediate in this dynamic process could be a distorted Δ-capped trigonal prismatic species as shown in Figure 5.

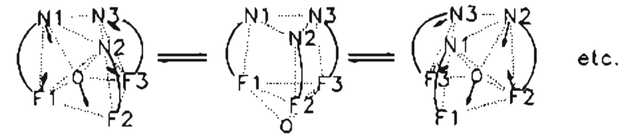


Figure 5. Proposed model for the chemical exchange responsible for the effective 3-fold symmetry of complex **3** in the NMR spectra recorded at ambient temperature.

On heating a sample of **3** in toluene-d_8 to above 330 K the ^{89}Y−^{19}F coupling breaks down, and the fluorine signal is observed as a broadened singlet above 350 K. This disappearance of the ^1J-coupling is probably a manifestation of rapid reversible dissociation of the F-donors on the time scale of the experiment.

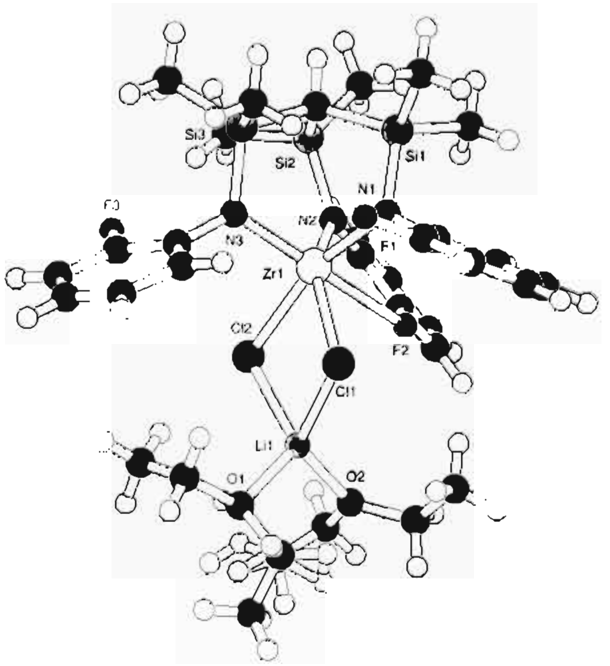


Figure 6. Molecular structure of HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$ZrCl$_2$Li(OEt$_2$)$_2$ (**4**) in the crystal.

Synthesis and Crystal Structure of HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$ZrCl$_2$Li(OEt$_2$)$_2$ (4). Reaction of **2** with ZrCl$_4$ in diethyl ether yields an amido zirconium complex **4** which precipitates as a highly crystalline solid upon slow removal of the ether solvent *in vacuo* and is almost insoluble in aliphatic or aromatic hydrocarbons. This method of isolation was chosen since extraction of the solid residue of the product mixture with toluene left most of the material undissolved and thus did not permit the isolation of the analogue to the complex CH$_3$Si{SiMe$_2$N(4-CH$_3$C$_6$H$_4$)}$_3$ZrCl.[11] On the basis of its analytical and spectroscopic data **4** is formulated as HC{SiMe$_2$N(2-FC$_6$H$_4$)}$_3$ZrCl$_2$Li(OEt$_2$)$_2$ (**4**). In spite of the apparent complexity of the system, the (albeit slightly broadened) resonance pattern in the ^{1}H-, ^{13}C-NMR spectra is consistent with a 3-fold symmetry of the molecule on the NMR time scale, however, the broad two-signal ^{19}F- and ^{29}Si-NMR spectra as well as the emergence of complicated exchange patterns upon cooling the sample in THF-d_8 which indicate a higher degree of structural complexity. As in the case of **3**, the high temperature limit, which is observed at temperatures above 320 K, reflects a dynamic behavior effecting overall 3-fold molecular symmetry on the NMR time scale.

In view of the unexpectedly complex formula of compound **4** and the complicated nature of its NMR spectra in solution, a single crystal X-ray diffraction study was carried out. A view of the molecular structure of **4** in the crystal is given in Figure 6, selected bond distances and interbond angles are given in Table 4, and the fractional coordinates of **4** are listed in Table 5.

As already inferred from the analytical data, compound **4** is to be seen as a {(Et$_2$O)$_2$LiCl}-adduct of the complex HC-

---

(19) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., McCleverty, J. A., Gillard, R. D. Eds.; Pergamon Press: Oxford, England, 1987; Vol. 2, p. 161.

(20) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1989; p 227.

(21) Lukevics, E.; Pudova, O.; Sturkovich, R. *Molecular Structures of Organosilicon Compounds*; Ellis Horwood: New York, 1989; p 93.

(22) See e.g.: Glidewell, C.; Robiette, A. G.; Sheldrick, G. M. *J. Mol. Struct.* **1971**, 9, 476. Hansen, H. D.; Mundt, O.; Kaim, W. *J. Organomet. Chem.* **1985**, *296*, 321. Martin, A. R.; Svensson, A.; Bates, R. B.; Ortega, R. B. *Acta Crystallogr., Sect. C* **1985**, *41*, 1804.

(23) Bradley, D. C.; Ghotra, J. S.; Hart, F. A. *J. Chem. Soc., Dalton Trans.*, **1973**, 1021; Duchateau, R.; van Wee, C. T.; Meetsma, A.; Teuben, J. H. *J. Am. Chem. Soc.* **1993**, *115*, 4931. Reger, D. L.; Lindeman, J. A.; Lebioda, L. *Inorg. Chem.* **1988**, *27*, 1891; 3923.

Table 4. Selected Bond Lengths (Å) and Interbond Angles (deg) of **4**

Zr(1)−Cl(1)	2.505(3)	O(2)−C(26)	1.31(2)
Zr(1)−Cl(2)	2.564(2)	O(2)−C(28)	1.60(3)
Zr(1)−F(2)	2.535(5)	O(2)−Li(1)	1.96(2)
Zr(1)−N(1)	2.072(7)	N(1)−C(8)	1.44(1)
Zr(1)−N(2)	2.125(6)	N(2)−C(14)	1.39(1)
Zr(1)−N(3)	2.040(7)	N(3)−C(20)	1.43(1)
Cl(1)−Li(1)	2.38(2)	Cl(2)−Li(1)	2.39(2)
Si(1)−N(1)	1.740(7)	Si(1)−C1	1.896(9)
Si(1)−C(2)	1.88(1)	Si(1)−C(3)	1.87(1)
Si(2)−N(2)	1.741(7)	Si(2)−C(1)	1.870(8)
Si(2)−C(4)	1.88(1)	Si(2)−C(5)	1.86(1)
Si(3)−N(3)	1.755(7)	Si(3)−C(1)	1.876(9)
Si(3)−C(6)	1.87(1)	Si(3)−C(7)	1.86(1)
F(1)−C(9)	1.35(1)	F(2)−C(21)	1.36(1)
F(3)−C(15)	1.381(9)	O(1)−C(30)	1.62(3)
O(1)−C(31)	1.60(3)	O(1)−Li(1)	1.92(2)
Cl(1)−Zr(1)−Cl(2)	81.58(8)	C(1)−Si(2)−C(4)	109.9(4)
Cl(1)−Zr(1)−F(3)	78.0(1)	C(1)−Si(2)−C(5)	115.7(4)
Cl(1)−Zr(1)−N(1)	87.2(2)	C(4)−Si(2)−C(5)	105.6(5)
Cl(1)−Zr(1)−N(2)	146.5(2)	N(3)−Si(3)−C(1)	103.4(4)
Cl(1)−Zr(1)−N(3)	110.9(2)	N(3)−Si(3)−C(6)	112.0(5)
Cl(2)−Zr(1)−F(3)	79.2(1)	N(3)−Si(3)−C(7)	109.5(4)
Cl(2)−Zr(1)−N(1)	164.4(2)	C(1)−Si(3)−C(6)	112.3(4)
Cl(2)−Zr(1)−N(2)	88.4(2)	C(1)−Si(3)−C(7)	114.6(5)
Cl(2)−Zr(1)−N(3)	95.8(2)	C(6)−Si(3)−C(7)	105.1(5)
F(3)−Zr(1)−N(1)	87.9(2)	Zr(1)−F(3)−C1(5)	108.7(5)
F(3)−Zr(1)−N(2)	68.7(2)	C(30)−O(1)−C(31)	100(2)
F(3)−Zr(1)−N(3)	169.2(2)	C(30)−O(1)−Li(1)	119(1)
N(1)−Zr(1)−N(2)	95.1(3)	C(31)−O(1)−Li(1)	112(1)
N(1)−Zr(1)−N(3)	98.4(3)	C(26)−O(2)−C(28)	109(2)
N(2)−Zr(1)−N(3)	101.8(3)	C(26)−O(2)−Li(1)	130(1)
Zr(1)−Cl(1)−Li(1)	94.7(5)	C(28)−O(2)−Li(1)	121(1)
Zr(1)−Cl(2)−Li(1)	92.9(5)	Zr(1)−N(1)−Si(1)	115.2(3)
N(1)−Si(1)−C(1)	104.4(4)	Zr(1)−N(1)−C(8)	128.1(6)
N(1)−Si(1)−C(29	109.2(4)	Si(1)−N(1)−C(8)	115.9(6)
N(1)−Si(1)−C(3)	111.6(4)	Zr(1)−N(2)−Si(2)	116.1(3)
C(1)−Si(1)−C(2)	114.8(4)	Zr(1)−N(2)−C(14)	120.5(6)
C(1)−Si(1)−C(3)	111.9(4)	Si(2)−N(2)−C(14)	123.4(6)
C(2)−Si(1)−C(3)	105.0(5)	Zr(1)−N(3)−Si(3)	117.4(4)
N(2)−Si(2)−C(1)	101.7(3)	Zr(1)−N(3)−C(20)	124.5(6)
N(2)−Si(2)−C(4)	115.1(4)	Si(3)−N(3)−C(20)	116.0(6)
N(2)−Si(2)−C(5)	109.2(4)	Si(1)−C(1)−Si(2)	111.6(4)
Si(1)−C(1)−Si(3)	113.6(4)	Si(2)−C(1)−Si(3)	114.9(5)
Cl(1)−Li(1)−Cl(2)	87.8(7)	Cl(1)−Li(1)−O(1)	107(1)
O(1)−C(30)−C(29)	92(2)	Cl(1)−Li(1)−O(2)	127(1)
Cl(2)−Li(1)−O(1)	118(1)	Cl(2)−Li(1)−O(2)	110(1)
O(1)−Li(1)−O(2)	107(1)		

Table 5. Fractional Atomic Coordinates of **4**

atom	*x*	*y*	*z*
Zr(1)	0.15731(6)	0.98791(5)	0.74174(5)
Cl(1)	0.0093(2)	0.9246(1)	0.7995(2)
Cl(2)	0.2428(2)	0.8670(1)	0.7837(2)
Si(1)	0.1133(2)	1.1383(1)	0.6467(2)
Si(2)	0.3284(2)	1.0734(1)	0.6403(2)
Si(3)	0.2515(2)	1.1462(2)	0.7943(2)
F(1)	−0.0613(6)	1.1217(4)	0.8119(5)
F(2)	0.4041(6)	1.0070(5)	0.8898(5)
F(3)	0.1034(4)	0.9014(3)	0.6342(3)
O(1)	0.0640(8)	0.7687(5)	0.9089(5)
O(2)	0.0701(9)	0.7221(6)	0.7368(7)
N(1)	0.0587(5)	1.0657(4)	0.6974(4)
N(2)	0.2573(5)	0.9929(4)	0.6476(4)
N(3)	0.2271(5)	1.0539(4)	0.8208(4)
C(1)	0.2452(6)	1.1436(4)	0.6864(5)
C(2)	0.1045(7)	1.1185(6)	0.5408(5)
C(3)	0.0442(8)	1.2273(6)	0.6604(7
C(4)	0.3583(7)	1.1030(5)	0.5392(6)
C(5)	0.4509(7)	1.0584(6)	0.6885(6)
C(6)	0.3756(8)	1.1787(6)	0.8307(6)
C(7)	0.1590(9)	1.2086(6)	0.8401(6)
C(8)	−0.0485(7)	1.0610(6)	0.6923(6)
C(9)	−0.106(1)	1.0901(7)	0.7505(8)
C(10)	−0.208(1)	1.0910(7)	0.752(1)
C(11)	−0.255(1)	1.056(1)	0.691(1)
C(12)	−0.200(1)	1.0269(9)	0.6317(9)
C(13)	−0.0965(9)	1.0258(7)	0.6304(7)
C(14)	0.2640(7)	0.9343(5)	0.5962(5)
C(15)	0.1845(7)	0.8872(5)	0.5880(5)
C(16)	0.1781(8)	0.8288(6)	0.5374(6)
C(17)	0.261(1)	0.8154(6)	0.4928(6)
C(18)	0.3441(8)	0.8583(6)	0.4997(6)
C(19)	0.3458(7)	0.9173(5)	0.5510(6)
C(20)	0.2343(9)	1.0376(5)	0.9014(6)
C(21)	0.323(1)	1.0155(7)	0.9352(8)
C(22)	0.335(1)	1.002(1)	1.012(1)
C(23)	0.252(2)	1.011(1)	1.0557(9)
C(24)	0.163(2)	1.031(1)	1.026(1)
C(25)	0.152(1)	1.0445(7)	0.9493(7)
C(26)	−0.006(2)	0.706(1)	0.692(1)
C(27)	−0.074(1)	0.761(1)	0.676(1)
C(28)	0.154(2)	0.660(2)	0.729(2)
C(29)	0.173(2)	0.809(1)	0.984(1)
C(30)	0.082(2)	0.824(2)	0.981(2)
C(31)	−0.050(2)	0.747(2)	0.922(2)
C(32)	−0.027(2)	0.677(2)	0.942(2)
C(33)	0.185(4)	0.654(3)	0.798(3)
Li(1)	0.088(2)	0.806(1)	0.807(1)

$\{SiMe_2N(2\text{-}FC_6H_4)\}_3ZrCl$, the analogue of the four-coordinate species $CH_3Si\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3ZrCl$.[11] The central zirconium atom displays 6-fold coordination in a distorted octahedral arrangement of donor atoms. As in **3**, the amido-N atoms occupy three positions within the inner coordination sphere, while two chloride ligands and one of the *ortho*-fluorine atoms (F2) of the 2-fluorophenyl groups of the amido ligand (at N2) are at the remaining three coordination sites. The other two *ortho*-fluoro atoms in the ligand periphery are uncoordinated. Whereas the two uncoordinated fluoro phenyl groups are twisted into an almost orthogonal position to the Si−N bonds [torsion angle between the phenyl-plane and the Si−N vectors 84(1)° at N(1) and 90(1)° at N3], the 2-fluorophenyl group at N(2) has a similar orientation [$\angle_{tors}$ = 24(1)°] as the three bound peripheral units in **3**. The other geometrical characteristics of the amido-metal cage are closely related to those observed in **3**.

The Zr−F(2) distance in **4** of 2.535(5) Å as well as the Y−F distances in **3** (2.482(6), 2.438(7), 2.517(7) Å) are clearly long M−F distances[4] and reflect the hemilabile nature of the coordinated peripheral donor atoms, as has been the target at the outset of this research.

The formally negatively charged tris(amido)dichlorozirconium moiety is bound to the $(Et_2O)_2Li^+$ through two bridging chloride ligands. This molecular unit is quite common in lanthanoid chemistry[25] but has thus far not been established in Zr-chemistry.[26] The four-membered ring Zr−Cl(1)−Li(1)−Cl(2) adopts a puckered geometry (interplane angle 167°), a situation which is probably a consequence of steric interaction between the diethyl ether molecules and the 2-fluorophenyl groups. Both the Li−Cl and Li−O distances [d_{av}(Li−Cl) = 2.38 Å, d_{av}(Li−O) = 1.94 Å] are comparable to those found in $Cp_2LnCl_2\{Li(OEt_2)_2\}$ compounds.[25]

Based on the results of the X-ray structure determination the observation of effective three fold symmetry in the NMR spectra recorded at high temperature may be interpreted on the basis of two dynamic models. A possible mechanism involves the reversible dissociation of $(Et_2O)_2LiCl$ generating a four- to

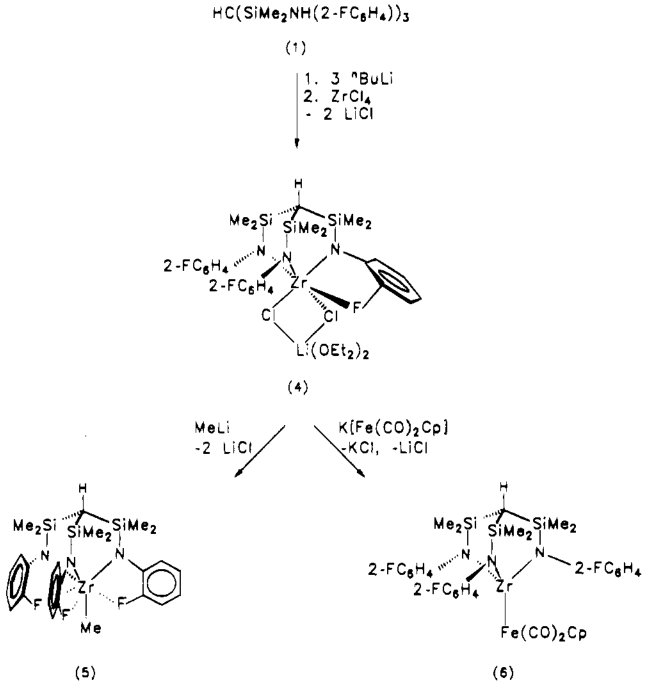
---

(24) See for instance the Zr−F bond lengths in "simple" zirconium fluorides or fluorocomplexes which lie in the range between 1.98 and 2.17 Å: (a) Sears, D. R.; Burns, J. H. *J. Chem. Phys.* **1964**, *41*, 3478. (b) Brunton, G. *Acta Crystallogr.* **1969**, *B25*, 2164. (c) Fischer, J.; Weiss, R. *Acta Crystallogr.* **1973**, *B29*, 1955. (d) Bush, M. A.; Sim, G. A. *J. Chem. Soc. A* **1971**, 2225.

(25) Atwood, J. L.; Hunter, W. E.; Rogers, R. D., *J. Chem. Soc., Chem. Commun.* **1978**, 140; Watson,P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1980**, *20*, 3271.

(26) Cambridge Structural Database, Cambridge University, 1994.

Scheme 1. Summary of the Synthesis and Chemical Conversions of **4**



seven-coordinate species. Rapid de- and reaggregation of this fragment would generate an effective 3-fold symmetry of **4** in solution. On the basis of our experience with related systems,[27] however, such a dissociation of a solvated LiCl-unit tends to be irreversible ultimately generating the "salt free" complex. We therefore favor an alternative mechanism of the exchange observed in **4** which leaves the molecule intact. Thermal dissociation of the Zr-F bond (as also observed for **3** under these conditions, *vide supra*) generates a five-coordinate species which is structurally nonrigid and may undergo rapid turnstile rotation. The coordinated 2-fluorophenyl group therefore acts as a "brake" in this dynamic process.

When **4** is reacted with 1 equiv of MeLi the thermally very stable methyl complex $HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3ZrCH_3$ (**5**) is formed (Scheme 1).

The ^1H-, ^{13}C-, and ^{19}F-NMR spectra of complex **5** show no significant temperature dependence and indicate C_{3v}-symmetry of the molecule. Particularly noteworthy are the ^1H- and ^{13}C resonances of the Zr-bonded methyl group (at $\delta = 0.56$ and $\delta = 47.3$, respectively). Due to coupling with three ^{19}F-nuclei both signals appear as quartets ($^3J_{FH} = 8.4$ Hz; $^2J_{FC} = 17.6$ Hz) which is indirect evidence for the coordination of all three F-atoms to the Zr-center. The methyl complex is therefore most probably seven-coordinate in solution with a (distorted) Δ-capped trigonal prismatic ligand arrangement. Complex **5** is therefore an example in which a sterically fairly undemanding ligand such as CH_3 allows for a participation of all peripheral F-donors in the coordination to the central metal atom.

On the other hand, the *ortho*-fluorophenyl ligand periphery indeed offers the necessary flexibility in its coordination behavior to allow for the interaction of both very bulky and small molecular fragments with the metal center. This capability, defined in the conceptual approach mentioned in the introduction, is exemplified by the metathesis of **4** with $[CpFe(CO)_2]^-$ to form the thermally stable but exceedingly air and moisture sensitive Fe−Zr-bonded dinuclear complex $HC\{SiMe_2N(2\text{-}FC_6H_4)\}_3ZrFe(CO)_2Cp$ (**6**)[28] along with small amounts (ca 5%) of $[CpFe(CO)_2]_2$ generated as SET-byproduct in the coupling reaction (Scheme 1).

Its spectroscopic characteristics are entirely analogous to those of the Fe−Ti and Ru−Ti compounds $HC\{SiMe_2N(4\text{-}CH_3C_6H_4)\}_3TiM(CO)_2Cp$ (M = Fe, Ru) both of which have been structurally characterized by X-ray crystallography.[6] The absence of ν(CO) absorptions attributable to bridging carbonyl or isocarbonyl ligands as well as the free internal rotation about the Zr−Fe bond inferred from the NMR spectra recorded at 295 K supports the the structural arrangement shown in Scheme 1. The high steric demand of the Fe-complex fragment precludes an involvement of the F-atoms in the coordination to the Zr-center. A detailed account of the chemistry and reactivity of the highly polar metal−metal bonds in a series of Zr−M (M = late transition metal) will be given elsewhere.[29]

Conclusions

This study has extended the design of tripodal amido ligands to include weak additional donor functions in the ligand periphery which, depending upon the electronic and steric situation in the complex may or may not participate in the bonding to the metal. The "reactive center" at the metal may therefore be masked by these anicillary donors. Examples which represent both extremes of the coordination of peripheral donors (**3**, **5**, and **6**) as well as an intermediate case (**4**) have demonstrated the viability of the conceptual approach.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (Grants 488/2−1, Ga 488/3−1), the Fonds der Chemischen Industrie, and the European Commission (ERASMUS scholarship to K.W.) for financial support and Wacker Chemie AG for a generous gift of basic chemicals. Thanks is also due to Professor H. Werner (Würzburg) for his continued interest and support of this work.

Supporting Information Available: Text detailing the structure determination and tables of crystallographic data, the positional and thermal parameters, interatomic distances, angles, and torsion angles for **3** and **4** (38 pages). Ordering information is given on any masthead page.

IC9501677

---

[27] Findeis, B.; Schubart, M.; Gade, L. H.; Möller, F.; Scowen, I.; McPartlin, M. Submitted for publication in *J. Chem. Soc., Dalton Trans.*

[28] Zr−Fe bonded complexes have been reported. See e.g.: Casey, C. P.; Jordan, R. F., Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *105*, 665. Casey, C. P.; Jordan, R. F.; Rheingold, A. L. *Organometallics* **1984**, *3*, 504. Casey, C. P. *J. Organomet. Chem.* **1990**, *400*, 205.

[29] Friedrich, S.; Memmler, H.; Gade, L. H.; Li, W.-S.; McPartlin, M.; Scowen, I. Manuscript in preparation.