

## Notizen / Notes

Functionalized Cyclopentadienyl Ligands, IV<sup>1)</sup>

## Synthesis and Complexation of Linked Cyclopentadienyl-Amido Ligands

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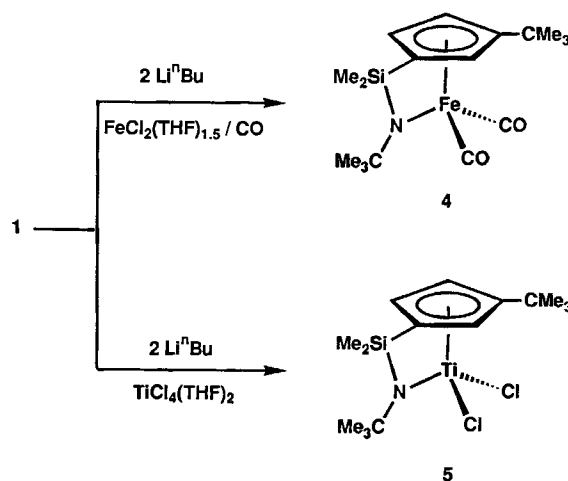
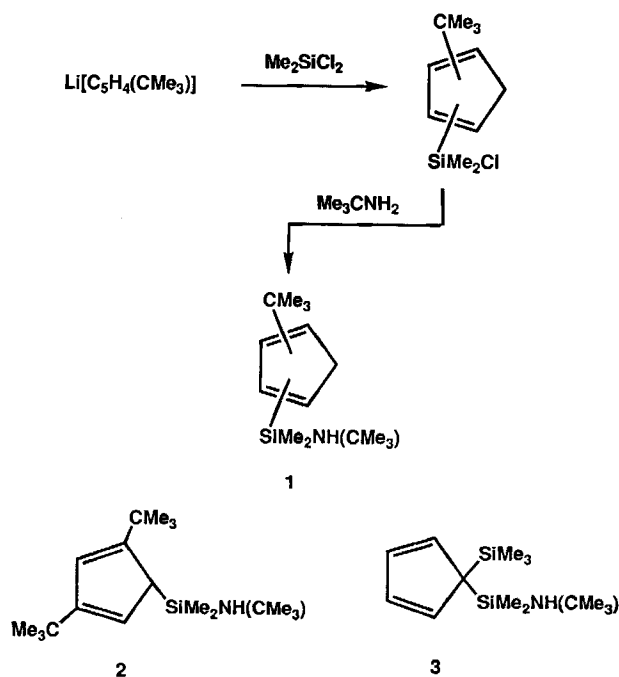
Received April 24, 1990

**Key Words:** Cyclopentadienyl ligand, functionalized / Amido ligands / Titanium complexes

[[*tert*-Butylamino]dimethylsilyl]cyclopentadienes  $C_5H_5-n-(CMe_3)_n(SiMe_2NHCMe_3)$  ( $n = 1, 2$ ) and  $C_5H_4(SiMe_3)(SiMe_2NHCMe_3)$  have been prepared and the complexation of their

lithium derivatives with  $FeCl_2(THF)_{1.5}$  and  $TiCl_4(THF)_2$  investigated.

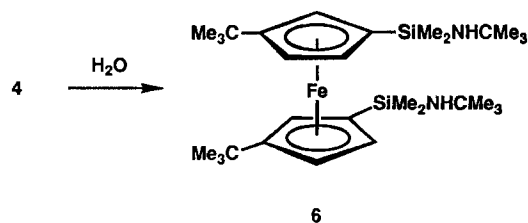
In an attempt to rationally design conformationally rigid ligand frameworks for transition metal centers, we have been studying the complexation properties of cyclopentadienyl ligands bearing sterically demanding substituents such as *tert*-butyl or trimethylsilyl groups<sup>2)</sup> as well as an additional functionality such as an alkenyl group<sup>1,3)</sup>. While bridged bis(cyclopentadienyl) ligands have been prepared mainly by Brintzinger et al. for the synthesis of ansa-metallocenes<sup>4)</sup>, Bercaw et al. have recently introduced a novel chelating ligand system in which one cyclopentadienyl moiety is linked via the  $SiMe_2$  group to an amido ligand, viz.  $\eta^5:\eta^1-C_5Me_4(SiMe_2NHCMe_3)$ <sup>5)</sup>. We report in this paper on the preparation and preliminary complexation behavior of related linked cyclopentadienyl-amido ligands in which the five-membered ring contains at least one *tert*-butyl<sup>6)</sup> or trimethylsilyl group.



Lithium *tert*-butylcyclopentadienide smoothly reacts with dichlorodimethylsilane to give  $C_5H_4(CMe_3)(SiMe_2Cl)$  that can be easily converted into  $C_5H_4(CMe_3)(SiMe_2NHCMe_3)$  (**1**) using two equivalents of *tert*-butylamine. Analogously, starting with di-*tert*-butylcyclopentadiene and trimethylsilylcyclopentadiene, related ligand precursors  $C_5H_3(CMe_3)_2(SiMe_2NHCMe_3)$  (**2**) and  $C_5H_4(SiMe_3)(SiMe_2NHCMe_3)$  (**3**) can be obtained by aminolysis of the corresponding chlorodimethylsilyl-substituted derivatives with *tert*-butylamine. **1**, **2**, and **3** are moisture-sensitive, distillable liquids and have been characterized by analysis,  $^1H$ -,  $^{13}C$ -NMR, and IR spectroscopic as well as mass spectrometric methods. NMR spectroscopic data reveal fluxionality as observed for the trimethylsilyl-substituted analogs<sup>7)</sup>.

Metalation of **1** with two equivalents of *n*-butyllithium gives the dilithium derivative  $Li_2[C_5H_3(CMe_3)(SiMe_2NHCMe_3)]$  which on mixing with ferrous chloride in THF at temperatures as low as  $-95^\circ C$  immediately leads to an intense purple solution. Bubbling CO gas through the solution followed by warming up to room temperature furnishes a dark orange mixture from which highly pentane-soluble dark brown crystals of  $[C_5H_3(CMe_3)(SiMe_2NHCMe_3)]Fe(CO)_2$  (**4**) can be isolated with difficulty. Although extreme moisture-sensitivity so far precluded complete characterization, **4** can be ascribed a

chelate structure of the  $\text{Fe}(\text{CO})_2$  fragment giving rise to two intense  $\nu(\text{CO})$  bands at 2027 and  $1974\text{ cm}^{-1}$  in the solution IR spectrum. When **4** is allowed to gradually hydrolyze, a mixture of orange crystals and off-white ferrous salts is obtained. Analytical,  $^1\text{H}$ -NMR, and IR spectroscopic as well as mass spectrometric data characterize the orange compound as the ferrocene derivative  $[\text{C}_5\text{H}_3(\text{CMe}_3)(\text{SiMe}_2\text{NHCMe}_3)]_2$  (**6**)<sup>9</sup>.



Reaction of the dilithium derivative with  $\text{TiCl}_4(\text{THF})_2$  results in the formation of the dichlorotitanium complex  $[\text{C}_5\text{H}_3(\text{CMe}_3)(\text{SiMe}_2\text{NHCMe}_3)]_2\text{TiCl}_2$  (**5**) which is isolated in moderate yields as brown, highly moisture-sensitive, pentane-soluble crystals and characterized by elemental analysis,  $^1\text{H}$ -,  $^{13}\text{C}$ -NMR, IR spectroscopy and mass spectrometry. NMR spectra clearly show a pattern as required for an asymmetric molecular structure. Thus, the  $^1\text{H}$ -NMR spectrum of **5** consists of two close singlets of intensity 3 at  $\delta = 0.24$  and  $0.25$  for the diastereotopic protons of the dimethylsilylene bridge, two distinct singlets of intensity 9 at  $\delta = 1.26$  and  $1.40$  for each of the *tert*-butyl groups, and three virtual triplets at  $\delta = 6.15$ ,  $6.18$ , and  $6.75$  for the three ring protons. The chemical shifts can be compared to those in  $[1,3\text{-C}_3\text{H}_5(\text{CMe}_3)(\text{SiMe}_3)]\text{TiCl}_3$ <sup>9</sup>.

We continue to study the ligand properties of these novel chelating systems and intend to delineate possible relevance to mechanism of metal-mediated stereoselective transformations using chelate complexes as described above.

Generous support by the *Volkswagen-Stiftung* and the *Bund der Freunde der Technischen Universität München* is gratefully acknowledged. We thank Prof. *W. A. Herrmann* for his continued interest and Prof. *J. E. Bercaw* and Dr. *P. J. Shapiro*, California Institute of Technology, Pasadena, for kindly providing us with unpublished results and crucial experimental details.

## Experimental

All experiments were carried out under dry nitrogen or argon using standard Schlenk technique. Solvents were purified, dried, and distilled under nitrogen. —  $^1\text{H}$ -NMR spectra: Jeol JNM-GX 270 or 400. — IR spectra: Nicolet 5-DX. — Mass spectra: Varian 311 A or Finnigan MAT 90. — Melting points were determined in sealed capillaries.

*[(tert-Butylamino)dimethylsilyl](tert-butyl)cyclopentadiene* (**1**): To a suspension of lithium *tert*-butylcyclopentadienide (25.63 g, 0.2 mol) in 50 ml of THF was quickly added at  $-78^\circ\text{C}$  dichlorodimethylsilane (38.72 g, 0.3 mol). The mixture was stirred for 1 h at  $-78^\circ\text{C}$  and then allowed to slowly warm up to  $0^\circ\text{C}$ . The solvent was removed in vacuo and the residue extracted with pentane (3  $\times$  20 ml). The extracts were filtered through a glass frit covered with sand and kieselguhr, and the volume of the filtrate was reduced to ca. 50 ml. To this solution of crude (*tert*-butyl)(chlorodimethylsilyl)cyclopentadiene was added dropwise at  $0^\circ\text{C}$  a solution of freshly distilled *tert*-butylamine (29.62 g, 0.4 mol) in pentane (20 ml). After completion of addition the white mixture was stirred 16 h at room temp., filtered, and pentane removed in vacuo. Vacuum distillation gave as main fraction 37.70 g (75%) of a pale yellow liquid, b.p.  $48^\circ\text{C}/10^{-3}$  Torr. —  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta =$

$-0.02$ ,  $0.01$  (s, 3H,  $\text{SiCH}_3$ ),  $1.22$  (s, 9H,  $\text{CCCH}_3$ ),  $1.23$  (s, 9H,  $\text{NCCH}_3$ ),  $3.04$  (s, 1H, NH),  $3.39$ ,  $6.10$ ,  $6.50$ ,  $6.65$  (m, 1H, ring H). —  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ):  $\delta = -0.19$ ,  $0.05$  ( $\text{SiCH}_3$ ),  $30.47$  ( $\text{CCCH}_3$ ),  $32.15$  ( $\text{CCCH}_3$ ),  $33.83$  ( $\text{NCCH}_3$ ),  $49.43$  ( $\text{NCCH}_3$ ),  $52.67$ ,  $124.11$ ,  $130.10$ ,  $134.21$ ,  $155.46$  (ring C). — IR (neat, KBr):  $\tilde{\nu} = 3386\text{ cm}^{-1}$  w (NH),  $2961$  s,  $1378$  ms,  $1361$  ms,  $1249$  s,  $1227$  s,  $961$  s,  $856$  s,  $812$  vs,  $654$  s. — GC/MS:  $m/z$  (%) =  $252$  (5) [ $\text{M}^+$ ],  $236$  (20) [ $\text{M}^+ - \text{CH}_4$ ],  $130$  (100) [ $\text{SiMe}_2\text{NHCMe}_3^+$ ].

$\text{C}_{15}\text{H}_{29}\text{NSi}$  (251.5) Calcd. C 71.64 H 11.62 N 5.57  
Found C 71.24 H 11.50 N 5.34

$\{\eta^5\text{-}\eta^1\text{-}3\text{-}(tert\text{-Butyl})\text{-}1\text{-}[(tert\text{-butylamido})dimethylsilyl]cyclopentadienyl\}dichlorotitanium$  (**4**) and  $3,3'\text{-Di}(tert\text{-butyl})\text{-}1,1'\text{-bis}(tert\text{-butylaminodimethylsilyl})ferrocene$  (**6**): To a solution of  $\text{Li}_2[\text{C}_5\text{H}_3(\text{CMe}_3)(\text{SiMe}_2\text{NHCMe}_3)]$  (1.32 g, 5 mmol) in 20 ml of THF was added at  $-95^\circ\text{C}$   $\text{FeCl}_2(\text{THF})_{1.5}$  (1.17 g, 5 mmol) as a solid. Immediately a purple mixture formed which was warmed to  $-78^\circ\text{C}$  and treated with CO gas. After warming up to room temp. under an atmosphere of CO, all volatiles were removed in vacuo, and the residue was extracted with pentane (30 ml). The extracts were filtered, concentrated, and cooled to  $-78^\circ\text{C}$  to give dark brown crystals; yield ca. 450 mg (25%). —  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta = 0.37$  (s, 6H,  $\text{SiCH}_3$ ),  $1.02$  (s, 9H,  $\text{CCCH}_3$ ),  $1.16$  (s, 9H,  $\text{NCCH}_3$ ),  $3.99$  (s, 1H,  $\text{C}_5\text{H}$ ),  $4.06$  (s, 2H,  $\text{C}_3\text{H}_2$ ). — IR (pentane):  $\tilde{\nu} = 2027$ ,  $1974\text{ cm}^{-1}$ . — EI-MS:  $m/z$  (%) =  $361$  (18) [ $\text{M}^+$ ],  $333$  (65) [ $\text{M}^+ - \text{CO}$ ],  $305$  (10) [ $\text{M}^+ - 2\text{CO}$ ],  $276$  (40) [ $\text{M}^+ - \text{C}_4\text{H}_9 - \text{CO}$ ]. — When a solution of **4** was left standing in moist pentane for 16 h, a flocculent white solid deposited and the color of the mixture turned orange. Filtration followed by concentration and cooling to  $-78^\circ\text{C}$  gave well-formed bright orange crystals in ca. 50% yield, m.p.  $119^\circ\text{C}$ . —  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta = 0.50$  (s, 6H,  $\text{SiCH}_3$ ),  $1.15$  (s, 9H,  $\text{CCCH}_3$ ),  $1.29$  (s, 9H,  $\text{NCCH}_3$ ),  $4.13$  (s, 1H,  $\text{C}_5\text{H}$ ),  $4.19$  (s, 2H,  $\text{C}_3\text{H}_2$ ). — IR (KBr):  $\tilde{\nu} = 3395\text{ cm}^{-1}$  w (NH),  $2965$  s,  $1361$  ms,  $1249$  s,  $1245$  s,  $1021$  s,  $850$  s. — EI-MS:  $m/z$  (%) =  $556$  (100) [ $\text{M}^+$ ],  $428$  (20) [ $\text{M}^+ - \text{C}_4\text{H}_9\text{N} - \text{C}_4\text{H}_9$ ].

$\text{C}_{30}\text{H}_{56}\text{N}_2\text{FeSi}_2$  (556.8) Calcd. C 64.71 H 10.14 N 5.03  
Found C 63.99 H 10.02 N 4.77

$\{\eta^5\text{-}\eta^1\text{-}3\text{-}(tert\text{-Butyl})\text{-}1\text{-}[(tert\text{-butylamido})dimethylsilyl]cyclopentadienyl\}dichlorotitanium$  (**5**): To a solution of  $\text{Li}_2[\text{C}_5\text{H}_3(\text{CMe}_3)(\text{SiMe}_2\text{NHCMe}_3)]$  (1.32 g, 5 mmol) in 30 ml of THF was treated with  $\text{TiCl}_4(\text{THF})_2$  (1.67 g, 5 mmol) at  $-78^\circ\text{C}$ . Gradually the yellow solid dissolved and the color of the mixture turned red. The mixture was allowed to warm up to room temp. and stirred for 2 h. After evaporation of the solvent, the residue was extracted with pentane (30 ml), the extracts were filtered, and the filtrate was concentrated to a few ml. Cooling to  $-78^\circ\text{C}$  afforded waxy brown crystals which were repeatedly recrystallized from pentane at  $-78^\circ\text{C}$ , yield 460 mg (35%), m.p.  $120^\circ\text{C}$ . —  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta = 0.24$ ,  $0.25$  (s, 3H,  $\text{SiCH}_3$ ),  $1.26$  (s, 9H,  $\text{CCCH}_3$ ),  $1.40$  (s, 9H,  $\text{NCCH}_3$ ),  $6.15$ ,  $6.18$ ,  $6.75$  (vt, splitting 2.6 Hz, 1H, ring H). —  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ,  $25^\circ\text{C}$ ):  $\delta = -0.25$ ,  $0.19$  ( $\text{SiCH}_3$ ),  $30.58$  ( $\text{CCCH}_3$ ),  $33.66$  ( $\text{CCCH}_3$ ),  $32.31$  ( $\text{NCCH}_3$ ),  $63.75$  ( $\text{NCCH}_3$ ),  $108.26$ ,  $120.52$ ,  $125.01$ ,  $156.48$  (ring C). — IR (KBr):  $\tilde{\nu} = 2980\text{ cm}^{-1}$  s,  $1250$  s,  $811$  vs,  $783$  s,  $440$ , m,  $429$  m. — EI-MS:  $m/z$  (%) =  $367$  (1) [ $\text{M}^+$ ],  $352$  (100) [ $\text{M}^+ - \text{Me}$ ],  $260$  (6) [ $\text{M}^+ - \text{Cl} - \text{C}_4\text{H}_9 - \text{Me}$ ].

$\text{C}_{15}\text{H}_{27}\text{Cl}_2\text{NSiTi}$  (368.3) Calcd. C 48.92 H 7.39 N 3.80  
Found C 48.56 H 7.36 N 3.21

## CAS Registry Numbers

**1**: 128000-00-0 / **4**: 128000-02-2 / **5**: 128000-03-3 / **6**: 128000-04-4 /  $\text{Li}[\text{C}_5\text{H}_3(\text{CMe}_3)]$ : 50356-03-1 /  $\text{Li}_2[\text{C}_5\text{H}_3(\text{CMe}_3)(\text{SiMe}_2\text{NHCMe}_3)]$ : 128000-01-1

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- <sup>8)</sup> Compound **6** is probably obtained as a mixture of *d,l* and *meso* isomers; cf. K. Schlögl, *J. Organomet. Chem.* **300** (1986) 219.
- <sup>9)</sup> J. Okuda, unpublished results.

[146/90]