ORGANOMETALLICS

Volume 16, Number 9, April 29, 1997

Communications

β-Si−H Agostic Rigidity in a Solvent-Free Indenyl-Derived *ansa*-Yttrocene Silylamide

Wolfgang A. Herrmann,[†] Jörg Eppinger,[†] Michael Spiegler,[†] Oliver Runte,[†] and Reiner Anwander*,[‡]

Institute of Inorganic Chemistry, Technische Universität München, D-85747 Garching, Germany, and Institute of Chemical Technology I, Universität Stuttgart, D-70550 Stuttgart, Germany

Received October 22, 1996[⊗]

Summary: The novel ansa-yttrocene complex $[(\eta^5\text{-}C_9H_5\text{-}2\text{-}Me)_2SiMe_2]Y[N(SiHMe_2)_2]$*, derived from a linked bis(indenyl) ligand, has been prepared by an amine elimination reaction. Utilization of* $Y[N(SiHMe_2)_2]_3(THF)_2$ *as a sterically flexible amide precursor ensures a high-yield synthesis, favorable solubility behavior, and the formation of two β-Si−H agostically fused metallacycles.*

Since the discovery that lanthanidocene (d^0f^n) complexes excellently model homogeneous Ziegler−Natta-type polymerization catalysts,[1] several chiral C_1- and C_2-symmetric *ansa*-bridged precatalysts have been developed to meet the demands of enantioselective synthesis of both polymers[2] and fine chemicals.[3] So far, salt metathesis starting from anhydrous lanthanide chlorides is the only well-established access to such lanthanidocene derivatives.[4−6] However, this route is encumbered by lengthy, tedious, often low-yield synthesis and *ate*-complex formation resulting in alkali-metal- and solvent-contaminated products.[7] Curiously, few efforts have been made to extend the ligand spectrum to indenyl or fluorenyl congeners,[4] considering the benefit to research and industry which evolved from Brintzinger-type C_2-symmetric *ansa*-zirconocenes.[8] We recently started the synthesis of such fused-ring lanthanidocene complexes.[9] Here we describe, as part of our studies on efficient precatalyst design by utilizing optimized synthesis conditions,[6b,10] a simple and effective method of preparing solvent-free complexes of rare-

---

[†] Technische Universität München.

[‡] Universität Stuttgart.

[⊗] Abstract published in *Advance ACS Abstracts*, April 1, 1997.

(1) Reviews: (a) Watson, P. L.; Parshall, G. W *Acc. Chem. Res.* **1985**, *18*, 51. (b) Yasuda, H.; Tamai, H. *Prog. Polym. Sci.* **1993**, *18*, 1097.

(2) (a) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103. (b) Mitchell, J. P.; Hajela, S.; Brookhart, S. K.; Hardcastle, K. I.; Henling, L. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1996**, *118*, 1045.

(3) Giardello, M. A.; Conticello, V. P.; Brard, L.; Gagné, M. R.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10241.

(4) For current reviews, see: (a) Schumann, H.; Meese-Marktscheffel, J. A.; Esser, L. *Chem. Rev.* **1995**, *95*, 865. (b) Edelmann, F. T. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 4, Chapter 2.

(5) Attempts to simplify the method of preparation of lanthanidocene complexes have only rarely been undertaken: (a) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271. (b) Booij, M.; Kiers, N. H.; Heeres, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1989**, *364*, 79. (c) For further non-salt metathesis routes to organolanthanide complexes, see: Schaverien, C. J. *Adv. Organomet. Chem.* **1994**, *36*, 283.

(6) The amine elimination reaction as a route to zirconocene complexes is meanwhile established: (a) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936. (b) Herrmann, W. A.; Morawietz, M. J. A.; Priermeier, T. *Angew. Chem.* **1994**, *106*, 2025. (c) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *Organometallics* **1996**, *15*, 4045 and references therein.

(7) For example, see: Haar, M. D.; Stern, C. L.; Marks, T. J. *Organometallics* **1996**, *15*, 1765.

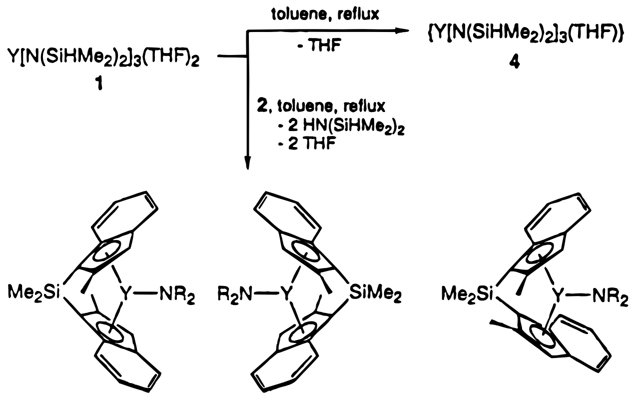
(8) For a recent review, see: Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. *Angew. Chem.* **1995**, *107*, 1255.

(9) Herrmann, W. A.; Anwander, R.; Riepl, H.; Scherer, W.; Whitaker, C. R. *Organometallics* **1993**, *12*, 4342.

(10) Runte, O.; Priermeier, T.; Anwander, R. *Chem. Commun.* **1996**, 1385.

S0276-7333(96)00892-8 CCC: $14.00

Scheme 1[a]



racemo-**3** meso-**3**

[a] Legend: **2** = $(C_9H_6\text{-}2\text{-}Me)_2SiMe_2$; R = $SiHMe_2$.

earth metals with *ansa*-bridged indenyl ligands, featuring an extraordinary β-Si−H agostic interaction.

$Y[N(SiHMe_2)_2]_3(THF)_2$ (**1**)[11] reacts with the bis(indenyl) ligand $(C_9H_6\text{-}2\text{-}Me)_2SiMe_2$ (**2**)[12] in toluene to form the yellow compound **3**, which can be isolated in 95% yield (Scheme 1).[13] As indicated by GC−MS analysis of the evaporated solvent, only refluxing of the reaction mixture for 18 h afforded total conversion. Application of the recently established extended silylamide route[10,11] turned out to be crucial in synthesizing the first *ansa*-bridged indenyl complex of the rare-earth metals. When $Y[N(SiMe_3)_2]_3$ is used instead of **1,** only decomposition without any further reaction is observed after prolonged heating.[14] Although the pK_a values of the bis(trimethylsilyl)amides should lead to deprotonation of **2**,[15] shielding of the bulky trimethylsilyl groups seems to prevent the exchange reaction (kinetic control).[11] On the other hand, the enhanced flexibility within **1**, originating from the sterically less demanding dimethylsilyl group and THF dissociation, ensures ligand approach and proton transfer. Most likely, ligand association proceeds via the mono-THF adduct **4**, which can be obtained by refluxing amide **1** in toluene (Scheme 1).[16]

The product is formed in a *rac*-**3**:*meso*-**3** ratio of 3:1, as detected by ^1H NMR. The pure *rac* form can be crystallized from toluene or *n*-hexane, where it easily redissolves upon heating. Spectroscopic data and elemental analysis are consistent with the displacement of THF in heteroleptic complex **3**. IR spectroscopy provided the first indication of an unusual bonding mode of the bis(dimethylsilyl)amide ligand in *rac*-**3**. The Si−H stretching frequency is shifted by 268 cm^{-1} to 1804 cm^{-1} compared to precursor **1** (2072 cm^{-1}). Such a distinct weakening of the Si−H bond is usually assigned to agostic interactions.[17,18]

^1H NMR spectroscopy clarifies the significant perturbation of the Si−H environment. The Si−H resonance of *rac*-**3** occurs at δ 2.97 and is thus 2 ppm upfield compared to the signal of **1**. Such drastic upfield shifts have also been found in related zirconocene complexes.[17] The Si−H resonance in *rac*-**3** resembles a nonet which is derived from a doublet of septets, as peak intensities suggest. The doublet splitting of 4.6 Hz in addition to the $^3J_{H,H}$ coupling (2.44 Hz) is to be assigned to a H···Y···H coupling.[19] Significant lengthening of the Si−H bond is also suggested by the comparably small value of the $^1H-^{29}Si$ coupling constant ($^1J_{Si,H}$ = 142 Hz).[20] The ^{29}Si NMR spectrum displays a doublet of septets at −22.4 ppm for the bis(dimethylsilyl)amide ligand. Perhaps the most striking feature of *rac*-**3** is its rigidity in solution, as evidenced by the H···Y···H coupling. Additionally, in the temperature range from −80 to +130 °C the ^1H and ^{13}C resonances of the silyl methyl (amido) group appear as two doublets and a doubled singlet, respectively, as expected for two methyl groups with different chemical environments. The signals of the bridged *meso*-**3** are rather broad at room temperature, clearly pointing to a flexible geometry. The chemical shift of the Si−H group of *meso*-**3** (δ 4.3 ppm) ranges between the shifts of *rac*-**3** and precursor **1**.

An X-ray crystal structure analysis of *rac*-**3**[21] revealed that the molecule is located on a 2-fold axis. The resulting *trans* coordination of the chelating bis(indenyl) ligand determines the C_2 symmetry of the thermodynamically more favorable *rac* complex (Figure 1). Bond distances (Y−C, 2.627(3)−2.697(3) Å) and bond angles (ring centroid−Y−ring centroid, 123.14(2)°) of the chelating moiety correlate well with the corresponding values

---

[11] Herrmann, W. A.; Anwander, R.; Munck, F. C.; Scherer, W.; Dufaud, V.; Huber, N. W.; Artus, G. R. J. *Z. Naturforsch., B* **1994**, *49*, 1789.

[12] For the preparation of **2**, see: Spaleck, W.; Antberg, M.; Rohrmann, J.; Winter, A.; Bachmann, B.; Kiprof, P.; Behm, J.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1347.

[13] In a glovebox, $Y[N(SiHMe_2)_2]_3(THF)_2$ (**1**; 630 mg, 1.00 mmol) and the bis(indenyl) ligand **2** (315 mg, 1.00 mmol) were dissolved in toluene (20 mL) and refluxed for 18 h, while the solution turned dark yellow. The solvent was removed in vacuo, leaving **3** (547 mg, 0.95 mmol, 95%) as a yellow powder. Pure *rac*-**3** (247 mg, 0.45 mmol, 45%) was obtained by fractional crystallization from hexane or toluene. IR (Nujol): 1804 m, 1410 w, 1344 m, 1333 m, 1279 m, 1246 s, 1150 m, 1037 m, 1000 m, 902 m, 876 s, 833 s, 807 s, 781 s, 765 s, 748 s, 690 m, 656 w, 644 m, 611 w, 571 w, 484 w, 460 m, 449 s, 429 m cm^{-1}. Anal. Calcd for $C_{26}H_{36}NSi_3Y$: C, 58.29; H, 6.77; N, 2.61. Found: C, 56.32; H, 6.80; N, 2.34. MS (CI): *m/e* 535 (M^+, 6%), 316 ($(SiMe_2(indenylMe)_2H^+$, 32%), 187 ($SiMe_2(indenylMe)H^+$, 100%). ^1H NMR (C_6D_6, 25 °C): δ 7.87 (d, 2H), 7.38 (d, 2H), 6.91 (t, 2H), 6.84 (t, 2H), 6.15 (s, 2H), 2.98 (n, 2H), 2.39 (s, 6H), 1.10 (s, 6H), 0.067 (d, 6H), 0.034 (d, 6H). ^{13}C NMR (C_6D_6, 25 °C): δ 138.0, 131.3, 131.0, 123.4, 123.3, 122.1, 121.9, 108.2, 99.29, 18.01, 3.15, 2.66, 2.64. ^{29}Si NMR (C_6D_6, 25 °C): δ 4.32 (Si_{bridge}), −22.41 (Si−N).

[14] (a) Mu, Y.; Piers, W. E.; MacDonald, M.-A.; Zaworotko, M. J. *Can. J. Chem.* **1995**, *73*, 2233. (b) Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G., Jr. *Organometallics* **1996**, *15*, 2720.

[15] pK_a(THF) = 25.8: Fraser R. R.; Mansour, T. S.; Savard, S. *J. Org. Chem.* **1985**, *50*, 3232.

[16] For full experimental and characterization details for **4**, see the Supporting Information.

[17] (a) Herrmann, W. A.; Huber, N. W.; Behm, J. *Chem. Ber.* **1992**, *125*, 1405. (b) Procopio, L. J.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 177.

[18] Luo, X. L.; Kubas, G. J.; Burns, C. J.; Bryan, J. C.; Unkefer, C. J. *J. Am. Chem. Soc.* **1995**, *117*, 1159. Thus, the Si−H−Y bond state seems to be comparable to that in Mo−(η^2-SiH) complexes (ν_{SiH} = 1730−1750 cm^{-1}).

[19] A final decision whether the doublet splitting of 4.6 Hz originates from $^1J_{Y,H}$ or through-space $J_{H,H}$ coupling via Y can only be reached by ^1H-coupled ^{89}Y NMR spectroscopy. However, no ^{89}Y NMR resonance could be observed for *rac*-**3**. Similar problems were reported for a cyclopentadienyl-derived yttrium complex: Schaverien, C. J. *Organometallics* **1994**, *13*, 69.

[20] Lukevics, E.; Pudowa, O.; Sturkovich, R. *Molecular Structure of Organosilicon Compounds*; Ellis-Horwood: Chichester, U.K., 1989. Silicon hydrides generally display $^1J_{Si,H}$ values in the range 160−200 Hz; $^1J_{Si,H}(\mathbf{1})$ = 164 Hz.

[21] Crystal data for *rac*-**3** ($C_{26}H_{36}Si_3NY$): monoclinic, *C*2/*c* with *a* = 15.110(4) Å, *b* = 11.731(2) Å, *c* = 15.699(5) Å, β = 108.55(1)°, *V* = 2638.2(11) Å^3, and D_{calcd} = 1.349 g cm^{-3} for *Z* = 4. Data were collected at 163 K on an Enraf-Nonius CAD4 diffractometer. The structure was solved by Patterson methods, and least-squares refinement of the model based on 2472 reflections ($I > 0.01\sigma(I)$) converged to a final R1 = 3.2% (wR2 = 7.4%) and GOF = 1.05. All hydrogen atoms were located in difference Fourier maps and refined with isotropic thermal parameters.

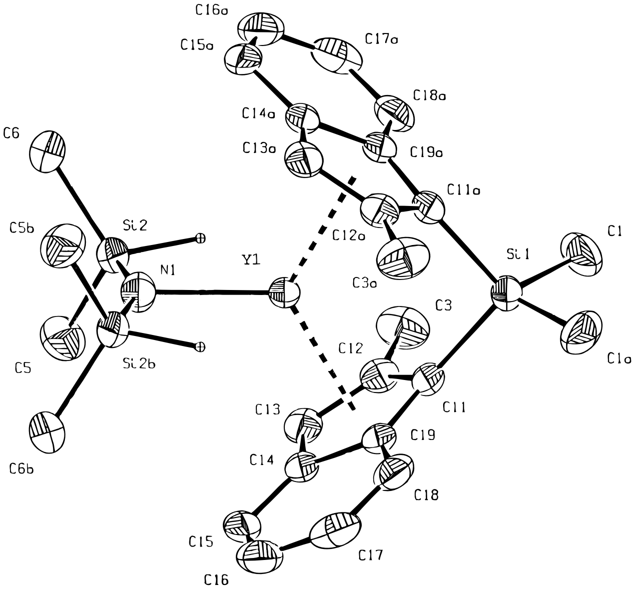


Figure 1. PLATON drawing of *rac*-**3**. Atoms are represented by thermal ellipsoids at the 50% level. Except for H(2) and H(2a), all hydrogen atoms are omitted for clarity. Pertinent distances (Å) and angles (deg): Y(1)−Si(2), 3.082(1); Y(1)−N(1), 2.237(4); Si(2)−H(2), 1.45(2); Si(2)−N(1), 1.666(1); Y(1)−N(1)−Si(2), 103.4(1); Si(2)−N(1)−Si(2)a, 153.3(2); Si(2)−Y(1)−N(1), 31.72(2); Y(1)−Si(2)−N(1), 44.9(1); N(1)−Si(2)−C(5), 114.6(1); N(1)−Si(2)−C(6), 117.1(2); C(5)−Si(2)−C(6), 109.0(2); N(1)−Si(2)−H(2), 100(1).

for other *ansa*-yttrocene complexes.[22] However, the bis(dimethylsilyl)amide fragment which completes the pseudotetrahedral coordination geometry revealed an unprecedented structural detail. Despite the quite normal Y−N bond length of 2.237(4) Å,[23] *both* "$SiHMe_2$" fragments seem to be sterically frozen by close *β*-Si−H−Y contacts and thus explain the ^1H and ^{13}C NMR findings. Usually, "$Cp_2Y[N(SiMe_3)_2]$" species display only one close Ln···Si contact.[23,24] The Y···Si distances of 3.082(1) Å are even in the range observed for Ln−Si *σ*-bonds, as exemplified by $Cp^*_2Sm[SiH(SiMe_3)_2]$ (Sm−Si, 3.052(8) Å).[25] The silicon hydride in *rac*-**3** could be located in a difference Fourier map and was successfully refined. The SiH−Y distance of 2.54(2) Å is slightly above the range recently reported for SiH−Er agostic interactions in $Er[N\mathit{t}Bu(SiHMe_2)]_3$ (2.32(3)−2.41(3) Å),[26] which can be explained by the changed covalent radius of yttrium, the changed coordination number, and a probably strained double-agostic interaction.

The unique agostic interaction is further documented in the bond angles of the $YNSi_2$ fragment, which are remarkably contracted for Y−N−Si (103.4(1)°) and extremely enlarged in the case of Si−N−Si (153.3(2)°). To our knowledge this is well above the values reported for Si−N−Si angles so far (121.6(4)−133(1)°).[22] All atoms participating in the agostically fused four-membered rings are located in one plane (torsion angle H2−Si2−N1−Y1, −2.79(11)°).

In summary, these preliminary results show that proper synthesis conditions such as precursor design are important for the preparation of indenyl-based *ansa*-yttrocene complexes. The steric and electronic peculiarities of the chelating bis(indenyl) moiety imply a remarkable bis(dimethylsilyl)amide bonding based on a 2-fold, strong Si−H−metal coordination. Si−H−metal interactions are assumed to be mechanistic intermediates in the dehydrogenative polymerization of hydrosilanes by lanthanidocene complexes.[25] Stimulated by the plethora of interesting spectroscopic and structural details of complex **3**, we are currently evaluating the preference and extent of this coordination mode by (i) steric and electronic fine-tuning of the chelating unit, (ii) ligand exchange reactions, and (iii) application in catalytic transformations.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft for the award of a fellowship to R.A.

Supporting Information Available: Text giving full experimental details for complexes **3** and **4** and tables of atomic coordinates, atomic displacement parameters, and bond distances and angles for *rac*-**3** (9 pages). Ordering information is given on any current masthead page.

OM9608925

---

(22) Giardello, M. A.; Conticello, V. P.; Brard, L.; Sabat, M.; Rheingold, A. L.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10212.

(23) (a) den Haan, K. H.; de Boer, J. L; Teuben, J. H.; Spek, A. L.; Kojic-Prodic, B.; Hays, G. R.; Huis, R. *Organometallics* **1986**, *5*, 1726. (b) Schumann, H.; Rosenthal, E. C. E.; Kociok-Köhn, G.; Molander, G. A.; Winterfeld, J. *J. Organomet. Chem.* **1995**, *496*, 233.

(24) For polyagostic Ln···Me interactions, see: (a) Tilley, T. D.; Andersen, R. A.; Zalkin, A. *Inorg. Chem.* **1984**, *23,* 2271. (b) Evans, W. J.; Anwander, R.; Ziller, J. W.; Khan, S. I. *Inorg. Chem.* **1995**, *34*, 5927.

(25) (a) Radu, N. S.; Tilley, T. D.; Rheingold, A. L. *J. Am. Chem. Soc.* **1992**, *114*, 8293. (b) Radu, N. S.; Tilley, T. D. *J. Am. Chem. Soc.* **1995**, *117*, 5863.

(26) Rees, W. S., Jr.; Just, O.; Schumann, H.; Weimann, R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 419.