Synthesis of highly soluble yttrium–salen complexes and the X-ray structure of *N,N′*-bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine-[bis(dimethylsilyl)amido]yttrium

Oliver Runte,[a] Thomas Priermeier[a] and Reiner Anwander*[b]

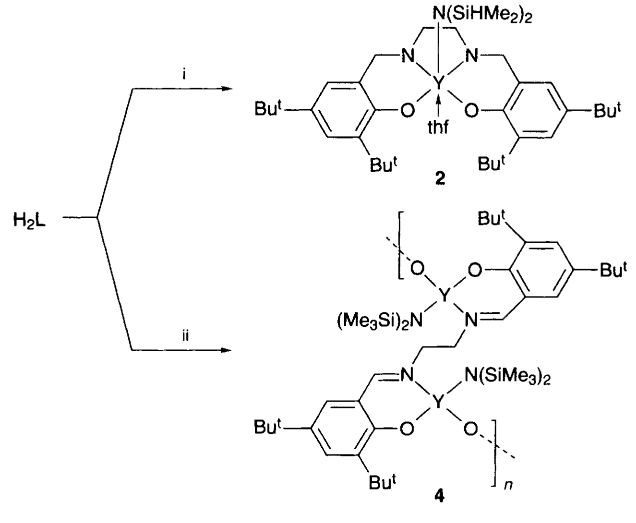
[a] *Institute of Inorganic Chemistry I, Technical University of Munich, D-85747 Garching, Germany*
[b] *Institute of Chemical Technology I, University of Stuttgart, D-70550 Stuttgart, Germany*

***N,N′*-Bis(3,5-di-*tert*-butylsalicylidene)ethylenediamine H_2L reacts with $[Y\{N(SiHMe_2)_2\}_3(thf)_2]$ in thf–hexane at ambient conditions to afford monomeric $[YL\{N(SiHMe_2)_2\}(thf)]$, the X-ray structure determination of which reveals a strongly bent coordination mode of the anionic salen derived ligand.**

Tailor-made cyclopentadienyl, β-diketonato and binaphthol ligands dominate the ligand environment of organolanthanide complexes with promising relevance to catalytic processes.[1–3] Schiff-base ligands, in particular salen derivatives, have been extensively employed as a stereochemically rigid ligand framework in highly efficient homogeneous precatalysts of first-row d-transition metals.[4] Use of flexible, easily tunable salen-type ligands should also put stimulus into the expanding field of organolanthanide catalysed transformations. However, hitherto the numerous studies on lanthanide Schiff-base complexation[5] comprise relatively few examples in nonaqueous media.[6]

Herein, we describe the synthesis and characterization of a highly hexane soluble yttrium–salen complex utilizing an extended silylamide route.[7] $[YL\{N(SiHMe_2)_2\}(thf)]$ **2** was obtained quantitatively by reaction of $[Y\{N(SiHMe_2)_2\}_3(thf)_2]$, **1** with H_2L, according to Scheme 1. Spectroscopic data and elemental analysis† for the product were consistent with the presence of both one thf and one bis(dimethylsilyl)amido ligand in the vicinity of the metal centre.

Crucial in the synthesis of this new type of discrete, mononuclear lanthanide complexes was the choice of an appropriate starting compound. Attempted preparation by the standard alcoholysis[8] of $[Y\{N(SiMe_3)_2\}_3]$ **3** with H_2L led to the formation of an oligomeric, thf insoluble product **4**.‡ The enhanced steric flexibility within **1**, originating from the sterically less demanding dimethylsilyl group and thf dissociation, might be responsible for the successful isolation of **2**. The bulkier trimethylsilyl group within **3** disfavours the intramolecular approach of the second phenol moiety, and rotation around the ethylene bridge affords such kinetically controlled intermolecular bonding within **4** (Scheme 1).[9]



Scheme 1 *Reagents and conditions*: thf–hexane, 20 °C, 5 d; i, **1**; ii, **3**

The monomeric assembly of **2** was unequivocally established by X-ray crystallography (Fig. 1),§ although a symmetrically imposed disordering excludes a detailed discussion of bond lengths and angles. Complex **2** to our knowledge represents the first structurally characterized heteroleptic monometallic yttrium salen-type complex.[10]

The yttrium atom is six-coordinate, the ligands adopting a distorted trigonal-prismatic geometry. The yttrium oxygen (salen) distances of 2.16 Å lie within the range of the terminal Y–O bond lengths in five-coordinate $[Y(OC_6H_3Bu^t{}_2\text{-}2,6)_2(\eta^5\text{-}C_5Me_5)]$ [2.096(4), 2.059(3) Å][11] and eight-coordinate $[\{CuYL'(NO_3)(Me_2SO)\}_2]$ [H_4L' = *N,N′*-ethylenebis(3-hydroxysalicylideneimine)] [2.29(1) Å].[12] The Y–N [bis(dimethylsilyl)amide] bond length of 2.27 Å matches the 2.229(4)–2.276(4) Å of the amide precursor.[7] Apart from mononuclearity, the most striking structural feature of **2** is the coordination mode of L^{2-}. In contrast to most salen complexes of the d-transition[4] and main group metals[13] which possess a square-planar geometry, the large yttrium ion imposes a strongly bent coordination. The deviation from planarity is best seen by the displacement of the yttrium by 0.95 Å from the O_2N_2 least-squares plane and by the decreased angle between the two phenyl groups (108°). Such an out-of-plane coordination is routinely detected in porphyrin-

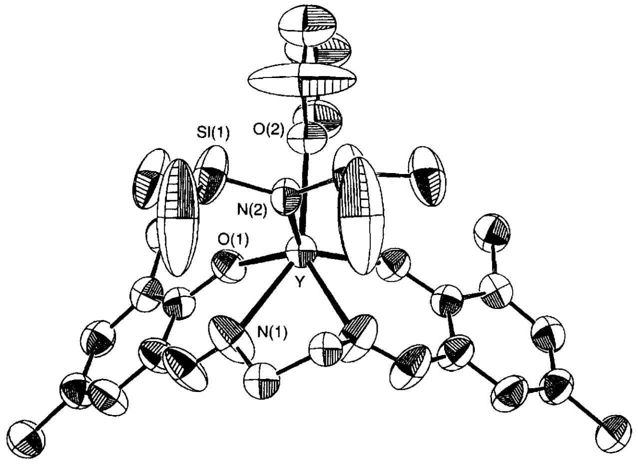


Fig. 1 Perspective view of the molecular structure of **2** (PLATON). Hydrogen atoms and the methyl groups of the *tert*-butyl substituents are omitted for clarity. For the same reason only one part of the disordered ethylene bridge is shown, the second half being created by the mirror plane through O(2), Y, N(2). Selected interatomic distances (Å) and angles (°): Y–O(1) 2.16, Y–N(2) 2.27; O(1)–Y–O(1A) 105, O(1)–Y–N(2) 126, N(1)–Y–O(1) 74, N(1)–Y–O(1A) 125.

$$\mathbf{2} \xrightarrow{\text{i}} \underset{\mathbf{5}}{[\mathrm{YL(OC_6H_3Bu^t{}_2\text{-}2,6)(thf)}]} \xrightarrow{\text{ii}} \underset{\mathbf{6}}{[\mathrm{YL\{CH(SiMe_3)_2\}(thf)}]}$$

Scheme 2 *Reagents and conditions*: i, $HOC_6H_3Bu^t{}_2$-2,6, hexane, room temp., 12 h; ii, Li[$CH(SiMe_3)_2$], hexane, room temp., 12 h

like complexes.[14] The salen ligand in **2** is sterically rather more demanding than the binaphthol ligand in [La{$CH(SiMe_3)_2$}{1,1′-(2-$OC_6H_2Bu^t{}_2$-3,5)$_2$}(thf)$_3$].[15] The intriguing structural motif of **2** also suggests comparison to tied-back ansa-lanthanocene complexes such as [(*R*)-Y(η^5-C_5Me_4)$SiMe_2${η^5-(−)-menthylC_5H_3}{$N(SiMe_3)_2$}] which display catalytically highly efficient building blocks.[16]

Subsequent work addresses variation of the Schiff-base ligand and the lanthanide centre, reactivity of the Ln–N(silylamide) bond and suitability of these complexes in catalysis. Preliminary substitution chemistry indicates a familiar pattern of reactivity as evidenced in the isolation of **5** and **6** (Scheme 2).

We thank Professor W. A. Herrmann for generous support and the Deutsche Forschungsgemeinschaft for the award of a DFG fellowship to R. A.

Footnotes

† All manipulations were performed under argon with rigorous exclusion of air and water. *Spectroscopic data* for **2**: IR (Nujol, ν/cm^{-1}): 2045s, 1633s, 1616vs, 1549s, 1535s, 1414m, 1341m, 1306m, 1275w, 1257m, 1242m, 1200w, 1167s, 1058w, 1026m, 988m, 922w, 890m, 877m, 831s, 786m, 758w, 746m, 677w, 638w, 608w, 525m, 442w. ^{1}H NMR (400 MHz, C_6D_6): δ 7.80 (2 H, s, CH=N), 7.70 (2 H, d, Ph), 7.06 (2 H, d, Ph), 5.00 (2 H, m, SiH), 4.26 (4 H, m, thf), 3.96 (4 H, s), 2.90 (4 H, m, thf), 1.67 (18 H, s, Bu^t), 1.36 (18 H, s, Bu^t), 0.28 (12 H, d, SiMe). ^{13}C (100.6 MHz, C_6D_6): δ 169.9, 164.8, 139.2, 136.5, 129.8, 129.7, 122.7, 70.4, 59.5, 35.7, 34.1, 31.8, 30.3, 25.3, 3.3. ^{29}Si (79.5 MHz, C_6D_6): δ −23.80. Satisfactory elemental analysis was obtained for **2** (C, H, N).

‡ IR spectroscopy and elemental analysis confirm the presence of silylamide moieties in **4**. Additionally, conventional synthetic methods such as salt metathesis of [$LnCl_3(thf)_x$] (Ln = Y, x = 3.5; La, x = 1.5) with Na_2L or alcohol exchange of [$Ln(OPr^i)_3$] with H_2L also yielded oligomeric, thf insoluble products.

§ *Crystal data* for **2**: $C_{40}H_{68}N_3O_3Si_2Y$, M = 784.07, orthorhombic, space group *Pnma*, a = 12.148(1), b = 22.520(1), c = 16.409(2) Å, U = 4489(1) Å^3, Z = 4, D_c = 1.16 g cm^{-3}, F(000) = 1680. IPDS (STOE) Mo-rotating anode (λ = 0.71073 Å), T = −80 °C. The structure was solved by direct methods. A crystallographically imposed pseudo-mirror plane bearing the thf ligand and the atoms Y and N(2) causes disordering of the amide ligand, both *tert*-butyl groups, the thf ligand and the ethylene moiety, the latter having been resolved into two equally populated positions. Least-squares refinement of the model based on 2029 reflections [$|F_o| > 2\sigma(|F_o|)$] and 231 parameters converged to a final R (R_w) value of 0.0575 (0.0540). Residual electron densities: +0.59, −0.54 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallograpic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/76.

References

1 M. A. Giardello, V. P. Conticelli, L. Brard, M. R. Gagne and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10241.
2 H. Tsukube, H. Shiba and J.-I. Uenishi, *J. Chem. Soc., Dalton Trans.*, 1995, 181.
3 H. Sasai, T. Arai, Y. Satow, K. N. Houk and M. Shibasaki, *J. Am. Chem. Soc.*, 1995, **117**, 6194.
4 E. N. Jacobsen, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, New York, 1995, vol. 12, ch. 11.1.
5 For recent comprehensive reviews, see: P. Guerriero, S. Tamburini and P. A. Vigato, *Coord. Chem. Rev.*, 1995, **139**, 17; V. Alexander, *Chem. Rev.*, 1995, **95**, 273.
6 P. Blech, C. Floriani, A. Chiesi-Villa and C. Guastini, *J. Chem. Soc., Dalton Trans.*, 1990, 3557.
7 W. A. Herrmann, R. Anwander, F. C. Munck, W. Scherer, V. Dufaud, N. W. Huber and G. R. J. Artus, *Z. Naturforsch., Teil B*, 1994, **49**, 1789.
8 P. B. Hitchcock, M. F. Lappert and A. Singh, *J. Chem. Soc., Chem. Commun.*, 1983, 1499.
9 L. Huang, C. Huang and G. Xu, *Jiegou Huaxue* (*J. Struct. Chem.*), 1989, **8**, 1.
10 For a homoleptic system, see: S. Mangani, A. Takeuchi, S. Yamada and P. Oriolo, *Inorg. Chim. Acta*, 1989, **155**, 149.
11 C. J. Schaverien, J. H. G. Frijns, H. J. Heeres, J. R. van den Hende, J. H. Teuben and A. L. Spek, *J. Chem. Soc., Chem. Commun.*, 1991, 642.
12 U. Casellato, P. Guerriero, S. Tamburini, S. Sitran and P. A. Vigato, *J. Chem. Soc., Dalton Trans.*, 1991, 2145.
13 D. A. Atwood, J. A. Jegier, K. J. Martin and D. Rutherford, *Organometallics*, 1995, **14**, 1453.
14 C. J. Schaverien and A. G. Orpen, *Inorg. Chem.*, 1991, **30**, 4968; J. W. Buchler and P. Hammerschmitt, *Liebigs Ann. Chem.*, 1991, 1177.
15 C. J. Schaverien, N. Meijboom and A. G. Orpen, *J. Chem. Soc., Chem. Commun.*, 1992, 124.
16 M. A. Giardello, V. P. Conticelli, L. Brard, M. Sabat, A. L. Rheingold, C. L. Stern and T. J. Marks, *J. Am. Chem. Soc.*, 1994, **116**, 10212.

Received, 16th February 1996; Com. 6/01152G