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O-Benzylated-calix[4]arenes as ancillary ligands in organolanthanide chemistry †

Frank Estler, Eberhardt Herdtweck and Reiner Anwander *

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstraße 4, D-85747 Garching, Germany. E-mail: reiner.anwander@ch.tum.de

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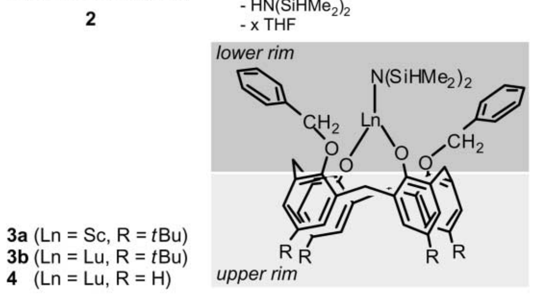
25,27-*O*-Benzylated-calix[4]arenes H_2L react with Ln[N(SiHMe$_2$)$_2$]$_3$(thf)$_x$ (Ln = Sc (x = 1), Lu (x = 2)) *via* an extended silylamide route to yield monomeric, heteroleptic calix[4]arene complexes with a N(SiHMe$_2$)$_2$ ligand bonded to the metal centre which is suitable for further ligand exchange reactions.

Linked alkoxide (aryloxide) ligands have attracted considerable attention in early transition metal chemistry as ancillary ligands of chiral precatalysts for olefin polymerization ("postmetallocenes") and organic synthesis.[1,2] Calix[4]arene derived anions comprise a set of oxygen donor atoms preorganized in a quasi-planar fashion making them interesting aryloxide ligands for rare earth metals.[3] The overall charge and steric demand of these ligands can be effectively tuned by partial functionalization of the O_4 set (at the *lower rim*), *e.g.*, *via* alkylation or silylation.[4] Moreover, derivatization at the *upper rim* affects the acidity of the phenol groups.[5] Complexes of rare earth metals with deprotonated calixarene ligands featuring various ring sizes were previously obtained by salt metathesis reactions in the presence of base molecules.[6–9] Herein, we describe the synthesis and characterization of 4-*tert*-butylcalix[4]arene and calix[4]arene supported lanthanide complexes utilising our extended silylamide route.[10] ‡

The *lower rim*-functionalized "divalent" precursors 25,27-dibenzyloxy-4-*tert*-butylcalix[4]arene **1a** and 25,27-dibenzyloxycalix[4]arene **1b** were synthesized from the corresponding calix[4]arenes using literature methods.[11] **1a** was reacted with one equivalent of the amide complexes Ln[N(SiHMe$_2$)$_2$]$_3$(thf)$_x$ (**2a**, Ln = Sc, x = 1; **2b**, Ln = Lu, x = 2) at ambient temperature to yield heteroleptic [LnL{N(SiHMe$_2$)$_2$}] (**3**) as shown in Scheme 1. Remarkably, derivatives **3** of the larger rare earth metal centers Y and La are not formed under the prevailing reaction conditions, probably due to an intrinsic steric misfit of the functionalized calix[4]arene bowl and the size of the lanthanide–silylamide moiety. §



Scheme 1 Synthesis of discrete metal–organic rare earth calix[4]arene complexes according to the extended silylamide route.

Compounds **3a** and **3b** can be crystallized from toluene in high yields (80–90%). Spectroscopic data and elemental analyses are consistent with the presence of one bis(dimethylsilyl)amido ligand at the metal centre. Displacement of all of the THF donor ligands occured which is probably due to the steric demand of the benzyloxo groups and the better chelating donor capabilities of its O(ether) atoms. The resulting steric and/or electronic saturation of the metal centres is also indicated by the absence of any Ln ··· H–Si ß-agostic interactions.[12] Non-agostic bis(dimethylsilyl)amide ligands are clearly indicated by the ν(Si–H) stretching vibration at ν = 2083 (**3a**) and ν = 2052 (**3b**) cm^{-1} in the IR spectrum and a SiH proton displaying a septet at δ = 5.79 (**3a**) and δ = 5.71 (**3b**), considerably downshifted compared to its synthetic precursors (**2a**, δ = 5.03; **2b**, δ = 4.95). The signals of the benzylic methylene groups also appear significantly downshifted at δ = 5.64 (**3a**) and δ = 5.44 (**3b**) (**1a**, δ = 4.71). Coordination of the metal renders the *ring* methylene groups diastereotopic as revealed by two doublets at δ = 4.30/2.93 (**3a**) and δ = 4.19/2.93 (**3b**). This pattern and the signals of the *tert*-butyl groups at δ = 1.41 (**3a**) and δ = 0.71 (**3b**) are in agreement with a *cone* or a *1,3-alternate* conformation. The ^{13}C NMR chemical shifts of the *ring* methylene groups of δ 33.8 (**3a**) and 34.1 (**3b**) propose a *cone* conformation in solution (*cf.*, δ(CH$_2$)$_{\text{cone}}$ = 32.7 for 4-*tert*-butylcalix[4]arene).[13] In the solid state, the *cone* conformation of the scandium derivative **3a** could be unequivocally established by an X-ray structure analysis (Fig. 1).¶

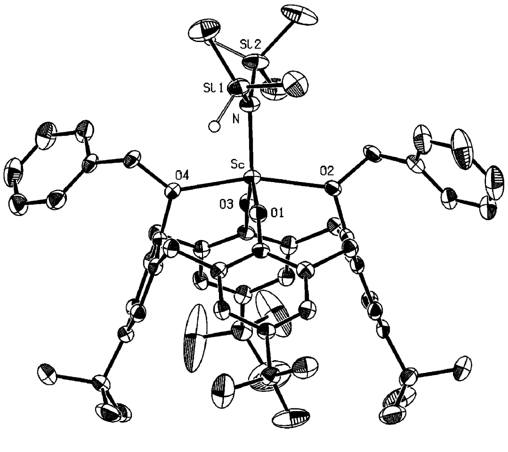


Fig. 1 Molecular structure of **3a**. Selected bond lengths (Å) and angles (°): Sc–N 2.060(2), Sc–O1 1.912(2), Sc–O2 2.278(2), Sc–O3 1.912(2), Sc–O4 2.248(2); O1–Sc–N 113.9(1), O2–Sc–N 100.0(1), O1–Sc–O3 126.2(1), O2–Sc–O4 162.65(8).

The coordination geometry at the metal centre is best described as distorted trigonal bipyramidal. Two aryloxide oxygen atoms (O1, O3) and the nitrogen atom form the equatorial plane, while the ethereal oxygen atoms (O2, O4) occupy the apical positions (O2–Sc–O4, 162.65(8)°). The Sc–O1/O3 bond lengths average 1.912 Å and as expected are considerably longer than those in the formally three-coordinate complex

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† Electronic supplementary information (ESI) available: synthesis and characterization data. See http://www.rsc.org/suppdata/dt/b2/b205200h/

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$Sc(OC_6H_2tBu_2\text{-}2,6\text{-}Me\text{-}4)_3$ (av. 1.869 Å)[14] and are comparable to those found in other formally five-coordinate scandium aryloxide complexes, *e.g.*, $[Sc_2(4\text{-}$*tert*-butyloxacalix[3]-arene$)_2\text{-}(DMSO)_2]\cdot 2DMSO$ (1.970 Å).[9b] The Sc–O2/O4 bond lengths average 2.263 Å and lie in the range for other metallated calix[4]arene complexes featuring a formally five-coordinate *exo* isomer, *e.g.*, Al[4-*tert*-butylcalix[4]arene$(OMe)_2$]H (2.125 Å)[15] or Fe[4-*tert*-butylcalix[4]arene$(OMe)_2$]CPh_2 (2.225 Å).[16] The Sc–N bond length of 2.060(2) Å compares to the av. 2.069 Å found in $Sc[N(SiHMe_2)_2]_3(thf)$.[17]

The reaction of **1b** with $Lu[N(SiHMe_2)_2]_3(thf)_2$ was carried out in toluene at ambient temperature according to Scheme 1 because of the poor solubility of **1b** in hexane. After crystallization from toluene, $[LuL\{N(SiHMe_2)_2\}]$ (**4**) was obtained in high yield (90%). Its spectroscopic details are almost identical to those of **3b**. The ν(Si–H) stretching vibration of the lutetium bonded bis(dimethylsilyl)amido ligand appears at $\nu = 2053\ cm^{-1}$ and the ^1H NMR spectrum shows a septet at $\delta = 5.74$. The signals for the *ring* methylene groups and for the benzylic methylene groups are at $\delta = 4.19/2.93$ and at $\delta = 5.49$, respectively. Also for complex **4**, the ^{13}C NMR chemical shift of the *ring* methylene groups of $\delta = 32.8$ suggests a *cone* conformation in solution (*cf.*, $\delta(CH_2) = 31.6$ for calix[4]arene).[13] The molecular structure of **4** could be unequivocally proven by X-ray crystallography (Fig. 2).¶

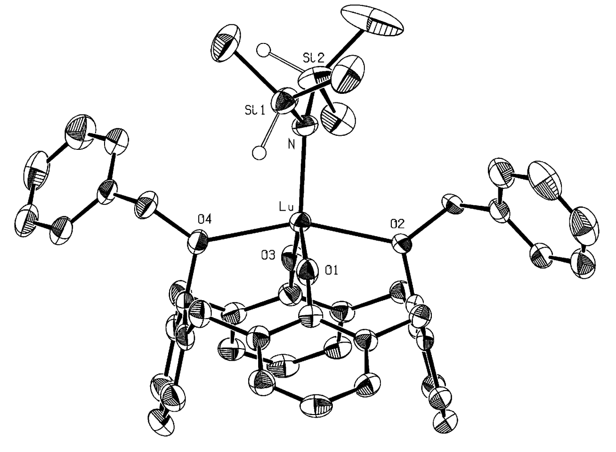

Fig. 2 Molecular structure of **4**. Selected bond lengths (Å) and angles (°): Lu–N 2.186(4), Lu–O1 2.011(3), Lu–O2 2.351(3), Lu–O3 2.011(3), Lu–O4 2.356(3); O1–Lu–N 121.1(1), O2–Lu–N 99.4(1), O1–Lu–O3 121.8(1), O2–Lu–O4 156.86(9).

The lutetium centre in **4** shows the same coordination geometry as scandium in **3a**. The Lu–O (aryloxide) and Lu–O (ether) bond lengths average 2.011 and 2.353 Å, respectively, and are comparable to those found in five-coordinate aryloxide complex $Lu(OC_6H_3iPr_2\text{-}2,6)_3(thf)_2$ (av. 2.044 and 2.296 Å)[18] and are in agreement with other five-coordinate lanthanide calix[4]arene complexes, *e.g.*, **3a** and [Y(4-*tert*-butylcalix[4]arene-$(OSiHMe_2)(thf)]_2$ (2.065 and 2.260 Å) taking into account the different ionic radii.[4b] The Lu–N bond length, 2.186(4) Å, equals those found in $Lu[N(SiHMe_2)_2]_3(thf)_2$ (2.184(3), 2.238(3) and 2.253(3) Å).[17] The different Ln–O bond lengths and the different substitution pattern at the *upper rim* of complexes **3a** and **4** implicate distinct conformational orientations of the phenyl rings. The two opposite *O*-alkylated phenyl rings form angles of 69.4° (**3a**) and 76.9° (**4**) with the least square plane formed by the four carbon atoms of the methylene groups. The phenolic rings are tilted against this C_4 plane by 45.5° (**3a**) and 48.6° (**4**), respectively. The overall *pinched cone* conformational arrangement is also revealed by the O ··· O distances of the ether moieties (O2 ··· O4, 4.475 Å (**3a**) and 4.611 Å (**4**)) and those of the more flattened phenol units (O1 ··· O3, 3.411 Å (**3a**) and 3.514 Å (**4**)).

Preliminary investigations show that activation of complexes **3** and **4** for catalytic applications can be achieved by silylamide ligand displacement involving Brønsted (HOMe) and Lewis acidic reagents (AlR_3).

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Notes and references

‡ For convenience, the term "lanthanide" is used synonymous with the rare earth elements Sc, Y, La and Ln = Ce–Lu.

§ We propose that also for reasons of steric discrimination, a more complicated reaction occurred when $Ln[N(SiMe_3)_2]_3$ was used as a synthetic precursor.

¶ Crystallographic data for **3a**: $C_{83}H_{104}NO_4ScSi_2$, $M = 1280.81$, monoclinic, space group *Cc*, $a = 17.5600(4)$, $b = 24.5441(7)$, $c = 17.2735(4)$ Å, $\beta = 92.577(2)°$, $V = 7437.3(3)$ Å^3, $Z = 4$, $\rho_{calc} = 1.144\ g\ cm^{-3}$, $F(000) = 2760$, $\mu(Mo\text{-}K\alpha) = 0.180\ mm^{-1}$, $\lambda = 0.71073$ Å, $T = 123$ K. The 20851 reflections measured on a Nonius Kappa CCD area detector yielded 12306 unique data ($\Theta_{max} = 25.34°$, $R_{int} = 0.037$), $R1 = 0.0532$, $wR2 = 0.1276$.

For **4**: $C_{53}H_{56}NO_4LuSi_2$, $M = 1002.14$, triclinic, space group $P\bar{1}$, $a = 11.3794(1)$, $b = 14.0015(2)$, $c = 16.9067(3)$ Å, $\alpha = 69.3972(6)$, $\beta = 75.8968(6)$, $\gamma = 69.8248(8)°$, $V = 2343.69(6)$ Å^3, $Z = 2$, $\rho_{calc} = 1.420\ g\ cm^{-3}$, $F(000) = 1024$, $\mu(Mo\text{-}K\alpha) = 2.203\ mm^{-1}$, $\lambda = 0.71073$ Å, $T = 173$ K. The 21461 reflections measured on a Nonius Kappa CCD area detector yielded 8139 unique data ($\Theta_{max} = 25.38°$, $R_{int} = 0.042$), $R1 = 0.0329$, $wR2 = 0.0748$. CCDC reference numbers 182440 (**3a**) and 182441 (**4**). See http://www.rsc.org/suppdata/dt/b2/b205200h/ for crystallographic data in CIF or other electronic format.

1 G. J. P. Britovsek, V. C. Gibson and D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428.
2 M. Shibasaki and H. Gröger, *Top. Organomet. Chem.*, 1999, **2**, 199.
3 J. M. Harrowfield, M. I. Odgen, W. R. Richmond and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1991, 2153.
4 (*a*) B. Castellano, E. Solari, C. Floriani, N. Re, A. Chiesi-Villa and C. Rizzoli, *Organometallics*, 1998, **17**, 2328; (*b*) R. Anwander, J. Eppinger, I. Nagl, W. Scherer, M. Tafipolsky and P. Sirsch, *Inorg. Chem.*, 2000, **39**, 4713.
5 K. Araki, K. Iwamoto, S. Shinkai and T. Matsuda, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 3480.
6 (*a*) I. L. Fedushkin, M. Weydert, A. A. Fagin, S. E. Nefedov, I. L. Eremenko, M. N. Bochkarev and H. Schumann, *Z. Naturforsch., Teil B*, 1999, **54**, 466; (*b*) L. M. Engelhardt, B. M. Furphy, J. M. Harrowfield, D. L. Kepert, A. H. White and F. R. Wilner, *Aust. J. Chem.*, 1988, **41**, 1465.
7 (*a*) P. D. Beer, M. G. Drew, A. Grieve, M. Kan, P. B. Leeson, G. Nicholson, M. I. Odgen and G. Williams, *Chem. Commun.*, 1996, 117; (*b*) P. D. Beer, M. G. Drew, A. Grieve, M. Kan, P. B. Leeson, G. Nicholson, M. I. Odgen and G. Williams, *Inorg. Chem.*, 1996, **35**, 2202.
8 M. B. Furphy, J. M. Harrowfield, M. I. Odgen, B. W. Skelton, H. A. White and F. R. Wilner, *J. Chem. Soc., Dalton Trans.*, 1989, 2217.
9 (*a*) Z. Asfari, J. M. Harrowfield, M. I. Odgen, J. Vicens and H. A. White, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 854; (*b*) C. E. Daitch, P. D. Hampton and E. N. Duesler, *Inorg. Chem.*, 1995, **34**, 5641.
10 R. Anwander, *Top. Organomet. Chem.*, 1999, **2**, 1.
11 J.-D. van Loon, A. Arduini, L. Coppi, W. Verboom, A. Pochini, R. Ungaro, S. Harkema and D. N. Reinhoudt, *J. Org. Chem.*, 1990, **55**, 5639.
12 J. Eppinger, M. Spiegler, W. Hieringer, W. A. Herrmann and R. Anwander, *J. Am. Chem. Soc.*, 2000, **122**, 3080.
13 C. Jaime, J. de Mendoza, P. Prados, P. M. Nieto and C. Sánchez, *J. Org. Chem.*, 1991, **56**, 3372.
14 P. B. Hitchcock, M. F. Lappert and A. Singh, *J. Chem. Soc., Chem. Commun.*, 1983, 1499.
15 M. G. Gardiner, G. A. Koutsantonis, S. M. Lawrence, P. J. Nichols and C. L. Raston, *Chem. Commun.*, 1996, 2035.
16 M. Giusti, E. Solari, L. Giannini, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *Organometallics*, 1997, **16**, 5610.
17 R. Anwander, O. Runte, J. Eppinger, G. Gerstberger, E. Herdtweck and M. Spiegler, *J. Chem. Soc., Dalton Trans.*, 1998, 847.
18 D. M. Barnhart, D. L. Clark, J. C. Gordon, J. C. Huffman, R. L. Vincent, J. G. Watkin and B. D. Zwick, *Inorg. Chem.*, 1994, **33**, 3487.