

# Yttrium half-sandwich complexes bearing the 2-(*N,N*-dimethylamino) ethyl-tetramethylcyclopentadienyl ligand



Lars N. Jende, Căcilia Maichle-Mössmer, Christoph Schädle, Reiner Anwander\*

Institut für Anorganische Chemie, Universität Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

## ARTICLE INFO

### Article history:

Received 10 April 2013

Received in revised form

2 May 2013

Accepted 3 May 2013

Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 65th Birthday.

### Keywords:

Alkyl

Silylamide

Cyclopentadienyl

Donor-functionalization

Yttrium

SiH activation

## ABSTRACT

The synthesis of bis(dimethylsilyl)amide and dimethyl half-sandwich complexes of yttrium bearing the 2-(*N,N*-dimethylamino)ethyl-tetramethylcyclopentadienyl ligand revealed unusual Si–H activation reactions and ate complex formation, respectively. Protonolysis of complex  $Y[N(SiHMe_2)_2]_3(thf)_2$  with cyclopentadiene  $C_5Me_4HCH_2CH_2NMe_2$  ( $HcP^{NMe_2}$ ) at elevated temperature yielded complex  $Cp^{NMe_2}Y[\eta^2-SiMe_2(NSiHMe_2)_2](thf)$  featuring a four-membered metallacycle. The bis(amido) ligand  $[\eta^2-SiMe_2(NSiHMe_2)_2]^{2-}$  is shown to form via separation of  $H_2SiMe_2$ . In contrast, the salt metathesis reaction of  $YCl_3(thf)_3$  with  $LiN(SiHMe_2)_2$  and  $LiCp^{NMe_2}$  in a 1/2/1 ratio at ambient temperature generated the non-activated complex  $Cp^{NMe_2}Y[N(SiHMe_2)_2]_2$ , exhibiting a distinct ligand activation at elevated temperatures, as evidenced by a comprehensive NMR spectroscopic study. Application of a sequential salt metathesis protocol involving  $YCl_3(thf)_3$ ,  $LiCp^{NMe_2}$ , and  $LiMe$  led to the isolation of ate complexes  $[Cp^{NMe_2}YCl_2][LiCl(thf)_2]$  and  $[Cp^{NMe_2}YMe_2(LiMe)]_2$ . Aforementioned half-sandwich complexes were all characterized by X-ray structure analyses and the respective silylamido and methyl derivatives are demonstrated to produce the half-sandwich yttrium bis(tetramethylaluminate) complex  $[Cp^{NMe_2}AlMe_3Y(AlMe_4)_2]$  in the presence of excess trimethylaluminum, by NMR spectroscopic studies.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Monocyclopentadienyl or half-sandwich-type complexes emerged as a prolific field in organo-rare-earth metal chemistry [1]. Particularly, highly reactive alkyl, hydrido, and amido derivatives and their cationic variants have revealed unique catalytic potential in polymerization reactions [1]. Approximately ten years ago, we set out to use tetramethylaluminate ligands as thermally robust alkyls in disguise and found that they are ideally suited to stabilize rare-earth metal half-sandwich complexes [2]. The corresponding complexes  $Cp^R Ln(AlMe_4)_2$  represent the first entries of the  $LLn(III)$  bis(tetramethylaluminate)-based postmetallocene library ( $L$  = monoanionic ancillary ligand), which is currently exploited for 1,3-diene polymerization [3]. Furthermore, donor-functionalized cyclopentadienyl ligands often ensure the formation of monolanthanide complexes via additional intramolecular coordination [1,4]. Amino functionalities are particularly effective for rare-earth metal(III) centres due to a good HSAB match and optimal steric shielding [5]. To date, bis(aluminate) complexes  $Cp^R Ln(AlMe_4)_2$  have been synthesized according to two main reaction sequences

(Scheme 1, A and B). While route A exploits the thermal stability of homoleptic tetramethylaluminate complexes  $Ln(AlMe_4)_3$  [6], route B refers to the well-defined bis(dimethylsilyl)amide derivatives  $Ln[N(SiHMe_2)_2]_3(thf)_x$  (extended silylamide route) [7]. Herein we examined synthesis strategies B and C for assessing the feasibility of yttrium bis(aluminate) complexes  $Cp^{NMe_2}Y(AlMe_4)_2$ , with  $Cp^{NMe_2}$  designating  $\eta^5-C_5Me_4CH_2CH_2NMe_2$  (1-[2-(*N,N*-dimethylamino)ethyl]-2,3,4,5-tetramethyl-cyclopentadienyl) [8].

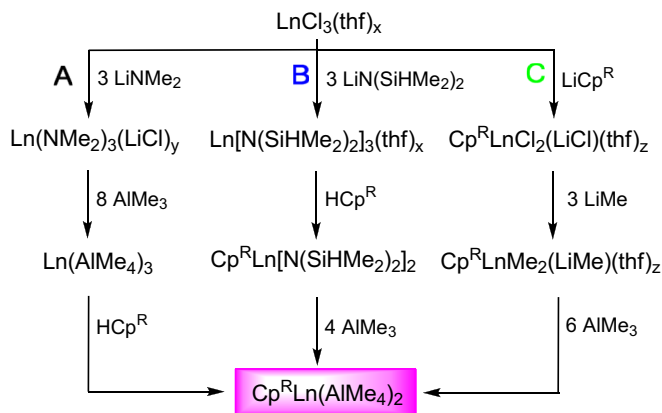
## 2. Results and discussion

### 2.1. Route B

Aiming at a bis(aluminate) half-sandwich complex with an amino-coordinated yttrium centre, we initially focused on pre-coordinating the cyclopentadienyl ligand in a  $\eta^5:\kappa^1$  fashion to the rare-earth metal. Thus formed complex  $Cp^{NMe_2}Y[N(SiHMe_2)_2]_2$  should engage in a trimethylaluminum-promoted silylamido/aluminate exchange under mild conditions and formation of the corresponding hydrocarbyl complexes [2]. It is noteworthy that very recently half-sandwich rare-earth metal bis(dimethylsilyl)amide complexes were successfully tested in styrene polymerization upon activation with perfluorated organoborate salts ( $[Ph_3C][B(C_6F_5)_4]$ ,  $[PhNMe_2H][B(C_6F_5)_4]$  [9,10]. However, the activity was low and

\* Corresponding author.

E-mail address: [reiner.anwander@uni-tuebingen.de](mailto:reiner.anwander@uni-tuebingen.de) (R. Anwander).

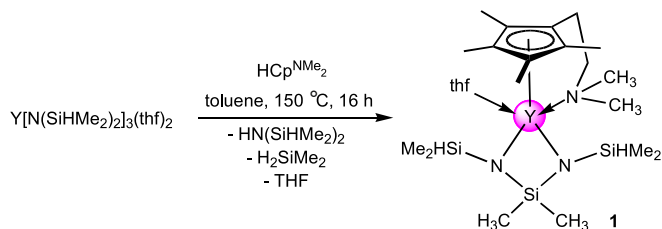


**Scheme 1.** Protocols considered for the synthesis of complexes  $\text{Cp}^{\text{R}}\text{Ln}(\text{AlMe}_4)_2$ .

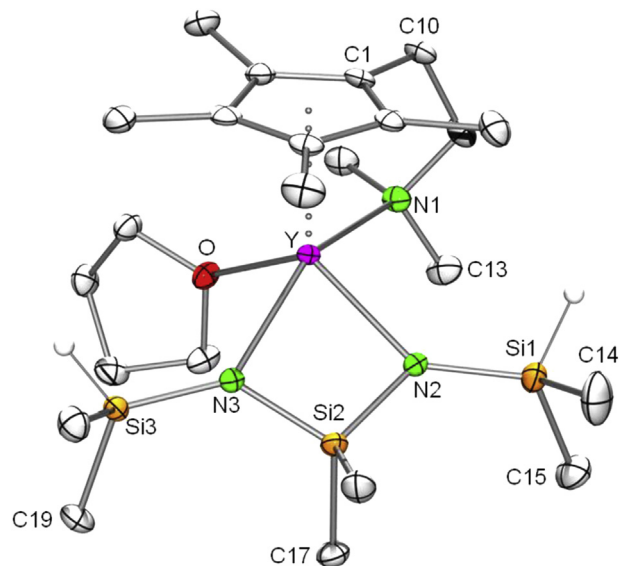
addition of trialkylaluminum was necessary to form a ternary catalyst system of complex/borate/ $\text{AlR}_3$  ( $\text{AlR}_3$ ;  $\text{R} = \text{Me}, \text{iBu}$ ). The protonolysis reaction of yttrium bis(dimethylsilyl)amide complex  $\text{Y}[\text{N}(\text{SiHMe}_2)_2]_3(\text{thf})_2$  [7a] with one equivalent of the N-donor functionalized cyclopentadiene  $\text{HCp}^{\text{NMe}_2}$  in toluene at  $150^\circ\text{C}$  yielded the Si–H bond activated complex  $\text{Cp}^{\text{NMe}_2}\text{Y}[\eta^2\text{SiMe}_2(\text{NSiHMe}_2)_2](\text{thf})$  (**1**) in moderate yields (68%) (Scheme 2). As previously observed for the synthesis of half-sandwich complex  $(\text{C}_5\text{Me}_5)\text{Y}[\text{N}(\text{SiHMe}_2)_2]_2$  [2] the silylamine elimination took place only at elevated temperature (according to an  $^1\text{H}$  NMR spectroscopic study the reaction did not occur below  $70^\circ\text{C}$ ).

Single crystals of **1** suitable for X-ray diffraction analysis were grown from saturated toluene solutions at  $-35^\circ\text{C}$  (space group  $P-1$ , Fig. 1). The yttrium centre is  $\eta^5:\kappa^1$  coordinated by the N-donor substituted cyclopentadienyl ligand via the Cp ring and the nitrogen atom. The dianionic bisamido ligand  $[\text{SiMe}_2(\text{NSiHMe}_2)_2]^{2-}$  coordinates in a  $\eta^2$  fashion via the two nitrogen atoms, while an additional thf molecule completes the coordination sphere of the yttrium centre.

The geometry of complex **1** is best described as distorted trigonal bipyramidal, with the nitrogen atoms N1 and N3 in the apical position disclosing an angle of  $145.2^\circ$  at the metal centre, while the centroid of the cyclopentadienyl together with the nitrogen atom N2 and the oxygen atom of the thf molecule are in the equatorial positions with angles close to trigonal planar ( $118.0$ ,  $120.1$  and  $121.5^\circ$ ). Interestingly, both Si–H units are oriented towards the electrophilic  $\text{Y}^{3+}$  centre, but  $\text{Y}\cdots\text{HSi}$   $\beta$ -agostic interactions can be ruled out since the  $\text{Y}\cdots\text{H}$  distances are longer than  $3.7\text{ \AA}$ . The absence of such secondary interactions is also evidenced by the lack of Si–H stretching vibrations at lower frequencies ( $2000\text{--}1800\text{ cm}^{-1}$ ) [11]. The most striking feature of complex **1** is the generation of the chelating (dimethylsilylene)-bis(dimethylsilylamido) ligand itself, although such Si–H bond activation along with the formation of a new Si–N bond under elimination of  $\text{H}_2\text{SiMe}_2$  has been observed previously. In 2009, Yuen and Marks observed the generation of a bidentate



**Scheme 2.** Synthesis of the bisamido yttrium half-sandwich complex **1**.



**Fig. 1.** ORTEP view of the molecular structure of **1**. Atomic displacement parameters are set at the 50% probability level. Hydrogen atoms (except for SiH) are omitted for clarity. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for **1**:  $\text{Y}-\text{Cp}_{\text{cent}} = 2.381$ ,  $\text{Y}-\text{O} = 2.388(4)$ ,  $\text{Y}-\text{N}1 = 2.629(3)$ ,  $\text{Y}-\text{N}2 = 2.249(3)$ ,  $\text{Y}-\text{N}3 = 2.276(3)$ ,  $\text{Si}1-\text{N}2 = 1.719(3)$ ,  $\text{Si}3-\text{N}3 = 1.719(3)$ ,  $\text{Si}2-\text{N}2 = 1.694(4)$ ,  $\text{Si}2-\text{N}3 = 1.683(3)$ ,  $\text{N}1-\text{Y}-\text{N}2 = 93.8(1)$ ,  $\text{N}2-\text{Y}-\text{N}3 = 71.6(1)$ ,  $\text{N}1-\text{Y}-\text{N}3 = 145.2(1)$ ,  $\text{N}1-\text{Y}-\text{O} = 77.5(1)$ ,  $\text{O}-\text{Y}-\text{N}3 = 83.8(1)$ ,  $\text{Cp}_{\text{cent}}-\text{Y}-\text{N}2 = 120.1(1)$ ,  $\text{Cp}_{\text{cent}}-\text{Y}-\text{O} = 118.0(1)$ ,  $\text{O}-\text{Y}-\text{N}2 = 121.5(1)$ .

amido-amine ligand during a transamination protocol, utilizing  $\text{Nd}[\text{N}(\text{SiMe}_3)_2]_3$  and  $\text{HN}(\text{SiHMe}_2)_2$  for the synthesis of  $\text{Nd}[\text{N}(\text{SiHMe}_2)_2]_3$ . The formation of monoanionic  $[\text{SiMe}_2(\text{NSiHMe}_2)(\text{NHSiHMe}_2)]^-$  ligand was confirmed by a ligand exchange reaction with a binuclear lanthanum complex and subsequent X-ray diffraction analysis (Chart 1, A) [12]. The same divalent ligand as present in complex **1** was reported by Buffet and Okuda in 2011, to result from a protonolysis reaction of  $\text{Sc}[\text{N}(\text{SiHMe}_2)_2]_3(\text{thf})$  with  $\text{Me}_3[12]\text{aneN}_4$  in  $\text{C}_6\text{D}_6$  at  $80^\circ\text{C}$  (Chart 1, B) [13]. Very recently, Chen et al. were able to isolate the cationic amidinate scandium amide complex  $[(\text{PhC}[\text{N}-2,6-\text{Pr}_2\text{C}_6\text{H}_3]_2)\text{Sc}(\text{N}(\text{SiHMe}_2)\{\text{SiMe}_2\text{N}(\text{SiHMe}_2)_2\})(\text{thf})_2][\text{B}(\text{C}_6\text{F}_5)_4]$  (Chart 1, C) [10a]. Treatment of the corresponding amidinate scandium bis(dimethylsilyl)amide complex with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in an aromatic solvent initiated the unexpected Si–H activation, but single crystals suitable for X-ray diffraction could only be obtained after addition of thf.

The metrical parameters of the bidentate bis(amido) (**1** and B) and amido-amine (A) are illustrated in Chart 2. The position of the hydrogen atoms is given by the torsion angle ( $\text{H}-\text{Si}-\text{N}-\text{M}$ , underlined) and bond lengths are set in brackets ( $\text{\AA}$ ).

The previously assumed elimination of dimethylsilane (during the synthesis of compound B), could be unambiguously proven by  $^1\text{H}$  and  $^1\text{H}-^1\text{H}$  COSY NMR spectroscopy in our reaction, showing a sharp septet at  $4.03\text{ ppm}$  for the  $\text{Me}_2\text{SiH}_2$  protons which couples with the triplet at  $0.07\text{ ppm}$  of the  $\text{Me}_2\text{SiH}_2$  protons. Furthermore, the  $^1\text{H}$  NMR spectrum of complex **1** showed the expected set of signals for the coordinated  $\text{Cp}^{\text{NMe}_2}$  ligand. The two aminomethyl groups appear as a singlet at  $1.95\text{ ppm}$  and the four methyl groups of the Cp ring display two singlets at  $2.18$  and  $2.4\text{ ppm}$ . The signals of the four ethylene-bridge protons are found as two multiplets at  $2.42$  and  $2.57\text{ ppm}$ . The SiH protons of the bis(amido) ligand are detected at  $5.18\text{ ppm}$ , while the silyl methyl groups give a broad signal at  $0.54\text{ ppm}$  (ESI, Fig. S1).

Efforts to synthesize the half-sandwich yttrium bis(dimethylsilyl)amide complex by applying a one-pot salt metathesis protocol, that is subsequent addition of  $\text{LiCp}^{\text{NMe}_2}$  and two

Download English Version:

<https://daneshyari.com/en/article/1324392>

Download Persian Version:

<https://daneshyari.com/article/1324392>

[Daneshyari.com](https://daneshyari.com)