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Published in: Chemical Communications

DOI: 10.1039/b606384e

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Document Version
Publisher's PDF, also known as Version of record

Publication date: 2006

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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The 6-amino-6-methyl-1,4-diazepine group as an ancillary ligand framework for neutral and cationic scandium and yttrium alkyls

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Received (in Cambridge, UK) 5th May 2006, Accepted 9th June 2006
First published as an Advance Article on the web 27th June 2006
DOI: 10.1039/b606384e

The 6-amino-6-methyl-1,4-diazepine framework is a readily available neutral 6-electron ligand moiety, suitable to support cationic group 3 metal alkyl catalysts; it also provides convenient access to tri- and tetradeutate monoanionic ligand derivatives.

In contrast to their transition-metal analogues (which have long been known as active catalysts for olefin polymerisation), the chemistry of cationic rare-earth metal alkyl species has only recently been developed.1 The use of nitrogen-based facial tridentate ligand moieties (such as 1,4,7-triazacyclonane, tris(pyrazolyl)methane and tris(oxazolinyl)methane) has played an important role in opening up this chemistry.2 A disadvantage of these ligand systems is that stepwise modification and extension of these moieties is synthetically quite elaborate. Very recently, the use of the 6-amino-6-methyl-1,4-diazepine group as a facially coordinating moiety in biomimetic complexes was described.3 This framework is readily obtained by reaction of 1,2-diaminoethanes with nitroethane and formaldehyde, followed by reduction of the nitro group. Here we show that this group provides an accessible and versatile basis for neutral and anionic tri- and tetradeutate ligands for use in rare-earth metal organometallic chemistry.

To test the suitability of the 6-amino-6-methyl-1,4-diazepine group as an ancillary ligand moiety for rare-earth metal alkyl chemistry, the known permethylated 6-amino-6-methyl-1,4-diazepine (L) was reacted with the group 3 metal trialkyls M(CH₂SiMe₃)₃(THF)₂ (M = Sc, Y). This afforded the complexes (L)M(CH₂SiMe₃)₃ (M = Sc 1a or Y 1b, Scheme 1) in high isolated yields (1a: 94%; 1b: 95%). Solution NMR spectroscopy of these compounds (C₆D₆) showed that the three alkyl groups on the metal centre are equivalent down to −50 °C. The M–CH₂ resonances (C₆D₆, 20 °C) for 1a are found at δ −0.14 ppm (¹H) and δ 40.0 ppm (¹³C), for 1b at δ −0.56 (δ, ³J_YH = 2.9 Hz) and δ 36.9 ppm (³J_YC = 35 Hz, ³J_CH = 97.9 Hz) respectively.

A crystal structure determination of 1a was performed, and its molecular structure is shown in Fig. 1.† The crystal contains two independent molecules in the asymmetric unit that do not differ significantly; only one is explicitly discussed here. The three nitrogen atoms of L are bound to the scandium centre in a fac-arrangement and the geometry at Sc is approximately octahedral. The average Sc–N bond length of 2.497 Å in 1a is slightly longer...
than that reported for the triazacyclonane complex ScMe₂[9mæneN₃(CH₂SiMe₃)$_3$] (average 2.463 Å), while the average Sc–CH₂ distances are very similar. There is no notable asymmetry in the bonding of the three amine donors in 1a: the Sc–N distance for the NMe₂-group is intermediate between the other two Sc–N distances in the complex. The smallest N–Sc–N angle involves the amine nitrogens linked by the (CH₂)₂-bridge, N(12)–Sc–N(13) of 66.45(8)°. 

The neutral trialkyl complexes 1 can be converted in THF solvent to the dialkyl cations [(L1)M(CH₂SiMe₃)$_2$(THF)]$^+$ (M = Sc, 2a; Y, 2b) by reaction with [PhMe₂NH][BAr₄] (Ar = Ph, C₆F₅). This was seen by NMR spectroscopy when performing these reactions in THF-d$_{8}$, and the BP$_{4}$-salt of the Sc cation 2a was isolated in 75% yield from THF-cyclohexane. The $^1$C NMR resonances of the M–CH₂ groups in 2 relative to those in 1 show the typical downfield shift and (for Y) increase in $^1$J$_{YC}$ associated with conversion to the cationic species (for 2b: $\delta$ 42.3 ppm, $J_{YC}$ = 41 Hz).

Ethene polymerisation experiments with 1a and 1b activated by [PhMe₂NH][B(C₆F₅)$_3$] were performed in toluene, and the results are listed in Table 1. For both metals active polymerisation catalysts are obtained. This shows that the 6-amino-6-methyl-1,4-diazepine group is suitable as an ancillary ligand moiety for cationic rare-earth metal alkyl catalysts. Remarkably, the activity of the Sc system increases substantially when the temperature is increased from 50 °C to 70 °C, but this is accompanied by a strong broadening of the polymer molecular weight distribution. This might be due to the transformation of the initially formed cation into another species that is also active, and of which the nature is presently unclear.

Two new ligand derivatives were prepared by the acid-catalysed condensation of the 1,4-dimethylated 6-amino-6-methyl-1,4-diazepine with benzaldehyde and with o-hydroxybenzaldehyde. This produced the 6-amino-6-methyl-1,4-diazepines 2b and 3 (Scheme 2).

Reaction of L2 with the yttrium trialkyl Y(CH₂SiMe₃)$_3$(THF)$_2$ is rapid and quantitative (NMR), and resulted in a product in which the imine carbon atom of the ligand has been alkylated to give the tridentate monoanionic ligand [(Me₂SiCH₂)Ph(C)NCMe₂(CH₂SiMe₃)$_2$]$.^+$ The coordination site on the metal that is vacated by the alkyl group that has migrated to the ligand is filled by one molecule of THF. The structure of this complex (3) was established by single-crystal X-ray diffraction (Fig. 2). The compound contains a monoanionic fac-tridentate ligand in which the nitrogen on the 6-position of the 1,4-diazepine skeleton is an amide with a phenyl(trimethylsilylmethyl)methyl substituent. The THF molecule is located in a trans position relative to the amide nitrogen. The Y–N(amide) distance of 2.215(3) Å is substantially shorter than the Y–N distances to the remaining ligand amine nitrogens. Low-temperature solution NMR studies on 3 show a fully asymmetric structure, with two resonances (δ 2.44, 2.12 ppm) for the diastereotopic methylene protons of the alkyl group transferred to the ligand, and four

![Scheme 2](image1.png)

**Scheme 2** Synthesis of ligand L₂ and L₃H and complex 3 and 4.

![Molecular structure](image2.png)

**Fig. 2** Molecular structure of one of the independent molecules of 3 (hydrogen atoms omitted for clarity, thermal ellipsoids drawn at 50% probability level). Selected bond distances (Å) and angles (°): Y1–N11 2.695(3), Y1–N12 2.589(3), Y1–N13 2.215(3), Y1–C120 2.469(3), Y1–C124 2.446(4), Y1–O1 2.487(3), N11–Y1–N12 62.94(10), N11–Y1–N13 74.85(10), N12–Y1–N13 71.39(11), C120–Y1–C124 110.10(14), O1–Y1–C120 87.37(11), O1–Y1–C124 85.74(13), N11–Y1–C120 157.45(10), N12–Y1–C124 151.54(14), O1–Y1–N13 152.13(10).

<table>
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<th>Trialkyl</th>
<th>PE yield/g</th>
<th>Productivity/$10^3$ kg(PE) mol(M)$^{-1}$ h$^{-1}$ bar$^{-1}$</th>
<th>$10^{-5}$ M$<em>{w}$/M$</em>{n}$</th>
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<td>1b</td>
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<tr>
<td>1b</td>
<td>70</td>
<td>4.57</td>
<td>5.48</td>
<td>1.43</td>
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</tbody>
</table>

* Conditions: 1 l steel autoclave (stirring rate 600 rpm), 250 ml toluene, 10 μmol trialkyl, 10 μmol [PhMe₂NH][B(C₆F₅)$_3$], 5 bar ethene, 10 min run time.
resonances (δ 0.18, −0.50, −0.74, −0.88 ppm) for the diastereotopic YCH2Si methylene protons. Intermolecular alkylation of ligand imino functionalities by metal alkyl species has been observed previously for early transition metals.

Reaction of L3H with Y(CH2SiMe3)2(THF)2 resulted in a product (4, Scheme 2) in which the phenolic −OH group of the ligand has been deprotonated, and where the imino ligand moiety remains intact (as evidenced by the 1H and 13C NMR resonances at δ 7.64 ppm and δ 161.1 ppm for the aldime −CH=N group and the v(C=N) IR band at 1622 cm⁻¹). Although suitable crystals of 4 for a single-crystal structure determination have not yet been obtained, the solution 1H and 13C spectra indicate a C3 asymmetric structure with a tetradentate iminophenolatedazepine ligand and two alkyl groups attached to the metal centre. The yttrium is again 6-coordinate, as no additional THF is bound. The NMR resonances for the YCH2Si groups are found at δ −0.51 and −0.55 ppm (1H; 2JHH = 11.5 Hz, 1JHH = 2.9 Hz) and δ 30.0 ppm (13C; 1JCH = 38 Hz). The compound is related to the triazacyclononanephenolato complexes of scandium reported by Mountford et al.4

In conclusion, the 6-amino-6-methyl-1,4-diazepine ligand framework proves to be a highly versatile and readily accessible ligand moiety for the synthesis of a range of neutral and monoanionic ancillary ligands that can be used in organo-rare-earth metal chemistry. We also expect these ligands to be useful for the early transition metals. The synthesis of derivatives with larger rare-earth metals (especially La) and the study of the reactive and catalytic properties of these compounds and their cationic derivatives is in progress.

This investigation was financially supported by the Chemical Sciences division of the Netherlands Organisation for Scientific Research (NWO-CW). The authors thank A. Jekel for polymer GPC analyses.

Notes and references