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Synthesis and structure of four-coordinate dimethyl aluminium complexes incorporating new N,O-chelating arylamido ligands

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Abstract

A new type of arylamido ligands with an intramolecular coordinating *ortho*-ether-substituent (i.e. a O,N^- chelating ligand) is introduced. The achiral and chiral 4-coordinate dimethyl aluminium complexes [2-ROC_6H_4NR']$AlMe_2$ (**4a**: R = R′ = Cy; **4b**: R = (−)-menthyl, R′ = Cy, **4c**: R = (−)-menthyl, R′ = CPh_3) have been prepared by reaction of the appropriate amido Li salt with $ClAlMe_2$. Complex **4a** could also be obtained, via methane elimination, by reaction of $AlMe_3$ with the corresponding ligand. The presence of two rotamers in solution at room temperature for **4b** and for **4c** is most likely due to a restricted rotation of the (−)-menthyl group at this temperature due to severe steric interactions with the rest of the complex.

Keywords: Synthesis; Dimethyl aluminium; N,O-Chelating arylamido ligands

1. Introduction

Mononuclear aluminum(III) complexes (L–X)AlR_2 (R = alkyl group) incorporating one monoanionic ligand of the $L–X^-$ type with a chelated four coordinate metal center have been widely investigated over the past 20 years due to their practical and fundamental importance [1]. For example, stable aluminium compounds containing nitrogen substituents are useful in the preparation of AlN-containing materials [2]. More recently, dialkyl complexes (L–X)AlR_2 ($L–X^- = N–O^-$, $N–N^-$; R = alkyl group) were found to be effective precursors to highly reactive cationic aluminum alkyls, which are of interest as epoxide and ethylene polymerization catalysts [3].

In contrast to the $N–O^-$ and $N–N^-$ bidentate ligands, monoanionic amido-ether bidentate ligands ($O–N^-$) appear to be rarely used for coordination to a Group 13 metal center. In fact, thus far, the generation of [$Me_2Si(O^tBu)(N^tBu)$]MR_2 (M = Al, Ga; R = Me, Cl; **A**, Chart 1) constitutes the only reports on that matter [4].

We are interested in the synthesis of mononuclear 4-coordinate dialkyl aluminium complexes incorporating one $O–N^-$ chelating ligand i.e. a N-anion with a pendant ethereal oxygen. The presence of an ethereal oxygen, which can be considered as a weak Lewis base center as compared to a neutral amine nitrogen or an alkoxide oxygen [1d], should, in turn, yield a more electrophilic, and thus more reactive, Al center. This feature is of interest for any potential application in Lewis acid catalysis of the derived Al complexes.

Arylamido ligands with an intramolecular coordinating *ortho*-ether-substituent (**B**, Chart 1) appeared suitable for this purpose because they may form a stable 5-membered ring Al metallocycle upon coordination to an Al(III) center. The *ortho*-ether-substituent in **B** is expected to provide steric shielding of the metal center as well as the electron donation to the metal center, and thus to favor the formation of mononuclear Al complexes. In addition, as presented in this work, the synthesis of chiral versions of such ligands is relatively easy, which opens the way to new chiral aluminium complexes.

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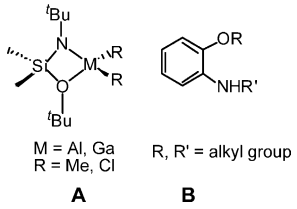


Chart 1.

Here we report our early findings on the synthesis and structure of new mononuclear dialkyl aluminium complexes incorporating achiral and chiral arylamido ligands with an intramolecular coordinating *ortho*-ether-substituent.

2. Results and discussion

2.1. Synthesis of 2-ROC_6H_4NHR' ligands 3a–c

The new achiral and chiral 2-alkoxy-*N*-alkylaniline ligands 2-ROC_6H_4NHR' **3a** (R = R′ = cyclohexyl), **3b** (R = (−)-menthyl, R′ = cyclohexyl) and **3c** (R = (−)-menthyl, R′ = CPh_3) were prepared by adapting literature methods [5]: 1-fluoro-2-nitrobenzene was reacted with the appropriate alcoholate potassium salt in THF at room temperature to give the corresponding 1-alkoxy-2-nitrobenzene (**1a**–**b**, Scheme 1), which after reduction of the nitro group with hydrazine on Pd led to the respective 2-alkoxyanilines (**2a**–**b**, Scheme 1).

Subsequent N-alkylation with $ClCPh_3$ or with cyclohexanone in a reducing medium afforded the 2-alkoxy-*N*-alkylaniline ligands (**3a**–**c**, Scheme 1) as white powders in moderate overall yields.

2.2. Synthesis and structure of $[ROC_6H_4NR']AlMe_2$ (4a–c)

The synthesis of **4a** was carried out using the two general methods employed for the obtention of such complexes: i.e. the salt metathesis and the methane elimination routes.

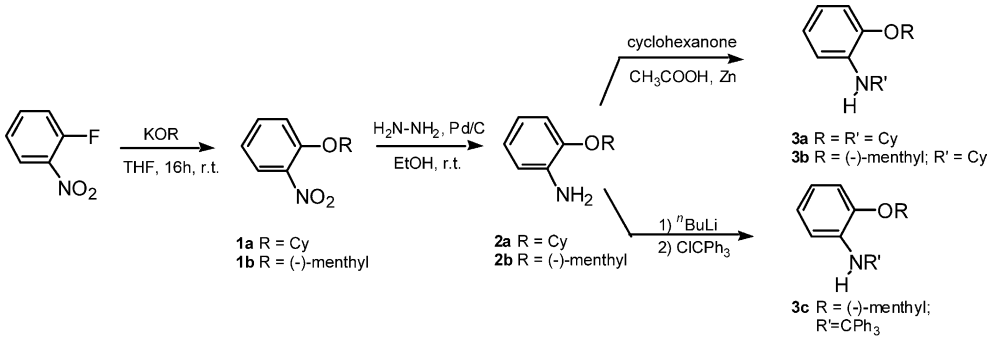
The reaction of the Li salt [2-$CyOC_6H_4NCy$][Li], generated by reaction of 2-$CyOC_6H_4NHCy$ with one equivalent of ^{n}BuLi, with one equivalent of $ClAlMe_2$ in toluene for 18 h at room temperature yields the formation of the chelate dimethyl complex [2-$CyOC_6H_4NCy$]$AlMe_2$ (**4a**, Scheme 2) isolated in good yield.

The molecular structure of **4a** was determined by X-ray crystallography analysis and is illustrated in Fig. 1. Compound **4a** crystallizes on a C_2 axis: i.e. the Al atom (4e position of the *C*2/*c* group) and the middle of the C(1)–C(1a) contact are on the C_2 axis. In these conditions, the atomic arrangement observed by X-ray diffraction must be considered as an average of two chemically true molecules, rotated by 180° around the C_2 axe in the crystal.

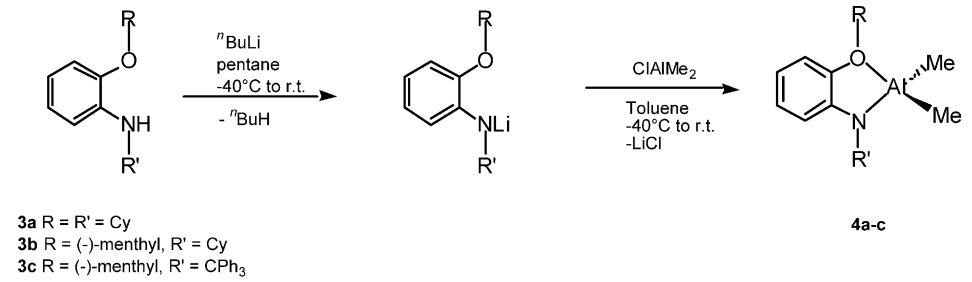
The ^{1}H- and ^{13}C-NMR spectra of **4a** in C_6D_6 both contain one resonance for the Al*Me*$_2$, one O–C*H* resonance and one N–C*H* resonance, which is consistent with an effective C_s symmetry of **4a** in solution and with the chelate solid state structure being retained in solution. In addition, no reaction was observed between **4a** and THF (one equivalent) after overnight at 75 °C in C_6D_6, which indicates the excellent stability in solution of the chelate complex in the presence of such a Lewis base.

The reaction of $AlMe_3$ with one equivalent of 2-$CyOC_6H_4NHCy$ (**3a**) at room temperature for 1 h leads to the quantitative formation of the adduct **3a**-$AlMe_3$ (Scheme 3).

The adduct **3a**-$AlMe_3$ was not isolated and was only characterized by ^{1}H-NMR spectroscopy. It is ^{1}H-NMR spectrum exhibits a characteristic N*H* doublet ($\delta = 5.29$, $^3J_{H-H} = 10$ Hz), which is significantly downfield shifted as compared to that of the free ligand (br, $\delta = 4.30$). The rest of the proton ligand resonances are nearly unchanged by the coordination to $AlMe_3$. Thus, the NMR data are consistent with the coordination of $AlMe_3$ to **3a** through the nitrogen atom. The adduct **3a**-$AlMe_3$ slowly decomposes at room temperature in pentane to yield **4a** over the course of several days with elimination of methane. This decomposition is quantitative after heating **3a**-$AlMe_3$ in C_6D_6 at 75 °C for 18 h (Scheme 3).



Scheme 1.



Scheme 2.

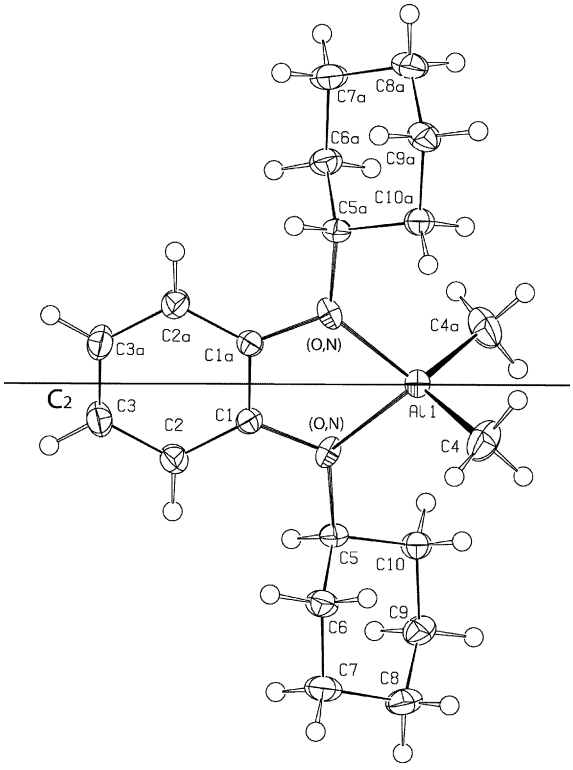
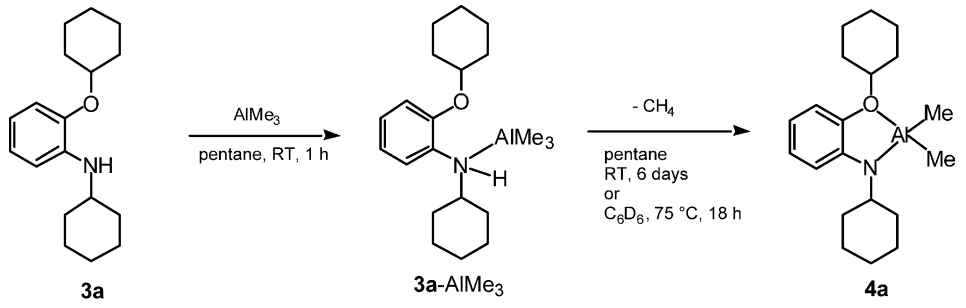


Fig. 1. Molecular structure of **4a** as determined by X-ray crystallography.

The synthesis of chiral dialkyl aluminium complexes [2-(−)-menthylOC$_6$H$_4$NR′]AlMe$_2$ (**4b**, R′ = Cy; **4c**, R′ = CPh$_3$) was carried out using the salt metathesis method. The pregenerated Li salts [2-(−)-menthylOC$_6$H$_4$NR′][Li] were reacted in toluene at room temperature with an equimolar amount of ClAlMe$_2$ to afford **4b** and **4c**, respectively (Scheme 2). Compounds **4b**–**c** are isolated as colorless solids and are both air- and moisture-sensitive, decomposing over a period of seconds in the solid state after exposure to air. Heating a C$_6$D$_6$ solution of **4b** at 70 °C for 5 h (or of **4c** for 8 h) yielded the quantitative decomposition of the corresponding Al complex to unidentified species, showing that **4b**–**c** are less stable than **4a** in solution. The decreased stability of **4b**–**c** vs. **4a** may be attributed to the increased steric hindrance around the metal center when changing from a O–Cy group to a *O*-menthyl group. As a consequence, the poor stability of **4b**–**c** precluded their obtention via the methane elimination method. As monitored by an NMR scale reaction, the formation of **4b** (or **4c**) did occur when an equimolar amount of AlMe$_3$ and **3b** (or **3c**) was heated in C$_6$D$_6$ at 70 °C; however, their formation was concomitant with their decomposition at this temperature [6].

Molecular weight measurements for **4b**–**c** in benzene suggest that both species are essentially monomeric in solution (**4b**: $M_{theo} = 385.29$, $M_{found} = 386.21$; **4c**: $M_{theo} = 545.32$, $M_{found} = 545.72$). Although the presence of a small amount of **4b**–**c** in a dimeric form cannot be entirely ruled out by these measurements, we assumed that compounds **4b**–**c** are exclusively monomeric and thus, adopt a chelate structure similar to that of **4a** in the solid state. Numerous attempts to obtain X-ray quality single crystals of either **4b** or **4c** remained unsuccessful.

The ^{1}H- and ^{13}C-NMR spectra of **4b**–**c** at room temperature contain two similar sets of resonances in a



Scheme 3.

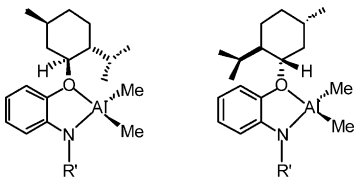


Chart 2.

10/1 ratio for **4b** and in a 4/1 ratio for **4c**, which are assigned to two different rotamers (**C** and **D**, Chart 2).

For example, the ^{1}H-NMR spectrum of **4c** contains two sets of two singlets in the AlMe region (δ −0.60, −0.57 for the major one; δ −0.81, −0.37 for the minor one) and two O–C*H* resonances also in a 4/1 ratio. Each rotamer exhibits two Al*Me* resonances by ^{1}H- and ^{13}C-NMR showing that the two methyl groups attached to the Al center are inequivalent, as expected by the presence of the chiral (−)-menthyl group in the coordination environment of the Al center. The coordination of the ethereal oxygen to the Al center in **4b**–**c** is also evident by NMR spectroscopy. In particular, for **4c**, the ^{1}H-NMR O–C*H* resonances (δ (average) 4.55) are significantly downfield shifted as compared to that of the free ligand **3c** (δ 4.00) [7], as expected by the chelate structure of **4c**.

The presence of two rotamers in **4b**–**c** at room temperature can be ascribed to a restricted rotation around the O–CH(menthyl) bond due to severe steric interactions of the menthyl group with the Ph group and/or with the methyl groups attached to the Al center. Similar hindered rotations were also observed for the related dimeric dialkyl Al complexes $\{R_2Al(\mu\text{-mentholate})\}_2$ (R = Me, ^{i}Bu) and for other organoaluminium complexes containing bulky alkoxide ligands [8]. To probe this issue further, high temperature NMR experiments were performed and are discussed in the case of **4c** (Fig. 2). As shown in Fig. 2, raising the temperature from 298 to 338 K, causes, in particular, the broadening and then the coalescence of all four AlMe resonances. Similarly, the two O–C*H* resonances coaslesce around 338 K. Finally, at 348 K, the presence of only one well-resolved O–C*H* resonance and two Al*Me* singlets show that the interconversion of the two rotamers is fast at this temperature on the NMR timescale.

Two possible mechanisms for the rotamers interconversion were considered: first, as the temperature is raised, fast rotation around the O–CH(menthyl) causes a rapid interconversion without modification of the chelate structure of **4c**; second, it was also considered that the exchange could proceed via initial de-coordination of the ethereal–menthyl oxygen followed by rotation around the O–CH(menthyl) bond and then re-coordination of the oxygen to the Al center. The second proposal appears unlikely to us because the high temperature ^{1}H-NMR spectra for **4c** in the presence of one equivalent of THF in C_6D_6 are essentially unchanged as compared to those of **4c** alone, suggesting that a putative de-coordination of the ethereal oxygen is slow on the NMR time scale under these conditions even in the presence of such a Lewis base. A de-/re-coordination exchange process may be markedly accelerated by Lewis bases due to facile cleavage of the Al–O(menthyl) bond by attack of Lewis bases on the Al center [9]. The de-coordination of the ethereal oxygen is thus unlikely to be involved in the interconversion process.

2.3. Conclusions

A new type of achiral and chiral O–N$^-$ bidentate arylamido-based ligands has been described. The derived Li salts readily react with $ClAlMe_2$ via salt metathesis to afford the corresponding dimethyl aluminium complexes. The presence of two rotamers in solution at room temperature for the chiral dimethyl Al complexes is due to steric interactions of the chiral group with the rest of the complex and suggests that the coordination sphere of the Al center in these complexes is severely crowded.

Further studies will focus on the conversion of the obtained complexes to alkyl aluminium cations and on reactivity studies of these cations.

3. Experimental

All experiments were carried out under N_2 using standard Schlenk techniques or in a Mbraun Unilab glovebox. Toluene, pentane and THF were distilled from Na/benzophenone and stored over activated molecular sieves (4 Å) in a glovebox prior to use. C_6D_6 was degassed under a N_2 flow and stored over activated molecular sieves (4 Å) in a glovebox prior to use. C_6D_6 was purchased from Eurisotope (CEA, Paris, France). All other chemicals were purchased from Aldrich and were used as received. All NMR spectra were recorded in $CDCl_3$ or in C_6D_6. The NMR data for **1a**–**c**, **2a**–**c** and **3a**–**c** were obtained on a Bruker AC 200 MHz. The NMR data for **4a**–**c** were obtained on a Bruker AC 400 MHz spectrometer, in Teflon-valved J-young tubes at ambient temperature, unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported vs. $SiMe_4$ and were determined by reference to the residual ^{1}H and ^{13}C solvent peaks. Molecular weights measurements for **4b** and **4c** were made in benzene with the use of an instrument similar to that described by Clark [10]. Elemental analysis were all performed by the microanalysis laboratory of the Université Pierre et Marie Curie (Paris, France), except those for **4a**–**c** performed

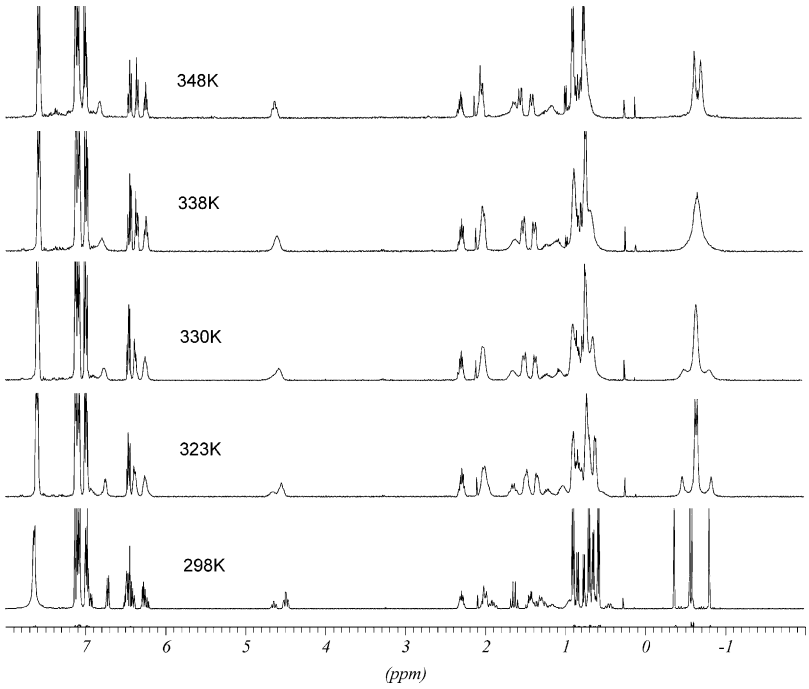


Fig. 2. Variable temperature of [2-(−)-menthylOC$_6$H$_4$NCPh$_3$]AlMe$_2$ (**4c**) in C$_6$D$_6$. The resonances are expanded off-scale for clarity.

by Mikroanalytisches Labor Pascher, Remagen–Bandorf, Germany. Silica gel Merck Gerudan SI (40–63 nm) was used for column chromatography.

3.1. Synthesis of 1-cyclohexyloxy-2-nitrobenzene (*1a*)

To a suspension of KH (2.12 g, 52.9 mmol) in 70 ml of THF was added dropwise at room temperature (r.t.) under argon cyclohexanol (5.59 ml, 52.9 mmol). The mixture was stirred for 16 h at r.t. and then cooled to −78 °C. 1-Fluoro-2-nitrobenzene (5.58 ml, 52.9 mmol) was then slowly added and the solution was allowed to warm to r.t. and stirred for 2 h. Fifty milliliters of CH_2Cl_2 were then added and the organic phase was washed with a saturated NH_4Cl solution. The aqueous phase was extracted with CH_2Cl_2 and the combined organic layers were dried over $MgSO_4$ and evaporated. Chromatography on silica gel (elution with Pentane/EtOAc 98/2) yielded 9.1 g (41.1 mmol, 78%) of **1a** as a white solid.

Anal. Calc. for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.68; H, 6.88; N, 6.11%. ^{1}H-NMR ($CDCl_3$): δ 1.25–1.95 (μ, 10H, XΨ), 4.44 (μ, 1H, XΨ*H*), 6.96 (τ, 1H, $\vartheta = 7.5$Hζ, Aρ), 7.08 (d, 1H, $J = 7.5$ Hz, Ar), 7.47 (t, 1H, $J = 7.5$ Hz, Ar), 7.75 (d, 1H, $J = 7.5$ Hz, Ar).

3.2. Synthesis of 1-(−)-menthyloxy-2-nitrobenzene (*1b*)

Following the same procedure as for **1a** from 7.44 g (47.6 mmol) of (−)-menthol, 1.91 g (47.6 mmol) of KH and 5.0 ml (48 mmol) of 1-fluoro-2-nitrobenzene. Chromatography on silica gel (elution with Pentane/EtOAc 98/2) yielded 8.72 g (31.4 mmol, 66%) of **1b** as a white solid.

Anal. Calc. for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05. Found: C, 69.13; H, 8.56; N, 5.03%. ^{1}H-NMR ($CDCl_3$): δ 0.73–2.30 (m, 18H, menthyl), 4.20 (t. of d, 1H, $J = 10.5$ and 4.1 Hz, C*H*–O), 6.95 (t, 1H, Ar), 7.09 (d, 1H, $J = 8.2$ Hz, Ar), 7.47 (t, 1H, Ar), 7.75 (d, 1H, $J = 8.1$ Hz, Ar). ^{13}C-NMR ($CDCl_3$): δ 16.3, 20.6, 21.9, 23.4, 25.7, 31.3, 34.1, 39.6, 47.5 (menthyl), 79.2 (*C*H–O), 115.0, 119.5, 125.4, 133.5, 140.8, 151.4 (Ar).

3.3. Synthesis of 2-cyclohexyloxyaniline (*2a*)

To a mixture of compound **1a** (4.5 g, 20.4 mmol) Pd (10 wt.%)/C (0.8 g) in EtOH (100 ml) was added very slowly 6.06 ml (125 mmol) of NH_2–$NH_2 \cdot H_2O$. After the addition was completed, the mixture was heated to reflux for 1 h. The suspension was then filtered through a pad of celite, and the solvent was evaporated. Chromatography on silica gel (elution with Pentane/EtOAc 95/5) yielded 3.23 g (16.9 mmol, 83%) of compound **2a** as a crystalline white solid.

Anal. Calc. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.36; H, 8.87; N, 7.23%. ^{1}H-NMR ($CDCl_3$): δ 1.33–2.05 (m, 10H, Cy), 3.81 (s large, 2H, N*H*$_2$), 4.25 (m, 1H, O–C*H*), 6.66–6.86 (m, 4H, Ar). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 23.8, 25.7, 32.1 (Cy), 76.0 (O–CH), 114.0, 115.4, 118.3, 121.1, 137.4, 145.2 (Ar).

3.4. Synthesis of 2-menthyloxyaniline (**2b**)

Following the same procedure as for **2a**, from 1.86 g (6.71 mmol) of compound **1b**, 0.29 g of Pd (10 wt.%)/C and 2 ml (41.2 mmol) of NH_2–$NH_2 \cdot H_2O$. Chromatography on silica gel (elution with Pentane/EtOAc 95/5) yielded 1.39 g (5.63 mmol, 84%) of compound **2b** as a crystalline white solid.

Anal. Calc. for $C_{16}H_{25}NO$: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.57; H, 10.14; N, 5.57%. ^{1}H-NMR ($CDCl_3$): δ 0.81–2.33 (m, 18H, menthyl), 3.80 (s large, 2H, NH_2), 4.08 (t. of d, 1H, $J = 10.4$ and 4.1 Hz, CH–O), 6.67–6.86 (m, 4H, Ar). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 16.6, 20.8, 22.0, 23.6, 26.0, 31.3, 34.5, 40.4, 48.1 (menthyl), 77.8 (*C*H–O), 113.0, 115.2, 118.3, 120.7, 137.3, 145.5 (Ar).

3.5. Synthesis of 2-cyclohexyloxy-N-cyclohexylaniline (**3a**)

To a suspension of Zn powder (2.23g) in 16.8 ml of AcOH was added 1.30 g (6.81 mmol) of compound **2a** and 0.85 ml (8.20 mmol) of cyclohexanone. The mixture was heated to 65–70 °C under argon for 40 h. The mixture was cooled to r.t. and 40 ml of MeOH were added. The suspension was filtered and the obtained white solid was washed with MeOH. To the combined organic layers were added 50 ml of dichloromethane and 30 ml of water. A NH_4OH solution was added until pH > 10. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried on Na_2SO_4 and the solvent was evaporated. Chromatography on silica gel (elution with Pentane/EtOAc 96/4) yielded 0.78 g (2.86 mmol, 42%) of compound **3a** as a white solid.

Anal. Calc. for $C_{18}H_{27}NO$: C, 79.07; H, 9.95; N, 5.12. Found: C, 79.43; H, 10.16; N, 5.03%. ^{1}H-NMR ($CDCl_3$): δ 1.21–2.15 (m, 20H, Cy), 3.33 (m, 1H, N–CH), 4.28 (m, 2H, O–CH and NH), 6.60–6.72 (m, 2H, Ar), 6.83–6.94 (m, 2H, Ar). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 23.8, 24.9, 25.7, 26.0, 32.0, 33.4 (Cy), 51.3 (N–*C*H), 76.2 (O–*C*H), 110.7, 113.3, 115.60, 121.3, 138.7, 144.6 (Ar).

3.6. Synthesis of 2-(−)-menthyloxy-N-cyclohexylaniline (**3b**)

The same procedure than that for **3a** was followed using 1 g (4.05 mmol) of **2b**, 1.33 g of Zn powder and 0.5 ml (4.82 mmol) of cyclohexanone in 10 ml of AcOH. Chromatography on silica gel (elution with Pentane/EtOAc 96/4) yielded 0.51 g (1.55 mmol, 38%) of compound **3b** as a white solid.

Anal. Calc. for $C_{22}H_{35}NO$: C, 80.19; H, 10.71; N, 4.25%. Found: C, 80.08; H, 10.88; N, 4.15%. ^{1}H-NMR ($CDCl_3$): δ 0.82–2.31 (m, 28H, Cy and menthyl), 3.28 (s large, 1H, CH–N), 4.05 (t. of d, 1H, $J = 10.5$ and 4.1 Hz, CH–O), 4.22 (br s, 1H, NH), 6.57–6.88 (m, 4H, Ar). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 16.8, 20.7, 22.0, 23.8, 24.9, 25.9, 26.2, 31.3, 33.3, 33.4, 34.5, 40.5, 48.1 (menthyl), 51.3 (N–*C*H), 78.2 (*C*H–O), 110.6, 112.5, 115.6, 121.0, 138.6, 144.9 (Ar).

3.7. Synthesis of 2-(−)-menthyloxo-N-triphenylmethylaniline (**3c**)

To a solution of 0.5 g (2.02 mmol) of compound **2b** in 6 ml of THF at −78 °C was added dropwise 0.9 ml (2.25 mmol) of ^{n}BuLi (2.5 M in hexanes). The solution was stirred at −78 °C for 0.5 h and a solution of 0.845 g (3.03 mmol) of Ph_3CCl in 3 ml of THF was added. The red suspension was allowed to warm to r.t. and was stirred at this temperature for 1 h. The solvent was evaporated. Chromatography of the residue on silica gel (elution with Pentane/EtOAc 98/2) yielded 0.32 g (0.65 mmol, 32%) of a slightly yellow oil which readily crystallized from MeOH at −20 °C.

Anal. Calc. for $C_{35}H_{39}NO$: C, 85.84; H, 8.03; N, 2.86%. Found: C, 85.76; H, 8.14; N, 2.58%. ^{1}H-NMR ($CDCl_3$): δ 0.84–2.35 (m, 18H, menthyl), 4.10 (t. of d, 1H, $J = 10.4$ and 4.1 Hz, CH–O), 5.94 (br s, 1H, NH), 6.08 (d, 1H, $J = 7.9$ Hz, Ar), 6.44 (t, 1H, $J = 7.7$ Hz, Ar), 6.55 (t, 1H, $J = 7.7$ Hz, Ar), 6.81 (d, 1H, $J = 7.9$ Hz, Ar), 7.21–7.46 (m, 15H, CPh_3). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 16.9, 20.6, 22.1, 23.8, 26.4, 31.4, 34.4, 40.9, 48.3 (menthyl), 70.8 (Ph_3C), 78.9 (*C*H–O), 111.7, 115.2, 116.2, 119.7, 126.5, 127.7, 129.0, 129.4, 137.0, 145.7 (Ar).

3.8. Synthesis of (2-$CyOC_6H_4NHCy$)-$AlMe_3$ (**3a**-$AlMe_3$)

In a glove box, compound **3a** (310 mg, 1.13 mmol) was added to a 15 ml vial sample and dissolved in 2 ml of pentane. The vial was then stored in the freezer at −35 °C for 30 min. After this time, it was taken out of the freezer and $AlMe_3$ (81.2 mg, 1.13 mmol) was quickly added. The colorless reaction mixture was allowed to warm to r.t. and stirred for 1 h at r.t., which resulted in the precipitation of a white crystalline solid. The vial was then stored at −35 °C overnight which provoked further precipitation. Filtration through a glass frit and drying under vacuum afforded the $AlMe_3$ adduct (**3a**-$AlMe_3$, 325 mg) along with minor impurities, according to the ^{1}H-NMR spectrum. ^{1}H-NMR (C_6D_6): δ −0.40 (s, 9H, Al–CH_3), 0.85–2.48 (m, 20H, Cy), 3.23 (m, 1H, N–CH), 3.94 (m, 1H, O–CH), 5.29 (d, 1H, $J_{H-H} = 10$ Hz, NH), 6.48–7.12 (m, 4H, Ar).

3.9. Synthesis of [2-CyOC$_6$H$_4$NCy]AlMe$_2$ (**4a**)

3.9.1. First method (via salt metathesis)

In a dry box, the ligand CyOC$_6$H$_4$-2-NHCy (**3a**, 840.0 mg, 3.070 mmol) was charged in a 50 ml round-bottom flask and dissolved in 10 ml of pentane. The resulting solution was cooled to −40 °C and ^{n}BuLi (3.070 mmol, 1.92 ml of a 1.6 M hexanes solution) was added dropwise via a pipette. Upon addition of ^{n}BuLi, the formation of a white precipitate and gas formation (^{n}BuH) are also immediately observed. After the addition, the reaction mixture was allowed to warm to r.t. and then stirred for 3 h. The mixture was filtered through glass frit and dried under vacuum to yield the extremely air-sensitive colorless solid Li salt CyOC$_6$H$_4$-2-N(Cy)(Li) (670 mg, 80% yield), which was used without further purification.

The Li salt CyOC$_6$H$_4$-2-N(Cy)(Li) (250.0 mg, 0.895 mmol) was charged in a 15 ml vial and dissolved in 5 ml of toluene to yield a pale yellow solution. The solution was cooled to −35 °C in a freezer for 30 min, after which it was taken out. ClAlMe$_2$ (0.895 mmol, 0.90 ml of 1 M of hexanes solution) was then rapidly added to the reaction mixture via a syringe. The resulting solution was allowed to warm to r.t. and stirred overnight causing the initial solution to turn into a colorless light suspension due to LiCl precipitation. The mixture was then filtered through frit and the volatiles removed under vacuum to give a colorless solid. Recrystallization of the crude product from a 1/1 toluene/ether mixture afforded analytically pure [CyOC$_6$H$_4$-2-NCy]AlMe$_2$ **4a** as an air-sensitive colorless crystalline solid (180 mg, 61% yield).

Anal. Calc. for C$_{20}$H$_{32}$AlNO: C, 72.91; H, 9.79. Found: C, 72.35; H, 9.56%. ^{1}H-NMR (C$_6$D$_6$): δ −0.23 (s, 6H, Al–CH_3), 0.68–2.30 (m, 20H, Cy), 3.25 (m, 1H, N–CH), 4.19 (m, 1H, O–CH), 6.43 (m, 2H, Ar), 6.66 (d, 1H, $J = 7$ Hz, Ar), 7.05 (t, 1H, $J = 7$ Hz, Ar). ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ −4.40 (Al–CH_3), 24.9, 26.2, 26.5, 31.3, 34.5 (Cy), 53.9 (N–CH), 81.9 (O–CH), 110.1, 110.6, 110.7, 125.5, 143.4, 144.2 (Ar).

3.9.2. Second method (via methane elimination)

In a glove box, a J-Young NMR tube was charged with CyOC$_6$H$_4$-2-NHCy (**3a**, 31.0 mg, 0.11 mmol) and 0.75 ml of C$_6$D$_6$ was added. AlMe$_3$ (8.2 mg, 0.11 mmol) was then added to the ligand solution via a microsyringe. The NMR tube was vigorously shaken and an ^{1}H-NMR spectrum was immediately recorded showing the quantitative formation of the AlMe$_3$ adduct **3a**-AlMe$_3$. The tube was then immersed in an oil bath pre-heated at 75 °C and the reaction was monitored by ^{1}H-NMR, which showed the complete conversion of **3a**-AlMe$_3$ to **4a** along with methane formation, after overnight at 75 °C.

3.10. Synthesis of [2-(−)-menthylOC$_6$H$_4$NCy]AlMe$_2$ (**4b**) and [2-(−)-menthylOC$_6$H$_4$NCPh$_3$]AlMe$_2$ (**4c**)

The aluminium dimethyl compounds **4b** and **4c** were synthesized following the salt metathesis route used for **4a**. The Li salts menthylOC$_6$H$_4$-2-NCyLi (255 mg, 0.774 mmol) and menthylOC$_6$H$_4$-2-NCPh$_3$Li (570.0 mg, 1.164 mmol) were synthesized and used as starting material for the obtention of **4b** and **4c**, respectively. In both cases, the ^{1}H-NMR spectrum of crude product in C$_6$D$_6$ clearly showed the presence of two rotamers in slow exchange on the NMR timescale in 1/10 and 1/4 ratios for **4b** and **4c**, respectively. Compound **4b** was isolated in a pure form as a colorless solid from recrystallization of the crude product from pentane at −35 °C (55% yield). Pure **4c** (colorless solid) was obtained by a pentane wash of the crude product followed by filtration through frit and drying under vacuum.

3.10.1. Data for **4b**

Anal. Calc. for C$_{24}$H$_{40}$AlNO: C, 74.76; H, 10.46. Found: C, 74.40; H, 10.70%. ^{1}H-NMR (C$_6$D$_6$) (minor rotamer): δ −0.27 (s, 3H, Al–CH_3), −0.17 (s, 3H, Al–CH_3), 4.62 (br, 1H, O–CH). ^{1}H-NMR (major rotamer): δ −0.23 (s, 3H, Al–CH_3), −0.18 (s, 3H, Al–CH_3), 0.56–2.30 (m, 28H, Cy and menthyl), 3.27 (m, 1H, N–CH), 4.56 (m, 1H, O–CH), 6.45 (t, 1H, $J = 7$ Hz, Ar), 6.70 (d, 1H, $J = 7$ Hz, Ar), 6.75 (d, 1H, $J = 7$ Hz, Ar), 7.07 (t, 1H, $J = 7$ Hz, Ar). ^{13}C{^{1}H}-NMR (C$_6$D$_6$): δ −5.3 (Al–CH_3), −3.6 (Al–CH_3), 15.6, 20.7, 21.7, 23.2, 25.2, 26.2, 26.3, 26.5, 32.0, 33.7, 34.6, 34.7, 39.6, 46.3 (Cy and menthyl), 54.0 (N–CH), 85.2 (O–CH), 110.8, 111.0, 111.1, 125.9, 144.6, 144.7 (Ar).

3.10.2. Data for **4c**

Anal. Calc. for C$_{37}$H$_{44}$AlNO: C, 81.43; H, 8.13. Found: C, 80.90; H, 7.90%. ^{1}H-NMR (C$_6$D$_6$) (major rotamer): δ −0.60 (s, 2.4H, Al–CH_3), −0.57 (s, 2.4H, Al–CH_3), 0.54–2.34 (m, 18H, menthyl), 4.48 (m, 1H, O–CH), 6.24–7.65 (m, 22H, Ar). ^{1}H-NMR (C$_6$D$_6$) (minor rotamer): δ −0.81 (s, 0.6H, Al–CH_3), −0.37 (s, 0.6H, Al–CH_3), 0.54–2.34 (m, 18H, menthyl), 4.63 (m, 1H, O–CH), 6.24–7.65 (m, 22H, Ar). ^{13}C{^{1}H}-NMR (C$_6$D$_6$) (major rotamer): δ −6.7 (Al–C), −5.2 (Al–C), 15.7, 20.9, 21.8, 23.3, 25.2, 32.3, 33.7, 33.7, 39.5, 46.2 (menthyl), 73.7 (N–CPh$_3$), 88.0 (O–CH), 111.8, 113.4, 120.5, 123.9, 143.4, 145.3 (Ar). ^{13}C{^{1}H}-NMR (C$_6$D$_6$) (minor rotamer): δ −8.8 (Al–C), −7.3 (Al–C), 16.6, 20.9, 21.9, 24.5, 25.5, 32.5, 33.9, 38.4, 47.7 (menthyl), 73.5 (N–CPh$_3$), 89.2 (O–CH), 113.0, 116.1, 120.3, 124.5, 142.3, 144.9 (Ar).

3.11. Crystal data for **4a**

Crystals of **4a** suitable for X-ray diffraction were obtained at r.t. by slow evaporation of a concentrated toluene solution of **4a**.

Compound **4a**: $C_{20}H_{32}AlNO$, $M = 329.45$ g mol^{-1}; colorless crystal; crystal size : $0.13 \times 0.10 \times 0.08$ mm^3; monoclinic; space groupe $C2/c$; $a = 12.271(5)$, $b = 12.313(5)$, $c = 12.480(5)$ Å; $\beta = 90.171(5)^\circ$; $Z = 4$; $D_{calc} = 1.16$ g cm^{-3}; μ (Mo–K$_\alpha$) $= 0.113$ mm^{-1}; a total of 6297 reflections; $2.34 < \theta < 30.02^\circ$, 2767 independent reflections with 2155 having $I > 2\sigma(I)$; 175 parameters; final results: $R(F) = 0.045$; $R_w(F) = 0.013$, Goodness-of-fit = 1.11, maximum residual electronic density = 0.384 e Å^{-3}. A selected crystal was mounted on a Nonius Kappa-CCD area detector diffractometer (Mo–K$_\alpha$, $\lambda = 0.71073$ Å). The complete conditions of data collection (Denzo software) and structure refinements are given below. The cell parameters were determined from reflections taken from one set of 10 frames (1.0° steps in phi angle), each at 20 s exposure. The structure was solved using direct methods (SIR97) and refined against F^2 using the SHELXL97 software. The absorption was not corrected. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereo-chemistry and refined using a riding model in SHELXL97. All hydrogen atoms were placed from fourier differences and refined isotropically. It is important to stress that this molecule crystallizes on a C_2 axe (i.e. the Al atom (4e position of the $C2/c$ group) and the middle of the C(1)–C(1a) contact are on the C_2 axe. In these conditions, the atomic arrangement observed by X-ray diffraction must be considered as an average of two chemically true molecules, rotate by 180° around the C_2 axe in the crystal. The structural resolution test in the triclinic system gives not realistic solutions.

4. Supplementary material

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 212662 for compound **4a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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