Group 13 metal complexes containing the bis-
(4-methylbenzoxazol-2-yl)-methane ligand†‡†‡

David-R. Dauer, Melchior Flügge, Regine Herbst-Irmer and Dietmar Stalke*

To focus on the high importance of low-valent main group metal complexes, which can be applied to catalytic transformations, this article deals with the promising new ligand system (4-MeNCOC6H3)2CH2 (1). It is patterned on the well known nacnac ligand and further development of the parent bis(heterocyclo) methanes. In comparison with the results of previous studies based on the bis(heterocyclo)methanes (NCOC6H3)2CH2 and (NCOC6H3)2CH2 derivative 1 was modified by adding a methyl group to the annulated benzene perimeters to enhance the steric protection of a potentially coordinated main group metal cation. On reaction of 1 with group 13 trimethyl reagents and dialkyl aluminium halides the ligand backbone gets deprotonated and the two endocyclic nitrogen donor atoms coordinate with the remaining organometallic fragment to form a six-membered metalla heterocycle. The synthesis of [Me2Al{(4-MeNCOC6H3)2CH}] (2), [Me2Ga{(4-MeNCOC6H3)2CH}] (3), [Me2In{(4-MeNCOC6H3)2CH}] (4), [ClMeAl{(4-MeNCOC6H3)2CH}] (5), [MeAl{(4-MeNCOC6H3)2CH}] (6) and [EtAl{(4-MeNCOC6H3)2CH}] (7) could be accomplished. A structural comparison of those metallated species based on single crystal X-ray analyses identifies them as ideal precursors generating new low-valent main group complexes.

Introduction

In the context of the ongoing increasing demand for the activation of small molecules like H2, N2, NH3 or CO2 the development of new synthetic approaches for generating catalytic active species is of high interest. Even though this research area of catalytic activation is mostly focused on the field of transition metal complexes the transfer to suitable main group metal complexes, which should adopt the same catalytic reactivity compared to the transition metals or even exceed them, plays a key role in current research.1

As a figurehead for efficient small molecule activation FLP (frustrated Lewis pairs) chemistry has developed to a promising research area over the last decade.2 In this way the usage of mainly phosphorus/boron, nitrogen/boron or carbon/boron FLP systems offers simple access to the efficient splitting of dihydrogen3 or the ring opening of THP.4 Also the aluminium based FLPs were found to be advantageous for B–H or N–H bond activation,5 polymerisation reaction of methyl methacrylate6 and conversion of CO2.7 Furthermore, the well-known nacnac ligand and the derived main group metal complexes, respectively, facilitate the stabilisation of metal ions in low oxidation states.8 The synthesis of the first Mg(II) compound9 and the corresponding β-diketiminate Ca(n) complexes,10 which were successfully applied for epoxide/CO2 copolymerisation11 or hydrogenation reactions of alkenes with H2,12 should be highlighted as alkaline earth metal complexes performing in catalysis. Switching to group 13 elements also a variety of Al(m) and Ga(n) containing complexes was synthesised and fully characterized.13 Subsequently also the low-valent Al(i)14 and Ga(i)15 species employing the Dipp-substituted (Dipp = 2,6-diisopropylphenyl) nacnac ligand were accessible. More recently the catalytic activity of the related alumoxanes was studied in detail.16 Other common ligand types, which are used for stabilisation of dimeric low-valent group 13 species involving metal–metal multiple bonds, are the substituted terphenyls, which are also prone to interaction with small molecules like H2.17

With this in mind in the field of main group transformation ligand design in particular and the choice of the suitable main group element have significant influence on the stability and the catalytic abilities of the resulting compounds. In this work we tried to mimic the omnipresent nacnac ligand by two methylene bridged substituted benzoxazole moieties. The corresponding group 13 metal complexes were synthesised to get the best from two worlds: the stabilisation abilities to get low-valent metal complexes and the reactivity of group
13 metals. To tie up with earlier studies concerning the related bis(heterocyclo) methanide and amide derivatives this work focuses on bis-[4-methylbenzoxazol-2-yl]-methane. The previous results of the methanide containing metal complexes have shown that upon deprotonation of the methylene bridge of the parent ligand systems the coordination of the metal cation is preferentially accomplished by the endocyclic nitrogen donor atoms in a chelating fashion. Due to this fact and to further shield the coordinated metal the bis-[benzoxazol-2-yl]-methane ligand was additionally methyl substituted in 1 to increase the kinetic stabilisation at the same side of the coordinating nitrogen atoms. Neither in the case of the methanide nor the amide derivatives a coordination via the other feasible O- or S-coordinating sites has been observed in the solid state yet.

The issue of steric shielding of metal centres within the group 13 complexes is an important aspect for further applications and reactions, because in the future we plan to convert these Al[III] containing species into the low-valent Al[I] compounds e.g. [Al(Dipp2nacnac)]. Because of the high electronegativity of the Al[II] species steric protection is essential to maintain the monomeric carbene-like structural motif and prevent dimerisation or nucleophilic attacks. The challenge for the synthesis of the low-valent species containing a bis(heterocyclo) methanide ligand backbone is still the guiding idea of ongoing research and 1 seems to be a promising ligand system for the subsequent reduction steps (vide infra).

Among the nacnac derivatives and the bis(heterocyclo) methanides efficient metal shielding is comparable within certain limits. In the case of the nacnac ligands the residues at the bulky imine moieties are twisted nearly perpendicularly with respect to the chelating C3N2M-plane, which causes the metal atoms to be most protected. In the case of the complexes derived from 1 the methyl groups shield as well but due to less steric congestion the metal centres are slightly more accessible for allowing some specific substitution reactions. The new metal complexes containing a central six-membered metalla heterocycle are reminiscent of the analogous metal complexes with the omnipresent nacnac ligand. The following similarities between the herein discussed bis(heterocyclo) methanides and the nacnac ligands can be stated due to the structural comparison of the corresponding metal complexes: Firstly the deprotonation of the bridging moiety leads to the formation of a negative charge in the ligand’s backbone, which is completely delocalised to give 6a electrons containing the metalla heterocycle (see Table 1). Secondly, the chelating coordination of the metal cation is achieved exclusively by the two nitrogen donor atoms in the ligand periphery.

Results and discussion

Ligand synthesis

The synthesis of the parent uncharged ligand system is achieved as reported earlier for the corresponding unsubstituted bis-benzoxazol-2-yl- and bis-benzothiazol-2-yl-

methanides. A cyclodehydration reaction of two equivalents of 2-amino-3-methylphenol and one equivalent of a C3-linker unit derived from malonic acid yields the ligand. Two different synthesis routes were performed and optimised to give a moderate overall yield of 56% (see Scheme 1).

The first route is through the synthesis of the unsubstituted bis-benzoxazol-2-yl-methane, in which a bisimidate linker was used for the coupling of the two phenol derivatives. This pathway, however, leads to a smaller yield of the desired product 1 and also promotes the formation of a specific side product 1a. The side product could be identified as 4-methylbenzoxazol-2-yl-carboxamide, which occurs, if just one equivalent of the starting material has cyclised and the remaining imidate unit has been hydrolysed upon further purification. On the second improved route malonic dinitrile was added to the phenolic starting material. In that case polyphosphoric acid (ppa) was added as a solvent and catalytically facilitates the cyclisation reaction to give the parent ligand system 1.

Compound 1 crystallises in the triclinic space group P1 and the asymmetric unit contains one molecule (Fig. 1). Like the other symmetrically substituted bis(heterocyclo) methanides the central carbon atom C1 is also coordinated in a distorted tetrahedral atom (1a) relative to each other. Due to

Table 1 Selected averaged bond lengths (Å) and angles (°) of the ligand backbone for compounds 1–4 and reference structures

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ci–Cj</th>
<th>Ci–Nj</th>
<th>Cj–Ck</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.487(2)</td>
<td>1.291(2)</td>
<td>1.487(2)</td>
</tr>
<tr>
<td>2</td>
<td>1.384(2)</td>
<td>1.351(2)</td>
<td>1.384(2)</td>
</tr>
<tr>
<td>3</td>
<td>1.388(3)</td>
<td>1.341(2)</td>
<td>1.388(3)</td>
</tr>
<tr>
<td>4</td>
<td>1.390(13)</td>
<td>1.337(12)</td>
<td>1.390(13)</td>
</tr>
</tbody>
</table>

Scheme 1 Synthetic routes to the parent ligand system 1 including the side product 1a.
the higher steric demand of the heterocycles the C1–C1′–C8 angle is widened to 110.8(1)°, whereas all other angles around C1′ are slightly compressed in comparison with an ideal tetrahedral angle. Interestingly in the solid state 1 forms a 3D network of quite remarkable C–H⋯N hydrogen bonds, in which the two acidic methylene hydrogen atoms of the bridge are coordinated by imine nitrogen atoms of two adjacent molecules (see Fig. 2). The experimentally determined values show two hydrogen bonds each, which are energetically more favourable (H1′B⋯N2: 2.39 Å; C1′–H1′B⋯N2: 171.1°), and two which are less pronounced (H1′A⋯N1: 2.62 Å; C1′–H1′A⋯N1: 150.9°).

Syntheses of the group 13 metal complexes

The reaction of 1 in toluene with pure trimethyl aluminium, gallium or indium leads to the formation of the monoanionic methanides containing the corresponding MMMe 2 fragment (see Scheme 2). By the addition of these organometallic reagents the acidic methylene bridge gets deprotonated with the evolution of gaseous methane and in a concerted manner the remaining dimethyl group 13 metal cation gets chelated by the two ring nitrogen donor atoms.

Upon deprotonation the concerned C-ipso–Cbridge distances are shortened in comparison with 1 and the C-ipso–N distances are slightly elongated (Table 1). This is caused by two facts, which are important for structural features. On the one hand the deprotonation of the central methylene moiety generates a free electron pair. Because of the adjacent conjugated π-systems of the two benzoxazole units this free electron pair tends to be delocalised over the whole ligand framework resulting in different feasible resonance structures: carbanionic, amidic or completely delocalised. On the other hand the hybridisation of the central carbon atom changes from sp3 in the starting material 1 to sp2 in the metallated species 2–4 based on the trigonal planar coordination geometry of C1′.

Structural comparison of 2–4

A closer look at the experimentally determined geometry of 1 shows that the C-ipso–Cbridge distance is slightly shorter than what is to be expected for a typical C(sp2)–C(sp3) single bond (1.51 Å). This deviation can be explained by the presence of the four electronegative adjacent heteroatoms, which cause the C-ipso–Cbridge bonds to shrink due to their electron withdrawing ability.

In comparison with compounds 2–4 the observed C-ipso–Cbridge distances (1.384 Å to 1.390 Å) are half way between a typical C(sp2)–C(sp3) single bond (1.47 Å) and a C(sp3)–N(sp2) double bond (1.34 Å), which is a result of the efficient delocalisation of the double bonds. The same explanation is valid for the C-ipso–N bond lengths, which are in a narrow range from 1.337 Å to 1.351 Å. These values for the C-ipso–N bond lengths can also be seen as the average of a typical C(sp2)–N(sp2) single bond (1.40 Å) and a C(sp2)–N(sp2) double bond (1.29 Å). In light of the previous results of the methanides [Me2Al{NCOC6H4,C2}H2] and [Me2Al{(NCS)C6H4,N}]18 and the analogous amide bridged species [Me2Al{(NCSC6H4,N)}] and [Me2Al{(4-MeNCSC6H4,N)}]19 the discussed structural values match well (Table 1).
Compounds 2 (Fig. 3) and 3 (Fig. 4) are equi-structural and crystallise each in the monoclinic space group $P_{2_1}/c$ and the asymmetric unit contains one molecule. 4 (Fig. 5) crystallises in the monoclinic space group $Pn$ and contains two metallated molecules in the asymmetric unit (Table 4).

The structural comparison of the MMe$_2$ derivatives shows that in each case the metal coordination again is accomplished by the two nitrogen atoms of the benzoxazole moieties and the oxygen atoms are pointing away from the metal (Fig. 3–5). In all three cases this leads to a distorted tetrahedral coordination geometry at the particular metal ion. As expected the ligand framework in 2–4 exhibits nearly no folding of the heterocyclic residues. Additionally the metal ion is located in the C$_3$N$_2$ plane of the central six-membered metalla heterocycle without any significant deviation (see Table 2). Only this arrangement facilitates total conjugation of the whole anionic ligand. Due to the fourfold coordination of the metal ion the methyl residues at that metal are aligned perpendicularly with respect to the N1–M–N2 plane. This V-shaped arrangement of the MMe$_2$ fragments allows the organometallic fragment to slot in between the methyl groups of the ligand. The four methyl groups frame the group 13 metal to stay in plane (see Fig. 6).

In the row of the investigated group 13 metal complexes 2–4 of the bis-(4-methylbenzoxazol-2-yl)-methanide ligand some clear trends from the obtained structural data could be deduced (see Table 3):

- The transannular N1⋯N2 distance, which is indicative of the size of the chelated metal atom, increases from 2 over 3 to 4 as expected, because the bigger the coordinated ion, the wider the chelating distance.
- Also the observed N–M distances increase according to the increasing ionic radii of the Al$^{3+}$, Ga$^{3+}$ or In$^{3+}$ ion, respectively.
- As a further consequence of this bond elongation and due to the fact that the metal stays in the ligand plane the resulting N1–M–N2 bite angles decrease from 2 over 3 to 4.

In Fig. 6 compound 2 is exemplary compared to the literature known nacnac derivatives [Me$_2$Al[$\text{Dipp}_{2}\text{nacnac}$]$^{13}$ (A) and [Al[$\text{Dipp}_{2}\text{nacnac}$]$^{14}$ (B) containing also the Al(m)Me$_2$ or Al(i) moiety, respectively. From the space filling model the steric

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**Table 2** Selected folding parameters for compounds 1–7

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Folding angle [°]</th>
<th>M-plane distance [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>3.721(20)</td>
<td>0.0054(22)</td>
</tr>
<tr>
<td>3</td>
<td>3.803(20)</td>
<td>0.0068(23)</td>
</tr>
<tr>
<td>4$^a$</td>
<td>4.925(122)</td>
<td>0.0572(287)</td>
</tr>
<tr>
<td>5</td>
<td>6.225(263)</td>
<td>0.1545(269)</td>
</tr>
<tr>
<td>6</td>
<td>3.394(20)</td>
<td>0.0090(19)</td>
</tr>
<tr>
<td>7</td>
<td>3.042(16)</td>
<td>0.0226(37)</td>
</tr>
<tr>
<td>7</td>
<td>4.423(71)</td>
<td>0.0483(20)</td>
</tr>
</tbody>
</table>

$^a$ Two values are given due to the discrepancy of the two molecules within the unit cell.
demand of each ligand can be visualised and provides a fair estimate of the shielding abilities of the metal atoms.

Starting with the crystal structure of the Al(i) species B it is evident that the metal atom is located almost ideally within the chelating C3N2 plane (Fig. 6, bottom). The N,N'-coordinated metal atom fits well into the pocket made up of the four iPr groups of the Dipp-substituents and the carbon atoms in the ortho-position of the associated phenyl rings. Furthermore, these phenyl rings are nearly perpendicularly aligned with respect to the C3N2 plane (89° and 91°). The ortho-carbon atoms provide the closest contact to the aluminium atom (averaged 3.606 Å) and presumably are equally important for the shielding of low-valent Al(i) species (listed in column C15/16→M in Table 3), because these distances are located between the nacnac species and the complexes derived from 1.

The bottom view also shows that the aluminium atom is not exhaustively coordinated so that coordination of the Lewis acidic site is facilitated. The side view highlights the good shielding abilities of the iPr groups, preventing the molecule from aggregation.

Continuing with the dimethyl aluminium species A the crystal structure clearly deviates from the reduced species B. The central six-membered metalla heterocycle is less planar than in B, because the AlMe2 unit is not located in the chelating C3N2 plane. Furthermore, one of the phenyl rings of the Dipp-substituents is considerably twisted away from orthogonality with respect to the C3N2 plane (112°). This deviation is caused by the additional methyl groups at the aluminium, which increases the steric demand compared to the naked metal in B. The formed pocket in B is not appropriate in size to accommodate the additional methyl groups. Instead of retaining the perpendicular alignment of the Dipp-substituents one of them is pushed away.

As mentioned earlier the methyl substituents of the chelating ligand in 2 adopt the shielding role of the Dipp residues of the comparable nacnac complexes. These efficient shielding abilities are visualised in the space filling model in the bottom view of 2 in Fig. 6: by chelation of the two nitrogen donor atoms of the ligand the AlMe2 fragment is aligned in the C3N2 plane without any significant deviation. This planarity is also supported by the ligand’s methyl groups, which fit nearly perfectly into the pocket made up of the V-shaped coordinated AlMe2 cation. So in comparison with A and B the kinetic shielding considered from the bottom view is even more pronounced. As opposed to this the side view of 2 shows that the planar arrangement of the complex leads to less steric congestion from this point of view. The shielding abilities in 2 are not that encompassing as in the case of A and B, so that beneficial, specific substitution reactions at the metal centre still can take place. This advantageous property is exploited by the synthesis of 5 described in the following paragraph.

Structural comparison of 5–7

In addition to the dimethyl substituted group 13 metal complexes 2–4 three Al(III) derivatives, in which one of the methyl groups is replaced by a halide, were successfully synthesised as well. This substitution is necessary to improve the reactivity of those species compared to the relatively high stability of the dimethyl aluminium complexes. These reaction products should facilitate access to Al(i) or Al(III) species upon reductive dehalogenation reactions.

The synthesis of compounds 5 and 7 parallels the procedures of the abovementioned dimethyl derivatives. To a solution of the parent ligand 1 in toluene the pure organometallic reagent AlMe2Cl or AlEt2I, respectively, was added in a slight excess at 0 °C (Scheme 3, pathway a). Differently 6 was prepared starting from the metallated species 2 by reaction with an excess of trimethyl silyl iodide to prompt a methyl iodide exchange at the metal atom (Scheme 3, pathway b).

Having a closer look at the geometrical data of those halide substituted species 5–7 the following conclusions can be
made: the derivatives 5 (Fig. 7) and 7 (Fig. 9) crystallise in the monoclinic space group $P2_1/c$ each and the asymmetric unit consists in both cases of one target molecule. Compound 6 (Fig. 8) crystallises in the orthorhombic space group $Pbcm$ and the asymmetric unit contains half a molecule (Table 4).

In the halogenated complexes the aluminium atom adopts also the distorted tetrahedral coordination by means of the two nitrogen donors and the remaining substituents at the metal atom. In direct comparison with the AlMe$_2$ derivative 2 the N–Al distances in 5–7 are increased and consequentially the corresponding N–Al–N bite angle is widened (see Table 3). These observed changes are caused by the electron withdrawing halide ligands Cl or I. These substituents increase the partial positive charge at the metal atom due to the negative inductive effect and their reduced electronegativity compared to carbon. The substituted aluminium atom needs less electron density from the donating nitrogen ring atoms and the nitrogen Lewis donors are less attractive.

The influence of the present halide atom on specific binding properties is displayed in Table 3. 5 compared to 6 shows the bigger halide iodide to cause the transannular N1⋯N2 distance to increase by about 0.03 Å (2.8500 Å in 5 vs. 2.8775 Å in 6). This widening of the coordination pocket is also displayed in the bite angle, which also gets enlarged from 96.52° to 97.84°. Predominantly the higher steric demand of the iodide compared to the chloride accounts for the structural changes in the ligand. The observed differences among the two iodide derivatives 6 and 7 concerning those values are negligible. Within the triple estimated standard deviations the values for both species are the same, indicating that the slightly enhanced steric demand in 7 due to the ethyl group instead of a methyl group has no significant effect on those structural features.

Conclusions

In this work the successful syntheses and solid state structure determination of six metallated bis-(4-methylbenzoxazol-2-yl)methanides 2–7 and the parent uncharged methane derivative 1 could be presented. As a consequence of tuning the pre-
viously reported bisheterocyclo methanes by introducing methyl groups to the benzannulated heterocycles (in this case benzoxazole) a promising ligand system for metal complexation could be obtained, which exhibits a nearly perfect planar coordination geometry with regard to the ligand side arms in all the discussed solid state structures. This fact is displayed by the small values in the folding angles between both heteroatomic planes and the just slight deviations of the metal cations from the chelating C3N2 plane in each complex, which is outstanding in the row of the previously investigated methanide and amide complexes. The observed arrangement in the is outstanding in the row of the previously investigated metha-

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Crystal structure data for 1–7</th>
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<tr>
<td></td>
<td>1</td>
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<tr>
<td>Formula</td>
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<tr>
<td>Mol. w., g mol⁻¹</td>
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<tr>
<td>wR₂(all refl.)</td>
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<tr>
<td>Rint</td>
<td>0.0369</td>
</tr>
<tr>
<td>Abs. stra. para.²⁶</td>
<td>P = (f² + 2g²)² / (g² + 3f²)</td>
</tr>
</tbody>
</table>

geometry should enable optimal orbital overlapping between the endocyclic nitrogen donors and the chelated future low-valent metal atom to obtain a more efficient delocalisation. Further substitution and reduction attempts on aluminium containing complexes of this promising ligand system are under investigation.

**Experimental section**

**General procedures**

All manipulations were carried out under an atmosphere of dried and purified N₂ or Ar by using Schlenk techniques. All solvents used within metallation reactions were distilled from Na or K prior to use. The starting materials were purchased commercially and used as received. ¹H, ¹³C, ¹⁵N and ²⁷Al NMR spectroscopic data were recorded on Bruker Avance 500 MHz, Bruker Avance 400 MHz and Bruker Avance 300 MHz spectrometers and referenced to the deuterated solvent (thf-d₈). Elemental analyses (C, H, N and S) were carried out on a Vario EL3 at the Mikroanalytisches Labor, Institut für Anorganische Chemie, University of Göttingen. All EI-MS spectra (70 eV) were recorded on a Finnigan MAT 95.

(4-MeNCOCH₃)₆CH₂ (1). **Method 1**: 2-Amino-3-methylphenol (2.91 g, 23.6 mmol, 2.00 eq.) and ethylbisimide dichloride (2.73 g, 11.8 mmol, 1.00 eq.) were dissolved in methanol (55 mL). The heating time of the reaction mixture was extended for reflux overnight and after cooling to rt stored at −32 °C in a refrigerator. The resulting crystalline material was filtered off, washed with saturated aqueous NaHCO₃ solution (3 × 50 mL) and water (3 × 50 mL) and dried under reduced pressure. Crystals suitable for X-ray diffraction experi-
mements could be obtained upon recrystallisation from toluene. Pale brown crystals were obtained in a yield of 1.43 g (5.15 mmol, 44%).

**Method 2:** A mixture of 2-amino-3-methylphenol (9.85 g, 80.0 mmol, 2.00 eq.) and malonic acid (4.16 g, 40.0 mmol, 1.00 eq.) was suspended in phosphoric acid (100 mL) with the use of a sealed precision glass (KPG) stirrer. Under vigorous stirring the reaction mixture was heated to 150 °C and the resulting dark blue viscous solution was kept under stirring at this elevated temperature for 5 h. Then the solution was allowed to cool to about 90 °C and poured over ice. The formed grey solid was filtered off, washed several times with saturated aqueous NaHCO₃ solution (9 × 50 mL) and distilled water (10 × 50 mL) to pH neutrality. The remaining solvent was evaporated in vacuo to obtain 1 (6.26 g, 22.5 mmol, 56%) as a pale grey powder.

Anal. Calcd for C₁₉H₁₉AlN₂O₂ (334.35 g mol⁻¹): C, 73.77; H, 5.07; N, 10.07. Found: C, 72.90; H, 5.14; N, 9.90; δ¹H (300 MHz, thf-d₈): 7.33 (d, JHH = 8.1 Hz, 2 H, H₃), 7.20 (t, JHH = 7.8 Hz, 2 H, H₄), 7.11 (d, JHH = 7.5 Hz, 2 H, H₅), 4.68 (s, 2 H, H₁), 2.55 (s, 6 H, H₁₅), δ¹³C¹H (75 MHz, thf-d₈): 160.62 (s, 2 C, C₁), 152.05 (s, 2 C, C₂), 141.74 (s, 2 C, C₇), 131.32 (s, 2 C, C₆), 125.62 (s, 2 C, C₄), 125.58 (s, 2 C, C₅), 108.38 (s, 2 C, C₃), 29.69 (s, 1 C, C₁₅), 16.41 (s, 2 C, C₁₅); δ¹⁵N¹H (30 MHz, thf-d₈): −135.9 (s); EI-MS, m/z (%): 278 (100) [M⁺], 146 (10) [M – NCOC₃H₇]⁺.

**Metallation reactions**

To a solution of the corresponding ligand 1 (1.00 eq.) in toluene a slight excess of the pure organometallic reactant AlMe₃, GaMe₃, InMe₃, AlMe₂Cl or AlEt₂I, respectively (1.10 eq.) were treated as stated in the general procedure above. Yellow crystals were obtained in a yield of 1.43 g (1.39 mmol, 11.3 mmol, 68%). Anal. Calcd for C₁₉H₁₉InN₂O₂ (777.1 g mol⁻¹): C, 60.52; H, 5.08; N, 4.73. Found: C, 60.84; H, 5.24; N, 4.75; δ¹H (400 MHz, thf-d₈): 7.22–7.13 (m, 2 H, H₃), 7.07–6.99 (m, 4 H, H₄ + H₅), 5.18 (s, 1 H, H₁), 2.57 (s, 6 H, H₁₅), 0.06 (s, 6 H, H₁₅); δ¹³C¹H (75 MHz, thf-d₈): 167.84 (s, 2 C, C₁), 140.29 (s, 2 C, C₂), 137.57 (s, 2 C, C₇), 127.27 (s, 2 C, C₅), 123.60 (s, 2 C, C₆), 123.15 (s, 2 C, C₄), 107.85 (s, 2 C, C₃), 58.83 (s, 1 C, C₁), 19.01 (s, 2 C, C₁₅), −0.95 (s, 2 C, C₁₇); δ¹⁵N¹H (40 MHz, thf-d₈): −229.7 (s); EI-MS, m/z (%): 376.1 (17) [M⁺], 361.0 (100) [M – Me⁺], 346.0 (20) [M – 2 Me⁺], 277.1 (12) [M – GaMe₃⁺], 68.9 (41) Ga⁺.

δ¹⁵N¹H (30 MHz, thf-d₈): 168.67 (s, 2 C, C₁), 149.14 (s, 2 C, C₂), 141.64 (s, 2 C, C₇), 131.32 (s, 2 C, C₆), 125.62 (s, 2 C, C₄), 125.58 (s, 2 C, C₅), 108.38 (s, 2 C, C₃), 29.69 (s, 1 C, C₁₅), 16.41 (s, 2 C, C₁₅); EI-MS, m/z (%): 278 (100) [M⁺], 146 (10) [M – NCOC₃H₇]⁺.
could be isolated as a brown powder (111 mg, 0.25 mmol, 25%). After recrystallization from toluene also crystals suitable for structure determination were obtained. Calculated for C_{19}H_{18}AlIN_{2}O_{2} (460.24 g mol\(^{-1}\)): C, 48.45; H, 3.61; N, 6.28. Found: C, 45.53; H, 3.32; N, 6.07 (deviation due to slight contamination with the AlI\(_2\) derivative); \(\delta\)H (300 MHz, thf-d\(_8\)): 7.29–7.25 (m, 2 H, H3), 7.14–7.10 (m, 4 H, H4 + H5), 5.47 (s, 1 H, H1), 2.77 (s, 6 H, H15), –0.47 (s, 3 H, H1M); \(\delta^{13}\)C{\(^1\)H} (125 MHz, thf-d\(_8\)): 168.90 (s, 2 C, C1), 149.13 (s, 2 C, C2), 136.66 (s, 2 C, C7), 127.72 (s, 2 C, C5), 125.12 (s, 2 C, C6), 124.11 (s, 2 C, C4), 108.05 (s, 2 C, C3), 60.58 (s, 1 C, C1'), 18.88 (s, 2 C, C15), –6.83 (s, 1 C, C1M); \(\delta^{15}\)N{\(^{1}\)H} (50 MHz, thf-d\(_8\)): –230.8 (s); El-MS, m/z (%): 278 (100) [M – AlEtI\(^{+}\)], 146 (37) [M – AlEt – NCOC\(_7\)H\(_4\)]\(^+\), 132 (9) [NCOC\(_7\)H\(_4\)]\(^+\).

X-ray crystallographic studies

Single crystals were selected from a Schlenk flask under an argon or a nitrogen atmosphere and covered with perfluorinated polyether oil on a microscope slide, which was cooled with a nitrogen gas flow using an X-TEMP2 device.\(^{27}\) An appropriate crystal was selected using a polarised microscope, mounted on the tip of a MiTeGen@MicroMount or glass fibre, fixed to a goniometer head and shock cooled by a crystal cooling device. The data for 1–7 were collected from shock-cooled crystals at 100(2) K. The data of 1, 2 and 7 were collected on an Incoatec Mo Microsource\(^{28}\) and compounds 3–6 were collected on an Incoatec Ag Microsource,\(^{29}\) each equipped with mirror optics and an APEX II detector with a D8 goniometer. All diffractometers were equipped with a low-temperature device and used either MoK\(_\alpha\) radiation of \(\lambda = 0.71073 \) Å or AgK\(_\alpha\) radiation of \(\lambda = 0.6896 \) Å. The data were integrated with SAINT\(^{10}\) and an semi-empirical absorption correction (SADABS)\(^{29}\) was applied. The structures were solved by direct methods (SHELXT)\(^{31}\) and refined by full-matrix least-squares methods against \(F^2\) (SHELX2014).\(^{32}\) All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their \(U_{iso}\) values constrained to equal 1.5 times the \(U_{eq}\) of their pivot atoms for terminal sp\(^3\) carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond length restraints and isotropic displacement parameter restraints. The positions of the amine hydrogen atoms are taken from the difference Fourier map and refined freely.

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The CCDC numbers, crystal data and experimental details for the X-ray measurements are listed in the ESL.\(^{\ddagger}\)

Conflict of interest

The authors declare no competing financial interest.

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Notes and references