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Amino–Organolithium Compounds and their Aggregation for the Synthesis of Amino–Organoaluminium Compounds

Alexander Bodach,[a] Jochen Ortmeyer,[a, b] Bastian Herrmann,[a] and Michael Felderhoff*[a]

Here, we present a thorough structural study of small, easily accessible amino–organolithium compounds with bridging phenyl and naphthyl moieties. Their crystal structures most likely represent their aggregation as tetramers and dimers in both hydrocarbon and ethereal solvents. These amino–organolithium compounds were further used to generate their corresponding aluminium compounds as a model system. Their crystal structures are reported too. All structures are discussed with a focus on the different steric demands and bridging moieties. Additionally, the crystal structures of neophyllithium and decomposition products of some of the compounds mentioned above are reported. This study provides additional data for the future design and synthesis of amine stabilised organolithium and -aluminium compounds.

Introduction

It has been more than 200 years since the discovery of lithium metal and 100 years since the first synthesis of an organolithium compound by Schlenk&Holtz.[1] This was followed by the report of a convenient synthesis strategy from lithium metal and alkyl halides by Ziegler in 1930.[2] Until now, chemists have learned to handle, modify, and apply organolithium compounds for a wide range of applications, even on an industrial scale.[3] One of the most determining parameters for organolithium compounds is their aggregation. Alkyllithium compounds are known to form mostly hexamers, e.g., (^{i}BuLi)$_6$,[4] (^{i}PrLi)$_6$,[5] (^{n}BuLi)$_6$,[6] and tetramers, e.g., (^{t}BuLi)$_4$,[6] (EtLi)$_4$,[7] (MeLi)$_4$.[8] In contrast, aryllithium compounds form insoluble coordination polymers of dimers, e.g., PhLi,[9] MesLi,[10] TolLi,[11] whose structures could only be determined from X-ray powder data. Nevertheless, the aggregation of NpLi (Np = neopentyl) and NphLi (Nph = neophyl, 2-methyl-2-phenylpropyl) in the solid-state has remained unclear. These compounds are widely used, e.g., for the synthesis of Schrock carbenes[12] and soluble Schlosser bases[13] because they lack a β-H moiety and therewith do not allow β-H elimination. The aggregation of organolithium compounds is strongly influenced by the electronic and steric properties of the ligand as well as the presence of bases and solvents.[3b,14] Here, especially amines and ethers play a vital role.[14c]

Currently, organolithium chemistry is evolving in several directions: First, experimental charge density studies revealed the nature of these unusual coordination bonds,[15] second, catalytic coupling reactions are still improved,[16] third, greener approaches try to avoid the usage of solvents and exploit solid organolithium compounds in mechanochemical reactions,[17] and fourth, they might be applied for syn-gas chemistry.[18]

Besides the crystallographic studies, which give the exact structure, but only of (single-)crystalline compounds, NMR spectroscopic studies reveal the aggregation in solution, which sometimes differs, depending on, e.g., concentration and solvent. Noteworthy for this study are several reported NMR investigations on a series of naphthyllithium compounds[19] and several ortho-dimethylamino–aryllithium compounds[20] in solution. Additionally, there are approaches to utilise ^{7}Li residual quadrupolar couplings to identify the degree of organolithium aggregation in gels,[21] DOSY,[22] classic ^{7}Li,[23] and scalar Li–Li couplings[24] in NMR spectroscopy.

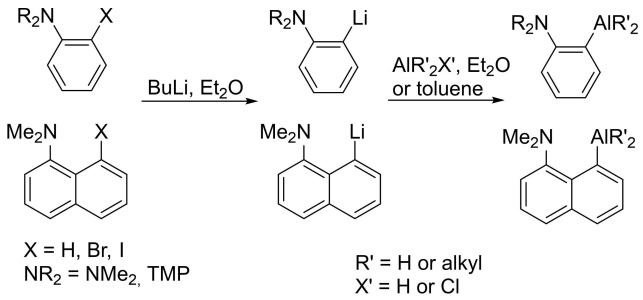
In addition to the many applications of organolithium compounds, they can also be used to synthesise organoaluminium compounds. These compounds garnered yet little attention aside from the well-known Ziegler polymerization.[25] This is now changing; several groups have recently started to explore nitrogen-stabilised organoaluminium compounds, including Al(I) and radical species, namely Power,[26] Braunschweig,[27] Aldridge,[28] Stephan,[17b] and Roesky.[29] Simultaneously, there are even reports on the activation of molecular hydrogen by Stephan and co-workers[30] using di-iso-butylaluminium-hydride and imines or by Aldridge and co-workers[31] using a complex aluminium imide. Also, we recently reported on the hydrogenation of metallic aluminium in the presence of piperidine[32] or TEDA (mechanochemical, TEDA = triethylenediamine)[33] and H_2 activation by inter- and intramolecular Al–N Lewis pairs.[34] Among the plenty of FLP (Frustrated Lewis Pair) literature,[35] the Al–N systems garnered far less attention. Nevertheless, there are noteworthy reports, e.g., by Uhl and co-workers,[36] and selected examples of reactions with chalcogen-containing double bonds (CO_2,[37] ketones,[38] isocyanates[39]), dehydrocoupling,[40] acryl and lac-

[a] A. Bodach, Dr. J. Ortmeyer, B. Herrmann, Dr. M. Felderhoff
Department of Heterogeneous Catalysis
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, 45470,
Mülheim an der Ruhr, Germany
E-mail: felderhoff@kofo.mpg.de
[b] Dr. J. Ortmeyer
Institute of Inorganic Chemistry,
RWTH Aachen University,
Landoltweg 1, 52074
Aachen, Germany

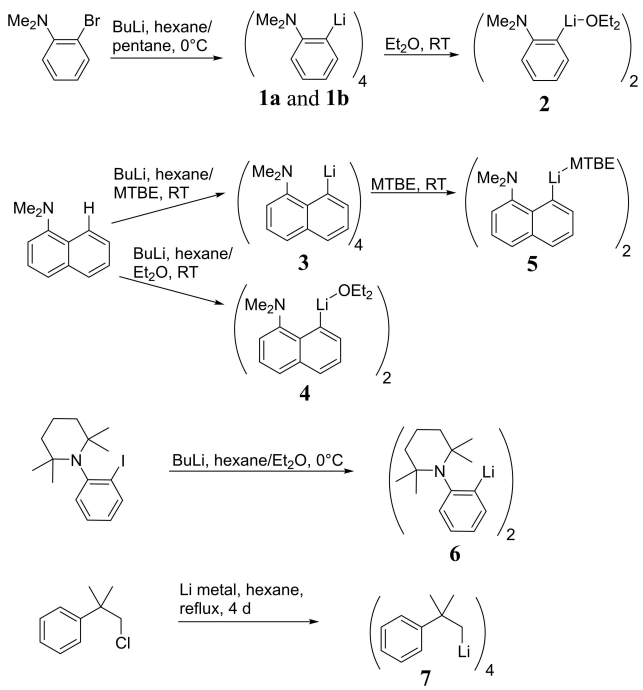
tone polymerisation are among the few that have been reported.[41]

Therefore, this study focuses on the syntheses and aggregations of intramolecular amine-stabilised organolithium compounds, which are common precursors for the syntheses of amine-group-13-element (frustrated) Lewis pairs. Generally, the organolithium compounds have been synthesised by directed ortho-metallation or lithium–halogen-exchange reactions and further reacted with alkylaluminium halides or aluminium hydride, Scheme 1.

A deeper understanding of the formation principles and geometrical changes in the aggregation of these organolithium compounds will define further applicability for syntheses of main-group-element compounds and serve as a model system. Here, we present a rare example where the organolithium compounds could be isolated donor-free and coordinated by ethers, which most likely reflect the species present in solution.



Scheme 1. General synthesis pathways of selected organolithium compounds towards organoaluminium compounds.



Scheme 2. Schematic syntheses and aggregations of amine-stabilised organolithium compounds **1**–**6** and neophyllithium **7**.

These organolithium compounds were, for demonstration purposes, used to synthesise intramolecular Al–N Lewis pairs and provide alkyl derivatives of the known (*o*-TMP–C_6H_4)AlH_2, which has been used for hydrogen[34] and alkyne[42] activation.

Results and Discussion

The organolithium compounds were synthesised by lithium–halogen-exchange reactions at low temperature or by directed *ortho*-metallation with *n*-butyllithium based on literature procedures,[34,43] Scheme 2.

Remarkably, $[Me_2NC_6H_4Li]_4$ (**1**) crystallised as large cubes from Et_2O/pentane as a tetramer in a cubic crystal structure (**1 a**) with small voids of ~30 Å^3 per unit cell, Figure 1a. Polymorph **1 a** slowly (~1 week) transformed into the respective monoclinic polymorph (**1 b**) without voids. Although these voids seem to be large enough to bear H_2O, its presence can be excluded due to the reactivity of **1 a** itself and the following phase transformation to **1 b**, which contains no voids/water. The metastable cubic phase **1 a** seems to undergo more likely a kinetically controlled crystallisation with reduced packing density, and therefore the phase transformation occurs to the more densely packed monoclinic polymorph.

The respective tetramer of $[Me_2NC_{10}H_6Li]_2$ (**3**) could only be crystallised in a monoclinic form from benzene, incorporating some benzene molecules, Figure 1b. In contrast, the crystallisation from ethereal solvents gave ether adducts $[Me_2NC_{10}H_6Li \cdot Et_2O]_2$ (**4**) and $[Me_2NC_{10}H_6Li \cdot MTBE]_2$ (**5**), solely, vide infra.

Furthermore, by increasing the steric demand from dimethylamino- in **1** to tetramethylpiperidinyl- in $[(o\text{-TMP–}C_6H_4)Li]_2$ (**6**), we could only crystallise a dimer in a monoclinic structure from Et_2O, surprisingly without incorporating ether, Figure 1c. It is

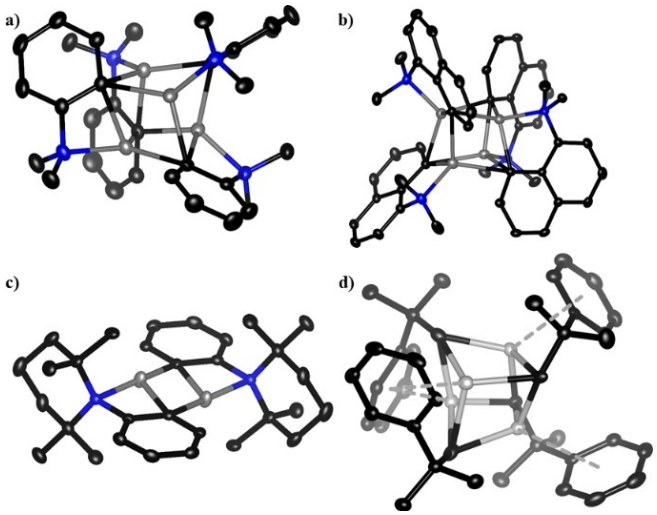


Figure 1. Molecular structures of (a) $[Me_2NC_6H_4Li]_4$ **1 a** (cubic polymorph), (b) $[Me_2NC_{10}H_6Li]_4$ **3** (benzene solvate, not shown), (c) $[(o\text{-TMP–}C_6H_4)Li]_2$ **6** and (d) $[NphLi]_4$ **7**, Ar···Li interactions shown as dashed lines, carbon (black), nitrogen (blue), lithium (grey), hydrogen atoms omitted for clarity, all displacement ellipsoids are shown with 50% probability.

Table 1. Selection of characteristic Li–E interatomic distances (E = Li, C, N), including min. and max. bond lengths to α- and γ-carbon atoms, found for "equivalent" bonds, space groups and Z′ (No of monomers in the asymmetric unit) for compounds **1 a**, **1 b**, **3**, **6**, and **7**.

	1 a	**1 b**	**3**	**6**	**7**
Formula Space group (No.)	$[Me_2NC_6H_4Li]_4$ $I\bar{4}3d$ (220)	$[Me_2NC_6H_4Li]_4$ $P2_1/c$ (14)	$[Me_2NC_{10}H_6Li\cdot C_6H_6]_4$ $P2_1/n$ (14)	$[(o\text{-TMP}–C_6H_4)Li]_2$ $P2_1/n$ (14)	$[C_{10}H_{13}Li]_4$ $I4_1/a$ (88)
Z′	1	4	4	1	4
d(Li–N)/Å	2.018(3)	Min 2.030(6) Max 2.041(6)	Min 1.984(3) Max 2.036(3)	2.026(3)	
d(Li–C)/Å	2.243(3) 2.283(3) 2.228(3)	Min 2.213(6) Max 2.263(6)	Min 2.184(3) Max 2.439(3)	2.138(3) 2.452(3)	Min α 2.21(3) Max α 2.337(3) Min γ 2.439(3) Max γ 2.550(3)
d(Li···Li)/Å	2.489(4) 2.622(5)	Min 2.488(8) Max 2.678(8)	Min 2.463(4) Max 2.629(4)	2.220(5)	Min 2.469(4) Max 2.505(4)

worth noting that we found a remarkable "shelf-life time" in the order of years for compounds **1–6**.

A closer look at the structures of these donor-free organolithium aggregates reveals that the tetrameric compounds **1 a**, **1 b**, and **3** each exhibit distorted heterocubanes as structure building motifs. A comparison of the bond lengths, Table 1, reveals that the Li–N bond length in cubic **1 a** is slightly shorter than in the monoclinic form **1 b** while the Li–C bond length is slightly increased and the Li···Li distances are similar. Overall these parameters are similar to the report of the co-crystal of $[Me_2NC_6H_4Li]_4$ (**1**) with ^{t}BuLi, by Stalke and co-workers.[44] In contrast, changing the phenyl (**1**) to a naphthyl (**3**) as a bridging motif, the bond lengths stay similar with respect to an increased deviation among approximately equal Li–C and Li–N bond lengths, Table 1.

Furthermore, we have synthesised neophyllithium NphLi (**7**), commonly used as a cheap replacement of neopentyllithium NpLi by direct synthesis from neophylchloride lithium metal analogously to the classic Schrock synthesis.[45] Both **7** and NpLi might be used to increase the steric demand on the Al site while offering high stability for future studies. It is worth noting that **7** and NpLi are colourless powders with a "shelf-lifetime" of several years due to their inability to undergo β-hydride elimination. Finally, we could elucidate the crystal structure of **7** in space group $I4_1/a$ (88) as a tetramer. The bond lengths are comparable to those of tetrameric (m-bicyclo[2.2.1]heptan-1,1,1-triyl)-lithium,[46] although the short Li–C_γ contacts in **7** are unique in the CCDC database for neat, tetrameric organolithium compounds (only H, Li, C), Table 1. In contrast, the structure of NpLi in the solid-state remains unclear, probably due to a plastic crystalline phase (long-range order, but no local order, e.g., molecules rotating on their position).[47] A similar study showed hexameric ^{i}BuLi[4] existing in a plastic crystalline phase at ambient temperature and an ordered crystalline phase at lower temperatures.

Since a significant fraction of organolithium compounds is used in ethereal solutions, especially for metathesis reactions, we carried on to study the ether adducts and their aggregation. This will allow predicting their reactivity for future synthetic protocols. The crystallisation of **1** from Et_2O led to a dimer (**2**) in a triclinic crystal structure with two monomers in the asymmetric unit, Figure 2a. The dimer consists of a Li_2C_2 diamond, where the Li-coordination is saturated in a distorted tetrahedral geometry by Et_2O and amine, respectively. This is probably the active form for the following metathesis reaction to the respective aluminium compounds, vide infra.

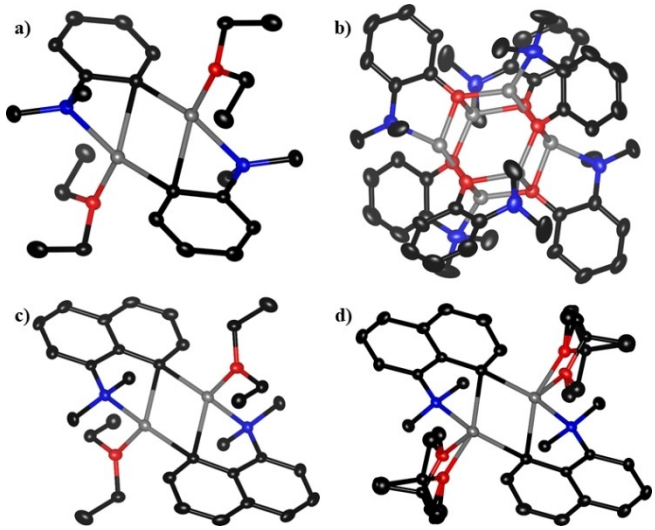


Figure 2. Molecular structures of (a) $[Me_2NC_6H_4Li\cdot Et_2O]_2$ **2**, (b) $[Me_2NC_6H_4OLi]_6$ **8**, (c) $[Me_2NC_{10}H_6Li\cdot Et_2O]_2$ **4** and (d) $[Me_2NC_{10}H_6Li\cdot MTBE]_2$ **5**, only one of the two disordered hexamers of **8** is shown, carbon (black), nitrogen (blue), oxygen (red), lithium (grey), hydrogen atoms omitted for clarity, all displacement ellipsoids are shown with 50% probability.

Analogously to **1**, **3** forms dimers upon crystallisation from Et_2O (**4**) and MTBE (**5**), respectively, Figure 2c and Figure 2d. Both **4** and **5** exhibit a similar coordination geometry despite the larger linker (naphthyl instead of phenyl), while the MTBE is disordered on two positions. Accordingly, the bond lengths of **2**, **4**, and **5** are very similar, as expected: The Li–N bonds are all ~2.1 Å long, the Li–C bonds are in the range of 2.1–2.3 Å, the Li–O bonds are ~2.0 Å, while the Li···Li distances are ~2.4 Å, Table 2. These bond lengths are also similar to $[(Me_2N)_2C_{10}H_5Li\cdot Et_2O]_2$[48] and $[(Me_2N)C_{10}H_6Li\cdot THF]_2$.[49]

Serendipitously, we obtained a decomposition product of **1** as hexamer $[Me_2NC_6H_4OLi]_6$ (**8**), which inserted oxygen atoms between each pair of lithium and carbon atoms, Figure 2b. Since we obtained **8** from a non-specific process, we could not evaluate in detail whether **1** cleaved Et_2O or oxygen "sneaked"

Table 2. Selection of characteristic Li–E interatomic distances (E = Li, C, N, O), including min. and max. bond lengths, found for "equivalent" bonds, space groups and Z′ (No of monomers in the asymmetric unit) for compounds **2**, **4**, **5**, and **8**.

	2	**4**	**5**	**8**
Formula	$[Me_2NC_6H_4Li\cdot Et_2O]_2$	$[Me_2NC_{10}H_6Li\cdot Et_2O]_2$	$[Me_2NC_{10}H_6Li\cdot MTBE]_2$	$[Me_2NC_6H_4OLi]_6$
Space group (No.)	$P\bar{1}$ (2)	$P2_1/c$ (14)	$P2_1/c$ (14)	$R\bar{3}$ (148)
Z′	2	1	1	1
d(Li–N)/Å	2.103(2) 2.138(2)	2.113(3)	2.164(2)	2.043(3) 2.065(3)
d(Li–C)/Å	Min 2.161(2) Max 2.238(2)	2.219(3) 2.189(3)	2.224(2) 2.261(2)	Min 2.667(4) Max 2.772(3)
d(Li···Li)/Å	2.448(4) 2.468(3)	2.344(5)	2.429(3)	2.597(3) 2.260(3)
d(Li–O)/Å	1.973(2)	1.930(3)	2.052(2)	Min 1.917(2) Max 1.985(2)

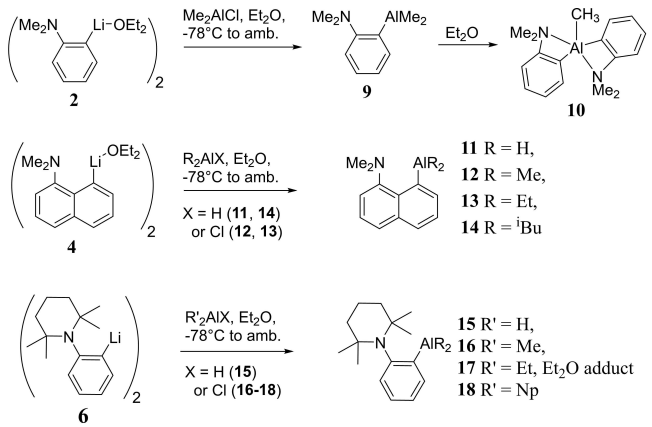
into the flask. Nevertheless, the crystal structure provides insights into the decomposition of amino–organolithium compounds. The hexamer **8** consists of two stacked Li_3O_3 rings, while the bridging 2-(dimethylamino)phenyl groups lead to a propeller arrangement. The crystal structure is described disordered in a trigonal system with the rarely observed space group $R\bar{3}$.

The hexamer of **8** can be described as two stacked cyclic trimers based on Li_3O_3 six-membered rings, while each amine group additionally coordinates to a Li atom within the same ring. This leads to a propeller shape and therewith to asymmetry. This asymmetry is compensated by a disorder where both possible orientations are similarly occupied, leading to a "pseudo-racemate". For visualisation, only one of those is shown in Figure 2b.

Similar hexamers with the similar or slightly distorted core structure of Li_6O_6 and a variety of coordinating amino ligands are also reported in the CCDB database with comparable bond lengths, e.g., ADATOP,[50] BUYSOF,[51] PIKCES[52] (CCDC Refcodes).

Since we know that different solvents do not only change the solubility of organolithium compounds but also change their aggregation (vide supra), we chose to use these organolithium compounds deliberately in Et_2O to increase their reactivity through smaller reactive dimers instead of tetramers (**1** and **3**) in hydrocarbon solvents. To investigate this reactivity, we chose a hitherto rarely studied and currently reviving field of simple main-group element compounds. Accordingly, Al–N compounds, where an increased Al–N distance could possibly lead to frustration, were selected as target molecules. Similar Al–N compounds recently garnered particular interest for their potential to activate molecular hydrogen as Lewis pairs with typical FLP reactivity.[34]

Subsequently, the above-mentioned organolithium compounds (mostly etherates) were reacted with dialkylaluminiumchlorides R_2AlCl or freshly prepared AlH_3, Scheme 3. First, $Me_2NC_6H_4AlMe_2$ (**9**) was synthesised and crystallised from hexane/Et_2O. Surprisingly, from an Et_2O-solution of the crude product of **9** within several weeks, the side-product $(Me_2NC_6H_4)_2AlCH_3$ (**10**) could be crystallised as minor species from Et_2O. This may point to a disproportionation reaction, where also $AlMe_3$ should have been formed and probably left to the gas phase. Analogously to **9**, the respective naphthalene-



Scheme 3. Syntheses of amine-stabilised organoaluminium compounds **9**–**18** from R–Li compounds.

bridged compounds **12** and **13** have been synthesised.[53] $[Me_2NC_{10}H_6AlH_2]$[54] (**11**) was synthesised by a different method using AlH_3 and its crystal structure confirmed with a higher qualty dataset (100 K instead of ambient measurement, Table 3), and additionally $Me_2NC_{10}H_6Al^iBu_2$ (**14**) was prepared similarly to **9**, Scheme 3. To investigate the influence of the steric demand of the amino group, the compounds (*o*-TMP–C_6H_4)AlR_2 (R = H, Me, Et, Np) (**15–18**) were synthesised. The synthesis of **15** has been reported previously,[34] while the others were synthesised analogously to above-mentioned compounds, see experimental section.

Noteworthy for the synthesis of **18** is that Np_2AlCl was synthesised from a modified solvothermal procedure,[55] and also mechanochemically using a common shaker mill and LiCl as milling medium.

However, up to now we did not obtain the desired scope of single crystals. Especially, **16–18** resisting our crystallisation attempts. Nevertheless, we could crystallise the ether adduct (*o*-TMP–C_6H_4)$AlEt_2\cdot Et_2O$ (**17**) from Et_2O and the decomposition product of **18** namely $[(o\text{-TMP–}C_6H_4)Al(Np)(ONp)]_2$ (**19**) from a pentane solution that was left open to air.

Remarkably, the crystal structure of **9** is described in the rarely observed space group $R\bar{3}$ (148) with an Al–N bond length of 2.103(2) Å, Figure 3a, Table 3. All bond lengths are comparable to the ones reported by Schumann et al.[53] for the

Table 3. Selection of characteristic Al–E interatomic distances (E = C, N, O, Al), including min. and max. bond lengths, found for "equivalent" bonds, space groups and Z' (No of molecules/monomers in the asymmetric unit) for compounds **9**, **10**, **17**, and **19**. For comparison, the respective entries for **12** and **13** are reported here as well.[53]

	9	**10**	**11**	**12**[53a]	**13**[53b]	**17**	**19**
Formula	$C_{10}H_{16}AlN$	$C_{17}H_{23}AlN_2$	$C_{12}H_{14}AlN$	$C_{14}H_{18}AlN$	$C_{16}H_{22}AlN$	$C_{22.50}H_{40.65}AlCl_{0.30}NO$	$[C_{25}H_{44}AlNO]_2$
Space group (No.)	$R^{-}3$ (148)	*Iba*2 (45)	$P2_1/c$, (14)	$P2_12_12_1$ (19)	$P2_1/c$ (14)	$P2_1/n$ (14)	$P2_1/n$ (14)
Z'	1	1	1	1	4	1	1
d(Al–N)/Å	2.103(2)	2.201(2) 2.237(2)	2.124(2)	2.069(2)	Min 2.056(3) Max 2.070(3)	3.293(2)	3.504(2)
d(Al–Al)/Å			2.7561(8)				2.002(2)
d(Al–C)/Å	1.965(2) 1.970(2) 1.996(2)	1.995(2) 1.998(2) 2.000(2)	1.979(2)	1.971(3) 1.972(3) 1.984(2)	Min 1.961(3) Max 1.981(3)	1.964(2) 1.989(2) 1.999(2)	2.003(2) 2.881(2) –
d(Al–O)/Å						1.964(2)	1.853(2) 1.883(2)

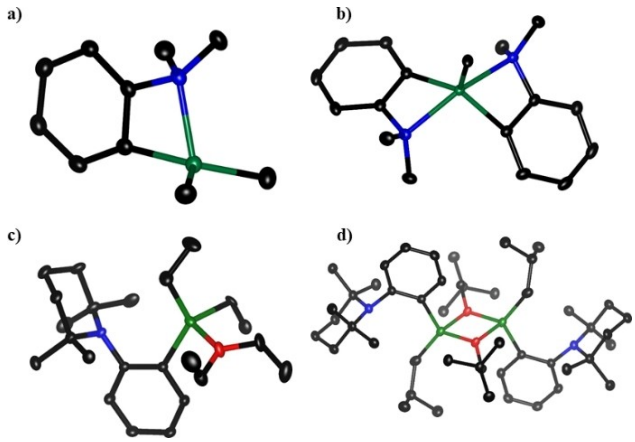


Figure 3. Molecular structures of (a) $Me_2NC_6H_4AlMe_2$ **9**, (b) $(Me_2NC_6H_4)_2AlCH_3$ **10**, (c) (*o*-TMP–C_6H_4)$AlEt_2 \cdot Et_2O$ **17** (disorder/Cl atom not shown for clarity), and (d) $[(o\text{-TMP–}C_6H_4)Al(Np)(ONp)]_2$ **19**, carbon (black), nitrogen (blue), oxygen (red), aluminium (green), hydrogen atoms omitted for clarity, all displacement ellipsoids are shown with 50% probability.

naphthylene-bridged derivative **12** and its respective Et-derivative **13** and within the expected range (*d*(Al–N) = 2.103(2) Å, *d*(Al–C) = 1.965(2) - 1.996(2) Å,), Table 3.

In contrast, the Al–N bond length in **10**, described in space group *Iba*2 (45), is slightly elongated to 2.201(2) Å in comparison to **9** as expected for a penta-coordinated Al species, Figure 3b, Table 3. The bond lengths in the crystal structure of **10** are similar to those of the chloro-derivative reported by Kannan et al.[38b] and the naphthylene bridged Et-derivative reported by Schumann et al..[53a]

Increasing the steric bulk to TMP, we could only crystallise the Et_2O-adduct **17**, Figure 3c, which has a drastically increased Al–N distance of 3.294(2) Å). On the one hand, this Al–N distance is in the range of FLPs reported, in the order of the sum of crystallographic van der Waals radii[56] (*d*(Al–N) = 3.39 Å). On the other hand, **17** is not representative of an FLP because an Et_2O molecule fills the free coordination site of the Al atom.

Notably, ~30% of one Al–**Et** group is described as a Cl atom, which may hint at an undesired side reaction. In this side reaction, both Et and Cl of the Et_2AlCl could react with **6** at approximately similar rates to give a mixed product with predominantly Et groups but also Cl atoms. This would be unexpected. However, Et and Cl both consist of seventeen electrons. Hence, our fitted Cl atom might be disordered Et group, but we could not obtain a suitable disordered model and the centre of the electron density should be more diffuse for an Et group.

The partly-oxidised product **19** forms inversion-symmetric oxygen-bridged dimers in a monoclinic crystal structure, Figure 3d. The bond lengths are all as expected, based on the sum of atomic radii.[57] Interestingly, the Al–N distance increases to 3.504(2) Å for this alcoholate compared to the ether adduct **17**.

Knowing that the above-mentioned Al–N compounds may be eligible for H_2 activation, based on our previous study,[34] the HD-activation was tested in the same manner. However, this did not lead to conclusive results. The reasons for this inactivity can be found in the crystal structures: The etherate **17** cannot act like an FLP with a coordinating Et_2O molecule, and **16** (as well as **9–14**) might not be sterically hindered enough. This may point out the need for synthesising compounds with sterically more demanding ligands, an AlH_2-moiety, or a suitable amine of lower basicity.

Conclusion

Here, a thorough structural study of aggregated amine-stabilised organolithium compounds and their respective dimeric ether adducts, which are most likely the soluble reacting species, is demonstrated. The discussed donor-free dimethylamino–phenyl or -naphthyl lithium compounds form tetramers while their ether adducts are dimers. In contrast, the TMP–phenyl lithium compound forms only dimers due to the increased steric bulk.

Furthermore, these organolithium compounds were used to synthesise the respective aluminium compounds. Based on our previous study,[34] we tested their ability to activate molecular hydrogen by HD isotope exchange reactions, which did not show any conclusive reactivity. Therefore, their crystal structures were analysed to investigate the reasons for their inactivity towards H_2/HD. This points strongly towards the need for the future development of compounds with steric more demanding ligands. Additionally, the structure of NphLi (**7**) as a common

alternative to NpLi and robust bulky ligand transferring agent as well as several decomposition products of the mentioned organolithium and -aluminium compounds are reported for a broader view on the described compounds. All reported organolithium compounds have a remarkable shelf-life time in the order of years, which is especially surprising for the ether adducts. This study presents valuable structural information for the future design and synthesis of these kinds of molecules.

Experimental Section

General procedures: All manipulations have been performed under inert argon atmosphere using standard Schlenk and glovebox techniques. All solvents were purified and dried by distillation from Na/benzophenone and stored over molecular sieves (3–4 Å, dried in vacuo at 250 °C for several hours). All chemicals, including organolithium and -aluminium compounds, were used as received from common suppliers or prepared vide infra. For a representative set of the described compounds, mass spectrometry and elemental analysis were attempted, but none of them was successful due to the high reactivity of these compounds, especially towards traces of water and air.

Caution: All organoaluminium and -lithium compounds, especially as neat liquids, as well as aluminium hydrides used for syntheses, are severely air-/moisture-sensitive and pyrophoric. Aluminium halides are air-/moisture-sensitive and decompose to volatile acids. Guidelines can be found in the literature for organolithium compounds,[3a,58] whereas the handling of organoaluminium compounds is similar with respect to their higher sensitivity and the possibility to use them as neat liquids in many cases.

NMR spectra were collected at 298 K on Bruker Avance III 300nano or AV400 spectrometers in 5 mm diameter NMR tubes. ^{1}H and ^{13}C chemical shifts (δ) are reported in ppm relative to non-deuterated solvent signals described by Fulmer et al.,[59] coupling constants are given in Hz common abbreviations are used. For ^{27}Al NMR spectra, an aring sequence of three pulses was used as described previously.[34]

Single-crystal structure analysis Suitable single crystals were selected under inert oil and mounted on a MiTeGen loop, and transferred into the cooled nitrogen stream (100 K, Oxford Cryostream 700, Oxford Cryosystems) on the goniometer. The three used instruments were Bruker AXS Mach3 instruments with a) Bruker AXS rotating Anode FR591 (45 kV, 30 mA, Cu–Kα_1 λ = 1.5406 Å) with Incoatec Montel 200 Optics and an APEX II CCD detector; b) Bruker AXS rotating Anode FR591 (50 kV, 40 mA, Mo–Kα_1 λ = 0.7093 Å) with Incoatec Montel 200 Optics and a Kappa CCD detector; c) Incoatec, Micro Focus IμS 1.0 (50 kV, 1 mA, Mo–Kα_1 λ = 0.7093 Å) with Incoatec Helios MX Optics and an APEX II CCD detector. The obtained diffraction data were evaluated with SuperGUI (collect and supergui, Bruker AXS BV, 1997–2009) and EVALCCD[60] or the APEX3 software package and a multi-scan absorption correction was applied using XREP (Version 2014/2, Bruker-AXS, 2014) or SADABS.[61] All Structures were solved with SHELXS or SHELXT and refined with SHELXL.[62] All non-hydrogen atoms were refined with anisotropic displacement parameters, while the hydrogen atoms were refined isotropically.

Syntheses

NpLi (neopentyllithium)[45] and **Np_3Al** (tris(neopentyl)aluminium) have been synthesised and characterised as described in literature.[17b] **12** ((8-(dimethylamino)naphthalenyl)-1-dimethylaluminium) and **13** ((8-(dimethylamino)naphthalenyl)-1-diethylaluminium) were prepared according to literature procedure.[53b] (**o-TMP–C_6H_4)I** ((2-(2,2,6,6-tetramethyl-piperidine-1-yl)phenyl)-iodide) and **6** ((2-(2,2,6,6-tetramethyl-piperidine-1-yl)phenyl)-lithium) have been synthesised according to literature procedures.[43b] **6** was recrystallised from Et_2O and the obtained single crystals were harvested for diffraction experiments. **15** has been described in our previous communication[34] as well as by Roesky and co-workers.[42a]

Np_2AlCl (bis(neopentyl)aluminium chloride) was synthesised based on a modified literature procedure.[55] A mixture of $AlCl_3$ (97 mg, 0.73 mmol, 1 eq.) and Np_3Al (350 mg, 1.5 mmol, 2 eq.) was heated in toluene to 80 °C for 3 h, then cooled to ambient and filtered. The residue was washed twice with 10 mL toluene. The filtrate was dried in vacuo and the product therein was purified by recrystallisation from pentane solution and sublimation in vacuo at 90 °C for several hours to yield 356 mg (1.7 mmol, 80 %) of the colourless product. ^{1}H NMR (300 MHz, C_6D_6) δ/ppm = 1.14 (s, 9H), 0.69 (s, 2H). ^{13}C NMR (75 MHz, C_6D_6) δ/ppm = 34.7, 31.5. ^{27}Al NMR could not be observed.

Np_2AlCl – mechanochemical approach: $AlCl_3$ (0.125 g, 0.93 mmol, 1 eq.), NpLi (0.45 g, 1.87 mmol, 2 eq.), 1.5 g LiCl as milling medium, and four balls (ø = 10 mm, steel) were charged into a 20 mL stainless steel milling vial and shook three times for (10 min + 5 min break) each in a Retsch MM200 shaker mill at 50 % power. The product was extracted with pentane and dried in vacuo to give a colourless solid. Yield: 0.51 g (2.49 mmol, 90 %).

1 [(2-(dimethylamino)phenyl)-1-lithium]$_4$. **1** was synthesised based on a modified literature procedure.[43b] 2-Bromo-dimethylaniline (5 mL, 3.75 g, 34.7 mmol, 1 eq.) was dissolved in 25 mL pentane, the solution cooled to 0 °C and ^{n}BuLi (14 mL, 2.5 M in hexanes, 35 mmol, 1.04 eq.) was added within 15 min. The reaction mixture was stirred for 3 h at 0 °C, then filtered and the residue washed with 6x4 mL pentane and dried in vacuo to yield the colourless product (3.75 g, 29.5 mmol, 85 %). Crystallisation by a gas-phase diffusion process (an Et_2O solution in a vial surrounded by pentane) yielded large blocks of the cubic polymorph **1 a** which transformed over several days to the monoclinic polymorph **1 b**. ^{1}H NMR (300 MHz, C_6D_6) δ/ppm = 8.29 (m, 1H), 7.26 (m, 2H), 7.03 (m, 1H), 2.08 (s, br, 6H). ^{7}Li NMR (117 MHz, C_6D_6) δ/ppm = 3.63. ^{13}C NMR (75 MHz, C_6D_6) δ/ppm = 166.3, 140.3, 126.2, 119.0, 46.7.

2 [(2-(dimethylamino)phenyl)-1-lithium-etherate]$_2$. **2** was obtained upon crystallisation from an Et_2O solution of **1** at −18 °C. **2** decomposes in C_6D_6 solution to Et_2O and **1**, indicated by its NMR spectrum.

3 [(8-(dimethylamino)naphthalenyl)-1-lithium]$_4$. To a solution of dimethylaminonaphthalene (3.0 mL, 3.1 g, 18 mmol, 1 eq.) in 8 mL MTBE, ^{n}BuLi (7.5 mL, 2.5 M in hexanes, 19 mmol, 1 eq.) was added within 10 min and the reaction mixture was stirred overnight, then filtered and the residue washed with 8x10 mL pentane. The filtrate was dried in vacuo to obtain the colourless product (2.61 g, 14.7 mmol, 81 %). Single crystals were grown from a benzene solution. ^{1}H NMR (300 MHz, C_6D_6) δ/ppm = 8.27 (dd, J = 6.0, 1.4 Hz, 1H), 7.70 (ddd, J = 8.2, 4.5, 1.3 Hz, 2H), 7.39–7.29 (m, 1H), 7.13–7.03 (m, 2H), 2.20 (s, 3H), 1.66 (s, 3H). ^{7}Li NMR (117 MHz, C_6D_6) δ/ppm = 4.88. ^{13}C NMR (75 MHz, C_6D_6) δ/ppm = 156.3, 143.5, 136.1, 135.8, 127.2, 125.3, 125.0, 116.5, 51.0, 55.6.

4 [(8-(dimethylamino)naphthalenyl)-1-lithium-etherate]$_2$. **4** was synthesised as described in the literature[43a] and crystallised from an Et_2O/hexane/pentane mixture. ^{1}H NMR (300 MHz, C_6D_6) δ/ppm = 7.70 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.2 Hz, 1H), 7.35 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.29 (m, 2H), 6.88 (d, J = 7.4 Hz, 1H), 3.26 (t, J = 7.0 Hz, 4H), 2.60 (s, 6H), 1.12 (t, J = 7.0 Hz, 6H). ^{7}Li NMR (117 MHz, C_6D_6) δ/

ppm = 1.75. ^{13}C NMR (75 MHz, C_6D_6) δ/ppm = 128.7, 126.1, 125.4, 124.7, 123.4, 114.4, 65.9, 60.8, 45.1, 15.6.

5 [(8-(dimethylamino)naphthalenyl)-1-lithium-(methyl-*tert*-butyl-) etherate]$_2$. Single-crystals of **5** were obtained upon recrystallisation of donor-free **3** in MTBE/pentane. **5** decomposes in C_6D_6 to **3** and MTBE.

7 Neophyllithium (2-methyl-2-phenylpropyl lithium). Neophylchloride (10 mL, 10.47 g, 62.1 mmol, 1 eq.) was added to a suspension of lithium granules (1% Na, 1.72 g, 248 mmol, 4 eq.) in 80 mL hexane. The reaction mixture was refluxed for 4 d. The resulting suspension was filtered over 1 cm of medium-coarse SiO_2. The residue was washed with pentane and toluene, and the filtrate was dried in vacuo. Recrystallisation of the crude product in 200 mL of pentane/hexane yielded 4.0 g of the desired product. Further concentration of the mother liquor resulted in additional 0.80 g. The product was obtained as colourless powder 4.80 g (34 mmol, 55%). Single crystals were grown from a toluene/pentane solution. ^{1}H NMR (300 MHz, C_6D_6) δ/ppm = 7.44–7.39 (m, 2H), 7.28–7.21 (m, 2H), 7.08–7.01 (m, 1H), 1.31 (s, 6H), −1.04 (s, 2H). ^{7}Li NMR (117 MHz, C_6D_6) δ/ppm = 0.76. ^{13}C NMR (75 MHz, C_6D_6) δ/ppm = 153.2, 129.9, 126.3, 124.9, 39.8, 35.8, 31.5.

8 [(lithium 2-(dimethylamino)phenolate)]$_6$. **8** was obtained serendipitously by a non-specific process upon attempting to crystallise **4** in Et_2O in a vial surrounded by pentane by a gas-diffusion process.

9 (2-(dimethylamino)phenyl)dimethylaluminium. Me_2AlCl (6.3 mL, 1 M in hexane, 6.3 mmol, 1 eq.) was added slowly to a solution of **1** (0.80 g, 6.3 mmol, 1 eq.) in 20 mL Et_2O at −78 °C within 10 min. The reaction mixture was warmed to -40 °C and stirred for 3 h. The suspension was filtered and the residue washed twice with 7 mL Et_2O. The filtrate was dried carefully in vacuo to grow single crystals of **9** (0.632 g, 3.57 mmol, 57%). ^{1}H NMR (400 MHz, C_6D_6) δ/ppm = 7.74–7.70 (m, 1H), 7.27 (ddd, *J* = 6.8, 4.6, 1.6 Hz, 2H), 6.93–6.89 (m, 1H), 2.54 (s, 6H), −0.26 (d, *J* = 22.1 Hz, 6H). ^{13}C NMR (101 MHz, C_6D_6) δ/ppm = 160.8, 137.9, 128.9, 127.4, 117.4, 116.3, 47.8, −9.9 (br). ^{27}Al NMR (78.21 MHz, C_6D_6) δ/ppm = 177 (FWHM could not be determined).

10 Bis(2-(dimethylamino)phenyl)(methyl)aluminium. **10** was only obtained as minor species upon a single recrystallisation experiment of crude **9** in Et_2O which may result from a disproportionation to **10** and $AlMe_3$.

11 (8-(dimethylamino)naphthalenyl)-1-aluminium hydride has been reported by Hair et al..[54] However, here we report a different synthesis procedure. $AlCl_3$ (0.62 g, 4.7 mmol, 0.25 eq.) in 15 mL Et_2O was added to a solution of $LiAlH_4$ (0.54 g, 14 mmol, 0.75 eq.) in 45 mL Et_2O at 0 °C and the resulting suspension stirred for 20 min. The suspension was filtered onto a suspension of **4** (3.00 g, 11.9 mmol, 1 eq.) in 60 mL Et_2O within 5 min. The resulting suspension was stirred at ambient temperature overnight, then filtered, and the residue was washed twice with 10 mL Et_2O. The residue was collected as pure colourless product (0.39 g, 16%). The filtrate was dried in vacuo and the obtained residue extracted with toluene, filtered off, and washed twice with 10 mL toluene. This second filtrate was dried in vacuo, and the crude product sublimated at up to 170 °C/0.02 mbar to obtain additional product (1.66 g, 70%). Total yield 2.05 g (10.3 mmol, 86%). ^{1}H NMR (300 MHz, C_6D_6) δ/ppm = 8.09 (dd, *J* = 6.3, 0.8 Hz, 1H), 7.62 (ddd, *J* = 20.6, 8.3, 1.1 Hz, 2H), 7.44 (dd, *J* = 8.2, 6.4 Hz, 1H), 7.15 (m, 1H), 6.79 (dd, *J* = 7.4, 1.1 Hz, 1H), 4.81(s, br, 2H, Al–H), 2.46(s, br, 6H). ^{13}C NMR (75 MHz, C_6D_6) δ/ppm = 136.8, 133.9, 128.2, 127.7, 127.3, 125.1, 115.5, 49.5. ^{27}Al NMR could not be observed.

14 (8-(dimethylamino)naphthalenyl)-1-di-iso-butylaluminium. Di-iso-butyl-aluminium hydride (8 mL, 25% in hexanes, 11.3 mmol, 1 eq.) was slowly added to a suspension of **4** (2.80 g, 11.1 mmol, 1 eq.) in 30 mL Et_2O at −78 °C. After stirring for 1 h, the reaction mixture was slowly warmed to ambient and stirred overnight, filtered and the filtrate dried in vacuo. The product was obtained after distillation under reduced pressure (145 °C/0.01 mbar) as colourless oil (1.82 g, 5.9 mmol, 53%). ^{1}H NMR (300 MHz, C_6D_6) δ/ppm = 8.11 (dd, *J* = 6.4, 1.2 Hz, 1H), 7.68–7.47 (m, 3H), 7.09–7.17 (m, 1H), 6.71 (dd, *J* = 7.5, 1.0 Hz, 1H), 2.25 (s, 6H), 2.08 (hept, *J* = 6.8 Hz, 2H), 1.20 (d, *J* = 6.5 Hz, 12H), 0.48–0.18 (m, 4H). ^{13}C NMR (75 MHz, C_6D_6) δ/ppm = 151.4, 137.5, 135.9, 133.8, 127.9, 126.0, 124.6, 114.2, 49.0, 28.9, 28.8, 22.8. ^{27}Al NMR (78.21 MHz, C_6D_6) δ/ppm = 175 (FWHM ~5.7 kHz).

16 (2-(2,2,6,6-tetramethyl-piperidine-1-yl)phenyl)-dimethyl aluminium. A solution/slurry of **6** (0.50 g, 2.24 mmol, 1 eq.) in 15 mL toluene was cooled to −78 °C and Me_2AlCl (2.24 mL, 1 M in hexane, 2.24 mmol, 1 eq.) was added slowly. The reaction mixture was stirred cooled for 10 min, then warmed naturally to ambient and stirred for additional 4 h after reaching ambient. The resulting suspension was filtered and the residue washed twice with 5 mL toluene. The filtrate was dried in vacuo to yield the yellowish solid 0.425 g (1.56 mmol, 69%). ^{1}H NMR (300 MHz, C_6D_6) δ/ppm = 7.69 (dt, *J* = 6.9, 1.3 Hz, 1H), 7.23–7.17 (m, 1H), 7.09–7.02 (m, 2H), 1.58 (m, 4H), 1.38 (s, 6H), 1.03–0.94 (m, 2H), 0.90 (s, 6H), 0.03 (s, 6H). Partial ^{13}C NMR (75 MHz, C_6D_6) δ/ppm = 155.8, 135.9, 130.6, 127.3, 127.0, 122.7, 59.6, 35.6, 33.3, 29.6, 16.8. Al–**C**H$_3$ could not be observed due to broadening. ^{27}Al NMR (78 MHz, C_6D_6) δ/ppm = 175.6 (FWHM could not be determined due to overlap with the artificial signal of the probe).

17 (2-(2,2,6,6-tetramethyl-piperidine-1-yl)phenyl)-diethyl aluminium-etherate. A solution/slurry of **6** (0.370 g, 1.66 mmol, 1 eq.) in 15 mL Et_2O was cooled to −78 °C and Et_2AlCl (1.66 mL, 1 M in hexane, 1.66 mmol, 1 eq.) was added slowly. The reaction mixture was stirred cooled for 10 min, then warmed naturally to ambient and stirred overnight. The resulting suspension was filtered, the residue washed twice with 5 mL Et_2O and the filtrate dried in vacuo to yield yellowish oil and crystals. The colourless crystals were harvested as the etherate **17** of the desired product 0.165 g (0.44 mmol, 26%). ^{1}H NMR (300 MHz, C_6D_6) δ/ppm = 7.56 (ddd, *J* = 6.9, 1.9, 0.7 Hz, 1H), 7.40–7.23 (m, 1H), 7.20–7.05 (m, 1H), 7.02–6.84 (m, 1H), 3.28 (q, *J* = 7.0 Hz, 4H, Et_2O), 1.48 (m, 6H), 1.37 (t, *J* = 8.1 Hz, 6H), 1.07 (s, 12H), 0.78 (t, *J* = 7.0 Hz, 6H, Et_2O), 0.47 (q, *J* = 8.1 Hz, 4H). ^{13}C NMR (75 MHz, C_6D_6) δ/ppm = 155.2, 137.4, 130.7, 129.7, 127.1, 125.7, 66.1, 57.0, 39.4, 32.6, 30.0, 29.1, 18.1, 14.2, 10.3, 4.8. ^{27}Al NMR (78 MHz, C_6D_6) δ/ppm = 179.3 (FWHM could not be determined due to overlap with the artificial signal of the probe).

18 (2-(2,2,6,6-tetramethyl-piperidine-1-yl)phenyl)-di-neopentyl aluminium etherate. Np_2AlCl (367 mg, 1.79 mmol, 1 eq.) was added as toluene solution to a slurry of **6** (0.40 g, 1.78 mmol, 1 eq.) in toluene and the reaction mixture stirred for 4 h at ambient temperature. The resulting suspension was filtered and the residue washed twice with toluene and the filtrate was dried in vacuo. The crude product was extracted subsequently with Et_2O and then pentane and the filtrate dried in vacuo to yield a yellowish compound of the Et_2O adduct. Yield 367 mg (0.80 mmol, 45%). ^{1}H NMR (300 MHz, C_6D_6) δ/ppm = 7.76–7.67 (m, 1H), 7.24–7.18 (m, 1H), 7.11–6.98 (m, 2H), 3.28 (q, *J* = 7.0 Hz, 4H, Et_2O), 1.75–1.43 (m, 6H), 1.36 (s, 6H), 1.34 (s, 18H), 1.10 (t, *J* = 7.0 Hz, 6H, Et_2O), 1.00 (s, 6H), 0.91 (s, 4H). Partial ^{13}C NMR (75 MHz, C_6D_6) δ/ppm = 155.9, 136.4, 130.3, 127.4, 127.0, 124.2, 65.8, 58.7, 36.7, 35.6, 33.2, 33.0, 31.2, 17.0, 15.1. Al–**C**H$_2$ could not be observed due to broadening. ^{27}Al NMR could not be observed.

19 (2-(2,2,6,6-tetramethyl-piperidine-1-yl)phenyl)-neopentyl-neopentoxy aluminium. Single crystals of **19** were harvested from a sample of **18** in pentane after leaving it open to air.

Deposition Numbers 2070399 (for **11**), 2070400 (for **4**), 2070401 (for **1b**), 2070402 (for **5**), 2070403 (for **9**), 2070404 (for **10**), 2070405 (for **8**), 2070406 (for **1a**), 2070407 (for **2**), 2070408 (for **19**), 2070409 (for **17**), 2070410 (for **7**), 2070411 (for **6**), and 2070412 (for **3**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

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