



Re-investigation of *ortho*-metalated *N,N*-dialkylbenzylamine complexes of rare-earth metals. First structurally characterized arylates of neodymium and gadolinium $\text{Li}[\text{LnAr}_4]$

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ABSTRACT

The influence of the ether ligand in $[\text{LnCl}_3(\text{sol})_n]$, $\text{sol} = \text{THF}, \text{DME}$; $n = 1-3$ in reactions with *ortho*-lithiated dimethyl-benzylamine $\text{Li}(\text{dmba})$ has been studied. An improved protocol towards homoleptic *tris*-aryl complexes of the type $[\text{Ln}(\text{dmba})_3]$, $\text{Ln} = \text{Y}, \text{Er}$ and Yb has been developed and molecular structures of these complexes have been established by X-ray crystallography. For the first time stable homoleptic lithium ate-complexes of the type $\text{Li}[\text{Ln}(\text{dmba})_4]$ ($\text{Ln} = \text{Gd}, \text{Nd}$) have been isolated and structurally characterized. The success in their synthesis strongly depends on the choice of the appropriate $[\text{LnCl}_3(\text{sol})_n]$ precursor, such as $[\text{GdCl}_3(\text{dme})_2]$, $[\text{NdCl}_3(\text{dme})]$, and THF-free reaction conditions. Factors influencing on possible degradation pathways of lanthanide *tris*-aryl complexes with *dmba*-type ligands are discussed.

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1. Introduction

Due to the lanthanide contraction the atomic radii in the row of the lanthanides gradually decrease from 1.07 Å for Ce to 0.86 Å for Lu (Scheme 1) [1]. Due to their different ion potential the chemistry of the larger and the smaller cations Ln^{3+} shows differences and for a systematic discussion the group of 4f elements is subdivided into three sub-groups – early (Ce–Sm), middle (Eu–Ho) and late (Er–Lu) lanthanides. This subdivision not only takes the structural and reactivity differences of the organolanthanide compounds into account but also has consequences for the synthetic accessibility of the starting materials.

1.1. Aryl complexes with *ortho*-metallated benzylamine ligand

The bidentate monoanionic *ortho*-metallated *N,N*-dimethylbenzylamine ligand (*dmba*) found broad application in the organometallic chemistry. Complexes with this ligand motif are known for almost every transition metal. The ligand may be introduced using

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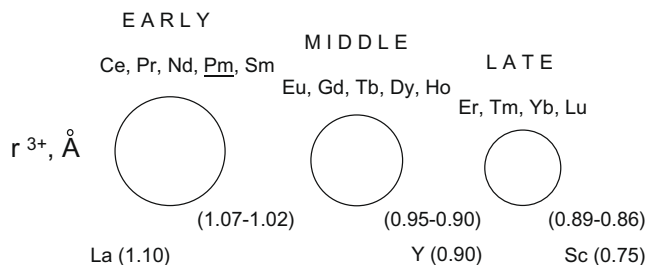
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the aryllithium reagent 2-lithio-*N,N*-dimethylbenzylamine $\text{Li}(\text{dmba})$ which itself is conveniently prepared by lithiation of *N,N*-dimethylbenzylamine. This bidentate ligand can perfectly provide kinetic stabilization of its metal complexes by strongly σ -donating dimethylamino-group (Scheme 2) [2].

1.2. *Tris*-aryl complexes of late lanthanides as well as Sc and Y

First attempts on the isolation of *tetrakis*-phenyl-ate-complexes $\text{Li}[\text{LaPh}_4]$ and $\text{Li}[\text{PrPh}_4]$ were reported in 1970 [3], however, no complete analysis or structural confirmation by physical methods was given. Homoleptic *tris*-aryl complex of group 3 elements – $[\text{Sc}(\text{dmba})_3]$ and $[\text{Y}(\text{dmba})_3]$ – have been reported early [4,5]. Unfortunately, both complexes were not crystallographically characterized. The scandium complex is not commonly used as precursor since it shows very low solubility in common organic solvents and no crystalline product suitable for crystallographic characterization could be obtained.

In 1984 Wayda et al. [6] have reported that molecular complexes of lanthanides stabilized by *dmba* as ligand can only be obtained for the lanthanides with smaller ionic radii, e.g. Er (1), Yb (2) and Lu (3). Only one of them, namely $[\text{Lu}(\text{dmba})_3]$ (3), was crystallographically characterized. The erbium and ytterbium complexes



Scheme 1. Sub-groups of rare earth metals discussed in this contribution.

were characterized solely by elemental analysis and IR spectroscopy. Up to date all attempts to isolate *tris*-dmba derivatives of early (Pr, Nd, Sm) and middle (Tb) lanthanide metals failed and resulted only in uncharacterizable mixtures of products.

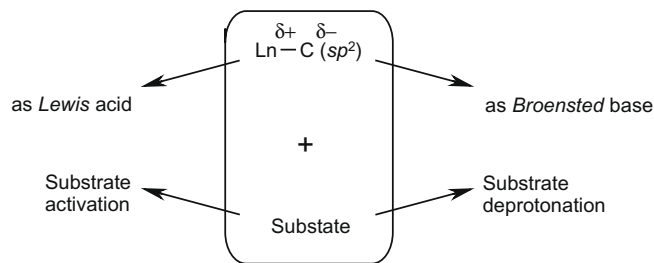
Both diamagnetic *tris*-aryl complexes of yttrium [Y(dm_{ba})₃] (**4**) and lutetium [Lu(dm_{ba})₃] (**3**) are broadly applied as pre-catalysts for intra-molecular hydroamination/cyclization reactions and as precursors for the synthesis of other organolanthanide complexes [7]. This supported our growing interest towards rare-earth *tris*-aryl and *tetrakis*-arylate complexes with dm_{ba}-type ligands.

1.3. Considerations of possible degradation pathways of dm_{ba}-ligand

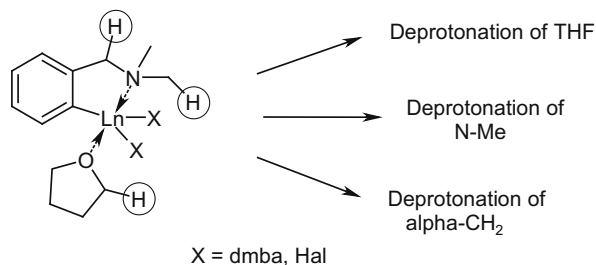
The pronounced *Lewis* acidity of a Ln-metal center combined with the high *Bronsted* basicity of the aryl ligands cause the high reactivity of lanthanide complexes (Scheme 3). Compared to the late lanthanides that have sterically unsaturated ligands, the early and middle lanthanides reveal higher coordination numbers which provides an enhanced tendency to coordinate molecules with donor functionalities (ether solvents, amines). The following ligand activation can cause rapid degradation reactions.

The common decomposition pathways of the sterically unsaturated lanthanide complexes are often indicated by solvent- [8], ligand-degradation [9], and/or occurrence of secondary agostic interactions [10]. In the case of the dm_{ba} ligand there are three possible pathways of degradation of the formed aryl complexes (Scheme 4): (1) decomposition of coordinated solvent molecules (e.g. ether cleavage) or dm_{ba} ligand deprotonation on (2) benzylic- or (3) dimethylamino-positions. Deprotonation pathways can proceed via an *inter*- or *intra*-molecular mechanism Scheme 4.

Decomposition of coordinated solvent molecules, especially of those of THF, is not unusual in lanthanide and early transition metal chemistry [11]. The possibility of working under THF-free con-



Scheme 3. Side reactions of highly polar Ln-C(sp^2) bond containing species.

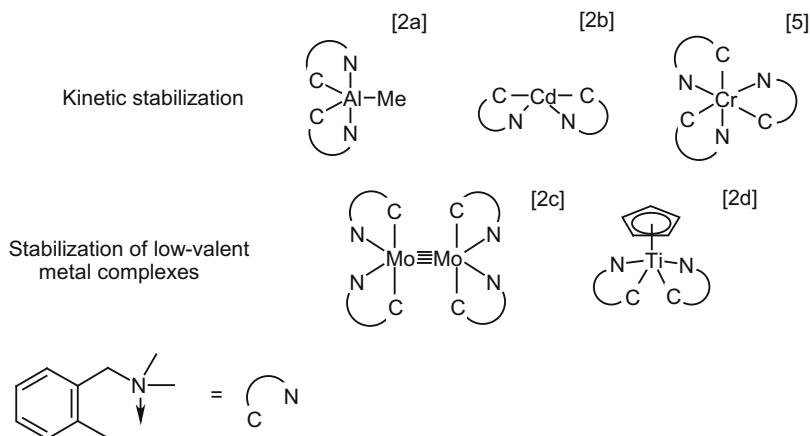


Scheme 4. Possible degradation pathways of complexes with dm_{ba} as ligand.

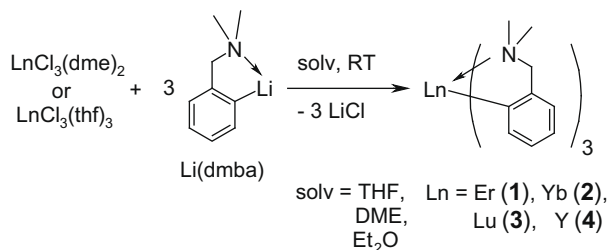
ditions put hard limitations on the choice of appropriate starting materials and acceptable solvents for reactions and purifications. Application of alternative high polarity solvents instead of THF, like 1,2-dimethoxyethane (DME) is promising, but up to now there are no reports on the application of anhydrous DME-solvated lanthanide trihalides in organometallic synthesis. Mostly all dme-solvated lanthanide trihalides were characterized by X-ray diffraction in 2004 with the aim to understand structural aspects [12]. Here we describe our results on a re-investigation of the syntheses of lanthanide aryl complexes under THF-free conditions.

1.4. Lanthanide *tris*-aryl-complexes with dm_{ba} and pyba ligands

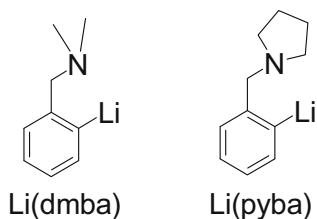
Searching for novel and versatile precursors for the lanthanide metallations we have investigated the reactions of *ortho*-lithiated *N,N*-dimethylbenzylamine Li(dm_{ba}) with different lanthanide and group 3 element trihalides. Additionally, the structurally similar new *ortho*-lithiated amine *N*-benzylpyrrolidine Li(pyba) [13] with stronger σ -donating and less CH-acidic *N*-alkyl group was investigated.



Scheme 2. Typical examples of dm_{ba} complexes.



Scheme 5. Synthesis of the homoleptic complexes $[\text{M}(\text{dmmba})_3]$, $\text{M} = \text{Er}$ (1), Yb (2), Lu (3) and Y (4).



The *salt-metathesis* reactions of $\text{Li}(\text{dmmba})$ with the late lanthanide (Er , Yb , Lu) and yttrium trichlorides as both thf [$\text{LnCl}_3(\text{thf})_3$] and dme [$\text{LnCl}_3(\text{dme})_2$] solvates are straightforward and furnish the corresponding *tris*-aryl-complexes in high analytical purity after crystallization (Scheme 5). For these late lanthanides the yields were found to be invariant to the type of solvated precursor applied. Only for **4** better yield was achieved when $[\text{YCl}_3(\text{dme})_2]$, rather $[\text{YCl}_3(\text{thf})_3]$ was used.

According to Wayda both early (Pr , Nd , Sm) and middle (Tb) lanthanides give no stable *tris*-aryl complexes in reactions of their thf -solvated adducts with $\text{Li}(\text{dmmba})$. Our re-investigation has confirmed these results even at THF -free conditions. However, the Y^{3+} ion by its size (0.90 \AA) is associated with the middle lanthanides' sub-group and this is the largest ion in the whole series that forms stable $[\text{Y}(\text{dmmba})_3]$ (**4**) complex.

Due to efficient paramagnetic relaxation, caused by the Er^{3+} metal center, NMR spectroscopy was not informative for complex **1**. However for its neighbour, the paramagnetic ytterbium complex **2** ^1H NMR spectroscopy in C_6D_6 at 23°C reveals three moderately up-field shifted, relatively "sharp" resonances at -8.7 ($\nu_{1/2} = 100 \text{ Hz}$), -17.0 ($\nu_{1/2} = 23 \text{ Hz}$) and -30.9 ($\nu_{1/2} = 45 \text{ Hz}$) ppm as well as a highly up-field shifted broad resonance at -99.1 ($\nu_{1/2} = 360 \text{ Hz}$) ppm (Fig. 1). The latter resonance should be assigned to the *ortho*-Ar proton, since it is the closest to the paramagnetic center. The assignment of other aromatic resonances is not trivial. Furthermore, two very broad resonances downfield shifted to 28.7 and 97.2 ppm ($\nu_{1/2} = \text{ca. } 1900 \text{ Hz}$ and $\text{ca. } 1200 \text{ Hz}$, respectively) at an integral ratio of 2:6 were observed, which can be assigned to the protons of the side-arm CH_2NMe_2 -group.

Despite the fact that **4** is known for almost 20 years [5] and used as a precursor in the synthesis of catalysts [7], there neither complete spectroscopic nor crystallographic data are reported to date. The room temperature ^1H NMR (toluene- d_8) spectrum of **4** is analogous to that one of **3** and reveals two sharp resonances in the aliphatic region at 3.37 and 2.12 ppm at an integral ratio of 2:6 assigned to benzylic methylene and Me_2N -groups. A low temperature NMR investigation reveals very weak temperature dependence and shows no resonance broadening down to 230 K . The slow broadening of resonances occurs beneath that temperature, but no complete splitting of resonances is observed down to 200 K . Such behaviour in solution is due to high conformational flexibility of dmmba ligands in **4**.

Among the whole series of homoleptic dmmba lanthanide complexes a molecular structure analysis has only been reported for the $[\text{Lu}(\text{dmmba})_3]$ (**3**) so far. We report here the X-ray single crystal structure determinations of **1**, **2** and **4** complexes. All these complexes crystallize in the monoclinic space group $\text{C}2/c$ with eight molecules in the unit cell – similar to the known parent Lu -complex **3**. The rare-earth metal atoms display coordination number six: three carbon atoms of the pendant amine arms form a distorted octahedron (Fig. 2). Interestingly, *ipso*-carbon atoms as well as the nitrogen atoms give a *pseudo*-meridional arrangement. The selected bond lengths and angles, compared with those of

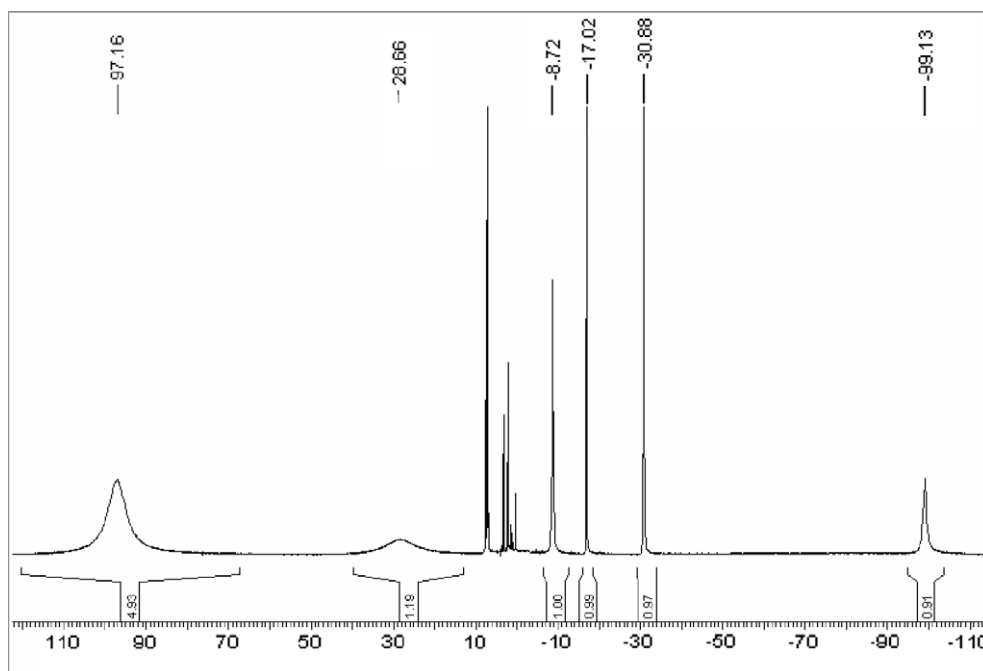


Fig. 1. The ^1H NMR spectrum (300.1 MHz) of ytterbium complex $[\text{Yb}(\text{dmmba})_3]$ (**2**) dissolved in C_6D_6 at $+25^\circ\text{C}$.

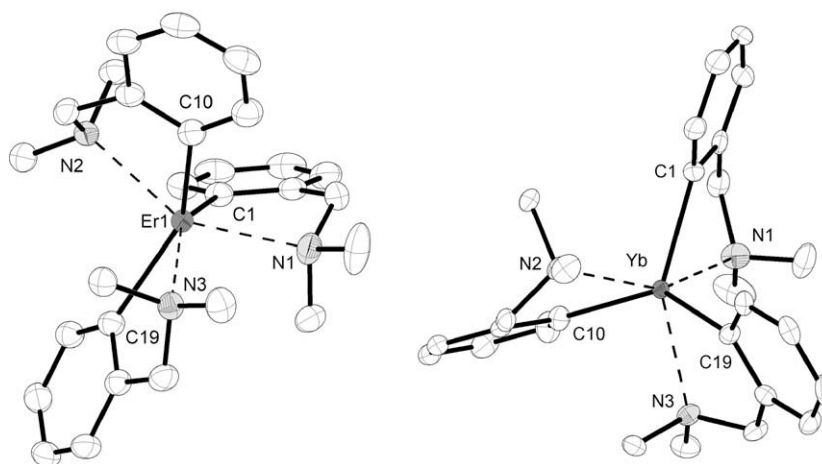


Fig. 2. The molecular structures of $[\text{Ln}(\text{dmmba})_3]$, $\text{Ln} = \text{Er}$ (1) and Yb (2). Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles ($^\circ$) in the homoleptic complexes $[\text{M}(\text{dmmba})_3]$ of Y (4), Er (1) and Yb (2), compared with those, found in $[\text{Lu}(\text{dmmba})_3]$ (3).

	4 (M = Y) [15]	1 (M = Er)	2 (M = Yb)	3 (M = Lu) [6]
M–N1	2.514(3)	2.505(2)	2.488(5)	2.588
M–N2	2.524(3)	2.496(2)	2.481(5)	2.478
M–N3	2.601(4)	2.594(2)	2.564(5)	2.468
M–C1	2.475(2)	2.457(2)	2.433(6)	2.427
M–C10	2.479(4)	2.483(2)	2.454(6)	2.425
M–C19	2.504(3)	2.456(3)	2.434(6)	2.456
C1–M–C10	96.4(1)	96.7(1)	120.4(2)	140.2(3)
C10–M–C19	121.4(2)	138.8(1)	140.03(19)	119.9(3)
C1–M–C19	138.7(1)	121.0(1)	96.1(2)	96.6(2)
$\Sigma(\text{C}_A\text{–M–C}_B)$	356.5(4)	356.5(3)	356.5(5)	356.6(7)
N1–M–N2	91.8(1)	148.2(1)	148.82(16)	114.0(2)
N2–M–N3	147.9(1)	115.0(1)	114.58(16)	149.8(3)
N1–M–N3	115.0(1)	91.4(1)	91.40(17)	91.2(2)
$\Sigma(\text{N}_A\text{–M–N}_B)$	354.8(3)	354.6(2)	354.8(5)	355.0(7)
M...CCC	0.259(1)	0.256(1)	0.252(1)	0.247(1)
M...NNN	0.304(1)	0.305(1)	0.297(1)	0.289(1)

$[\text{Lu}(\text{dmmba})_3]$ (3), are presented in Table 1. The lanthanide atoms are very close to the planes formed by three *ipso*-carbon atoms (CCC-plane) and planes formed by three nitrogen atoms (NNN-plane). Their distances vary in the range from 0.252(1) to 0.259(1) Å in case of the CCC-plane and from 0.297(1) to 0.305(1) Å in case of the NNN-plane. Deviation from ideal arrangement is also supported by the values of C–M–C and N–M–N angular sums which are not 360° but $355\text{--}356^\circ$ for all investigated compounds.

The Er–C bond lengths in the erbium complex $[\text{Er}(\text{dmmba})_3]$ (1) are in the range of 2.456(3)–2.483(2) Å and only for ca. 0.04 Å longer than in earlier reported $[\text{Ph}_3\text{Er}(\text{thf})_3]$ [14]. The Er–N bond lengths fit to the “two-short, one-long” bond pattern reported for 3 [6]: 2.496(2), 2.505(2), 2.592(2) Å. Essentially the same pattern was found for the ytterbium complex 2: 2.433(5)–2.454(6) Å for the Yb–C bond lengths and 2.481(5), 2.488(5), 2.564(5) Å for the Yb–N bond lengths and for the yttrium complex 4 [15]: 2.475(2)–2.504(3) Å for the Y–C bond lengths and 2.514(3), 2.524(3) Å and 2.601(4) Å for the Y–N bond lengths. Interestingly, the long M–C19 and M–N3 bonds in the structure of 4 belong to the one and the same dmmba ligand.

The origin of the “two-short, one-long” Ln–N bond length pattern can be explained by packing effects in the solid state. Analysis of the packing in the unit cell reveals that molecules are arranged with respect to a center of inversion, as shown below on example of 4 (Fig. 3).

Consequently, one among three M–C σ -bonds and one among three M–N bonds in these dmmba ligands has been found to be ca. 0.2 Å and 0.8 Å longer than two other corresponding M–C and M–N bonds.

1.5. Lanthanide tetrakis-aryl-ate-complexes with dmmba and pyba ligands

Our observations denote the crucial role of coordinated solvent in $[\text{LnCl}_3(\text{sol})_n]$ on the nature of the transmetalated products. Thus we found that the use of $[\text{GdCl}_3(\text{dme})_2]$ instead of its THF-sol-

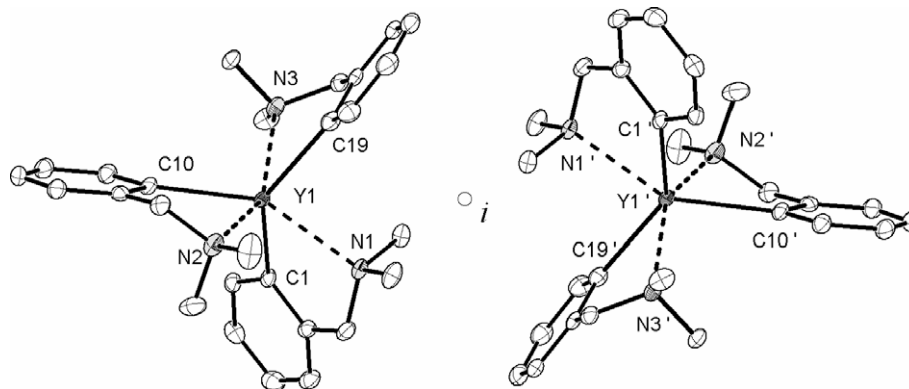
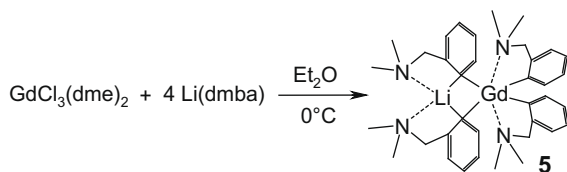
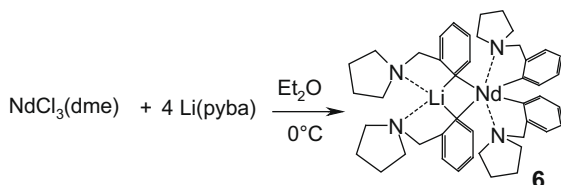


Fig. 3. The molecular structure of $[\text{Y}(\text{dmmba})_3]$ (4) [15]. Hydrogen atoms have been omitted for clarity.



Scheme 6. Synthesis of the $\text{Li}[\text{Gd}(\text{dmmba})_4]$ (**5**).



Scheme 7. Synthesis of the $\text{Li}[\text{Nd}(\text{pyba})_4]$ (**6**).

ated analogue in the reaction with 4 equivalents of $\text{Li}(\text{dmmba})$ allows the isolation of colourless crystalline product of the ate complex $\text{Li}[\text{Gd}(\text{dmmba})_4]$ (**5**) in 56% yield (Scheme 6).

Earlier, Wayda et al. reported that they failed to achieve a characterizable Nd ate-complex by reaction with four equivalents of $\text{Li}(\text{dmmba})$. Based on this experience and in order to minimize chances for ether cleavage or ligand deprotonation as the degradation pathways we have used $[\text{NdCl}_3(\text{dme})]$ under THF-free conditions in the reaction with $\text{Li}(\text{pyba})$ [13] in Et_2O and were able to isolate highly air- and moisture sensitive pale green ate-complex $\text{Li}[\text{Nd}(\text{pyba})_4]$ (**6**) in 13% yield which as solid is stable at room temperature (Scheme 7).

The composition of **5** and **6** as molecular binuclear lithium ate complexes of gadolinium and neodymium was confirmed by elemental analysis and their molecular structures were determined by X-ray diffraction analysis.

It is worth to mention, that although in the solid state the substances are stable even at room temperature their solutions should be worked-up at low temperatures ($<0^\circ\text{C}$) and can be stored at -30°C without decomposition for months.

Crystals of **5** and **6** suitable for X-ray diffraction analysis were obtained by cooling of their saturated solutions in ether and toluene, respectively. The crystal structures are depicted in Fig. 4.

The compound **6** crystallizes with additional two toluene molecules per unit cell. Both **5** and **6** are heterobinuclear and crystallize in the monoclinic ($P2_1/n$) and triclinic $P\bar{1}$ space groups, respectively.

In their structures a slightly distorted propeller-like arrangement of ligands around each metal with a non-crystallographic *pseudo*- C_2 axis through lithium and the lanthanide atoms is observed. In both structures terminal and bridging aryl-groups are present. The sixfold coordinated lanthanide atom is best described as distorted octahedron. Both terminal aryl groups and corresponding dialkylamino groups coordinate in κ^2 -fashion. The bridging aryl groups coordinate to lithium and lanthanide atoms to form an almost planar heterobimetallic core with $\text{Li}-\mu\text{-C}_{\text{Ar}}-\text{Ln}-\mu\text{-C}_{\text{Ar}}$ torsion angles of $4.2(5)^\circ$ and $6.5(2)^\circ$. The lithium atom is tetra-coordinated by the two bridging aryl groups and their dialkylamino groups. Due to the steric bulk of the aryl groups, the terminal aryl substituents occupy antiperiplanar positions relative to dialkylamino groups coordinated to the lithium atom. The $\text{C}-\text{Ln}-\text{Li}-\text{N}$ torsion angles are close to 180° (Nd: $167.2(5)^\circ$, $160.9(5)^\circ$; Gd: $162.7(2)^\circ$, $169.9(2)^\circ$). The selected bond lengths and angles are given in Table 2.

This slight modification of the ligand framework ($\text{dmmba} \rightarrow \text{pyba}$) has allowed us for the first time to stabilize one of the large early lanthanide metals (Nd) in the form of its homoleptic *tetrakis*-aryl-ate complex and to establish its molecular structure.

For the attempted reactions of both, $\text{Li}(\text{dmmba})$ and $\text{Li}(\text{pyba})$, with $[\text{PrCl}_3(\text{dme})]$ the usage of the same protocol was not success-

Table 2
Selected bond lengths (Å) and angles ($^\circ$) for the lithium ate complexes **5** and **6** $\times \frac{1}{2}\text{PhMe}$.

	5 (Ln = Gd)	6 $\times \frac{1}{2}\text{PhMe}$ (Ln = Nd)
$\text{Ln}-\text{C}_{\text{Ar}}$	2.521(3), 2.517(3)	2.567(9), 2.578(7)
$\text{Ln}-\mu\text{-C}_{\text{Ar}}$	2.597(3), 2.594(3)	2.626(9), 2.634(10)
$\text{Li}-\mu\text{-C}_{\text{Ar}}$	2.180(5), 2.185(6)	2.250(18), 2.144(16)
$\text{Ln}-\text{NR}_2$	2.694(2), 2.629(2)	2.739(9), 2.734(13)
$\text{Li}-\text{NR}_2$	2.063(6), 2.068(5)	2.124(15), 2.091(15)
$\mu\text{-C}_{\text{Ar}}-\text{Ln}-\mu\text{-C}'_{\text{Ar}}$	87.3(1)	87.2(3)
$\mu\text{-C}_{\text{Ar}}-\text{Li}-\mu\text{-C}'_{\text{Ar}}$	110.3(3)	111.3(6)
$(\text{N}-\text{CH}_2-\text{C}_{\text{Ar}})_{\text{Ln}}$	112.9(3), 112.4(3)	112.8(8), 111.4(11)
$(\text{N}-\text{CH}_2-\text{C}_{\text{Ar}})_{\text{Li}}$	109.7(3), 109.9(3)	112.5(8), 111.6(8)
$\text{C}_{\text{Ar}}-\text{Ln}-\text{Li}-\text{N}'_{\text{Ar}}$	162.7(2), 169.9(2)	167.2(5), 160.9(5)
$\text{Li}-\text{C}_{\text{Ar}}-\text{Ln}-\text{C}_{\text{Ar}}$	6.5(2)	4.2(5)

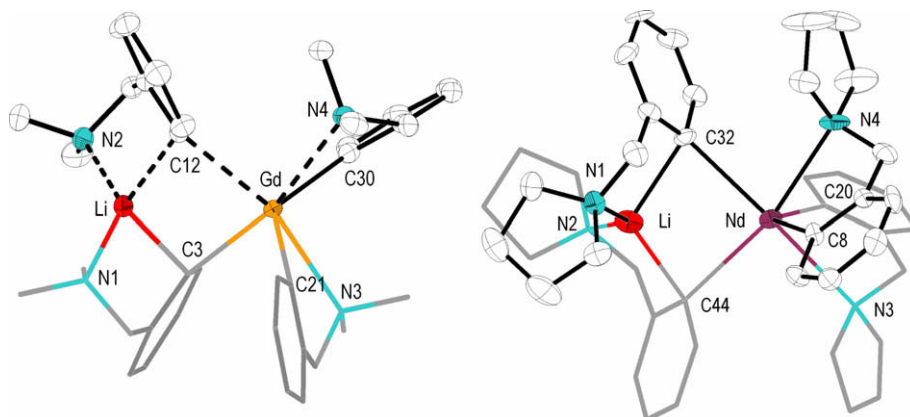


Fig. 4. The molecular structures of $\text{Li}[\text{Gd}(\text{dmmba})_4]$ (**5**, left) and $\text{Li}[\text{Nd}(\text{pyba})_4]$ (**6** $\times \frac{1}{2}\text{PhMe}$, right) drawn with 50% probability ellipsoids. Toluene molecules in compound **6** $\times \frac{1}{2}\text{PhMe}$, as well as all hydrogen atoms, have been omitted for clarity and some ligand molecules are presented as sticks model.

ful any more – a progressive darkening of the reaction mixture was observed immediately after the beginning of the reaction, even at low temperatures. This indicates that for stabilization of dmbs-like complexes of early lanthanides further modification of the dmbs ligand is required. The effects of α methylation of the dmbs ligands on stability of lanthanide complexes will be the subject of the forthcoming account [16].

2. Experimental

2.1. General considerations

Starting lanthanide chlorides [$\text{LnCl}_3 \times 6\text{H}_2\text{O}$] were prepared by dissolving their oxides in conc. hydrochloric acid (p.a.) followed by continuous evaporation in an evaporating dish at 90 °C. 1,2-Dimethoxyethane (DME), ether, hexane and toluene were purified by conventional methods.

Lanthanide content in solvated lanthanide trichlorides was determined by complexometric titration with EDTA in the presence of xylenol orange as indicator [17], Chloride content by precipitation with aqueous AgNO_3 . Elemental analyses (CHN) were performed in microanalytical laboratory at chemistry department of Philipps-Universität Marburg. IR spectra of $\text{Ln}(\text{dmbs})_3$ (Ln = Lu, Er, Yb) were measured in analytical laboratory of the Institute of Chemistry of the Humboldt-University of Berlin and were found to be identical with the earlier reported [6]. Measurement of IR spectra of the ate-complexes **5** and **6** because of their instability against nujol was failed.

Following compounds were synthesized as reported in the literature: $\text{Li}(\text{dmbs})$ [18], $[\text{Er}(\text{dmbs})_3]$ [6] (**1**), $[\text{Yb}(\text{dmbs})_3]$ (**2**) [6], $[\text{LnCl}_3(\text{dme})_2]$ (Ln = Nd, Sm, Gd) [12]. *N,N*-Dimethylbenzylamine, *N*-benzylpyrrolidine and *tert*-BuLi (15% solution in pentane) – were used as supplied (Acros, Aldrich).

2.1.1. Synthesis of starting materials

N-Synthesis of *o*-(pyrrolidylmethyl)-phenyllithium ($\text{Li}(\text{pyba})$): To *N*-benzylpyrrolidine (10.0 g, 62.1 mmol) in ca. 120 mL ether, solution of *tert*-BuLi (50 mL, 1.5 M in hexane, 75 mmol, 1.2 equiv.) was added at ambient temperature and stirred for 48 h. The precipitated solid was filtered off from deep yellow mother liquor and thoroughly washed with hexane (3 \times 50 mL). The product was obtained as colorless, crystalline solid in 94% yield (9.8 g).

$^1\text{H NMR}$ (C_6D_6 , 300.1 MHz): δ = ppm. 0.70 (s br, 1H), 1.09 (s br, 1H), 1.24 (s br, 2H), 1.57 (dd, 1H, $J = 8.4$ Hz, $J = 17.2$ Hz), 1.81 (dd, 1H, $J = 8.5$ Hz, $J = 17.4$ Hz), 2.27 (m br, 1H), 2.71 (m br, 1H), 3.19 (d, $J = 13.1$ Hz, 1H), 4.48 (d, $J = 13.0$ Hz, 1H), 7.20 (m, Ar, 4H), 8.38 (d, $J = 5.3$ Hz, 1H, *o*-Ar) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 75.5 MHz): δ = 22.6, 23.5 (NCH_2CH_2), 54.1, 55.1 (NCH_2CH_2), 67.7 (ArCH₂N), 125.3 (Ar), 126.1 (Ar), 126.7 (Ar), 139.3 ($\text{C}_{2\text{Ar}}$), 152.8 ($\text{C}_{6\text{Ar}}\text{CH}_2$), 174.7 (br s, $\text{C}_{1\text{Ar}}$) ppm. Anal. Calc. for $\text{C}_{11}\text{H}_{14}\text{LiN}$ (167.18): C, 79.03; H, 8.44; N, 8.38. Found: C, 77.94; H, 8.92; N, 8.24%.

Synthesis of $[\text{YCl}_3(\text{dme})_2]$: To a suspension of $[\text{YCl}_3 \times 6\text{H}_2\text{O}]$ (12.0 g, 40 mmol) in ca. 120 mL DME thionyl chloride (25 mL, 360 mmol, 9.0 equiv.) was added during 0.5 h. The reaction mixture was heated 2 h at 70 °C till no gas evolution observed. The solid formed was filtered off, washed thoroughly with ether (5 \times 20 mL) and dried in vacuum. A colorless, compact microcrystalline solid was obtained in 97% yield (14.5 g). Anal. Calc. for $\text{C}_8\text{H}_{20}\text{Cl}_3\text{O}_4\text{Y}$ (375.50): Cl, 28.32; Y, 23.68. Found: Cl, 28.38; Y, 23.52%.

2.1.2. Synthesis of aryl-complexes

Synthesis of $[\text{Er}(\text{dmbs})_3]$ [6] (**1**): The erbium complex **1** was synthesized analogous to the method reported in the literature using

DME as solvent. Crystallization from ether yields a pink, microcrystalline solid in yield of 69%. Anal. Calc. for $\text{C}_{27}\text{H}_{36}\text{ErN}_3$ (569.87): C, 56.91; H, 6.37; N, 7.37. Found: C, 56.80; H, 6.51; N, 7.24%.

Synthesis of $[\text{Yb}(\text{dmbs})_3]$ [6] (**2**): The ytterbium complex **2** was synthesized analogous to the method reported in the literature using DME as solvent. Crystallization from ether yields a bright yellow, microcrystalline solid in yield of 87%. $^1\text{H NMR}$ (C_6D_6 , 400.1 MHz): δ = 97.2 (br s, $\nu_{1/2} = \text{ca. } 1200$ Hz, 6H, NMe_2), 28.7 (br s, $\nu_{1/2} = \text{ca. } 1900$ Hz, 2H, CH_2NMe_2), -8.7 (br s, $\nu_{1/2} = 50$ Hz, 1H, $\text{HC}_{3\text{Ar}}$), -17.0 (s, 1H, $\text{HC}_{4\text{Ar}}$), -30.9 (s, 1H, $\text{HC}_{5\text{Ar}}$), -99.1 (br s, $\nu_{1/2} = 170$ Hz, 1H, $\text{HC}_{6\text{Ar}}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.1 MHz): δ = -7.6 (br s, CH_2NMe_2), 54.1 (s, $\text{C}_{5\text{Ar}}$), 76.6 (CH_2NMe_2), 82.1 (s, $\text{C}_{4\text{Ar}}$), 143 (br s, $\text{C}_{3\text{Ar}}$), 210 (br s, $\text{C}_{5\text{Ar}}$), 372 (br s, $\text{C}_{2\text{Ar}}$) ppm. Anal. Calc. for $\text{C}_{27}\text{H}_{36}\text{N}_3\text{Yb}$ (575.65): C, 56.34; H, 6.30; N, 7.30. Found: C, 56.21; H, 6.61; N, 7.35%.

Synthesis of $[\text{Y}(\text{dmbs})_3]$ [5] (**4**): The yttrium complex **4** was synthesized analogous to the method reported in the literature using THF or DME as solvent. Crystallization from hot hexane yields a colorless, crystalline solid in yield of 91%. $^1\text{H NMR}$ (C_7D_8 , 400.1 MHz): δ = 2.12 (s, 6 H, Me_2N), 3.37 (s, 2 H, $\text{C}_{\text{Ar}}\text{CH}_2$), 6.83 (d, $^2J_{\text{HH}} = 7.3$ Hz, $\text{HC}_{5\text{Ar}}$), 7.10 (t, $^3J_{\text{HH}} = 7.0$ Hz, $\text{HC}_{4\text{Ar}}$), 7.20 (t, $^3J_{\text{HH}} = 7.0$ Hz, $\text{HC}_{3\text{Ar}}$), 8.06 (d, $^3J_{\text{HH}} = 6.6$ Hz, $\text{HC}_{2\text{Ar}}$) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 100.1 MHz): δ = 45.9 (Me_2N), 69.7 ($\text{C}_{\text{Ar}}\text{CH}_2$), 124.8 (Ar), 125.2 (Ar), 125.7 (Ar), 138.7 ($\text{C}_{2\text{Ar}}$), 146.8 ($\text{C}_{6\text{Ar}}\text{CHMe}$), 186.9 (d, $^1J_{\text{CY}} = 44$ Hz, $\text{C}_{1\text{Ar}}\text{Y}$) ppm. Crystallographic data for yttrium complex **4**: monoclinic, space group $\text{C}2/c$, $a = 24.170(3)$ Å, $b = 9.362(1)$ Å, $c = 23.880(2)$ Å, $\beta = 113.47(1)^\circ$, $V = 4955.9(8)$ Å³, $Z = 4$, $D_c = 1.317$ g/cm³, $\mu = 2.372$ mm⁻¹, $F(000) = 2064$. Anal. Calc. for $\text{C}_{27}\text{H}_{36}\text{N}_3\text{Y}$ (491.52): C, 65.98; H, 7.38; N, 8.55%. Found: C, 64.48; H, 7.55; N, 8.34%.

Synthesis of $[\text{Li}(\text{dmbs})_4]$ (**5**): To a stirred suspension of $\text{Li}(\text{dmbs})$ (568 mg, 4.0 mmol) in 40 mL ether, solid $[\text{GdCl}_3(\text{dme})_2]$ (442 mg, 1.0 mmol) was added at ambient temperature. The color of the reaction mixture turned slowly yellowish depositing a colorless heavy microcrystalline solid. It was filtered off and dried in vacuum. This solid was triturated with toluene (20 mL) whereupon LiCl precipitates. The solution was filtered through a Celite[®]-pad and the filtrate was concentrated to 20% of the original volume. Addition of ether (20 mL) at 0 °C causes formation of colorless crystalline solid. It was filtered off and dried in vacuum. Yield: 56% (450 mg, 0.56 mmol). Anal. Calc. for $\text{C}_{36}\text{H}_{48}\text{GdLiN}_4$ (701.00): C, 61.68; H, 6.90; N, 7.99. Found: C, 63.89; H, 6.83; N, 7.02%.

Synthesis of $[\text{LiNd}(\text{pyba})_4]$ (**6**): To a suspension of $\text{Li}(\text{pyba})$ (668 mg, 4.00 mmol) in 20 mL of ether $[\text{NdCl}_3(\text{dme})]$ (340 mg, 1.00 mmol) was added. The obtained green suspension was stirred for 10 min at ambient temperature and the solution over precipitate of LiCl was decanted into a flask pre-cooled to 0 °C. Stirring for 1/2 h resulted in formation of blue green crystalline precipitate that was filtered off and dried in vacuum. A sky blue, microcrystalline solid was obtained in 13% yield (96 mg). The complex is stable at ambient temperature for couple of days and therefore was stored at -30 °C. $^1\text{H NMR}$ (C_6D_6 , 300.1 MHz): δ = -0.4 (br s, $\nu_{1/2} = 780$ Hz), 11.4 (br s, $\nu_{1/2} = 1000$ Hz), 29.5 (br s, $\nu_{1/2} = 1300$ Hz) ppm. Anal. Calc. for $\text{C}_{44}\text{H}_{56}\text{LiNd}_4$ (792.14): C, 66.72; H, 7.13; N, 7.07. Found: C, 64.32; H, 6.81; N, 6.82%.

2.1.3. X-ray crystallographic studies

The structures of **1**, **2**, **4**–**6**, were solved by direct methods and expanded by difference-Fourier syntheses using SHELX-97 software package. G.M. Sheldrick, Program for solution of crystal structures, SHELXS-97, Universität Göttingen, 1997; G.M. Sheldrick, Program for the refinement of crystal structures, SHELXL-97, Universität Göttingen, 1997. Crystallographic data for all compounds are summarized in Table 3.

Table 3
Crystallographic data for **1**, **2**, **4**, **5** and **6**.

	[Er(dmba) ₃] (1)	[Yb(dmba) ₃] (2)	[Y(dmba) ₃] (4)	Li[Gd(dmba) ₃] (5)	Li[Nd(pyba) ₃] × 0.5 C ₇ H ₈ (6)
Empirical formula	C ₂₇ H ₃₆ ErN ₃	C ₂₇ H ₃₆ N ₃ Yb	C ₂₇ H ₃₆ N ₃ Y	C ₃₆ H ₄₈ GdLiN ₄	C _{47.50} H ₆₀ LiN ₄ Nd
Crystal habit	Irregular plate	Prism	Prism	Prism	Prism
Crystal colour	Gray brown	Yellow	Colourless	Colourless	Pale blue
Crystal size (mm)	0.3 × 0.23 × 0.15	0.09 × 0.08 × 0.04	0.3 × 0.12 × 0.09	0.18 × 0.12 × 0.03	0.24 × 0.09 × 0.06
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	C 2/c	C 2/c	C 2/c	P $\bar{1}$	P 2 ₁ /n
Z	8	8	8	2	4
a (Å)	24.1766(16)	24.098(11)	24.170(3)	9.7595(12)	12.5989(11)
b (Å)	9.3438(5)	9.312(4)	9.3613(7)	12.0826(16)	24.3261(19)
c (Å)	23.8596(15)	23.758(7)	23.880(2)	15.8362(19)	13.6311(13)
α (°)	90	90	90	82535(10)	90
β (°)	113.567(5)	113.48(3)	113.474(11)	75095(9)	95.336(11)
γ (°)	90	90	90	70257(10)	90
Volume (Å ³)	4940.4(5)	4890(3)	4955.9(8)	1696.6(4)	4159.6(6)
θ range (°)	1.8–27.1	2.0–26.0	1.9–26.0	1.3–25	2.0–25
hkl ranges	–30 28, –11 11, –29 30	–29 29, 0 11, –29 29	–29 29, –11 11, –27 28	–11 11, –14 14, –19 19	–14 14, –28 28, –16 16
Formula weight	569.85	575.63	491.50	700.97	838.17
λ (Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
μ (Mo Kα) (mm ^{–1})	3.415	3.843	2.372	1.983	1.285
D _{calc} (g cm ^{–3})	1.532	1.564	1.317	1.372	1.338
F(000)	2296	2312	2064	718	1744
Diffraction type	IPDS2	IPDS2	IPDS1	IPDS2	IPDS1
T (K)	173(2)	150(2)	193(2)	173(2)	193(2)
N	18448	8513	19038	14409	27227
N _{ind} [R _{i(int)}]	5237 [0.0286]	4811 [0.0345]	4794 [0.0944]	6549 [0.0382]	7312 [0.2045]
N _{obs} [I > 2σ(I)]	4583	4231	3147	5479	2799
N _{var}	425	280	280	571	502
Absorption correction	Integration	Semi-empirical	Semi-empirical	Integration	Gaussian
T _{min} , T _{max}	0.4673, 0.6736	0.701, 0.912	0.5989, 0.7399	0.7277, 0.9164	0.8144, 0.9248
GOF (F ²)	1.025	1.162	0.914	0.905	0.723
R ₁ (F), wR ₂ (F ²)	0.0173, 0.0388	0.0340, 0.0941	0.0415, 0.1048	0.0252, 0.0471	0.0570, 0.1054
Residual extrema (e Å ^{–3})	–0.774, 0.512	–2.017, 1.344	–0.533, 1.125	–0.573, 0.749	–0.606, 0.815

Supplementary material

CCDC 699271, 699272, 699273, 699274 and 699275 contain the supplementary crystallographic data for **1**, **2**, **4**, **5** and **6**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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