



## Dramatic enhancement of the stability of rare-earth metal complexes with $\alpha$ -methyl substituted *N,N*-dimethylbenzylamine ligands

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### ABSTRACT

Stepwise substitution of benzylic CH<sub>2</sub> protons in *ortho*-metallated *N,N*-dimethylbenzylamine (dm<sub>ba</sub>) ligands leads to chiral *ortho*-metallated *N,N*, $\alpha$ -trimethylbenzylamine (tm<sub>ba</sub>) and cumyl-*N,N*-dimethylamine (cu<sub>da</sub>) ligands. These larger ligands with less or no acidic protons in benzylic position prove to stabilize some of those homoleptic *tris*-aryls of the larger (middle) and largest (early) rare-earth metal cations, for which such *tris*-aryl or *tris*-dm<sub>ba</sub> complexes could not be synthesized so far. The syntheses, characterization and crystal structures of [Li(cu<sub>da</sub>)], [(tm<sub>ba</sub>)<sub>2</sub>Lu( $\mu$ -Cl)]<sub>2</sub> (**1**), [(tm<sub>ba</sub>)<sub>2</sub>Y( $\mu$ -Cl)]<sub>2</sub> (**2**), [Y(tm<sub>ba</sub>)<sub>3</sub>] (**3**), [Dy(tm<sub>ba</sub>)<sub>3</sub>] (**4**), [Nd(tm<sub>ba</sub>)<sub>3</sub>] (**5**), [Sm(tm<sub>ba</sub>)<sub>3</sub>] (**6**), and [Sm(cu<sub>da</sub>)<sub>3</sub>] (**7**) are reported, trends in complex stability are discussed.

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### 1. Introduction

The bidentate monoanionic *ortho*-metallated *N,N*-dimethylbenzylamine ligand (dm<sub>ba</sub>) found broad application in the organometallic chemistry. Complexes with this ligand motif are known for almost every transition metal. This ligand may be introduced using the aryllithium reagent 2-lithio-*N,N*-dimethylbenzylamine Li(dm<sub>ba</sub>) which itself is conveniently prepared by *ortho*-directed lithiation of *N,N*-dimethylbenzylamine [1]. This chelate ligand can perfectly provide kinetic stabilization of its metal aryl complexes by the strongly  $\sigma$ -donating dimethylamino group. Homoleptic *tris*-aryls [Ln(dm<sub>ba</sub>)<sub>3</sub>] are known for late rare-earth metals with small ionic radii (Er, Yb and Lu [2], Sc [3], Y [4]). Furthermore it was reported that due to not identified decomposition paths no such complexes with larger cations of the early or middle lanthanides exist [2].

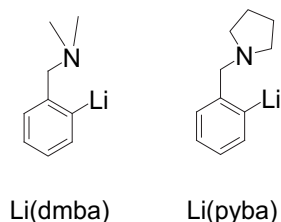
Recently we reported a reinvestigation of the reactions of *ortho*-lithiated *N,N*-dimethylbenzylamine [Li(dm<sub>ba</sub>)] and *N*-benzylpyrrolidine [Li(py<sub>ba</sub>)] ligands with different lanthanide and group 3 metal complexes (Scheme 1).

Our observations denote the crucial role of coordinated solvent in the lanthanide precursors [LnCl<sub>3</sub>(sol<sub>v</sub>)<sub>*n*</sub>] on the formation of the transmetallated products. The use of [NdCl<sub>3</sub>(dme)] or [GdCl<sub>3</sub>(dme)<sub>2</sub>] instead of their THF-solvated pendants and a slight modification of the ligand framework (dm<sub>ba</sub>  $\rightarrow$  py<sub>ba</sub>) allowed the isolation and XRD structural characterization of highly air-sensitive, crystalline lithium *tetrakis*-aryl-ate complexes of early and middle lanthanide metals, namely Li[Nd(py<sub>ba</sub>)<sub>4</sub>] and Li[Gd(tm<sub>ba</sub>)<sub>4</sub>] (Scheme 2) [5].

The existence of *tris*-dm<sub>ba</sub> complexes only for smaller (or late) lanthanides (Er–Lu) and the smaller group 3 metals Y and Sc indicates that for stabilization of such homoleptic aryls of early (La–Sm) and middle (Eu–Ho) lanthanides further modification of the dm<sub>ba</sub> ligand is required.

In this context it is interesting to note, that deprotonation of *N,N*-dimethylbenzylamine with *n*-BuLi in ether takes place exclusively at the *ortho*-position of the phenyl ring as a result of a kinetically as well as thermodynamically controlled reaction. When alkylsodium compounds (e.g. *n*-BuNa or *n*-AmNa) suspended in hexane are used, deprotonation of *N,N*-dimethylbenzylamine under kinetic control occurs at the *ortho*-position (Scheme 3), however, the *ortho*-sodio aryl derivative is unstable and isomerizes into thermodynamically more stable benzyl or  $\alpha$ -sodio species within 20 h, respectively [6]. The softer metal cation Na<sup>+</sup> (vs. Li<sup>+</sup>) tends to better stabilize the softer benzyl (and not aryl) carbanion. The preference of even softer

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**Scheme 1.** Earlier studied benzylamine-derived ligands.

cation  $K^+$  to interact with benzylic carbanions in highly aggregated structures is well documented by XRD structural analyses of  $[PhCH_2K(pmdta)]_\infty$  [7],  $[PhCH_2K(thf)]_\infty$  [8],  $[Ph(Me_3Si)_2CK]_\infty$  [9] and  $[Me_2NC_6H_4CHSiMe_3K(thf)]_\infty$  [10].

On the other hand the  $\alpha$ -lithio derivative being prepared from the  $\alpha$ -sodio compound by metathesis with lithium bromide is stable at 25–30 °C for at least 24 h. At higher temperatures (45 °C/45 h), this species slowly isomerizes forming the thermodynamically more stable *ortho*-lithio derivative. We anticipated that the availability of acidic benzylic protons would strongly influence the stability of the primary products with larger and softer early rare-earth metals obtained via transmetalation with Li(dmmba). Therefore substitution of benzylic protons by one or two methyl groups should have a strong impact on complex stability of larger cations.

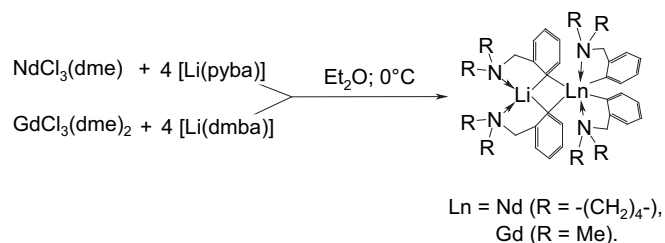
Here we report our achievements in organometallic chemistry of early, middle and late lanthanide complexes with *mono*- and *bis*- $\alpha$ -methyl substituted dmmba ligands.

### 1.1. Synthesis of aryllithium reagents Li(tmmba) and Li(cuda)

The  $\alpha$ -methyl- and  $\alpha,\alpha$ -dimethyl substituted benzylamine precursors are *N,N*, $\alpha$ -trimethyl-benzylamine (tmmba)H and *cumyl-N,N*-dimethylamine (cuda)H (Scheme 4). Both amines were synthesized according to the literature procedures from (*S*)-phenylethylamine and *tert*-cumylamine [11] by the standard protocol for methylation under *Eschweiler-Clark* conditions [12].

The synthesis and properties of aryllithium reagent Li(tmmba) were first reported in 2004 by van Koten et al. [13]. It was shown that the appearance, reactivity and physicochemical properties of *ortho*-lithiated racemic and enantiopure amine differ dramatically. Therefore, the metallation was investigated with (*S*)-phenylethylamine instead of the racemate. The synthesis of the aryllithium reagent was performed using *tert*-BuLi as deprotonating agent in pentane at room temperature [14].

The second aryllithium reagent – *ortho*-lithiated cumyl-*N,N*-dimethylamine, Li(cuda) (2) – was previously generated *in situ* by



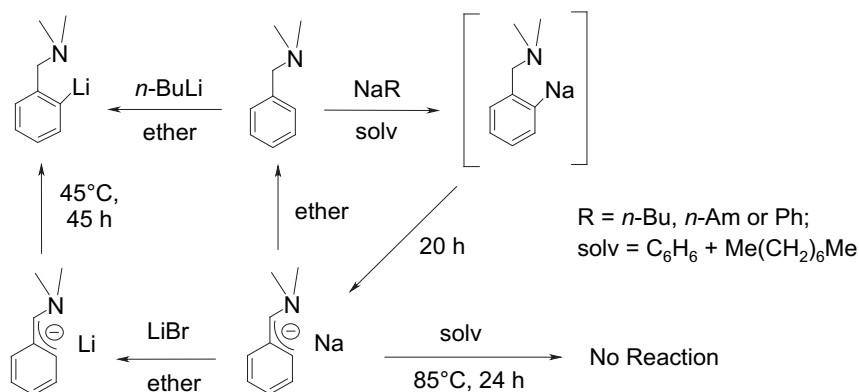
**Scheme 2.** Synthesis of the lithium ate-complexes  $Li[Nd(pyba)_4]$  and  $Li[Gd(dmmba)_4]$ .

metallation of (*o*-BrC<sub>6</sub>H<sub>4</sub>)C(Me)<sub>2</sub>NMe<sub>2</sub> with *n*-BuLi and further used for a following reaction in boron chemistry. No isolation or characterization of the compound was attempted [15].

We have synthesized and completely characterized Li(cuda) by deprotonation of *N,N*-dimethyl-cumylamine with *tert*-BuLi in multigram scale. The product shows higher solubility in ethereal and aliphatic solvents than Li(tmmba). The isolation of this lithium reagent was achieved by storing its pentane solution at –30 °C. The product was isolated in 55% yield. Crystallisation from ether leads to an etherate of the composition  $Li(cuda) \times \frac{1}{2}Et_2O$ . Attempts to remove the coordinated ether molecule by drying in vacuum at  $10^{-2}$  mbar/20 °C were unsuccessful. This stable etherate could also be used as a convenient precursor. In the <sup>1</sup>H NMR spectrum of Li(cuda), sharp resonances for NMe<sub>2</sub> and CMe<sub>2</sub> at 2.16 and 1.35 ppm respectively were observed. The fluxional behavior of the cuda ligands in those Li etherates is reflected by significant broadening of Me<sub>2</sub>C and Me<sub>2</sub>N group resonances (1.42 and 1.76 ppm respectively).

### 1.2. Rare-earth complexes with tmmba ligand

In first experiments on transmetalation with the aryllithium reagent Li(tmmba), the synthesis of the homoleptic lutetium complex  $[Lu(tmmba)_3]$  was attempted. The salt metathesis reaction of three equiv. of this aryllithium reagent with one equiv.  $[LuCl_3(thf)_3]$  [16] did not lead to expected  $[Lu(tmmba)_3]$ , the homologue of  $[Lu(dmmba)_3]$ . Cooling the hexane extract of non-volatile reaction products leads to precipitation of a crystalline solid, that was identified as  $[(tmmba)_2Lu(\mu-Cl)]_2$  (1). This is the first heteroleptic *bis*-aryl-chloro lanthanide complex in this series. Even prolonged reaction times (24 d at 20 °C) did not result in the substitution of the third chlorine atom in this complex. The composition of 1 was also confirmed by elemental analysis (Fig. 1). The <sup>1</sup>H NMR spectrum of 1 reveals three broad resonances for diastereotopic methyl groups of Me<sub>2</sub>N and for C(H)Me suggesting a *cis* coordination of both ligands in an octahedral chlorine bridged dinuclear complex,



**Scheme 3.** Deprotonation of *N,N*-dimethylbenzylamine with lithio- and sodio-organyls and their following transmetalation/isomerization reactions.

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