**Benzyllanthanide Chemistry: Revival of Manzer’s ortho-Me₂N-Benzyl Ligand**

Sjoerd Harder*[^a]

**Keywords:** Rare earths; Benzyl ligand; Synthetic methods; Half sandwich complexes; Organometallic chemistry

**Abstract.** The Manzer benzyl ligand, ortho-Me₂N-benzyl (DMA), has been introduced in lanthanide (Ln) chemistry more than three decades ago with the syntheses of Sc(DMA)₃ and Er(DMA)₃ but no reaction chemistry or structures have been described. Only recently it was shown that a Ln(DMA)₃ complex can also be obtained for the largest Ln metal lanthanum and first crystal structures appeared. At present crystal structures of many Ln(DMA)₃ complexes throughout the series have been determined and were found to be isomorphous. This report describes the improvement of synthetic methods for Ln(DMA)₃ complexes, a discussion on structures and trends and more important, the wide scope of Ln(DMA)₃ reagents as versatile building-blocks in lanthanide chemistry: the fast-growing number of complexes and catalysts that have been made starting from a Ln(DMA)₃ reagent are summarized. Despite the intramolecular chelating Me₂N arm, half-sandwich catalysts containing the DMA fragment are still active in alkene polymerizations or other catalytic conversions. The main advantages of Ln(DMA)₃ complexes are: i) easy syntheses from commercially available starting materials, ii) convenient crystallization which warrants high purity, iii) high stability on account of intramolecular coordination while sufficient reactivity for further conversions is maintained and iv) availability of these reagents over the full Ln range which is advantageous for catalyst screening.

**Introduction**

The benzyl ligand plays an important role throughout organometallic chemistry. It is popular in early main group chemistry as a resonance-stabilized carbanion. Charge delocalization reduces extreme reactivity and facilitates handling to a level that is sufficient for most applications. The benzyl ligand is similarly popular in transition metal chemistry. As it does not have any β-hydrogen atoms, it prevents decomposition by β-hydrogen elimination. Manzer et al. introduced the benzyl ligand in organolanthanide chemistry (for convenience we abbreviate “lanthanide” with Ln and define this group as the elements Ce–Lu and include the group 3 metals Sc, Y and La) [1–4]. They used a ligand with a “built-in” chelating Me₂N group that insures additional stabilization (1). Thus the complexes Sc(DMA)₃ and Er(DMA)₃ have been prepared already at an early stage in the development of organolanthanide chemistry (DMA = ortho-Me₂N-benzyl).

Considering their ease of preparation from commercially available precursors, it is surprising that this chemistry never achieved much further attention. In this respect, it should be noted that the most common, highly reactive, organolanthanide precursors were based on the (Me₃Si)₂CH and (Me₃Si)CH₂ ligands. Homoleptic complexes with these ligands are not always available for the larger lanthanide metals and generally show high air and thermal sensitivity [5–8]. In 2003, the synthesis of Nd(DMA)₃ appeared in a patent [9], but up to then...
no crystal structure data of any \( Ln(DMA)_3 \) complex was available. In 2005 we showed that the early work of Manzer could be applied to the largest of all lanthanide metals and reported the synthesis and crystal structure of \( La(DMA)_3 \) [10]. The same paper describes also synthesis and structure of \( Y(DMA)_3 \), a complex with one of the smallest lanthanide metals. As both crystallize isomorphous, it was anticipated that these complexes would be easily available over the whole lanthanide range.

It was questioned whether the \( Ln \) metals in these \( Ln(DMA)_3 \) complexes, which are stabilized by intramolecular coordination, would still be accessible for further reactivity. In addition, functionalization by ligand deprotonation would form an amine by-product (DMA-H) which possibly could coordinate or disturb further reactivity. However, it could be shown that the least reactive \( Y(DMA)_3 \) complex can be easily converted to a constrained geometry catalyst which under hydrogen pressure reacted further to a dimeric hydride complex that does not contain the original DMA ligand or any of the amine side-product DMA-H (Scheme 1).

**Results and Discussion**

**Syntheses**

Complexes \( Ln(DMA)_3 \) can be obtained by simple metathesis between \( LnCl_3 \) and three equivalents of the alkalimetalsalt of the DMA anion. Manzer’s original synthetic procedures for \( Sc(DMA)_3 \) and \( Er(DMA)_3 \) made use of Li(DMA) and complexes could be obtained in yields of 81% and 44%, respectively [2, 4]. Likewise, \( Nd(DMA)_3 \) was obtained by metathesis with Li(DMA) in 40% yield [9].

The use of lithium reagents generates LiCl which could complicate isolation of the product. First of all, LiCl dissolves well in organic solvents, especially in the presence of polar ethereal cosolvents like Et\(_2\)O and THF. As is often seen in lanthanide chemistry [15–18], reaction of a \( LnCl_3 \) with an organolithium reagent \( RLi \) can result in formation of “ate” complexes like \( [LnR_3Cl_x][Li^+]_x \) or \( [LnR_4][Li^+] \). This is especially a problem for large \( Ln \) metals that possess considerably sized coordination spheres. For this reason we chose to use the potassium reagent K(DMA) which would produce the much less soluble KCl and avoid contamination of the product with alkali metal salts. Reaction of the appropriate \( LnCl_3 \) with three equivalents of K(DMA) gave \( Y(DMA)_3 \) and \( La(DMA)_3 \) in crystallized yields of 59% and 41%, respectively [10]. Complexes with other \( Ln \) metals like Yb, Tm, Sm, Nd, Dy, Ho were made by the same procedure and have been isolated in crystalline purity in yields between 21% and 40% (these yields are based on unoptimized small scale synthetic procedures, < 1 mmol) [12, 19].

\( Hou \) et al. published a modified procedure for the synthesis of \( La(DMA)_3 \) in which LaBr\(_3\) is used instead of LaCl\(_3\). This increased the crystalline yield from 41% up to 87% and gave good yields for other metals like praseodymium and neodymium (92% and 83%, respectively) [14]. It was further found
that reaction of LnCl₃ precursors with Li(DMA) also gave satisfactory crystalline yields for the metals yttrium (75%), samarium (92%), gadolinium (85%), and lutetium (77%) [14]. Additionally, Xie et al. reported that Y(DMA)₃ and Er(DMA)₃ were prepared from LnCl₃ and Li(DMA) in yields of 81 % and 55 %, respectively [20]. It is therefore not a necessity to use K(DMA); Li(DMA) conveniently can be used instead. Apparently formation of “ate” complexes is not an issue for Ln(DMA)₃ complexes. This is likely due to the three chelating Me₂N substituents, which block the metal for further interactions with halide ions. This is supported by crystal structures of these complexes (vide infra). The ease of crystallization of Ln(DMA)₃ facilitates the isolation of these complexes in high purity and is an added advantage to the use of this precursor. Despite these factors, in cases where it is crucial to obtain absolute halide free Ln(DMA)₃, the use of K(DMA) is highly recommended.

Attempted synthesis of Eu(DMA)₃ by the same established salt metathesis route, i.e. reaction of EuCl₃ with K(DMA), led to the formation of an orange-brown powder that is insoluble in common polar solvents [19]. As the mother liquor contained considerable quantities of the C–C coupled DMA-DMA, (ortho-Me₂N-C₆H₄CH₂)₂, it is presumed that oxidation of the DMA anion is accompanied by spontaneous Eu³⁺ → Eu²⁺ reduction. Considering the low reduction potential of -0.35 V (Eu²⁺/Eu³⁺ [22]), this is a likely process. The product of this reduction process, Eu(DMA)₃, could be a coordination polymer on account of the much larger ionic radius for Eu²⁺ (1.20 Å, cf. Eu³⁺ 0.95 Å; both for hexacoordinate metal ions) [22].

Hitherto, Ln(DMA)₃ complexes of nearly all 17 lanthanide metals have been prepared by a very similar salt metathesis route. So far only cerium, radioactive promethium, terbium, and europium are missing. All complexes show excellent solubility in aromatic solvents and are remarkably stable. Toluene solutions of Y(DMA)₃ that are kept at 20 °C show after one year only minor decomposition (< 5 %). Keeping a solution overnight at reflux temperature, also hardly gives any decomposition. This contrasts with the instability of the unchelated benzyllanthanide complexes: THF solutions of Ln(Bn)₃(THF)₃ darken within hours at room temperature. The exact nature of this decomposition reaction has not been established but it has been proposed that carbene-like intermediates (Bn)Ln=CPh₃ are formed by α-elimination [23].

**Structures and Trends**

The hitherto structurally known Ln(DMA)₃ complexes crystallize isomorphic in the monoclinic space group P2₁/c. The molecular structures show a paddlewheel structure in which the metal has a distorted trigonal prismatic coordination arrangement (Figure 1). The three Me₂N substituents are not arranged in a facial manner, but surround the metal in a planar trigonal conformation. The potential threefold symmetry of the molecule is broken by “up-side-down” coordination of one of the chelating DMA ligands. This asymmetry is likely caused by repulsion between the more sterically demanding Me₂N substituents.

The crystal structures also show that part of the aryl ring is coordinated to the Ln metal (Cipso and Cortho). This side-on benzylic–Ln interaction is especially important for the larger metals like lanthanum. The Ln–C and Ln–N bond lengths naturally increase with metal size; however, the increment in Ln–C bond lengths is much steeper than that for the Ln–N bond lengths (Figure 2). The 0.150(3) Å difference between the longest (La) and shortest (Yb) Ln–N bonds agrees well with the difference of 0.164 Å in their ionic radii. The difference between their respective Ln–Cₐ bonds, 0.226(3) Å, is significantly larger. Additional lengthening of the Ln–C bonds with metal size is explained by the increasing importance of benzyl side-on coordination. The graph in Figure 2 shows that the average Ln-ring contact (Cipso, Cortho) hardly increases with metal size (0.061(3) Å), i.e. this contact becomes more important for the larger metals.

![Figure 1. Crystal structure of La(DMA)₃. All other Ln(DMA)₃ structures are isomorphic and show slightly different Ln–Cipso and Ln–N bonds as well as a less pronounced side-on coordination of the aryl ring (Ln–Cipso and Ln–Cortho).](image)

![Figure 2. Trends for the Ln–C, Ln–N and Ln–ring contacts in the series of Ln(DMA)₃ complexes.](image)
delocalization decreases with increasing metal Lewis acidity. Small, highly charged, cations polarize the negative charge on the benzyl carbon atom. Much weaker Lewis acids, like the larger alkali metal ions, lead to extensive charge delocalization of which the extent can be qualitatively estimated by several structural or spectroscopic features. It is well-known that the $C_{ax}$–$C_{ipso}$ bond length decreases with increasing importance of delocalization [24]. This goes hand in hand with aryl ring distortions: the endocyclic angle at $C_{ipso}$ is squeezed considerably. Although these features are also present in the structures of $Ln(DMA)_{3}$ complexes, the change in Lewis acidity from La$^{3+}$ to Yb$^{2+}$ is too small for a clear correlation between aryl ring distortion and metal size. In line with increased Lewis acidity (and decreased charge delocalization) the endocyclic C–C–C distortion and metalsize. In line with increased Lewis acidity (and decreased charge delocalization) the endocyclic C–C–C angle increases from 115.0(2)$^\circ$ (La) to 115.5(3)$^\circ$ (Yb) and the $C_{ax}$–$C_{ipso}$ bond length increases from 1.432(4) Å (La) to 1.454(5) Å (Yb). However, with the relatively large standard deviations, differences are too small to be significant.

The extent of charge delocalization is also connected to the hybridization state of the benzyl carbon which can be evaluated by the sum of the valence angles at this atom and should be dependent on metal size (Scheme 2). As the hydrogen atom positions in the crystal structures of $Ln(DMA)_{3}$ could not always be reliably established, this parameter does not provide precise information on the hybridization of $C_{ax}$. However, the $^{1}J_{CH}$ coupling constants at $C_{ax}$ correlate with its hybridization and some information could be obtained from these. In La(DMA)$_{3}$ and Y(DMA)$_{3}$, these coupling constants measure 142.8 Hz and 133.2 Hz, respectively [10]. Thus, the benzyl carbon in La(DMA)$_{3}$ is somewhat less pyramidalized than that in Y(DMA)$_{3}$. This is in agreement with more ionic bonding and more extensive charge delocalization in the lanthanum complex.

Another probe for charge delocalization is the $^{1}$H NMR chemical shift for the ring proton in $para$-position of the benzyl carbon. The shift for this hydrogen atom is highly sensitive to the nature of the metal cation. Large, soft electropositive metal cations result in extensive charge delocalization and cause a significant high-field shift of this signal. For ortho-Me$_{2}$N-$a$-Me$_{2}$Si-benzylmetal compounds the following shifts were measured (ppm): 5.77 (K$^+$) [25, 6.29 (Li$^+$) 19, 6.33 (Ca$^{2+}$) 25, 6.36 (Yb$^{3+}$) 26]. Whereas the potassium complex shows an unusually low chemical shift for an aryl proton, the smaller Li$^+$ localizes the negative charge much more on the benzyl carbon. For the compound with the larger Ca$^{2+}$, the increased 2$^{+}$ charge counterbalances the size effect and a similar chemical shift is found as for the lithium compound. It is interesting to note that the Yb$^{3+}$ and Ca$^{2+}$ complexes show very similar chemical shifts. This is in line with their similar ion sizes (1.02 Å vs. 1.00 Å) [22]. Therefore, Yb$^{1}$ complexes show very similar structures and properties as their analogous calcium compounds [26]. In the series of $Ln(DMA)_{3}$ complexes, we compared the chemical shifts of this $para$-hydrogen atom for the metals Y$^{3+}$ and La$^{3+}$. The values of 6.66 (Y$^{3+}$) and 6.43 (La$^{3+}$) indicate that the latter is significantly more ionic (and reactive). Thus, the chemical shift for the $para$-hydrogen atom, as well as the $^{1}J_{CH}$ coupling constant, are much more sensitive probes for ionicity (charge delocalization) as structural distortions in the aryl ring.

**Conversions and Applications**

From the early work of Manzer on Sc(DMA)$_{3}$ and Er(DMA)$_{3}$ [1–4], it was not clear what the synthetic potential of these complexes is. The 2003 patent on the use of Nd(DMA)$_{3}$ in butadiene polymerization also does not describe further reaction chemistry [9]. The Nd(DMA)$_{3}$ itself is activated with non-hydrolytic methyl alumoxane (i.e. Me$_{3}$Al-poor PMAO-IP) and produces polybutadiene with a high cis-1,4-content [9]. Our earlier study described the reactivity of Y(DMA)$_{3}$ with a combined fluorene-amine ligand and its subsequent conversion with hydrogen (Scheme 1). This demonstrates that the $Ln$–DMA functionality is highly reactive. Protection of the metal atom by intramolecular Me$_{2}$N–$Ln$ coordination apparently does not diminish its synthetic potential and even H$_{2}$, with a $pK_a$ value of circa 35 [27, 28], could be efficiently deprotonated. As yttrium is one of the smaller $Ln$ metals, the remaining $Ln(DMA)_{3}$ complexes are expected to be even more reactive. Only Sc(DMA)$_{3}$ might show lower reactivity. Hou et al. showed that Sc(DMA)$_{3}$ also efficiently reacts with a combined cyclopentadiene–amine ligand and a constrained geometry catalyst of type 5 (Scheme 3) could be isolated [14]. Access to $Ln(DMA)_{3}$ complexes over the full range of the $Ln$ series enabled the syntheses of 5 with various metals (La, Pr, Nd, Sm, Gd, Lu, Y, and Sc). This series of catalysts was tested in the addition of the phosphane P–H bond to carbodiimides and allowed screening of the metal size: an increase in the size of the metal results in increased activity. The same type of catalysts has shown good activity in the cross-coupling of various alkynes with isocyanide and shows an unprecedented Z-selectivity [29]. Catalysts of type 5, which contain the DMA ligand as the active part, showed the same activity as similar catalysts with CH$_{3}$SiMe$_{3}$ as the active group. This demonstrates that the activity of DMA-containing catalysts is not significantly affected by the initially chelating benzyl fragment.
The compound Sc(DMA)$_3$ was also shown to react with differently substituted CpH compounds and is a convenient precursor for half-sandwich complexes of the type Cp'Sc(DMA)$_2$ (6, Scheme 3) [30]. Although these complexes were prepared in THF, the products are THF-free on account of the chelating side-arms. These half-sandwich complexes were further activated by reaction with Ph$_3$C$^+$/[(C$_6$F$_5$)$_4$B] $^-$. One of the products, ([Me$_3$Si]MeCp)Sc(DMA)$^+$/[(C$_6$F$_5$)$_4$B] $^-$(type 7) could be characterized by X-ray diffraction [30]. It represents the first example of a cationic rare-earth metal species that is free of external Lewis bases. It was questioned whether intramolecular Me$_2$N coordination would inhibit its activity for olefin polymerization, however, 7 could initiate the polymerization of a variety of olefins such as ethylene, 1-hexene, styrene, norbornene (NB) and dicyclopentadiene (DCPD). More remarkably, it could copolymerize 1-hexene with NB or DCPD to give random copolymers. This demonstrates that the DMA ligand is an excellent scaffold for the stabilization of external-Lewis-base-free cationic Ln species. The coordinating side-arm does not hinder olefin coordination and polymerization and apparently walks away from the metal during the progress of the polymerization reaction. External THF ligands would continuously coordinate to the metal site and seriously hinder the polymerization reaction. Similar Cp'Sc(DMA)$_2$ (6) complexes were used as catalysts for the carbaolumination of alkylox substituted alkynes or alkenes and display unique regio- and stereoselectivity [31].

Half-sandwich complexes could also be obtained by the in situ reaction of Sc(DMA)$_3$ with a sterically hindered phosphine (8) [32]. The resulting compound, which could not be obtained by the alternative salt metathesis route, was activated with Ph$_3$C$^+$/[(C$_6$F$_5$)$_4$B] $^-$. One of the products, which was inactive in styrene polymerization [33]. This demonstrates the importance of $\eta^2$ face-on coordination of the ligand for catalyst activity.

Reaction of Y(DMA)$_3$ with a sterically hindered amidine gave access to the amide complex 11 (Ln = Y) [34]. Once activated with Ph$_3$C$^+$/[(C$_6$F$_5$)$_4$B] $^-$. It polymerizes isoprene with high 3,4-regioselectivity and some isotacticity ($mm \approx 50\%$), 11 could be activated with Ph$_3$C$^+$/[(C$_6$F$_5$)$_4$B] $^-$. It gave a switch in selectivity and largely 1,4-cis-polyisoprene was isolated (up to 98% selective) [34,35]. The analogous scandium complex of 11 has been used for the synthesis of a cyclized polyisoprene [36].

Other conversions of Ln(DMA)$_3$ complexes include the reaction with an indenyl ligand that contains a chelating arm with the bulky anion cage 1,2-closo-B$_{10}$C$_2$H$_{10}$ (12, Ln = Sc or Er) [21], with a partially hydrogenated fluorene ligand (13, Ln = Sc) [37] or with a cyclopentadiene ligand containing a pendant arm (14, Ln = Sc or Y) [37]. Activation of the scandium complex 14 with MAO gives a catalyst that is active for ethylene/1-hexene copolymerization or for the polymerization of lactones. Activation of 14 with Al($i$Bu)$_3$ and Ph$_3$C$^+$/[(C$_6$F$_5$)$_4$B] $^-$. It gives a catalyst for ethylene/styrene copolymerization (the ratio PE/PS can be effectively tuned by ethylene pressure). The latter catalyst also allows for the synthesis of PE/PS block-copolymers in which PS blocks have significant syndiotacticity [37].

Reaction of Ln(DMA)$_3$ with sulfur-bridged biphenol compounds gave complexes of type 15 (Ln = Sc, Y) [38]. Activation with MAO resulted in catalysts for the polymerization of ethylene or for copolymerization of ethylene and 1-hexene.

Reaction of Ln(DMA)$_3$ complexes with superbulky cyclopentadiene (Ar$_3$CphH, Ar = 4-nBu-C$_6$H$_4$; abbreviated in here as...
Cp\textsuperscript{BIG}H was investigated [39]. For \( Ln = Y \) the half-sandwich complex of type 6 was obtained: Cp\textsuperscript{BIG}Y(DMA)\(_3\). This demonstrates that the less reactive Y(DMA)\(_3\) efficiently deprotonates the superbulky Cp\textsuperscript{BIG}H ligand. For \( Ln = \text{Yb and Sm} \), however, spontaneous reduction to the metallocene (Cp\textsuperscript{BIG})\(_2\)Ln was observed [39]. As the reduction potential for samarium is highly negative (\( E_{1/2} \text{Sm}^{3+}/\text{Sm}^{2+} = -1.55 \text{ V} \)) [22], this spontaneous metal reduction should be considered remarkable (especially when one considers that Cp*\(_2\)Sm is oxidized by nitrogen [40]). The detection of large amounts of the C–C coupled DMA-DMA, (\textit{ortho}-Me\(_2\)N-C\(_5\)H\(_4\)CH\(_2\))\(_2\), indicates that the mechanism of formation could be sterically induced (SIR) [41].

Conclusions

The early work of Manzer has produced Ln(DMA)\(_3\) complexes of the metals scandium and erbium. This chemistry has been revived three decades later with the syntheses of the Ln(DMA)\(_3\) complexes containing either one of the smallest Ln metals, yttrium, or the largest Ln metal lanthanum. The crystal structures of these two complexes are isomorphous and suggested that the whole series would crystallize similar. With few exceptions, Ln(DMA)\(_3\) complexes over the whole metal size range were obtained: Sc, Y, La, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb, and Lu. These complexes indeed all crystallize isomorphous. The DMA ligand represents the first (resonance-stabilized) alkyl system that allows access to highly reactive lanthanide precursors for the complete Ln series. Optimization of synthetic procedures has led to convenient methods for their syntheses from cheap commercially available starting materials. As all Ln(DMA)\(_3\) complexes crystallize nicely in the form of large blocks, the purity of the final products is warranted.

The availability of Ln(DMA)\(_3\) complexes over the whole series does not only allow for a discussion of trends in their molecular structures but also for screening of metal size effects in catalysis. All Ln(DMA)\(_3\) complexes can be easily converted by reaction with mono-protic (LH) or diprotic (LH\(_2\)) ligands and various products LLn(DMA)\(_2\) or LLn(DMA) were routinely obtained. Bulky ligands do not pose a problem and dihydrogen can be deprotonated to give a Ln–H functionality.

The catalytic behavior of the resulting complexes is not negatively influenced by the presence of the intramolecular chelating Me\(_2\)N arm. In contrast, this chelating substituent allows for isolation of compounds that are free of external Lewis bases like THF. In the time frame 2007–2010, DMA-containing complexes have emerged as efficient catalysts for the polymerization of a wide variety of monomers. The system is also increasingly popular for other catalytic conversions like the hydrophosphonation of carbodiimides, carboalumination of alkoxyl substituted alkynes (or alkynes) and cross-coupling of various alkynes with isocyaniands. The fast-growing number of patents which make use of Ln(DMA)\(_3\) precursors, shows that interest is not only academic. In conclusion, the Manzer ligand system has been shown to be very versatile in Ln chemistry and its rapid progress during the last few years promises an even brighter future.

Acknowledgement

S. Harder acknowledges the Deutsche Forschungsgemeinschaft for generous support within the framework of the high priority program SPP1166 “lanthanide-specific functionalities in molecule and material”.

References

Revival of Manzer’s ortho-Me₂N-Benzyl Ligand


Received: April 29, 2010
Published Online: June 28, 2010