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

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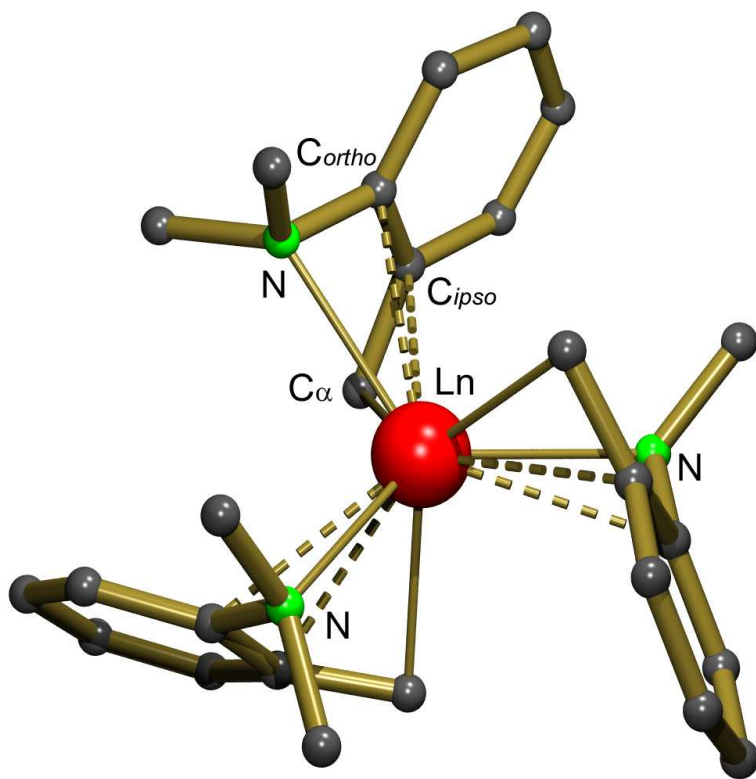
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**Benzylanthanide Chemistry: Revival of Manzer's ortho-
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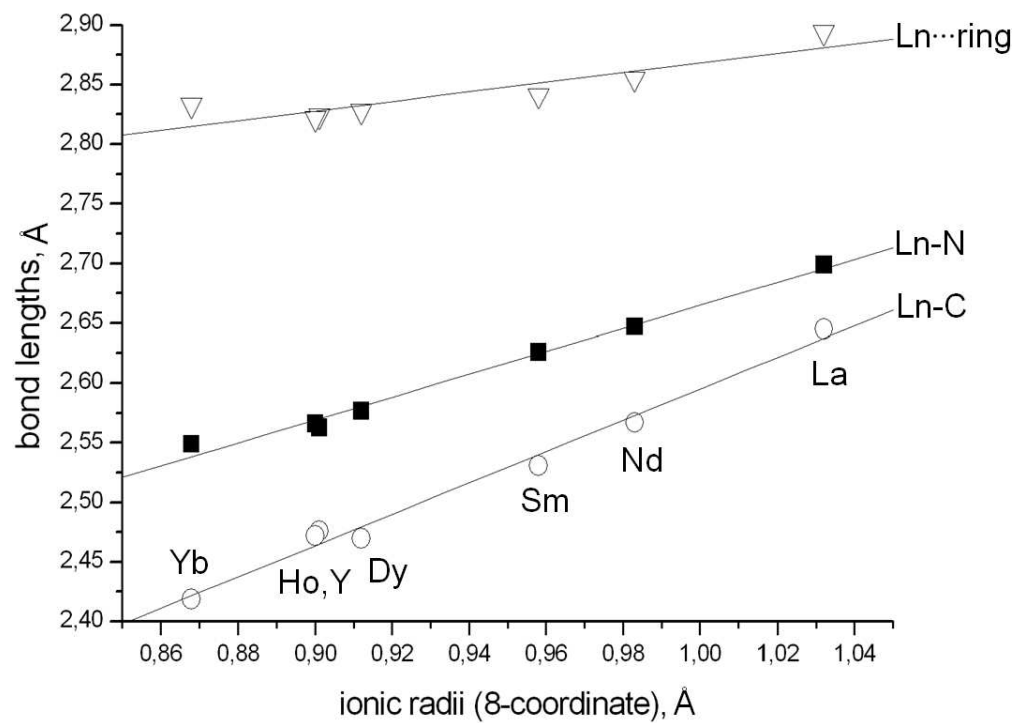
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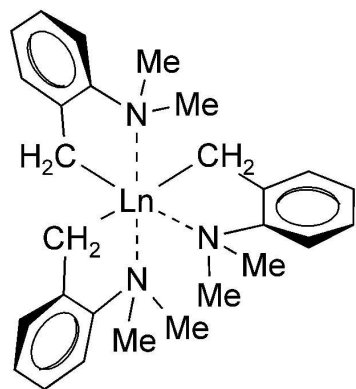
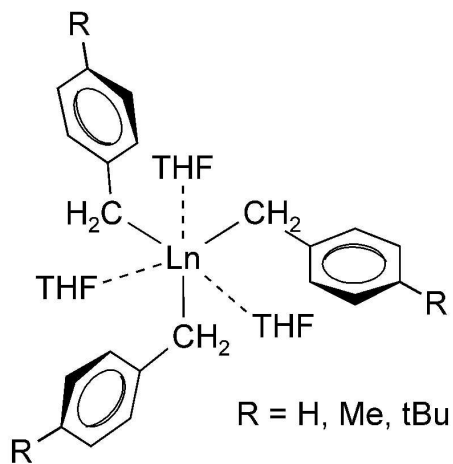
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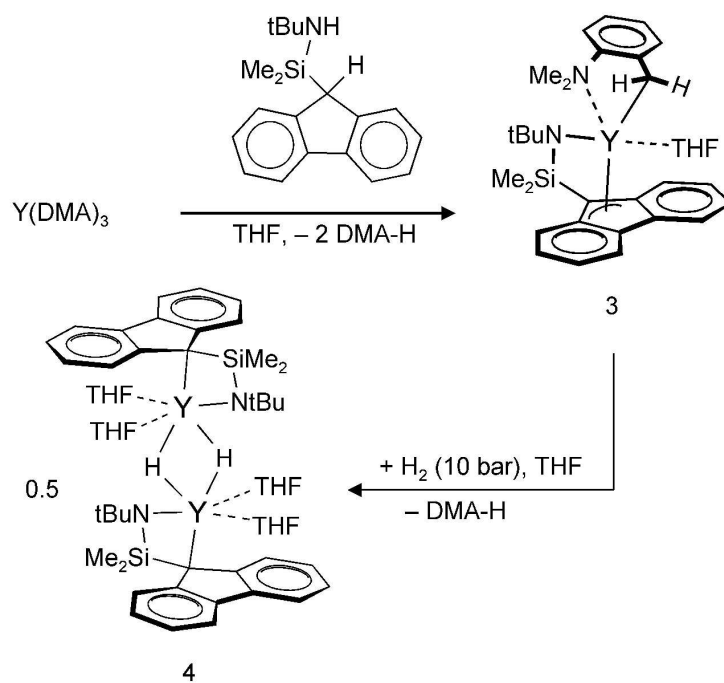
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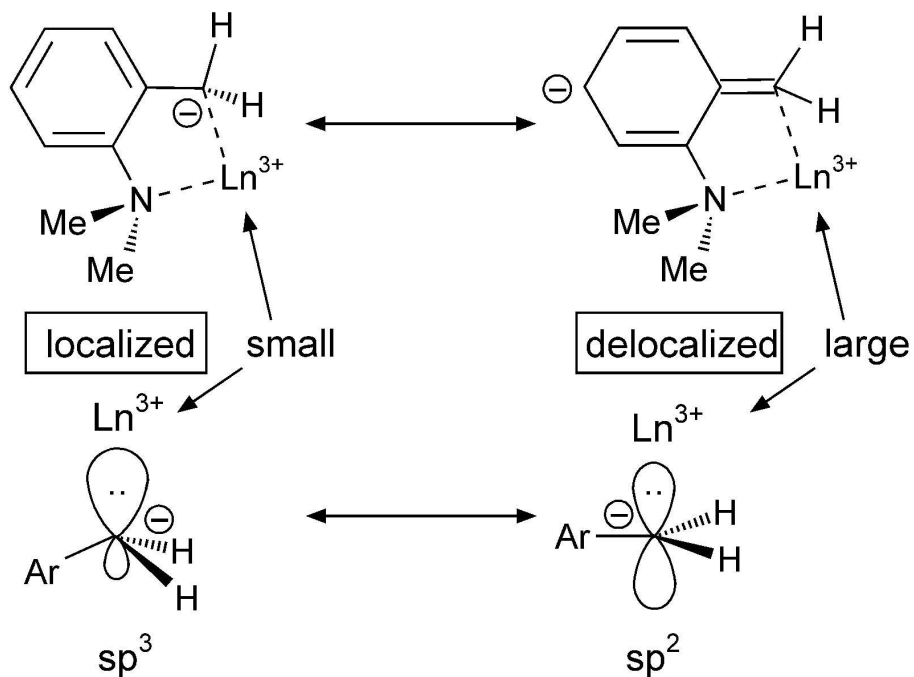
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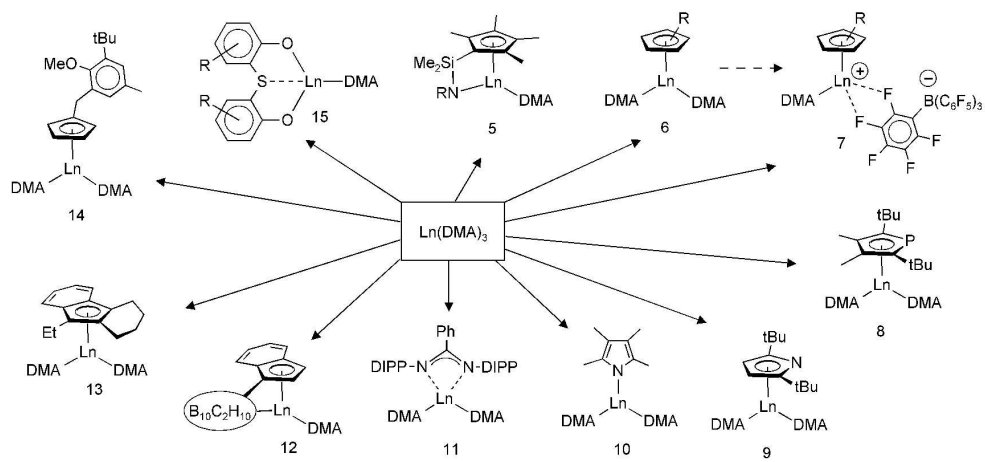
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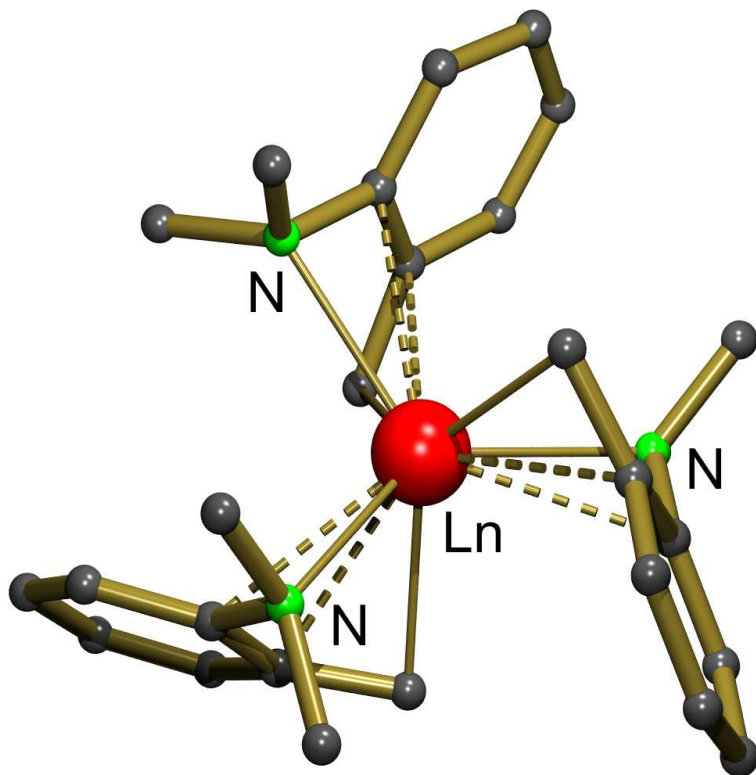


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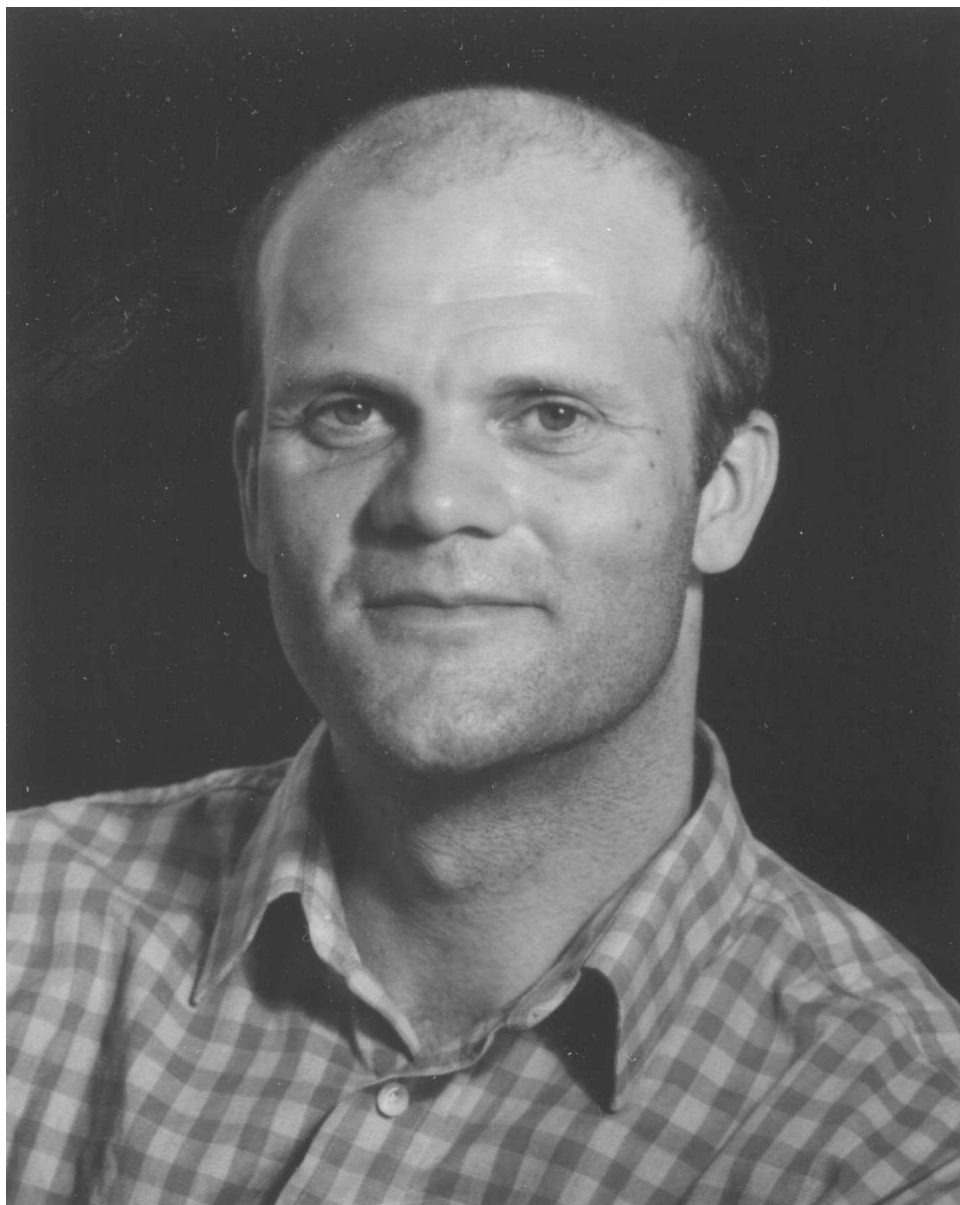
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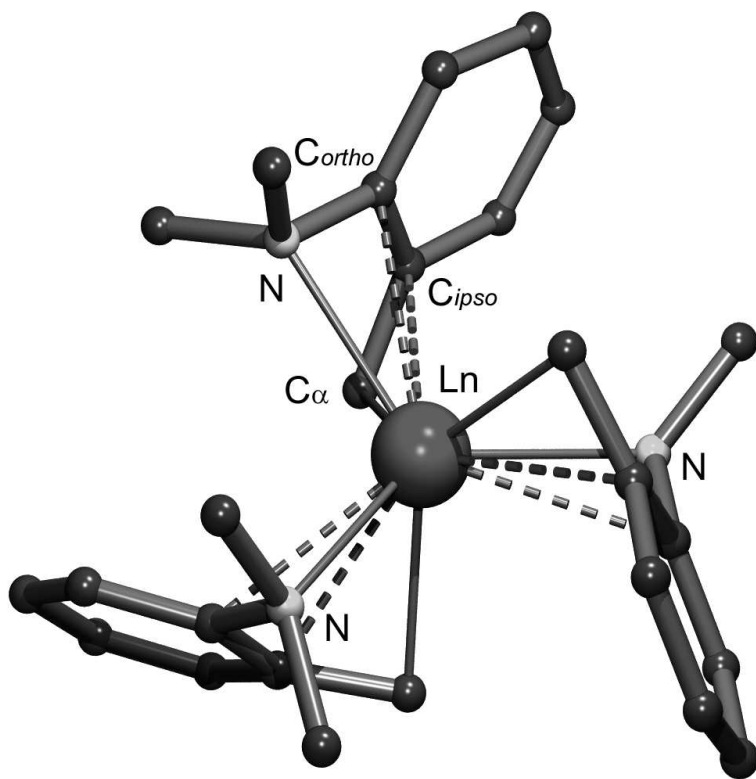
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RESEARCH REPORT

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Benzylanthanide Chemistry: Revival of Manzer's *ortho*-Me₂N-Benzyl Ligand

Sjoerd Harder^[a]

Keywords: lanthanide; benzyl; synthesis

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 La 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 reports 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.

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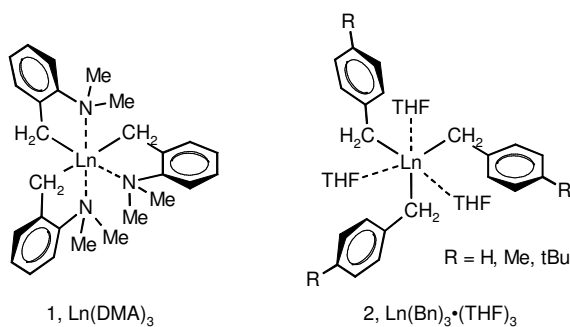


Introduction

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 possess 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 Me_2N group that insures additional stabilization (**1**). Thus the complexes $\text{Sc}(\text{DMA})_3$ and $\text{Er}(\text{DMA})_3$ have been prepared already at an early stage in the development of organolanthanide chemistry (DMA = *o*- Me_2N -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 $(\text{Me}_3\text{Si})_2\text{CH}$ and $(\text{Me}_3\text{Si})\text{CH}_2$ 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 $\text{Nd}(\text{DMA})_3$ appeared in a patent [9], but up to then no crystal structure data of any $\text{Ln}(\text{DMA})_3$ 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 $\text{La}(\text{DMA})_3$ [10]. The same paper describes also synthesis and structure of $\text{Y}(\text{DMA})_3$, 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



Scheme 1.

Despite the unproblematic functionalization of $\text{Ln}(\text{DMA})_3$ complexes, benzyl lanthanide complexes that do not contain intramolecularly chelating side-arms (**2**) have been introduced and were prepared according to the same synthetic route, i.e. reaction of benzylpotassium precursor with a lanthanide(III) halide salt. Hessen *et al.* and our group reported syntheses and crystal structures of the following compounds: $\text{La}(\text{benzyl})_3$ [11], $\text{La}(\textit{para}\text{-Me-benzyl})_3$ [11], $\text{La}(\textit{para}\text{-tBu-benzyl})_3$ [12] and $\text{Y}(\text{benzyl})_3$ [12]. All crystallize as THF-adducts of general formula $\text{Ln}(\text{Bn})_3 \cdot (\text{THF})_3$ with distorted octahedral metal coordination environments. The three benzyl ligands, as well as the three THF ligands, are in a facial arrangement. It is not clear why the negatively charged benzyl ligands are in close proximity.

Five years after the report on the syntheses and structures of $\text{La}(\text{DMA})_3$ and $\text{Y}(\text{DMA})_3$ [10], many intermediate members in the $\text{Ln}(\text{DMA})_3$ family have been prepared and were shown to form isomorphous crystals [12-14]. Although this series of complexes is not as reactive as the unstabilized $\text{Ln}(\text{Bn})_3$ complexes, they are reactive enough for further functionalization (*vide infra*). There seems to be a good compromise between stability (ease of handling) and reactivity (functionalization/catalysis). This manuscript gives a short overview on the syntheses, structures, trends, reactivity and use of $\text{Ln}(\text{DMA})_3$ complexes.

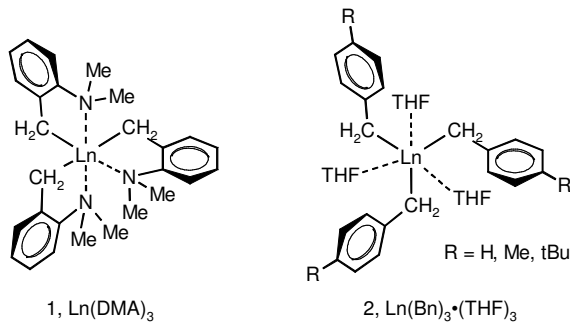
Results and Discussion

Syntheses

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

The use of Li 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_2O and THF. As is often

$\text{Ln}(\text{DMA})_3$ 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 $\text{Y}(\text{DMA})_3$ 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).



seen in lanthanide chemistry [15-18], reaction of a LnCl_3 with an organolithium reagent RLi can result in formation of "ate" complexes like $[\text{LnR}_3\text{Cl}_x^-][\text{Li}^+]_x$ or $[\text{LnR}_4^-][\text{Li}^+]$. 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 (the yields of the raw products were 92 % and 85 %, 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 Pr and Nd (92 % and 83 %, respectively) [14]. It was further found that reaction of LnCl_3 precursors with Li(DMA) also gave satisfactory crystalline yields for the metals Y (75 %), Sm (92 %), Gd (85 %) and Lu (77 %) [14]. Also Xie *et al* report that Y(DMA)_3 and Er(DMA)_3 have been prepared from LnCl_3 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 Me_2N -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 EuCl_3 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*- $\text{Me}_2\text{N-C}_6\text{H}_4\text{CH}_2$)₂, it is presumed that oxidation of the DMA anion is accompanied by spontaneous $\text{Eu(III)} \rightarrow \text{Eu(II)}$ reduction. Considering the low reduction potential of -0.35 V ($E_{1/2} \text{Eu}^{3+}/\text{Eu}^{2+}$ [22]), this is a likely process. The product of this reduction process, Eu(DMA)_2 , could be a coordination polymer on account of the much larger ionic radius for Eu^{2+} (1.20 Å, *cf.* Eu^{3+} 0.95 Å; both for 6-coordinate 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 Ce, radioactive Pm, Tb and Eu 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 stability of the unchelated benzyl lanthanide complexes: THF solutions of $\text{Ln(Bn)}_3 \cdot (\text{THF})_3$ 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 $(\text{Bn})\text{Ln}=\text{CHPr}_4$ are formed by α -elimination [23].

Structures and Trends

The hitherto structurally known Ln(DMA)_3 complexes crystallize isomorphous in the monoclinic space group $P2_1/c$. The molecular structures show a paddlewheel geometry in which the metal has a distorted trigonal prismatic coordination geometry (Figure 1). The three Me_2N substituents are not arranged in a facial geometry but surround the metal in a planar trigonal conformation. The potential three-fold 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 Me_2N -substituents.

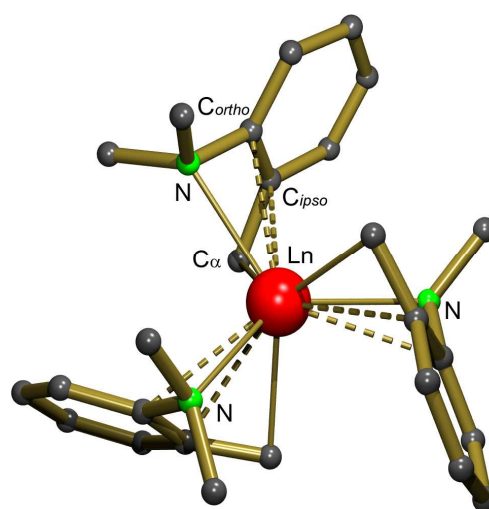


Figure 1. Crystal structure of La(DMA)_3 . All other Ln(DMA)_3 structures are isomorphous and show slightly different Ln-C_α and Ln-N bonds as well as a less pronounced side-on coordination of the aryl ring ($\text{Ln-C}_{\text{ipso}}$ and $\text{Ln-C}_{\text{ortho}}$).

The crystal structures also show that part of the aryl ring is coordinated to the Ln metal (C_{ipso} and C_{ortho}). This side-on benzyl-Ln interaction is especially important for the larger metals like La. The Ln-C and Ln-N bond distances naturally increase with metal size, however, the increment in Ln-C bond distances is much steeper than that for the Ln-N bond distances (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-C_α 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 (C_{ipso} , C_{ortho}) hardly increases with metal size (0.061(3) Å), *i.e.* this contact becomes more important for the larger metals.

Typical for benzyl ligands in polar organometallic compounds is delocalization of the negative charge on the benzylic carbon into the aryl ring. The extent of

delocalization is highly dependent on the nature of the metal. The importance of charge delocalization decreases with increasing metal Lewis-acidity. Small, highly charged, cations polarize the negative charge on the benzylic 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_{α} - C_{ipso} bond distance 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 $\text{Ln}(\text{DMA})_3$ complexes, the change in Lewis-acidity from La^{3+} to Yb^{3+} 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 angle increases from $115.0(2)^\circ$ (La) to $115.5(3)^\circ$ (Yb) and the C_{α} - C_{ipso} bond distance 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.

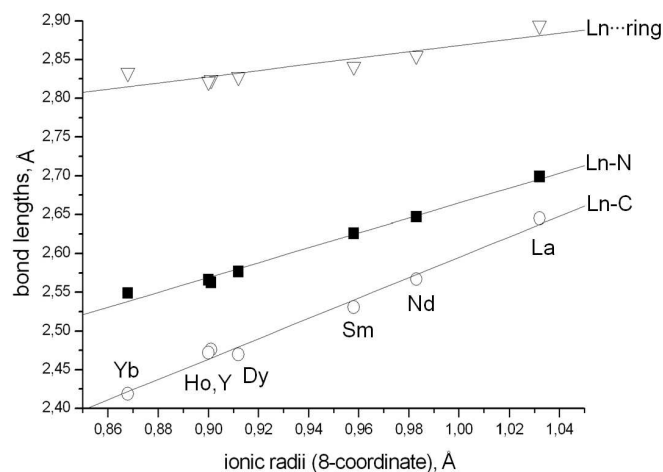
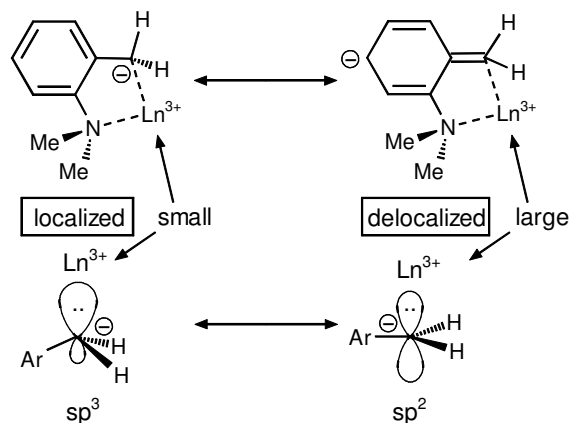


Figure 2. Trends for the Ln-C, Ln-N and Ln...ring contacts in the series of $\text{Ln}(\text{DMA})_3$ complexes.

The extent of charge delocalization is also connected to the hybridization state of the benzylic 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 $\text{Ln}(\text{DMA})_3$ could not always be reliably established, this parameter does not provide precise information on the hybridization of C_{α} . However, the $^1J_{\text{CH}}$ coupling constants at C_{α} correlate with its hybridization and some information could be obtained from these. In $\text{La}(\text{DMA})_3$ and $\text{Y}(\text{DMA})_3$, these coupling constants measure 142.8 Hz and 133.2 Hz, respectively [10]. Thus, the benzylic carbon in $\text{La}(\text{DMA})_3$ is somewhat less pyramidalized than that in $\text{Y}(\text{DMA})_3$. This is in agreement with more ionic bonding and more extensive charge delocalization in the La complex.

Another probe for charge delocalization is the ^1H NMR chemical shift for the ring proton in *para*-position of the benzylic 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_2N -*a*- Me_3Si -benzylmetal compounds the following shifts have been measured (ppm): 5.77 (K^+) [25], 6.29 (Li^+) [19], 6.33 (Ca^{2+}) [25], 6.36 (Yb^{2+}) [26]. Whereas the K complex shows an unusually low chemical shift for an aryl proton, the smaller Li^+ localizes the negative charge much more on the benzylic 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 Li compound. It is interesting to note that the Yb^{2+} 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(II) complexes show very similar structures and properties as their analogous Ca compounds [26]. In the series of $\text{Ln}(\text{DMA})_3$ complexes, we compared the chemical shifts of this *para*-H 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*-H atom, as well as the $^1J_{\text{CH}}$ coupling constant, are much more sensitive probes for ionicity (charge delocalization) as structural distortions in the aryl ring.



Scheme 2

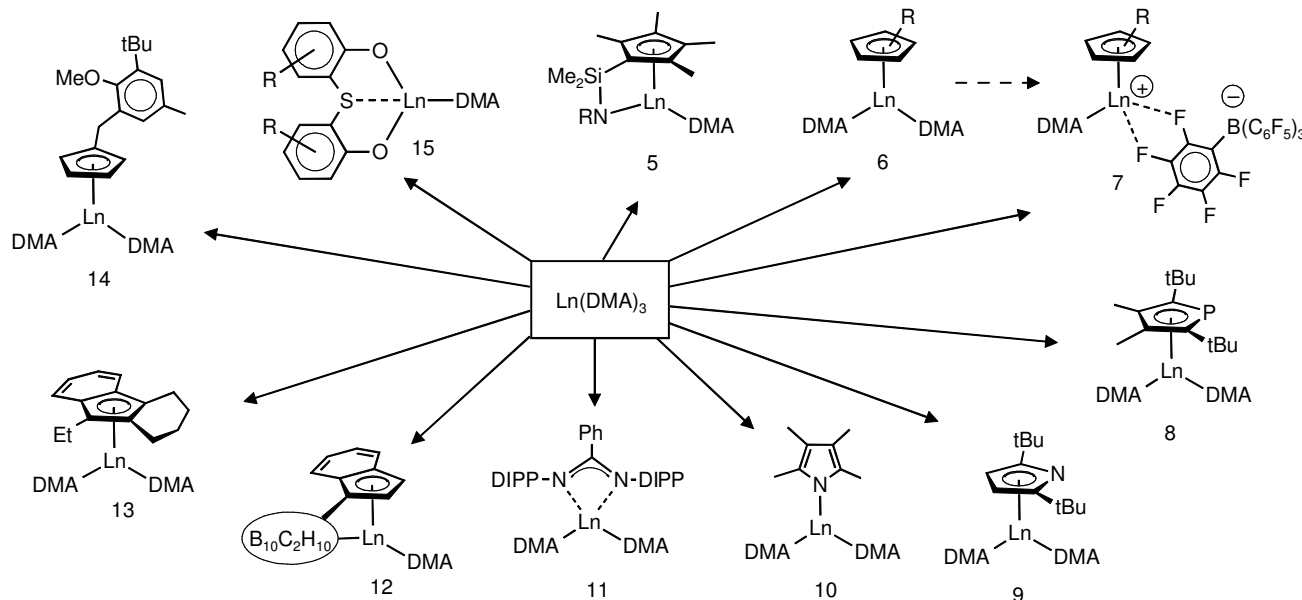
Conversions and Applications

From the early work of Manzer on $\text{Sc}(\text{DMA})_3$ and $\text{Er}(\text{DMA})_3$ [1-4], it was not clear what the synthetic potential of these complexes is. The 2003 patent on the use of $\text{Nd}(\text{DMA})_3$ in butadiene polymerization also does not describe further reaction chemistry [9]. The $\text{Nd}(\text{DMA})_3$ itself is activated with non-hydrolytic methyl alumoxane (*i.e.* Me_3Al -poor PMAO-IP) and produces polybutadiene with a high *cis*-1,4-content [9]. Our earlier study described the reactivity of $\text{Y}(\text{DMA})_3$ 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 center by intramolecular Me_2N -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 Y is one of the smaller Ln metals, the

remaining $\text{Ln}(\text{DMA})_3$ complexes are expected to be even more reactive. Only $\text{Sc}(\text{DMA})_3$ might show lower reactivity.

Hou *et al.* showed that $\text{Sc}(\text{DMA})_3$ 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 $\text{Ln}(\text{DMA})_3$ complexes over the full

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 olefine 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



Scheme 3

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 phosphine 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_2SiMe_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 $\text{Sc}(\text{DMA})_3$ was also shown to react with differently substituted $\text{Cp}'\text{H}$ compounds and is a convenient precursor for half-sandwich complexes of the type $\text{Cp}'\text{Sc}(\text{DMA})_2$ (**6**, Scheme 3) [30]. Although these complexes have been prepared in THF, the products are THF-free on account of the chelating side-arms. These half-sandwich complexes have been further activated by reaction with $\text{Ph}_3\text{C}^+(\text{C}_6\text{F}_5)_4\text{B}^-$ and one of the products, $[(\text{Me}_3\text{Si})\text{Me}_4\text{Cp}]\text{Sc}(\text{DMA})^+(\text{C}_6\text{F}_5)_4\text{B}^-$ (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_2N -coordination would inhibit its activity for olefine 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

polymerization reaction. Similar $\text{Cp}'\text{Sc}(\text{DMA})_2$ (**6**) complexes have been used as catalysts for the carboalumination of alkoxy substituted alkynes or alkenes and display unique regio- and stereoselectivity [31].

Half-sandwich complexes could also be obtained by the *in situ* reaction of $\text{Sc}(\text{DMA})_3$ with a sterically hindered phosphole (**8**) [32]. The resulting compound, which could not be obtained by the alternative salt metathesis route, was activated with $\text{Ph}_3\text{C}^+(\text{C}_6\text{F}_5)_4\text{B}^-$ and found to be an excellent catalyst for syndiospecific styrene polymerization. Reaction of various $\text{Ln}(\text{DMA})_3$ complexes with a similar sterically hindered pyrrole gave the analogous complex (**9**) which is also active in syndiospecific styrene polymerization [33]. The availability of a set of catalysts ($\text{Ln} = \text{Sc}, \text{Y}, \text{La}$) allowed for screening of the effect of metal size: activities increase with decreasing metal size along the row $\text{La} < \text{Y} < \text{Sc}$. Use of a less sterically hindered phosphole gave the η^1 edge-on coordinated complex **10** which is inactive in styrene polymerization [33]. This demonstrates the importance of η^5 face-on coordination of the ligand for catalyst activity.

Reaction of $\text{Y}(\text{DMA})_3$ with a sterically hindered amidine gave access to the amidinate complex **11** ($\text{Ln} = \text{Y}$) [34]. Once activated with $\text{Ph}_3\text{C}^+(\text{C}_6\text{F}_5)_4\text{B}^-$, it polymerizes isoprene with high 3,4-regioselectivity and some isotacticity ($mm \approx 50\%$). Reaction of **11** with excess Me_3Al led to exchange of the DMA^- ions for Me_4Al^- ions. Interestingly, subsequent activation with $\text{Ph}_3\text{C}^+(\text{C}_6\text{F}_5)_4\text{B}^-$ gave a switch in selectivity and largely 1,4-*cis*-polyisoprene was isolated (up to 98% selective) [34, 35]. The analogous Sc complex of **11** has been used for the synthesis of a cyclized polyisoprene [36].

Other conversions of Ln(DMA)₃ complexes include the reactions with an indene ligand that contains a chelating arm with the bulky anion cage 1,2-*closo*-B₁₀C₂H₁₀ (**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 Sc 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 Ph₃C⁺/(C₆F₅)₄B⁻ 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 sulphur 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 (Ar₅CpH, Ar = 4-*n*Bu-C₆H₄; abbreviated in here as Cp^{BIG}H) has been investigated [39]. For Ln = Y the half-sandwich complex of type **6** was obtained: Cp^{BIG}Y(DMA)₂. This demonstrates that the less reactive Y(DMA)₃ efficiently deprotonates the superbulky Cp^{BIG}H ligand. For Ln = Yb and Sm, however, spontaneous reduction to the metallocene (Cp^{BIG})₂Ln has been observed [39]. As the reduction potential for Sm is highly negative (E_{1/2} Sm³⁺/Sm²⁺ = -1.55 V) [22], this spontaneous metal reduction should be considered remarkable (especially when one considers that Cp*₂Sm is oxidized by N₂ [40]). The detection of large amounts of the C-C coupled DMA-DMA, (*ortho*-Me₂N-C₆H₄CH₂)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 Sc and Er. 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, Y, or the largest Ln metal La. 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 have been 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 (LH₂) ligands and various products LLn(DMA)₂ or LLn(DMA) have been routinely obtained. Bulky ligands do

not pose a problem and H₂ can be deprotonated to give a Ln-H functionality.

The catalytic behaviour of the resulting complexes is not negatively influenced by the presence of the intramolecular chelating Me₂N-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 hydrophosphination of carbodiimides, carboalumination of alkoxy substituted alkynes (or alkenes) and cross-coupling of various alkynes with isocyanides. 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

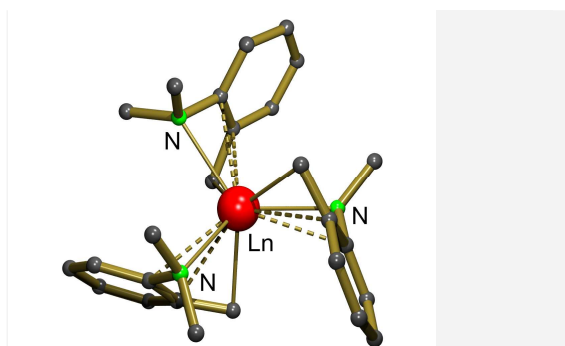
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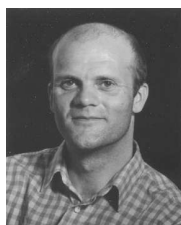
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Entry for the Table of Contents



S. Harder Page No. – Page No.

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

Sjoerd Harder, born in The Netherlands, obtained his Ph.D. degree in experimental organolithium chemistry under the supervision of Lambert Brandsma (1990, Utrecht) and was awarded the H.J. Backer prize in organic chemistry for this contribution. After post-doc work in theoretical organic chemistry with Paul R. von Schleyer (1991, Erlangen) he moved to the group of Andrew Streitwieser (1992, Berkeley) to work on superbases. His third post-doc stay in the group of Hans Brintzinger (1993, Konstanz) was extended and he received his habilitation on investigations of group 1 sandwich complexes (lithocene, sodocene and cesocene) in 1998. He intensified his work on the heavier group 2 metals (Ca, Sr, Ba) and cooperated in a BASF project on highly reactive alkaline-earth metal benzyl complexes for styrene polymerization. In 2004 he became a professor of Inorganic Chemistry at the university of Duisburg-Essen. Since 2010 he holds the chair of inorganic chemistry at the university of Groningen. His current research interests include: catalysis with early main group organometallics, hydrogen elimination in metal amidoborane and hydride complexes, multi-metallic catalysts, lanthanide chemistry (catalysis and luminescence) and Cp^{BIG} chemistry, i.e. chemistry with superbuly cyclopentadienyl ligands.