



Account/Revue

## Discrete allyl complexes of group 3 metals and lanthanides

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## ABSTRACT

Allyl complexes based on group IIIb metals (Sc, Y, La) and lanthanides are reviewed. The diversity, synthesis, and main structural and reactivity features of discrete, well-defined homoleptic and pseudo-homoleptic neutral, anionic and cationic bis-, tris- and tetra(allyl)-lanthanide complexes, as well as heteroleptic allyl-lanthanidocenes and allyl-lanthanide complexes supported by non-Cp ligands are covered. Brief comments on the catalytic performances of some key compounds in polymerization processes are also provided.

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## 1. Introduction

Allyl-lanthanide complexes are compounds of fundamental interest, notably due to their intermediacy in a number of important catalytic processes. This class of compounds has been studied since the 1960s but “simple” compounds have remained elusive for a long time. For instance, homoleptic tris( $\eta^3$ -allyl)-lanthanide complexes, which have remained as other homoleptic tris(alkyl)-lanthanides over the years one major challenge in organolanthanide chemistry, were unknown until the late 1990s. In fact, the chemistry of allyl-lanthanide complexes has made significant progress in recent years in terms of preparative results as well as of applications in organic synthesis and catalysis. The aim of this short review article is to outline general trends around discrete, well-defined allyl-lanthanide complexes<sup>1</sup> in terms of compounds

diversity, synthetic procedures and main structural and reactivity features.<sup>2</sup> Brief comments on the catalytic performances of some key compounds in polymerization processes are also provided.

## 2. Allyl-lanthanide complexes: simple homoleptic and pseudo-homoleptic neutral, “ate” and cationic complexes

## 2.1. Synthesis, reactivity and structural features of unsubstituted allyl complexes

The synthesis of homoleptic and pseudo-homoleptic neutral tris(allyl)-lanthanide, anionic “ate” tetrakis(allyl)-lanthanide and cationic allyl-lanthanide complexes was essentially stimulated from the very beginning by the valuable performance of some mixed rare earth-based systems in the stereoselective polymerization of conjugated dienes and the assumed intermediacy of allyl-lanthanide species in those processes (*vide infra*, section 2.1). Early works focused accordingly on the isolation of putative active species or on the synthesis of model complexes.

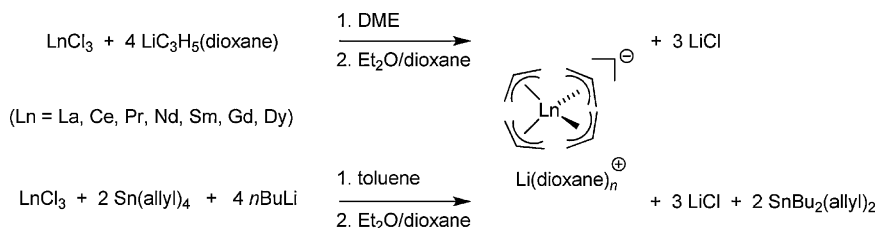
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(J.-F. Carpentier).

<sup>1</sup> Only well-defined allyl-lanthanide complexes are included in this review, which is not aimed to be fully comprehensive; accordingly, special focus is given onto structurally (or spectroscopically for the very first compounds) characterized complexes. Also, only regular allyl ligands are addressed. Thus, heteroallyl ligands such azaallyls or diphosphino-methanides are not included in this manuscript.

<sup>2</sup> For general reviews in organolanthanide chemistry, with highlights on allyl-lanthanide complexes, see [1].

Scheme 1. Preparation of  $[\text{Li}(1,4\text{-dioxane})_n][\text{Ln}(\text{allyl})_4]$  “ate” complexes [2,3,5].

The first reports on homoleptic “ate” tetra(allyl)-lanthanide complexes appeared in the 1980s. Mazzei and Lugli prepared  $[\text{Li}(1,4\text{-dioxane})_n][\text{Ln}(\text{allyl})_4]$  ( $\text{Ln} = \text{Ce, Pr, Nd, Sm, Gd, Dy}$ ;  $n = 2$ ) complexes from the reaction of  $\text{LnCl}_3$  and 4 equiv. of allyllithium (Scheme 1) [2,3]. Those compounds were characterized spectroscopically, in particular by variable temperature NMR studies that evidenced the dynamic behavior of these species in solution. At the same time, but using five equiv. of allyllithium, Wu et al. reported the synthesis of  $[\text{Li}_2(\mu\text{-C}_3\text{H}_5)(1,4\text{-dioxane})_n][\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_4]$  complexes ( $\text{Ln} = \text{Ce, Nd, Sm, Gd, Dy, Ho, Er}$ ;  $n = 1, 3$ ), of which the cerium congener constituted the first structurally characterized example of this type of anionic allyl-lanthanide complexes [4]. Using an analogous synthetic procedure involving the *in situ* preparation of the allyllithium reagent from tetraallyltin and *n*-butyllithium, Taube and Schumann prepared  $[\text{Li}(1,4\text{-dioxane})_{1.5}][\text{La}(\eta^3\text{-C}_3\text{H}_5)_4]$  (Scheme 1), which was also characterized in the solid state by single-crystal X-ray diffraction studies [5]. The structure of this compound features a pair of discrete ions, with the La center in the anion coordinated in a strongly distorted tetrahedral environment (range of C–La–C bond angles involving the central C atom of each allyl group:  $78.7\text{--}133.4^\circ$ ) by four  $\eta^3$ -bonded allyl groups (range of La–C bond distances involving all C atoms of the allyl groups:  $2.722(9)\text{--}2.84(1) \text{ \AA}$ ).

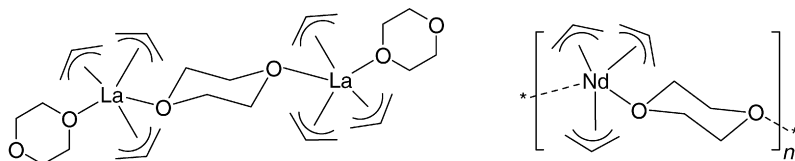
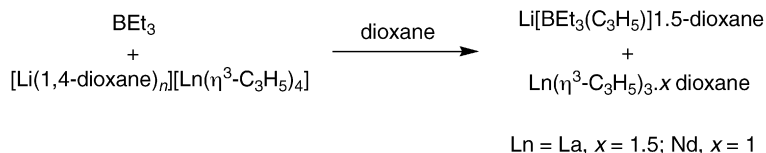
A significant breakthrough in this chemistry came from the group of Taube who disclosed an effective entry toward homoleptic neutral tris(allyl)-lanthanide complexes. A first route involves allyllithium abstraction of  $[\text{Li}(1,4\text{-dioxane})_n][\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_4]$  ( $\text{Ln} = \text{La or Nd}$ ) with  $\text{BET}_3$  as the Lewis acidic acceptor, in dioxane, affording  $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_3 \cdot x \text{ dioxane}]_n$  ( $\text{Ln} = \text{La}$ ,  $x = 1.5$ ;  $\text{Ln} = \text{Nd}$ ,  $x = 1$ ) in 60–70% yield

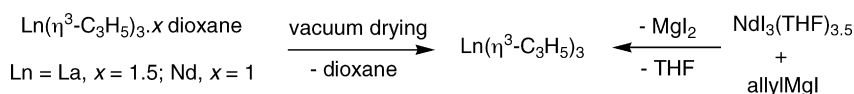
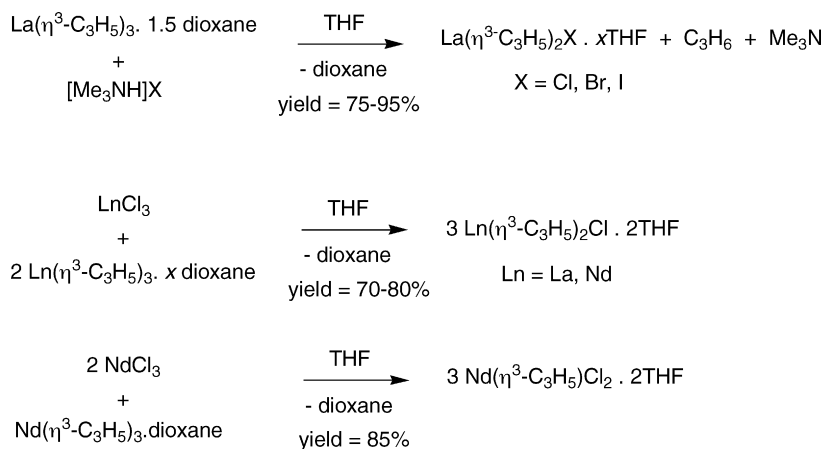
(Scheme 2) [6]. As revealed by NMR and X-ray crystal structure analyses, in both complexes, the three allyl anions are  $\eta^3$ -coordinated. In the solid state, the lanthanum compound features a dimeric structure,  $[\{\text{La}(\eta^3\text{-C}_3\text{H}_5)_3(\eta^1\text{-}1,4\text{-dioxane})\}_2(\mu\text{-}1,4\text{-dioxane})]$ , due to the bridging coordination mode of one dioxane molecule, while the same phenomenon induced a polymeric structure for the neodymium complex,  $[\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_3(\mu\text{-}1,4\text{-dioxane})]_\infty$ .

The dioxane molecules can easily be removed from these complexes at  $50^\circ\text{C}$  without further decomposition to give the corresponding unsolvated tris(allyl) complexes  $\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_3$  ( $\text{Ln} = \text{La or Nd}$ ) (Scheme 3) [6]. In the presence of THF, DME or dioxane, they form the corresponding solvates again. This series of neutral tris(allyl)s, as well as the anionic allyl-lanthanum complexes, has been studied by  $^{139}\text{La}$  NMR spectroscopy. Typical ranges of the chemical shifts were found for the different types of complex independent of the number and the nature kind of organic groups directly bonded to lanthanum [7].

Another straightforward preparation of the dioxane adduct of tris(allyl)neodymium involves the reaction of  $\text{NdI}_3(\text{THF})_{3.5}$  with three equiv. of  $\text{C}_3\text{H}_5\text{MgBr}$  (or allylmagnesium iodide) in THF, followed by recrystallization from dioxane. This procedure affords the halide-free product in more than 70% yield [8]. Vacuum drying further affords the unsolvated  $\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_3$  (Scheme 3).

The dimeric molecular structure of  $(\mu\text{-dioxane})[\text{La}(\eta^3\text{-C}_3\text{H}_5)_3(\text{dioxane})]_2$  can be broken up into monomeric units by addition of hexamethylphosphoramide (HMPA) or chelating ligands such as 1,2-dimethoxyethane (DME) or tetramethylethylenediamine (TMEDA). The mononuclear nature of  $\text{La}(\eta^3\text{-C}_3\text{H}_5)_3(\text{TMEDA})$  was confirmed by a single-crystal X-ray structure analysis [9].

Scheme 2. Synthesis and structure of homoleptic neutral  $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_3 \cdot x \text{ dioxane}]_n$  complexes [6].

Scheme 3. Synthesis of unsolvated homoleptic  $\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_3$  complexes [6,8].

Scheme 4. Synthesis of neutral bis- and mono(allyl)-lanthanide halides [10,11].

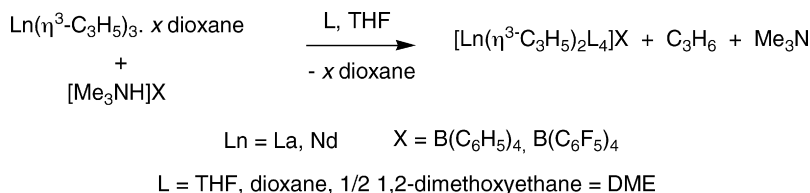
The solvated tris(allyl)lanthanide complexes serve as a source toward neutral bis- and mono(allyl)-lanthanide halides, either by partial protolysis with trimethylammonium halides as the Brønsted acid or by comproportionation with the lanthanide trichloride in the corresponding 2:1 and 1:2 molar ratio, respectively (Scheme 4) [10,11]. The structures of the bis(allyl)-lanthanide chloride complexes  $[\{\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_2\text{Cl}(\text{THF})_2\}_2]$  (Ln = La, Nd) were determined to be dimeric in the solid state, via  $\mu$ -bridging chloride ligands.

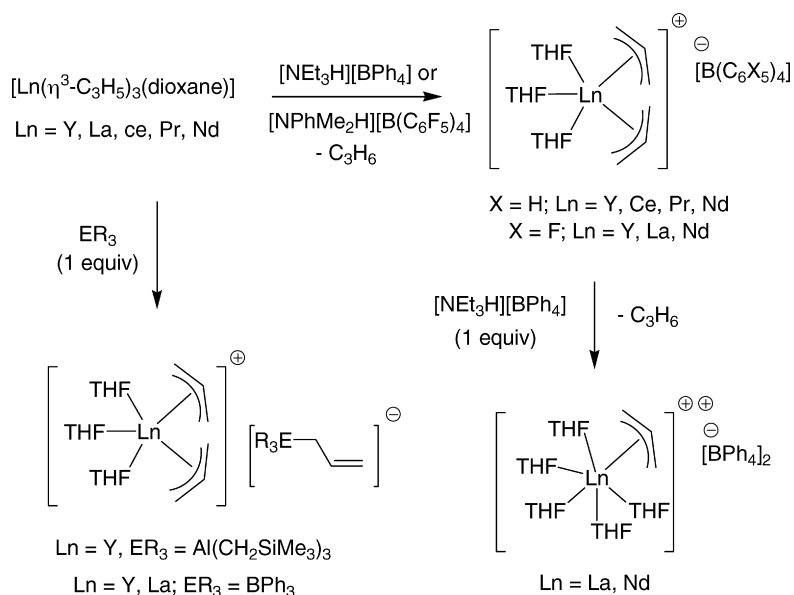
The group of Taube further demonstrated that these solvate tris(allyl)lanthanide complexes are also valuable precursors for the synthesis of cationic bis(allyl)-lanthanide derivatives  $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_2\text{L}_4]\text{X}$  (X = B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>, B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>). The preparation involves partial protolysis with trimethylammonium salts of the tetrakis(phenyl)- or tetrakis(pentafluorophenyl)borate anion as “non”-coordinating counteranion, in proper donor solvents (L) (Scheme 5) [8,12]. A set of such compounds was fully characterized and single-crystal structures were obtained for the lanthanum complexes. The latter compounds exist in the solid state as well-separated ion pairs, with the lanthanum center in the cation coordinated by two  $\eta^3$ -allyl groups and four  $\eta^1$ -THF ligands.

Very recently, Okuda et al. reported the synthesis and comprehensive structural characterization of a series of

mono- and dicationic allyl complexes [13]. Monocationic bis(allyl) complexes  $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_2(\text{THF})_3][\text{B}(\text{C}_6\text{X}_5)_4]$  (Ln = Y, La, Nd; X = H, F) and dicationic mono(allyl) complexes of yttrium and the early lanthanides  $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)(\text{thf})_6][\text{BPh}_4]_2$  (Ln = La, Nd) were prepared by protolysis of the trisallyl complexes  $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_3(\text{dioxane})]$  (Ln = Y, La, Ce, Pr, Nd, Sm), which were isolated and structurally characterized as a 1,4-dioxane bridged dimer (Ln = Ce) or THF adducts  $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_3(\text{THF})_2]$  (Ln = Ce, Pr) (Scheme 6). Allyl abstraction from the neutral tris(allyl) complex by a Lewis acid, ER<sub>3</sub> (Al(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>, BPh<sub>3</sub>) gave the ion pair  $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_2(\text{THF})_3][\text{ER}_3(\eta^1\text{-CH}_2\text{CH}=\text{CH}_2)]$  (Ln = Y, La). Also, it was found that benzophenone inserts into the La–C(allyl) bond of  $[\text{La}(\eta^3\text{-C}_3\text{H}_5)_2(\text{THF})_3][\text{BPh}_4]$  to form the alkoxy complex  $[\text{La}\{\text{OCPh}_2(\text{CH}_2\text{CH}=\text{CH}_2)\}_2(\text{THF})_3][\text{BPh}_4]$ .

Another interesting contribution, considering the possible relevance of the prepared complexes to Ziegler-Natta polymerization catalysis, came from Wu et al. [14]. They prepared a series of mixed halide-allyl-lanthanide-magnesium complexes,  $(\eta^3\text{-C}_3\text{H}_5)_2\text{LnX}_5\text{Mg}_2(\text{Et}_2\text{O})$  and  $(\eta^3\text{-C}_3\text{H}_5)_2\text{LnX}_5\text{Mg}_2(\text{TMEDA})$  (Ln = La, Ce, Pr, Nd, Sm; X = Cl, Br), by the reaction of anhydrous LnCl<sub>3</sub> with allyl Grignard reagents in diethylether, or in THF in the presence of TMEDA (Scheme 7). The preparation of such complexes was further extended to Y, La and Nd derivatives with THF

Scheme 5. Synthesis of cationic bis(allyl)-lanthanide derivatives  $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_2\text{L}_4]\text{X}$  [12].



Scheme 6. Synthesis of monocationic bis(allyl)- and dicationic mono(allyl)-lanthanide derivatives [13].

ligands [15]. Because in some cases, lanthanide trischlorides and allyl-magnesium bromide were used, compounds having both Cl and Br were obtained, making X-ray diffraction studies somewhat complicated [14]. The determination of the solid-state structure of three of such compounds established that they all have triangular metallic (i.e., two Mg and one Ce or Nd) skeletons bonded together by three bridging and two capping halide atoms. The two allyl groups are  $\eta^3$ -bonded to the lanthanide ions. The quite high decomposition temperatures (higher than 160 °C) of these complexes indicated the stabilities of such heteropolymetallic structures.

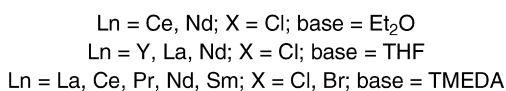
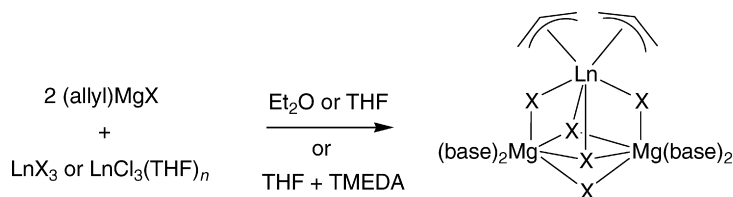
Bochmann et al. showed that the reaction of  $\text{LnI}_3(\text{THF})_n$  ( $\text{Ln} = \text{La}$ ,  $n = 4$ ;  $\text{Ln} = \text{Y}$ ,  $n = 3.5$ ) with three equiv. of allylMgI in THF/1,4-dioxane proceeds in moderate yields to give the unexpected mixed-metal complexes  $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_3(\mu\text{-dioxane})_n\text{Mg}(\eta^1\text{-C}_3\text{H}_5)_2(\mu\text{-dioxane})_{1.5}]_{\infty}$ . The solid-state structures of these compounds contain distorted trigonal-bipyramidal lanthanide centers with three  $\eta^3$ -allyl ligands and distorted trigonal-bipyramidal magnesium centers with two  $\eta^1$ -bonded allyl groups. Both metal

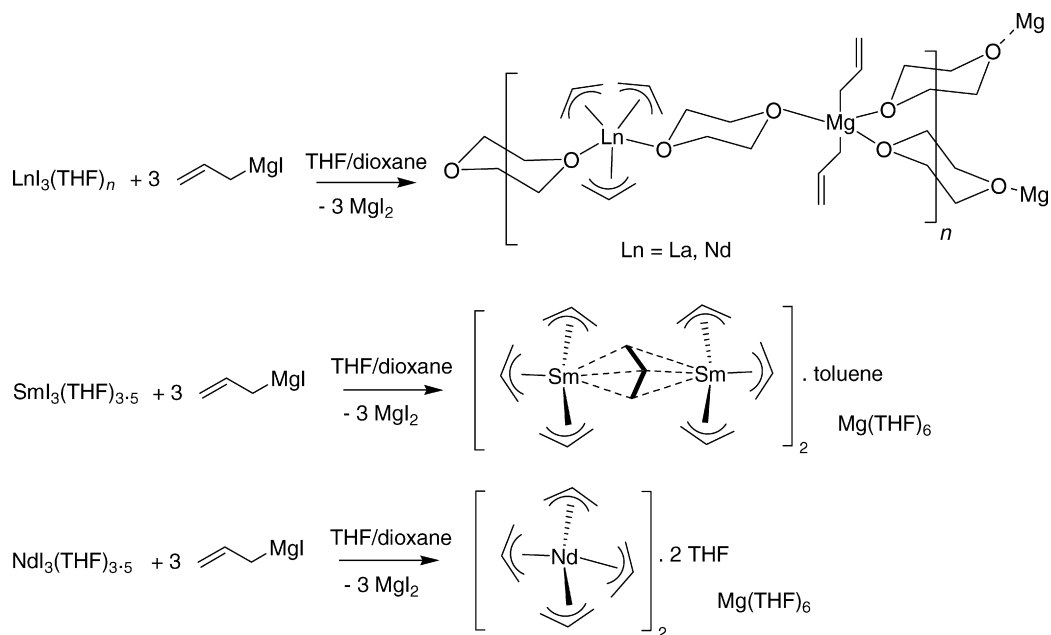
centers are connected by bridging 1,4-dioxane molecules building a planar polymeric network (Scheme 8) [16].

In contrast, samarium(III) iodide gives a salt containing a new allyl-bridged anion,  $[\text{Mg}(\text{THF})_6][\text{Sm}_2(\eta^3\text{-C}_3\text{H}_5)_6(\mu\text{-}\eta^3\text{:}\eta^2\text{-C}_3\text{H}_5)_2\text{.toluene}]$ , while neodymium(III) iodide affords  $[\text{Mg}(\text{THF})_6][\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_4]_2 \cdot 2\text{THF}$  under the same reaction conditions (Scheme 8) [14]. The solid-state structure of the samarium compound consists of well-defined discrete ions, with an unprecedented type of binuclear anion containing two samarium centers bridged by a  $\eta^3\text{:}\eta^3$ -allyl ligand.

## 2.2. Catalytic properties of trivalent homoleptic and pseudo homoleptic allyl-lanthanide complexes in stereospecific diene polymerization

A significant part of synthetic rubber is currently produced by homogeneous catalytic liquid phase stereospecific polymerization of 1,3-dienes (typically butadiene and isoprene) to 1,4-*cis*-polydienes using Ziegler–Natta mixed catalysts based on neodymium precursors, Lewis

Scheme 7. Synthesis of mixed halide-allyl-lanthanide-magnesium complexes ( $\eta^3\text{-C}_3\text{H}_5)_2\text{LnX}_2\text{Mg}_2(\text{base})$  [14,15].



Scheme 8. Preparation of mixed-metal complexes  $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_3(\mu\text{-dioxane}).\text{Mg}(\eta^1\text{-C}_3\text{H}_5)_2(\mu\text{-dioxane})_{1.5}]_n$  complexes [16].

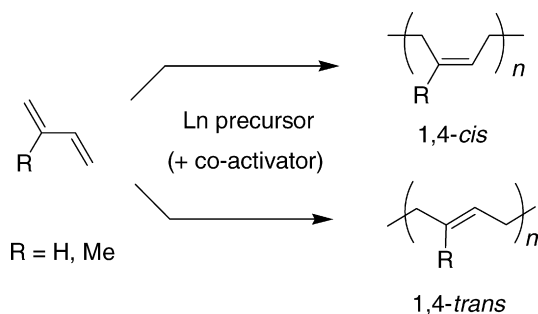
acidic co-catalysts such as  $\text{AlEt}_2\text{Cl}$  and possible other promoters (Scheme 9) [17]. The nature of the active rare-earth-metal species generated from these (binary, ternary and quaternary) systems has been controversial since the early discoveries of their superior performance in these polymerization processes. As mentioned in the introduction, the synthesis and isolation of the putative active species have been a driving force for the preparation of well-defined allyl-lanthanide compounds. The aim of this short section is to give a brief overview of the catalytic performance that the aforementioned different classes of simple allyl-lanthanide compounds feature in stereospecific polymerization of dienes. For more comprehensive studies and detailed comments on mechanistic issues, the readers shall refer to some leading articles [12,17–19].

Anionic and neutral allyl-lanthanide complexes with or without different donor ligands are active homogeneous catalysts for the polymerization of butadiene (BD) (and isoprene) in solution. Usually, these complexes catalyze the *trans*-polymerization of butadiene, while the addition

of Lewis-acidic aluminum organic compounds results in a change of the selectivity to *cis*-polybutadiene. Neodymium-based compounds most often lead to the highest stereoselectivities, as compared to other rare-earths, regardless of the ionic radius (lanthanum, yttrium...). For instance,  $\text{La}(\eta^3\text{-allyl})_3 \cdot 1.5(\text{dioxane})$ ,  $\text{Nd}(\eta^3\text{-allyl})_3 \cdot (\text{dioxane})$  and  $\text{Nd}(\eta^3\text{-allyl})_3$  polymerize butadiene in toluene at  $50^\circ\text{C}$  with turnovers frequencies (TOFs, in  $\text{mol}(\text{BD}) \cdot \text{mol}(\text{Ln})^{-1} \cdot \text{h}^{-1}$ ) of 500, 600, and 1,300, and *trans* selectivities of 83, 94 and 89%, respectively [12]. Obviously, donor ligands act as competitors/inhibitors in the catalytic reaction and also diminish the *cis* selectivity.

Once the tris(allyl)lanthanides are combined with a Lewis acid like  $\text{AlEt}_2\text{Cl}$  or MAO (methylalumoxane) (2–30 equiv. vs Ln), a significant increase in activity and a dramatic reversal in stereoselectivity, to the benefit of the desired 1,4-*cis* polymer, are observed. Thus,  $\text{La}(\eta^3\text{-allyl})_3 \cdot 1.5(\text{dioxane})$  and  $\text{Nd}(\eta^3\text{-allyl})_3 \cdot (\text{dioxane})$  combined with 30 equiv. of MAO give TOFs of 4700 and 14,000  $\text{h}^{-1}$  and *cis* selectivities of 65 and 79%, respectively. Using the bis and mono(allyl)neodymium chloride precursors  $\text{Nd}(\eta^3\text{-allyl})_2\text{Cl} \cdot 1.5(\text{THF})$  and  $\text{Nd}(\eta^3\text{-allyl})\text{Cl}_2 \cdot 2(\text{THF})$ , still combined with 30 equiv. of MAO, afforded even better performances; i.e., TOFs of 575,000 and 570,000  $\text{h}^{-1}$  and *cis* selectivities of 98 and 98%, respectively [12]. Very high performances were also reached with bimetallic precursors of the type  $(\eta^3\text{-allyl})_2\text{NdCl}_5\text{Mg}_2(\text{THF})$  combined with MAO [15]. These results strongly suggested that the active species in the stereoselective polymerization of dienes is a dicationic mono(allyl)-lanthanide fragment, probably stabilized by coordinative interactions with donor atoms of the activator (e.g., heterobridging chloroaluminate ligands) [20].

The cationic bis(allyl)-lanthanide complexes developed by Taube et al. are single-component active catalysts, i.e.,



Scheme 9. Stereospecific polymerization of 1,3-dienes promoted by Ziegler-Natta mixed catalysts.

they do not require any coactivator that can perform a high *cis* selectivity. Thus,  $[\text{Nd}(\eta^3\text{-allyl})_2(\text{dioxane})_4][\text{B}(\text{C}_6\text{F}_5)_4]$  feature, under the same conditions as above, TOF up to  $11,200 \text{ h}^{-1}$  and a *cis* selectivity higher than 90% [12]. On the other hand, no control of the stereoselectivity was observed with the THF complexes  $[\text{Ln}(\eta^3\text{-allyl})_2(\text{THF})_4][\text{B}(\text{C}_6\text{F}_5)_4]$  ( $\text{Ln} = \text{La}, \text{Nd}$ ) (*cis* selectivity = 27–36% and 42–45%, respectively). In addition, comparison of theoretical and experimental molecular weights established that all the lanthanide centers in those compounds are active, and that two polymer chains are formed per lanthanum while a single chain is formed at the neodymium. The authors interpreted those results as a corroboration that the *cis* selectivity in the allyl-lanthanide-catalyzed diene polymerization is structurally determined by the formation and reactivity of a dicationic mono(allyl)-lanthanide species [12]. However, the reaction pathway leading to the latter dicationic mono(allyl) species from the cationic di(allyl) species (in the absence of other activator) was not addressed.

Controlled 1,3-butadiene polymerization was observed using the cationic allyl complexes prepared recently by Okuda et al. [13] (Scheme 6), giving polybutadiene with ca. 90% 1,4-*cis* stereoselectivity. The results further corroborated the assumption of a dicationic rare-earth-metal center in  $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)(s\text{-cis-C}_4\text{H}_6)_2]^{2+}$  as the active site of insertion. Somewhat unexpectedly, the yttrium catalysts were found to be more active than their homologues based on the larger lanthanum and neodymium centers. Narrower molecular weight distributions were achieved by the less active lanthanum and neodymium catalysts.

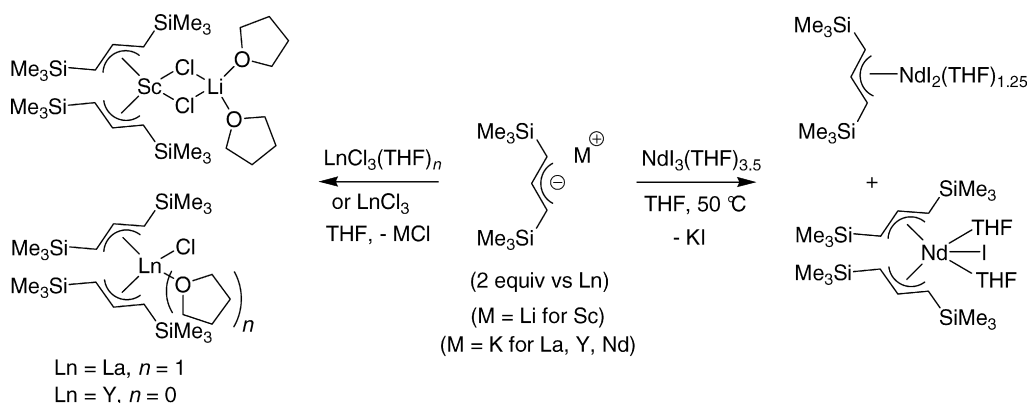
### 2.3. Homoleptic and pseudo-homoleptic neutral lanthanide complexes bearing silyl-substituted allyl ligands

Studies on the coordination of silyl-substituted allyl groups, typically 1,3-bis(trimethylsilyl) allyl, onto lanthanide metal centers arose from two main expectations: First, it is known that the application of such ligand imparts additional thermal stability relative to the parent transition metals complexes. Furthermore, the confirmed ability of 1,3-bis(trimethylsilyl) allyl to adopt a  $\sigma$  geometry is in line with the potential for  $\sigma/\pi$  interconversion of the

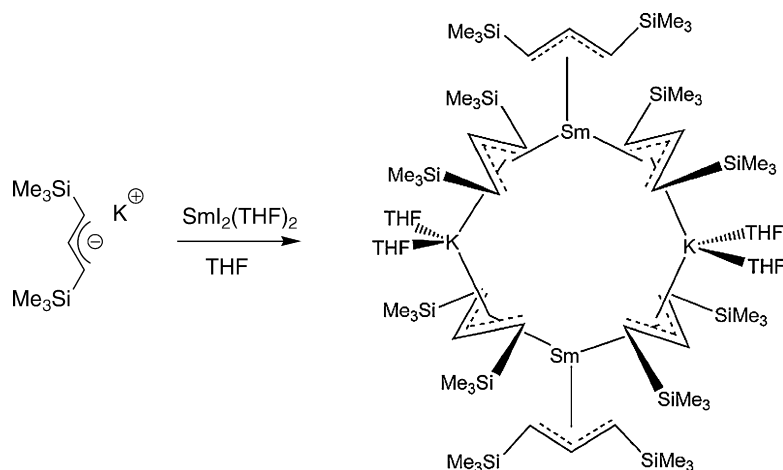
parent allyl moiety to open up coordination sites for catalytic reactions.

The group of Bochmann intensively investigated the preparation of lanthanide complexes supported by allyl ligands having trisalkylsilyl substituents at diverse positions. As for their unsubstituted analogues, those complexes were usually prepared by direct salt metathesis reactions of the adequate allyl anion (as the potassium salt) with trishalide precursors  $\text{LnX}_3(\text{THF})_n$  or  $\text{LnX}_3$  in THF. The nature of the final compound(s) recovered in these reactions varied considerably according to the nature of the lanthanide precursor. Thus, the reaction of trichloride group 3 metal precursors ( $\text{Ln} = \text{Sc}, \text{Y}, \text{La}$ ) with two equiv. of the bulky 1,3-bis(trimethylsilyl)allyl anion,  $[\text{1,3-C}_3\text{H}_3(\text{SiMe}_3)_2]^-$ , yielded the corresponding bis(allyl) compounds (Scheme 9). “Ate” or neutral mononuclear complexes, with a variable number of THF donor ligands, were obtained according to the nature of the metal center [21]. A similar reaction with  $\text{NdI}_3(\text{THF})_{3.5}$  yielded a mixture of the mono(allyl) and bis(allyl) iodide complexes (Scheme 10) [22]. The latter complex adopts in the solid state a distorted trigonal-bipyramidal structure with the THF ligands in *trans* position.

The analogous reaction of  $[\text{1,3-C}_3\text{H}_3(\text{SiMe}_3)_2]^-$  with  $\text{SmI}_2(\text{THF})_2$  proceeded to give a dark green solution from which a compound of composition  $\text{KSm}(\text{C}_3\text{H}_3(\text{SiMe}_3)_2)_3(\text{THF})_2$  was isolated. Single-crystal X-ray diffraction showed that this compound is the allyl-bridged dimer  $[\text{Sm}(\eta^3\text{-1,3-C}_3\text{H}_3(\text{SiMe}_3)_2)_3\{\mu\text{-K}(\text{THF})_2\}]_2$  (the first structurally authenticated Sm(II) allyl complex), which possesses a cyclic structure, comprising two samarium and two potassium ions bridged by four  $\eta^3$ -allyl ligands (Scheme 11) [23]. Interestingly, the addition of THF- $d_8$  to a toluene solution of this compound had very little effect on the NMR spectra, suggesting that the cyclic structure is maintained in solution.  $[\text{Sm}(\eta^3\text{-1,3-C}_3\text{H}_3(\text{SiMe}_3)_2)_3\{\mu\text{-K}(\text{THF})_2\}]_2$  is an highly effective single-component catalyst for the polymerization of methyl methacrylate (TOFs >  $80,000 \text{ mol}(\text{MMA})\cdot\text{mol}(\text{Ln})^{-1} \text{ h}^{-1}$  at  $0^\circ\text{C}$ ) and of  $\epsilon$ -caprolactone (TOFs >  $58,000 \text{ h}^{-1}$  at  $20^\circ\text{C}$ ) (the bis(allyl) iodide complex  $[\text{Nd}(\eta^3\text{-1,3-C}_3\text{H}_3(\text{SiMe}_3)_2)_2(\text{THF})_2]$  is also highly active in this process), producing high molecular weights polymers with relatively narrow molecular weight distributions.



Scheme 10. Synthesis of silylated allyl-lanthanide-halide complexes [21,22].



Scheme 11. Synthesis of  $[\text{Sm}(\eta^3\text{-}1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2)_3\{\mu\text{-K}(\text{THF})_2\}_2]$  [23].

Note that earlier, Ihara et al. reported samarium(II) complexes formulated as  $(1,3\text{-C}_3\text{H}_3\text{R}_2)_2\text{Sm}(\text{THF})_2$  ( $\text{R} = \text{Ph}$ ,  $\text{SiMe}_3$ ), obtained by reaction of  $\text{K}\{1,3\text{-C}_3\text{H}_3\text{R}_2\}$  with  $\text{SmI}_2(\text{THF})_2$  [24]. However, these compounds were not fully characterized and did not show the same catalytic reactivity towards methyl methacrylate than the aforementioned  $\text{Sm}\text{-K}$ -allyl complex.

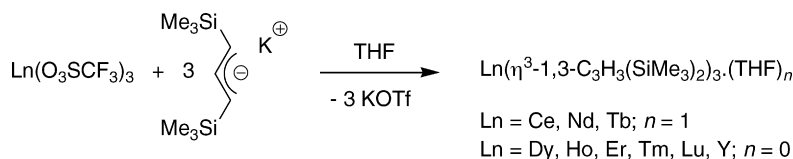
All attempts to obtain halide-free products and generate neutral homoleptic tris(allyl) complexes of the type  $\text{Ln}\{1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2\}_3$  from  $\text{LnX}_3$  failed (e.g.,  $\text{Ln} = \text{La}$ ,  $\text{Y}$ ;  $\text{X} = \text{Cl}$ , [23]). For instance, Kuehl et al. isolated allyl-lanthanide salts of the type  $[\text{K}(\text{THF})_4][\{\eta^3\text{-}1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2\}_3\text{LnI}]$  ( $\text{Ln} = \text{Ce}$ ,  $\text{Pr}$ ,  $\text{Nd}$ ,  $\text{Gd}$ ,  $\text{Tb}$ ,  $\text{Dy}$ ,  $\text{Er}$ ) by reaction of three equiv. of  $\text{K}\{1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2\}$  with  $\text{LnI}_3$  in THF [25]. Similarly, when lanthanide trisiodides and the lithium allyl  $\text{Li}\{1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2\}$  were combined, the corresponding lanthanate species  $[\text{Li}(\text{THF})_4][\{\eta^3\text{-}1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2\}_3\text{LnI}]$  were formed [26]. The former cerium(III), terbium(III) and erbium(III) congeners were characterized by X-ray diffraction studies and found to be isostructural. In these three complexes, all three allyl ligands are bonded to the lanthanide center in a trihapto, slightly asymmetric fashion, with the  $\text{SiMe}_3$  groups from all three allyl ligands in a *syn,syn* configuration. These authors also observed that the reaction of four equiv. of  $\text{K}\{1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2\}$  with  $\text{LnI}_3$  does not lead to  $[\text{K}(\text{THF})_x][\{1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2\}_4\text{Ln}]$  (which could have been precursors toward homoleptic neutral tris(allyl) complex by allyl lithium abstraction following Taube's procedure [6], *vide supra*), but only  $[\text{K}(\text{THF})_4][\{1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2\}_3\text{LnI}]$  and excess  $\text{K}\{1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2\}$  were obtained.

Successful preparation of neutral homoleptic complexes bearing silylated-allyl ligands was achieved using

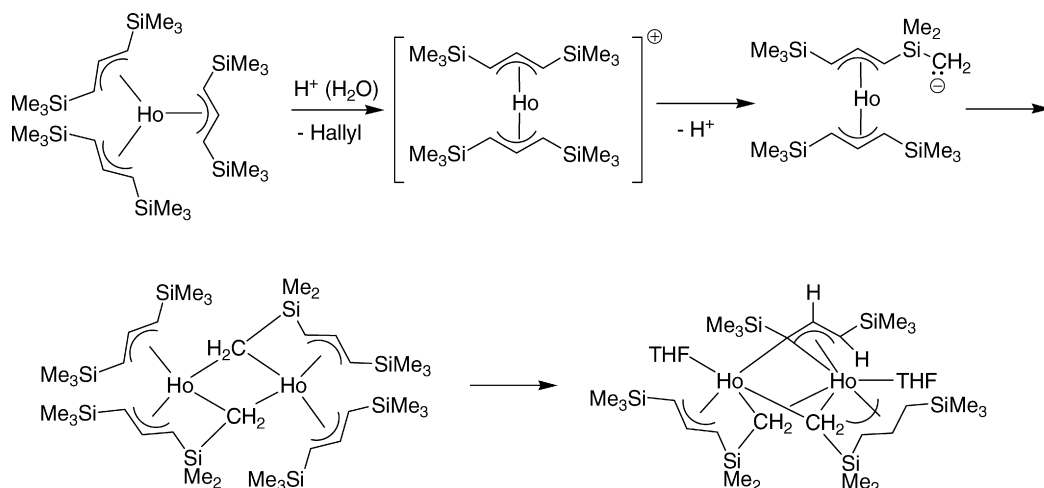
triflate salts. Hence, a series of complexes  $\{1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2\}_3\text{Ln}(\text{THF})_n$  could be isolated in moderate yields from the reaction of rigorously anhydrous  $\text{Ln}(\text{O}_3\text{SCF}_3)_3$  with three equiv. of the 1,3-bis(trimethylsilyl)allyl anion (Scheme 12) [25,26].

Thanks to a significant number of crystal structures obtained in the studies mentioned above, trends in the bonding of lanthanide allyl complexes with the 1,3-bis(trimethylsilylated)allyl ligand could be explored and compared with those of cyclopentadienyl lanthanide complexes [26]. It was concluded that despite the geometrically irregular shape of the substituted allyl anion, metal–ligand distances in monomeric lanthanide allyl complexes appear to be reasonably predictable based on metal radius and oxidation state. This is an expected consequence of a high degree of ionic character in the bonding.

Traces of coordinated water in holmium triflate proved to have a major influence in the fate of reactions with the 1,3-bis(trimethylsilyl)allyl anion (Scheme 13); this eventually leads to the unexpected generation of dimethylsilylene and allylidene holmium complexes [27]. It was found that, even long vacuum-dried,  $\text{Ho}(\text{O}_3\text{SCF}_3)_3$  may retain up to ca. 3% of water that induces the formation of a complex isolated in 74% yield, which is quite different from the expected homoleptic tris(allyl) compound. An X-ray diffraction study revealed a dimer in which one  $\eta^3$ -coordinated allyl ligand is bound to each metal, but hydrogen abstraction from a trimethylsilyl group had occurred on a second allyl ligand associated with each metal center, forming dimethylsilylene units that bridge the holmium atoms (Scheme 13). When the reaction that produced the dimeric dimethylsilylene complex was



Scheme 12. Synthesis of neutral homoleptic complexes  $\{1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2\}_3\text{Ln}(\text{THF})_n$  [25,26].



Scheme 13. Decomposition pathway of the tris(silylated allyl)holmium complex [27].

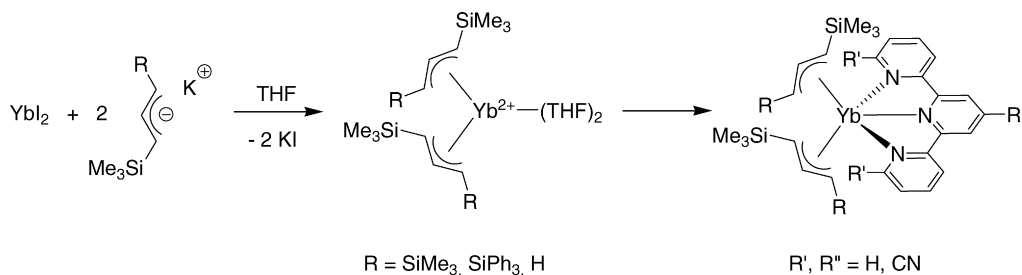
prolonged for more than 20 h before workup, a second yellow-orange dinuclear product was isolated. The X-ray structure analysis revealed that, in addition to two dimethylsilylene bridges, the metal centers are joined with a  $\mu$ - $\eta^1, \eta^3$ -allylidene ligand (Scheme 13). This study clearly showed that trimethylsilyl groups on allyl ligands cannot always be assumed to be completely unreactive in f-element complexes.

Salt metathesis of silylated allyl anions with  $\text{YbI}_2$  afforded the corresponding homoleptic bis(allyl)-ytterbium complexes as THF solvates. These were subsequently reacted with a series of bulky terpyridines to determine the effect of allyl ligands on the internal charge-transfer process that exists in these terpyridyl-bis(allyl) complexes (Scheme 14) [28]. Single-crystal X-ray characterization of  $[\eta^3\text{-}1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2]_2\text{Yb}(\text{tpy})$  revealed that the allyl moiety possesses shorter Yb–C and Yb–N bond lengths than the  $\text{Cp}^*$  analogue. The magnetic susceptibility data for  $[\eta^3\text{-}1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2]_2\text{Yb}(\text{tpy})$  departs dramatically from the Curie law, with a room-temperature magnetic moment of 2.95  $\mu\text{B}$ .

In contrast to mono(allyl) ligands, the *ansa*-bis(allyl) ligand  $\{\text{Me}_2\text{Si}(\text{CHCHCHSiMe}_3)_2\}^{2-}$  readily gives halide-free compounds. Thus, the reactions of lanthanide trisilides with an equimolar amount of the dipotassium salt  $\text{K}_2\{3\text{-}(\text{C}_3\text{H}_3\text{-SiMe}_3\text{-}1)_2\text{SiMe}_2\}$  in THF lead to the formation of the

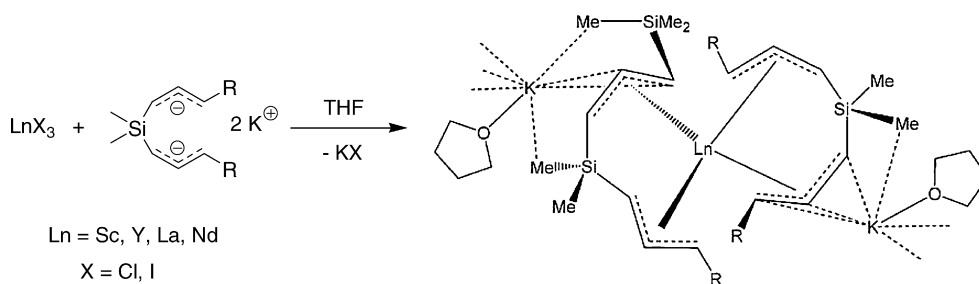
*ansa*-bis(allyl)-lanthanide “ate” complexes  $[\text{Ln}\{3\text{-}(\eta^3\text{-}1\text{-C}_3\text{H}_3\text{SiMe}_3)_2\text{SiMe}_2\}_2\text{-}\{\mu\text{-K}(\text{THF})\}\cdot(\text{THF})_n]_\infty$  ( $\text{Ln} = \text{La}, n = 0.5$ ;  $\text{Sc}, \text{Y}, n = 1$ ) (Scheme 15) [29]. These compounds are highly effective single-component catalysts for the polymerization of methyl methacrylate (TOFs > 80,000 mol (MMA).mol(Ln) $^{-1}$  h $^{-1}$  at 0 °C), producing high molecular weights polymers with relatively narrow molecular weight distributions.

An X-ray diffraction study on the lanthanum complex revealed that each lanthanum atom is coordinated to two *ansa*-bis(allyl) ligands, both of which bind to the metal in a  $\eta^3$  fashion. The coordination environment of the lanthanum consists of 12 carbon atoms, with La–C bond lengths (2.769(3)–2.902(3) Å) similar to those observed in the related unsubstituted lanthanum complex  $[\text{Li}(1,4\text{-dioxane})_{1.5}][\text{La}(\eta^3\text{-C}_3\text{H}_5)_4]$  (2.721–2.842 Å) [5] and slightly larger than those observed in the neutral complex  $[\{\text{La}(\eta^3\text{-C}_3\text{H}_5)_3(\eta^1\text{-}1,4\text{-dioxane})\}_2(\mu\text{-}1,4\text{-dioxane})]$  (2.751(3) to 2.829(5) Å) [6]. The allyl ligands adopt an *anti,syn* arrangement and feature bond lengths very similar to the aforementioned unsubstituted allyl compounds. A potassium cation, that balances the charge of the tetra(allyl)-lanthanide “ate” moiety, is coordinated to two allyl moieties of two different lanthanum atoms, resulting in the formation of a coordination polymer with infinite chain structure. This potassium ion binds one THF ligand and

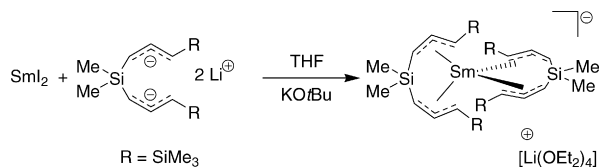


Scheme 14. Synthesis of terpyridyl-bis(silylated-allyl)ytterbium(II) complexes [28].





**Scheme 15.** Synthesis of *ansa*-bis(allyl)-lanthanide “ate” complexes  $[\text{Ln}\{3\text{-}(\eta^3\text{-1-C}_3\text{H}_3\text{SiMe}_3\text{)}_2\text{SiMe}_2\text{]}_2\{\mu\text{-K(THF)}\}\cdot(\text{THF})_n\}_\infty$  [29].



**Scheme 16.** Formation of samarium(III) complex  $[\text{Li(OEt}_2\text{)}_4][\text{Sm}\{3\text{-}(\eta^3\text{-1-C}_3\text{H}_3\text{SiMe}_3\text{)}_2\text{SiMe}_2\text{]}_2$  [29].

features as well complex bonding interactions with the allyl ligands and close  $\text{K}\cdots\text{CH}_3\text{Si}$  contacts.

Although X-ray quality crystals for the analogous Sc and Y complexes were not obtained, all other methods of analysis suggested they have a structure closely similar to that of the lanthanum compound [29]. Also, similar reaction of  $\text{K}_2\{3\text{-}(1\text{-C}_3\text{H}_3\text{SiMe}_3\text{)}_2\text{SiMe}_2\}$  with  $\text{NdI}_3(\text{THF})_{3.5}$  and subsequent recrystallization from toluene afforded the polymeric complex  $[\text{Nd}\{\eta^3\text{-C}_3\text{H}_3\text{SiMe}_3\text{)}_2\text{SiMe}_2]_2\{\mu\text{-K(THF)}\}(\text{THF})(\text{toluene})_\infty$ , which can be transformed upon drying under vacuum into the solvent-free coordination polymer  $[\text{Nd}\{3\text{-}(\eta^3\text{-1-C}_3\text{H}_3\text{SiMe}_3\text{)}_2\text{SiMe}_2\text{]}_2\{\mu\text{-K}\}]_\infty$ .

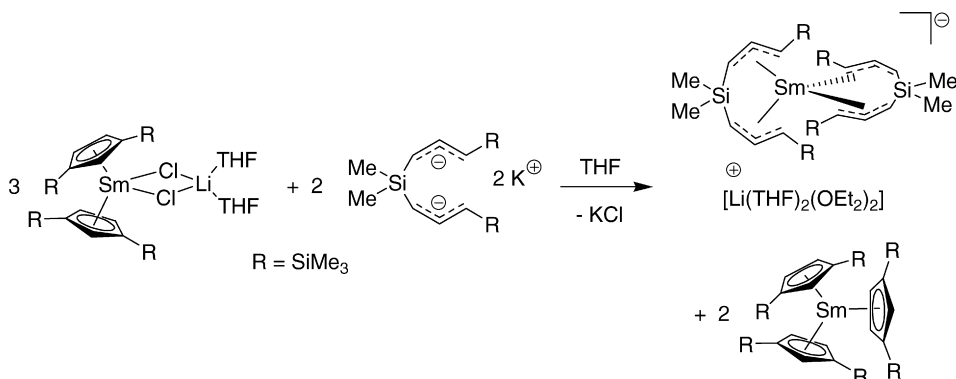
On the other hand, treatment of  $\text{SmI}_2(\text{THF})_2$  with  $\text{Li}_2\{3\text{-}(1\text{-C}_3\text{H}_3\text{SiMe}_3\text{)}_2\text{SiMe}_2\}/\text{KOtBu}$  afforded, in small yield, the samarium(III) complex  $[\text{Li(OEt}_2\text{)}_4][\text{Sm}\{3\text{-}(\eta^3\text{-1-C}_3\text{H}_3\text{SiMe}_3\text{)}_2\text{SiMe}_2\text{]}_2$ ; this one shows up in the crystal structure as discrete ions, with no close interionic contacts (Scheme 16) [29]. Apparently, the lithium salt crystallized more easily and this change in the nature of the alkali cation accounts for the formation of a non-polymeric complex. The arrangement of the allyl ligands around the samarium

atom ion in this compound is closely similar to that observed in the polymeric lanthanum complex, with the same *anti,syn* conformation.

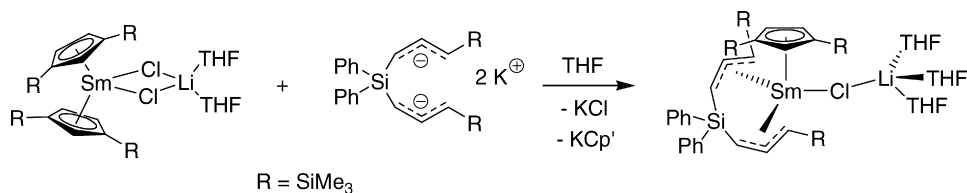
#### 2.4. Towards allyl-lanthanidocenes

Installation of such *ansa*-bis(silylated allyl) ligands into lanthanidocenes proved to be difficult. The reaction of  $\text{Cp}'_2\text{LnCl}_2\text{Li}(\text{THF})_2$  ( $\text{Cp}' = 1,3\text{-C}_5\text{H}_3(\text{SiMe}_3)_2$ ;  $\text{Ln} = \text{Y}$  or  $\text{Sm}$ ) with  $\text{K}_2\{3\text{-}(1\text{-C}_3\text{H}_3\text{SiMe}_3\text{)}_2\text{SiMe}_2\}$  in THF leads, upon workup (crystallization from diethyl ether), to ligand redistribution, to give  $[\text{Li(OEt}_2\text{)}(\text{THF})_3][\text{Ln}\{3\text{-}(\eta^3\text{-1-C}_3\text{H}_3\text{SiMe}_3\text{)}_2\text{SiMe}_2\text{]}_2]$  (Scheme 17) [22]. The latter yttrium compound was characterized by X-ray single crystal diffraction, which revealed a structure close to that observed for the above-mentioned samarium(III) complex  $[\text{Li(OEt}_2\text{)}_4][\text{Sm}\{3\text{-}(\eta^3\text{-1-C}_3\text{H}_3\text{SiMe}_3\text{)}_2\text{SiMe}_2\text{]}_2$ , with the same *anti,syn* arrangement of the *ansa*-bis(allyl) ligands around the metal [29]. Ligand redistribution was also encountered in the reaction of  $\text{Cp}'_2\text{YCl}_2\text{Li}(\text{THF})_2$  with  $\text{K}_2\{3\text{-}(1\text{-C}_3\text{H}_3\text{SiMe}_3\text{)}_2\text{SiPh}_2\}$ . In this case, a potassium atom was retained as the counteranion, even in the presence of lithium cations, to afford the polymeric complex  $[\text{Y}\{3\text{-}(\eta^3\text{-1-C}_3\text{H}_3\text{SiMe}_3\text{)}_2\text{SiPh}_2\text{]}_2\{\mu\text{-K}\}(\text{THF})_{0.5}(\text{Et}_2\text{O})_{1.5}]_\infty$  [22].

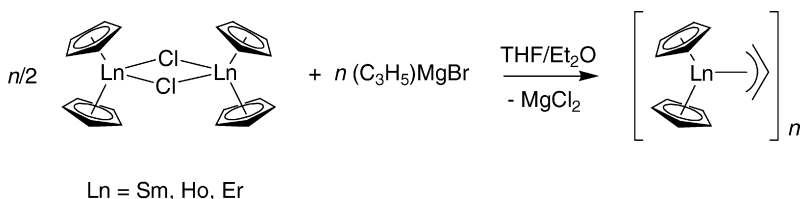
Only in the reaction of  $\text{Cp}'_2\text{SmCl}_2\text{Li}(\text{THF})_2$  and  $\text{K}_2\{3\text{-}(1\text{-C}_3\text{H}_3\text{SiMe}_3\text{)}_2\text{SiPh}_2\}$ , a red crystalline solid was isolated, which was authenticated by NMR and single-crystal X-ray analysis as the heteroleptic mono-Cp complex  $[\text{Cp}'\{3\text{-}(\eta^3\text{-1-C}_3\text{H}_3\text{SiMe}_3\text{)}_2\text{SiMe}_2\text{]}_2(\mu\text{-Cl})\text{Li}(\text{THF})_3]$  (Scheme 18) [22]. The formation of this compound is an unusual example of the displacement of a cyclopentadienyl ligand while a



**Scheme 17.** Ligand redistribution processes in reaction of chlorolanthanidocenes with bis(silylated allyl) dianion [22].



Scheme 18. Preparation of a silylated bis(allyl)-samarocene complex [22].



Scheme 19. Synthesis of allyl-lanthanidocenes [30].

chloride ligand has been retained, a phenomenon which was proposed to arise from the steric congestion at the lanthanide center. Again, as in other *ansa*-allyl complexes, the allyl ligand in this heteroleptic compound adopts an *anti,syn* configuration, with bond lengths very similar to those observed in related samarium(III)-allyl complexes.

### 3. Allyl-lanthanidocenes and cyclopentadienyl-supported allyl-lanthanides

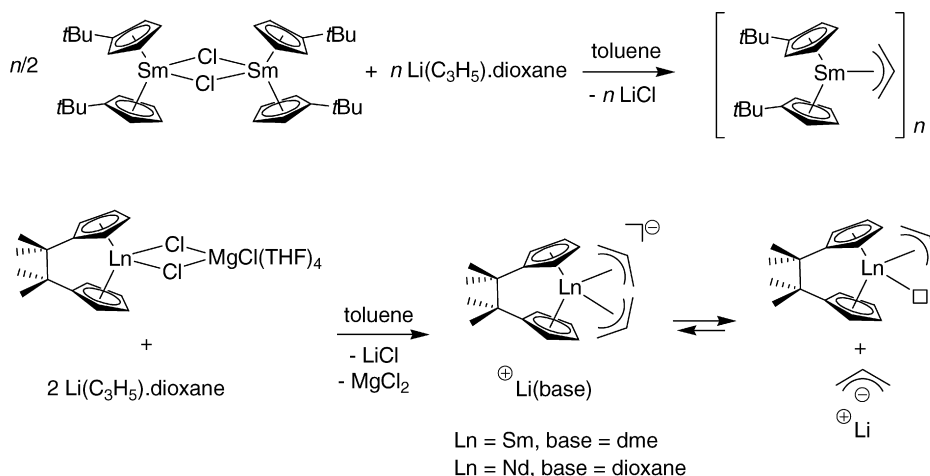
#### 3.1. Neutral and ate allyl-lanthanidocenes and half-sandwich complexes

Allyl-lanthanidocenes and related complexes supported by cyclopentadienyl ancillaries were actually the first allyl-lanthanide compounds reported. The field was pioneered by Tsutsui in 1975 who reported that reactions of Cp<sub>2</sub>LnCl complexes (Ln = Sm, Ho, Er) with allylmagnesium bromide in THF/ether solution at –78 °C, followed by workup with dioxane to precipitate MgCl<sub>2</sub>, afford the corresponding allyl-lanthanidocene derivatives, Cp<sub>2</sub>Ln(C<sub>3</sub>H<sub>5</sub>) [30] (Scheme 19).

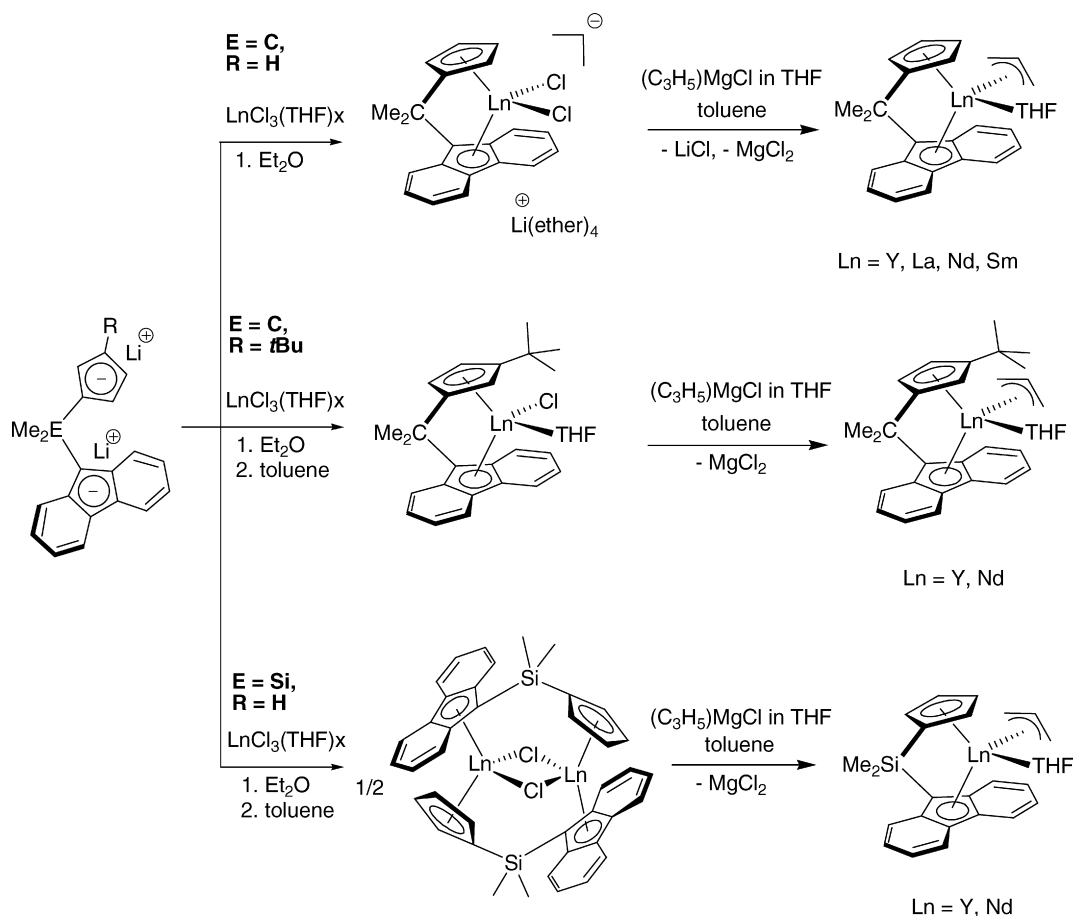
Although very sensitive to air and moisture, these compounds were found to be quite thermally stable, decomposing at temperatures above 200 °C. IR studies indicated a η<sup>3</sup>-coordination mode of the allyl moiety. The IR spectrum of the samarium(III)-allyl complex in THF showed the C–C stretch to be essentially unshifted, indicating that there is little tendency for the allyl group to undergo a σ–π rearrangement in the presence of a strongly coordinating solvent.

This methodology proved to be quite general and a variety of allyl-lanthanidocenes was prepared efficiently following similar transmetalation protocols.

For instance, Baudry et al. described the synthesis of neutral allyl complex [Cp<sub>2</sub>Sm(C<sub>3</sub>H<sub>5</sub>)]<sub>n</sub> (Cp' = *t*BuC<sub>5</sub>H<sub>4</sub>) and *ansa*-“ate” allyl complexes [Me<sub>4</sub>C<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>]Ln(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>Li(-base) (Ln = Sm, Nd; base = DME, dioxane) from [Cp<sub>2</sub>SmCl]<sub>2</sub> and the magnesium derivatives [Me<sub>4</sub>C<sub>2</sub>(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>]LnCl.MgCl<sub>2</sub>(THF)<sub>4</sub>, respectively (Scheme 20) [31,32]. The anionic *ansa*-samarocene complex exhibited moderate activity for the polymerization of isoprene (TOF = 260 mol(IP) mol(Ln)<sup>–1</sup> h<sup>–1</sup> at 50 °C), giving 1,4-*trans*-enriched (95%) polymers. The



Scheme 20. Synthesis of allyl-samarocene and -neodymocene complexes used for isoprene and styrene polymerization [31,32].



**Scheme 21.** Synthesis of neutral allyl *ansa*-lanthanidocenes supported by fluorenyl-cyclopentadienyl ligands and used in syndiospecific homo and copolymerization of styrene [35].

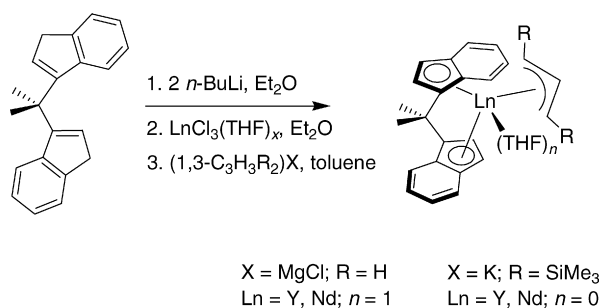
polymerization of an equimolar mixture of isoprene and 1-hexene with  $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{Ln}(\text{C}_3\text{H}_5)_2\text{Li}(\text{DME})$  ( $\text{Ln} = \text{Sm}, \text{Nd}$ ) as single component catalysts led to a co-polymer (1-hexene/isoprene = 1:10) essentially formed of 1,4-*trans*-polyisoprene blocks separated by only one inserted hexyl group [33]. It was proposed that these polymerization reactions proceed via prior dissociation of allyl-lithium [18], generating a neutral species “ $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{Ln}(\eta^3\text{-C}_3\text{H}_5)^3$ ”<sup>3</sup> having a vacant site for isoprene coordination and subsequent polymerization (Scheme 18); allyl-lithium cogenerated in this equilibrium would account for the imperfect 1,4-*trans* stereoselectivity, as this compound was shown to produce 1,4-*cis*-polyisoprene under those conditions.

Also, it was observed that  $[\text{Me}_4\text{C}_2(\text{C}_5\text{H}_4)_2]\text{Nd}(\text{C}_3\text{H}_5)_2\text{Li}(\text{DME})$  is a moderately active catalyst for the polymerization of styrene, affording isotactic-enriched polystyrenes [32]. On the other hand, the neutral allyl derivative  $[\text{Cp}_2\text{Sm}(\text{C}_3\text{H}_5)]_n$  was inactive towards isoprene.

<sup>3</sup> Attempts to isolate such neutral complex (or a related Lewis base adduct) were performed but the species could not be fully authenticated, see [34].

The lack of reactivity of this compound was related to its associated structure: isoprene probably does not possess a sufficiently strong coordination ability [unlike, for example, the nucleophilic carbene  $\text{C}(\text{NiPr})_2(\text{CMe}_2)$ ] to dissociate the starting polymeric material.

Our group also reported the preparation via salt metathesis protocols of well-defined allyl-*ansa*-lanthanidocenes that proved especially useful for styrene polymerization. Neutral allyl complexes bearing *ansa*-bridged fluorenyl/cyclopentadienyl ligands  $[\text{FluEMe}_2(3\text{-R-Cp})]\text{Ln}(\eta^3\text{-C}_3\text{H}_5)(\text{THF})$  ( $\text{E} = \text{C}, \text{R} = \text{H}, \text{Ln} = \text{Y}, \text{La}, \text{Nd}, \text{Sm}$ ;  $\text{R} = \text{tBu}, \text{Ln} = \text{Y}, \text{Nd}$ ;  $\text{E} = \text{Si}, \text{R} = \text{H}, \text{Ln} = \text{Y}, \text{Nd}$ ) were prepared in good yields (Scheme 21) [35]. The complexes were characterized by elemental analysis, NMR spectroscopy for diamagnetic complexes, and single-crystal X-ray diffraction studies for several members. The allyl fragment is coordinated in an  $\eta^3$ -mode, though in a rather non-symmetric manner, as judged by the *ca.* 0.1–0.2 Å difference in the M–C(allyl) and also the C–C bonds in the allyl ligands distances. This peculiarity could arise from either severe steric congestion induced by the neighboring coordinated THF molecule and/or non-equal participation of the  $\text{sp}^2$ -carbon atoms in bonding with the metal center.



**Scheme 22.** Synthesis of neutral allyl *ansa*-lanthanidocenes supported by bis(indenyl) ligands and used in isospecific polymerization of styrene [39].

Considering a  $\eta^3$ -coordination mode for the allyl fragment and fluorenyl ligand, those eight-coordinate allyl complexes are formal 16-electron species.

Some of these allyl *ansa*-lanthanidocenes, especially  $\{\text{FluCMe}_2\text{C}_5\text{H}_4\}\text{Nd}(\eta^3\text{-C}_3\text{H}_5)(\text{THF})$ , are effective single-component (i.e., they do not require any activator) catalysts for the polymerization of styrene, giving pure syndiotactic polystyrenes (*rrrr* > 99% on the crude *unfractionated* polymers) with high molecular weights and narrow polydispersities [35].<sup>4</sup> Note that the corresponding alkyl and hydrido complexes  $\{[\text{FluCMe}_2\text{C}_5\text{H}_4]\text{Nd}(\text{R})(\text{THF})_n$  ( $\text{R} = \text{CH}_2\text{SiMe}_3$ ,  $\text{CH}(\text{SiMe}_3)_2$ ,  $n = 1$ ;  $\text{R} = \text{H}$ ,  $n = 2$ ) are inactive toward styrene [37]. The allyl-lanthanidocene catalysts are remarkably stable, capable of polymerizing styrene up to 120 °C, while maintaining high activities and high syndiotacticity. Also, highly effective copolymerization of styrene with ethylene was achieved (activity up to 2530 kg(PS-PE) mol<sup>-1</sup> h<sup>-1</sup>) to give, for styrene-rich true copolymers void of homopolymers with high molecular weights and narrow polydispersities. These P(*S-co-E*) copolymers have a microstructure predominantly made of long highly syndiotactic PS sequences separated by single or few ethylene units. The mechanism of the initiation step of styrene polymerization promoted by those single-component allyl *ansa*-lanthanidocene catalysts has been studied from a combined experimental/computational (DFT) perspective [38]. Key results include that (i) insertion of styrene proceeds directly in the  $\eta^3$ -coordinated allyl group and (ii) the insertion of styrene proceeds selectively in a secondary (2,1) fashion, both at the initiation and propagation steps.

$\text{C}_2$ -symmetric allyl *ansa*-lanthanidocenes supported by a bis(indenyl) ligand were efficiently prepared using a similar salt metathesis approach (Scheme 22) [39]. The one-pot reaction proceeded with selective *rac*-coordination of the indenyl ligand. A diffraction study performed on the bis(silylated)allyl-yttrium complex showed that the allyl group is  $\eta^3$ -coordinated with the  $\text{SiMe}_3$  groups arranged in a *syn, syn* fashion; i.e., the same conformation as in  $\{\eta^3\text{-1,3-C}_3\text{H}_3(\text{SiMe}_3)_2\}_2\text{Sc}(\mu\text{-Cl})_2\text{Li}(\text{THF})$  [21]. These

species turned out to be efficient single-component catalysts for highly isospecific polymerization of styrene (> 99% *mmmmmm* on the crude *unfractionated* polymers, even up to 100 °C), operable under industrially relevant conditions (bulk, 60–120 °C).

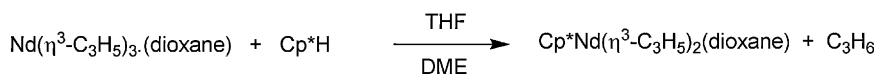
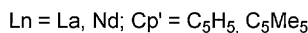
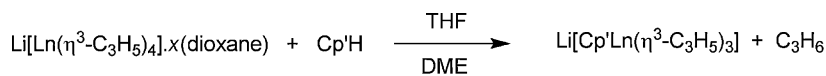
Another synthetic entry to allyl-lanthanidocenes involves partial protolysis of one allyl ligand in homoleptic tris or tetra(allyl)-lanthanide compounds with a proteo cyclopentadiene derivative Cp'H. Thus,  $[\text{Li}(\mu\text{-dioxane})_{1.5}][\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_4]$  ( $\text{Ln} = \text{La, Nd}$ ) reacts with a stoichiometric amount of Cp'H ( $\text{Cp}' = \text{C}_5\text{H}_5$ ,  $\text{C}_5\text{Me}_5 = \text{Cp}^*$ , indenyl, fluorenyl) to yield selectively the complexes  $[\text{Li}(\text{dioxane})_2][\text{Cp}'\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_3]$  (Scheme 23) [40,41]. Similarly, the synthesis of  $\text{Cp}^*\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_2(\text{dioxane})$  has been achieved by protonation of  $\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_3(\text{dioxane})$  with penta-methylcyclopentadiene [8]. The ease of these protolytic reactions reflects the predominantly ionic nature of the tris(allyl)-lanthanide precursors.

A most important, pioneering study in the field of early metallocene chemistry was reported by Watson et al. at Dupont [42]. This group conducted spectroscopic studies aimed at the establishment of propene polymerization by  $[\text{Cp}_2^*\text{LuMe}]_2$  and obtained at that time one of the clearest experimental model for coordination catalysis of olefin polymerization. Among the numerous interesting results gathered in this study, it was demonstrated that termination processes occur by C–H activation; i.e., abstraction of an allylic methyl C–H from propene or isobutylene gives allylic complexes, which do not react further with propene (Scheme 24).

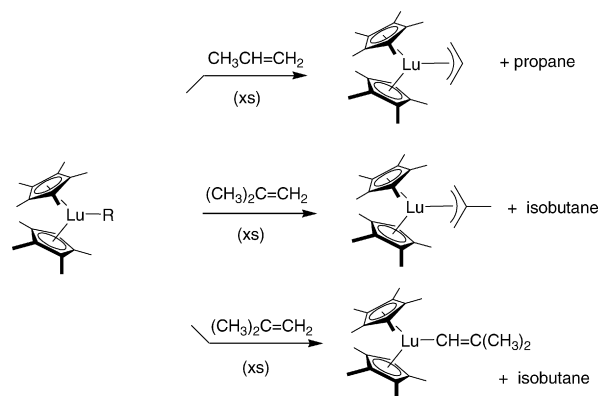
Marks and Schumann [43] and later Evans et al. [44] further expanded on these results, demonstrating that  $[\text{Cp}_2^*\text{Ln}(\mu\text{-H})_2]$  ( $\text{Ln} = \text{La, Nd}$ ) and  $[\text{Cp}_2^*\text{Sm}(\mu\text{-H})_2]$  react with propene, butene, and allylbenzene in hexane to form the corresponding allyl complexes  $\text{Cp}_2^*\text{Ln}(\text{CH}_2\text{CHCH}_2)$ ,  $\text{Cp}_2^*\text{Ln}(\text{CH}_2\text{CHCHMe})$ , and  $\text{Cp}_2^*\text{Sm}(\text{CH}_2\text{CHCHPh})$  in high yields (Scheme 25). In these reactions, the corresponding alkane was formed as a byproduct in equal quantities, as observed in the lutetium case (*vide supra*). All of these allyl complexes were fully characterized, in particular in the solid state by X-ray diffraction studies for the samarocene compounds which confirmed the trihapto coordination of the allyl moieties. The presence of two  $\text{Cp}^*$  signals and separate signals for the *syn* and *anti* protons of the allyl group in the <sup>1</sup>H NMR spectrum of  $\text{Cp}_2^*\text{Sm}(\text{C}_3\text{H}_5)$  indicated that, in the absence of coordinating solvents, this compound exists in solution as a static  $\eta^3$ -allyl structure. The addition of a coordinating solvent, such as THF, causes both the  $\text{C}_5\text{Me}_5$  signals and the *syn* and *anti* signals to coalesce. This coalescence was proposed to occur through a THF adduct in which the allyl moiety can shift to a  $\eta^1$ -mode of binding. The chemistry of  $\text{Cp}_2^*\text{Sm}(\text{C}_3\text{H}_5)$  is indeed consistent with the availability of an  $\eta^1$ -allyl binding mode. For example,  $\text{Cp}_2^*\text{Sm}(\text{C}_3\text{H}_5)$  dissolved in hexane reacts with 1 atm of H<sub>2</sub> to produce  $[\text{Cp}_2^*\text{Sm}(\mu\text{-H})_2]$ , it reacts with toluene to form the corresponding benzyl complex with elimination of propene (Scheme 25), and catalyzes the polymerization of ethylene.

Later on, Casey et al. conducted a similar detailed study on the reactivity of yttrium alkyl complexes of the type  $[\text{Cp}_2^*\text{YR}]$  with  $\alpha$ -olefins [45]. The selectivity of the reaction

<sup>4</sup> Syndiotactic oligostyrenes were also obtained by the in situ combination of the *ansa*-chloroneodymocene precursor  $[(\text{CpCMe}_2\text{Flu})\text{Nd}(\mu\text{-Cl})_2]$  with  $(\text{allyl})_2\text{Mg}$  or a regular dialkylmagnesium, see [36].



Scheme 23. Protolysis of homoleptic lanthanide-allyls with Cp\*H pro-ligands [8,40,41].



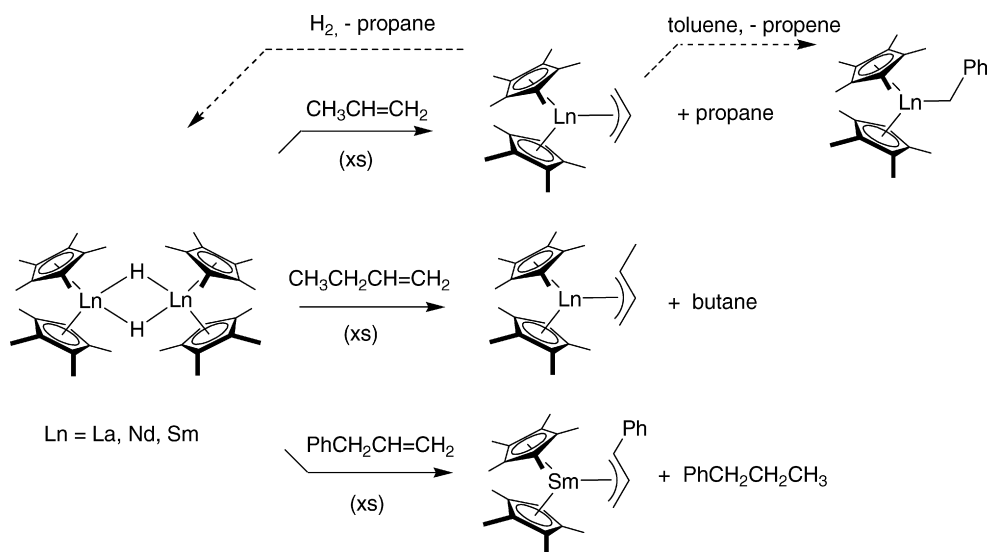
Scheme 24. Reaction of alkyl-lanthanidocene  $[\text{Cp}_2\text{Lu}(\text{R})]_2$  with  $\alpha$ -olefins [42].

of  $[\text{Cp}_2^*\text{YR}]$  with C–H bonds is allylic  $\text{CH}_3 > \text{vinyl C-H} > \text{allylic CH}_2$ , leading eventually to either allyl or vinyl yttrium complexes. Less substituted alkenes react faster, consistent with prior alkene coordination. Thus, propene is also readily metallated by  $[\text{Cp}_2^*\text{YR}]$  giving the allyl complex  $[\text{Cp}_2^*\text{Y}(\eta^3\text{-C}_3\text{H}_5)]$ , which does not react further with propene.

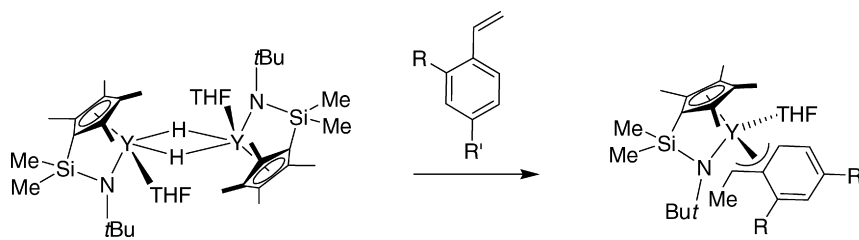
All these studies gave an efficient access to a range of allyl-lanthanidocene complexes and, even more importantly, they explained why  $[\text{Cp}_2^*\text{LnR}]$  ( $\text{R} = \text{H, alkyl}$ ) complexes make such poor propene polymerization catalysts.

Okuda et al. showed that the “constrained geometry” hydrido complex  $[(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NtBu})\text{Y}(\text{THF})(\mu\text{-H})]_2$  smoothly reacts with stoichiometric amounts of styrenes to give the corresponding allyl complexes (Scheme 26) [46]. Styrenes with no more than one *ortho*-substituent give 1-phenethyl complexes. An X-ray diffraction study of  $[\text{Y}(\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2\text{NtBu})(\text{THF})(\text{CHMeC}_6\text{H}_4\text{tBu-4})]$  confirmed that the insertion occurred in a 2,1-fashion and that the phenyl ring is engaged in an  $\eta^3$ -coordination. Variable-temperature NMR spectroscopy further revealed fluxional behavior that includes THF dissociation, phenyl ring coordination, and rotation about the ipso- and  $\alpha$ -carbon atom. When larger amounts of styrene (or dienes) were used, polymerization does not occur, reflecting the stability of these mono(insertion) products, possibly due to the presence of the coordinated THF molecule that cannot be displaced by styrene.

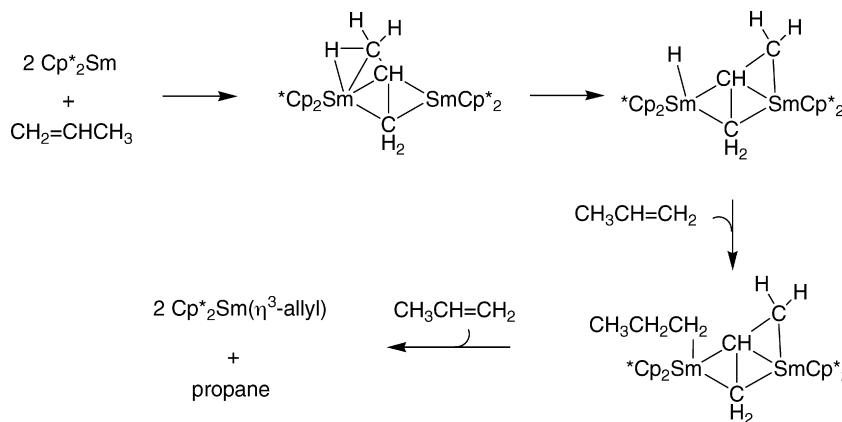
Another effective entry to allyl-samarocenes relies on the reaction of alkenes with the divalent precursor  $\text{Cp}_2^*\text{Sm}$  [44]. In fact, this latter complex reacts rapidly and quantitatively with alkenes (propene, butene, and allyl-



Scheme 25. Reaction of  $[\text{Cp}_2^*\text{Ln}(\mu\text{-H})]_2$  with  $\alpha$ -olefins, nature of the structurally characterized allyl-samarocene products and reactivity of  $\text{Cp}_2^*\text{Sm}(\text{C}_3\text{H}_5)$  [43,44].



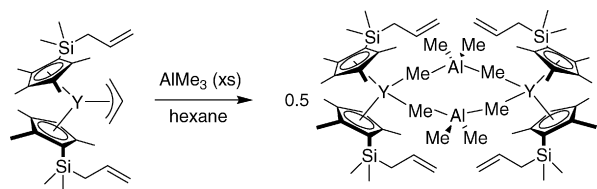
Scheme 26. Insertion of styrenes in "constrained geometry" hydrido yttrium complexes [46].



Scheme 27. Possible reaction pathway for conversion of 3 mol of propene to propane and two allyl complexes within a tetracyclopentadienyl cavity generated from two  $\text{Cp}_2^*\text{Sm}$  units [44].

benzene) in hexane or toluene to form the corresponding allyl complexes and alkane byproducts. Several possible routes were discussed to account for the formation of such allyl compounds. Based on the observed reactivity, notably towards styrene and dienes, it was concluded that allyl complexes form via pathways which do not involve free  $\text{Cp}_2^*\text{SmH}$  or  $\text{Cp}_2^*\text{Sm}(\text{alkyl})$  intermediates. A bimetallic mechanism was eventually proposed (Scheme 27).

Relevant to diene polymerization catalysis, a structurally proven example of [allyl]  $\rightarrow$  [alkyl] exchange reaction was reported by Evans et al. [47]. The addition of excess  $\text{AlMe}_3$  to the Cp-functionalized monoallyl-yttrocene complex quantitatively yields a dimeric aluminate, which was X-ray crystallographically characterized (Scheme 28). Bochmann et al. previously proposed on the basis of NMR spectroscopic investigations a similar allyl exchange reaction between lanthanide bis(allyl) complexes  $\text{LnCl}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2](\text{THF})_x$  ( $\text{Ln} = \text{La}$ ,  $x = 1$ ;  $\text{Ln} = \text{Y}$ ,  $x = 0$ ) and triisobutylaluminum [21].



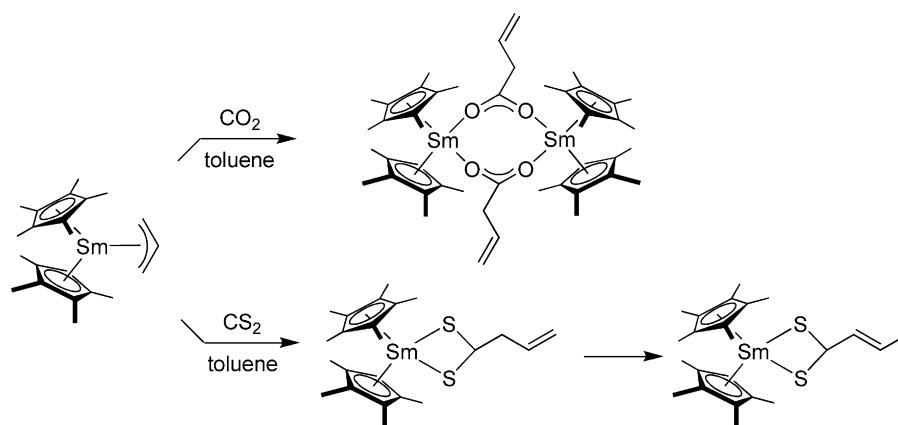
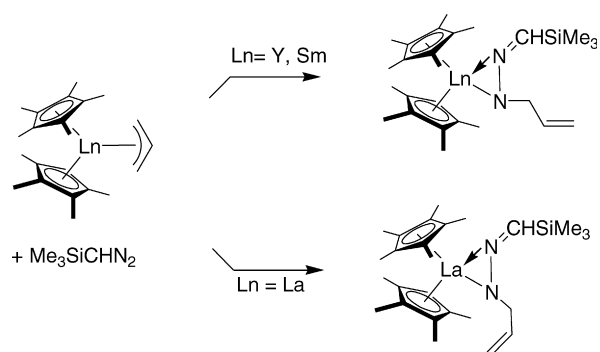
Scheme 28. [allyl]  $\rightarrow$  [alkyl] exchange reaction in a Cp-functionalized monoallyl-yttrocene complex [47].

Mono(allyl)-lanthanidocenes can react with protic compounds via a sigma-bond metathesis process, eventually releasing propene. For instance, Evans et al. showed that the mono(allyl)-lanthanidocene complexes  $\text{Cp}_2^*\text{Ln}(\eta^3\text{-C}_3\text{H}_5)(\text{THF})$  ( $\text{Ln} = \text{Ce}$ ,  $\text{Sm}$ ,  $\text{Y}$ ) react with proligand 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine (Hhpp) to form heteroallylic NCN metallocene complexes,  $\text{Cp}_2^*\text{Ln}(\text{hpp})$ , in which the (hpp)<sup>1-</sup> anion coordinates as a terminal bidentate ligand [48].

Evans et al. investigated also  $\text{CO}_2$  and  $\text{CS}_2$  insertion chemistry of mono(allyl)-samarocenes [49].  $\text{CO}_2$  reacted with  $\text{Cp}_2^*\text{Sm}(\eta^3\text{-C}_3\text{H}_5)$  to form  $[\text{Cp}_2^*\text{Sm}(\mu\text{-O}_2\text{CCH}_2\text{CH}=\text{CH}_2)]_2$  in > 90% yield (Scheme 29).  $\text{CS}_2$  reacted analogously with  $\text{Cp}_2^*\text{Sm}(\eta^3\text{-C}_3\text{H}_5)$  to form  $[\text{Cp}_2^*\text{Sm}(\eta^2\text{-S}_2\text{CCH}_2\text{CH}=\text{CH}_2)]_2$ , which subsequently isomerized to  $\text{Cp}_2^*\text{Sm}(\eta^2\text{-S}_2\text{CCH}=\text{CHCH}_3)$  (Scheme 29). The same reactivity was observed with COS.

Recently, the reactivity of allyl-lanthanidocenes  $\text{Cp}_2^*\text{Ln}(\text{C}_3\text{H}_5)$  ( $\text{Ln} = \text{Y}$ ,  $\text{La}$ ,  $\text{Sm}$ ) with (trimethylsilyl)diazomethane,  $\text{Me}_3\text{SiCHN}_2$ , was studied [50]. This latter reagent is not metallated by the allyl-metallocene complexes but instead inserts to form the lanthanide hydrazone complexes  $\text{Cp}_2^*\text{Ln}[\eta^2\text{-}(N,N')\text{-RNN}=\text{CHSiMe}_3]$  ( $\text{R} = \text{CH}_2=\text{CHCH}_2$ ) (Scheme 30). Although the La, Y, and Sm complexes are isomorphous, the double bond in the allyl substituent is oriented toward La and away from Y and Sm.

A fundamental work about the fluxional behavior of allyl moieties in neutral allyl group 3 metallocenes was performed by Bercaw et al. using variable-temperature  $^1\text{H}$  NMR spectroscopy combined with spectral simulations

Scheme 29. CO<sub>2</sub> and CS<sub>2</sub> insertion with Cp<sub>2</sub>Sm( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>) [49].Scheme 30. Reaction of allyl-lanthanidocenes Cp<sub>2</sub>Ln(C<sub>3</sub>H<sub>5</sub>) (Ln = Y, La, Sm) with (trimethylsilyl)diazomethane [50].

and line shape analyses [51]. Spectroscopic data for a number of allyl-lanthanidocenes (( $\eta^5$ -Cp\*)<sub>2</sub>Sc( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>), *meso*-Me<sub>2</sub>Si( $\eta^5$ -3-*t*Bu-C<sub>5</sub>H<sub>3</sub>)<sub>2</sub>Sc( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>), *meso*-Me<sub>2</sub>Si( $\eta^5$ -2,4-(*i*Pr)<sub>2</sub>-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>Sc( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>), *meso*-Me<sub>2</sub>Si( $\eta^5$ -3-[2-(2-Me)-adamantyl]-C<sub>5</sub>H<sub>3</sub>)<sub>2</sub>Ln( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>) (Ln = Sc, Y) and *rac*-Me<sub>2</sub>Si( $\eta^5$ -2,4-(*i*Pr)<sub>2</sub>-C<sub>5</sub>H<sub>2</sub>)<sub>2</sub>Sc( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)) indicated an allyl rearrangement mechanism involving rate determining C=C dissociation from the metal center, i.e., an  $\eta^3$  to  $\eta^1$  change in coordination (Scheme 31). Donor solvents do not significantly affect the rate of olefin dissociation. A second rearrangement mechanism that involves 180° rotation of the  $\eta^3$ -allyl moiety has been found to operate in those metallocenes whose ancillary ligand arrays adopt rigid *meso* geometries. Line shape analysis indicated that the rate of  $\eta^3$ -allyl rotation is generally more than one order of magnitude faster than olefin dissociation for a given *meso* metallocene. On the other hand, no unambiguous assessments of the mechanism(s) were found for the fluxional

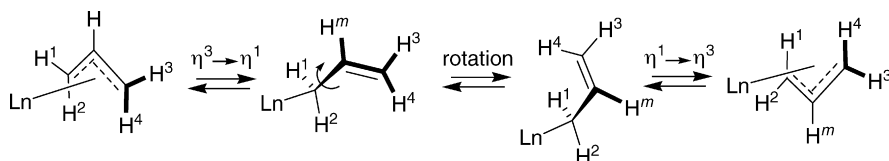
behavior for the allyl derivatives of the racemic metallocenes.

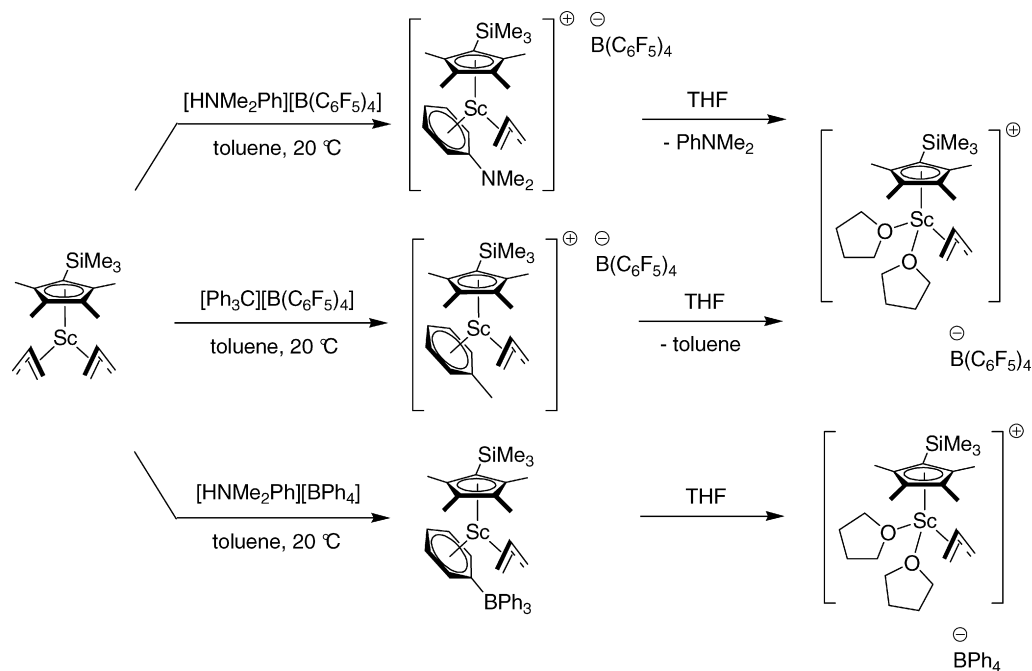
### 3.2. Mono- and dicationic half-sandwich allyl-lanthanide complexes

Quite recently, important contributions on cationic group 3 metal and lanthanide allyl complexes bearing mono(cyclopentadienyl) ligands have been reported independently by the groups of Xi and Hou [52] and Okuda [13]. This work was essentially motivated by the involvement of mono- and dicationic allyl complexes in diene polymerization catalysis evidenced in Taube's contributions (*vide supra*) and the topical excitement around cationic rare-earth-metal alkyl complexes.

Xi and Hou reported novel families of monocationic mono(cyclopentadienyl)scandium allyl complexes generated by the reactions of neutral di(allyl) precursors with various activators such as [PhNMe<sub>2</sub>H][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>], and [PhNMe<sub>2</sub>H][BPh<sub>4</sub>]. Well-defined cationic half-sandwich allyl complexes with various Lewis base ligands such as toluene, *N,N*-dimethylaniline, and THF were isolated under appropriate conditions (Scheme 32). Recrystallization of these compounds in THF yielded the corresponding THF separated ion pair complexes.

These monocationic complexes were examined as catalysts for the polymerization and copolymerization of isoprene and norbornene, which demonstrated significant influence of the Lewis base ligands and the counteranions on the catalytic activity of the polymerization. Thus, [( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)( $\eta^6$ -PhNMe<sub>2</sub>)] [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] and [( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>3</sub>)Sc( $\eta^3$ -C<sub>3</sub>H<sub>5</sub>)( $\eta^6$ -toluene)] [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] are highly active, affording random copolymers previously unavailable with a broad range of isoprene content

Scheme 31. *Syn*  $\leftrightarrow$  *anti* interconversion in allyl-lanthanidocenes [51].



Scheme 32. Monocationic half-sandwich allyl-scandium complexes [52].

(33–86 mol%), while the tight ion pair  $[(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)\text{Sc}(\eta^3\text{-C}_3\text{H}_5)(\mu, \eta^6\text{-PhBPh}_3)]$  and the THF complexes are inactive.

The group of Okuda reported similar observations on corresponding yttrium and lanthanum complexes [13]. The monocationic half-sandwich complexes  $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\eta^3\text{-C}_3\text{H}_5)(\text{THF})_2][\text{B}(\text{C}_6\text{X}_5)_4]$  (Ln = Y, La; X = H, F) were synthesized from the neutral precursors  $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\eta^3\text{-C}_3\text{H}_5)_2(\text{THF})]$  by protonolysis with the corresponding reagents.

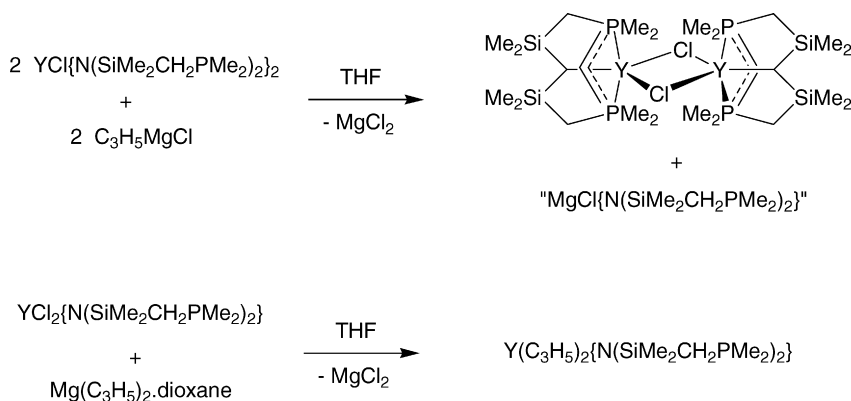
#### 4. Heteroleptic allyl-lanthanide complexes supported by non-Cp ancillaries

Surprisingly enough, there are few examples of well-characterized, allyl-lanthanide complexes supported by

non-Cp ancillaries. Apparently, synthetic problems involving ligand transfer reactions and/or ligand redistribution processes have so far hampered the preparation of a large variety of such compounds.

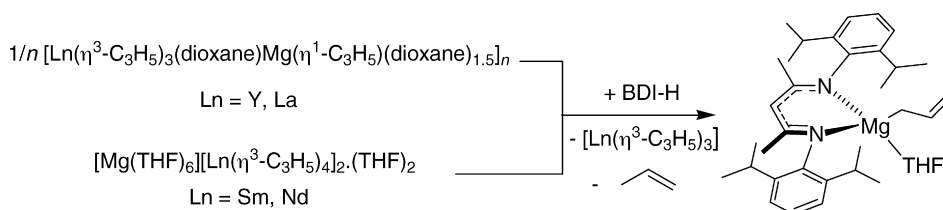
Fryzuk et al. reported that the bis{amido(diphosphino)}-chloride complex  $[\{\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2\text{YCl}\}_2]$  reacts with allylmagnesium chloride or diallylmagnesium with elimination of one  $\{\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2\}^-$  ligand (and not of the  $\text{Cl}^-$ ) and formation of  $[\{(\eta^3\text{-C}_3\text{H}_5)\{\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2\text{Y}(\mu\text{-Cl})\}_2]$  (Scheme 33) [53]. On the other hand, the reaction of  $[\{\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2\text{YCl}\}_2]$  with diallylmagnesium occurred with elimination of  $\text{MgCl}_2$  and  $[(\eta^3\text{-C}_3\text{H}_5)_2\{\text{N}(\text{SiMe}_2\text{CH}_2\text{PMe}_2)_2\text{Y}]$  was obtained. This latter compound acts as a catalyst precursor for the polymerization of ethylene.

Also, Bochmann et al. investigated reactions of different magnesium/lanthanide allyl complexes with the weakly

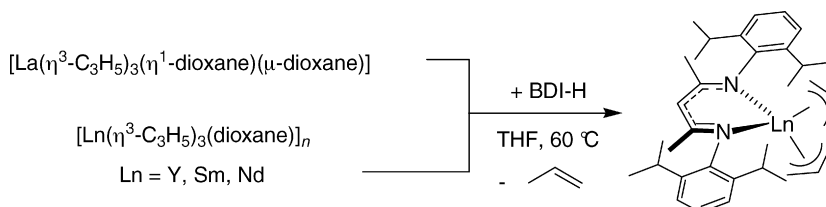


Scheme 33. Transmetalation reactions between allyl Grignard and diallylmagnesium and chloroyttrium complexes supported by amidodiphosphine ligands [53].





Scheme 34. Reactions of a  $\beta$ -diketimine pro-ligand with mixed lanthanide-magnesium allyls [54].



Scheme 35. Synthesis of bis(allyl)( $\beta$ -diketiminato)-lanthanide complexes [55].

acidic diketimine pro-ligand BDI-H (BDI-H = 2-(2,6-diisopropylphenyl)amino-4-(2,6-diisopropylphenyl) imino-2-pentene). However, no lanthanide-containing product could be isolated. Instead, magnesium  $\beta$ -diketiminato complexes were formed as a result of ligand transfer reactions (Scheme 34) [54]. On the other hand, when the “ate” allyl-samarium complex  $[\text{Mg}(\text{THF})_6][\text{Sm}_2(\eta^3\text{-C}_3\text{H}_5)_6(\mu\text{-}\eta^3\text{:}\eta^2\text{-C}_3\text{H}_5)_2.\text{toluene}]$  was treated with BDI-H,  $[\text{Mg}(\text{THF})_6][\text{Sm}(\eta^3\text{-C}_3\text{H}_5)_4]_2.2\text{THF}$ , alongside  $\text{Sm}(\eta^3\text{-C}_3\text{H}_5)_2\{\eta^3\text{-HC}(\text{MeCNC}_6\text{H}_3\text{iPr}_2\text{-2,6})_2\}$  were produced [16].

Effective access to bis(allyl)( $\beta$ -diketiminato)-lanthanide complexes was achieved through the reaction of  $[\text{La}(\eta^3\text{-C}_3\text{H}_5)_3(\eta^1\text{-dioxane})_2(\mu\text{-dioxane})]$  and  $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_3(\eta^1\text{-dioxane})]_\infty$  (Ln = Y, Sm, Nd) with the proteo diketimine pro-ligand BDI-H in THF at 60 °C [55]. These reactions proceeded cleanly with propene elimination (Scheme 35). The solid-state structure of the samarium complex showed that the allyl fragment opposite the N atoms is  $\eta^3$ -bonded, with three very similar Sm–C bond lengths, while bonding of the second allyl moiety is less symmetrical. All of these complexes are highly effective single-component catalysts for the ring-opening polymerization of  $\epsilon$ -caprolactone and *rac*-lactide giving poly( $\epsilon$ -caprolactone) and atactic poly(lactide) with controlled molecular weights and narrow molecular weights distributions. Polymer end-group analysis shows that the polymerization process is initiated by allyl transfer to the monomer.

## 5. Conclusions

Allyl complexes have attracted considerable interest over the past four decades. Efficient synthetic methodologies have allowed access to quite a large variety of compounds. The span of compounds now readily available includes “simple” homoleptic neutral, anionic and also cationic bis, tris and tetra(allyl) compounds and mono(-allyl)-lanthanidocene complexes. The preparation of allyl complexes of group 3 metals and lanthanides supported by non-Cp ancillaries is much less mature. Considering the

obvious interest of allyl-lanthanides in catalysis, notably in (co)polymerization of dienes and styrenics, one can expect that development of effective procedures for accessing new derivatives of such allyl postmetallocene complexes shall be the focus of future research.

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