

Cationic Organometallic Complexes of Scandium, Yttrium, and the Lanthanoids

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1. Introduction

The organometallic chemistry of the rare-earth metals (the term “rare-earth metal” in this article will include scandium and yttrium alongside the elements from lanthanum to lutetium, the lanthanoids in the strictest sense) is dominated by neutral and anionic compounds, as documented in recent review articles.^{1–9} The emergence of cationic alkyl complexes of group 4 metals as key intermediates in homogeneous olefin polymerization and related catalytic reactions¹⁰ has recently prompted interest in cationic rare-earth organometallic complexes.¹¹ This may also be a result of increased attention to the development of catalytically active complexes of the rare-earth metals in general.^{12,13} However, in contrast to the large number of neutral and anionic organolanthanoid complexes, cationic complexes have continued to appear in the literature at a relatively steady rate in recent years only. The large ionic radii of the rare-earth metals¹⁴ initially appeared to require the robust metallocenium structure $[\text{Ln}(\eta^5\text{-C}_5\text{R}_5)_2]^+$ ($\text{R} = \text{H}$, alkyl) to tolerate positively charged fragments. The presence of appropriate donor ligands L has only recently enabled the isolation of surprisingly “simple” hydrocarbyl mono- and dications of the type $[\text{LnR}_m(\text{L})_n]^{(3-m)+}$ ($\text{R} = \text{hydrocarbyl}$; $m = 1, 2$; $\text{L} = \text{neutral Lewis base}$).^{11,15,16}

This review summarizes work related to the chemistry of cationic rare-earth organometallic complexes, that is, molecular compounds of the rare-earth metals that contain at

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Stefan Arndt was born in Teheran, Iran, in 1973. He received his Diploma in 2000 at the Johannes Gutenberg-University Mainz, Germany, and his Dr. rer. nat. degree in 2004 at the RWTH Aachen University, Germany, both on rare-earth metal polymerization catalysts under the supervision of Professor J. Okuda. In 2005, he joined Professor R. R. Schrock's group at MIT as a Feodor Lynen fellow of the Alexander von Humboldt Foundation, investigating decomposition and regeneration of metathesis catalysts. His research interests include the catalysis of organic and polymerization reactions via well-defined organometallic complexes.

least one metal–carbon bond and that carry a positive ionic charge. Relevant literature is covered up until the end of 2005. The synthesis, structure, and reactivity of the compounds, as well as their applications will be presented. Both the chemistry of organometallic cations in the gas phase^{17–21} and that of rare-earth metal fullerene compounds²² are outside the scope of this review.

2. Overview of Synthesis, Structure, and Properties

2.1. Synthesis

In principle, any neutral metal complex that contains a polar metal–ligand bond L_nM-X is capable of dissociating into cationic and anionic fragments $[ML_n]^+$ and X^- , provided charge separation between these parts is sufficient in a given



Ben R. Elvidge studied Natural Sciences at Downing College, Cambridge, carrying out a final year research project on phosphorus-containing cage complexes with Dominic Wright. He then went to Sussex University for his doctoral studies, working on yttrium chelating diamide complexes under the supervision of Professor G. Cloke. During this time, he spent three months at the Johannes Gutenberg-University Mainz as a visiting researcher in Professor J. Okuda's lab. His postdoctoral work he spent with Professor J. Okuda on cationic lanthanoid alkyl complexes at the RWTH Aachen University. In December 2005, he moved back to the U.K. and started working for Infineum on the application of molybdenum–sulfur compounds as lubricant additives.



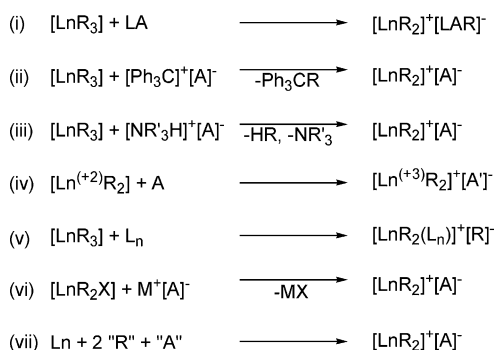
Jun Okuda was born in 1957 in Osaka, Japan. At the RWTH Aachen University, Germany, he received his Diploma in 1982 and his Dr. rer. nat. degree in 1984, both in organomolybdenum chemistry under the supervision of Gerhard E. Herberich. After postdoctoral research on carbon monoxide reduction catalysts with Dick Schrock at MIT, he obtained his "habilitation" on metallocenes in 1991 from the Technical University of Munich, Germany, and held academic positions at SUNY Albany, at the Philipps Universität Marburg, and at the Johannes Gutenberg-Universität Mainz. He has held the chair for Organometallic Chemistry at the RWTH Aachen University since 2003. His research interests include ligand design for reactive organometallic compounds and the development of coordinative polymerization catalysts.

medium. This behavior is promoted by solvent media with a high dielectric constant, pronounced Lewis basicity, or both. Thus the molecular chemistry of rare-earth metal ions, in particular in aqueous solutions, is dominated by ionic species.^{23,24} The adoption of "molecular" or "ionic" forms is governed by very subtle effects. For example, crystals of $YCl_3(THF)_{3.5}$ take the ion pair structure $[YCl_2(THF)_5]^+ [YCl_4(THF)_2]^-$,²⁵ whereas $[YCl_3(pyridine)_4]$ is "molecular" in the solid state.²⁶

By contrast, *organometallic* complexes of large, highly electropositive metals such as the lanthanoids require efficient charge distribution and stabilization by a weakly coordinating (less nucleophilic) anion to induce the charge separation

necessary for ion formation.^{27,28} The following synthetic methods have been shown to give cationic organo-rare-earth metal complexes from neutral or anionic precursors (Scheme 1):

Scheme 1^a



^a Ln = rare-earth metal; LA = Lewis acid; [A]⁻ = anion; R = hydrocarbyl.

(i) alkyl group abstraction by strong Lewis acids such as triarylboranes BR₃ (R = Ph, C₆F₅) or trialkylaluminum AIR₃ (R = CH₂SiMe₃);

(ii) alkyl group abstraction by the trityl cation [Ph₃C]⁺;

(iii) alkyl group abstraction by weak Brønsted acids such as [NR'₃H]⁺ (R' = Me, Et; R'₃ = PhMe₂);

(iv) oxidation of divalent lanthanoid alkyl complexes by transition metal carbonyl or borate complexes;

(v) rearrangement/dissociation of a neutral complex induced by a neutral ligand;

(vi) salt metathesis;

(vii) one-pot procedures from metallic starting materials.

2.2. Solid State Structures

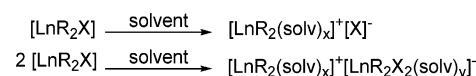
The coordination geometry of cationic rare-earth metal complexes is not fundamentally different from that of their neutral counterparts. The anionic X-type ligand that was abstracted is usually replaced in the coordination sphere by an L-type ligand such as a solvent molecule. The smallest element in the series, scandium, occupies a special position because a lower coordination number is commonly preferred compared with the larger lanthanoids. Saturation of the coordination sphere is important in all cases for stability, leading to coordination numbers up to nine. The counteranion can adopt a number of positions with respect to the cation. In "contact ion pair" structures, electron-deficient bonding joins the two units covalently. Some structures show electrostatic cation-anion interactions, while other complexes have essentially separate ions. A variety of different ion pair interactions involving the same class of anion have been observed. Details will be given alongside the description of the relevant compound.

2.3. Ion Pair Interactions in Solution

There is a continuum in solution from neutral molecules via contact ion pairs (sometimes referred to as zwitterions) to solvent-separated ion pairs.^{29,30} These ion pair dynamics are of interest both fundamentally and in terms of reactivity. Such a situation often results in a rather complicated, multidimensional network of numerous structures that are in equilibrium and subject to subtle influences. For instance, addition of donor solvents to a neutral complex or a contact

ion pair leads to the formation of solvent-separated ion pairs (Scheme 2). The nature of the ion pair becomes crucial for

Scheme 2



applications in polymerization catalysis, as shown for the d-block transition metals. The reactivity for a given cation is usually higher when the anion is more weakly coordinating.^{31,32} Organometallic complexes of the s-block elements such as organolithium compounds^{33,34} and Grignard reagents^{35,36} are well studied examples of complicated association/dissociation equilibria in solution that affect the reactivity considerably.

3. Cationic Cyclooctatetraene Complexes

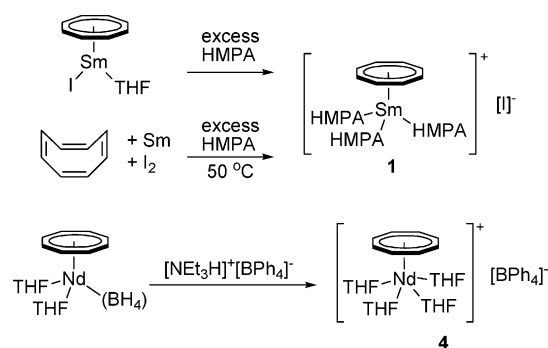
Cyclooctatetraene complexes form a group of compounds among the neutral non-cyclopentadienyl organolanthanoid complexes that have been investigated thoroughly, because the cyclooctatetraene dianion acts as a robust ancillary ligand.^{4,37} The known cationic cyclooctatetraene lanthanoid complexes are listed in Table 1.

Table 1. Cationic Cyclooctatetraene Rare-Earth Metal Complexes

| no. | compound | characterization | refs |
|-----|---|-------------------------------|-------|
| 1 | [Sm(η ⁸ -C ₈ H ₈)(HMPA) ₃] ⁺ [I] ⁻ | X-ray, ¹ H NMR | 38 |
| 2 | [La(η ⁸ -C ₈ H ₈)(HMPA) ₄] ⁺ [La(η ⁸ -C ₈ H ₈) ₂] ⁻ | ¹ H NMR | 38 |
| 3 | [Sm(η ⁸ -C ₈ H ₈)(HMPA) ₃] ⁺ [Sm(η ⁸ -C ₈ H ₈) ₂] ⁻ | X-ray, mp, ¹ H NMR | 38 |
| 4 | [Nd(η ⁸ -C ₈ H ₈)(THF) ₄] ⁺ [BPh ₄] ⁻ | X-ray, ¹ H NMR, EA | 39–42 |
| 5 | [Nd(η ⁸ -C ₈ H ₈)(HMPA) ₃] ⁺ [BPh ₄] ⁻ | X-ray, ¹ H NMR, EA | 41,43 |

The synthesis of a cationic cyclooctatetraene samarium complex [Sm(η⁸-C₈H₈)(HMPA)₃]⁺[I]⁻ (**1**) was reported in 1998.³⁸ It proceeds either by a simple one-pot reaction of stoichiometric amounts of metallic samarium, cyclooctatetraene, and iodine in the presence of excess hexamethylphosphoric triamide (HMPA) at 50 °C, or by reaction of the neutral complex [Sm(η⁸-C₈H₈)I(THF)] with excess HMPA (Scheme 3). The reaction of metallic lanthanum or samarium

Scheme 3



with cyclooctatetraene and a catalytic amount of iodine in the presence of HMPA afforded the ionic complexes [Ln(η⁸-C₈H₈)(HMPA)_n]⁺[Ln(η⁸-C₈H₈)₂]⁻ (Ln = La, n = 4 (**2**); Ln = Sm, n = 3 (**3**)). The structure of these cationic complexes was determined by ¹H NMR spectroscopy; crystal structure

analysis for both samarium complexes showed that the ion pairs are well-separated in the solid state (Figure 1).

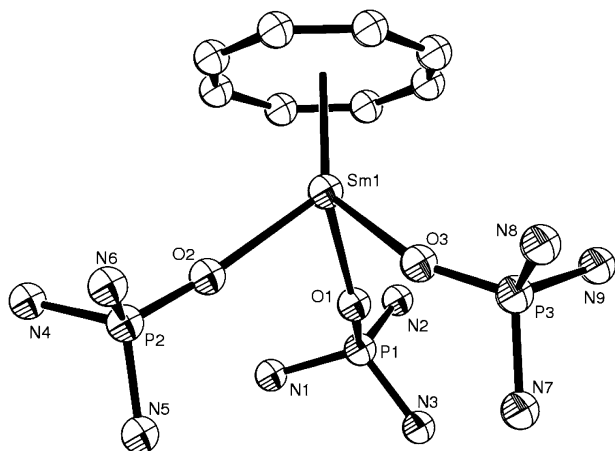


Figure 1. Molecular structure of the cationic part of $[\text{Sm}(\eta^8\text{-C}_8\text{H}_8)\text{-(HMPA)}_3]^+[\text{Sm}(\eta^8\text{-C}_8\text{H}_8)_2]^-$ (**3**). Hydrogen atoms and methyl groups in HMPA are omitted for clarity. Drawn from data in ref 38.

The syntheses of two cationic cyclooctatetraene neodymium complexes, $[\text{Nd}(\eta^8\text{-C}_8\text{H}_8)(\text{THF})_4]^+[\text{BPh}_4]^-$ (**4**)^{39–42} and $[\text{Nd}(\eta^8\text{-C}_8\text{H}_8)(\text{HMPA})_3]^+[\text{BPh}_4]^-$ (**5**),^{41,43} have been presented. The reaction of the neutral borohydride complex $[\text{Nd}(\eta^8\text{-C}_8\text{H}_8)(\text{BH}_4)(\text{THF})_2]$ with a slight excess of $[\text{NET}_3\text{H}]^+[\text{BPh}_4]^-$ in THF afforded **4** in good yield. Its discrete ion pair structure was confirmed by ¹H NMR spectroscopy and X-ray crystal structure analysis. Substitution of the THF ligands in **4** with HMPA in pyridine led to **5** in modest yield. Characterization by ¹H NMR spectroscopy and X-ray crystal structure analysis revealed well-separated ion pairs. Treating these neodymium complexes with $\text{K}(\text{C}_5\text{Me}_5)$ afforded the mixed ring sandwich complex $[\text{Nd}(\eta^8\text{-C}_8\text{H}_8)(\eta^5\text{-C}_5\text{Me}_5)(\text{THF})]$. Reaction with appropriate sodium salts gave the alkoxide complex $[\text{Nd}(\eta^8\text{-C}_8\text{H}_8)(\text{OEt})(\text{THF})_2]$ and depending on the reaction conditions the thiolate complexes $\text{Na}[\text{Nd}(\eta^8\text{-C}_8\text{H}_8)(\text{S}^i\text{Bu})_2]$ or $[\text{Na}(\text{THF})_2]^+[\{\text{Nd}(\eta^8\text{-C}_8\text{H}_8)\}_2(\text{S}^i\text{Bu})_3]^-$.

4. Cationic Bis(cyclopentadienyl) Complexes

In 1992, a theoretical investigation into the bending potentials of the postulated bis(cyclopentadienyl) rare-earth metal cations $[\text{Ln}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ ($\text{Ln} = \text{La}, \text{Sc}$) highlighted their usefulness as model compounds for neutral heavy alkaline earth and lanthanoid(II) metallocenes.⁴⁴ Previous and subsequent work has shown that both solvent-free and solvated contact ion pairs $[\text{Ln}(\eta^5\text{-C}_5\text{R}_5)_2(\mu\text{-A})(\text{solv})_x]$ and solvent-separated ion pairs $[\text{Ln}(\eta^5\text{-C}_5\text{R}_5)_2(\text{solv})_y]^+[\text{A}]^-$ are isolable species (Table 2). However, bis(cyclopentadienyl) rare-earth metal cations $[\text{Ln}(\eta^5\text{-C}_5\text{R}_5)_2]^+$ free of any further stabilization still remain elusive.

4.1. Metallocenium Carbonylmetalate Complexes

The initial interest in cationic rare-earth metal complexes that contain transition metal–carbonyl compounds arose from investigations into the Lewis acidity of tris(cyclopentadienyl) rare-earth metal complexes $[\text{Ln}(\eta^5\text{-C}_5\text{H}_4\text{R})_3]$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{Gd}, \text{Dy}, \text{Ho}, \text{Er}, \text{Yb}$; $\text{R} = \text{H}, \text{Me}$).⁴⁵ Such compounds have been shown to form adducts with terminal nitrosyl and carbonyl ligands of transition metal complexes such as $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)(\text{NO})_2\text{Cl}]$. Furthermore, the reaction of

$[\text{Ln}(\eta^5\text{-C}_5\text{H}_4\text{R})_2\text{Cl}]$ ($\text{R} = \text{Me}, \text{Ln} = \text{Dy}; \text{Ho}; \text{R} = \text{H}, \text{Ln} = \text{Er}, \text{Yb}$) with $\text{Na}[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]$ in THF yields $[\text{Ln}(\eta^5\text{-C}_5\text{H}_4\text{R})_2(\text{THF})_n]^+[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]^-$ ($\text{R} = \text{Me}, \text{Ln} = \text{Dy}$ (**6**), Ho (**7**); $\text{R} = \text{H}, \text{Ln} = \text{Er}$ (**8**), Yb (**9**)), which are highly thermally stable crystalline solids. Solution IR spectra (THF) show CO stretching bands consistent with the free metal carbonyl anion, whereas in the mull additional bands and a lowering of the frequency of the lowest energy band from the solution phase were observed. These data suggest a polymeric structure in the solid state with lone-pair donation from the carbonyl oxygen to the rare-earth metal center (isocarbonyl bond) but solvent-separated ion pairs in THF solution. No X-ray crystallographic data were given.

Preparation of a series of heterobimetallic Yb(III) transition metal complexes that exist either as carbonyl-bridged molecular species or solvent-separated ion pairs was achieved by oxidation of the divalent ytterbium precursor $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{L})]$ ($\text{L} = \text{THF}, \text{OEt}_2$) with $[\text{Co}_2(\text{CO})_8]$, $[\text{Fe}_3(\text{CO})_{12}]$, $[\text{Mn}_2(\text{CO})_{10}]$, and $[\text{Re}_2(\text{CO})_{10}]$ (Scheme 4). In the case of $[\text{Co}_2(\text{CO})_8]$, the paramagnetic bimetallic complex containing a bridging carbonyl unit in the solid state $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})\text{Co}(\mu\text{-CO})(\text{CO})_3]$ (**10**) was isolated and characterized by X-ray crystallography (Figure 2).⁴⁶ With $[\text{Fe}_3(\text{CO})_{12}]$, the complex $[\{\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2\}_2\text{Fe}_3(\mu\text{-CO})_4(\text{CO})_7]$ (**11**) could be isolated as violet crystals from a toluene solution.⁴⁷ X-ray crystallography confirmed this structure, in which two $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2]^+$ units are connected by the dianion $[\text{Fe}_3(\mu\text{-CO})_4(\text{CO})_7]^{2-}$. The inequivalence of the C_5Me_5 resonances in the ¹H NMR spectrum (toluene-*d*₈) suggests that the structure in the solid state is retained in solution. By contrast, reaction of $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{OEt}_2)]$ with half an equivalent of $[\text{Fe}(\text{CO})_5]$ gave $[\{\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})\}_2\text{Fe}(\mu\text{-CO})_2(\text{CO})_2]$ (**12**) after recrystallization from THF. Based on the ¹H NMR spectrum (THF-*d*₈) the authors proposed a structure in which two $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})]^+$ cations are connected via single carbonyl bridges to the dianion $[\text{Fe}(\text{CO})_4]^{2-}$, similar to $\text{Na}_2[\text{Fe}(\text{CO})_4]$.^{48–50} No X-ray diffraction data were reported. A similar complex incorporating manganese instead of iron, $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mn}(\mu\text{-CO})_x(\text{CO})_{5-x}]_2$ (**13**), offers an IR spectrum in THF solution consistent with a bridging carbonyl ligand.⁵¹ The molecular structure, determined by X-ray crystallography in the absence of THF, consists of layers of infinite, planar, polymeric sheets in which dimeric molecules of the formula $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mn}(\mu\text{-CO})_2(\text{CO})_3]_2$ are packed between polymeric sheets of the composition $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Mn}(\mu\text{-CO})_3(\text{CO})_2]_\infty$. The IR spectrum in the solid state or in cyclohexane is much more complicated than that in THF, suggesting that the unusual structure in the crystalline state is maintained in noncoordinating solvents. The reactivity of $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{OEt}_2)]$ toward $[\text{Re}_2(\text{CO})_{10}]$ to yield $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Re}(\mu\text{-CO})(\text{CO})_4]$ (**14**) is similar to that of $[\text{Mn}_2(\text{CO})_{10}]$.⁵¹

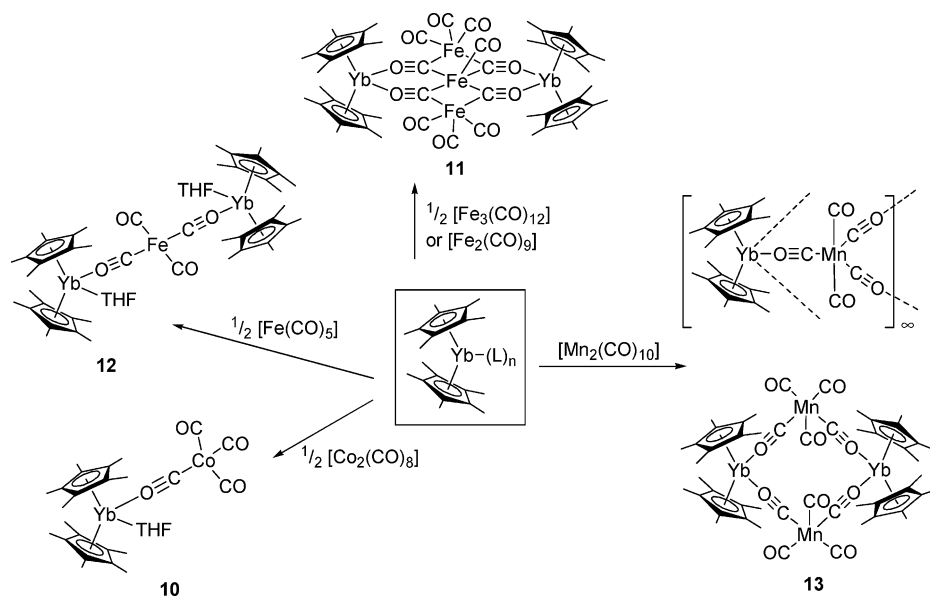
An analogous redox reaction of $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})_2]$ with $[\text{Co}_2(\text{CO})_8]$ formed $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})(\mu\text{-CO})_n\text{Co}(\text{CO})_{4-n}]$ (**15**).⁵² Since the structure of **15** could not be confirmed by X-ray crystallography, it is not clear whether the ions are separate ($n = 0$) or joined by isocarbonyl linkages ($n \geq 1$). The authors note that the carbonyl region of the IR spectra contains several strong bands, suggestive of a low-symmetry, linked structure. By contrast, the ions in the similar complex $[\text{SmI}_2(\text{THF})_5]^+[\text{Co}(\text{CO})_4]^-$ are separate in the solid state; the coordination geometry around the samarium atom is roughly pentagonal bipyramidal with the iodine atoms at the two apical positions.⁵²

Table 2. Cationic Bis(cyclopentadienyl) Rare-Earth Metal Complexes

| no. | compound | characterization | refs |
|--------------------------------|---|---|--------------|
| M(CO) _x Counterions | | | |
| 6 | [Dy(η^5 -C ₅ H ₄ Me) ₂ (THF) _n] ⁺ [W(η^5 -C ₅ H ₅)(CO) ₃] ⁻ | IR | 45 |
| 7 | [Ho(η^5 -C ₅ H ₄ Me) ₂ (THF) _n] ⁺ [W(η^5 -C ₅ H ₅)(CO) ₃] ⁻ | IR | 45 |
| 8 | [Er(η^5 -C ₅ H ₅) ₂ (THF) _n] ⁺ [W(η^5 -C ₅ H ₅)(CO) ₃] ⁻ | IR | 45 |
| 9 | [Yb(η^5 -C ₅ H ₅) ₂ (THF) _n] ⁺ [W(η^5 -C ₅ H ₅)(CO) ₃] ⁻ | IR | 45 |
| 10 | [Yb(η^5 -C ₅ Me ₅) ₂ (THF)Co(μ -CO)(CO) ₃] | X-ray, ¹ H NMR, IR | 46 |
| 11 | [{Yb(η^5 -C ₅ Me ₅) ₂ } ₂ Fe ₃ (μ -CO) ₄ (CO) ₇] | X-ray, ¹ H NMR, IR, EA | 47 |
| 12 | [{Yb(η^5 -C ₅ Me ₅) ₂ (THF)} ₂ Fe(μ -CO) ₂ (CO) ₂] | ¹ H NMR, IR, EA | 47 |
| 13 | [Yb(η^5 -C ₅ Me ₅) ₂ Mn(μ -CO) _x (CO) _{5-x}] _y | X-ray, ¹ H NMR, IR, EA, mp | 51 |
| 14 | [Yb(η^5 -C ₅ Me ₅) ₂ Re(μ -CO)(CO) ₄] | ¹ H NMR, IR, EA, mp | 51 |
| 15 | [Sm(η^5 -C ₅ Me ₅) ₂ (THF)(μ -CO) _n Co(CO) _{4-n}] | ¹ H NMR, IR, EA, mp, susc. ^a | 52 |
| 16 | [Ce{ η^5 -C ₅ H ₃ (SiMe ₃) ₂ -1,3} ₂ (μ -CO) ₂ W(η^5 -C ₅ H ₅)(CO) ₂] | X-ray, emission | 53 |
| 17 | [Ce{ η^5 -C ₅ H ₃ (SiMe ₃) ₂ -1,3} ₂ (MeCN) _x] ⁺ [W(η^5 -C ₅ H ₅)(CO) ₃] ⁻ | IR, emission | 53 |
| 18 | [Sm{ η^5 -C ₅ H ₄ (CH ₂ CH ₂ OMe) ₂ (THF)}] ⁺ [Co(CO) ₄] ⁻ | X-ray, ¹ H NMR, IR | 54 |
| 19 | [Yb{ η^5 -C ₅ H ₄ (CH ₂ CH ₂ OMe) ₂ (THF)}] ⁺ [Co(CO) ₄] ⁻ | X-ray, ¹ H NMR, IR | 54 |
| Borate Counterions | | | |
| 20 | [La{ η^5 -C ₅ H ₃ (SiMe ₃) ₂ -1,3} ₂ (MeCN)(DME)] ⁺ [BPh ₄] ⁻ | X-ray, ¹ H NMR, IR | 55 |
| 21 | [Ce{ η^5 -C ₅ H ₃ (SiMe ₃) ₂ -1,3} ₂ (MeCN)(DME)] ⁺ [BPh ₄] ⁻ | ¹ H NMR, IR | 55 |
| 22 | [Sm(η^5 -C ₅ Me ₅) ₂ (THF) ₂] ⁺ [BPh ₄] ⁻ | X-ray, ¹ H, ¹³ C, ¹¹ B NMR, IR, EA, susc. ^a | 56,63 |
| 23 | [Ce(η^5 -C ₅ Me ₅) ₂ (THF) ₂] ⁺ [BPh ₄] ⁻ | ¹ H NMR, IR, EA | 58,69 |
| 24 | [Ce(η^5 -C ₅ Me ₅) ₂ (THT) ₂] ⁺ [BPh ₄] ⁻ | X-ray, IR, EA | 58 |
| 25 | [Sm(η^5 -C ₅ H ₄ ^t Bu) ₂ (THF) ₂] ⁺ [BPh ₄] ⁻ | ¹ H, ¹³ C NMR, EA | 59 |
| 26 | [Sm(η^5 -C ₅ H ₄ SiMe ₃) ₂ (THF) ₂] ⁺ [BPh ₄] ⁻ | ¹ H, ¹³ C NMR, EA | 59 |
| 27 | [Sm(η^5 -NC ₄ H ₂ ^t Bu ₂ -2,5) ₂ (THF)] ⁺ [BPh ₄] ⁻ | ¹ H, ¹³ C NMR, EA | 59 |
| 28 | [Y(η^5 -C ₅ Me ₅) ₂ (THF) ₂] ⁺ [BPh ₄] ⁻ | ¹ H, ¹³ C NMR, EA | 59 |
| 28 | [Yb(η^5 -C ₅ Me ₅) ₂ (THF) ₂] ⁺ [BPh ₄] ⁻ | X-ray, EA | 59 |
| 30 | [Y(η^5 -C ₅ Me ₄ Et) ₂ (THF) ₂] ⁺ [BPh ₄] ⁻ | ¹ H, ¹³ C NMR, EA | 59 |
| 31 | [Sm(η^5 -C ₅ Me ₄ Et) ₂ (THF) ₂] ⁺ [BPh ₄] ⁻ | ¹ H, ¹³ C NMR, EA | 59 |
| 32 | [Yb(η^5 -C ₅ H ₄ ^t Bu) ₂ (THF) ₂] ⁺ [BPh ₄] ⁻ | X-ray, IR, EA, mp | 60 |
| 33 | [Sm(η^5 -C ₅ H ₄ Me) ₂ (THF) ₂] ⁺ [BPh ₄] ⁻ | IR, mp, EA, conductivity | 61 |
| 34 | [Yb(η^5 -C ₅ H ₄ Me) ₂ (THF) ₂] ⁺ [BPh ₄] ⁻ | X-ray, mp, EA, conductivity | 61 |
| 35 | [Sm(η^5 -C ₅ Me ₅) ₂ (η^2 -H ₂ NNH ₂)(THF)] ⁺ [BPh ₄] ⁻ | X-ray, ¹ H, ¹³ C, ¹¹ B NMR, EA | 62 |
| 36 | [Sm(η^5 -C ₅ Me ₅) ₂ (μ -Ph) ₂ BPh ₂] | X-ray, ¹ H, ¹³ C NMR, IR, EA | 63,65,69 |
| 37 | [La(η^5 -C ₅ Me ₅) ₂ (μ -Ph) ₂ BPh ₂] | no data available | 64,65,69,171 |
| 38 | [Ce(η^5 -C ₅ Me ₅) ₂ (μ -Ph) ₂ BPh ₂] | ¹ H NMR, IR | 66,69 |
| 39 | [Pr(η^5 -C ₅ Me ₅) ₂ (μ -Ph) ₂ BPh ₂] | ¹ H NMR | 66 |
| 40 | [Nd(η^5 -C ₅ Me ₅) ₂ (μ -Ph) ₂ BPh ₂] | X-ray, ¹ H NMR, IR, EA | 63 |
| 41 | [Tm(η^5 -C ₅ Me ₅) ₂ (μ -Ph) ₂ BPh ₂] | IR, EA | 63 |
| 42 | [Lu(η^5 -C ₅ Me ₅) ₂ (μ -Ph) ₂ BPh ₂] | no data available | 65 |
| 43 | [La(η^5 -C ₅ Me ₄ Et) ₂ (μ -Ph) ₂ BPh ₂] | ¹ H NMR | 64 |
| 44 | [La(η^5 -C ₅ Me ₄ Pr) ₂ (μ -Ph) ₂ BPh ₂] | ¹ H NMR | 64 |
| 45 | [La(η^5 -C ₅ Me ₄ SiMe ₃) ₂ (μ -Ph) ₂ BPh ₂] | ¹ H, ¹³ C NMR | 64 |
| 46 | [Lu(η^5 -C ₅ Me ₄ H) ₂ (μ -Ph) ₂ BPh ₂] | X-ray, ¹ H, ¹³ C NMR, EA | 67 |
| 47 | [Ce(η^5 -C ₅ Me ₅) ₂ (μ -C ₆ F ₅) _n B(C ₆ F ₅) _{4-n}] | no data available | 69 |
| 48 | [Sm{ η^5 -C ₅ Me ₄ (SiMe ₂ CH ₂ CH=CH ₂) ₂ }] ⁺ [BPh ₄] ⁻ | X-ray, ¹ H NMR, IR, EA | 70 |
| 49 | [{Y(η^5 -C ₅ H ₅) ₂ }(μ -Me)] ⁺ [B(C ₆ F ₅) ₄] ⁻ | in situ, ¹ H NMR | 71 |
| 50 | [Y(η^5 -C ₅ H ₅) ₂ (THF) ₂] ⁺ [B(C ₆ F ₅) ₄] ⁻ | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 71 |
| 51 | [Y(η^5 -C ₅ H ₄ SiMe ₃) ₂ (THF) ₂] ⁺ [B(C ₆ F ₅) ₄] ⁻ | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR | 71 |
| 52 | [Y(η^5 -C ₅ H ₅) ₂ (μ -Me)(μ -C ₆ F ₅)B(C ₆ F ₅) ₂] | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 71 |
| 53 | [Y(η^5 -C ₅ H ₄ SiMe ₃) ₂ (μ -Me)(μ -C ₆ F ₅)B(C ₆ F ₅) ₂] | X-ray, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 71 |
| 54 | [Y(η^5 -C ₅ H ₅) ₂ (THF) ₂] ⁺ [B(C ₆ F ₅) ₃ Me] ⁻ | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 71 |
| 55 | [Y(η^5 -C ₅ H ₄ SiMe ₃) ₂ (THF) ₂] ⁺ [B(C ₆ F ₅) ₃ Me] ⁻ | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR | 71 |
| 56 | [Y(η^5 -C ₅ H ₄ SiMe ₃) ₂] ⁺ [B(C ₆ F ₅) ₄] ⁻ | in situ, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR | 71 |
| 57 | [Pr(η^5 -C ₅ Me ₅) ₂ (μ -C ₆ F ₅) ₂ B(C ₆ F ₅) ₂] ₂ | X-ray, ¹ H NMR | 76 |
| 58 | [Nd(η^5 -C ₅ Me ₅) ₂ (μ -C ₆ F ₅) ₂ B(C ₆ F ₅) ₂] ₂ | X-ray, ¹ H NMR | 76 |
| 59 | [Gd(η^5 -C ₅ Me ₅) ₂ (μ -C ₆ F ₅) ₂ B(C ₆ F ₅) ₂] ₂ | no data available | 76 |
| 60 | [Ce(η^5 -C ₅ Me ₅) ₂ (μ -C ₆ F ₅) ₂ B(C ₆ F ₅) ₂] ₂ | no data available | 77 |
| 61 | [Sm(η^5 -C ₅ Me ₅) ₂ (μ -C ₆ F ₅) ₂ B(C ₆ F ₅) ₂] ₂ | X-ray, data not available | 77 |
| 62 | [Sc(η^5 -C ₅ Me ₅) ₂ (THF) ₂] ⁺ [BPh ₄] ⁻ | X-ray, ¹ H NMR, IR, EA | 78 |
| 63 | [Sc(η^5 -C ₅ Me ₅) ₂ (μ -Ph)BPh ₃] | X-ray, IR, EA | 78 |
| 64 | [Sc(η^5 -C ₅ Me ₅) ₂ (FC ₆ H ₅) ₂] ⁺ [BPh ₄] ⁻ | X-ray, EA | 78 |
| 65 | [Sc(η^5 -C ₅ Me ₅) ₂ (<i>o</i> -F ₂ C ₆ H ₄) ₂] ⁺ [BPh ₄] ⁻ | X-ray, IR, EA | 78 |
| 66 | [{Sc(η^5 -C ₅ Me ₅) ₂ }(μ -Me)] ⁺ [B(C ₆ F ₅) ₄] ⁻ | X-ray | 78 |
| 67 | [Sc(η^5 -C ₅ Me ₅) ₂ (μ -C ₆ F ₅)B(C ₆ F ₅) ₃] | X-ray, IR, EA | 78 |
| 68 | [Sc(η^5 -C ₅ Me ₅) ₂ (OCMe ₂) ₂] ⁺ [BPh ₄] ⁻ | X-ray, ¹ H NMR | 79 |
| 69 | [Sc(η^5 -C ₅ Me ₅) ₂ (OCPh ₂) ₂] ⁺ [BPh ₄] ⁻ | X-ray, ¹ H NMR, IR | 79 |
| Other Counterions | | | |
| 70 | [Ce{ η^5 -C ₅ H ₃ (SiMe ₃) ₂ -1,3} ₂ (solvent) _x] ⁺ [BF ₄] ⁻ | ¹⁹ F NMR, luminescence | 53 |
| 71 | [Sm(η^5 -C ₅ Me ₅) ₂ Cl(μ -Cl)Sm(η^5 -C ₅ Me ₅) ₂ - { μ , η^4 -Me(OCH ₂ CH ₂) ₄ OMe}Sm(η^5 -C ₅ Me ₅) ₂] ⁺ - [Sm(η^5 -C ₅ Me ₅) ₂ Cl] ₂ (μ -Cl)] ⁻ | X-ray | 80 |

^a Magnetic susceptibility.

Scheme 4



The heterobimetallic cerium–tungsten compound $[\text{Ce}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}_2(\mu\text{-CO})_2\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2]$ (**16**), synthesized by salt metathesis of $[\text{CeI}_3(\text{THF})_x]$ with 4 equiv of $[\text{K}\{\text{C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}]$ and 2 equiv of $[\text{K}\{\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\}]$ in THF, is dimeric in the solid state, forming a $\{\text{Ce}(\mu\text{-CO})\text{W}(\mu\text{-CO})\}_2$ square (Scheme 5).⁵³ The authors determined the configuration in the solution state by IR and luminescence measurements. No luminescence was observed in THF or toluene solution, due to quenching of excited cerium states by tungsten centers (consistent with Förster-type energy transfer). Since similar behavior of the solid material was observed, the contact ion-pair structure revealed by X-ray crystallography is retained in solution. In acetonitrile solution however, strong luminescence was observed. IR spectroscopy also indicated a pseudo- C_{3v} -symmetrical anion $[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]^-$. Thus the structure $[\text{Ce}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}_2(\text{MeCN})_x]^+[\text{W}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3]^-$ (**17**) was proposed. Treatment of **16** with AgBF_4 resulted in $[\text{Ce}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}_2(\text{solv})_x]^+[\text{BF}_4]^-$ (**70**). The extent of ion pair aggregation in toluene- d_8 could not be conclusively determined by ^{19}F NMR spectroscopy. Luminescence spectroscopy for **70** in acetonitrile or THF, however, is consistent with dissociated ion pairs.

Crystallographic confirmation for the structure of $[\text{Ln}\{\eta^5\text{-C}_5\text{H}_4(\text{CH}_2\text{CH}_2\text{OMe})\}_2(\text{THF})]^+[\text{Co}(\text{CO})_4]^-$ ($\text{Ln} = \text{Sm}$ (**18**),

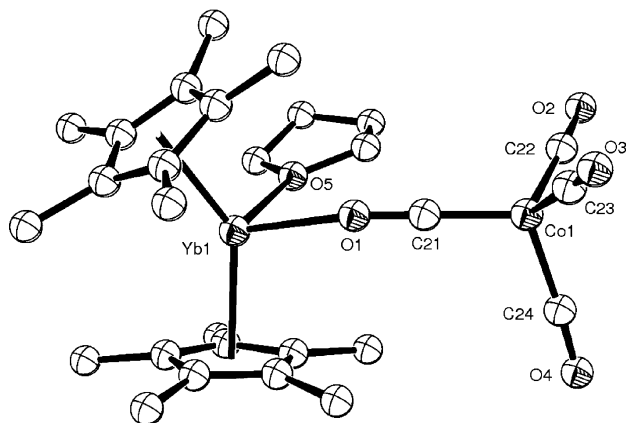
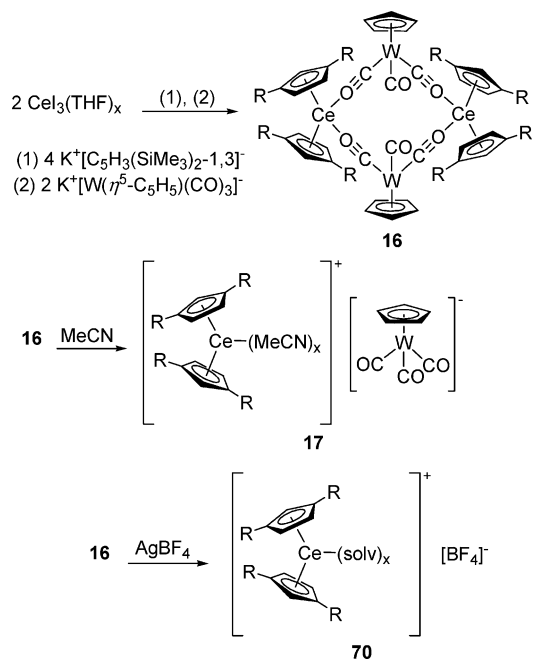


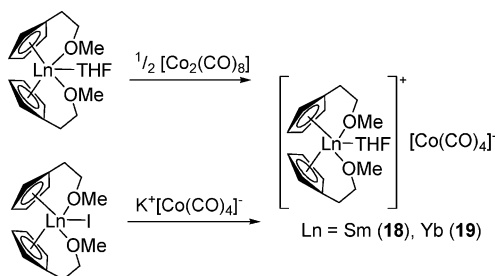
Figure 2. Molecular structure of $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})\text{Co}(\mu\text{-CO})(\text{CO})_3]$ (**10**). Hydrogen atoms are omitted for clarity. Drawn from data in ref 46.

Scheme 5



Yb (**19**)), which are both comprised of solvent-separated ion pairs, has been presented.⁵⁴ Complexes **18** and **19** were reported to have been formed either by the reaction of $[\text{Ln}\{\eta^5\text{-C}_5\text{H}_4(\text{CH}_2\text{CH}_2\text{OMe})\}_2\text{I}]$ with $[\text{K}[\text{Co}(\text{CO})_4]]$ or one electron oxidation of $[\text{Ln}\{\eta^5\text{-C}_5\text{H}_4(\text{CH}_2\text{CH}_2\text{OMe})\}_2(\text{THF})]$ with $[\text{Co}_2(\text{CO})_8]$ (Scheme 6). The data from both IR spectroscopy (mull) and X-ray crystallography (Figure 3) are

Scheme 6



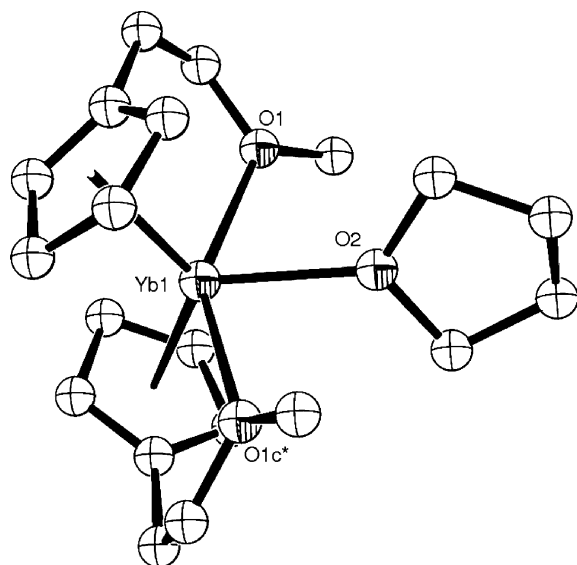


Figure 3. Molecular structure of the cationic part of $[\text{Yb}\{\eta^5\text{-C}_5\text{H}_4(\text{CH}_2\text{CH}_2\text{OMe})_2\}_2(\text{THF})_2][\text{Co}(\text{CO})_4]^-$ (**19**). Hydrogen atoms are omitted for clarity. Drawn from data in ref 54.

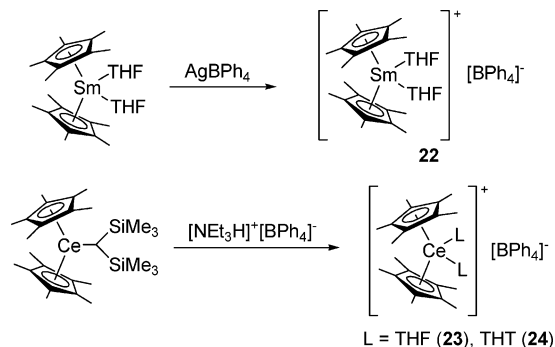
in accordance with separate ion pairs. Complexes **18** and **19** are isostructural and adopt a distorted trigonal-bipyramidal configuration with the two Cp-bound oxygen atoms occupying the axial positions. The NMR spectra indicate that these species are highly fluxional in solution. The fluxionality involves coordinative competition between THF and the chelating arm of the substituted Cp, rotation of the Cp ring, or a Berry pseudorotation.

4.2. Metallocenium Borate Complexes

The complexes $[\text{Ln}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_{2-1,3}\}_2\text{I}(\text{MeCN})_2]$ ($\text{Ln} = \text{La}, \text{Ce}$) were used as starting materials for the ionic compounds $[\text{Ln}(\eta^5\text{-C}_5\text{H}_3\text{SiMe}_3)_{2-1,3}\}_2(\text{MeCN})(\text{DME})]^+[\text{BPh}_4]^-$ ($\text{Ln} = \text{La}$ (**20**), Ce (**21**)) by reaction with AgBPh_4 in THF.⁵⁵ Crystal structure analysis, following recrystallization by slow diffusion of diethyl ether into a DME solution with a few drops of acetonitrile, confirmed the structure of **20** in the solid state.

A samarium THF adduct $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})_2]^+[\text{BPh}_4]^-$ (**22**) that is similar to **20** and **21** was reported to form by oxidation of $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})_2]$ with AgBPh_4 in THF (Scheme 7).⁵⁶ X-ray crystallography shows that the C_5Me_5

Scheme 7



ring centroids (Cn) and the THF oxygen atoms form a distorted tetrahedron with a Cn–Sm–Cn angle of 134.2°. The authors report that the synthetic route involving the Sm(III) species $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}(\text{THF})_2]$ and AgBPh_4 in

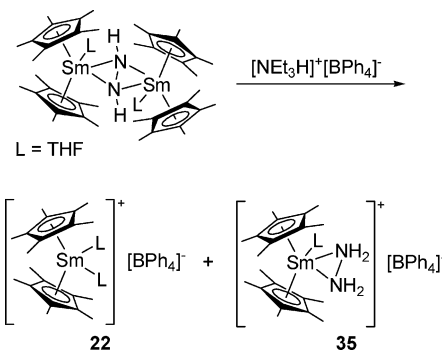
THF is less favorable. They also discuss the synthetic utility of **22** and its ring-opening of THF on reaction with $\text{K}(\text{C}_5\text{Me}_5)$. This area has been comprehensively reviewed elsewhere.⁵⁷ Similar cerium complexes were prepared by protonolysis of the neutral alkyl complex $[\text{Ce}(\eta^5\text{-C}_5\text{Me}_5)_2\{\text{CH}(\text{SiMe}_3)_2\}]$ with $[\text{NEt}_3\text{H}]^+[\text{BPh}_4]^-$ in THF or THT to give the cationic compounds $[\text{Ce}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{L})_2]^+[\text{BPh}_4]^-$ ($\text{L} = \text{THF}$ (**23**), THT (**24**)).⁵⁸ The crystal structure of the THT derivative **24** was determined by X-ray diffraction, which showed that it consists of discrete ions. In a manner similar to **22**, the Cp ring centroids (Cn) and the sulfur atoms in the cation form a distorted tetrahedron with a Cn–Sm–Cn angle of 134.57(6)°, although unlike the earlier compound the Cp rings are staggered rather than eclipsed.

An extension of both the oxidation and protonolysis routes toward these complexes led to $[\text{Sm}(\eta^5\text{-C}_5\text{H}_4\text{R})_2(\text{THF})_2]^+[\text{BPh}_4]^-$ ($\text{R} = \text{tBu}$ (**25**), SiMe_3 (**26**)), $[\text{Sm}(\eta^5\text{-NC}_4\text{H}_2\text{tBu}-2,5)_2(\text{THF})]^+[\text{BPh}_4]^-$ (**27**), $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})_2]^+[\text{BPh}_4]^-$ ($\text{Ln} = \text{Y}$ (**28**), Yb (**29**)), and $[\text{Ln}(\eta^5\text{-C}_5\text{H}_4\text{Et})_2(\text{THF})_2]^+[\text{BPh}_4]^-$ ($\text{Ln} = \text{Y}$ (**30**), Sm (**31**)).⁵⁹ Complexes **25**–**31** were synthesized by oxidation of the divalent complexes $[\text{Sm}(\eta^5\text{-C}_5\text{H}_4\text{R})_2(\text{THF})_2]$, $[\text{Sm}(\eta^5\text{-2,5-tBu-NC}_4\text{H}_2)_2(\text{THF})]$, $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})]$, and $[\text{Sm}(\eta^5\text{-C}_5\text{H}_4\text{Et})_2(\text{THF})]$ with AgBPh_4 or by protonolysis of the trivalent alkyl compounds $[\text{Y}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Me}(\text{THF})]$, $[\text{Yb}(\eta^5\text{-C}_5\text{Me}_5)_2\{\text{CH}(\text{SiMe}_3)_2\}(\text{THF})]$, and $[\text{Ln}(\eta^5\text{-C}_5\text{H}_4\text{Et})_2\{\text{CH}(\text{SiMe}_3)_2\}(\text{THF})]$ ($\text{Ln} = \text{Y}, \text{Sm}$) with $[\text{NEt}_3\text{H}]^+[\text{BPh}_4]^-$. The diamagnetic compounds all give rise to single resonances in the ^1H and ^{13}C NMR spectra (pyridine- d_5), indicating solvent-separated, high-symmetry ions in solution. The crystal structure of **29** is similar to the analogous compounds described above, wherein a distorted tetrahedral center shows a Cn–Sm–Cn angle of 135.83(16)°.

Further advances include the cationic ytterbium species $[\text{Yb}(\eta^5\text{-C}_5\text{H}_4\text{tBu})_2(\text{THF})_2]^+[\text{BPh}_4]^-$ (**32**),⁶⁰ which was also made by oxidation of the divalent species $[\text{Yb}(\eta^5\text{-C}_5\text{H}_4\text{tBu})_2(\text{THF})_2]$ with AgBPh_4 , as were the Sm and Yb complexes incorporating the less bulky methylcyclopentadienyl ligand $[\text{Ln}(\eta^5\text{-C}_5\text{H}_4\text{Me})_2(\text{THF})_2]^+[\text{BPh}_4]^-$ ($\text{Ln} = \text{Sm}$ (**33**), Yb (**34**)).⁶¹ Both **32** and **34** have also been characterized by X-ray crystallography and show similar structures.

A mixture of **22** and the hydrazine complex $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2(\eta^2\text{-H}_2\text{NNH}_2)(\text{THF})]^+[\text{BPh}_4]^-$ (**35**) was formed in a 1:1 ratio when the Sm(III) complex $[\{\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2\}_2(\mu\text{-}\eta^2\text{-}\eta^2\text{-HNNH})]$ reacted with $[\text{NEt}_3\text{H}]^+[\text{BPh}_4]^-$ (Scheme 8).⁶²

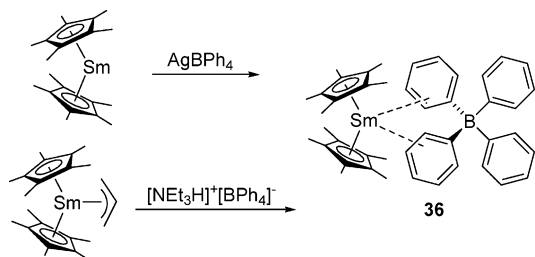
Scheme 8



The novel hydrazine complex **35** was characterized by X-ray crystallography. If the chelating hydrazine ligand is considered as a single unit, the cationic portion of the Sm complex adopts a slightly distorted tetrahedral geometry; two phenyl groups of the borate anion are aligned with the hydrazine ligand in the solid state.

A complex free of THF or other strongly Lewis basic solvents was synthesized by reaction of $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2]$ with AgBPh_4 in toluene followed by extraction with hot toluene or benzene.⁶³ This gave the crystallographically characterized contact ion pair $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-Ph})_2\text{BPh}_2]$ (**36**) in 60% yield (Scheme 9). Complex **36** contains

Scheme 9



electrostatic cation–anion interactions via two phenyl groups of the tetraphenylborate in the crystalline state. The closest approach of the phenyl groups occurs at the *ortho* position, although the *meta* carbon atoms are also within coordination distance. Synthesis of the analogous THF-free cationic complexes $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-Ph})_2\text{BPh}_2]$ ($\text{Ln} = \text{La}$ (**37**), Ce (**38**), Pr (**39**), Nd (**40**), Tm (**41**), Lu (**42**)) was also possible from the trivalent precursors $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2\{\text{CH}(\text{SiMe}_3)_2\}]$ and $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)_2(\eta^3\text{-C}_3\text{H}_5)]$ ($\text{Ln} = \text{La}$, Ce , Pr , Sm , Nd , Tm , Lu) via reaction with $[\text{NEt}_3\text{H}]^+[\text{BPh}_4]^-$.^{63–66} The neodymium complex was characterized by X-ray crystallography (Figure 4).⁶³ A further series of similar lanthanum compounds

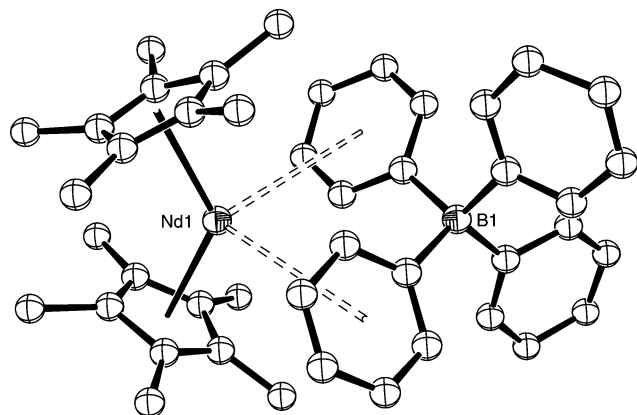


Figure 4. Molecular structure of $[\text{Nd}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-Ph})_2\text{BPh}_2]$ (**40**). One of two crystallographically independent molecules is shown; hydrogen atoms are omitted for clarity. Drawn from data in ref 63.

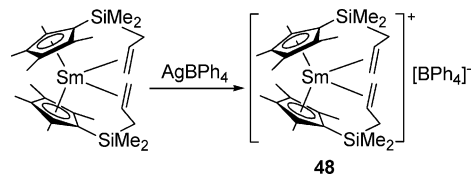
with various substituted cyclopentadienyl ligands $[\text{La}(\eta^5\text{-C}_5\text{Me}_4\text{R})_2(\mu\text{-Ph})_2\text{BPh}_2]$ ($\text{R} = \text{Et}$ (**43**), Pr (**44**), SiMe_3 (**45**)) has been reported.⁶⁴ X-ray crystallography indicated that the structures of **43** and **45** are similar to the parent pentamethylcyclopentadienyl compound. Recently, this series could be further extended on the Lu complex $[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{H})_2(\mu\text{-Ph})_2\text{BPh}_2]$ (**46**) with a sterically less demanding cyclopentadienyl ligand.⁶⁷ The reaction chemistry of this family of contact ion pairs has been extended to a number of organometallic reagents, leading to unsolvated complexes otherwise inaccessible via conventional synthetic routes (section 9.4).⁶⁵ The samarium complex **36** reacted with LiCH_2Bu in an unexpected manner to yield $[\{\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2\}_2(\mu\text{-}\eta^3\text{-}\eta^3\text{-C}(\text{CH}_2)_3)]$, a rare example of lanthanoid-based β -alkyl elimination.⁶⁸

Complexes **36**, **37**, and **38**, as well as the solvated cerium complex **23** and the contact ion pair $[\text{Ce}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-}$

$\text{C}_6\text{F}_5)_n\text{B}(\text{C}_6\text{F}_5)_{4-n}]$ (**47**), have been used as precatalysts in hetero-Diels–Alder reactions (section 9.2.3).⁶⁹

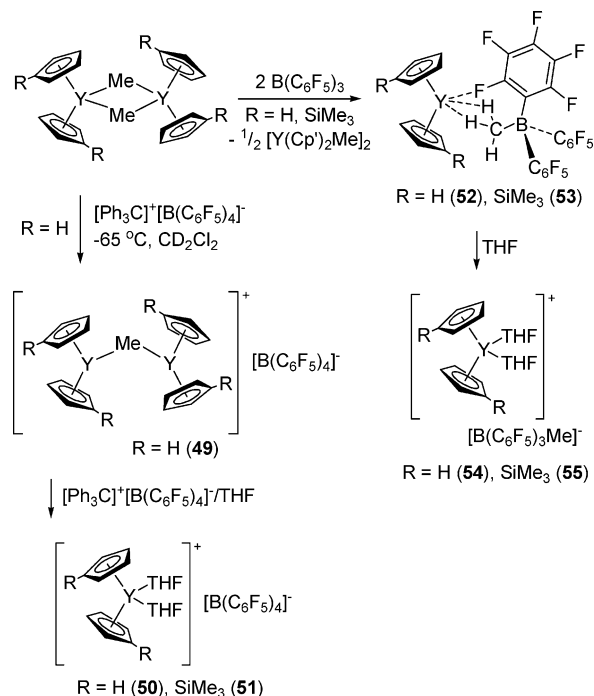
The samarium complex $[\text{Sm}\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\}^+[\text{BPh}_4]^-$ (**48**), incorporating a cyclopentadienyl ligand with a tethered olefin unit, can be isolated via reaction of the divalent precursor $[\text{Sm}\{\eta^5\text{-C}_5\text{Me}_4(\text{SiMe}_2\text{CH}_2\text{CH}=\text{CH}_2)_2\}]$ with AgBPh_4 in toluene.⁷⁰ Interestingly, coordination of the two olefin units is preferred over that of the phenyl groups from the borate anion in the solid state (Scheme 10).

Scheme 10



A series of cationic rare-earth metallocenium complexes was isolated using $[\text{Y}(\eta^5\text{-C}_5\text{H}_4\text{R})_2(\mu\text{-Me})_2]$ ($\text{R} = \text{H}$, SiMe_3) as a starting material (Scheme 11).⁷¹ Reaction of $[\text{Y}(\eta^5\text{-}$

Scheme 11



$\text{C}_5\text{H}_5)_2(\mu\text{-Me})_2]$ with 1 equiv of $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ at -65 °C in CD_2Cl_2 gave the bimetallic cation $[\{\text{Y}(\eta^5\text{-C}_5\text{H}_5)_2\}_2(\mu\text{-Me})^+[\text{B}(\text{C}_6\text{F}_5)_4]^-]$ (**49**). The use of 2 equiv of $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in toluene gave an oily precipitate. Addition of THF to this material gave the expected discrete ion pairs $[\text{Y}(\eta^5\text{-C}_5\text{H}_4\text{R})_2(\text{THF})_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ($\text{R} = \text{H}$ (**50**), SiMe_3 (**51**)).

When 2 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene was used to activate $[\text{Y}(\eta^5\text{-C}_5\text{H}_4\text{R})_2(\mu\text{-Me})_2]$ ($\text{R} = \text{H}$, SiMe_3), the contact ion pairs $[\text{Y}(\eta^5\text{-C}_5\text{H}_4\text{R})_2(\mu\text{-Me})(\mu\text{-C}_6\text{F}_5)\text{B}(\text{C}_6\text{F}_5)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ($\text{R} = \text{H}$ (**52**), SiMe_3 (**53**)) were formed. An X-ray structure analysis of **53** revealed that the anion coordinates in a chelating fashion via one *ortho*-fluorine and two methyl hydrogens (Figure 5). NMR studies showed that the complexes are highly fluxional in solution. The solvent-separated ion pairs $[\text{Y}(\eta^5\text{-C}_5\text{H}_4\text{R})_2(\text{THF})_2]^+[\text{B}(\text{C}_6\text{F}_5)_3\text{Me}]^-$ ($\text{R} = \text{H}$ (**54**), SiMe_3 (**55**)) were formed on the addition of THF to **52** or **53**, respectively.

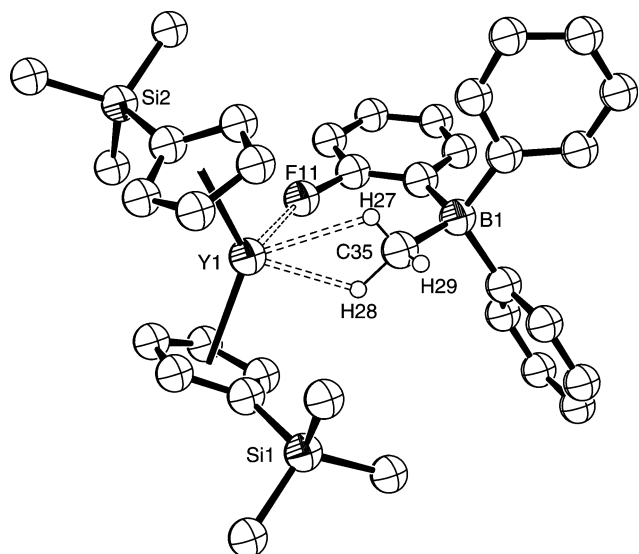


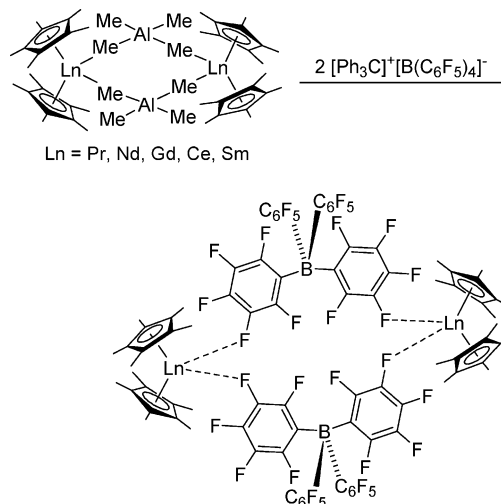
Figure 5. Molecular structure of $[Y(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2(\mu\text{-Me})(\mu\text{-C}_6\text{F}_5)\text{B}(\text{C}_6\text{F}_5)_2]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**53**). Remaining hydrogen atoms and remaining fluorine atoms of $\text{B}(\text{C}_6\text{F}_5)_3$ are omitted for clarity. Drawn from data in ref 71.

The in situ generated THF-free cationic complex $[Y(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**56**) was active in isobutylene polymerization (section 9.1.4).

Although no organometallic species were fully characterized, it can be postulated that the reaction of the Sm(III) compound $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-Me})_2\text{AlMe}_2]$ and indeed that of the Sm(II) species $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})_2]$ with MMAO (MMAO = modified methylaluminumoxane containing isobutylaluminumoxane) or $\text{Al}^i\text{Bu}_3/[\text{Ph}_3\text{C}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ resulted in the formation of bis(cyclopentadienyl) samarium(III) cation/organaluminatate contact or solvent-separated ion pairs.^{72,73} The reaction is likely to proceed in the latter case via one electron oxidation of the Sm(II) center by the aluminum reagent to give an intermediate heterobimetallic Sm–Al complex. It is noteworthy that complexes such as $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-Me})_2\text{AlMe}_2]$ can be cleaved by THF to form neutral $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Me}(\text{THF})_n]$ and AlMe_3 and not the ion pair $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})_x]^+ [\text{AlMe}_4]^-$.⁷⁴ A later study showed that the variation of substituents at the cyclopentadienyl ring has a profound effect on the reactivity of the Sm(II) complexes on activation with MMAO.⁷⁵ Furthermore, the Lewis base-free ion pairs $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-C}_6\text{F}_5)_2\text{B}(\text{C}_6\text{F}_5)_2]_2$ (Ln = Pr (**57**), Nd (**58**), Gd (**59**)) were prepared by reaction of the aluminate complexes $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-Me})_2\text{AlMe}_2]$ with $[\text{Ph}_3\text{C}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ in toluene (Scheme 12).⁷⁶ X-ray crystallography of **57** showed that two $[\text{Pr}(\eta^5\text{-C}_5\text{Me}_5)_2]^+$ units are linked by two $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ units via Pr–F interaction. The corresponding cerium and samarium complexes **60** and **61** were synthesized in an analogous manner and used as catalysts for 1,3-butadiene polymerization (section 9.1.3).⁷⁷

The reaction of $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Me}]$ with $[\text{PhNMe}_2\text{H}]^+ [\text{BPh}_4]^-$ in THF yielded $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})_2]^+ [\text{BPh}_4]^-$ (**62**).⁷⁸ The solid-state structure of its THF-*d*₈ analogue, which was obtained after recrystallization from THF-*d*₈/pentane, was determined by X-ray crystallography and shows well-separated ion pairs. The same reaction carried out in toluene instead of THF afforded the base-free cationic compound $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-Ph})\text{BPh}_3]$ (**63**). In contrast to the compounds with larger lanthanoids above, only one phenyl group of the $[\text{BPh}_4]^-$ anion interacts with the cationic metal center

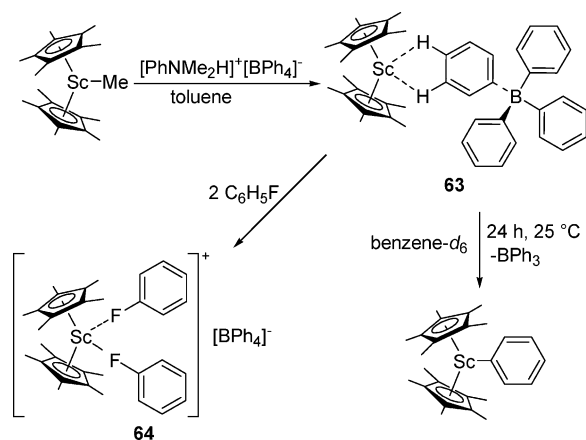
Scheme 12^a



Ln = Pr, Nd, Gd, Ce, Sm

^a Ln = Pr (**57**), Nd (**58**), Gd (**59**), Ce (**60**), Sm (**61**).

Scheme 13

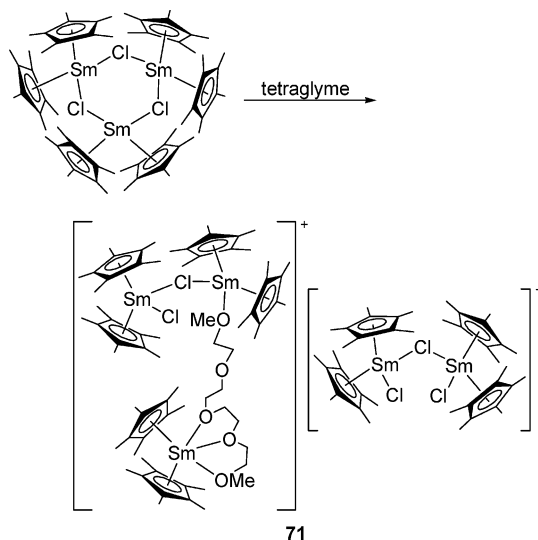


(Scheme 13). Addition of THF to **63** afforded the corresponding THF adduct **62**. Addition of fluorobenzene or *o*-difluorobenzene to **63** yielded the adducts $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{FC}_6\text{H}_5)_2]^+ [\text{BPh}_4]^-$ (**64**) and $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{o-F}_2\text{C}_6\text{H}_4)]^+ [\text{BPh}_4]^-$ (**65**). Their X-ray structure analysis revealed well-separated anions and coordination of the fluorobenzenes to the metal center via the fluorine atoms. Complex **63** reacted via C–F activation with α,α,α -trifluorotoluene to yield the neutral bis(cyclopentadienyl) fluoro complex $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)_2\text{F}]$. The reaction of $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Me}]$ with half an equivalent of $[\text{PhNMe}_2\text{H}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ in toluene yielded the methyl-bridged dimer $[\{\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)_2\}_2(\mu\text{-Me})]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**66**); monomeric $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-C}_6\text{F}_5)\text{B}(\text{C}_6\text{F}_5)_3]$ (**67**) was isolated in the presence of additional $[\text{PhNMe}_2\text{H}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$. The X-ray structure of **66** shows a trigonal bipyramidal, bridging methyl group with a Sc–C–Sc angle close to linear and a noncoordinating anion. In **67**, the anion coordinates to the metal center via two fluorine atoms, comparable to the coordination of the *o*-difluorobenzene molecule in **65**. Addition of a slight excess of acetone or benzophenone to a fluorobenzene solution of **63** yielded the cationic, crystallographically characterized bis(acetone) and mono(benzophenone) adducts **68** and **69**, respectively.⁷⁹ Decomposition of **63** in C_6D_6 suspension within 24 h at room temperature afforded $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ph}]$ and BPh_3 as the major products as monitored by ¹H and ¹³C NMR spectroscopy.

4.3. Metallocenium Cluster Complex

Tetraglyme has been shown to induce a rearrangement of the solvent-free samarocene chloride $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}]_3$ from its trimeric structure with an approximately hexagonal $(\text{Sm}-\text{Cl})_3$ core to the unusually complex ion pair structure $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}(\mu\text{-Cl})\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2\{\mu,\eta^4\text{-Me}(\text{OCH}_2\text{CH}_2)_4\text{OMe}\}]\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2]^+[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}(\mu\text{-Cl})\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}]^-$ (**71**).⁸⁰ The three different Sm centers in the cationic portion of the ion pair structure are connected via tetraglyme and chloride bridges, while in the anion a chloride bridge links two equivalent $\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Cl}$ units (Scheme 14).

Scheme 14



5. Cationic Mono(cyclopentadienyl) Complexes

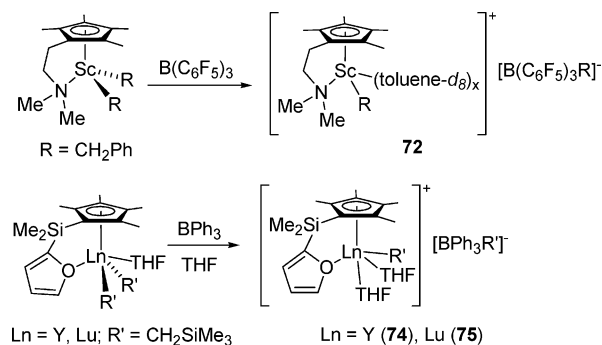
Significantly fewer neutral rare-earth metal half-sandwich compounds are known compared to the extensive range of bis(cyclopentadienyl) complexes, due in part to the greater thermodynamic stability of the metallocene derivatives.⁸¹ The neutral complexes containing one Cp and two σ -bound alkyl

groups have the advantage that the cationic derivatives retain a σ -alkyl group, potentially useful in polymerization or organic transformation reactions. Published examples of cationic organolanthanoid half-sandwich complexes are listed in Table 3.

5.1. Donor-Functionalized Mono(cyclopentadienyl) Complexes

$[\text{Sc}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2\text{CH}_2\text{NMe}_2)\}(\text{CH}_2\text{Ph})]^+[\text{B}(\text{C}_6\text{F}_5)_3\text{-}(\text{CH}_2\text{Ph})]^-$ (**72**) was synthesized in situ by addition of $\text{B}(\text{C}_6\text{F}_5)_3$ to a toluene-*d*₈ solution of the neutral, crystallographically characterized complex $[\text{Sc}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2\text{CH}_2\text{NMe}_2)\}(\text{CH}_2\text{Ph})_2]$ (Scheme 15).⁸² No detailed characteriza-

Scheme 15



tion was given for this compound, but addition of ethylene gave noticeable polyethylene formation within several minutes.

Similar complexes with a furyl-functionalized cyclopentadienyl ligand $[\text{Ln}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2(\text{C}_4\text{H}_3\text{O}-2)\}(\text{CH}_2\text{SiMe}_3)\text{-}(\text{THF})_x]^+[\text{BPh}_3(\text{CH}_2\text{SiMe}_3)]^-$ ($\text{Ln} = \text{Y}$ (**74**), Lu (**75**)) were prepared in situ by the reaction of the corresponding neutral bis(alkyl) complexes with BPh_3 in THF (Scheme 15).⁸³ The NMR spectroscopic data indicated the formation of solvent-separated ion pairs.

Reaction of the neutral binuclear bis(alkyl) complexes $[\text{Ln}(\eta^5\text{-}\eta^1\text{-}\mu\text{-C}_5\text{Me}_4\text{SiMe}_2\text{PCy})(\text{CH}_2\text{SiMe}_3)]_2$ ($\text{Cy} = \text{cyclo-}$

Table 3. Cationic Mono(cyclopentadienyl) Rare-Earth Metal Complexes

| no. | compound | characterization | refs |
|---|---|---|-------|
| Donor-Functionalized Cyclopentadienyl Ligands | | | |
| 72 | $[\text{Sc}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2\text{CH}_2\text{NMe}_2)\}(\text{CH}_2\text{Ph})]^+[\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{Ph})]^-$ | in situ, no data available | 82 |
| 73 | $[\text{Sc}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4(\text{CH}_2\text{CH}_2\text{NMe}_2)\}(\text{CH}_2\text{Ph})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | in situ, no data available | 82 |
| 74 | $[\text{Y}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2(\text{C}_4\text{H}_3\text{O}-2)\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{BPh}_3(\text{CH}_2\text{SiMe}_3)]^-$ | ¹ H, ¹³ C, ¹¹ B NMR | 83 |
| 75 | $[\text{Lu}\{\eta^5\text{-}\eta^1\text{-C}_5\text{Me}_4\text{SiMe}_2(\text{C}_4\text{H}_3\text{O}-2)\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{BPh}_3(\text{CH}_2\text{SiMe}_3)]^-$ | ¹ H, ¹³ C, ¹¹ B NMR | 83 |
| 76 | $[\{\text{Y}(\eta^5\text{-}\eta^1\text{-}\mu\text{-C}_5\text{Me}_4\text{SiMe}_2\text{PCy})\}_2(\mu\text{-CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^a | in situ, no data available | 84 |
| 77 | $[\{\text{Lu}(\eta^5\text{-}\eta^1\text{-}\mu\text{-C}_5\text{Me}_4\text{SiMe}_2\text{PCy})\}_2(\mu\text{-CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^a | in situ, no data available | 84 |
| 78 | $[\{\text{Y}(\eta^5\text{-}\eta^1\text{-}\mu\text{-C}_5\text{Me}_4\text{SiMe}_2\text{PCy})\}_2(\mu\text{-CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{SiMe}_3)]^-$ ^a | in situ, no data available | 84 |
| Nonfunctionalized Cyclopentadienyl Ligands | | | |
| 79 | $[\text{La}(\eta^5\text{-C}_5\text{Me}_5)\{\text{CH}(\text{SiMe}_3)_2\}(\mu\text{-Ph})_2\text{BPh}_2]$ | ¹ H, ¹³ C, ²⁹ Si NMR, ¹³ C CP MAS, EA | 85 |
| 80 | $[\text{La}(\eta^5\text{-C}_5\text{Me}_5)\{\text{CH}(\text{SiMe}_3)_2\}(\text{THF})_3]^+[\text{BPh}_4]^-$ | ¹ H, ¹³ C, ²⁹ Si NMR, ¹³ C CP MAS, EA | 85 |
| 81 | $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{BPh}_4]^-$ | ¹ H, ¹³ C NMR | 86b |
| 82 | $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}(\text{tBu}_3\text{P}=\text{O})(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$ | X-ray, ¹ H, ¹¹ B, ¹⁹ F NMR | 87 |
| 83 | $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | in situ, ¹ H NMR | 89–91 |
| 84 | $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | in situ, no data available | 89 |
| 85 | $[\text{Gd}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | in situ, no data available | 89 |
| 86 | $[\text{Lu}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | in situ, no data available | 89 |
| 87 | $[\text{Sc}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | in situ, no data available | 90 |
| 88 | $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | in situ, no data available | 90 |
| 89 | $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | ¹ H NMR | 90 |
| 90 | $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^3\text{-ArNC}(\text{Me})\text{CHC}(\text{Me})\text{NAr}\}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]^+$ | ¹ H NMR, mp, EA | 92 |
| 91 | $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{THF})_4]^{2+}[\text{BPh}_4]_2^-$ | X-ray, ¹ H, ¹¹ B NMR, EA | 93 |

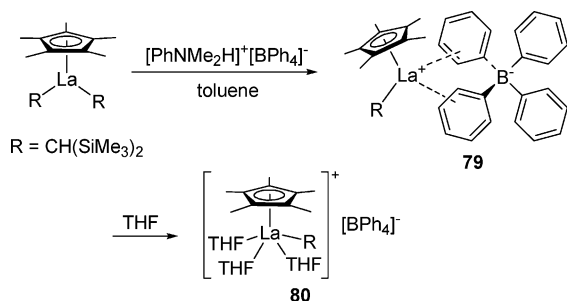
^a Cy = cyclohexyl. ^b Ar = C₆H₃Pr₂-2,6.

hexyl; Ln = Y, Lu) with 1 equiv of $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, $[\text{PhNMe}_2\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, or $\text{B}(\text{C}_6\text{F}_5)_3$ in $\text{C}_6\text{H}_5\text{Cl}$ afforded the corresponding binuclear monocationic mono(alkyl) species $[\{\text{Ln}(\eta^5\text{-}\eta^1\text{-}\mu\text{-C}_5\text{Me}_4\text{SiMe}_2\text{PCy})\}_2(\mu\text{-CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_3\text{R}]^-$ ($\text{R} = \text{C}_6\text{F}_5$, $\text{Ln} = \text{Y}$ (**76**), Lu (**77**); $\text{R} = \text{CH}_2\text{SiMe}_3$, $\text{Ln} = \text{Y}$ (**78**)).⁸⁴ These monocations, generated in situ, were used for the polymerization of isoprene (section 9.1.3). Since the isolation of these compounds was not possible due to their high instability, DFT calculations were carried out, which corroborated their proposed structures.

5.2. Nonfunctionalized Mono(cyclopentadienyl) Complexes

The first example of a cationic lanthanoid alkyl complex was reported by Schaverien in 1992.⁸⁵ The complex $[\text{La}(\eta^5\text{-C}_5\text{Me}_5)\{\text{CH}(\text{SiMe}_3)_2\}(\mu\text{-Ph})_2\text{BPh}_2]$ (**79**) was synthesized in good yield by protonolysis of $[\text{La}(\eta^5\text{-C}_5\text{Me}_5)\{\text{CH}(\text{SiMe}_3)_2\}_2]$ with an equimolar amount of $[\text{PhNMe}_2\text{H}]^+[\text{BPh}_4]^-$ in toluene (Scheme 16). During the reaction, the formation of PhNMe_2

Scheme 16



and $\text{CH}_2(\text{SiMe}_3)_2$ was monitored by ^1H NMR spectroscopy. The stoichiometry of **79** was confirmed by elemental analysis as well as by ^1H , ^{13}C , and ^{29}Si NMR spectroscopy. A small upfield shift of the *ipso* carbons in the ^{13}C NMR spectrum compared to the uncoordinated borate anion was explained by π -coordination in weakly donating solvents with rapid inter- or intramolecular exchange. Addition of 3 equiv of THF to a toluene solution of **79** afforded $[\text{La}(\eta^5\text{-C}_5\text{Me}_5)\{\text{CH}(\text{SiMe}_3)_2\}(\text{THF})_3]^+[\text{BPh}_4]^-$ (**80**) by irreversible displacement of the coordinated tetraphenylborate anion. Here, the resonances of the *ipso* carbons of the anion are in agreement with a noncoordinating, tetrahedral $[\text{BPh}_4]^-$ anion. Reaction of **79** with $\text{LiCH}(\text{SiMe}_3)_2$ gave the neutral bis(alkyl) mono(cyclopentadienyl) complex $[\text{La}(\eta^5\text{-C}_5\text{Me}_5)\{\text{CH}(\text{SiMe}_3)_2\}_2]$; reaction with $\text{LiOC}_6\text{H}_3\text{Bu}_2\cdot\text{Et}_2\text{O}$ yielded the mixed alkyl-alkoxide complex $[\text{La}(\eta^5\text{-C}_5\text{Me}_5)\{\text{CH}(\text{SiMe}_3)_2\}(\text{OC}_6\text{H}_3\text{Bu}_2)]$.

$[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{BPh}_4]^-$ (**81**) was generated by the reaction of $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]^{86a}$ with 1 equiv of $[\text{PhNMe}_2\text{H}]^+[\text{BPh}_4]^-$ in $\text{C}_6\text{D}_5\text{Br}$ at -20°C .^{86b} In situ characterization by ^1H and ^{13}C NMR spectroscopy indicated the formation of SiMe_4 and PhNMe_2 besides **81**. The complex decomposes in solution at room temperature within 24 h.

The reaction of $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}_2(\text{tBu}_3\text{P}=\text{O})]$ with the Lewis acid $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene formed the contact ion pair $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)\text{Me}(\text{tBu}_3\text{P}=\text{O})(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$ (**82**).⁸⁷ The difference of 4.1 ppm between the *meta* and *para* fluorine signals in the ^{19}F NMR spectrum, by analogy to related zirconium complexes $[\text{Zr}\{\text{Me}_3\text{SiN}(\text{CH}_2\text{CH}_2\text{NSiMe}_3)_2\}\text{R}(\mu\text{-R})\text{B}(\text{C}_6\text{F}_5)_3]$ ($\text{R} = \text{Me}, \text{CH}_2\text{Ph}$),⁸⁸ as well as the X-ray crystal structure clearly show that **82** exists as a contact ion pair.

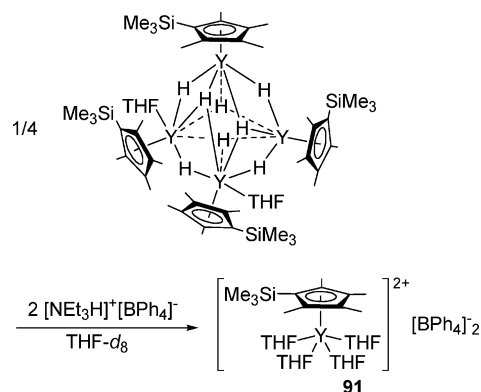
Despite the relatively high thermal stability of **82** in solution, polymerization of ethylene at elevated temperatures showed a decline in activity probably due to catalyst decomposition, whereas the activity at room temperature is quite high ($1.3 \times 10^2 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$).

The in situ generation of cationic mono(cyclopentadienyl) complexes of the lanthanoids for the polymerization of different nonpolar substrates has been described. The reaction of $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ with 1 equiv of $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in benzene afforded the cationic complex $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**83**).⁸⁹ The ^1H NMR spectrum of the complex generated in situ in C_6D_6 showed resonances due to $\text{Ph}_3\text{CCH}_2\text{SiMe}_3$, as well as two sets of THF resonances, but the methylene protons of the trimethylsilylmethyl ligand were not observed. Ion pair **83** shows excellent activity for syndiospecific styrene homopolymerization and styrene-ethylene copolymerization (section 9.1). Analogously, the cationic lanthanoid complexes $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ($\text{Ln} = \text{Y}$ (**84**), Gd (**85**), Lu (**86**)) were generated in situ and their polymerization activity examined. Nevertheless, efforts to isolate the cationic species were unsuccessful. In a few hours, the formation of a benzene-insoluble oily product was observed. Complex **83** and the related cationic half-sandwich scandium complexes $[\text{Sc}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_{2-1,3}\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**87**) and $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**88**) (generated in situ from the corresponding neutral bis(alkyl) complexes with 1 equiv of $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in benzene) were reported to be highly active in the homo- and copolymerization of various nonpolar monomers (section 9.1).^{90,91} The bis(THF)-coordinated cationic species $[\text{Sc}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**89**) is more stable but inactive toward ethylene and norbornene polymerization.⁹⁰

Reaction of $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^3\text{-ArNC}(\text{Me})\text{CHC}(\text{Me})\text{NAr}\}\text{Me}]$ ($\text{Ar} = \text{C}_6\text{H}_3\text{Pr}_2\text{-2,6}$) with $\text{B}(\text{C}_6\text{F}_5)_3$ in toluene afforded $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)\{\eta^3\text{-ArNC}(\text{Me})\text{CHC}(\text{Me})\text{NAr}\}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$ (**90**), which was analyzed by ^1H NMR spectroscopy.⁹² Complex **90** is relatively poorly soluble in toluene and shows no reactivity under CO atmosphere in toluene or toward ethylene or MMA at room temperature.

A unique example of an yttrium mono(cyclopentadienyl) dication, $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{THF})_4]^{2+}[\text{BPh}_4]_2^-$ (**91**), was formed upon reaction of the neutral hydride cluster $[\{\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_4(\mu\text{-H})_4(\mu_3\text{-H})_4(\text{THF})_2\}]$ with an excess of $[\text{NEt}_3\text{H}]^+[\text{BPh}_4]^-$ in THF-d_8 (Scheme 17).⁹³ X-ray structure analysis (Figure 6) revealed no close ion-ion interactions in the solid state.

Scheme 17



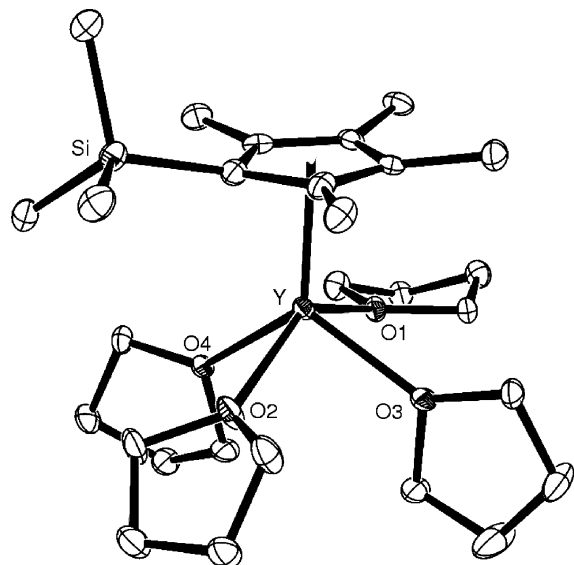


Figure 6. Molecular structure of the cationic part of $[Y(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)(\text{THF})_4]^{2+}[\text{BPh}_4]^{-}_2$ (**91**). Hydrogen atoms are omitted for clarity. Drawn from data in ref 93.

6. Cationic Complexes with Monoanionic, Non-Cyclopentadienyl Ligands

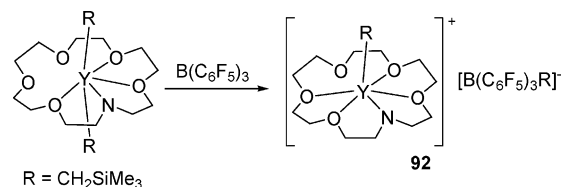
6.1. Complexes with L_nX -Type Ligands ($n = 3\text{--}5$)

This class of compounds contains azacrown ether and triazacyclononane complexes as well as complexes with analogous “open” chelating ligands (Table 4).

6.1.1. Deprotonated Aza-18-crown-6 Complex

The reaction of the structurally characterized complex $[Y(\text{MAC})(\text{CH}_2\text{SiMe}_3)_2]$ (MAC = deprotonated aza-18-crown-6) with $\text{B}(\text{C}_6\text{F}_5)_3$ afforded the highly unstable cationic complex $[Y(\text{MAC})(\text{CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{SiMe}_3)]^-$ (**92**) (Scheme 18).⁹⁴ Comparison of the *meta/para* fluorine chemical shift values in the ^{19}F NMR spectra recorded in THF- d_8 indicates the presence of noncoordinating anions.

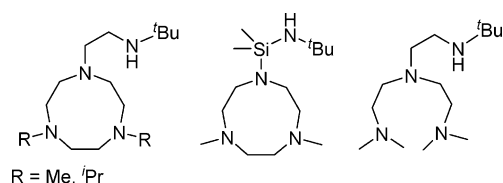
Scheme 18



6.1.2. Functionalized Triazacyclononane and Triamino-amide Complexes

The macrocyclic six-electron donor 1,4,7-triazacyclononane (TACN) has been widely used as a facially coordinating ancillary ligand in coordination chemistry and homogeneous catalysis.^{95–97} Various syntheses of cationic rare-earth organometallic complexes with donor-functionalized triazacyclononane and other related ligands have been reported (Chart 1).

Chart 1



The reaction of $[\text{PhNMe}_2\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ with the neutral dialkyl complex $[Y\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-R}_2\text{-TACN-}N''\text{-(CH}_2)_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)_2]$ (TACN = 1,4,7-triazacyclononane) in $\text{C}_6\text{D}_5\text{Br}$ gave SiMe_4 , free PhNMe_2 , and the cation $[Y\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-R}_2\text{-TACN-}N''\text{-(CH}_2)_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ($\text{R} = \text{Me}$ (**93**)).⁹⁸ The mono-THF adduct could be obtained in the presence of excess of THF- d_8 ($\text{R} = \text{tPr}$ (**94**)). In analogous reactions using $\text{C}_6\text{D}_5\text{Br}$ as solvent, $[\text{PhNMe}_2\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ was added to the respective neutral complexes to afford a series of cationic rare-earth metal complexes (**95–106**).⁹⁹ All of these in situ generated cationic complexes are active in the homo- or copolymerization of ethylene and ethylene/ α -olefins. Additionally, the related cationic lanthanum monoalkyl complex $[\text{La}(\eta^3\text{-}\eta^1\text{-}N,N'\text{-Me}_2\text{-TACN-}N''\text{-(CH}_2)_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)(\text{THF-}d_8)_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**107**) showed rare *cis*-selective behavior in the linear dimerization of phenylacetylene.¹⁰⁰

Table 4. Cationic Rare-Earth Organometallic Complexes That Contain L_nX -Type Ligands ($n = 3\text{--}5$)

| no. | compound | characterization | refs |
|------------|--|---|------------|
| 92 | $[Y(\text{MAC})(\text{CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{SiMe}_3)]^-$ ^a | in situ, ^1H , ^{13}C , ^{19}F NMR | 94 |
| 93 | $[Y\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-Me}_2\text{-TACN-}N''\text{-(CH}_2)_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, ^1H , ^{13}C NMR | 98,99,169 |
| 94 | $[Y\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-tPr}_2\text{-TACN-}N''\text{-(CH}_2)_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)(\text{THF-}d_8)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, ^1H NMR | 98,99,169 |
| 95 | $[Y\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-Me}_2\text{-TACN-}N''\text{-SiMe}_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, ^1H , ^{13}C , ^{19}F NMR | 99 |
| 96 | $[\text{Nd}\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-Me}_2\text{-TACN-}N''\text{-SiMe}_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, no data available | 99 |
| 97 | $[\text{Sc}\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-Me}_2\text{-TACN-}N''\text{-SiMe}_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, no data available | 99 |
| 98 | $[Y\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-Me}_2\text{-TACN-}N''\text{-SiMe}_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, no data available | 99 |
| 99 | $[\text{Nd}\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-Me}_2\text{-TACN-}N''\text{-SiMe}_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, no data available | 99 |
| 100 | $[Y\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-Pr}_2\text{-TACN-}N''\text{-SiMe}_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)(\text{THF-}d_8)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, ^1H NMR | 99 |
| 101 | $[\text{Nd}\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-Me}_2\text{-TACN-}N''\text{-(CH}_2)_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, no data available | 99 |
| 102 | $[\text{La}\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-Me}_2\text{-TACN-}N''\text{-(CH}_2)_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, ^1H NMR | 99,100 |
| 103 | $[Y\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-Me}_2\text{-TACN-}N''\text{-(CH}_2)_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, no data available | 99 |
| 104 | $[\text{Nd}\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-Me}_2\text{-TACN-}N''\text{-(CH}_2)_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, no data available | 99 |
| 105 | $[\text{La}\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-Me}_2\text{-TACN-}N''\text{-(CH}_2)_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, ^1H NMR | 99 |
| 106 | $[Y\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-Me}_2\text{-TACN-}N''\text{-(CH}_2)_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, no data available | 99 |
| 107 | $[\text{La}\{\eta^3\text{-}\eta^1\text{-}N,N'\text{-Me}_2\text{-TACN-}N''\text{-(CH}_2)_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)(\text{THF-}d_8)_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, ^1H , ^{13}C NMR | 100 |
| 108 | $[Y\{\{\text{Me}_2\text{N}(\text{CH}_2)_2\}_2\text{N}(\text{CH}_2)_2N^t\text{Bu}\}\text{(CH}_2\text{SiMe}_3)(\text{THF-}d_8)_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | in situ, ^1H , ^{13}C NMR | 99,101,169 |

^a MAC = deprotonated aza-18-crown-6. ^b TACN = 1,4,7-triazacyclononane.

Table 5. Cationic Rare-Earth Organometallic Complexes That Contain Non-Cyclopentadienyl L₂X-Type Ligands

| no. | compound | characterization | refs |
|-----|--|--|---------|
| 109 | [Sc{ η^3 -ArNC(Me)CHC(Me)NAr}(CH ₂ C ₆ H ₅) ₂ { μ , η^6 -C ₆ H ₅ CH ₂ B(C ₆ F ₅) ₃ }] ^a | X-ray, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 103 |
| 110 | [Sc{ η^3 -ArNC(Me)CHC(Me)NAr}Me(η^6 -C ₆ H ₅ Br)] ⁺ [B(C ₆ F ₅) ₄] ⁻ ^a | X-ray, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 105 |
| 111 | [Sc{ η^3 -ArNC(Me)CHC(Me)NAr}Me(η^6 -C ₆ H ₆)] ⁺ [B(C ₆ F ₅) ₄] ⁻ ^a | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 105 |
| 112 | [Sc{ η^3 -ArNC(Me)CHC(Me)NAr}Me(η^6 -toluene)] ⁺ [B(C ₆ F ₅) ₄] ⁻ ^a | X-ray, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 105 |
| 113 | [Sc{ η^3 -ArNC(Me)CHC(Me)NAr}Me(η^6 -mesitylene)] ⁺ [B(C ₆ F ₅) ₄] ⁻ ^a | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 105 |
| 114 | [ScMe{ η^3 -ArNC(Me)CHC(Me)NAr}(μ -Me)B(C ₆ F ₅) ₃] ^a | in situ, ¹ H, ¹¹ B, ¹⁹ F NMR | 105,106 |
| 115 | [Sc(C ₆ F ₅) ₃ { η^3 -ArNC(Me)CHC(Me)NAr}(μ -Me)B(C ₆ F ₅) ₂ Me] ^a | in situ, ¹ H, ¹¹ B, ¹⁹ F NMR | 105,106 |
| 116 | [Sc{ η^3 -ArNC(Me)CHC(Me)NAr}{(μ -Me)B(C ₆ F ₅) ₂ }] ^a | in situ, ¹ H, ¹¹ B, ¹⁹ F NMR | 105,106 |
| 117 | [Sc(C ₆ F ₅) ₃ { η^3 -ArNC(Me)CHC(Me)NAr}(μ -Me)B(C ₆ F ₅) ₃] ^a | X-ray, ¹ H, ¹¹ B, ¹⁹ F NMR | 105,106 |
| 118 | [(Sc{ η^3 -ArNC('Bu)CHC('Bu)NAr}Me) ₂ (μ -Me)] ⁺ [B(C ₆ F ₅) ₃ Me] ⁻ ^a | in situ, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR | 107 |
| 119 | [ScMe{ η^3 -ArNC('Bu)CHC('Bu)NAr}(μ -Me)B(C ₆ F ₅) ₃] ^a | X-ray, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 107 |
| 120 | [Sc{ η^3 -ArNC('Bu)CHC('Bu)NAr}{(μ -Me)B(C ₆ F ₅) ₂ }] ^a | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 107 |
| 121 | [Sc{ η^3 -ArNC('Bu)CHC('Bu)NC ₆ H ₃ (ⁱ Pr)(CH(Me)CH ₂) ₂ }{(μ -Me)B(C ₆ F ₅) ₃ }] ^a | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 107 |
| 122 | [Sc{ η^3 -ArNC('Bu)CHC('Bu)NAr}Me] ⁺ [B(C ₆ F ₅) ₄] ⁻ | in situ, no data available | 107 |
| 123 | [ScMe{ η^3 -ArNC('Bu)CHC('Bu)NAr}(μ -Me)B(C ₁₂ F ₈)(C ₆ F ₅) ₃] ^a | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 106 |
| 124 | [Sc{ η^3 -ArNC('Bu)CHC('Bu)NAr}{(μ -Me)B(C ₁₂ F ₈)(C ₆ F ₅) ₂ }] ^a | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 106 |
| 125 | [Sc{ η^3 -ArNC('Bu)CHC('Bu)NAr}(CH ₂ SiMe ₂ CH ₂ SiMe ₃)(μ -Me)B(C ₆ F ₅) ₃] ^a | X-ray, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 106 |
| 126 | [Sc{ η^3 -ArNC('Bu)CHC('Bu)NAr}(CH ₂ SiMe ₂ CH ₂ 'Bu)(μ -Me)B(C ₆ F ₅) ₃] ^a | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 106 |
| 127 | [Sc{ η^3 -ArNC('Bu)CHC('Bu)NAr}(CH ₂ SiMe ₂ CH ₂ SiMe ₃)(μ -Me)B(C ₁₂ F ₈)(C ₆ F ₅) ₃] ^a | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 106 |
| 128 | [Sc{ η^3 -ArNC('Bu)CHC('Bu)NAr}(CH ₂ SiMe ₂ CH ₂ 'Bu)(μ -Me)B(C ₁₂ F ₈)(C ₆ F ₅) ₃] ^a | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 106 |
| 129 | [Sc{ η^3 -ArNC('Bu)CHC('Bu)NAr}(NCH ₂ CPh ₂ CH ₂ CHMe)] ⁺ [B(C ₆ F ₅) ₃ Me] ⁻ ^a | in situ, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR | 108 |
| 130 | [Tm{ η^3 -ArNC('Bu)CHC('Bu)NAr} ₂] ⁺ [BPh ₄] ⁻ ^a | ¹ H NMR | 109 |
| 131 | [Tm{ η^3 -ArNC('Bu)CHC('Bu)NAr} ₂] ⁺ [B(C ₆ F ₅) ₄] ⁻ ^a | X-ray, ¹ H NMR, EA | 109 |
| 132 | [Y{2-NAr-C ₆ H ₄ (CH=NAr)}(CH ₂ SiMe ₂ Ph)(THF) ₂] ⁺ [B(C ₆ F ₅) ₃ (CH ₂ SiMe ₂ Ph)] ⁻ ^a | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR, EA | 110 |
| 133 | [Y{2-NAr-C ₆ H ₄ (CH=NAr)}(CH ₂ SiMe ₂ Ph)(THF)] ⁺ [B(C ₆ F ₅) ₃ (CH ₂ SiMe ₂ Ph)] ⁻ ^a | in situ, no data available | 110 |
| 134 | [Lu{2-(ArN=CM ₂)-6-(ArNCMe ₂)C ₅ H ₃ N}(CH ₂ SiMe ₂ CH ₂ SiMe ₃)(THF)] ⁺ [B(C ₆ F ₅) ₃ Me] ⁻ ^a | ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR | 111 |
| 135 | [La{P(C ₆ H ₄ -2-CH ₂ NMe ₂){CH(SiMe ₃)(SiMe ₂ CH ₂) ₂ }(THF) ₄] ⁺ [BPh ₄] ⁻ | X-ray, ¹ H, ¹¹ B, ³¹ P NMR | 112 |

^a Ar = C₆H₃ⁱPr₂-2,6.

The generation of [Y({Me₂N(CH₂)₂)₂N(CH₂)₂N'Bu)-(CH₂SiMe₃)(THF-*d*₈)₁]⁺[B(C₆F₅)₄]⁻ (**108**) was possible using an analogous, conformationally less rigid monoanionic tetradentate ligand based on a linear triamine moiety.^{99,101} ¹H and ¹³C NMR spectroscopy revealed resonances similar to the related substituted TACN complexes. However, THF is required for sufficient stability to allow ¹³C NMR spectra to be measured. Polymerization of ethylene could be monitored despite rapid catalyst deactivation when the cationic complex was generated in situ upon reaction with [Ph₃C]⁺[B(C₆F₅)₄]⁻.

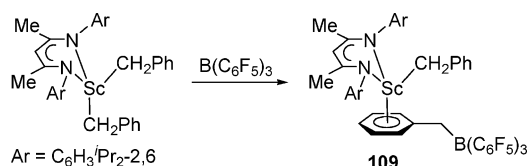
6.2. Complexes with L₂X-Type Ligands

6.2.1. β -Diketiminato Complexes

The monoanionic β -diketiminato ligands ArNC(R)CHC(R)NAr (R = 'Bu, Me; Ar = C₆H₃ⁱPr₂-2,6) have witnessed a surge in interest as ancillary ligands for transition metal complexes in recent years.¹⁰² Table 5 contains cationic lanthanoid complexes with β -diketiminato and related ligands.

Addition of B(C₆F₅)₃ to a benzene solution of [Sc{ η^3 -ArNC(Me)CHC(Me)NAr}(CH₂C₆H₅)₂](Ar = C₆H₃ⁱPr₂-2,6) yielded crystals of [Sc{ η^3 -ArNC(Me)CHC(Me)NAr}(CH₂-C₆H₅)₂]{ μ , η^6 -C₆H₅CH₂B(C₆F₅)₃}] (**109**) suitable for X-ray crystallography (Scheme 19).¹⁰³ The structure clearly shows

Scheme 19



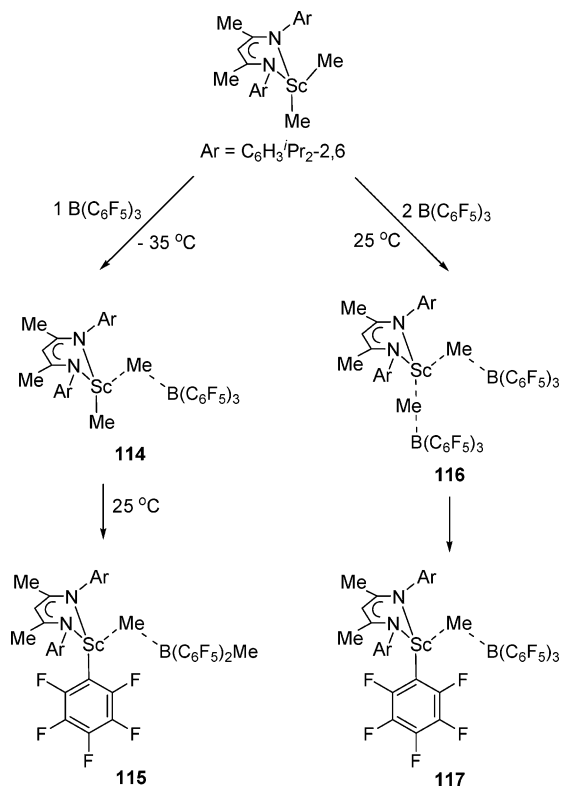
a contact ion pair arising from η^6 -bonding of the abstracted benzyl group to the scandium center. The presence of a

contact ion pair was also noted by the chemical shift difference of 3.9 ppm between the *meta* and *para* fluorines of the anion in the ¹⁹F NMR spectrum. This could also explain the inactivity of **109** toward H₂ and ethylene, because the binding of toluene to cationic titanium complexes decreases their polymerization activity.¹⁰⁴ As evidenced by the short Sc–C distances (C1 2.835(2) and C3 2.787(2) Å) and the large extent to which the metal center lies out of the ligand plane (1.114 Å), the β -diketiminato ligand appears to have more π -bonding character in this cation than in the neutral complex.

A series of related complexes, [Sc{ η^3 -ArNC(Me)CHC(Me)NAr}Me(η^6 -Ar')]⁺[B(C₆F₅)₄]⁻ (Ar = C₆H₃ⁱPr₂-2,6; Ar' = C₆H₅Br (**110**), C₆H₆ (**111**), toluene (**112**), mesitylene (**113**)), was synthesized from [Sc{ η^3 -ArNC(Me)CHC(Me)NAr}Me₂]₂ using [Ph₃C]⁺[B(C₆F₅)₄]⁻.¹⁰⁵ This enabled the thermodynamic parameters for the arene exchange to be studied, thus rationalizing the characteristics of η^6 -coordination of arenes to complexes such as **109**. The order of arene coordination was found by competition experiments to be bromobenzene \ll benzene < mesitylene < toluene. This was explained by the interplay of basicity and steric factors. A mechanism for the displacement of mesitylene by toluene invoking partial slippage of the η^6 -coordinated arene to lower hapticity and adjacent exchange by the more basic toluene was backed up by kinetic measurements via NMR spectroscopy at low temperature. Multinuclear NMR experiments as well as X-ray structure analysis (**110**, **112**) showed the existence of well-separated ion pairs for complexes **110**–**113**.

By comparison, β -diketiminato-supported alkyl cations derived from [Sc{ η^3 -ArNC(Me)CHC(Me)NAr}Me₂]₂ using B(C₆F₅)₃ instead of [Ph₃C]⁺[B(C₆F₅)₄]⁻ are relatively unstable.^{105,106} The addition of B(C₆F₅)₃ at –33 °C led to the formation of the contact ion pair [ScMe{ η^3 -ArNC(Me)CHC(Me)NAr}(μ -Me)B(C₆F₅)₃] (**114**) (Scheme 20). However, at

Scheme 20

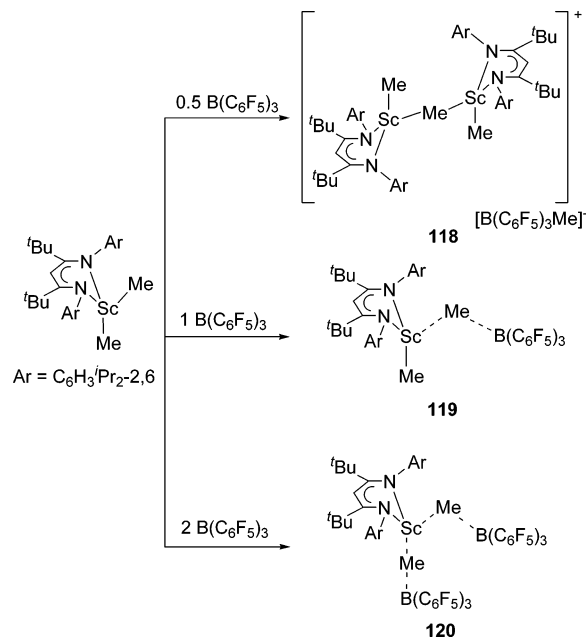


room temperature rapid C₆F₅ transfer gave the contact ion pair [Sc(C₆F₅)₃{η³-ArNC(Me)CHC(Me)NAr}(μ-Me)B(C₆F₅)₂-Me] (**115**). Addition of a second equivalent of B(C₆F₅)₃ to **114** gave the more stable contact ion pair [Sc{η³-ArNC(Me)CHC(Me)NAr}{(μ-Me)B(C₆F₅)₃}₂] (**116**). Over longer periods of time, this compound also decomposed via aryl group transfer to give [Sc(C₆F₅)₃{η³-ArNC(Me)CHC(Me)NAr}(μ-Me)B(C₆F₅)₃] (**117**), whose structure was confirmed by multinuclear NMR spectroscopy and X-ray structure analysis.¹⁰⁶

The reaction of varying amounts of B(C₆F₅)₃ with a similar dimethyl scandium complex [Sc{η³-ArNC(^tBu)CHC(^tBu)NAr}Me₂] (Ar = C₆H₃(Pr)₂-2,6) containing a sterically more bulky β-diketiminato ligand resulted in the formation of different ion pairs (Scheme 21).¹⁰⁷ Half an equivalent of B(C₆F₅)₃ yielded a methyl-bridged dimer [(Sc{η³-ArNC(^tBu)CHC(^tBu)NAr}Me)₂(μ-Me)]⁺[B(C₆F₅)₃Me]⁻ (**118**) that could not be isolated as a solid. A monomeric, crystallographically characterized contact ion pair [ScMe{η³-ArNC(^tBu)CHC(^tBu)NAr}(μ-Me)B(C₆F₅)₃] (**119**) was isolated by addition of 1 equiv of B(C₆F₅)₃. A dicationic contact ion triple [Sc{η³-ArNC(^tBu)CHC(^tBu)NAr}{(μ-Me)B(C₆F₅)₃}₂] (**120**) resulted from the addition of 2 equiv of B(C₆F₅)₃. The ¹H NMR spectrum of **119** shows broad signals at room temperature but is consistent with the presence of two diastereomers at -60 °C. The interconversion of the diastereomers was proposed to occur either via a ligand flipping mechanism or via an associative ion pair process. The exchange barrier was estimated to be 51.9(11) kJ mol⁻¹ at -10 °C. In solution, metalation of an isopropyl group via loss of methane in **119** resulted in the formation of [Sc{η³-ArNC(^tBu)CHC(^tBu)NC₆H₃(Pr)(CH(Me)CH₂)}{(μ-Me)B(C₆F₅)₃}] (**121**), as indicated by multinuclear NMR spectroscopy and elemental analysis.

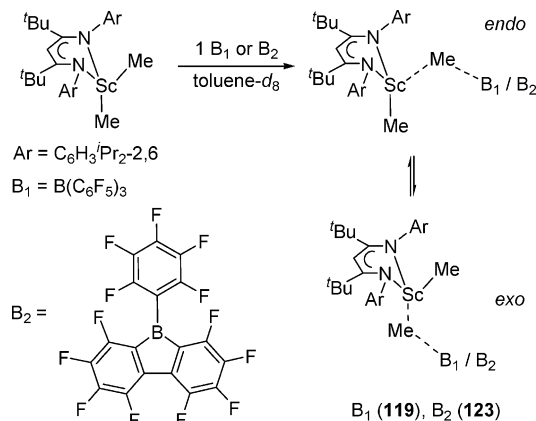
A further study of ion pair dynamics in solution involving complexes **119** and **120** and others also having a ^tBu-

Scheme 21



substituted backbone has recently been presented.¹⁰⁶ These compounds were generated with either B(C₁₂F₈)(C₆F₅) or B(C₆F₅)₃ from the neutral bis(alkyl) β-diketiminato complexes [Sc{η³-ArNC(^tBu)CHC(^tBu)NAr}RR'] (Ar = C₆H₃(Pr)₂-2,6; R = R' = Me, CH₂SiMe₃; R = CH₂SiMe₃, R' = CH₂^tBu) in toluene (Scheme 22). Thus for R = Me, [ScMe-

Scheme 22



{η³-ArNC(^tBu)CHC(^tBu)NAr}(μ-Me)B(C₁₂F₈)(C₆F₅)] (**123**) and [Sc{η³-ArNC(^tBu)CHC(^tBu)NAr}{(μ-Me)B(C₁₂F₈)(C₆F₅)₂}] (**124**) were synthesized. Interestingly, no cations could be made when R = R' = CH₂^tBu. Furthermore, when cationic complexes starting from the bulkier alkyl complexes formed, these groups coupled to give [Sc{η³-ArNC(^tBu)CHC(^tBu)NAr}(R)(μ-Me)B(C₆F₅)₃] (R = CH₂SiMe₂CH₂-SiMe₃ (**125**), CH₂SiMe₂CH₂^tBu (**126**)) and [Sc{η³-ArNC(^tBu)CHC(^tBu)NAr}(R)(μ-Me)B(C₁₂F₈)(C₆F₅)] (R = CH₂SiMe₂-CH₂SiMe₃ (**127**), CH₂SiMe₂CH₂^tBu (**128**)). It was found that the compounds with methyl coligands exist in solution at room temperature as an exchanging pair of diastereomers with indistinguishable ¹H and ¹⁹F NMR spectra. However, at lower temperature coalescence behavior between the *exo* and *endo* isomers could be observed and the barriers to exchange estimated. Interestingly, the ion pairs with the bulkier coupled alkyl group exist as only one diastereomer

at all temperatures (X-ray structure analysis of **125** showed this to be the *exo* isomer). Neither **125** nor **127** reacted with a second equivalent of either $B(C_{12}F_8)(C_6F_5)_3$ or $B(C_6F_5)_3$.

The cationic β -diketiminato scandium complex **119** showed high activity for catalytic intramolecular hydroamination of both α,ω -aminoalkynes and α,ω -aminoalkenes.¹⁰⁸ The mechanism was proposed to proceed via olefin insertion into the Sc–N σ -bond formed upon substrate protonolysis. A cationic N-bound heterocyclic product $[Sc\{\eta^3\text{-ArNC}(\text{tBu})\text{CHC}(\text{tBu})\text{NAr}\}(\text{NCH}_2\text{CPh}_2\text{CH}_2\text{CHMe})]^+[\text{B}(\text{C}_6\text{F}_5)_3\text{Me}]^-$ (**129**) could be observed by multinuclear NMR spectroscopy in the reaction of **119** and 2,2-diphenyl-4-pentenylamine under stoichiometric conditions (section 9.2.1).

Recently, the syntheses of cationic homoleptic thulium complexes $[\text{Tm}\{\eta^3\text{-ArNC}(\text{tBu})\text{CHC}(\text{tBu})\text{NAr}\}_2]^+[\text{BPh}_4]^-$ (**130**) and $[\text{Tm}\{\eta^3\text{-ArNC}(\text{tBu})\text{CHC}(\text{tBu})\text{NAr}\}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**131**) by reaction of appropriate ammonium tetraarylborates and a thulium precursor containing both the monoanionic β -diketiminato ligand $\text{ArNC}(\text{tBu})\text{CHC}(\text{tBu})\text{NAr}$ ($\text{Ar} = \text{C}_6\text{H}_3^i\text{Pr}_{2,6}$) and its deprotonated dianionic derivative were described.¹⁰⁹ Whereas the formation of **130**, which is thermally unstable, was confirmed by ^1H NMR spectroscopy, **131** could be isolated in good yield and its structure determined by single-crystal X-ray diffraction. The structure shows π -interactions between two ligand carbon atoms and the cationic metal center ($\text{Tm}-\text{C}2 = 2.717(3)$ and $\text{Tm}-\text{C}31 = 2.826(3)$ Å, Figure 7).

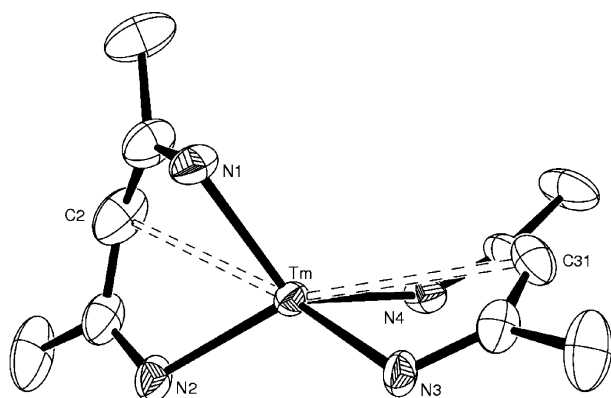
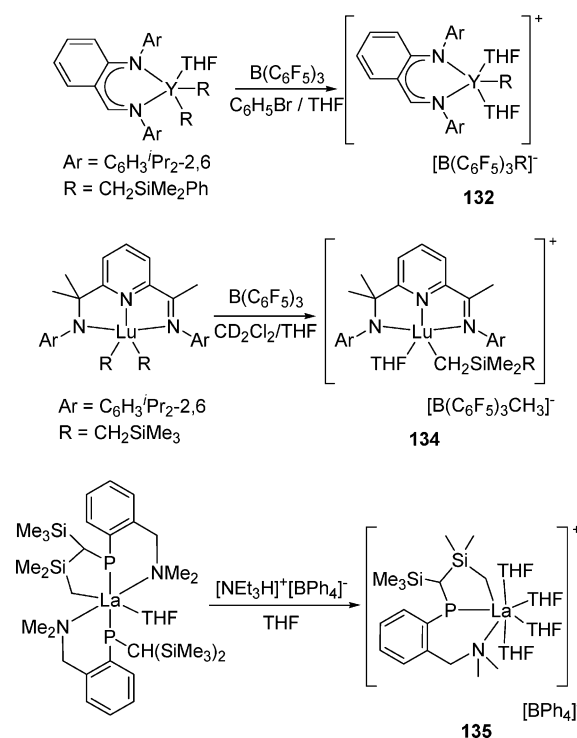


Figure 7. Molecular structure of the cationic part of $[\text{Tm}\{\eta^3\text{-ArNC}(\text{tBu})\text{CHC}(\text{tBu})\text{NAr}\}_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**131**). One of two crystallographically independent molecules is shown; hydrogen atoms and aryl substituents of the ligands are omitted for clarity. Drawn from data in ref 109.

6.2.2. Complexes with Other Related Ligands

A bulky anilido-imine ligand, which combines the properties of β -diketiminato and salicylaldimine ligands, has been used to support organoyttrium complexes.¹¹⁰ Reaction of $[\text{Y}\{2\text{-NAr-C}_6\text{H}_4(\text{CH}=\text{NAr})\}(\text{CH}_2\text{SiMe}_2\text{Ph})_2(\text{THF})]$ ($\text{Ar} = \text{C}_6\text{H}_3^i\text{Pr}_{2,6}$) with $B(\text{C}_6\text{F}_5)_3$ in bromobenzene resulted in the formation of $[\text{Y}\{2\text{-NAr-C}_6\text{H}_4(\text{CH}=\text{NAr})\}(\text{CH}_2\text{SiMe}_2\text{Ph})(\text{THF})_2]^+[\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{SiMe}_2\text{Ph})]^-$ (**132**) as a thermally stable solid (Scheme 23). ^{19}F NMR measurements were in accordance with separate ion pairs in the presence of excess THF. Formation of $[\text{Y}\{2\text{-NAr-C}_6\text{H}_4(\text{CH}=\text{NAr})\}(\text{CH}_2\text{SiMe}_2\text{-Ph})(\text{THF})]^+[\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{SiMe}_2\text{Ph})]^-$ (**133**) as a mixture of three isomers, which may be geometrical in nature or result from ion pair interactions, in the absence of excess THF was postulated from in situ NMR spectroscopic measurements.

Scheme 23



Treatment of a CD_2Cl_2 solution of $[\text{Lu}\{2\text{-(ArN}=\text{CMe)-6-(ArNCMe}_2\text{)C}_5\text{H}_3\text{N}\}(\text{CH}_2\text{SiMe}_3)_2]$ ($\text{Ar} = \text{C}_6\text{H}_3^i\text{Pr}_{2,6}$) with $B(\text{C}_6\text{F}_5)_3$ in the presence of THF led to the cationic monoalkyl derivative $[\text{Lu}\{2\text{-(ArN}=\text{CMe)-6-(ArNCMe}_2\text{)C}_5\text{H}_3\text{N}\}(\text{CH}_2\text{SiMe}_2\text{CH}_2\text{SiMe}_3)(\text{THF})]^+[\text{B}(\text{C}_6\text{F}_5)_3\text{Me}]^-$ (**134**), in which two trimethylsilylmethyl groups have been coupled together (Scheme 23).¹¹¹ The cation, which is stable in solution, was analyzed by multinuclear NMR spectroscopy. The small difference between *meta* and *para* aryl fluorine resonances of only 2.6 ppm in the ^{19}F NMR spectrum indicates a solvent-separated ion pair. The coupling was explained by concerted silylmethyl group extraction by $B(\text{C}_6\text{F}_5)_3$ accompanied by alkyl group migration.

The cationic alkyl lanthanum complex $[\text{La}\{\text{P}\{\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2\}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{CH}_2)\}(\text{THF})_4]^+[\text{BPh}_4]^-$ (**135**) resulted from the reaction of the cyclometalated lanthanum phosphide complex $[\text{La}\{\text{(Me}_3\text{Si)}_2\text{CH}\}(\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2)\text{P}]^+[\text{P}\{\text{C}_6\text{H}_4\text{-2-CH}_2\text{NMe}_2\}\{\text{CH}(\text{SiMe}_3)(\text{SiMe}_2\text{-CH}_2)\}]^-$ with $[\text{NEt}_3\text{H}]^+[\text{BPh}_4]^-$ in THF (Scheme 23).¹¹² In this reaction, protonolysis of the bidentate, monoanionic ligand instead of the tridentate, dianionic CPN-type ligand occurred, as confirmed by multinuclear NMR spectroscopy and X-ray structure analysis.

6.3. Complexes with LX-Type Ligands

The compounds of this class, including cationic lanthanoid benzamidinato and allyl complexes, are compiled in Table 6.

6.3.1. Benzamidinato Complexes

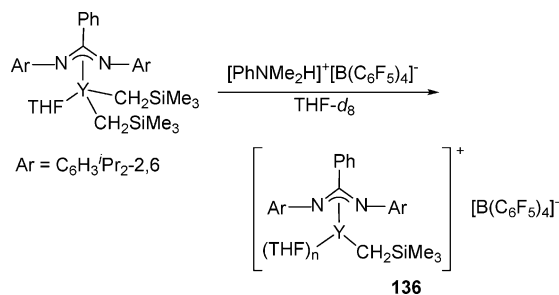
The reaction of $[\text{Y}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})]$ ($\text{Ar} = \text{C}_6\text{H}_3^i\text{Pr}_{2,6}$) with 1 equiv of $[\text{PhNMe}_2\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in THF-d_8 yielded SiMe_4 , PhNMe_2 , and the cationic yttrium alkyl species $[\text{Y}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF-d}_8)_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**136**), as shown by in situ ^1H and ^{13}C NMR spectroscopy (Scheme 24).¹¹³ The isolation of complexes

Table 6. Cationic Rare-Earth Organometallic Complexes That Contain LX-Type Ligands

| no. | compound | characterization | refs |
|-----|---|---|---------|
| 136 | $[Y\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF-}d_8)_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^a | in situ, ¹ H, ¹³ C NMR | 113,169 |
| 137 | $[\text{Sc}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]^+[\text{BPh}_4]^-$ | X-ray, ¹ H, ¹³ C NMR, EA | 114 |
| 138 | $[Y\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_3]^+[\text{BPh}_4]^-$ | X-ray, ¹ H, ¹³ C NMR, EA | 114 |
| 139 | $[\text{La}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_4]^+[\text{BPh}_4]^-$ | X-ray, ¹ H, ¹³ C NMR, EA | 114 |
| 140 | $[\text{Nd}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_4]^+[\text{BPh}_4]^-$ | X-ray, EA | 114 |
| 141 | $[\text{Gd}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_3]^+[\text{BPh}_4]^-$ | X-ray, EA | 114 |
| 142 | $[\text{Lu}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_3]^+[\text{BPh}_4]^-$ | X-ray, ¹ H, ¹³ C NMR, EA | 114 |
| 143 | $[\text{Sc}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF-}d_8)_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | in situ, ¹ H NMR | 114,169 |
| 144 | $[\text{La}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF-}d_8)_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | in situ, ¹ H, ¹³ C NMR | 114 |
| 145 | $[\text{Nd}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | in situ, no data available | 114,115 |
| 146 | $[\text{Gd}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | in situ, no data available | 114 |
| 147 | $[\text{Lu}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | in situ, no data available | 114 |
| 148 | $[Y\{\eta^3\text{-}(\text{C}_6\text{F}_5)\text{C}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF-}d_8)_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | in situ, ¹ H, ¹³ C, ¹⁹ F NMR | 115 |
| 149 | $[\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_2(\text{THF})_4]^+[\text{BPh}_4]^-$ | no data available | 116,161 |
| 150 | $[\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_2(\text{THF})_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | no data available | 116 |
| 151 | $[\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_2(\text{DME})_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | no data available | 116 |
| 152 | $[\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_2(\text{dioxane})_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | no data available | 116 |
| 153 | $[\text{La}(\eta^3\text{-C}_3\text{H}_5)_2(\text{THF})_4]^+[\text{BPh}_4]^-$ | X-ray, data not available | 116 |
| 154 | $[\text{La}(\eta^3\text{-C}_3\text{H}_5)_2(\text{THF})_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ | X-ray, data not available | 116 |
| 155 | $[\text{Nd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{THF})_5]^+[\text{BPh}_4]^-$ | X-ray, EA | 117 |

^a Ar = C₆H₃ⁱPr₂-2,6.

Scheme 24



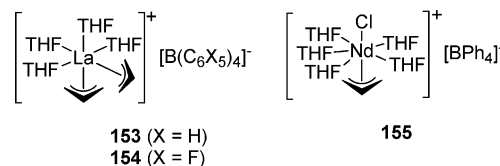
$[\text{Ln}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{BPh}_4]^-$ (Ar = C₆H₃ⁱPr₂-2,6; Ln = Sc, $x = 2$ (**137**); Ln = Y, $x = 3$ (**138**); Ln = La, $x = 4$ (**139**); Ln = Nd, $x = 4$ (**140**); Ln = Gd, $x = 3$ (**141**); Ln = Lu, $x = 3$ (**142**)) was possible from the corresponding bis(alkyl) complexes with $[\text{PhNMe}_2\text{H}]^+[\text{BPh}_4]^-$ in THF.¹¹⁴ The structures for all of these complexes could be determined by X-ray crystallography. As expected, the number of THF molecules bound to the metal increases with the ionic radii¹⁴ of the metal centers. Since **136** was shown to be an active ethylene polymerization catalyst, producing polyethylene with a narrow polydispersity,¹¹³ analogous complexes $[\text{Ln}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (Ln = Sc (**143**), La (**144**), Nd (**145**), Gd (**146**), Lu (**147**)) were generated by in situ activation of the bis(alkyl) complexes with $[\text{PhNMe}_2\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in toluene in the presence of 20 equiv of isobutylaluminumoxane (TIBAO) at 30 °C and also tested for their activities (section 9.1.1).^{114,115} The intermediate-sized metals (Y and Gd) were found to be the most active within this series. Another analogous yttrium complex with a perfluorinated backbone $[Y\{\eta^3\text{-}(\text{C}_6\text{F}_5)\text{C}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF-}d_8)_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**148**) (Ar = C₆H₃ⁱPr₂-2,6) showed similar properties in ethylene polymerization under the same conditions.¹¹⁵

6.3.2. Allyl Complexes

Cationic bis(allyl) neodymium and lanthanum complexes $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_2(\text{L})_n]^+[\text{A}]^-$ (Ln = Nd; L = THF, $n = 4$, A = BPh₄ (**149**); L = THF, $n = 4$, A = B(C₆F₅)₄ (**150**); L = DME, $n = 4$, A = B(C₆F₅)₄ (**151**); L = dioxane, $n = 4$, A = B(C₆F₅)₄ (**152**); Ln = La; L = THF, $n = 4$, A = BPh₄

(**153**); L = THF, $n = 4$, A = B(C₆F₅)₄ (**154**)) have been synthesized by partial protonolysis of the neutral tris(allyl) complexes with different trimethylammonium borates in appropriate solvents (Chart 2).¹¹⁶ The compounds were fully

Chart 2



characterized, but no spectroscopic data were published. Complexes **153** and **154** were characterized by X-ray crystal structure analysis. The two allyl groups in the cation of **154** adopt a *cis* arrangement. Polymerization of 1,4-butadiene in toluene using **150**, **152**, and **154** as one-component catalysts showed high *cis*-1,4-selectivity. Additionally, **152** (with the more labile dioxane donor ligand) exhibited the highest activity, with a TOF of about 10 000 h⁻¹ (section 9.1.3).

The comproportionation of the neutral tris(allyl) neodymium complex $[\text{Ln}(\eta^3\text{-C}_3\text{H}_5)_3(\text{dioxane})]$ with NdCl₃ in a 1:1 molar ratio followed by protonolysis with 1 equiv of $[\text{NMe}_3\text{H}]^+[\text{BPh}_4]^-$ yielded $[\text{Nd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}(\text{THF})_5]^+[\text{BPh}_4]^-$ (**155**) as a green solid.¹¹⁷ X-ray structure analysis revealed a well-separated ion pair. The metal center adopts a pentagonal-bipyramidal coordination geometry with a *trans* configuration for the allyl group and the chloride ligand. No catalytic activity toward 1,4-butadiene was observed, probably due to rapid decomposition of the complex in toluene at room temperature or to coordination of THF or the counterion in solution.

6.4. Complexes with X-Type Ligands

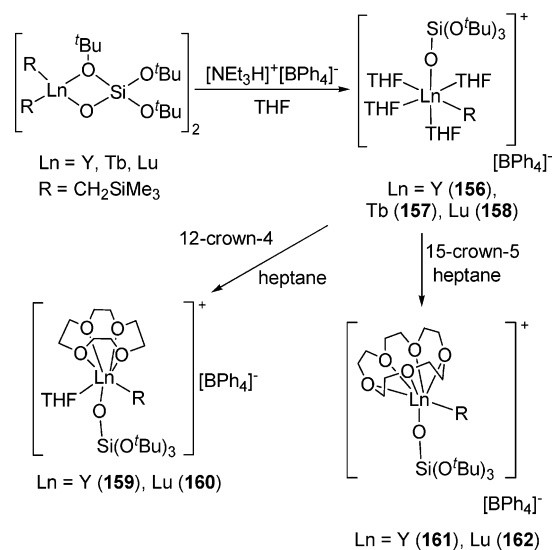
The cationic complexes known of this type, which all contain a tri(*tert*-butoxy)silanolate ligand, are compiled in Table 7.

Reaction of the dimeric, THF-free rare-earth metal silanolate complexes $[\text{Ln}\{\mu\text{-}\eta^2\text{-OSi}(\text{O}^t\text{Bu})_3\}(\text{CH}_2\text{SiMe}_3)_2]$ (Ln = Y, Tb, Lu) with 2 equiv of $[\text{NEt}_3\text{H}]^+[\text{BPh}_4]^-$ yielded the cationic derivatives $[\text{Ln}\{\text{OSi}(\text{O}^t\text{Bu})_3\}(\text{CH}_2\text{SiMe}_3)-$

Table 7. Cationic Rare-Earth Organometallic Complexes That Contain an X-Type Ligand

| no. | compound | characterization | ref |
|------------|---|--|-----|
| 156 | $[Y\{OSi(O^tBu)_3\}(CH_2SiMe_3)(THF)_4]^+[BPh_4]^-$ | 1H , ^{13}C , ^{11}B NMR, EA | 118 |
| 157 | $[Tb\{OSi(O^tBu)_3\}(CH_2SiMe_3)(THF)_4]^+[BPh_4]^-$ | EA | 118 |
| 158 | $[Lu\{OSi(O^tBu)_3\}(CH_2SiMe_3)(THF)_4]^+[BPh_4]^-$ | 1H , ^{13}C , ^{11}B NMR, EA | 118 |
| 159 | $[Y\{OSi(O^tBu)_3\}(CH_2SiMe_3)(12\text{-crown-4})(THF)]^+[BPh_4]^-$ | 1H , ^{13}C , ^{11}B NMR, EA | 118 |
| 160 | $[Lu\{OSi(O^tBu)_3\}(CH_2SiMe_3)(12\text{-crown-4})(THF)]^+[BPh_4]^-$ | 1H , ^{13}C , ^{11}B NMR, EA | 118 |
| 161 | $[Y\{OSi(O^tBu)_3\}(CH_2SiMe_3)(15\text{-crown-5})]^+[BPh_4]^-$ | 1H , ^{13}C , ^{11}B NMR, EA | 118 |
| 162 | $[Lu\{OSi(O^tBu)_3\}(CH_2SiMe_3)(15\text{-crown-5})]^+[BPh_4]^-$ | 1H , ^{13}C , ^{11}B NMR, EA | 118 |
| 163 | $[Y\{OSi(O^tBu)_3\}(CH_2SiMe_3)(THF)_4]^+[B(C_6F_5)_4]^-$ | 1H , ^{13}C , ^{11}B , ^{19}F NMR, EA | 118 |
| 164 | $[Y\{OSi(O^tBu)_3\}(CH_2SiMe_3)(THF)_4]^+[Al(CH_2SiMe_3)_4]^-$ | 1H , ^{13}C , ^{11}B , ^{27}Al , ^{29}Si , ^{89}Y NMR | 118 |
| 165 | $[Y\{OSi(O^tBu)_3\}(CH_2SiMe_3)(THF)_4]^+[BPh_3(CH_2SiMe_3)]^-$ | in situ, 1H , ^{13}C , ^{11}B NMR | 118 |

$(THF)_4]^+[BPh_4]^-$ (Ln = Y (**156**), Tb (**157**), Lu (**158**)) in THF (Scheme 25).¹¹⁸ Further derivatives were obtained by adding

Scheme 25

stoichiometric amounts of 12-crown-4 or 15-crown-5 to give $[Ln\{OSi(O^tBu)_3\}(CH_2SiMe_3)(L)(THF)_n]^+[BPh_4]^-$ (L = 12-crown-4, $n = 1$; Ln = Y (**159**), Lu (**160**); L = 15-crown-5, $n = 0$; Ln = Y (**161**), Lu (**162**)). Reaction of $[Y\{\mu,\eta^2\text{-OSi(O}^t\text{Bu)}_3\}(CH_2SiMe_3)_2\}_2$ with $[PhNMe_2H]^+[B(C_6F_5)_4]^-$, $[Al(CH_2SiMe_3)_3]$ or BPh₃ yielded the expected cationic yttrium compounds $[Y\{OSi(O^tBu)_3\}(CH_2SiMe_3)(THF)_4]^+[A]^-$ (A = $B(C_6F_5)_4$ (**163**), $Al(CH_2SiMe_3)_4$ (**164**), $BPh_3(CH_2SiMe_3)$ (**165**)). Multinuclear NMR spectroscopy gave resonances indicative of solvent-separated ion pairs in solution. 1H and ^{13}C NMR spectroscopy indicated the presence of small amounts of the bis(alkyl) and bis(silanolate) complexes $[Ln(CH_2SiMe_3)_2(THF)_n]^+[A]^-$ and $[Ln\{OSi(O^tBu)_3\}_2-$

$(THF)_m]^+[A]^-$, which presumably formed by ligand redistribution processes.

7. Cationic σ -Alkyl Complexes Bearing Neutral Coligands

A series of mono- and dicationic rare-earth metal alkyl complexes that contain THF, macrocyclic, or tripodal ligands have become accessible. These complexes are in some cases thermally more robust than the neutral parent compounds and have been characterized in the solution and solid state. In contrast to the bulky tris(alkyl) complex $[Ln\{CH(SiMe_3)_2\}_3]$,^{119–122} tris(trimethylsilylmethyl) derivatives $[Ln(CH_2SiMe_3)_3(THF)_n]$ ^{123–126} are reactive toward alkyl group abstraction by Lewis or Brønsted acids.

7.1. Monocationic σ -Alkyl Complexes

7.1.1. Complexes with Neutral L_n -Type Coligands ($n = 4–6$)

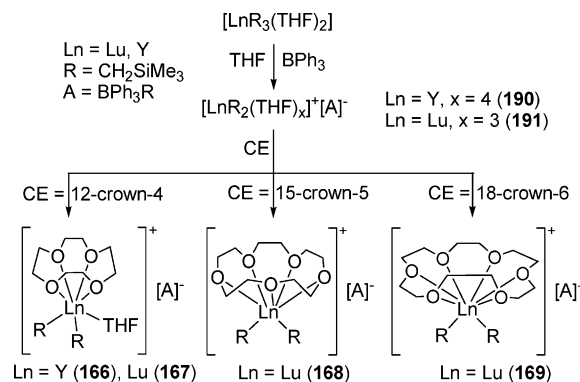
Crown ethers comprise a family of neutral macrocyclic donor ligands suitable for coordination at lanthanoid centers.¹²⁷ Complexes incorporating these coligands are compiled in Table 8.

Complexes of the general type $[LnR_2(CE)(THF)_x]^+[A]^-$ (Ln = Sc, Y, Lu; R = CH_2SiMe_3 ; CE = 12-crown-4, 15-crown-5, 18-crown-6; $x = 0, 1$; A = AlR_4 , BPh_3R , BPh_4) were readily prepared in THF from either their parent THF adducts $[LnR_3(THF)_x]$ or the thermally more robust crown ether complexes $[LnR_3(12\text{-crown-4})]$.^{128,129} Treatment of in situ generated THF-supported alkyl cations $[LnR_2(THF)_x]^+[BPh_3(CH_2SiMe_3)]^-$ (Ln = Y (**190**), Lu (**191**)) with crown ethers gave the ion pairs $[Ln(CH_2SiMe_3)_2(CE)(THF)_x]^+[BPh_3(CH_2SiMe_3)]^-$ (Ln = Y; CE = 12-crown-4, $x = 1$ (**166**); Ln = Lu; CE = 12-crown-4, $x = 1$ (**167**); CE = 15-crown-5, $x = 0$ (**168**); CE = 18-crown-6, $x = 0$ (**169**)) in

Table 8. Monocationic Alkyl Rare-Earth Metal Complexes That Contain Neutral L_n -Type Ligands ($n = 4–6$)

| no. | compound | characterization | ref |
|------------|---|---|-----|
| 166 | $[Y(CH_2SiMe_3)_2(12\text{-crown-4})(THF)]^+[BPh_3(CH_2SiMe_3)]^-$ | 1H , ^{13}C , ^{11}B NMR, EA | 130 |
| 167 | $[Lu(CH_2SiMe_3)_2(12\text{-crown-4})(THF)]^+[BPh_3(CH_2SiMe_3)]^-$ | X-ray, 1H , ^{13}C , ^{11}B NMR, EA | 130 |
| 168 | $[Lu(CH_2SiMe_3)_2(15\text{-crown-5})]^+[BPh_3(CH_2SiMe_3)]^-$ | X-ray, 1H , ^{13}C , ^{11}B NMR, EA | 130 |
| 169 | $[Lu(CH_2SiMe_3)_2(18\text{-crown-6})]^+[BPh_3(CH_2SiMe_3)]^-$ | X-ray, 1H , ^{13}C , ^{11}B NMR, EA | 130 |
| 170 | $[Y(CH_2SiMe_3)_2(12\text{-crown-4})(THF)]^+[Al(CH_2SiMe_3)_4]^-$ | 1H , ^{13}C NMR, EA | 129 |
| 171 | $[Sc(CH_2SiMe_3)_2(12\text{-crown-4})]^+[BPh_4]^-$ | 1H , ^{13}C , ^{11}B NMR, EA | 128 |
| 172 | $[Y(CH_2SiMe_3)_2(12\text{-crown-4})]^+[BPh_4]^-$ | 1H , ^{13}C , ^{11}B NMR, EA | 128 |
| 173 | $[Lu(CH_2SiMe_3)_2(12\text{-crown-4})(THF)]^+[BPh_4]^-$ | 1H , ^{11}B , ^{13}C NMR, EA | 128 |
| 174 | $[Sc(CH_2SiMe_3)_2(12\text{-crown-4})]^+[BPh_3(CH_2SiMe_3)]^-$ | 1H , ^{13}C , ^{11}B NMR, EA | 129 |
| 175 | $[Y(CH_2SiMe_3)_2(12\text{-crown-4})(THF)_x]^+[B(C_6F_5)_3(CH_2SiMe_3)]^-$ | in situ, 1H , ^{13}C , ^{11}B , ^{19}F NMR | 129 |
| 176 | $[Lu(CH_2SiMe_3)_2(12\text{-crown-4})(THF)_x]^+[B(C_6F_5)_3(CH_2SiMe_3)]^-$ | in situ, 1H , ^{13}C , ^{11}B , ^{19}F NMR | 129 |
| 177 | $[Y(CH_2SiMe_3)_2(12\text{-crown-4})(THF)_x]^+[B(C_6F_5)_4]^-$ | in situ, 1H , ^{13}C , ^{11}B , ^{19}F NMR | 129 |
| 178 | $[Lu(CH_2SiMe_3)_2(12\text{-crown-4})(THF)_x]^+[B(C_6F_5)_4]^-$ | in situ, 1H , ^{13}C , ^{11}B , ^{19}F NMR | 129 |
| 179 | $[YMe_2(12\text{-crown-4})(THF)_2]^+[BPh_4]^-$ | X-ray, 1H , ^{13}C , ^{11}B NMR, EA | 131 |

Scheme 26



high yield (Scheme 26).¹³⁰ The Ln–CH₂ resonances were observed at higher field in the ¹H and ¹³C NMR spectra with increasing size of the crown ether in agreement with an enhanced shielding along this series. ¹¹B NMR spectra at room temperature in THF-*d*₈ are consistent with identical anions separate from the cation in each case. According to X-ray structure analysis, the cationic lutetium complex **167** exhibits a seven-coordinate capped trigonal prismatic metal center (Figure 8). 15-Crown-5 stabilizes the (4 + *n*) electron

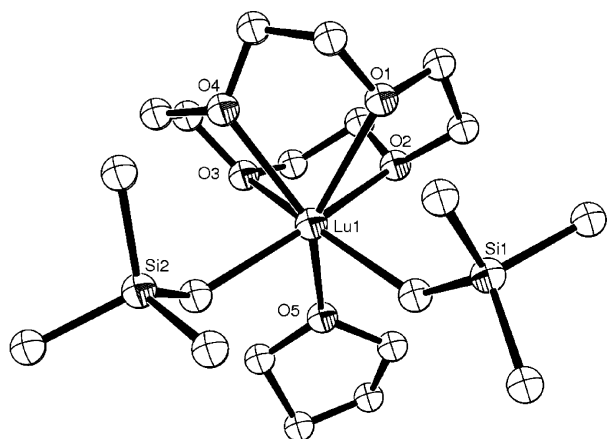


Figure 8. Molecular structure of the cationic part of $[\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(12\text{-crown-4})(\text{THF})]^+[\text{BPh}_3(\text{CH}_2\text{SiMe}_3)]^-$ (**167**). Hydrogen atoms are omitted for clarity. Drawn from data in ref 130.

fragment $[\text{LnR}_2]^+$ (*n* = number of f-electrons) without additional THF to give $[\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(15\text{-crown-5})]^+[\text{BPh}_3(\text{CH}_2\text{SiMe}_3)]^-$ (**168**). The (14 + 14) electron cation in **168** also has a seven-coordinate metal center with a capped trigonal prismatic coordination geometry. The (16 + 14) electron lutetium center in $[\text{Lu}(\text{CH}_2\text{SiMe}_3)_2(18\text{-crown-6})]^+[\text{BPh}_3(\text{CH}_2\text{SiMe}_3)]^-$ (**169**) adopts a doubly capped trigonal

prismatic coordination geometry, where all six oxygen atoms of 18-crown-6 are coordinated to the eight-coordinate lutetium ion.

The yttrium complex $[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$ reacted with $[\text{Al}(\text{CH}_2\text{SiMe}_3)_3]$ in THF to give microcrystalline $[\text{Y}(\text{CH}_2\text{SiMe}_3)_2(12\text{-crown-4})(\text{THF})]^+[\text{Al}(\text{CH}_2\text{SiMe}_3)_4]^-$ (**170**).¹²⁹ The tris(alkyl) complexes $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_3(12\text{-crown-4})]$ of scandium, yttrium, and lutetium also reacted with $[\text{NEt}_3\text{H}]^+[\text{BPh}_4]^-$ in THF to give the alkyl cations $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(12\text{-crown-4})(\text{THF})_x]^+[\text{BPh}_4]^-$ (Ln = Sc, *x* = 0 (**171**); Ln = Y, *x* = 0 (**172**); Ln = Lu, *x* = 1 (**173**))¹²⁸ or with BPh₃ to give $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(12\text{-crown-4})]^+[\text{BPh}_3(\text{CH}_2\text{SiMe}_3)]^-$ (**174**).¹²⁹ The reactions of the neutral 12-crown-4 adducts with $\text{B}(\text{C}_6\text{F}_5)_3$ or $[\text{PhNMe}_2\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in THF-*d*₈ yielded $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(12\text{-crown-4})(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{SiMe}_3)]^-$ (Ln = Y (**175**), Lu (**176**)) and $[\text{Ln}(\text{CH}_2\text{SiMe}_3)_2(12\text{-crown-4})(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (Ln = Y (**177**), Lu (**178**)), respectively, and were monitored in situ by multinuclear NMR spectroscopic experiments.¹²⁹

Addition of 12-crown-4 to a THF solution of the in situ generated monocation $[\text{YMe}_2(\text{THF})_5]^+[\text{BPh}_4]^-$ (**199**), prepared from the dication $[\text{YMe}(\text{THF})_6]^{2+}[\text{BPh}_4]^{2-}$ (**214**) and LiMe, allowed the isolation of the crown ether adduct $[\text{YMe}_2(12\text{-crown-4})(\text{THF})_2]^+[\text{BPh}_4]^-$ (**179**) in 80% yield as thermally robust, colorless crystals.¹³¹ The ligands around the yttrium center adopt a square antiprismatic configuration in the solid state.

7.1.2. Complexes with Neutral L₃-Type Coligands

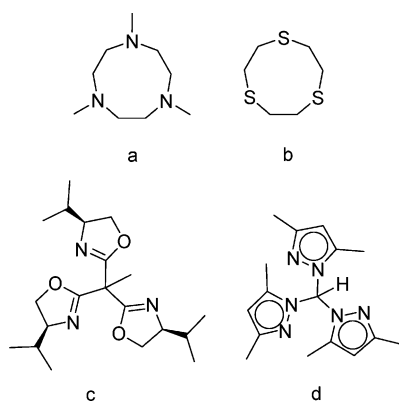
Macrocyclic and tripodal ligands that contain nitrogen or sulfur donors have been shown to stabilize cationic scandium alkyl complexes (Table 9, Chart 3). In situ generated complexes containing these ligands were used as catalyst precursors for olefin polymerization (section 9).

The scandium trimethyl complex $[\text{ScMe}_3(\text{Me}_3\text{-TACN})]$ with the 1,4,7-trimethyl-1,4,7-triazacyclononane ligand Me₃-TACN, prepared by salt metathesis of the corresponding scandium trichloride $[\text{ScCl}_3(\text{Me}_3\text{-TACN})]$ with methyl-lithium, reacted with $\text{B}(\text{C}_6\text{F}_5)_3$ in THF to give the contact ion pair $[\text{ScMe}_2(\text{Me}_3\text{-TACN})(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$ (**180**) (Scheme 27).⁹⁶ The ¹H NMR spectrum of **180** in THF-*d*₈ shows a broad singlet at δ 0.50 ppm for the μ-Me group and a sharp singlet at δ 0.66 ppm due to the terminal Sc–Me groups. Furthermore, $[\text{ScMe}_3(\text{Me}_3\text{-TACN})]$ reacted with $[\text{PhNMe}_2\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in THF to form the ion pair $[\text{ScMe}_2(\text{Me}_3\text{-TACN})(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**181**). Although the ¹H NMR spectrum of **181** in THF-*d*₈ indicates the formation of the expected byproducts, free *N,N*-dimethylaniline and methane, the Sc–Me resonance of the cation was not detected. Experimental observations suggest the formation of a liquid clathrate.

Table 9. Monocationic Alkyl Rare-Earth Metal Complexes That Contain Neutral L₃-Type Ligands

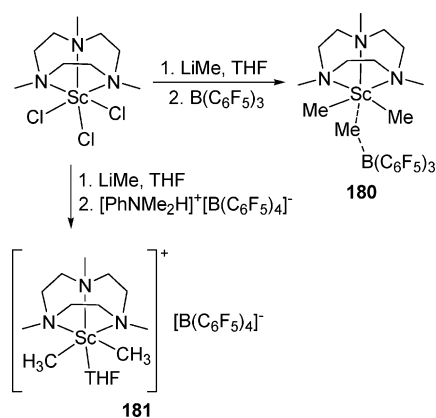
| no. | compound | characterization | ref |
|------------|---|---|-----|
| 180 | $[\text{ScMe}_2(\text{Me}_3\text{-TACN})(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$ ^a | in situ, ¹ H NMR | 96 |
| 181 | $[\text{ScMe}_2(\text{Me}_3\text{-TACN})(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^a | in situ, ¹ H NMR | 96 |
| 182 | $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{Me}_3\text{-TACN})]^+[\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{SiMe}_3)]^-$ ^a | in situ, no data available | 132 |
| 183 | $[\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{Me}_3\text{-TACN})]^+[\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{SiMe}_3)]^-$ ^a | in situ, no data available | 132 |
| 184 | $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{Me}_2\text{-pz})(\text{THF})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^b | ¹ H, ¹³ C, ¹⁹ F NMR, IR, MS | 132 |
| 185 | $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{Me}_2\text{-pz})]^+[\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{SiMe}_3)]^-$ ^b | in situ, no data available | 132 |
| 186 | $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{Pr-trisox})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^c | in situ, ¹ H, ¹³ C, ¹⁹ F, ²⁹ Si NMR | 133 |
| 187 | $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{TTCN})(\text{THF})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ^d | in situ, ¹ H, ¹³ C, ¹⁹ F NMR | 134 |
| 188 | $[\text{Sc}(\text{CH}_2\text{SiMe}_3)_2(\text{TTCN})]^+[\text{B}(\text{C}_6\text{F}_5)_3(\text{CH}_2\text{SiMe}_3)]^-$ ^d | in situ, no data available | 134 |

^a TACN = 1,4,7-triazacyclononane. ^b Me₂-pz = tris(3,5-dimethylpyrazolyl)methane. ^c Pr-trisox = 1,1,1-tri{2-[4-(*S*)-isopropylloxazolyl]}ethane. ^d TTCN = 1,4,7-trithiacyclononane.

Chart 3^a

^a (a) 1,4,7-trimethyl-1,4,7-triazacyclononane (TACN); (b) 1,4,7-trithiacyclononane (TTCN); (c) 1,1,1-tri-[2-(4-(*S*)-isopropylloxazolyl)]ethane (Pr-trisox); (d) tris(3,5-dimethylpyrazolyl)methane (Me₂-pz).

Scheme 27



The reaction of [Sc(CH₂SiMe₃)₃(Me₂-pz)] (Me₂-pz = tris(3,5-dimethylpyrazolyl)methane), in which (Me₂-pz) is facially coordinating, and [Ph₃C]⁺[B(C₆F₅)₄]⁻ in CD₂Cl₂/THF afforded the ion pair [Sc(CH₂SiMe₃)₂(Me₂-pz)(THF)]⁺[B(C₆F₅)₄]⁻ (**184**).¹³²

NMR spectroscopic investigations into the reactivity of the tris(oxazolyl)ethane-supported scandium tris(alkyl) derivative [Sc(CH₂SiMe₃)₃(Pr-trisox)] (Pr-trisox = 1,1,1-tri-[2-(4-(*S*)-isopropylloxazolyl)]ethane) suggested its transformation into an alkyl cation [Sc(CH₂SiMe₃)₂(Pr-trisox)]⁺[B(C₆F₅)₄]⁻ (**186**) upon treatment with [Ph₃C]⁺[B(C₆F₅)₄]⁻ in CD₂Cl₂.¹³³

The 1,4,7-trithiacyclononane (TTCN) supported scandium derivative [Sc(CH₂SiMe₃)₂(TTCN)(THF)]⁺[B(C₆F₅)₄]⁻ (**187**) was generated in situ in dichloromethane and characterized by multinuclear NMR spectroscopy.¹³⁴

7.1.3. Complexes with Neutral L-Type Ligands

Monocationic σ -alkyl complexes containing solely THF are listed in Table 10.

The reaction of [Y(CH₂SiMe₃)₃(THF)₂] with [Al(CH₂SiMe₃)₃] gave the thermally robust ion pair [Y(CH₂SiMe₃)₂(THF)₄]⁺[Al(CH₂SiMe₃)₄]⁻ (**189**) in THF.^{129,135} The ⁸⁹Y NMR chemical shift correlated well with the charge at yttrium, being significantly shifted to higher field when compared to that of the neutral complex. Likewise, the ¹J_{YC} coupling constants increased with the charge at the yttrium center. Crystallographic characterization of **189** revealed a distorted octahedral coordination geometry around the yttrium center with *cis*-arrangement of the two trimethylsilylmethyl groups.^{130,136}

A mixture of [Ln(CH₂SiMe₃)₃(THF)₂] (Ln = Y, Lu) and 1 equiv of BPh₃ in THF gave the ion pairs [Ln(CH₂SiMe₃)₂(THF)_n]⁺[BPh₃(CH₂SiMe₃)]⁻ (Ln = Y, n = 4 (**190**); Ln = Lu, n = 3 (**191**)).^{129,130} When the stronger Lewis acid B(C₆F₅)₃ was used, the ion pairs [Ln(CH₂SiMe₃)₂(THF)_x]⁺[B(C₆F₅)₃(CH₂SiMe₃)]⁻ (Ln = Y (**192**), Lu (**193**)) could be prepared in situ and characterized by NMR spectroscopy (THF-*d*₈) but required forcing conditions (several hours at 40–50 °C) due to the greater stability of the adduct B(C₆F₅)₃(THF).^{137–139} The ¹⁹F NMR spectra of [Ln(CH₂SiMe₃)₂(THF)_x]⁺[B(C₆F₅)₃(CH₂SiMe₃)]⁻ exhibited *meta/para* chemical shift differences of 2.2 ppm, consistent with the presence of solvent-separated ion pairs.

The tris(alkyl) complexes [Ln(CH₂SiMe₃)₃(THF)₂] (Ln = Y, Sc, Lu) underwent protonolysis with equimolar amounts of [NEt₃H]⁺[BPh₄]⁻ to give the ion pairs [Ln(CH₂SiMe₃)₂(THF)_x]⁺[BPh₄]⁻ (Ln = Sc, x = 3 (**194**); Ln = Y, x = 4 (**195**); Ln = Lu, x = 3 (**196**)) in THF (Scheme 28).^{129,135} The ¹H, ¹³C, and ¹¹B NMR spectroscopic data for **195** are consistent with the presence of solvent-separated ions in solution. The coupling constant ¹J_{CH} of 97.2 Hz was similar to that found for the neutral tris(alkyl) complex (¹J_{CH} = 98.4 Hz) and does not appear to indicate an α -agostic interaction.^{140–143}

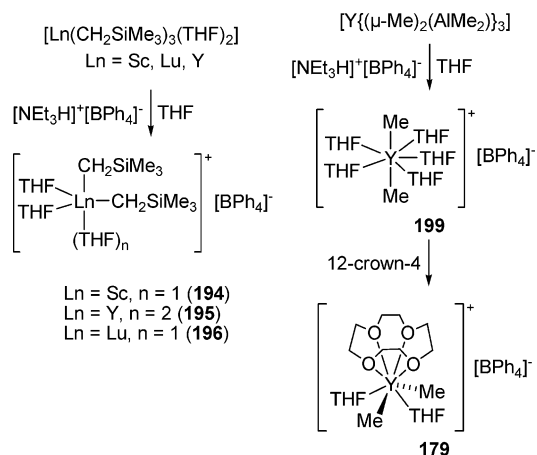
Analogous yttrium and lutetium complexes containing the anion [B(C₆F₅)₄]⁻ could be generated and observed by NMR spectroscopy.¹²⁹ Equimolar amounts of the tris(alkyl) complexes [Ln(CH₂SiMe₃)₃(THF)₂] and [PhNMe₂H]⁺[B(C₆F₅)₄]⁻ underwent reaction in THF-*d*₈ to form [Ln(CH₂SiMe₃)₂(THF)_x]⁺[B(C₆F₅)₄]⁻ (Ln = Y (**197**); Ln = Lu (**198**)).

The aluminate [Y{(μ-Me)₂AlMe₂}]₃ reacted with [NEt₃H]⁺[BPh₄]⁻ in THF to give the dimethyl derivative [YMe₂(THF)₅]⁺[BPh₄]⁻ (**199**) as thermally robust crystals.¹³¹ Formation of the related complex [YMe₂(THF)_x]⁺[B(C₆F₅)₄]⁻ (**200**) was monitored in situ during the reaction of [Y{(μ-Me)₂AlMe₂}]₃ and 1 equiv of [PhNMe₂H]⁺[B(C₆F₅)₄]⁻ in

Table 10. Monocationic Alkyl Rare-Earth Metal Complexes That Contain Neutral L-Type Ligands

| no. | compound | characterization | refs |
|------------|---|---|---------|
| 189 | [Y(CH ₂ SiMe ₃) ₂ (THF) ₄] ⁺ [Al(CH ₂ SiMe ₃) ₄] ⁻ | X-ray, ¹ H, ¹³ C, ²⁷ Al, ⁸⁹ Y NMR, EA | 129,135 |
| 190 | [Y(CH ₂ SiMe ₃) ₂ (THF) ₄] ⁺ [BPh ₃ (CH ₂ SiMe ₃)] ⁻ | ¹ H, ¹³ C, ¹¹ B, ⁸⁹ Y NMR, EA | 129,130 |
| 191 | [Lu(CH ₂ SiMe ₃) ₂ (THF) ₃] ⁺ [BPh ₃ (CH ₂ SiMe ₃)] ⁻ | ¹ H, ¹³ C, ¹¹ B NMR, EA | 130 |
| 192 | [Y(CH ₂ SiMe ₃) ₂ (THF) _x] ⁺ [B(C ₆ F ₅) ₃ (CH ₂ SiMe ₃)] ⁻ | in situ, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR | 129,130 |
| 193 | [Lu(CH ₂ SiMe ₃) ₂ (THF) _x] ⁺ [B(C ₆ F ₅) ₃ (CH ₂ SiMe ₃)] ⁻ | in situ, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR | 129,130 |
| 194 | [Sc(CH ₂ SiMe ₃) ₂ (THF) ₃] ⁺ [BPh ₄] ⁻ | ¹ H, ¹³ C, ¹¹ B NMR, EA | 129 |
| 195 | [Y(CH ₂ SiMe ₃) ₂ (THF) ₄] ⁺ [BPh ₄] ⁻ | ¹ H, ¹³ C, ¹¹ B, ⁸⁹ Y NMR, EA | 129,135 |
| 196 | [Lu(CH ₂ SiMe ₃) ₂ (THF) ₃] ⁺ [BPh ₄] ⁻ | ¹ H, ¹³ C, ¹¹ B NMR, EA | 129 |
| 197 | [Y(CH ₂ SiMe ₃) ₂ (THF) _x] ⁺ [B(C ₆ F ₅) ₄] ⁻ | in situ, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR | 129 |
| 198 | [Lu(CH ₂ SiMe ₃) ₂ (THF) _x] ⁺ [B(C ₆ F ₅) ₄] ⁻ | in situ, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR | 129 |
| 199 | [YMe ₂ (THF) ₅] ⁺ [BPh ₄] ⁻ | X-ray, ¹ H, ¹³ C, ¹¹ B NMR, EA | 131 |
| 200 | [YMe ₂ (THF) _x] ⁺ [B(C ₆ F ₅) ₄] ⁻ | in situ, ¹ H NMR | 131 |

Scheme 28



THF-*d*₈. Single-crystal X-ray structure analysis of **199** revealed a pentagonal bipyramidal coordination geometry around the yttrium center in the solid state with methyl groups arranged in a *trans* fashion. Notably, THF readily displaced three molecules of AlMe₃ when the aluminate [Y{(μ-Me)₂AlMe₂}₃] was converted into the ion pair [YMe₂(THF)₅]⁺[BPh₄]⁻.

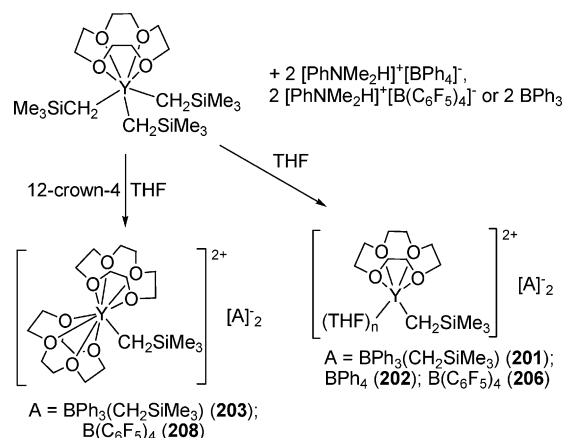
7.2. Dicationic σ-Alkyl Complexes

7.2.1. Complexes with Neutral L_n-Type Coligands (*n* = 3, 4)

Dicationic complexes of the rare-earth metals containing one σ-alkyl group are rather unusual species, because they were not expected and were discovered in the context of homogeneous α-olefin polymerization catalysis. Those containing neutral chelating L_n-type ligands (*n* = 3, 4) are compiled in Table 11.

Dicationic yttrium and lutetium mono(trimethylsilylmethyl) complexes with [BPh₃(CH₂SiMe₃)]⁻ and [BPh₄]⁻ counterions were isolated as both mono- and bis(12-crown-4) complexes: [Y(CH₂SiMe₃)(12-crown-4)(THF)_{*x*}]²⁺[A]⁻² (*x* = 2, A = BPh₃(CH₂SiMe₃) (**201**); *x* = 3, A = BPh₄ (**202**)) and [Ln(CH₂SiMe₃)(12-crown-4)₂]²⁺[A]⁻² (Ln = Y, A = BPh₃(CH₂SiMe₃) (**203**); Ln = Lu, A = BPh₄ (**204**)) (Scheme 29).¹²⁹ These complexes are highly soluble in pyridine, but their solubility in other solvents such as THF and dichloromethane is highly dependent on the choice of anion and the number of 12-crown-4 ligands. They were prepared in high yield from THF solutions of the parent neutral crown-ether derivatives and the corresponding Lewis or Brønsted acids, BPh₃ or [NEt₃H]⁺[BPh₄]⁻. The crystal structure of **202** has

Scheme 29



a face-capping 12-crown-4 and three THF units, giving an eight-coordinate yttrium center of square antiprismatic coordination geometry. Although thermally robust as isolated compounds, these complexes were not stable in pyridine solution. Complex **202** reacted with pyridine within 10 h with concomitant formation of [Y(η²-(C,N)-C₅D₄N)(12-crown-4)(C₅D₅N)_{*x*}]²⁺[BPh₄]⁻² (**205**). Dicationic mono(trimethylsilylmethyl) complexes of yttrium and lutetium [Ln(CH₂SiMe₃)(12-crown-4)_{*n*}(THF)_{*x*}]²⁺[B(C₆F₅)₄]⁻² (*n* = 1; Ln = Y (**206**), Ln = Lu (**207**); *n* = 2; Ln = Y (**208**), Ln = Lu (**209**)) were prepared in situ and characterized by multinuclear NMR spectroscopy. These complexes with the [B(C₆F₅)₄]⁻ anion showed a much higher solubility in THF than those with the [BPh₄]⁻ anion. Interestingly, the bis(12-crown-4) complexes, but notably not the mono(12-crown-4) analogues, reacted with [PhNMe₂H]⁺[B(C₆F₅)₄]⁻ to give trimethylsilylmethyl-free complexes, tentatively assigned as [Ln(12-crown-4)₂(THF)_{*x*}]³⁺[B(C₆F₅)₄]⁻³ (Ln = Y, Lu).

The reaction of [Sc(Pr-trisox)(CH₂SiMe₃)₃] with 2 equiv of [Ph₃C]⁺[B(C₆F₅)₄]⁻ was monitored by multinuclear NMR spectroscopy.¹³³ The formation of 2 equiv of Ph₃CCH₂SiMe₃ was observed and the scandium-containing species tentatively assigned as the dicationic complex [Sc(Pr-trisox)(CH₂SiMe₃)₂]²⁺[B(C₆F₅)₄]⁻² (**210**). This complex was proposed as the active species in 1-hexene polymerization when generated in situ (section 9.1) but was not isolated.

[Sc(CH₂SiMe₃)(TTCN)]²⁺[B(C₆F₅)₄]⁻² (**211**) was generated in situ upon reaction of the neutral tris(alkyl) complex with 2 equiv of [Ph₃C]⁺[B(C₆F₅)₄]⁻ and used as catalyst for the polymerization of 1-hexene and styrene (section 9.1).¹³⁴

7.2.2. Complexes with Neutral L-Type Coligands

Dicationic rare earth metal alkyl complexes that contain THF or pyridine are collected in Table 12.

Table 11. Dicationic Alkyl Rare-Earth Metal Complexes That Contain Neutral L_n-Type Ligands (*n* = 3, 4)

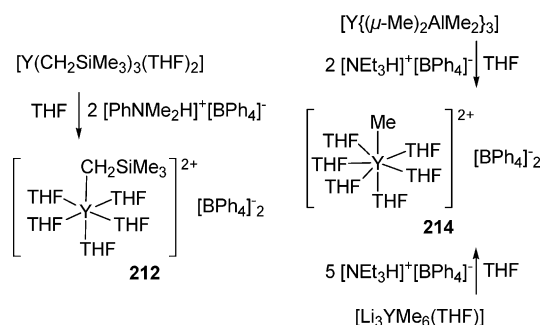
| no. | compound | characterization | ref |
|------------|--|---|-----|
| 201 | [Y(CH ₂ SiMe ₃)(12-crown-4)(THF) ₂] ²⁺ [BPh ₃ (CH ₂ SiMe ₃)] ⁻² | ¹ H, ¹³ C NMR, EA | 129 |
| 202 | [Y(CH ₂ SiMe ₃)(12-crown-4)(THF) ₃] ²⁺ [BPh ₄] ⁻² | X-ray, ¹ H, ¹³ C, ¹¹ B NMR, EA | 129 |
| 203 | [Y(CH ₂ SiMe ₃)(12-crown-4) ₂] ²⁺ [BPh ₃ (CH ₂ SiMe ₃)] ⁻² | ¹ H, ¹³ C, ¹¹ B NMR, EA | 129 |
| 204 | [Lu(CH ₂ SiMe ₃)(12-crown-4) ₂] ²⁺ [BPh ₄] ⁻² | ¹ H, ¹³ C, ¹¹ B NMR, EA | 129 |
| 205 | [Y(η ² -(C,N)-C ₅ D ₄ N)(12-crown-4)(C ₅ D ₅ N) _{<i>x</i>}] ²⁺ [BPh ₄] ⁻² | in situ, ¹ H, ¹³ C, ¹¹ B NMR | 129 |
| 206 | [Y(CH ₂ SiMe ₃)(12-crown-4)(THF) _{<i>x</i>}] ²⁺ [B(C ₆ F ₅) ₄] ⁻² | in situ, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR | 129 |
| 207 | [Lu(CH ₂ SiMe ₃)(12-crown-4)(THF) _{<i>x</i>}] ²⁺ [B(C ₆ F ₅) ₄] ⁻² | in situ, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR | 129 |
| 208 | [Y(CH ₂ SiMe ₃)(12-crown-4) ₂ (THF) _{<i>x</i>}] ²⁺ [B(C ₆ F ₅) ₄] ⁻² | in situ, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR | 129 |
| 209 | [Lu(CH ₂ SiMe ₃)(12-crown-4) ₂ (THF) _{<i>x</i>}] ²⁺ [B(C ₆ F ₅) ₄] ⁻² | in situ, ¹ H, ¹³ C, ¹¹ B, ¹⁹ F NMR | 129 |
| 210 | [Sc(CH ₂ SiMe ₃)(Pr-trisox)] ²⁺ [B(C ₆ F ₅) ₄] ⁻² ^a | in situ, ¹ H, ¹³ C, ¹⁹ F, ²⁹ Si NMR | 133 |
| 211 | [Sc(CH ₂ SiMe ₃)(TTCN)] ²⁺ [B(C ₆ F ₅) ₄] ⁻² ^b | in situ, no data available | 134 |

^a Pr-trisox = 1,1,1-tri[2-[4-(S)-isopropylloxazolyl]]ethane. ^b TTCN = 1,4,7-trithiacyclononane.

Table 12. Dicationic Alkyl Rare-Earth Metal Complexes That Contain Neutral L-Type Ligands

| no. | compound | characterization | refs |
|-----|--|---|---------|
| 212 | $[Y(CH_2SiMe_3)(THF)_5]^{2+}[BPh_4]^{-}_2$ | 1H , ^{13}C , ^{11}B , ^{89}Y NMR, EA | 129,135 |
| 213 | $[Lu(CH_2SiMe_3)(THF)_4]^{2+}[BPh_4]^{-}_2$ | 1H , ^{13}C , ^{11}B NMR, EA | 129 |
| 214 | $[YMe(THF)_6]^{2+}[BPh_4]^{-}_2$ | X-ray, 1H , ^{13}C , ^{11}B , ^{89}Y NMR, EA | 131,135 |
| 215 | $[YMe(THF)_x]^{2+}[B(C_6F_5)_4]^{-}_2$ | in situ, 1H NMR | 131 |
| 216 | $[LuMe(THF)_6]^{2+}[BPh_4]^{-}_2$ | 1H , ^{13}C , ^{11}B NMR, EA | 131 |
| 217 | $[YbMe(THF)_6]^{2+}[BPh_4]^{-}_2$ | EA | 131 |
| 218 | $[HoMe(THF)_6]^{2+}[BPh_4]^{-}_2$ | X-ray, EA | 131 |
| 219 | $[ScMe(THF)_5]^{2+}[BPh_4]^{-}_2$ | 1H , ^{13}C , ^{11}B NMR, EA | 131 |
| 220 | $[NdMe(THF)_7]^{2+}[BPh_4]^{-}_2$ | EA | 131 |
| 221 | $[YMe(C_5H_5N)_6]^{2+}[BPh_4]^{-}_2$ | 1H , ^{13}C , ^{11}B NMR, EA | 153 |
| 222 | $[Y\{\eta^2-(C,N)-C_5H_4N\}(C_5H_5N)_6]^{2+}[BPh_4]^{-}_2$ | X-ray, 1H , ^{13}C , ^{11}B NMR, EA | 153 |

Treatment of a THF solution of the yttrium tris(alkyl) complex $[Y(CH_2SiMe_3)_3(THF)_2]$ with 2 equiv of $[NEt_3H]^+[BPh_4]^-$ or $[PhNMe_2H]^+[BPh_4]^-$ gave the dicationic alkyl complex $[Y(CH_2SiMe_3)(THF)_5]^{2+}[BPh_4]^{-}_2$ (**212**) as thermally robust, colorless microcrystals (Scheme 30).^{129,135} The lute-

Scheme 30

tium complex $[Lu(CH_2SiMe_3)(THF)_4]^{2+}[BPh_4]^{-}_2$ (**213**) was prepared by the reaction of $[Lu(CH_2SiMe_3)_3(THF)_2]$ with 2 equiv of $[PhNMe_2H]^+[BPh_4]^-$.¹²⁹ The remaining alkyl groups at the rare-earth metal in **212** and **213** were resistant to Brønsted acids.^{105,135,144,145} The ^{89}Y NMR resonance at δ 409.2 ppm for **212** in THF- d_8 was shifted to a significantly higher field compared to that for the corresponding monocations and the neutral precursor, respectively.

When the tris(aluminate) $[Y\{(\mu-Me)_2AlMe_2\}_3]^{146}$ was treated with 2 equiv of $[NEt_3H]^+[BPh_4]^-$ in THF, the ion triple $[YMe(THF)_6]^{2+}[BPh_4]^{-}_2$ (**214**) containing the methyl dication was obtained as thermally robust colorless crystals (Scheme 30).^{131,135} Formation of the related complex $[YMe(THF)_x]^{2+}[B(C_6F_5)_4]^{-}_2$ (**215**) was monitored in situ during the reaction of $[Y\{(\mu-Me)_2AlMe_2\}_3]$ and 2 equiv of $[PhNMe_2H]^+[B(C_6F_5)_4]^-$ in THF- d_8 .¹³¹ Alternatively, **214** was prepared from the ate complex $[Li_3YMe_6(THF)]^{147}$ and 5 equiv of $[NEt_3H]^+[BPh_4]^-$ in THF.¹³⁵ The analogous lutetium (**216**), ytterbium (**217**), and holmium (**218**) derivatives as well as the scandium derivative $[ScMe(THF)_5]^{2+}[BPh_4]^{-}_2$ (**219**) were also prepared from the appropriate hexamethylates $[Li_3LnMe_6(THF)]$ by protonolysis;^{147–150} reaction of $[Nd\{(\mu-Me)_2AlMe_2\}_3]$ with 2 equiv of $[NEt_3H]^+[BPh_4]^-$ afforded $[NdMe(THF)_7]^{2+}[BPh_4]^{-}_2$ (**220**). Crystal structure analysis of **214** revealed that the methyl dication exhibits a pentagonal bipyramidal coordination geometry around the yttrium center with the methyl group in the apical position (Figure 9). The holmium derivative **218** is isostructural with its yttrium analogue **214** in the solid state. Although the 1H and ^{13}C NMR spectroscopic data for **214** do not indicate any agostic interactions, the high value of $^1J_{YC}$ (53.6 Hz) is remarkable.^{151,152} The role of these alkyl

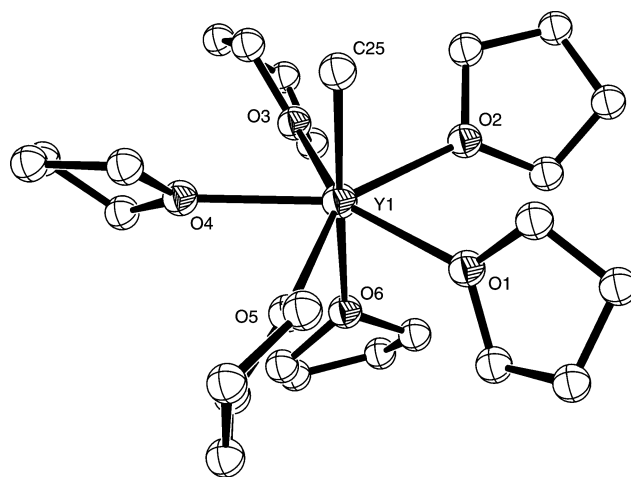


Figure 9. Molecular structure of the cationic part of $[YMe(THF)_6]^{2+}[BPh_4]^{-}_2$ (**214**). Hydrogen atoms are omitted for clarity. Drawn from data in ref 135.

dications with pentafluorophenylborate anions in ethylene and 1,3-diene polymerization is described in section 9.1.

A ligand exchange reaction was carried out by dissolving the dicationic yttrium methyl complex **214** in excess pyridine and immediately precipitating with pentane to give the analogous pyridine adduct $[YMe(C_5H_5N)_6]^{2+}[BPh_4]^{-}_2$ (**221**). When **214** was left in pyridine at room temperature, C–H activation proceeded to give the structurally characterized dicationic rare-earth metal η^2 -pyridyl complex $[Y\{\eta^2-(C,N)-C_5H_4N\}(C_5H_5N)_6]^{2+}[BPh_4]^{-}_2$ (**222**).¹⁵³ X-ray crystallography revealed that the pyridyl complex **222** adopts a pentagonal bipyramidal coordination geometry with the pyridyl ligand in an axial position. Kinetic data demonstrate that this complex forms by an associative mechanism in the presence of excess pyridine after rapid exchange of the Lewis bases to give **221**.

8. Divalent Cationic Rare-Earth Organometallic Complexes

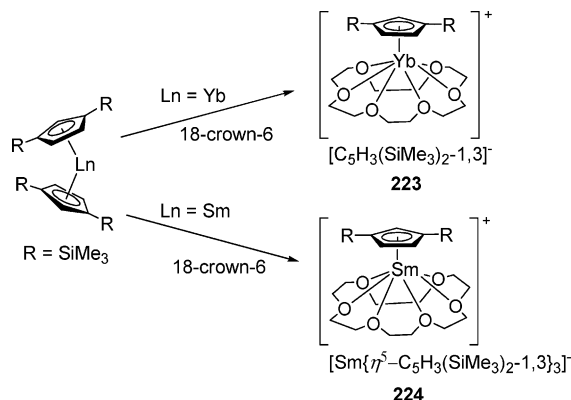
Divalent cationic rare-earth organometallic metal complexes are extremely rare species and in some cases appear to have formed serendipitously upon the addition of neutral ligands. Those few compounds to have been reported are compiled in Table 13.¹⁷⁵

The first examples of cationic organolanthanoid(II) complexes to be published, $[Yb\{\eta^5-C_5H_3(SiMe_3)_2-1,3\}(18-crown-6)]^+[C_5H_3(SiMe_3)_2-1,3]^-$ (**223**) and $[Sm\{\eta^5-C_5H_3(SiMe_3)_2-1,3\}(18-crown-6)]^+[Sm\{\eta^5-C_5H_3(SiMe_3)_2-1,3\}_3]^-$ (**224**), were formed upon treatment of the bis(cyclopentadienyl) lanthanoid(II) complexes $[Ln\{\eta^5-C_5H_3(SiMe_3)_2-1,3\}_2]$ with 18-crown-6 in benzene (Scheme 31).¹⁵⁴ The displacement of

Table 13. Divalent Cationic Organolanthanoid Complexes

| no. | compound | characterization | ref |
|-----|---|---|-----|
| 223 | $[\text{Yb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}(18\text{-crown-6})]^+[\text{C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}]^-$ | X-ray, ^1H , ^{29}Si , ^{171}Yb NMR | 154 |
| 224 | $[\text{Sm}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}(18\text{-crown-6})]^+[\text{Sm}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}_3]^-$ | X-ray, ^{29}Si NMR | 154 |
| 225 | $[\text{Yb}(\eta\text{-C}_{13}\text{H}_9)(\text{THF})_4]^+[\text{AlMe}_4]^-$ | X-ray, ^1H NMR, EA | 155 |
| 226 | $[\text{Eu}(\text{C}_6\text{F}_5)(\text{THF})_6]^+[\text{BPh}_4]^-$ | X-ray, ^1H NMR, IR, EA | 156 |
| 227 | $[\text{Yb}(\text{C}_6\text{F}_5)(\text{THF})_5]^+[\text{BPh}_4]^-$ | X-ray, ^1H , ^{19}F , ^{171}Yb NMR, IR, EA | 156 |
| 228 | $[\text{Yb}(\text{C}_6\text{F}_5)(\text{THF})_5]^+[\text{Yb}(\text{C}_6\text{F}_5)_2\{\text{N}(\text{SiMe}_3)_2\}_2]^-$ | X-ray, IR | 156 |

Scheme 31



one cyclopentadienyl ligand by the crown ether afforded **223** and **224** as crystalline salts. Characterization by multinuclear NMR spectroscopy and X-ray structure analysis revealed well-separated ions. The cations contain one cyclopentadienyl ligand and one crown ether in a sandwich-like structure with the cyclopentadienyl ligand and one oxygen donor adopting the apical positions of a pseudo-pentagonal bipyramid (Figure 10).

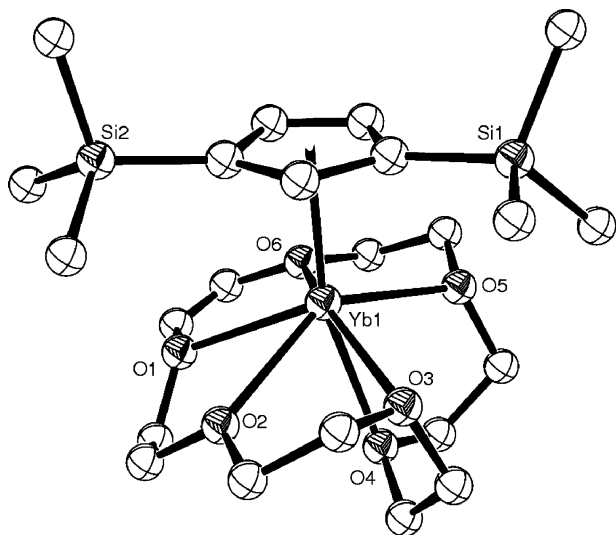
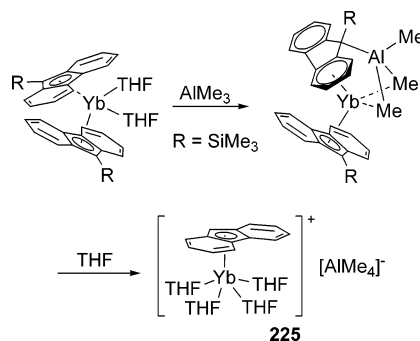


Figure 10. Molecular structure of the cationic part of $[\text{Yb}\{\eta^5\text{-C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}\}(18\text{-crown-6})]^+[\text{C}_5\text{H}_3(\text{SiMe}_3)_2\text{-1,3}]^-$ (**223**). Hydrogen atoms are omitted for clarity. Drawn from data in ref 154.

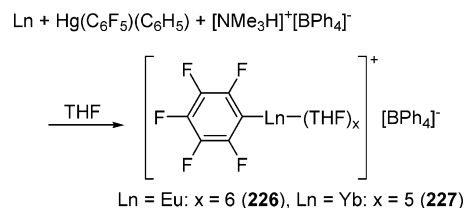
Addition of excess THF to the unsymmetrical bis(1-trimethylsilylfluorenyl) ytterbium complex $[\text{Yb}(\eta^5\text{-C}_{13}\text{H}_8\text{SiMe}_3)\{\eta^6\text{-C}_{13}\text{H}_8(\text{SiMe}_3)(\text{AlMe}_3)\}]$ gave the crystallographically characterized ion pair $[\text{Yb}(\eta\text{-C}_{13}\text{H}_9)(\text{THF})_4]^+[\text{AlMe}_4]^-$ (**225**) in low yield (Scheme 32).¹⁵⁵ Experiments with a deuterium labeled indenyl group and THF-*d*₈ indicated that the SiMe₃ group was eliminated from the indenyl group by the attack of THF, although the exact reaction pathway remains obscure.

Scheme 32



The one-pot reaction of metallic ytterbium or europium with $\text{HgPh}(\text{C}_6\text{F}_5)$ and $[\text{NMe}_3\text{H}]^+[\text{BPh}_4]^-$ in THF gave the tetraphenylborate salts of solvated pentafluorophenyl lanthanoid(II) cations $[\text{Ln}(\text{C}_6\text{F}_5)(\text{THF})_x]^+[\text{BPh}_4]^-$ (Ln = Eu, $x = 6$ (**226**); Ln = Yb, $x = 5$ (**227**); Scheme 33).¹⁵⁶ The

Scheme 33



same divalent ytterbium cation as in **227** was found in the mixed-valent complex $[\text{Yb}^{\text{II}}(\text{C}_6\text{F}_5)(\text{THF})_5]^+[\text{Yb}^{\text{III}}(\text{C}_6\text{F}_5)_2\{\text{N}(\text{SiMe}_3)_2\}_2]^-$ (**228**), isolated in low yield from the reaction of ytterbium, $\text{HgPh}(\text{C}_6\text{F}_5)$, and $\text{HN}(\text{SiMe}_3)_2$ in THF. X-ray structure analysis revealed well-separated ions; complex **228** is notably highly thermally stable. The Eu–C bond distance is shorter in the cationic compound **226** than in the comparable neutral complex $[\text{Eu}(\text{C}_6\text{F}_5)_2(\text{THF})_5]$.¹⁵⁷ Complex **227** exhibits ^1H and ^{19}F spectra typical of an $\text{Yb}^{\text{II}}\text{-C}_6\text{F}_5$ species. A slightly asymmetric multiplet with the coupling constants $^3J_{\text{YbF}} \approx 48$ Hz, $^4J_{\text{YbF}} \approx 33$ Hz, and $^5J_{\text{YbF}} \approx 8$ Hz arising from $^{171}\text{Yb}\text{-}^{19}\text{F}$ coupling was observed in the ^{171}Yb NMR spectrum at -30 °C.

9. Applications

Cationic organolanthanoid complexes have been used in a number of catalytic and stoichiometric reactions. These include homo- and copolymerization catalysis of nonpolar substrates, catalysis of organic transformations, reduction of dinitrogen and synthesis of unsolvated neutral rare-earth organometallics.

9.1. Polymerization Catalysis

The initial studies into the polymerization catalysis of cationic organolanthanoids exclusively addressed homogeneous ethylene polymerization. Recent investigations have

Table 14. Ethylene Polymerization with Cationic Organolanthanoid Catalysts Generated in Situ by the Reaction of a Neutral Precursor with an Activator

| catalyst | precursor | activator | cocatalyst | <i>t</i> (min) | activity (kg mol ⁻¹ h ⁻¹ bar ⁻¹) | <i>M</i> _n (× 10 ³ g mol ⁻¹) | <i>M</i> _w / <i>M</i> _n | ref |
|----------|--|---|---------------------------------|-------------------|--|--|---|-----|
| 143 | [Sc{η ³ -PhC(NAr) ₂ }(CH ₂ SiMe ₃) ₂ (THF)] ^a | [PhNMe ₂ H] ⁺ [B(C ₆ F ₅) ₄] ⁻ | TIBAO | 20 | 24 ^b | 58 | 1.6 | 114 |
| 136 | [Y{η ³ -PhC(NAr) ₂ }(CH ₂ SiMe ₃) ₂ (THF)] ^a | [PhNMe ₂ H] ⁺ [B(C ₆ F ₅) ₄] ⁻ | | 5 | 1040 ^c | 360 | 1.2 | 113 |
| 136 | [Y{η ³ -PhC(NAr) ₂ }(CH ₂ SiMe ₃) ₂ (THF) ₂] ^a | [PhNMe ₂ H] ⁺ [B(C ₆ F ₅) ₄] ⁻ | TIBAO | 5 | 2670 ^c | 170 | 2.1 | 113 |
| 136 | [Y{η ³ -PhC(NAr) ₂ }(CH ₂ SiMe ₃) ₂ (THF) ₂] ^a | [PhNMe ₂ H] ⁺ [B(C ₆ F ₅) ₄] ⁻ | TIBAO | 20 | 1666 ^b | 833 | 2.0 | 114 |
| 144 | [La{η ³ -PhC(NAr) ₂ }(CH ₂ SiMe ₃) ₂ (THF)] ^a | [PhNMe ₂ H] ⁺ [B(C ₆ F ₅) ₄] ⁻ | TIBAO | 20 | 470 ^b | 835 | 2.5 | 114 |
| 145 | [Nd{η ³ -PhC(NAr) ₂ }(CH ₂ SiMe ₃) ₂ (THF)] ^a | [PhNMe ₂ H] ⁺ [B(C ₆ F ₅) ₄] ⁻ | TIBAO | 20 | 1596 ^b | 725 | 2.2 | 114 |
| 146 | [Gd{η ³ -PhC(NAr) ₂ }(CH ₂ SiMe ₃) ₂ (THF)] ^a | [PhNMe ₂ H] ⁺ [B(C ₆ F ₅) ₄] ⁻ | TIBAO | 20 | 1753 ^b | 188 | 2.1 | 114 |
| 147 | [Lu{η ³ -PhC(NAr) ₂ }(CH ₂ SiMe ₃) ₂ (THF)] ^a | [PhNMe ₂ H] ⁺ [B(C ₆ F ₅) ₄] ⁻ | TIBAO | 20 | 496 ^b | 354 | 1.4 | 114 |
| 182 | [Sc(CH ₂ SiMe ₃) ₃ (Me ₃ -TACN)] | B(C ₆ F ₅) ₃ | Al ⁱ Bu ₃ | 60 | 240 ^d | <i>e</i> | <i>e</i> | 132 |
| 183 | [Y(CH ₂ SiMe ₃) ₃ (Me ₃ -TACN)] | B(C ₆ F ₅) ₃ | Al ⁱ Bu ₃ | 60 | 10 ^d | <i>e</i> | <i>e</i> | 132 |
| 185 | [Sc(CH ₂ SiMe ₃) ₃ (Me ₂ -pz)] | B(C ₆ F ₅) ₃ | Al ⁱ Bu ₃ | 60 | 290 ^d | <i>e</i> | <i>e</i> | 132 |
| 188 | [Sc(CH ₂ SiMe ₃) ₃ (TTCN)] | B(C ₆ F ₅) ₃ | Al ⁱ Bu ₃ | 60 | 110 ^d | <i>e</i> | <i>e</i> | 134 |
| | [Sc{η ³ -ArNC('Bu)CHC('Bu)NAr}Me ₂] | PMAO-IP | | <i>e</i> | 58 ^c | 940 | 2.0 | 107 |
| 119 | [Sc{η ³ -ArNC('Bu)CHC('Bu)NAr}Me ₂] | B(C ₆ F ₅) ₃ | PMAO-IP | <i>e</i> | 15 ^c | 620 | 1.7 | 107 |
| 122 | [Sc{η ³ -ArNC('Bu)CHC('Bu)NAr}Me ₂] | [Ph ₃ C] ⁺ [B(C ₆ F ₅) ₄] ⁻ | PMAO-IP | <i>e</i> | 23 ^c | 340 | 2.5 | 107 |
| 82 | [Sc(η ⁵ -C ₅ Me ₅)Me ₂ ('Bu ₃ P=O)] | B(C ₆ F ₅) ₃ | | <i>e</i> | 130 | <i>e</i> | <i>e</i> | 87 |
| | [Sc{η ³ :η ¹ -C ₅ Me ₄ (CH ₂ CH ₂ NMe ₂)Cl ₂] | MAO | | 15 | 771 ^f | 180 | 2.1 | 82 |
| 73 | [Sc{η ³ :η ¹ -C ₅ Me ₄ (CH ₂ CH ₂ NMe ₂)(CH ₂ Ph) ₂] | [PhNMe ₂ H] ⁺ [B(C ₆ F ₅) ₄] ⁻ | AlEt ₃ | 15 | 25 ^f | 4 | 1.9 | 82 |
| 93 | [Y{η ³ :η ¹ -N,N'-Me ₂ -TACN-N''-(CH ₂) ₂ N'Bu)-(CH ₂ SiMe ₃) ₂] | [PhNMe ₂ H] ⁺ [B(C ₆ F ₅) ₄] ⁻ | | 10 | 1180 ^c | 70 | 4.9 | 98 |
| 108 | [Y{(Me ₂ N(CH ₂) ₂) ₂ N(CH ₂) ₂ N'Bu)-(CH ₂ SiMe ₃) ₂] | [Ph ₃ C] ⁺ [B(C ₆ F ₅) ₄] ⁻ | | 15 | 60 ^c | 30 | 2.2 | 101 |

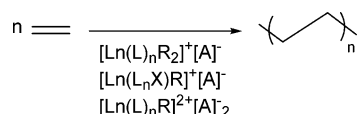
^a Ar = C₆H₃Pr₂-2,6. ^b *T* = 30 °C. ^c *T* = 50 °C. ^d *T* = 33 °C. ^e No information available. ^f *T* = 80 °C.

also covered α-olefins and conjugated dienes. Mono- and dicationic alkyl complexes were shown to be plausible candidates for the active species. In certain cases, dicationic derivatives were especially promising, since their activity and selectivity were significantly higher with respect to their monocationic relatives. Polymerization activity often increases with ionic radius, although in many respects scandium is exceptional due to its much smaller size.

9.1.1. Ethylene and α-Olefins

Ethylene Polymerization. Scandium and yttrium alkyl complexes containing both neutral and monoanionic ancillary ligands have been reported as precursors for efficient ethylene polymerization catalysts (Table 14, Scheme 34). The active

Scheme 34



monocationic species [Ln(L)_nR₂]⁺ or [Ln(L_nX)R]⁺ are commonly generated in situ by the reaction of the parent neutral complexes with Lewis acid or Brønsted acid activators. In some cases, further cocatalysts are also used (Table 15). No detailed mechanistic studies have been reported so far, but the role of an alkyl dication [Ln(L_n)R(solv)_x]²⁺ is highly intriguing.^{131,133–135}

Narrow molecular weight distributions of around 1.1 suggested a living character for ethylene polymerization with

Table 15. Ethylene Polymerization with [Ln(CH₂SiMe₃)(THF)₂] as Catalyst Precursors Activated in Situ with [PhNMe₂H]⁺[B(C₆F₅)₄]⁻ in the Presence of AlⁱBu₃¹³⁵

| Ln | <i>r</i> (Å) ^a | yield (g) | activity (kg mol ⁻¹ h ⁻¹ bar ⁻¹) | <i>M</i> _n (g mol ⁻¹) | <i>M</i> _w / <i>M</i> _n | <i>T</i> _m (°C) |
|-----------------|------------------------------|--------------|--|---|---|-------------------------------|
| Sc ^b | 0.89 | 0.03 | 1 | | | |
| Lu ^b | 1.00 | <i>d</i> | | | | |
| Yb | 1.01 | | | | | |
| Tm | 1.02 | 0.76 | 183 | 22030 | 4.1 | 136.7 |
| Er | 1.03 | 0.85 | 205 | 13430 | 5.3 | 134.7 |
| Y ^c | 1.04 | 0.91 | 272 | 14150 | 2.9 | 135.5 |
| Ho | 1.04 | 1.15 | 275 | 44850, 3450 ^e | 1.7, 1.8 | 132.5 |
| Dy | 1.05 | 3.51 | 842 | 3650 | 3.6 | 126.3 |
| Tb | 1.06 | 3.74 | 899 | 3820 | 2.9 | 126.3 |

^a Effective ionic radius of Ln³⁺ for CN = 6 (ref 14). ^b *t* = 60 min. ^c *t* = 8 min. ^d Traces. ^e Bimodal molecular weight distribution.

in situ generated [Y{η³-PhC(NAr)₂}(CH₂SiMe₃)(THF-*d*₈)_x]⁺[B(C₆F₅)₄]⁻ (Ar = C₆H₃Pr₂-2,6 (**136**)).¹¹³ Interestingly, the yttrium precursor appeared to provide the most effective catalyst for ethylene polymerization, because both larger and smaller metals showed lower activity under standardized conditions.¹¹⁴

Activation of the scandium complex [ScMe₃(Me₃-TACN)] (TACN = 1,4,7-triazacyclononane) with B(C₆F₅)₃ or [PhNMe₂H]⁺[B(C₆F₅)₄]⁻ gave the cationic scandium species [ScMe₂(Me₃-TACN)(μ-Me)B(C₆F₅)₃] (**180**) and [ScMe₂(Me₃-TACN)(THF)_x]⁺[B(C₆F₅)₄]⁻ (**181**), which catalyzed the polymerization of ethylene.⁹⁶ The tris(trimethylsilylmethyl) derivative [Sc(CH₂SiMe₃)₃(Me₃-TACN)] showed a significantly enhanced activity (220–240 vs 30 kg mol⁻¹ h⁻¹ bar⁻¹)

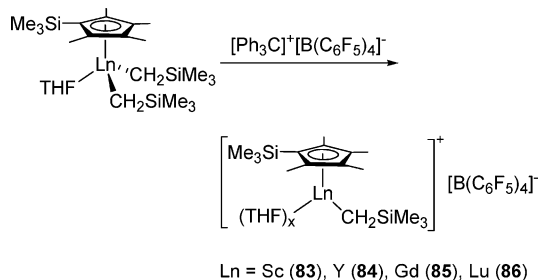
upon activation with $B(C_6F_5)_3/Al^iBu_3$.¹³² Under identical conditions, $[Sc(CH_2SiMe_3)_3(Me_2-pz)]$ produced polyethylene at a slightly higher activity ($290 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$), whereas the 1,4,7-trithiacyclononane derivative $[Sc(CH_2SiMe_3)_3\text{-}(TTCN)]$ ($TTCN = 1,4,7\text{-trithiacyclononane}$) was found to be less active ($110 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$).^{132,134}

The scandium methyl cations that contain a β -diketiminato ligand $[(Sc\{\eta^3\text{-ArNC}(\text{t}Bu)\text{CHC}(\text{t}Bu)\text{NAr}\}Me)_2(\mu\text{-Me})]^+ [B(C_6F_5)_3Me]^-$ ($Ar = C_6H_3^iPr_2\text{-}2,6$, **118**), as well as the dicationic contact ion triple $[Sc\{\eta^3\text{-ArNC}(\text{t}Bu)\text{CHC}(\text{t}Bu)\text{NAr}\}\{(\mu\text{-Me})B(C_6F_5)_3\}_2]$ (**120**), were effective in homogeneous ethylene polymerization but somewhat lower in activity when the dichloride $[Sc\{\eta^3\text{-ArNC}(\text{t}Bu)\text{CHC}(\text{t}Bu)\text{NAr}\}Cl_2]$ ($Ar = C_6H_3^iPr_2\text{-}2,6$) was activated by methylaluminumoxane (MAO).¹⁰⁷ The contact ion pair $[Sc(\eta^5\text{-}C_5Me_5)Me(\text{t}Bu_3P=O)(\mu\text{-Me})B(C_6F_5)_3]$ (**82**), generated in situ in toluene from the parent dialkyl and $B(C_6F_5)_3$, catalyzed ethylene polymerization at $130 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$.⁸⁷

Toluene solutions of the rare-earth metal tris(alkyl) complexes $[Ln(CH_2SiMe_3)_3(THF)_2]$ efficiently catalyzed ethylene polymerization upon activation with at least 2 equiv of $[Ph_3C^+][B(C_6F_5)_4]^-$ in the presence of Al^iBu_3 .^{135,158} Linear polyethylenes with molecular weights $M_n = 3500\text{--}45000 \text{ g mol}^{-1}$ and polydispersities $M_w/M_n = 2\text{--}6$ were produced after short run times (10 min) at 25°C under 5 bar of ethylene. The activity correlated well with the effective ionic radius¹⁴ of the rare-earth metal.¹⁵⁹ No significant activity was observed for tris(alkyl) complexes of the smaller elements scandium, lutetium, and ytterbium; the highest activity ($899 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$) was found for terbium, the largest metal examined. An alkyl dication $[Ln(CH_2SiMe_3)(\text{solvent})_2]^{2+}$, formed via the bis(alkyl) monocation $[Ln(CH_2SiMe_3)_2(\text{solvent})_y]^+$, is thought to be the active species in these reactions, since the polymerization required at least a 2-fold excess of $[Ph_3C^+][B(C_6F_5)_4]^-$. The isolated monocation $[Y(CH_2SiMe_3)_2(THF)_4]^+[Al(CH_2SiMe_3)_4]^-$ (**189**), while not active by itself, can be activated by addition of another equivalent of $[Ph_3C^+][B(C_6F_5)_4]^-$ to exhibit ethylene polymerization with an activity similar to that obtained with the mixture $[Y(CH_2SiMe_3)_3(THF)_2]/[Ph_3C^+][B(C_6F_5)_4]^-/[Al(CH_2SiMe_3)_3]$.

Synthesis of Copolymers Incorporating Ethylene. The scandium half-sandwich bis(alkyl) complex $[Sc(\eta^5\text{-}C_5Me_4\text{-}SiMe_3)(CH_2SiMe_3)_2(THF)]$ can be converted into the cationic species $[Sc(\eta^5\text{-}C_5Me_4SiMe_3)(CH_2SiMe_3)(THF)_x]^+[B(C_6F_5)_4]^-$ (**83**) upon treatment with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (Scheme 35).⁸⁹

Scheme 35



When generated in situ in toluene at room temperature, **83** catalyzed the copolymerization of styrene with ethylene to give a polymer with syndiotactic styrene sequences connected by repeated ethylene units. Copolymers with narrow molecular weight distributions ($M_w/M_n = 1.14\text{--}1.26$) and a styrene content up to 87 mol % were isolated. The same catalyst

could also be used for the alternating copolymerization of ethylene with dicyclopentadiene and the terpolymerization of ethylene, dicyclopentadiene, and styrene.⁹¹ The in situ generated cationic scandium alkyl species $[Sc(\eta^5\text{-}Cp')(CH_2SiMe_3)(THF)_x]^+[B(C_6F_5)_4]^-$ ($Cp' = C_5Me_4(SiMe_3)$ (**83**), $Cp' = C_5H_3(SiMe_3)_2\text{-}1,3$ (**87**), $Cp' = C_5Me_5$ (**88**)) catalyzed the alternating copolymerization of ethylene and norbornene.⁹⁰ In these systems, the successive insertion of the cyclic olefin is sluggish in comparison with a very fast insertion of the cyclic olefin into a $Sc\text{-}CH_2CH_2R$ bond; the latter process is preferred over successive ethylene insertion.

The half-sandwich complex $[Sc\{\eta^5\text{-}\eta^1\text{-}C_5Me_4(CH_2CH_2NMe_2)\}Cl_2]$ and the amido-functionalized triazacyclononane derivative $[Y(\eta^3\text{-}\eta^1\text{-}N,N'\text{-}Me_2\text{-}TACN\text{-}N''\text{-}SiMe_2N^iBu)(CH_2SiMe_3)_2]$ catalyze the copolymerization of ethylene with 1-hexene upon activation with MAO.^{82,99}

α -Olefin Polymerization. Bercaw et al. were the first to show that α -olefin polymerization can be catalyzed by cationic rare-earth metal alkyl derivatives. They demonstrated that the activation of the scandium complex $[ScMe_3(Me_3TACN)]$ with $B(C_6F_5)_3$ or $[Ph_3C^+][B(C_6F_5)_4]^-$ gives 1-pentene oligomerization ($M_n = 2800 \text{ g mol}^{-1}$, $M_w/M_n = 1.3$).⁹⁶

In situ generation of $[Sc(CH_2SiMe_3)_2(TTCN)]^+[B(C_6F_5)_4]^-$ (**187**, $TTCN = 1,4,7\text{-trithiacyclononane}$) followed by addition of 1-hexene led to the slow formation of poly(1-hexene) (ca. 30% conversion after 15 min), whereas the experiment with the mono(alkyl) dication $[Sc(CH_2SiMe_3)(TTCN)]^{2+}[B(C_6F_5)_4]^{2-}$ (**211**) was highly exothermic, rapidly forming atactic poly(1-hexene) with 90% conversion after 2.5 min even at -30°C (activity $3660 \text{ kg of poly(1-hexene) mol}^{-1} \text{ h}^{-1}$).¹³⁴

The in situ generated scandium cations $[Sc(CH_2SiMe_3)_2(\text{Pr-trisox})]^+[B(C_6F_5)_4]^-$ (**186**) and $[Sc(CH_2SiMe_3)(\text{Pr-trisox})]^{2+}[B(C_6F_5)_4]^{2-}$ (**210**, $\text{Pr-trisox} = 1,1,1\text{-tri}\{2\text{-}[4\text{-}(S)\text{-isopropyl-oxazolyl}]\}$ ethane) were used for 1-hexene polymerization catalysis.¹³³ The activity of $36\,200 \text{ kg mol}^{-1} \text{ h}^{-1}$ at 21°C observed for the dication was greater by 3 orders of magnitude than that of the monocation. Unlike the atactic polymers obtained with the TTCN complexes,¹³⁴ the poly(1-hexenes) produced by this chiral dicationic scandium species at -30°C were highly isotactic ($m\text{mmm} > 90\%$) and exhibited narrow monomodal molecular weight distribution ($M_w = 750\,000$, $M_w/M_n = 1.18$).

9.1.2. Styrene

The heterobimetallic complex $[Sm(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}Me_2)\text{-}AlMe_2]$ catalyzed styrene polymerization with low activity (16% conversion after 24 h at 50°C , $M_n = 7900$, $M_w/M_n = 1.54$) upon activation with $[Ph_3C]^+[B(C_6F_5)_4]^-$ in the presence of Al^iBu_3 .⁷³ The same system was also used for the block and random copolymerization of butadiene and styrene with *cis*-1,4-polybutadiene microstructure. The active species in this system was proposed to be an alkyl-bridged $Sm(III)\text{-}Al(III)$ heterometallic cation.¹²

When generated in situ, the mono(cyclopentadienyl) derivatives $[Ln(\eta^5\text{-}C_5Me_4SiMe_3)(CH_2SiMe_3)(THF)_x]^+[B(C_6F_5)_4]^-$ ($Ln = Sc$ (**83**), Y (**84**), Gd (**85**), Lu (**86**)) were active for the syndiospecific polymerization of styrene.⁸⁹ The scandium complex showed the highest activity ($1.36 \times 10^4 \text{ kg mol}^{-1} \text{ h}^{-1}$, $M_w/M_n = 1.29\text{--}1.55$).

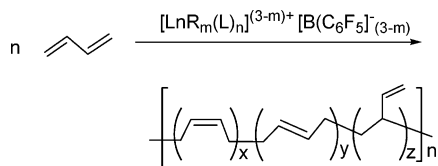
The scandium complex $[Sc(CH_2SiMe_3)_3(TTCN)]$, when activated by 2 equiv of $[Ph_3C]^+[B(C_6F_5)_4]^-$, is very active toward styrene polymerization (100% conversion after 1 min,

$1.36 \times 10^4 \text{ kg mol}^{-1} \text{ h}^{-1}$). The dicationic complex $[\text{Sc}(\text{CH}_2\text{SiMe}_3)(\text{TTCN})]^{2+}[\text{B}(\text{C}_6\text{F}_5)_4]^{-2}$ (**211**) was proposed to be the active species.¹³⁴

9.1.3. 1,3-Dienes

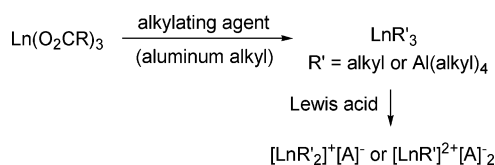
Some Ziegler-type catalysts, consisting of a transition metal or neodymium carboxylate, a Lewis acid, or an alkylating reagent, efficiently catalyze 1,3-butadiene polymerization with high *cis*-1,4-selectivity (Scheme 36).^{160,161} The

Scheme 36



complicated composition of these multicomponent catalysts has so far hampered a comprehensive elucidation of the polymerization mechanism, although recent work has shown that rare-earth metal alkyl species are involved in this catalysis (Scheme 37).¹⁶¹ There is also considerable evidence

Scheme 37



for the involvement of cationic rare-earth metal species in this catalysis, as detailed below.^{162–164} Rare-earth organo-metallic catalyst precursors for 1,3-diene polymerization are collated in Table 16.

The reaction of the neodymium tris(allyl) complex $[\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_3(\text{THF})_2]$ with $[\text{NMe}_3\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in the absence of any aluminum alkyls to give the initiator $[\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_2(\text{THF})_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**150**) indicates that cationic allyl derivatives play an important role in the activation step of homogeneous 1,3-diene polymerization.¹⁶² Moreover, the formation of a dicationic mono(allyl) lanthanoid complex as the active species responsible for the high *cis*-1,4-selectivity was proposed in this context.¹¹⁶

The activation of the cationic bis(pentamethylcyclopentadienyl) complexes $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-C}_6\text{F}_5)_2\text{B}(\text{C}_6\text{F}_5)_2]_2$ ($\text{Ln} = \text{Pr}$ (**57**), Nd (**58**), Gd (**59**), Ce (**60**), Sm (**61**)) with Al^iBu_3 afforded highly *cis*-1,4-selective initiators for 1,3-butadiene polymerization, further supporting the involvement of a cationic active species.^{76,77,165–167}

Alternatively, $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2\text{Me}(\text{THF})_2]$, $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-Me})_2\text{AlMe}_2]_2$ ($\text{Ln} = \text{Gd}, \text{Sm}, \text{Pr}$), or $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})_2]$ were used as catalyst precursors to yield *cis*-1,4-polybutadiene upon activation with either MMAO or $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-/\text{Al}^i\text{Bu}_3$.^{72,73,75} Furthermore, $[\text{Gd}(\eta^5\text{-C}_5\text{Me}_4\text{Pr})_2(\mu\text{-Me})_2\text{AlMe}_2]_2$ catalyzed the *cis*-1,4-specific polymerization of isoprene and allowed for butadiene–isoprene copolymerization.¹⁶⁴ The active species in these systems is probably an alkyl-bridged $\text{Ln}(\text{III})\text{–Al}(\text{III})$ heterometallic cation.¹²

The in situ generated cationic yttrium methyl complexes $[\text{YMe}_2(\text{solv})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**200**) and $[\text{YMe}(\text{solv})_x]^{2+}[\text{B}(\text{C}_6\text{F}_5)_4]^{-2}$ (**215**) are also active in 1,3-diene polymerization.¹³¹ The monocationic compound **200** yielded 100% polybutadiene after 14 h with 90% *cis* selectivity in the presence of Al^iBu_3 , whereas the dicationic compound **215** afforded 97% *cis* selectivity under the same conditions. An insertion mechanism was proposed by comparison of the molecular weights ($M_n = 50 \times 10^3 \text{ g mol}^{-1}$ for **200**, $100 \times 10^3 \text{ g mol}^{-1}$ for **215**) and the assumption that depending on the experimental conditions the active species is either a dication with one growing chain or a monocation with two. Isoprene was also polymerized by **200** and **215**. Here, the presence of Al^iBu_3 increased the *cis* selectivity; the polymers obtained again showed different microstructures depending on the cationic catalyst system used.

The in situ generated complexes $[(\text{Ln}(\eta^5\text{-}\eta^1\text{-}\mu\text{-C}_5\text{Me}_4\text{SiMe}_2\text{-PCy})_2(\mu\text{-CH}_2\text{SiMe}_3))^+[\text{B}(\text{C}_6\text{F}_5)_3\text{R}]^-$ ($\text{Cy} = \text{cyclohexyl}$, $\text{R} = \text{C}_6\text{F}_5$, $\text{Ln} = \text{Y}$ (**76**), Lu (**77**); $\text{R} = \text{CH}_2\text{SiMe}_3$, $\text{Ln} = \text{Y}$ (**78**)) showed unprecedented isospecific 3,4-polymerization of isoprene with extremely high stereo- and regioselectivity (3,4-selectivity 100%; *mmmm* > 99%).⁸⁴ This new, crystalline polymer has a melting temperature at 162 °C. A cationic dinuclear complex with a bridging alkyl group was proposed to be the active species.

9.1.4. Isobutylene

The yttrocenium cations $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2(\mu\text{-Me})(\mu\text{-C}_6\text{F}_5)\text{B}(\text{C}_6\text{F}_5)_2]^+$ (**53**) and $[\text{Y}(\eta^5\text{-C}_5\text{Me}_4\text{SiMe}_3)_2]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**56**) are initiators for the carbocationic polymerization of isobutylene.⁷¹ The yields of polymer and their molecular weights were rather higher than those obtained with the comparable group 4 metal system $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)\text{Me}_3]/\text{B}(\text{C}_6\text{F}_5)_3$.¹⁶⁸

9.2. Catalysis of Organic Transformations

In a manner similar to homogeneous olefin polymerization catalysis, the activity of rare-earth metal catalyzed organic

Table 16. 1,3-Butadiene Polymerization with Cationic Organolanthanoid Precursors

| precursor | activator | <i>T</i> (°C) | <i>t</i> (min) | yield (%) | selectivity <i>cis/trans</i> /1,2 | <i>M_n</i> ($\times 10^3 \text{ g mol}^{-1}$) | <i>M_w/M_n</i> | ref |
|---|------------------------------------|------------------|-------------------|--------------|--------------------------------------|--|------------------------------------|-----|
| $[\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_2(\text{THF})_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (150) | Al^iBu_3 | 20 | 60 | 59 | 57:41:2 | <i>a</i> | <i>a</i> | 162 |
| $[\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_3(\text{dioxane})]$ | $\text{B}(\text{C}_6\text{F}_5)_3$ | 20 | 20 | 43 | 97:1:2 | <i>a</i> | <i>a</i> | 162 |
| $[\text{Nd}(\eta^3\text{-C}_3\text{H}_5)_2(\text{dioxane})_4]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (152) | | 50 | 35 | 40 | 92:7:1 | 254 | 1.6 | 116 |
| $[\text{Pr}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-C}_6\text{F}_5)_2\text{B}(\text{C}_6\text{F}_5)_2]_2$ (57) | Al^iBu_3 | 50 | 300 | 95 | 90:7:3 | 80 | 1.7 | 76 |
| $[\text{Nd}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-C}_6\text{F}_5)_2\text{B}(\text{C}_6\text{F}_5)_2]_2$ (58) | Al^iBu_3 | 50 | 25 | 96 | 91:6:3 | 130 | 1.4 | 76 |
| $[\text{Sm}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-C}_6\text{F}_5)_2\text{B}(\text{C}_6\text{F}_5)_2]_2$ (61) | Al^iBu_3 | 50 | 5 | 80 | 96% <i>cis</i> ^b | 130 | 1.7 | 77 |
| $[\text{Gd}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-C}_6\text{F}_5)_2\text{B}(\text{C}_6\text{F}_5)_2]_2$ (59) | Al^iBu_3 | 50 | 3 | 100 | 98:1:1 | 250 | 1.7 | 76 |
| $[\text{YMe}_2(\text{THF})_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (200) | Al^iBu_3 | 20 | 840 | 100 | 90:8:2 | 50 | 2.6 | 131 |
| $[\text{YMe}(\text{THF})_x]^{2+}[\text{B}(\text{C}_6\text{F}_5)_4]^{-2}$ (215) | Al^iBu_3 | 20 | 840 | 100 | 97:2:1 | 100 | 2.1 | 131 |
| $[\text{YMe}(\text{THF})_x]^{2+}[\text{B}(\text{C}_6\text{F}_5)_4]^{-2}$ (215) | Al^iBu_3 | 20 | 30 | 18 | 95:3:2 | 61 | 1.7 | 131 |

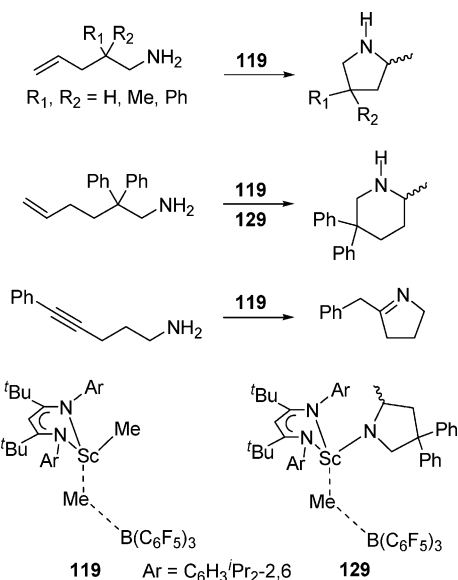
^a Not available. ^b Details of the microstructure not available.

transformations may be enhanced by the use of cationic derivatives. The number of examples remains limited so far.

9.2.1. Intramolecular Hydroamination

The contact ion pair $[\text{ScMe}\{\eta^3\text{-ArNC}(\text{tBu})\text{CHC}(\text{tBu})\text{NAr}\}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3]$ (**119**) catalyzed the intramolecular hydroamination/cyclization of α,ω -aminoalkenes to give pyrrolidine and piperidine products (Scheme 38).¹⁰⁸ The neutral

Scheme 38



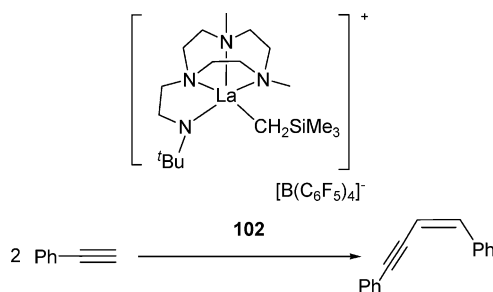
dimethyl complex $[\text{Sc}\{\eta^3\text{-ArNC}(\text{tBu})\text{CHC}(\text{tBu})\text{NAr}\}\text{Me}_2]$ ($\text{Ar} = \text{C}_6\text{H}_3^i\text{Pr}_{2-2,6}$) is less efficient by several orders of magnitude. Since the stoichiometric reaction of the cationic scandium complex with an α,ω -aminoalkene gives the cationic pyrrolidinato complex $[\text{Sc}\{\eta^3\text{-ArNC}(\text{tBu})\text{CHC}(\text{tBu})\text{NAr}\}(\text{NCH}_2\text{CPh}_2\text{CH}_2\text{CHMe})^+[\text{B}(\text{C}_6\text{F}_5)_3\text{Me}]^-$ (**129**), as characterized by NMR spectroscopy, the catalytically active species appears to be an amido cation.

Recently, the catalytic activity of the in situ generated cationic complexes $[\text{Y}\{\eta^3\text{-}N,N',N''\text{-R}_2\text{-TACN-}N''\text{-(CH}_2)_2\text{N}^i\text{Bu}\}(\text{CH}_2\text{SiMe}_3)(\text{THF-}d_8)_n]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (TACN = 1,4,7-triazacyclononane, $\text{R} = \text{Me}$, $n = 0$ (**93**); $\text{R} = ^i\text{Pr}$, $n = 1$ (**94**)), $[\text{Y}\{\{\text{Me}_2\text{N}(\text{CH}_2)_2\}_2\text{N}(\text{CH}_2)_2\text{N}^i\text{Bu}\}(\text{CH}_2\text{SiMe}_3)(\text{THF-}d_8)_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**108**), and $[\text{Ln}\{\eta^3\text{-PhC}(\text{NAr})_2\}(\text{CH}_2\text{SiMe}_3)(\text{THF-}d_8)_x]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ ($\text{Ar} = \text{C}_6\text{H}_3^i\text{Pr}_{2-2,6}$, $\text{Ln} = \text{Y}$ (**136**); $\text{Ln} = \text{Sc}$ (**143**)) in the intramolecular hydroamination/cyclization of 2,2-dimethyl-4-pentenylamine was compared with that of the parent neutral bis(alkyl) compounds.¹⁶⁹ Whereas the cationic complexes **93**, **94**, and **108** with triamine-amide ligands are more active than the neutral species, the amidinate complexes **136** and **143** show a much lower activity compared to the respective neutral complexes, thus showing a strong dependency on the nature of the monoanionic ancillary ligand.

9.2.2. Alkyne Dimerization

The lanthanum alkyl cation $[\text{La}\{\eta^3\text{-}N,N',N''\text{-Me}_2\text{-TACN-}N''\text{-(CH}_2)_2\text{N}^i\text{Bu}\}(\text{CH}_2\text{SiMe}_3)]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**102**), generated in situ from the neutral bis(alkyl) complex $[\text{La}\{\eta^3\text{-}N,N',N''\text{-Me}_2\text{-TACN-}N''\text{-(CH}_2)_2\text{N}^i\text{Bu}\}(\text{CH}_2\text{SiMe}_3)_2]$ and $[\text{PhNM}_2\text{H}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ in phenylbenzene, efficiently catalyzed the dimerization of phenylacetylene to give the linear head-to-head *cis*-enyne (Scheme 39) with high regio- and stereo-

Scheme 39

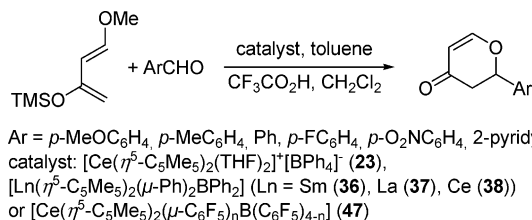


selectivity (99% *cis* content; TOF > 100 h⁻¹).¹⁰⁰ An alkynyl cation $[\text{La}\{\eta^3\text{-}N,N',N''\text{-Me}_2\text{-TACN-}N''\text{-(CH}_2)_2\text{N}^i\text{Bu}\}(\text{C}\equiv\text{CPh})]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$, which may be a dimer, was proposed to be the active species. An insoluble oily compound was obtained upon reaction of **102** with 1 equiv of phenylacetylene or upon treating the dinuclear dialkynyl complex $[\text{La}\{\eta^3\text{-}N,N',N''\text{-Me}_2\text{-TACN-}N''\text{-(CH}_2)_2\text{N}^i\text{Bu}\}(\text{C}\equiv\text{CPh})(\mu\text{-C}\equiv\text{CPh})_2]$ with $[\text{PhNM}_2\text{H}]^+[\text{BPh}_4]^-$. A similar catalysis was previously reported using the neutral rare-earth metal complexes with a linked amido-cyclopentadienyl ligand such as $[\text{Lu}(\eta^5\text{-}C_5\text{Me}_4\text{SiMe}_2\text{NPh})(\text{CH}_2\text{SiMe}_3)(\text{THF})_2]$.¹⁷⁰ A dinuclear bis(μ -alkynyl) active species was suggested in this case.

9.2.3. Hetero-Diels–Alder Reactions

The cationic bis(pentamethylcyclopentadienyl) rare-earth metal derivatives $[\text{Ce}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})_2]^+[\text{BPh}_4]^-$ (**23**), $[\text{Ln}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-Ph})_2\text{BPh}_2]$ ($\text{Ln} = \text{Sm}$ (**36**), La (**37**), Ce (**38**)), and $[\text{Ce}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-C}_6\text{F}_5)_n\text{B}(\text{C}_6\text{F}_5)_{4-n}]$ (**47**) catalyzed the hetero-Diels–Alder reaction between Danishefsky's diene and substituted benzaldehydes (Scheme 40).⁶⁹ The isolated

Scheme 40



yield of the dihydropyranone depended on the anion ($[\text{BPh}_4]^-$ (**38**) 93%; $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (**47**) 15%), whereas the choice of the rare-earth metal (La (**37**) or Ce (**38**)) did not unambiguously affect the performance of the catalyst. Interestingly, the THF adduct $[\text{Ce}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})_2]^+[\text{BPh}_4]^-$ (**23**) gave similar results to the unsolvated derivative **38**.

9.3. Reduction of Dinitrogen

The first example of a lanthanum dinitrogen complex was obtained when the contact ion pair $[\text{La}(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-Ph})_2\text{BPh}_2]$ (**37**) was reacted under dinitrogen with potassium graphite in THF to produce red-orange crystals of $[\{\text{La}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)\}]$.¹⁷¹ The N–N separation of 1.233(5) Å in $[\{\text{La}(\eta^5\text{-C}_5\text{Me}_5)_2(\text{THF})_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-N}_2)\}]$ was consistent with the reduction of dinitrogen to $[\text{N}=\text{N}]^{2-}$. The high yield for this reaction was mainly ascribed to the formation of the insoluble byproduct KBPh_4 , which (unlike alternative byproducts such as $\text{KN}(\text{SiMe}_3)_2$ for the $[\text{Ln}\{\text{N}(\text{SiMe}_3)_2\}_3/\text{KC}_8/\text{N}_2\text{-systems}]$) did not interact with either the starting material or the dinitrogen reduction product that may be formed initially.

9.4. Synthesis of Unsolvated Neutral Complexes

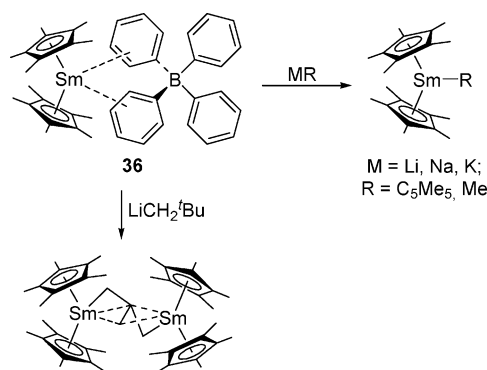
9.4.1. Tris(pentamethylcyclopentadienyl) Complexes [Ln(η^5 -C₅Me₅R)₃]

The reaction of [Ln(η^5 -C₅Me₅)₂(μ -Ph)₂BPh₂] with K(C₅Me₅) in the absence of THF allowed for a general synthesis of [Ln(η^5 -C₅Me₅)₃] complexes that applies for all rare-earth metals.⁵⁷ In an analogous manner, the reaction of [Lu(η^5 -C₅Me₄H)₂(μ -Ph)₂BPh₂] (**46**) with 1 equiv of K(C₅Me₄H) yielded [Lu(η^5 -C₅Me₄H)₃].⁶⁷ The absence of THF is crucial, since [Sm(η^5 -C₅Me₅)₂(THF)₂]⁺[BPh₄]⁻ (**22**) reacted with K(C₅Me₅) to give the neutral alkoxide [Sm(η^5 -C₅Me₅)₂-{O(CH₂)₄C₅Me₅}(THF)] formed by the ring opening of THF.^{56,172,173} For [Ln(η^5 -C₅Me₅)₂(μ -Ph)₂BPh₂] (Ln = Ce (**38**), Pr (**39**)), silylated glassware was required to prevent the formation of the oxides [{Ln(η^5 -C₅Me₅)₂(μ -O)].⁶⁶ [Ln(η^5 -C₅Me₅)₃] (Ln = Ce, Pr) react with AgBPh₄ via “sterically induced reduction” to give **38** and **39**, half an equivalent of (C₅Me₅)₂, and Ag. These tris(pentamethylcyclopentadienyl) complexes also react with [NEt₃H]⁺[BPh₄]⁻ via protonolysis to yield **38** and **39**, C₅Me₅H, and NEt₃.

9.4.2. Unsolvated Metallocenium Complexes [Ln(η^5 -C₅Me₅)₂]_nR

The unsolvated species [Ln(η^5 -C₅Me₅)₂(μ -Ph)₂BPh₂] reacted with alkyl potassium or lithium reagents to give unsolvated alkyl bis(pentamethylcyclopentadienyl) complexes of the rare-earth metals (Scheme 41).⁶⁴ This route

Scheme 41



allows for the synthesis of methyl, benzyl, trimethylsilylmethyl, and phenyl derivatives. Alternatively, benzyl, trimethylsilylmethyl, and phenyl derivatives could be prepared from highly reactive [Sm(η^5 -C₅Me₅)₂Me]₃ by C–H bond activation of toluene, tetramethylsilane, or benzene. The synthesis of these unsolvated complexes has not been reported by more conventional synthetic routes.

Reaction of [Sm(η^5 -C₅Me₅)₂(μ -Ph)₂BPh₂] (**36**) with LiCH₂^ᵀBu in methylcyclohexane afforded the trimethylenemethane complex [Ln(η^5 -C₅Me₅)₂]₂{ μ - η^3 : η^3 -C(CH₂)₃}] instead of the expected neopentyl complex [Sm(η^5 -C₅Me₅)₂(CH₂^ᵀBu)]_x (Scheme 41).⁶⁷ This rare example of lanthanoid-based β -methyl elimination most likely proceeds from sequential reactions involving β -methyl elimination and isobutene formation from [Sm(η^5 -C₅Me₅)₂(CH₂^ᵀBu)]_x followed by subsequent C–H activation of the isobutene to give a 2-methyl complex, which can be metalated again to generate the final trimethylenemethane ligand. This mechanism was supported by deuterium labeling studies, which also suggest an additional C–H activation pathway.

10. Conclusion

As a consequence of interest in homogeneous olefin polymerization catalysis based on group 4 metal catalysts, cationic organometallic complexes of the rare-earth metals have attracted increasing attention since the 1990s. With the realization that Lewis basic solvents and weakly coordinating anions lead to the formation of isolable alkyl cations, the development of the chemistry of cationic complexes was triggered, fueled by the expectation that cationic species would be generally more electrophilic and thus more active homogeneous catalysts.

Various classes of neutral and monoanionic ligands have been employed to stabilize these cations. The large size of the rare-earth metals has necessitated in most cases imaginative use of not only highly Lewis basic solvents such as THF but also macrocycles to allow these complexes to be isolated. Recent work has demonstrated that the counteranion itself sometimes provides sufficient stabilization by weak coordination to the metal center in the absence of Lewis bases. The evolution of other appropriate ligands to saturate the large coordination sphere of the rare-earth metals and to stabilize cationic organolanthanoid complexes remains a key issue in this developing field of chemistry.

The majority of cationic rare-earth organometallic complexes have been synthesized by the reaction of neutral hydrocarbyl complexes with Brønsted or Lewis acids in appropriate solvents. The reactivity of cationic organolanthanoid complexes in catalytic and stoichiometric reactions has often led to improved activity with respect to their neutral analogues and in some cases allowed the development of completely new synthetic pathways.

As found for the organometallic chemistry of the electropositive s-block metals and group 13 elements,¹⁷⁴ the development of cationic complexes of the rare-earth metals has clearly added a new dimension to the chemistry of the group 3 and f-block elements. Further analogy to the extensively studied cationic organotransition metal complexes may help accelerate the bridging of the gap between s-, f-, and d-block chemistry in the near future.

11. Glossary

| | |
|---------------------|-------------------------------------|
| Bu | butyl |
| ⁱ Bu | isobutyl |
| ⁿ Bu | <i>n</i> -butyl |
| ^s Bu | secondary butyl |
| ^t Bu | tertiary butyl |
| CE | crown ether |
| Cn | ring centroid |
| CN | coordination number |
| Cp | cyclopentadienyl |
| Cy | cyclohexyl |
| DME | 1,2-dimethoxyethane |
| EA | elemental analysis |
| equiv | equivalent(s) |
| Et | ethyl |
| Et ₂ O | diethyl ether |
| HMPA | hexamethylphosphoramide |
| IR | infrared (spectroscopy) |
| <i>J</i> | coupling constant |
| Ln | rare-earth metal (Sc, Y, La; Ce–Lu) |
| M | metal |
| MAC | deprotonated aza-18-crown-6 |
| MAO | methylaluminoxane |
| Me | methyl |
| Me ₂ -pz | tris(3,5-dimethylpyrazolyl)methane |

| | |
|------------------------|---|
| Me ₃ -TACN | 1,4,7-trimethyl-1,4,7-triazacyclononane |
| MMA | methyl methacrylate |
| MMAO | modified methylaluminoxane containing isobutylaluminumoxane |
| M _n | number-average molecular weight |
| M _w | weight-average molecular weight |
| MeCN | acetonitrile |
| mp | melting point |
| NMR | nuclear magnetic resonance |
| <i>o</i> | ortho |
| Ph | phenyl |
| PMAO-IP | polymethylaluminoxane |
| ⁱ Pr | isopropyl |
| ⁱ Pr-trisox | 1,1,1-tri[2-[4-(<i>S</i>)-isopropylloxazolyl]]ethane |
| <i>r</i> | effective ionic radius |
| R | alkyl group |
| solv | solvent |
| TACN | 1,4,7-triazacyclononane |
| tetraglyme | tetraethyleneglycoldimethyl ether |
| THF | tetrahydrofuran |
| THT | tetrahydrothiophene |
| TIBAO | triisobutylaluminoxane |
| T _m | melting temperature |
| TOF | turnover frequency |
| TTCN | 1,4,7-trithiacyclononane |

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