Cationic Alkyl Complexes of the Rare-Earth Metals: Synthesis, Structure, and Reactivity

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This contribution is dedicated to Dick Schrock on the occasion of his 60th birthday.

Abstract: Cationic alkyl complexes of the rare-earth metals $[LnR_m(L)_n]^{(3-m)+}$ (R = alkyl; m = 1, 2; L = Lewis base) were virtually unknown species until recently. Because of their increased Lewis acidity/electrophilicity they should have considerable potential as homogeneous catalysts in olefin polymerization and in organic transformations. They can be generated by treating the neutral rare-earth metal precursors containing at least two alkyl groups R with suitable Lewis or Brønsted acids in the presence of weakly coordinating anions. Not only monocationic but also dicationic alkyl derivatives have been shown to be accessible. In the context of modeling homogeneous ethylene polymerization using a mixture consisting of $LnR_3/AlR_3/[NMe_2HPh][B(C_6F_5)_4]$, such dications were discovered. Some thermally robust examples of mono- and dicationic alkyl complexes have been structurally characterized as solvent-separated ion pairs. Neutral and monoanionic macrocycles such as crown ethers or aza-crown ethers as well as amidinato, β-diketiminato, and substituted cyclopentadienyl ligands are suitable ancillary ligands to stabilize the cationic alkyl fragments.

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Keywords: alkyl complexes; cations; homogeneous catalysis; ligand effects; polymerization; rare-earth metals

1 Introduction

Neutral and anionic alkyl complexes of group 3 metals and the lanthanides $[LnR_m(L)_n]^{(m-3)-}$ (R = alkyl; m = 3–6; L = Lewis base) have been known since the early stages in the development of the organometallic chemistry of these elements.[1] However, cationic complexes bearing nucleophilic alkyl groups at an extremely Lewis acidic rare-earth metal center remained elusive. A series of rare-earth cations containing aromatic ligands such as cyclopentadienyl ligands of the type $[Ln(\eta^5\text{-}C_5R_5)_2(L)_x]^+$ (L = Lewis base) has recently become known and their reactivity has been studied in some detail.[2–20] As isoelectronic analogues of the group 4 metallocenium alkyl and hydride cations $[M(\eta^5\text{-}C_5R_5)_2(X)]^+$ neutral rare-earth metallocene alkyls and hydrides $[Ln(\eta^5\text{-}C_5R_5)_2(X)]$ (X = alkyl, H) have been studied for quite some time. They have successfully been utilized as hydrometalation catalysts as well as single component, single-site olefin polymerization catalysts without the necessity of cocatalysts.[21] A similar isoelectronic relationship exists with the 14-electron cationic half-sandwich complex of the type $[Ln(\eta^5\text{-}C_5R_5)(L)_3(X)]^+$, which should also polymerize olefins.[22] Further generalization implies that in princi-

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Stefan Arndt was born 1973 in Teheran, Iran. He received his Diploma in 2000 at the Johannes Gutenberg-Universität Mainz, Germany and his Dr. rer. nat. degree in 2004 at the RWTH Aachen University, Germany; both on neutral and cationic alkyl and hydrido complexes of the rare-earth metals under the supervision of Prof. J. Okuda. In 1997/98 he was a DAAD (German Academic Exchange Service) fellow for 6 months in Professor J. Sunamoto's group at Kyoto University, Japan. In 2001 he spent 4 months as a Marie Curie Fellow in Professor F. G. N. Cloke's Group at the University of Sussex, England. His current research interests include the activation of small molecules, catalysis of organic reactions and polymerization catalysis via well defined, Lewis acidic organometallic complexes.

ple any monoanionic ligand would support alkyl cations of the general formula $[Ln(L_mX)(R)]^+$ (L_mX: monoanionic ligand set). In the context of developing single-site olefin polymerization catalysts, such rare-earth metal alkyl cations with non-metallocene ligand frameworks have recently attracted some attention.[21,23–27] We summarize here the chemistry of cationic complexes of the rare-earth metals that contain hydrocarbyl ligands R other than cyclopentadienyl ligands, in particular in the context of developing efficient homogeneous catalysts.

2 Cationic Alkyl Complexes Containing Neutral Ligands

2.1 Cationic Alkyl Complexes with THF Ligands

2.1.1 Monocationic Alkyl Complexes

In contrast to the sterically encumbered tris(alkyl) complex $[Ln\{CH(SiMe_3)_2\}_3]$,[28–31] the rather easily accessible tris(trimethylsilylmethyl) derivative $[Ln(CH_2SiMe_3)_3(THF)_n]$[32–35] is highly reactive and undergoes alkyl group abstraction/elimination when treated with Lewis acids or Brønsted acids in the strongly Lewis-basic solvent THF. According to Equation (1), the reaction of the yttrium tris(alkyl) complex $[Y(CH_2SiMe_3)_3(THF)_2]$ with $Al(CH_2SiMe_3)_3$ yields the thermally robust ion pair $[Y(CH_2SiMe_3)_2(THF)_4]^+[Al(CH_2SiMe_3)_4]^-$.[36]

$$[Y(CH_2SiMe_3)_3(THF)_2] \xrightarrow[\text{THF}]{Al(CH_2SiMe_3)_3} [Y(CH_2SiMe_3)_2(THF)_4]^+[Al(CH_2SiMe_3)_4]^- \quad (1)$$

Pertinent NMR spectroscopic data for the cation in $[Y(CH_2SiMe_3)_2(THF)_4]^+[Al(CH_2SiMe_3)_4]^-$ are compiled in Table 1 and can be compared with those of the neutral and other cationic yttrium alkyl complexes. Most strikingly, the ^{89}Y NMR chemical shift correlates well with the charge at the yttrium, as chemical shifts of the cationic derivatives are significantly shifted to higher field when compared with those of the neutral complexes. Likewise, in analogy to the crown ether complexes (*vide infra*), the coupling constants $^1J_{Y,C}$ values increase with the charge at the yttrium.

Crystallographic characterization of the cation in $[Y(CH_2SiMe_3)_2(THF)_4]^+$ $[Al(CH_2SiMe_3)_4]^-$ revealed a distorted octahedral coordination geometry around the yttrium center with *cis*-arrangement of the two trimethylsilylmethyl groups (Table 2).[40,41]

When the yttrium tris(alkyl) complex $[Y(CH_2SiMe_3)_3(THF)_2]$ is reacted with an equimolar amount of the Lewis acid BPh_3 in THF-d_8, the formation of an ion pair $[Y(CH_2SiMe_3)_2(THF)_4]^+$ $[BPh_3(CH_2SiMe_3)]^-$ is observed (Scheme 1).[39,41]

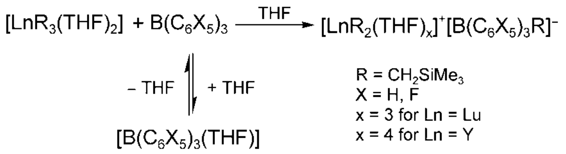
The lutetium complex $[Lu(CH_2SiMe_3)_3(THF)_2]$ reacts with BPh_3 in an analogous manner in THF yielding the ion pair $[Lu(CH_2SiMe_3)_2(THF)_3]^+$ $[BPh_3(CH_2SiMe_3)]^-$. The ^1H NMR spectrum in CD_2Cl_2 indicates

Table 1. NMR spectroscopic data for YCH fragments in yttrium alkyl complexes at 25 °C.

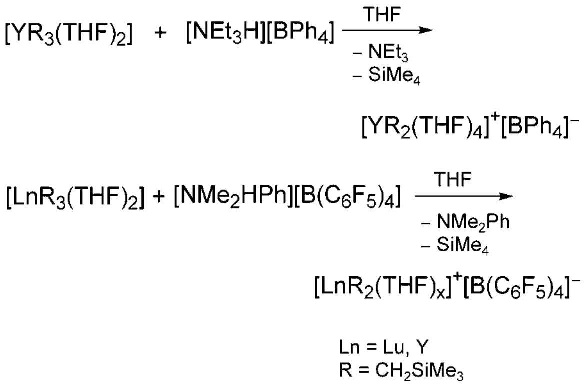
Compound	Solvent	$\delta(^1H)$ [ppm]	$^2J_{Y,H}$ [Hz]	$\delta(^{13}C)$ [ppm]	$^1J_{Y,C}$ [Hz]	$^1J_{C,H}$ [Hz]	$\delta(^{89}Y)$ [ppm]	Refs.
Neutral complexes								
$[Y\{CH(SiMe_3)_2\}_3]$	C_6D_6	–0.62	2.0	55.0	30.4	–	895.0	[29,37,38]
$[Y(CH_2SiMe_3)_3(THF)_2]$	THF-d_8	–0.92	2.9	32.5	35.4	98.4	882.7	[32]
Monocations								
$[Y(CH_2SiMe_3)_2(THF)_4]^+$ $[Al(CH_2SiMe_3)]^-$	THF-d_8	–0.73	3.1	37.2	42.1	–	666.4	[36]
$[Y(CH_2SiMe_3)_2(THF)_4]^+$ $[BPh_3(CH_2SiMe_3)]^-$	THF-d_8	–0.80	3.2	36.7	41.6	–	660.2	[39]
$[Y(CH_2SiMe_3)_2(THF)_x]^+$ $[B(C_6F_5)_3(CH_2SiMe_3)]^-$	THF-d_8	–0.70	2.9	37.3	43.0	–	–	[39]
$[Y(CH_2SiMe_3)_2(THF)_4]^+$ $[BPh_4]^-$	THF-d_8	–0.78	3.3	36.9	41.2	–	660.0	[39]
	pyr-d_5	–0.08	2.3	30.9	36.5	97.2	–	
$[Y(CH_2SiMe_3)_2(THF)_x]^+$ $[B(C_6F_5)_4]^-$	THF-d_8	–0.69	3.2	37.4	41.6	–	–	[39]
$[Y(CH_3)_2(THF)_5]^+$ $[BPh_4]^-$	pyr-d_5	–0.38, 0.11	– 1.2	17.7	39.3	102.5	–	[39]
Dications								
$[Y(CH_2SiMe_3)(THF)_4]^{2+}$ $[BPh_4]^-{}_2$	THF-d_8	–	–	–	–	–	409.2	[36]
	pyr-d_5	0.73	3.3	44.5	44.9	93.8	–	
$[Y(CH_3)(THF)_6]^{2+}$ $[BPh_4]^-{}_2$	pyr-d_5	0.69	2.1	32.8	53.6	105.5	433.2	[36]

Table 2. Yttrium-carbon(alkyl) bond lengths.

Compound	Y–C [Å]	Refs.
$[Y(CH_2SiMe_3)_2(THF)_4]^+$ $[Al(CH_2SiMe_3)_4]^-$	2.384(6), 2.411(6)	[36]
$[Y(L\text{-}3)(CH_2SiMe_3)(THF)_3]^+$ $[BPh_4]^-$	2.363(5)	[42]
$[Y(CH_3)_2(THF)_5]^+$ $[BPh_4]^-$	2.526(2), 2.508(2)	[39]
$[Y(CH_3)(THF)_6]^{2+}$ $[BPh_4]^-{}_2(THF)$	2.418(3)	[36]



Scheme 1.



Scheme 2.

that in accordance with the smaller ionic radius of lutetium as compared with that of yttrium, the cation in $[Lu(CH_2SiMe_3)_2(THF)_3]^+$ $[BPh_3(CH_2SiMe_3)]^-$ contains only three THF ligands (Scheme 1).[39,41]

When the strong Lewis acid $B(C_6F_5)_3$ is used, the ion pairs $[Ln(CH_2SiMe_3)_2(THF)_x]^+$ $[B(C_6F_5)_3(CH_2SiMe_3)]^-$ (Ln = Y, Lu) can be prepared *in situ* and characterized by NMR spectroscopy (Table 1).[39,41] The reaction of the yttrium and lutetium tris(alkyl) complexes $[Ln(CH_2SiMe_3)_3(THF)_2]$ (Ln = Lu, Y) with $B(C_6F_5)_3$ in THF-d_8 requires forcing conditions (several hours at 40–50 °C).[43–45] This decrease in reactivity compared with that when using BPh_3 may be explained by the formation of inert THF adducts $[B(C_6F_5)_3(THF)]$, as indicated in Scheme 1.[46] The ^{19}F NMR spectra of $[Ln(CH_2SiMe_3)_2(THF)_x]^+$ $[B(C_6F_5)_3(CH_2SiMe_3)]^-$ exhibit *meta*/*para* chemical shift differences $\Delta\delta$ of 2.2 ppm for the anion part, consistent with the presence of solvent-separated ion pairs.[47,48]

According to Scheme 2, the yttrium tris(alkyl) $[Y(CH_2SiMe_3)_3(THF)_2]$ undergoes protonolysis with an equimolar amount of the Brønsted acid $[NEt_3H]$ $[BPh_4]$ in THF to give the ion pair $[Y(CH_2SiMe_3)_2(THF)_4]^+$ $[BPh_4]^-$, isolable as thermally fairly robust, colorless microcrystals.[36]

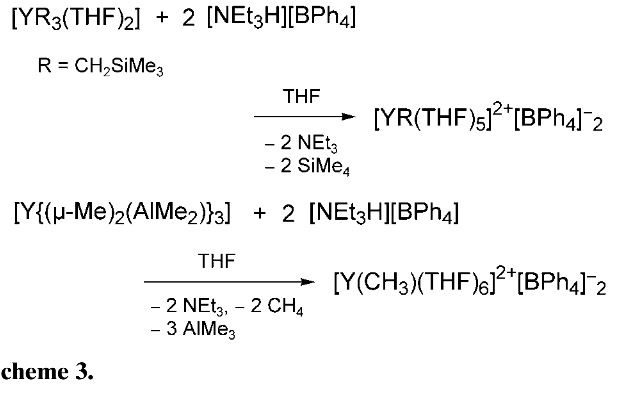
The ^{1}H, ^{13}C and ^{89}Y NMR spectroscopic data for the cation in $[Y(CH_2SiMe_3)_2(THF)_4]^+$ $[BPh_4]^-$ agree with the presence of solvent-separated ions in solution (Table 1). The coupling constant $^1J_{C,H}$ of 97.2 Hz is similar to that found for the neutral tris(alkyl) complex ($^1J_{C,H} = 98.4$ Hz) and does not appear to indicate an α-agostic interaction.[49–52]

Analogous yttrium and lutetium complexes containing the anion $[B(C_6F_5)_4]^-$ can be generated and observed by NMR spectroscopy. As shown in Scheme 2, equimolar amounts of tris(alkyl) complexes $[Ln(CH_2SiMe_3)_3(THF)_2]$ and the $[NMe_2HPh]$ $[B(C_6F_5)_4]$ undergo reaction in THF-d_8 to form $[Ln(CH_2SiMe_3)_2(THF)_x]^+$ $[B(C_6F_5)_4]^-$ (Ln = Lu, Y). Their isolation as pure compounds is not possible due to the concomitant formation of poly(THF) which is difficult to separate.[39]

2.1.2 Dicationic Alkyl Complexes

Treatment of a THF solution of the yttrium tris(alkyl) complex $[Y(CH_2SiMe_3)_3(THF)_2]$ with two equivalents of the ammonium tetraphenylborate $[NEt_3H]$ $[BPh_4]$ or $[NMe_2HPh]$ $[BPh_4]$ results in the clean formation of the dicationic alkyl complex $[Y(CH_2SiMe_3)(THF)_5]^{2+}$ $[BPh_4]^-_2$ as thermally robust colorless microcrystals.[36,39] The residual alkyl group is resistant to Brønsted acids.[53–56] Even in the presence of a third equivalent of $[NMe_2HPh]$ $[BPh_4]$, the ion triple $[Y(CH_2SiMe_3)(THF)_5]^{2+}$ $[BPh_4]^-_2$ can be isolated after 24 h at 25 °C as the only yttrium-containing species in virtually quantitative yield.[36] As shown in Table 1, the ^{89}Y NMR resonance at 409.2 ppm for $[Y(CH_2SiMe_3)(THF)_5]^{2+}$ $[BPh_4]^-_2$ in THF-d_8 is shifted to a significantly higher field compared with that for the corresponding monocations or the neutral precursor.

When the tris(aluminate) $[Y\{(\mu\text{-}Me)_2(AlMe_2)\}_3]$[57] is treated with two equivalents of $[NEt_3H]$ $[BPh_4]$ in THF, the ion triple $[Y(CH_3)(THF)_6]^{2+}$ $[BPh_4]^-_2$ containing the methyl dication is obtained as thermally robust colorless crystals (Scheme 3). Crystal structure analysis revealed that the methyl dication exhibits a pentagonal bipyramidal coordination geometry around the yttrium center with the methyl group in the apical position. The yttrium-carbon distance of 2.418(3) Å does not appear to be elongated. Although the ^{1}H and ^{13}C NMR spectroscopic data do not indicate any agostic interaction, the high value for $^1J_{Y,C}$ of 53.6 Hz is remarkable.[58,59] The high reactivity of $[Y(CH_3)(THF)_6]^{2+}$ $[BPh_4]^-_2$ can be judged by its ready decomposition in pyridine.



Scheme 3.

2.2 Cationic Alkyl Complexes Containing L_3-Type Ligands

The macrocyclic 6-electron donor 1,4,7-triazacyclononane has been broadly used as facially coordinating ancillary ligand in coordination chemistry and homogenous catalysis. The scandium trimethyl complex $[Sc(L\text{-}1)(CH_3)_3]$ with the *N,N′,N″*-trimethyl-1,4,7-triazacyclononane ligand L-1 (Figure 1), prepared by salt metathesis of the corresponding scandium trichloride $[Sc(L\text{-}1)Cl_3]$ with methyllithium, reacts in THF with $B(C_6F_5)_3$ under alkyl abstraction. The ^{1}H NMR spectrum in THF-d_8 shows a broad singlet at 0.50 ppm for $[Sc(\mu\text{-}CH_3)B]$ and a sharp singlet at 0.66 ppm due to $Sc(CH_3)_2$, indicating the formation of the zwitterionic complex $[Sc(L\text{-}1)(CH_3)_2(\mu\text{-}CH_3)B(C_6F_5)_3]$. Furthermore, $[Sc(L\text{-}1)(CH_3)_3]$ reacts with $[NMe_2HPh]$ $[B(C_6F_5)_4]$ in THF to form the ion pair $[Sc(L\text{-}1)(CH_3)_2(THF)_x]^+$ $[B(C_6F_5)_4]^-$(Scheme 4).

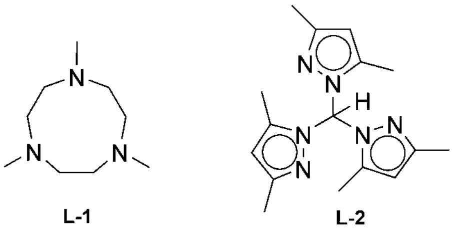
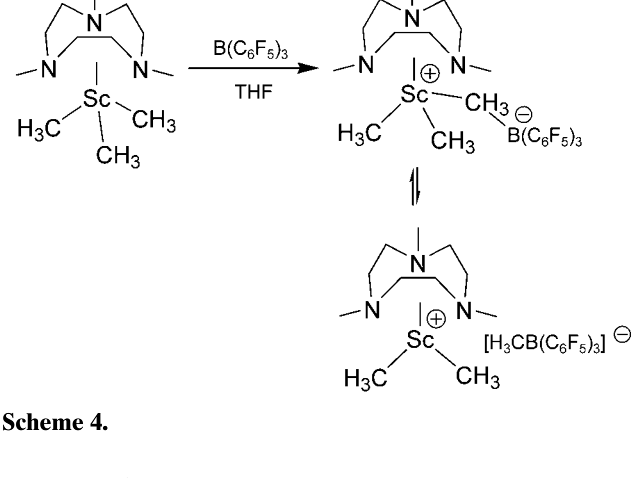


Figure 1.



Scheme 4.

Although the ^{1}H NMR spectrum in THF-d_8 indicates the formation of the expected by-products, free *N,N*-dimethylaniline and methane, the $ScCH_3$ resonance of the cation was not detected. The experimental findings indicate the formation of a liquid clathrate.[60]

The reaction of a tris(trimethylsilylmethyl)scandium complex $[Sc(CH_2SiMe_3)_3(THF)_2]$ with a facially coordinating tris(pyrazolyl-3,5-dimethyl)methane ligand L-2 with $[Ph_3C]$ $[B(C_6F_5)_4]$ in CD_2Cl_2/THF affords the ion pair $[Sc(L\text{-}2)(CH_2SiMe_3)_2(THF)]^+$ $[B(C_6F_5)_4]^-$.[61]

2.3 Cationic Alkyl Complexes Containing L_n-Type Ligands (n = 4, 5, 6)

Another family of neutral macrocylic donor ligands suitable for coordination of lanthanide centers are crown ethers. When a solution of the tris(alkyl) complex $[Ln(CH_2SiMe_3)_3(THF)_2]$ (Ln = Lu, Y) is treated at 25 °C with one equivalent of BPh_3, followed by addition of one equivalent of crown ether (CE), colorless crystals of the thermally robust ion pairs $[Ln(CH_2SiMe_3)_2(CE)(THF)_n]^+$ $[BPh_3(CH_2SiMe_3)]^-$ (Ln = Y, CE = 12-crown-4, n = 1; Ln = Lu, CE = 12-crown-4, n = 1; Ln = Lu, CE = 15-crown-5, n = 0; Ln = Lu, CE = 18-crown-6, n = 0) are isolated (Figure 2, Scheme 5).[41]

The $LuCH_2$ resonances shift to higher field in the ^{1}H and ^{13}C NMR spectra with increasing size of the crown ether. This is in agreement with an enhanced shielding along this series. In analogy to the cationic alkyl complexes with THF ligands, the crown ether-coordinated derivatives exhibit a resonance at –10.4 ppm in the ^{11}B NMR spectra at 25 °C in THF-d_8, indicating the presence of the identical anion.

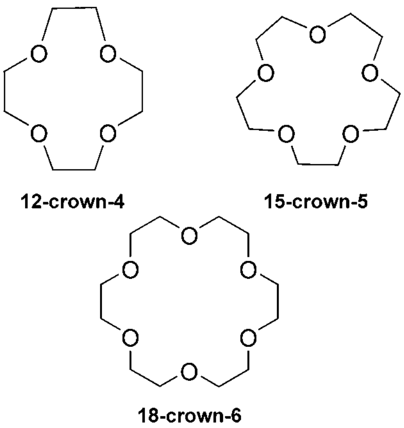
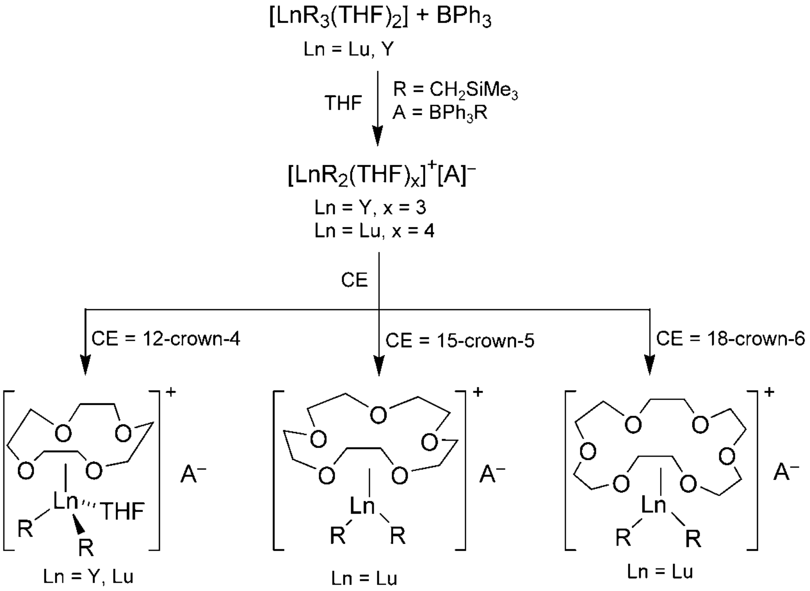


Figure 2.

2.3.1 Cationic Alkyl Complexes Supported by 12-Crown-4

NMR spectroscopy confirms that the cationic lutetium complex derived from 12-crown-4 $[Lu(CH_2SiMe_3)_2(12\text{-crown-}4)(THF)]^+$ $[BPh_3(CH_2SiMe_3)]^-$ contains one THF ligand which is labile on the NMR timescale, whereas the crown ether is rigidly coordinated at the metal center.

According to the X-ray structure analysis, the cationic lutetium complex $[Lu(CH_2SiMe_3)_2(12\text{-crown-}4)(THF)]^+$ $[BPh_3(CH_2SiMe_3)]^-$ exhibits a seven-coordinate metal center that can be best described as a capped trigonal prism. The lutetium-carbon bond lengths [2.340(2) and 2.354(2) Å] are the shortest found within the examined cationic crown ether complexes and are slightly shorter than those reported for neutral lutetium alkyl derivatives (Table 3).[41]



Scheme 5.

Table 3. Lutetium-carbon(alkyl) bond lengths.

Compound	Lu–C [Å]	Refs.
$[Lu(CH_2SiMe_3)_3(THF)_2]$	2.358(3), 2.380(3)	[62]
$[Lu(CH_2SiMe_3)_2(12\text{-crown-4})(THF)]^+ [BPh_3(CH_2SiMe_3)]^-$	2.340(2), 2.354(2)	[41]
$[Lu(CH_2SiMe_3)_2(15\text{-crown-5})]^+ [BPh_3(CH_2SiMe_3)]^-$	2.364(7), 2.345(7)	[41]
$[Lu(CH_2SiMe_3)_2(18\text{-crown-6})]^+ [BPh_3(CH_2SiMe_3)]^-$	2.366(8), 2.371(8)	[41]

The use of the neutral crown ether tris(alkyl) complexes $[Ln(CH_2SiMe_3)_3(12\text{-crown-4})]$ as starting materials for cation formation instead of the corresponding bis(THF) complexes is advantageous because of their enhanced thermal stability.[63] The tris(alkyl) complexes $[Ln(CH_2SiMe_3)_3(12\text{-crown-4})]$ of scandium, yttrium and lutetium smoothly react with $[NEt_3H]$ $[BPh_4]$ in THF to give the alkyl cations $[Ln(CH_2SiMe_3)_2(12\text{-crown-4})(THF)_x]^+$ $[BPh_4]^-$ (Ln = Sc, x = 0; Ln = Y, x = 0, Ln = Lu, x = 1) in high yields (Scheme 6).[63]

In contrast to the lutetium complex, the isolated scandium and yttrium complexes do not contain a THF ligand. For the scandium complex, this may be due to steric factors. The yttrium complex $[Y(CH_2SiMe_3)_2(12\text{-crown-4})]$ $[BPh_4]$ was isolated THF-free after drying under vacuum, since yttrium is less Lewis acidic/electrophilic than lutetium.

2.3.2 Cationic Alkyl Complexes Supported by 15-Crown-5 and 18-Crown-6

15-Crown-5 stabilizes the formally four-electron bis(alkyl) cation fragment $[LnR_2]^+$ without additional THF. Again, the coordination geometry around the seven-coordinate metal center in $[Lu(CH_2SiMe_3)_2(15\text{-crown-5})]^+$ $[BPh_3(CH_2SiMe_3)]^-$ is a capped trigonal prism.[41]

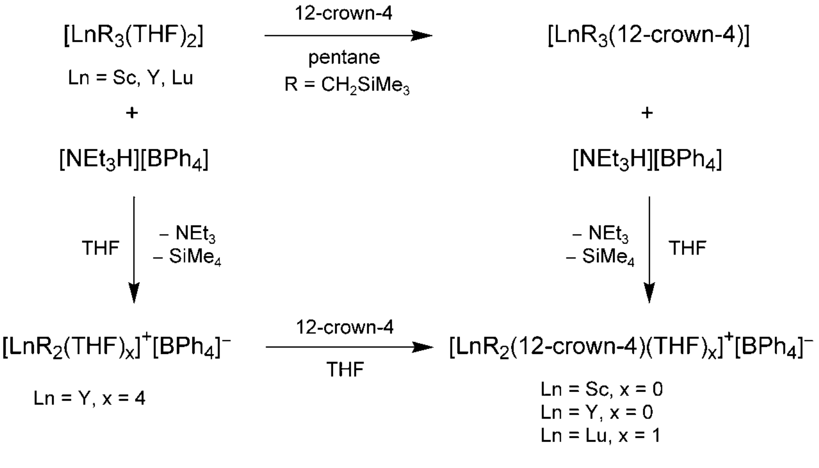
Use of 18-crown-6 makes further expansion of the coordination sphere of the bis(alkyl) lanthanide complex possible. The ion pair $[Ln(CH_2SiMe_3)_2(18\text{-crown-6})]^+$ $[BPh_3(CH_2SiMe_3)]^-$ is a rare example of a complex with direct coordination of 18-crown-6 to lutetium. Coordination of 18-crown-6 to rare-earth metal centers smaller than terbium is observed only infrequently, as these ions are too small to effectively fill the cavity.[64] As a result, the crown ether conformation is significantly distorted: the lutetium center adopts a coordination geometry of a doubly capped trigonal prism, where all six oxygen atoms of 18-crown-6 are coordinated to the eight-coordinate lutetium ion.[41]

3 Cationic Alkyl Complexes Containing Monoanionic Ligands

Amidinato, β-diketiminato-type, and cyclopentadienyl ligands have widely been used as supporting ligands for monocationic alkyl derivatives of the rare-earth metals. Monoanionic ancillary ligands used in the literature to support cationic rare-earth metal alkyl fragments are compiled in Figure 3.

3.1 Cationic Alkyl Complexes Containing LX-Type Ligands

The yttrium benzamidinato complexes $[Y(L\text{-}3)(CH_2SiMe_3)_2(THF)_x]$ (x = 1, 2) react in THF-d_8 with $[NMe_2HPh]$ $[B(C_6F_5)_4]$ to give the alkyl cation $[Y(L\text{-}3)(CH_2SiMe_3)(THF\text{-}d_8)_y]^+$ $[B(C_6F_5)_4]^-$ (Scheme 7).



Scheme 6.

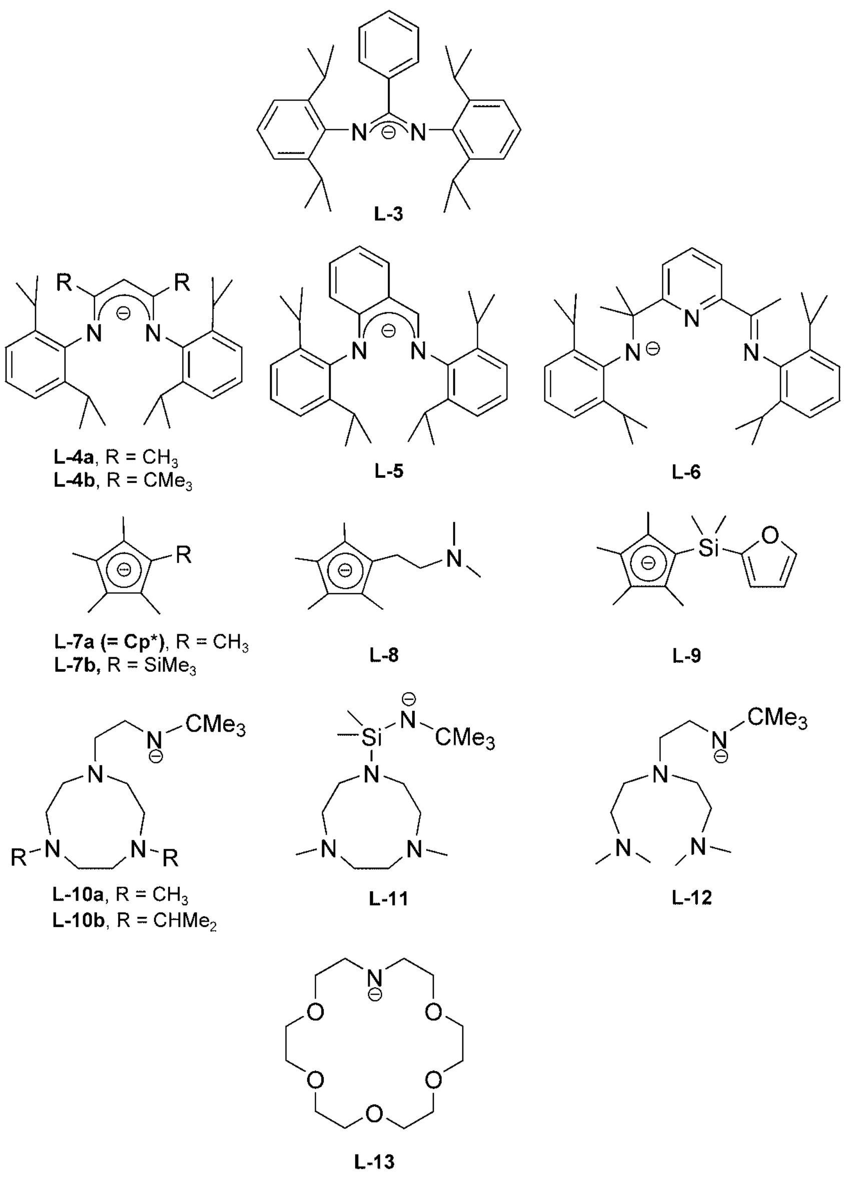
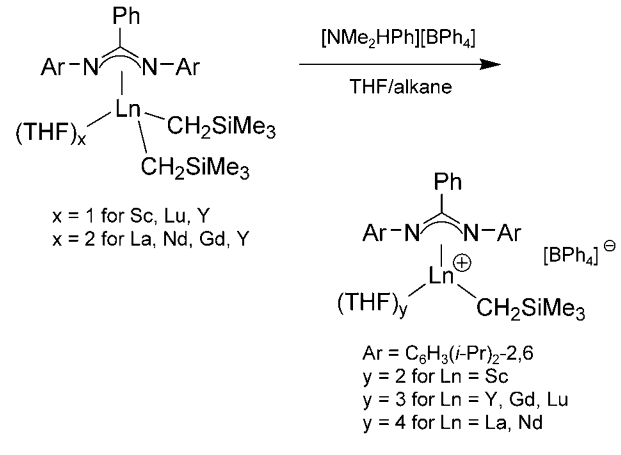
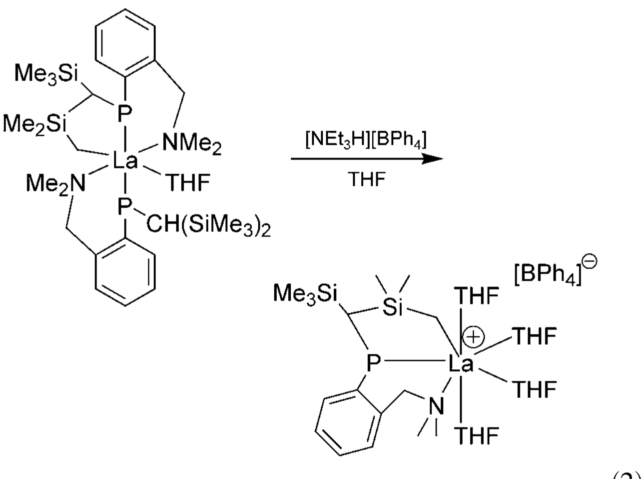


Figure 3.



Scheme 7.

This ion pair is generated *in situ* and characterized by ^{1}H and ^{13}C NMR spectroscopy.[65] The reaction of the neutral bis(alkyl) complexes of the lanthanides $[Ln(L\text{-}3)(CH_2SiMe_3)_2(THF)_x]$ (x=2 for Ln=La, Nd, Gd, Y; x=1 for Ln=Sc, Lu, Y) with $[NMe_2HPh]$ $[BPh_4]$ in THF/alkane yields the thermally robust ion pairs $[Ln(L\text{-}3)(CH_2SiMe_3)(THF)_y]^+$ $[BPh_4]^-$ (y=2 for Ln=Sc; y=3 for Y, Gd, Lu; y=4 for La, Nd) (Scheme 7). Crystallographic characterization of the cationic benzamidinato derivatives (Ln=Sc, Y, Gd, Nd, La) confirmed the increasing coordination number with the increasing ionic radius[66] of the metal center by the binding of additional THF molecules.[42]

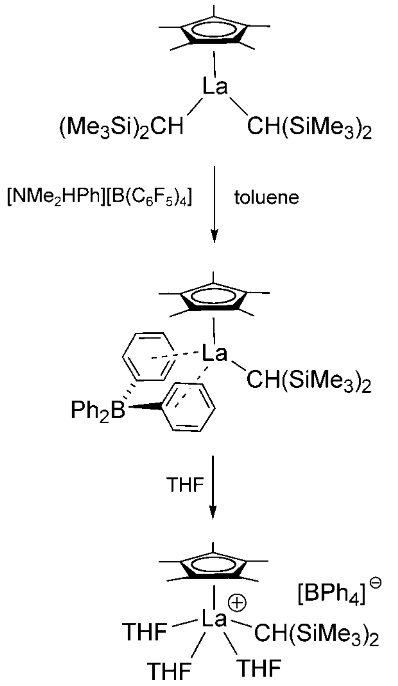


(2)

Treatment of the lanthanum mono(alkyl) complex $[La\{\eta^2\text{-}C_6H_4(PR)\text{-}1\text{-}(CH_2NMe_2)_2\}\{\eta^3\text{-}C_6H_4[PC(H)(SiMe_3)SiMe_2CH_2]\text{-}1\text{-}(CH_2NMe_2)\text{-}2\}(THF)]$ $[R{=}CH(SiMe_3)_2]$ with one equivalent of $[NEt_3H][BPh_4]$ results in the protonolysis of the bidentate aminophosphido ligand, Equation (2). X-ray crystallography of the ion pair $[La\{\eta^3\text{-}C_6H_4[PC(H)(SiMe_3)SiMe_2\text{-}CH_2]\text{-}1\text{-}(CH_2NMe_2)\text{-}2\}(THF)_4]^+$ $[BPh_4]^-$ revealed a pentagonal-bipyramidal structure for the cation in the solid state.[67]

3.2 Cationic Alkyl Complexes Containing L_2X-Type Ligands

Protonolysis of the pentamethylcyclopentadienyl lanthanum bis(alkyl) complex $[LaCp^*\{CH(SiMe_3)_2\}_2]$ with $[NMe_2HPh]$ $[BPh_4]$ in toluene affords the contact ion pair $[LaCp^*\{CH(SiMe_3)_2\}\{(\eta^n\text{-}Ph_2)BPh_2\}]$ in quantitative yield. In spite of the absence of any coordinating (Lewis basic) solvents, this compound is surprisingly robust. ^1H and ^{13}C NMR spectroscopy in CD_2Cl_2 as well as solid-state NMR spectra suggest a η^n-coordination of the tetraphenylborate anion at the lanthanide center. The contact ion pair irreversibly reacts with THF to form the THF-containing cationic complex $[LaCp^*\{CH(SiMe_3)_2\}(THF)_3]^+$ $[BPh_4]^-$ in almost quantitative yield (Scheme 8). The ^1H and ^{13}C NMR spectra of the THF adduct suggest the presence of a weakly coordinating anion in solution.[22]



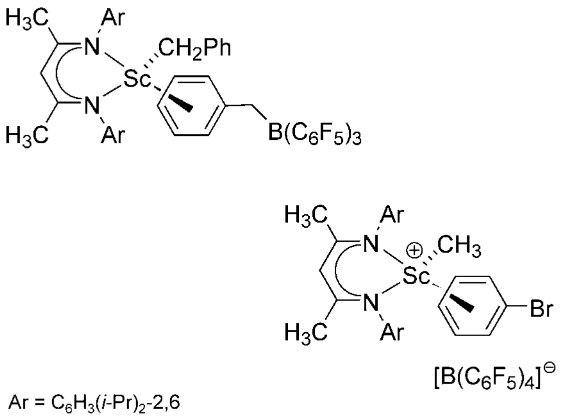
Scheme 8.

Treatment of the scandium derivative $[ScCp^*(CH_3)_2\{O{=}P(CMe_3)_3\}]$ with one equivalent of $B(C_6F_5)_3$ in toluene gives the crystallographically characterized contact ion pair $[ScCp^*(CH_3)\{O{=}P(CMe_3)_3\}(\mu\text{-}CH_3)B(C_6F_5)_3]$ as a relatively thermally stable compound.[68]

The β-diketiminato-supported dibenzylscandium complex $[Sc(L\text{-}4a)(CH_2Ph)_2]$ reacts with $B(C_6F_5)_3$ to form the zwitterionic complex $[Sc(L\text{-}4a)(CH_2Ph)\{(\eta^6\text{-}C_6H_5)(CH_2)\}B(C_6F_5)_3]$ (Scheme 9). X-ray structural analysis shows that the abstracted benzyl group is coordinated through a strong η^6-bonding to the scandium center.[69]

The dimethyl derivative of scandium $[Sc(L\text{-}4b)(CH_3)_2]$ forms the crystallographically characterized zwitterionic complex $[Sc(L\text{-}4b)(CH_3)(\mu\text{-}CH_3)\{(\mu\text{-}F)\text{-}C_6F_4\}B(C_6F_5)_2]$ upon treatment with one equivalent of $B(C_6F_5)_3$ in hexanes. In contrast, the thermally sensitive dimer $[\{Sc(L\text{-}4b)CH_3\}_2(\mu\text{-}CH_3)]$ is produced when $[Sc(L\text{-}4b)(CH_3)_2]$ is treated with 0.5 equivalents of $B(C_6F_5)_3$, whereas in the presence of an excess of $B(C_6F_5)_3$ the dicationic contact ion triple $[Sc(L\text{-}4b)\text{-}\{(\mu\text{-}CH_3)B(C_6F_5)_3\}_2]$ is formed.[54]

The reaction of $[Sc(L\text{-}4a)(CH_3)_2]_2$ with one equivalent of $[Ph_3C][B(C_6F_5)_4]$ in bromobenzene produces the sol-

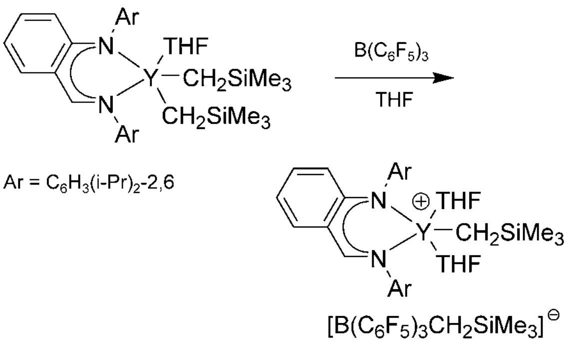


Ar = $C_6H_3(i\text{-}Pr)_2\text{-}2,6$

Scheme 9.

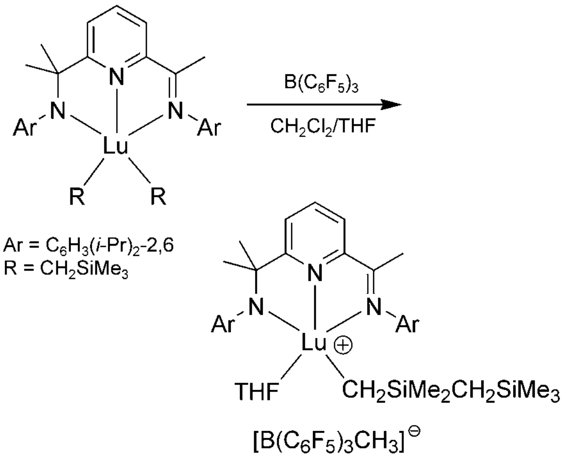
vent separated ion pair $[Sc(L\text{-}4a)(CH_3)(\eta^6\text{-}C_5H_5Br)]^+$ $[B(C_6F_5)_4]^-$ (Scheme 9). X-ray crystallography gives evidence for the η^6-coordination of the arene group in the solid state, whereas ^1H NMR spectroscopy indicates rapid exchange of free and coordinated arene in solution. By NMR spectroscopy, analogous solvent-separated ion pairs $[Sc(L\text{-}4a)(CH_3)(\eta^6\text{-arene})]^+$ $[B(C_6F_5)_4]^-$ (arene = benzene, toluene, mesitylene) are characterized, generated *in situ* by replacement of labile bromobenzene by the corresponding arene.[70]

The anilido-imine-supported yttrium bis(alkyl) complex $[Y(L\text{-}5)(CH_2SiMe_3)_2(THF)]$, upon reaction with $B(C_6F_5)_3$ in bromobenzene, forms a complex mixture of isomers of the thermally unstable ion pair $[Y(L\text{-}5)(CH_2SiMe_3)(THF)]^+$ $[B(C_6F_5)_3(CH_2SiMe_3)]^-$, whereas the bis(THF) complex $[Y(L\text{-}5)(CH_2SiMe_3)(THF)_2]^+$ $[B(C_6F_5)_3(CH_2SiMe_3)]^-$ is isolated as a thermally stable compound, Equation (3).[71]



(3)

The lutetium bis(alkyl) complex $[Lu(L\text{-}6)(CH_2SiMe_3)_2]$ containing the anilido-pyridine-imine ligand reacts with $B(C_6F_5)_3$ in CH_2Cl_2/THF to form the thermally stable ion pair $[Lu(L\text{-}6)(CH_2SiMe_2CH_2SiMe_3)(THF)]^+$ $[B(C_6F_5)(CH_3)]^-$, Equation (4).

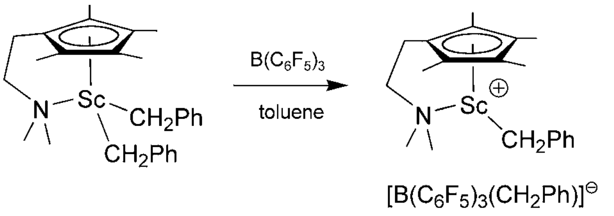


(4)

A concerted silyl methyl group extraction by $B(C_6F_5)_3$ accompanied by alkyl migration is proposed to explain the formation of the $CH_2SiMe_2CH_2SiMe_3$ fragment, although the mechanistic details remain somewhat obscure.[72]

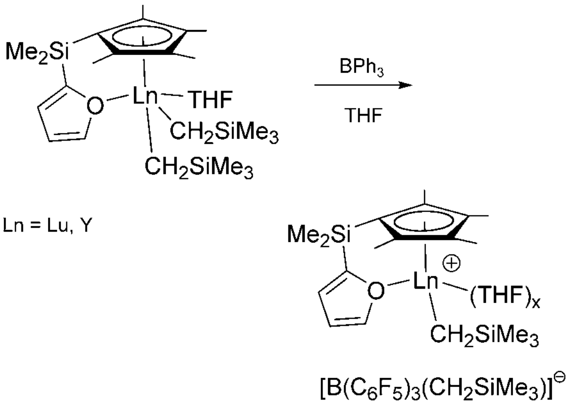
3.3 Cationic Alkyl Complexes Containing L_3X-Type Ligands

Treatment of the amino-functionalized tetramethylcyclopentadienyl complex $[Sc(L\text{-}8)(CH_2Ph)_2]$ with $B(C_6F_5)_3$ in toluene forms an oily product, formulated as $[Sc(L\text{-}8)(CH_2Ph)]^+$ $[B(C_6F_5)_3(CH_2Ph)]^-$, Equation (5). Cationic alkyl complexes of the rare-earth metals supported by cyclopentadienyl ligands are compiled in Table 4.



(5)

The reaction of the bis(alkyl) complexes $[Ln(L\text{-}9)(CH_2SiMe_3)_2(THF)]$ (Ln = Lu, Y) with triphenylborane in THF results in the clean formation of the alkyl cations $[Ln(L\text{-}9)(CH_2SiMe_3)(THF)_x]^+$ $[BPh_3(CH_2SiMe_3)]^-$, Equation (6).[73]

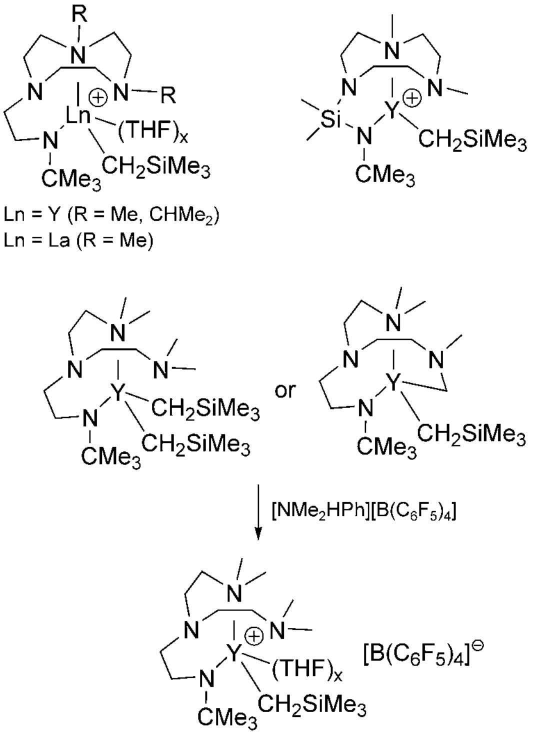


(6)

The amido-functionalized triazacyclononane complex $[Y(L\text{-}10a)(CH_2SiMe_3)_2]$ reacts with $[NMe_2HPh]$ $[B(C_6F_5)]$ in bromobenzene to form the thermally stable ionic compound $[Y(L\text{-}10a)(CH_2SiMe_3)]^+$ $[B(C_6F_5)_4]^-$ (Scheme 10).[75] The analogous complex supported by a dimethylsilanediyl-linked amido-triazacyclononane ligand $[Y(L\text{-}11)(CH_2SiMe_3)]^+$ $[B(C_6F_5)_4]^-$ is obtained by a similar procedure,[76] whereas the reaction of $[Y(L\text{-}10b)(CH_2SiMe_3)_2]$ with $[NMe_2HPh]$ $[B(C_6F_5)]$ requires the presence of THF to stabilize the ion pair $[Y(L\text{-}10b)(CH_2SiMe_3)(THF)_x]^+$ $[B(C_6F_5)_4]^-$.[75] Likewise, THF stabilizes the ionic lanthanum complex $[La(L\text{-}10a)(CH_2SiMe_3)(THF)_x]^+$ $[B(C_6F_5)_4]^-$, which is characterized in solution by NMR spectroscopy (Scheme 10).[77]

Table 4. Cationic alkyl complexes of the rare-earth metals supported by cyclopentadienyl ligands.

Compound	Characterization	Ref.
$[LaCp^*\{CH(SiMe_3)_2\}(THF)_x]^+ [BPh_4]^-$; x = 0, 3	^1H, ^{13}C, ^{13}C CPMAS NMR, EA	[22]
$[Y(L\text{-}7b)(CH_2SiMe_3)(THF)_x]^+ [BPh_4]^-$	^1H, ^{13}C NMR	[37]
$[ScCp^*\{O{=}P(CMe_3)_3\}(CH_3)]^+ [B(C_6F_5)_3(CH_3)]^-$	X-ray, ^1H NMR	[68]
$[Sc(L\text{-}8)(CH_2Ph)]^+[B(C_6F_5)_3(CH_2Ph)]^-$	no data available	[74]
$[Ln(L\text{-}9)(CH_2SiMe_3)(THF)_x]^+ [BPh_3(CH_2SiMe_3)]^-$; Ln = Y, Lu	^1H, ^{13}C, ^{11}B NMR	[73]

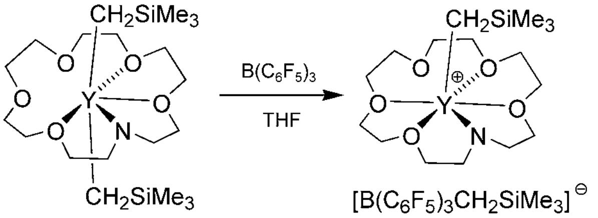


Scheme 10.

The reaction of the triamino-amide bis(alkyl) complex $[Y(L\text{-}12)(CH_2SiMe_3)_2]$ or its metalated compound with $[NMe_2HPh]$ $[B(C_6F_5)_4]$ in THF results in the formation of $[Y(L\text{-}12)(CH_2SiMe_3)(THF)_x]^+$ $[B(C_6F_5)_4]^-$ (Scheme 10) which, unlike the triazacyclononane derivatives, is not stable in the absence of THF.[78]

3.4 A Cationic Alkyl Complex Containing an L_5X Ligand

The yttrium bis(alkyl) complex $[Y(L\text{-}13)(CH_2SiMe_3)_2]$ containing the deprotonated aza-18-crown-6 undergoes alkyl abstraction with $B(C_6F_5)_3$ in THF to yield a colorless compound assigned as the ion pair $[Y(L\text{-}13)(CH_2SiMe_3)(THF)_x]^+$ $[B(C_6F_5)_3(CH_2SiMe_3)]^-$ (Equation 7). It rapidly decomposes to give $SiMe_4$ and unidentified products at room temperature, as shown by NMR spectroscopy.[79] It is noteworthy that the related crown ether derivatives are far less thermally sensitive.



(7)

4 Applications in Homogeneous Catalysis

4.1 Polymerization of Ethylene and α-Olefins

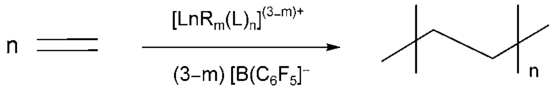
The majority of the cationic alkyl complexes so far reported have been studied in the context of homogenous ethylene polymerization catalysts. As compiled in Table 5, scandium and yttrium alkyl complexes containing both neutral and monoanionic ancillary ligands are precursors for efficient ethylene polymerization catalysts (Scheme 11). The active monocationic species $[Ln(L_m)(R)_2]^+$ or $[Ln(L_mX)(R)]^+$ are commonly generated *in situ* by the reaction of Lewis acid or Brønsted acid activators, optionally in the presence of further cocatalysts. No detailed mechanistic studies have been reported so far. Narrow molecular weight distributions and catalyst efficiencies of around 1.1 indicate a living character of the polymerization when the benzamidinato complex $[Y(L\text{-}3)R_2(THF)]$ is activated with $[NMe_2HPh]$ $[B(C_6F_5)_4]$.[65] Interestingly, the yttrium precursor appears to provide the most effective catalyst for ethylene polymerization, as both larger and smaller metals show lower activity under standardized conditions.[42]

Activation of the triazacyclononane derivative $[Sc(L\text{-}1)(CH_3)_3]$ with $B(C_6F_5)_3$ or $[NMe_2HPh][B(C_6F_5)_4]$ gives cationic scandium species that catalyze ethylene homopolymerization and 1-pentene oligomerization ($M_n = 2800$ g mol^{-1}, $M_w/M_n = 1.3$).[60] Interestingly, the tris(trimethylsilylmethyl) derivative $[Sc(L\text{-}1)(CH_2SiMe_3)_3]$ showed a significantly enhanced activity.[61] The scandium methyl cations supported by a β-diketiminato ligand $[Sc(L\text{-}4b)(CH_3)(\mu\text{-}CH_3)\{(\mu\text{-}F)C_6F_4\}B(C_6F_5)_2]$ as well as the dicationic species $[Sc(L\text{-}4b)]$ $[B(C_6F_5)_3(CH_3)]_2$ are effective in homogeneous ethylene polymerization, but somewhat lower in activity when the dichloride $[Sc(L\text{-}4b)Cl_2]$ is activated by methylaluminoxane

Table 5. Ethylene polymerization with *in situ* generated cationic alkyl derivatives of the rare-earth metals.

Precursor	Activator	Cocatalyst	t[a]	Activity[b]	M_n[c]	M_w/M_n	Refs.
$[Sc(L\text{-}1)R_3]$[d]	$B(C_6F_5)_3$	$Al(i\text{-}Bu)_3$	60	240[e]	n.a.[f]	n.a.[f]	[61]
$[Y(L\text{-}1)R_3]$[d]	$B(C_6F_5)_3$	$Al(i\text{-}Bu)_3$	60	10[e]	n.a.[f]	n.a.[f]	[61]
$[Sc(L\text{-}2)R_3]$[d]	$B(C_6F_5)_3$	$Al(i\text{-}Bu)_3$	60	290[e]	n.a.[f]	n.a.[f]	[61]
$[Y(L\text{-}3)R_2(THF)]$[d]	$[NMe_2HPh]\ [B(C_6F_5)_4]$	–	5	1040[g]	360	1.2	[65]
$[Y(L\text{-}3)R_2(THF)_2]$[d]	$[NMe_2HPh]\ [B(C_6F_5)_4]$	TIBAO	5	2670[g]	170	2.1	[65]
$[Sc(L\text{-}4b)(CH_3)_2]$	PMAO-IP	–	n.a.[f]	58[g]	940	2.0	[54]
$[Sc(L\text{-}4b)(CH_3)_2]$	$B(C_6F_5)_3$	PMAO-IP	n.a.[f]	15[g]	620	1.7	[54]
$[Sc(L\text{-}4b)(CH_3)_2]$	$[Ph_3C]\ [B(C_6F_5)_4]$	PMAO-IP	n.a.[f]	23[g]	340	2.5	[54]
$[Sc(L\text{-}8)Cl_2]$	MAO	–	15	771[h]	180	2.1	[74]
$[Sc(L\text{-}8)(CH_2Ph)_2]$	$[NMe_2HPh]\ [B(C_6F_5)_4]$	$AlEt_3$	15	25[h]	4	1.9	[74]
$[Y(L\text{-}10a)R_2]$[d]	$[NMe_2HPh]\ [B(C_6F_5)_4]$	–	10	1180[g]	70	4.9	[75]
$[Y(L\text{-}12)R_2]$[d]	$[Ph_3C]\ [B(C_6F_5)_4]$	–	15	60[g]	30	2.2	[78]

[a] Reaction time in min.
[b] In kg $mol^{-1}\ h^{-1}\ bar^{-1}$.
[c] $\times 10^{-3}$ g mol^{-1}.
[d] $R = CH_2SiMe_3$.
[e] $T = 33\,°C$.
[f] No information available.
[g] $T = 50\,°C$.
[h] $T = 80\,°C$.



Scheme 11.

(MAO). The half-sandwich complex $[Sc(L\text{-}8)Cl_2]$ and the amido-functionalized triazacyclononane derivative $[Y(L\text{-}11)(CH_2SiMe_3)_2]$ have been claimed to catalyze the copolymerization of ethylene with 1-hexene upon activation with MAO.[74,76]

Toluene solutions of the rare-earth metal tris(alkyl) complexes $[Ln(CH_2SiMe_3)_3(THF)_2]$ efficiently catalyze ethylene polymerization upon activation with five equivalents of the Brønsted acid $[NMe_2HPh]\ [B(C_6F_5)_4]$ in the presence of a 200-fold excess of $Al(i\text{-}Bu)_3$ (Table 6).[36]

After short run times (10 min) at 25 °C and 5 bar of ethylene pressure, linear polyethylenes with molecular weights $M_n = 3500-45000$ g mol^{-1} and polydispersities $M_w/M_n = 2-6$ are produced with activities up to 899 kg $mol^{-1}\ h^{-1}\ bar^{-1}$ (Table 6). As illustrated in Figure 4, the catalyst performance can be adjusted by the choice of the rare-earth metal, as the activity is well correlated with the effective ionic radius[66] of the rare-earth metal.[80]

Table 6. Ethylene polymerization with $[Ln(CH_2SiMe_3)_3(THF)_2]$ as catalyst precursor activated with $[NMe_2HPh]\ [B(C_6F_5)_4]$ in the presence of $Al(i\text{-}Bu)_3$.[36]

Ln	r[a] [Å]	Yield [g]	Activity [kg $mol^{-1}\ h^{-1}\ bar^{-1}$]	M_n [g mol^{-1}]	M_w/M_n	T_m [°C]
Sc[b]	0.89	0.03	1	–	–	–
Lu[b]	1.00	traces	–	–	–	–
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[d]	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

Conditions: 5 μmol Ln; B:Ln = 5:1; Al:Ln = 200:1; $T = 25\,°C$; $p = 5$ bar; $t = 10$ min; $V = 30$ mL (toluene).
[a] Effective ionic radius of Ln^{3+} for $CN = 6$, see ref.[66]
[b] $t = 60$ min.
[c] $t = 8$ min.
[d] Bimodal molecular weight distribution.

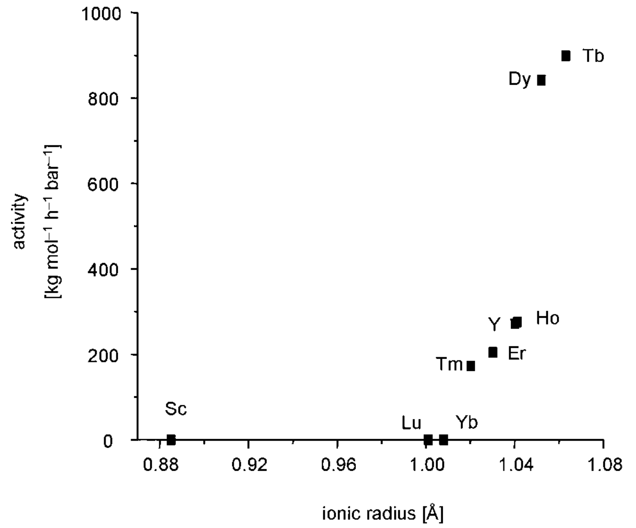
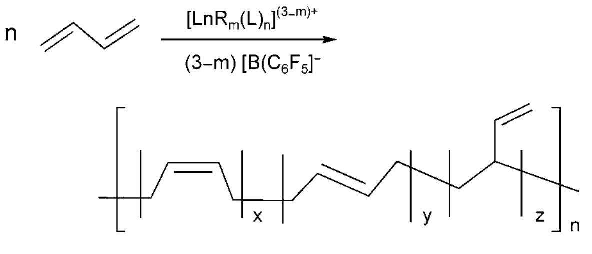


Figure 4. Plot of the ethylene polymerization activity *vs.* the effective ionic radius R of the trivalent rare-earth metal for $CN=6$ according to Table 6.

For the tris(alkyl) complexes of the smaller elements scandium, lutetium and ytterbium, no significant activity is observed, whereas the thulium derivative produces polyethylene with 183 kg mol^{-1} h^{-1} bar^{-1}. For terbium, the element with the largest radius within the examined series, an activity of 899 kg mol^{-1} h^{-1} bar^{-1} is found. An alkyl dication $[Ln(CH_2SiMe_3)(solv)_z]^{2+}$, formed *via* the bis(alkyl) monocation $[Ln(CH_2SiMe_3)_2(solv)_y]^+$, is thought to be most probably the active species, since the polymerization requires at least twofold excess of $[NMe_2HPh]$ $[B(C_6F_5)_4]$. The isolated monocation $[Y(CH_2SiMe_3)_2(THF)_4]^+$ $[Al(CH_2SiMe_3)_4]^-$, while not active by itself, can be activated by addition of another equivalent of $[NMe_2HPh]$ $[B(C_6F_5)_4]$ to exhibit ethylene polymerization activity similar to that obtained with the mixture $[Y(CH_2SiMe_3)_3(THF)_2]/[NMe_2HPh]$ $[B(C_6F_5)_4]/[Al(CH_2SiMe_3)_3]$.[36]



Scheme 12.

4.2 1,3-Butadiene Polymerization.

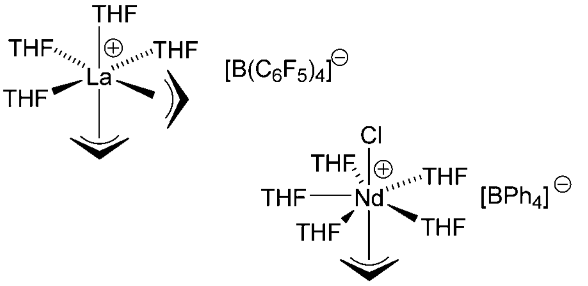
The regio- and stereospecific polymerization of conjugated dienes is of great significance for the elastomer synthesis (Scheme 12). *cis*-1,4-Polybutadiene in particular exhibits excellent elastomeric properties and has gained considerable importance for the production of synthetic rubbers. Some Ziegler-type catalysts consisting of transition metal or neodymium carboxylate, Lewis acid and/or alkylating reagent have been reported to efficiently catalyze 1,3-butadiene polymerization with high *cis*-1,4-selectivity.[81,82] The complicated composition of these multicomponent catalysts has so far hampered a comprehensive elucidation of the polymerization mechanism, although there is no doubt that rare-earth metal alkyl species are involved in this catalysis.[82]

In the context of homogeneously catalyzed polymerizations, the reaction of the neodymium tris(allyl) complex $[Nd(\eta^3\text{-}C_3H_5)_3]$ with $B(C_6F_5)_3$ in the absence of any aluminum alkyls to give the initiator $[Nd(\eta^3\text{-}C_3H_5)_2]^+$ $[B(C_6F_5)_3(C_3H_5)]^-$ (Table 7) indicates that the generation of cationic allyl derivatives plays an important role in the activation step.[84] The crystal structure of $[La(\eta^3\text{-}C_3H_5)_2(THF)_4]^+$ $[B(C_6F_5)_4]^-$ clearly shows the presence of solvent separated ion pairs in the lattice (Scheme 13). Moreover, the formation of a dicationic mono(allyl) lanthanide complex as the active species responsible for the high *cis*-1,4-selectivity was proposed in this context.[85] The reaction of $[Nd(\eta^3\text{-}C_3H_5)_3]$ with $[NMe_2HPh]$ $[B(C_6F_5)_4]$ generates the ionic

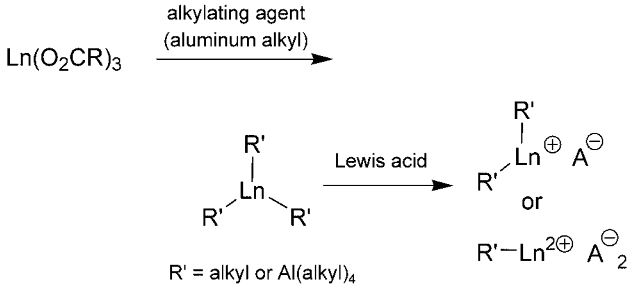
Table 7. 1,3-Butadiene polymerization with cationic rare-earth metal derivatives with π-bound hydrocarbyl ligands.

Precursor	Activator	T [°C]	t[a]	Yield [%]	Selectivity *cis*:*trans*:1,2	M_n[b]	M_w/M_n	Refs.
$[PrCp*_2B(C_6F_5)_4]_2$	$Al(i\text{-}Bu)_3$	50	300	95	90:7:3	80	1.7	[12]
$[NdCp*_2B(C_6F_5)_4]_2$	$Al(i\text{-}Bu)_3$	50	25	96	91:6:3	130	1.4	[12]
$[SmCp*_2B(C_6F_5)_4]_2$	$Al(i\text{-}Bu)_3$	50	5	80	96% *cis*[c]	130	1.7	[83]
$[GdCp*_2B(C_6F_5)_4]_2$	$Al(i\text{-}Bu)_3$	50	3	100	98:1:1	250	1.7	[12]
$[Nd(\eta^3\text{-}C_3H_5)_2(THF)_4]^+$ $[B(C_6F_5)_4]^-$	$Al(i\text{-}Bu)_3$	20	60	59	57:41:2	n.a.	n.a.	[84]
$[Nd(\eta^3\text{-}C_3H_5)_3]$	$B(C_6F_5)_3$	20	20	43	97:1:2	n.a.	n.a.	[84]
$[Nd(\eta^3\text{-}C_3H_5)_2(C_4H_8O_2)_4]^+$ $[B(C_6F_5)_4]^-$	–	50	35	40	92:7:1	254	1.6	[85]

[a] Reaction time in min.
[b] In $\times 10^{-3}$ g mol^{-1}.
[c] Details of the microstructure are not provided.



Scheme 13.



Scheme 14.

derivative $[Nd(\eta^3\text{-}C_3H_5)_2]^+$ $[B(C_6F_5)_4]^-$, which also catalyzes the polymerization of isoprene.[84] When a 1:1 mixture of the neodymium tris(allyl) complex $[Nd(\eta^3\text{-}C_3H_5)_3(C_4H_8O_2)]$ and $[NdCl_3(THF)_2]$ is treated with $[NMe_2HPh]$ $[BPh_4]$ in THF, the cationic allyl complex $[Nd(\eta^3\text{-}C_3H_5)Cl(THF)_5]^+$ $[BPh_4]^-$ is produced. Single crystal X-ray structure analysis shows the presence of solvent separated ion pairs in the solid state, with a pentagonal bipyramidal coordination geometry around the cationic neodymium center and the chloro and allyl ligands arranged in a *trans* fashion (Scheme 13).[86]

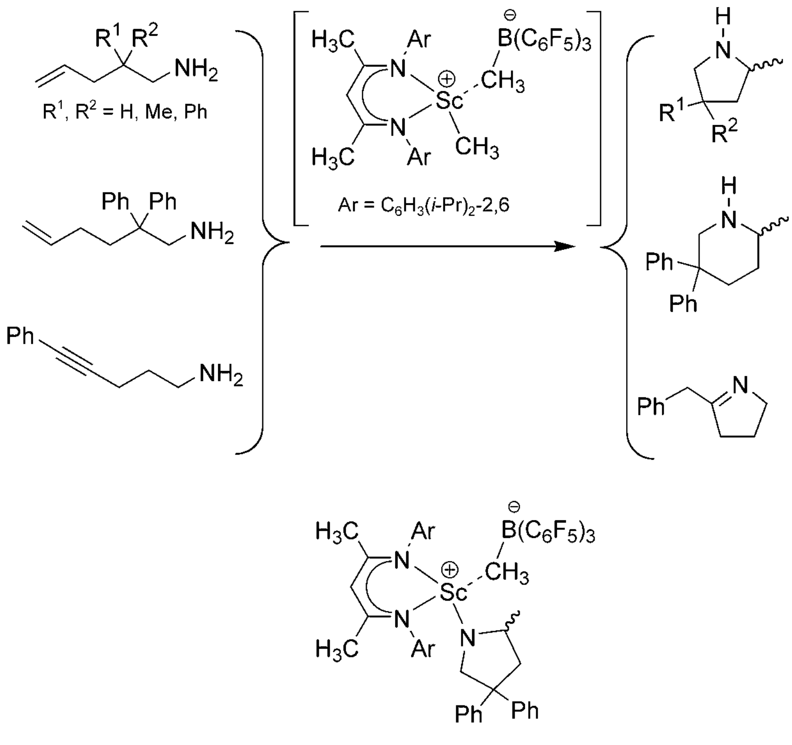
Further evidence that cationic hydrocarbyl complexes act as the active species is given by the following observation: The activation of the cationic bis(pentamethylcyclopentadienyl) complexes $[LnCp^*_2][B(C_6F_5)_4]$ (Ln = Pr, Nd, Sm) with Al(*i*-Bu)$_3$ was reported to afford highly *cis*-1,4 selective initiators for 1,3-butadiene polymerization (Table 7).[12,83,87]

The above findings may also imply that, in the case of the industrially applied multicomponent catalysts typically consisting of lanthanide carboxylate, aluminum alkyl and Lewis acid, discrete cationic alkyl species may be formed *in situ* or exist in equilibrium with non-ionic compounds (Scheme 14).[88,89]

4.3 Intramolecular Hydroamination

As has been established for homogeneous olefin polymerization catalysis, one can anticipate that the catalytic activity for a variety of rare-earth metal catalyzed transformations will be enhanced by using cationic derivatives.

The zwitterionic compound $[Sc(L\text{-}4b)(CH_3)(\mu\text{-}CH_3)\{(\mu\text{-}F)C_6F_4\}B(C_6F_5)_2]$ catalyzes the intramolecular

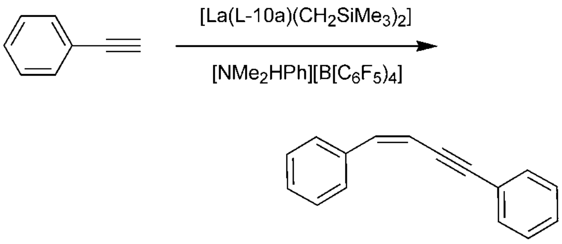


Scheme 15.

hydroamination/cyclization of aminoalkenes to give pyrrolidine and piperidine products (Scheme 15). The neutral dimethyl complex $[Sc(L\text{-}4b)(CH_3)_2]$ is by orders of magnitude less efficient. Since the stoichiometric reaction of the cationic scandium complex with an aminoalkene gives a cationic pyrrolidinato complex, as characterized by NMR spectroscopy, the catalytically active species appears to be an amido cation.[90]

4.4 Alkyne Dimerization

The cationic lanthanum alkyl complex $[La(L\text{-}10a)(CH_2SiMe_3)]^+ [B(C_6F_5)_4]^-$, generated *in situ* from the neutral bis(alkyl) complex $[La(L\text{-}10a)(CH_2SiMe_3)_2]$ and $[NMe_2HPh] [B(C_6F_5)_4]$ in bromobenzene, efficiently catalyzes the dimerization of phenylacetylene [Equation (8)] to give the linear head-to-head *cis*-enyne with high regio- and stereoselectivity (99% *cis* content, TOF > 100 h^{-1}).[77] As active species an alkynyl cation $[La(L\text{-}10a)(C{=}CPh)]^+ [B(C_6F_5)_4]^-$, possibly as a dimer, is invoked. An insoluble oily compound is obtained upon reaction of $[La(L\text{-}10a)(CH_2SiMe_3)]^+ [B(C_6F_5)_4]^-$ with one equivalent of phenylacetylene or upon treating the dinuclear dialkynyl complex $[La(L\text{-}10a)(C{=}CPh)(\mu\text{-}C{=}CPh)]_2$ with $[NMe_2HPh] [BPh_4]$. A similar catalysis was previously reported using the neutral rare-earth metal complexes with a linked amido-cyclopentadienyl ligand such as $[Lu(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2\text{-}NPh)(CH_2SiMe_3)(THF)_2]$. A dinuclear bis(μ-alkynyl) species is thought to be here the active species.[91]



(8)

5 Conclusion

The first rare-earth alkyl cation was reported not very long ago[22] and the chemistry of alkyl cations of the rare-earth metals is still in its infancy. Only a limited number of fully characterized mono- and dicationic alkyl complexes of the rare-earth metals has been described,[36,41,42] and the potential of such species in olefin polymerization catalysis remains unexplored.[36,42,54,60,61,65,68,75] For other organic transformations, two instructive examples have recently appeared in the literature.[77,90] Cationic lanthanide alkyl derivatives as homogeneous catalysts appear to be generally superior to their neutral precursors due to their increased electrophilicity towards substrate molecules. The future will hopefully witness a further expansion of the applications of this type of complexes. Some of these mono- and dicationic alkyl derivatives are easily accessible and thermally robust, at least in the presence of Lewis bases. Hence they promise to become useful starting materials for hitherto unknown species of rare-earth metals such as hydrido cations and alkylidene complexes. Salt metathesis reactions in analogy to lanthanocenium cations will probably also make new types of rare earth complexes accessible.[6]

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