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Coordination features of 1,3,5-triazapentadienyl ligand in alkyl complexes of rare-earth metals

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Abstract: The reactions of 1,3,5-triazapentadiene 2,6-$iPr_2C_6H_3NC(Ph)NC(Ph)NHC_6H_3iPr_2$-2,6 (**1**) with $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Lu) in hexane afford bis(alkyl) complexes [2,6-$iPr_2C_6H_3NC(Ph)NC(Ph)NC_6H_3iPr_2$-2,6]$Ln(CH_2SiMe_3)_2(THF)$ (Ln =Y (**2**), Lu (**3**)) in 58 (**2**) and 62 (**3**) % yields. The X-ray diffraction study revealed that in **3** the triazapentadienyl ligand coordinates with the Lu^{3+} ion in "amidinate" fashion resulting in the formation of a four-membered metallocycle. In contrast, the reaction of **1** with the scandium analogue $Sc(CH_2SiMe_3)_3(THF)_2$ in toluene proceeds with the cleavage of C-N bond of 1,3,5-triazapentadiene and leads to the formation of a dinuclear monoalkyl complex [{μ^2-2,6-$iPr_2C_6H_3NC(Ph)N$}$Sc(CH_2SiMe_3)(THF)$]$_2$ (**4**) in 43% yield. Complex **4** features κ^2-N,N-coordination of the residual dianionic {μ^2-2,6-$iPr_2C_6H_3NC(Ph)N$}$^{2-}$ ligand μ-bridging two Sc^{3+} centers. Alkyl complexes **2**–**4** were evaluated as pre-catalysts for isoprene polymerization and hydrosilylation of unsaturated substrates with $PhSiH_3$.

Introduction

The rational design of new ligand systems suitable for coordination to large ions[1] of electropositive[2] rare-earth metals which can allow for the synthesis of isolable complexes is still in the focus of organometallic and coordination chemistry of these elements.[3] Due to the hard Lewis acidity of rare-earth metals, polydentate N-containing ligands seem to be prospective and promising candidates for strong binding with these ions[3b,4] able to provide kinetic stability of their complexes. Indeed, a variety of N-containing ligands was successfully employed for the synthesis of highly reactive alkyl,[3a,3d,5] cationic alkyl,[3d,6] hydrido,[3a,7] borohydrido derivatives[8] of rare-earth metals. To date, amidinate,[3c,3d,9] guanidinate,[3a,3c,10] amidopyridinate[11] and β-diketoiminato[3c,12] ligands are among those which are most frequently and efficiently used in rare-earth chemistry. Strangely, despite the similarity of structural and electronic properties of β-diketoiminates (Fig. 1) and 1,3,5-triazapentadienes (also known as imidoylamidines) the latter remain completely beyond rare-earth chemistry and nothing was known about their coordination to large ions of these metals. 1,3,5-Triazapentadienes (tap) were discovered over a century ago, however their coordination chemistry with rare-earths still remains virtually unexplored.[13]

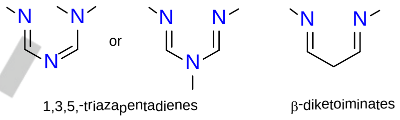


Figure 1. Key structural motifs of 1,3,5-triazapentadienes (*tap*) and isoelectronic counterpart β-diketoiminate.

Taps are polyfunctional nitrogen-containing analogues of pentadienes having unsaturated NCNCN fragment formed by formally fused amidine, imide and amine functions, capable of saturation of the metal center coordination environment.[13a] 1,3,5-Triazapentadienyl ligands have many advantages, such as large variety of possibilities for their geometry design and modification of steric and electronic properties by introducing different substituents onto nitrogen and carbon atoms of the NCNCN fragment. In addition, 1,3,5-triazapentadienyl ligands have three basic nitrogen sites for coordination with metal ion[14] (Fig. 2). However, no example of the application of 1,3,5-triazapentadienyl ligands in the synthesis of rare-earth metal complexes is known so far.

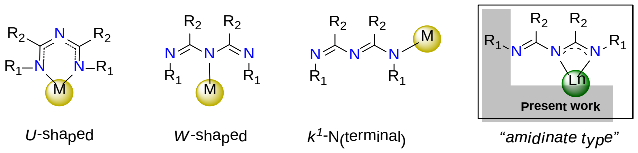


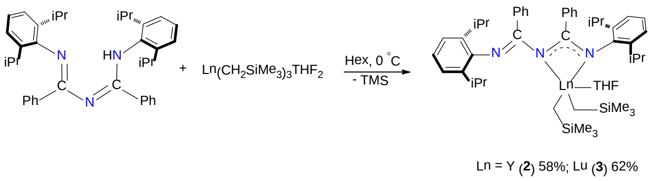
Figure 2. The coordination types of 1,3,5-triazapentadienyl ligands.

We report here on the synthesis and characterization of rare-earth alkyl complexes coordinated by 1,3,5-triazapentadienyl ligand. The synthesized compounds were scrutinized as pre-catalysts in reactions of isoprene polymerization and hydrosilylation of multiple C–C bonds.

Results and Discussion

Synthesis and characterization of complexes 2-4

1,3,5-Triazapentadiene 2,6-$iPr_2C_6H_3NC(Ph)NC(Ph)NHC_6H_3iPr_2$-2,6 (**1**) was synthesized according to the previously published method developed by Ley and Müller[15] in 1907. For the synthesis of bis(alkyl) rare-earth complexes supported by 1,3,5-triazapentadienyl ligand the alkane elimination approach was employed. The preparative-scale reactions of $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Lu) with equimolar amounts of **1** were carried out at 0°C in hexane and afforded bis(alkyl) derivatives [2,6-$iPr_2C_6H_3NC(Ph)NC(Ph)NC_6H_3iPr_2$-2,6]$Ln(CH_2SiMe_3)_2$(THF) (Ln = Y (**2**), Lu (**3**)) (Scheme 1). Bis(alkyl) complexes **2** and **3** were isolated as bright-yellow microcrystalline solids in 58 and 62 % yields, respectively. Complexes **2** and **3** are air-and moisture-sensitive, well-soluble in benzene, toluene and hexane.



Scheme 1. Synthesis of **2** and **3**.

The complexes **2** and **3** were characterized by ^1H and $^{13}C\{^1H\}$ spectroscopy. In the ^1H NMR spectra of **2** and **3**, the methylene protons of the alkyl groups attached to the metal ion appear as broadened singlets at −0.20 and −0.29 ppm, respectively. In the $^{13}C\{^1H\}$ spectrum, the appropriate carbons give rise to a doublet at 37.1 ($^1J_{Y,C}$ = 38.4 Hz) for **2**, while for the lutetium complex **3** they appear as a singlet at 46.3 ppm (see Experimental section for NMR details and Figs. S1–S4). The methyl protons of $SiMe_3$ groups give rise to the singlets in the ^1H NMR spectra of complexes **2** and **3** with chemical shifts 0.36 (**2**) and 0.37 (**3**) ppm, respectively. Two doublets with chemical shifts δ 0.98 ($^3J_{H\text{-}H}$ = 6.8 Hz), 1.32 ($^3J_{H\text{-}H}$ = 6.8 Hz) (for **2**) and δ 1.01 ($^3J_{H\text{-}H}$ = 5.6 Hz), 1.23 ($^3J_{H\text{-}H}$ = 5.6 Hz) (for **3**) ppm correspond to the methyl protons of iPr groups. The methine hydrogen atoms of the iPr groups appear as one septet at 3.45 ($^3J_{H\text{-}H}$ = 6.8 Hz) ppm for **2** and one multiplet at 3.37 ppm for **3**. The aromatic region of the spectrum of **2** contains a pattern of two multiplets at δ 6.60 and 7.00 ppm, a triplet at δ 6.67 ($^3J_{H\text{–}H}$ = 7.5 Hz) ppm and a doublet at δ 7.10 ($^3J_{H\text{–}H}$ = 7.5 Hz) ppm. In the case of **3**, aromatic protons appear as a set of multiplets in the low field region (6.71–7.34 ppm).

Thermostabilities of diamagnetic bis(alkyl) complexes **2** and **3** were evaluated. Complex **3** demonstrated rather good thermostability (in the scale appropriate for hydrocarbyl derivatives of rare-earths): in dry and degassed benzene-d_6 solution at room temperature no apparent decomposition was detected during 2 months. However, when heated in a benzene-d_6 solution to 60 °C **3** has a half-life time of 6 h. Yttrium complex **2** was found to be less stable with half-life time about 12 hours at 25 °C in benzene-d_6 solution. The process of decomposition of **2** is accompanied by the color change from yellow to bright red. Decompositions of **2** and **3** occur with the elimination of $SiMe_4$, unfortunately all the trials to isolate any metal containing products failed.

The bright-yellow crystals of complex **3** suitable for X-ray diffraction study were obtained by continuous cooling of the hexane solution at −20 °C. Complex **3** crystallizes in orthorhombic P*bca* space group with unique molecule of complex in the asymmetric unit (Fig. 3). The crystallographic data and structure refinement details are given in Table 1.

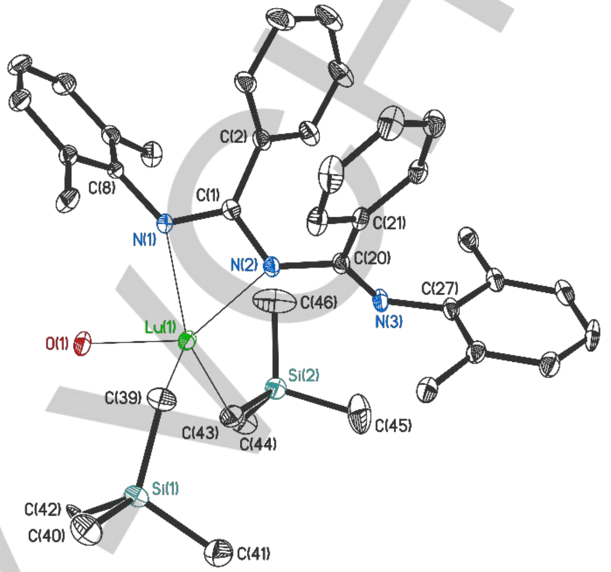


Figure 3. Molecular structure of **3**. Thermal ellipsoids are drawn at the 30% probability level. Me groups of the iPr substituents, CH_2 fragments of THF molecule and all hydrogen atoms are omitted for clarity.

The X-ray single crystal diffraction study of compound **3** revealed that the lutetium atom is bound with two nitrogen atoms of 1,3,5-triazapentadienyl ligand, two carbon atoms of the alkyl groups and one oxygen atom of the THF molecule. Thus, the formal coordination number of Lu cation is 5. It should be noted that in **3** an unusual bonding mode of the 1,3,5-triazapentadienyl ligand with metal ion is realized. In complexes of transition metals, the *tap* ligands either coordinate to metal centers in κ^2-N,N mode forming six-membered NCNCNM metallocycles[16] or bind only *via* one nitrogen atom in κ^1-N fashion resulting in W–shaped type or linear structures.[17] In contrast, in complex **3** previously unknown κ^2-N,N'-amidinate type of coordination of the *tap* ligand was discovered. Only two neighboring nitrogen atoms are involved into the metal-ligand interaction leading to the formation of a four-membered metallocycle, while the attached imino group remains pendant. The alkyl groups are arranged on opposite sides from the LuNCN plane; apparently, to minimize the interaction with 2,6-$iPr_2C_6H_3$ group. The Lu–N bonds in **3** (Lu(1)-N(1) 2.371(3) Å, Lu(1)-N(2) 2.264(3) Å) fall into the range typical for lutetium complexes supported by amidinate ligands [CyC(N-2,6-$iPr_2C_6H_3)_2$]$Lu(CH_2SiMe_3)_2$(THF) (2.317(3), 2.308(3) Å);[18] {2-[Ph_2P=O]$C_6H_4NC(tBu)N$(2,6-$iPr_2C_6H_3$)}$Lu(CH_2SiMe_3)_2$ (2.361(3), 2.343(3) Å).[9b] However, unlike the most amidinate complexes in which M-N bonds have close lengths, in **3** these bonds differ noticeably similarly to lutetium complex 2,6-$iPrC_6H_3NC(C_6H_5)NHCH_2CH_2(NCHCHN(C_6H_2Me_3$-2,4,6)CH)$Lu(CH_2SiMe_3)_2$ (2.352(3), 2.260(4) Å)[19]. At the same time, the C-N bond lengths in the amidinate fragment also slightly differ from each other (C(1)-N(1) 1.322(5) Å, C(1)-N(2) 1.357(5) Å), but still indicate delocalization of negative charge along the NCN fragment. The four-membered LuNCN cycle in **3** adopts nearly planar structure – the dihedral angle between the NLuN and NCN planes is 168.1(5)°.

Table 1. Selected bond lengths (*d*) and bond angles (*ω*) in complexes **3** (Lu) and **4** (Sc)*.

Compound	Bond	d/Å	Angle	ω/deg
3	Lu(1)-N(1)	2.371(3)	N(2)-Lu(1)-N(1)	57.9(2)
	Lu(1)-N(2)	2.264(3)	C(39)-Lu(1)-N(1)	101.9(2)
	N(1)-C(1)	1.322(5)	C(43)-Lu(1)-N(1)	107.7(2)
	N(2)-C(1)	1.357(5)	C(39)-Lu(1)-N(2)	101.5(2)
	N(2)-C(20)	1.390(5)	C(43)-Lu(1)-C(39)	107.5(2)
	N(3)-C(20)	1.270(5)	N(1)-C(1)-N(2)	113.9(3)
	N(3)-C(27)	1.414(5)	N(3)-C(20)-N(2)	117.1(3)
	Lu(1)-C(39)	2.390(7)	C(1)-N(1)-C(8)	121.0(3)
	Lu(1)-C(43)	2.275(7)	C(1)-N(2)-C(20)	121.6(3)
	Lu(1)-O(1)	2.275(3)	C(20)-N(3)-C(27)	122.8(3)
4	Sc(1)–N(1)	2.242(2)	N(1)–Sc(1)–N(2)	62.52(5)
	Sc(1)–N(2)	2.185(2)	N(2)–Sc(1)–N(2A)	84.64(6)
	Sc(1)–N(2A)	2.031(2)	N(1)–Sc(1)–C(20)	112.27(6)
	Sc(1)–C(20)	2.229(2)	N(2)–Sc(1)–C(20)	115.86(6)
	Sc(1)–O(1)	2.171(2)	N(1)–C(1)–N(2)	118.4(2)
	Sc(1)…Sc(1A)	3.1189(6)	C(1)–N(1)–C(8)	122.9(2)
	C(1)–N(1)	1.354(2)		
	C(1)–N(2)	1.321(2)		

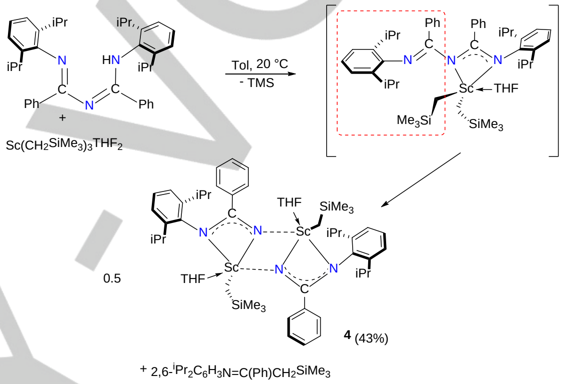
*)Symmetry transformations used to generate equivalent atoms in 4 is #1 -x+2,-y+1,-z

The Lu–C bonds lengths in **3** ((2.275(7)-2.390(7) Å) are comparable to the values previously measured in the related complexes [CyC(N-2,6-$iPr_2C_6H_3)_2$]Lu($CH_2SiMe_3)_2$(THF) (2.328(4), 2.327(4) Å);[18] [2,6-$iPrC_6H_3NC(C_6H_5)NHCH_2CH_2(NCHCHN(C_6H_2Me_3$-2,4,6)CH)]Lu($CH_2SiMe_3)_2$ (2.337(5), 2.359(5) Å),[19] {2-[Ph_2P=O]C_6H_4NC(tBu)N(2,6-$iPr_2C_6H_3$)}Lu($CH_2SiMe_3)_2$ (2.317(4), 2.360(4) Å).[9b] The Lu–O bond length in **3** (2.275(3) Å) is close to the distances in the formerly reported five-coordinate compounds CyC(N-2,6-$iPr_2C_6H_3)_2$]Lu($CH_2SiMe_3)_2$(THF) (2.315(3) Å);[18] [NPN]Lu(CH_2SiMe_3)(THF) (2.303(2) Å).[20]

It is noteworthy that, despite specific type of coordination of the *tap* ligand in crystalline state, in the ^{1}H NMR spectrum of complex **3** in benzene-d_6 the ligand appears as a single set of signals. The variable temperature ^{1}H NMR study of **3** in toluene-d_8 in the temperature range 213-293 K did not reveal dynamic process, most likely due to its high rate in NMR time-scale.

Although all our attempts to obtain crystals of **2** suitable for X–ray studies failed, the composition of the complex was unambiguously determined by means of spectroscopic methods and microanalysis (see ESI).

Similarly to **2** and **3**, the alkane elimination approach was used for the synthesis of bis(alkyl) complex of scandium. Surprisingly, the reaction of **1** with Sc($CH_2SiMe_3)_3(THF)_2$ in toluene at 20 °C is accompanied by the cleavage of one C−N bond of 1,3,5-triazapentadiene and affords a dimeric mono(alkyl) complex [{μ^2-$iPr_2C_6H_3$NC(Ph)N}Sc(CH_2SiMe_3)(THF)]$_2$ (**4**) coordinated by μ^2-bridging dianionic amidinate ligand (Scheme 2). Compound **4** was isolated in 43% yield as highly air- and moisture-sensitive light-yellow crystals. The reactions of **1** with Sc($CH_2SiMe_3)_3(THF)_2$ in toluene at -78 °C and in THF also afforded **4**.



Scheme 2. Synthesis of **4**.

The isolated complex **4** proved to be thermally stable: in benzene-d_6 solution at 20 °C no evidence of decomposition was observed during 2 weeks. Even after heating **4** at 60 °C during 6 h (benzene-d_6,) no decomposition took place. In the ^{1}H NMR spectrum of **4**, the methylene protons of the CH_2SiMe_3 appear as two broad peaks at 0.50 and 0.55 ppm. The carbons from the same methylene fragments give rise to a slightly broadened singlet in the ^{13}C NMR spectrum of **4** at δ_C = 47.0 ppm (see Experimental section for NMR details and Figs. S5–S6). The methyl protons of $SiMe_3$ groups give rise to a singlet in the ^{1}H NMR spectrum with chemical shift 0.35 ppm. The methyl protons of the iPr groups give rise to two doublets at 0.99 ($^3J_{H\text{-}H}$ = 6.8 Hz) and 1.26 ($^3J_{H\text{-}H}$ = 6.8 Hz) ppm. The methine hydrogen atoms of the iPr groups appear as one septet at 3.40 ($^3J_{H\text{-}H}$ = 6.8 Hz) ppm. The aromatic region of the spectrum contains a pattern of doublet at δ 7.35 ($^3J_{H\text{-}H}$ = 8.2 Hz) ppm and two multiplets at δ 7.00 and in the range of δ 6.64–6.84 ppm.

The NMR scale reaction of **1** with Sc($CH_2SiMe_3)_3(THF)_2$ performed in benzene-d_6 at room temperature allowed to observe (besides the signals of **4** mentioned above) additional peaks corresponding to the by-product 2,6-$iPr_2C_6H_3N$=C(Ph)CH_2SiMe_3 (see ESI). The reaction supposedly proceeds *via* the formation of a bis(alkyl) intermediate (Scheme 2), however, no evidence of this was obtained by means of ^{1}H NMR spectroscopy. A molecular peak with m/z 351.6 corresponding to $iPr_2C_6H_3$NC(Ph)CH_2SiMe_3 was detected in the mass spectrum of the reaction mixture after isolation of crystals of **4** (see ESI).

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Slow concentration of the saturated toluene solution of **4** at room temperature allowed for obtaining samples suitable for single crystal X-ray diffraction study. Complex **4** crystallizes in triclinic *P-1* space group with two structurally independent molecules in the unit cell. Each of the molecules is located at the inversion center. The geometric parameters of the molecules are close to each other, so below we discuss the bond lengths and angles of only one of them. X-ray analysis revealed that **4** adopts a dimeric structure (Fig. 4). Each scandium atom is bound with three nitrogen atoms of two amidinate groups: two of one chelating κ^2-amidinate ligand, and one μ^2-bridging nitrogen atom of other amidinate ligand. Moreover, Sc^{3+} is bound with one carbon atom of the alkyl group and an oxygen atom from a THF molecule. Thus, the formal coordination number of scandium cation is five.

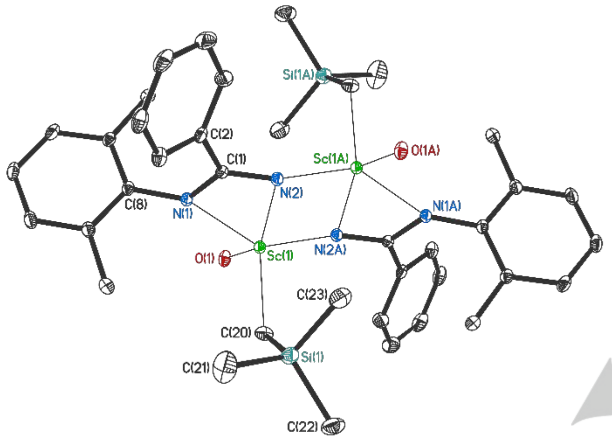


Figure 4. Molecular structure of **4**. Thermal ellipsoids are drawn at the 30% probability level. Me groups of the iPr substituents, CH_2 fragments of THF molecules and all hydrogen atoms are omitted for clarity.

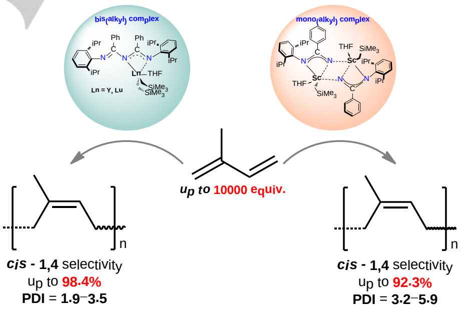
The bond lengths between Sc ions and nitrogen atoms of chelating κ^2-amidinate ligand in **4** are noticeably different (2.185(2) and 2.242(2) Å), but both have values close to those measured in the related scandium complex $[PhC(NC_6H_3iPr_2\text{-}2,6)_2]Sc(CH_2SiMe_3)_2(THF)$ (2.198(2) and 2.215(2) Å).[21] As in **3**, the C-N bond lengths in the amidine fragment also slightly differ from each other 1.321(2), 1.354(2) Å. The four-membered ScNCN cycle in **4** adopts nearly planar structure – the dihedral angle between the NScN and NCN planes is 166.2(2)°.

It should be noted that complex **4** also contains the μ^2-Sc–N bonds (2.031(3) Å), which are significantly shorter than the Sc–$N_{amidinate}$ bonds. The μ^2-Sc–N bond lengths in **4** (2.031(2) Å) are shorter than the values measured in dimeric scandium complex comprising μ^3-bridging nitrogen atom $[MeC(N(2,6\text{-}(iPr)_2C_6H_3))CHCMe(NCH_2CH_2NMe)ScNH(2,6\text{-}(iPr)_2C_6H_3)]_2$ (2.205(3) and 2.212(3) Å).[22] The Sc–C bond lengths in **4** (2.229(2) Å) is comparable with those found in pentacoordinate scandium bis(alkyl) derivatives coordinated by amidopyridinate $Ap^*Sc(CH_2SiMe_3)_2(THF)$ (2.207(4) and 2.229(4) Å)[23] and benzamidinate ligands $[PhC(NC_6H_3iPr_2\text{-}2,6)_2]Sc(CH_2SiMe_3)_2(THF)$ (2.195(3) and 2.229(3) Å).[21] The Sc–O bond distance in **4** (2.171(2) Å) is close to the distance measured in the formerly reported five-coordinate compounds $Ap^*Sc(CH_2SiMe_3)_2(THF)$ (2.194(3) Å)[23] $[PhC(NC_6H_3iPr_2\text{-}2,6)_2]Sc(CH_2SiMe_3)_2(THF)$ (2.203(2) Å).[21]

Catalytic activity of complexes 2-4 in isoprene polymerization and hydrosilylation of double and triple C-C bonds

Cis-1,4 stereoregular polyisoprene (PIP) is known as one of the most important elastomers used for production of tires and other elastic materials. Generally, single-component neutral organo-rare-earth compounds are inactive in polymerization of conjugated dienes.[24] However, in the presence of co-catalysts, such as aluminum alkyls and organoborates, highly reactive initiator systems for regio- and/or stereoselective polymerization of conjugated dienes are formed.[11a,25] Structure and electronic properties of the "supporting" ligands, ion size and nature of lanthanide metal as well as co-catalysts are among the factors dramatically affecting both activity and selectivity of the catalytic systems and proved to be useful tools for providing control of the polymerization.[24a,25a,26]

Catalytic activity of complexes **2**–**4** in isoprene polymerization was evaluated at room temperature in toluene. The results of the catalytic tests are summarized in Table 2. The complexes **2**–**4**, as well as the binary systems **2**–**4**/$AliBu_3$, **2**–**4**/$[Ph_3C][B(C_6F_5)_4]$, **2**–**4**/$[PhNHMe_2][B(C_6F_5)_4]$ performed no activity. However, when **2** and **3** were activated with borate ($[Ph_3C][B(C_6F_5)_4]$ or $[PhNHMe_2][B(C_6F_5)_4]$) and $AliBu_3$ (1:1:10 molar ratio) (Table 2, Entries 3–5, 7–9,12–14, 16–18) the resulting ternary systems were found to enable isoprene polymerization and to provide 91–100% conversion of 10000 equiv. of monomer within the period of 24 h (Scheme 3).



Scheme 3. Selective polymerization of isoprene catalyzedby ternary systems (**2**-**4**)/borate/$AliBu_3$.

Mono(alkyl) scandium complex **4** provides higher reaction rate: when the ternary systems containing **4** (**4**/$[Ph_3C][B(C_6F_5)_4]$, $[PhNHMe_2][B(C_6F_5)_4]$/10$AliBu_3$) were applied, only 0.2-1.0 h were needed to convert into a polymer 10000 equivalents of monomer with quantitative conversions (see Table 2, Entries 21–23, 25–27).

The systems **2**–**3**/$[Ph_3C][B(C_6F_5)_4]$, $[PhNHMe_2][B(C_6F_5)_4]$/10 Al^iBu_3 afford the PIPs having similar microstructures, predominantly composed of *cis*-1,4 and 3,4-units (see Entry 3–5, 7–9, 12–14, 16–18). No *trans*-1,4 units were detected in the synthesized PIPs. The ternary catalytic systems (**2**–**3**/$[Ph_3C][B(C_6F_5)_4]$, $[PhNHMe_2][B(C_6F_5)_4]$/10$AliBu_3$) provide the formation of polymers featuring moderate molecular weight distributions (M_w/M_n = 1.9–3.5). It is noteworthy that the system (**2**/$[PhNHMe_2][B(C_6F_5)_4]$/10$AliBu_3$) provides content of *cis*-1,4

Table 2. Catalytic tests in isoprene polymerization initiated by systems (**2**–**4**)/borate/AliBu$_3$. (borate: [Ph$_3$C][B(C$_6$F$_5$)$_4$] (TB), [PhNHMe$_2$][B(C$_6$F$_5$)$_4$] (HNB), [Ln]/[borate]/[AliBu$_3$] = 1/1/10).[a]

Entry	Cat	[Ln]/[IP]	Borate	AlR$_3$	t(h)[b]	Conv. (%)	M_n×10^{-3}[c]	M_w/M_n[c]	1,4-*cis* (%)[d]	1,4-*trans* (%)[d]	3,4 (%)[d]
1	**2**	1/1000	—	Al*i*Bu$_3$	48	trace	—	—	—	—	—
2	**2**	1/1000	HNB	—	48	trace	—	—	—	—	—
3	**2**	1/1000	HNB	Al*i*Bu$_3$	1	100	24.7	2.4	73.3	—	26.7
4	**2**	1/5000	HNB	Al*i*Bu$_3$	4	100	91.5	2.6	77.4	—	22.6
5	**2**	1/10000	HNB	Al*i*Bu$_3$	48	100	152.5	2.0	89.5	—	10.5
6	**2**	1/1000	TB	—	48	trace	—	—	—	—	—
7	**2**	1/1000	TB	Al*i*Bu$_3$	1	98	52.2	2.1	79.5	—	20.5
8	**2**	1/5000	TB	Al*i*Bu$_3$	4	100	74.3	2.0	79.9	—	20.1
9	**2**	1/10000	TB	Al*i*Bu$_3$	24	100	93.1	1.9	81.5	—	18.5
10	**3**	1/1000	—	Al*i*Bu$_3$	48	trace	—	—	—	—	—
11	**3**	1/1000	HNB	—	48	trace	—	—	—	—	—
12	**3**	1/1000	HNB	Al*i*Bu$_3$	1	91	92.2	3.1	66.3	—	33.7
13	**3**	1/5000	HNB	Al*i*Bu$_3$	4	100	291.3	3.5	77.9	—	22.1
14	**3**	1/10000	HNB	Al*i*Bu$_3$	24	100	471.1	3.0	98.4	—	1.6
15	**3**	1/1000	TB	—	48	trace	—	—	—	—	—
16	**3**	1/1000	TB	Al*i*Bu$_3$	1	99	85.8	2.3	67.2	—	32.8
17	**3**	1/5000	TB	Al*i*Bu$_3$	4	100	178.4	2.2	82.6	—	17.4
18	**3**	1/10000	TB	Al*i*Bu$_3$	24	100	248.3	2.1	94.9	—	5.1
19	**4**	1/1000	—	Al*i*Bu$_3$	48	trace	—	—	—	—	—
20	**4**	1/1000	HNB	—	48	trace	—	—	—	—	—
21	**4**	1/1000	HNB	Al*i*Bu$_3$	0.2	92	133.5	5.5	87.7	4.9	7.4
22	**4**	1/5000	HNB	Al*i*Bu$_3$	0.5	95	469.8	3.4	90.1	4.5	5.4
23	**4**	1/10000	HNB	Al*i*Bu$_3$	1	100	871.6	5.5	92.3	2.9	4.8
24	**4**	1/1000	TB	—	48	trace	—	—	—	—	—
25	**4**	1/1000	TB	Al*i*Bu$_3$	0.2	90	125.6	5.9	78.3	7.9	13.8
26	**4**	1/5000	TB	Al*i*Bu$_3$	0.5	93	493.7	3.2	81.8	8.7	9.5
27	**4**	1/10000	TB	Al*i*Bu$_3$	1	99	955.9	5.6	88.9	3.9	7.2

[a] Conditions: complex (10 μmol) in toluene, [M]:[Borate]:[AliBu$_3$] = 1/1/10, (T = 20 °C, Borate: [Ph$_3$C][B(C$_6$F$_5$)$_4$] (TB), [PhNHMe$_2$][B(C$_6$F$_5$)$_4$] (HNB)). [b] Reaction times are not optimized. [c]M_n determined by GPC against polystyrene standard. [d]Determined by ^{1}H NMR and ^{13}C{^{1}H} NMR spectroscopy in CDCl$_3$ at rt.

units up to 89.5% (Entries 3–5). The use of [Ph$_3$C][B(C$_6$F$_5$)$_4$] leads to a slight decrease of *cis*-1,4 selectivity to 81.5% (Entries 7–9). Lutetium complex **3** turned out to be more selective than its yttrium counterpart **2**. The system (**3**/[PhNHMe$_2$][B(C$_6$F$_5$)$_4$]/10 AliBu$_3$) allows to obtain PIPs containing up to 98.4% of *cis*-1,4 units, therefore providing the best selectivity (Entries 12–14).

Application of [Ph$_3$C][B(C$_6$F$_5$)$_4$] provides polyisoprenes with the *cis*-1,4 units content up to 94.9% (Entries 16–18). Ternary systems including bis(alkyl) yttrium and lutetium complexes make it possible to obtain polymers with molecular weights 85.8–471.1×10^3 for complex **3** and 24.7–152.5×10^3 for complex **2**. The ternary catalytic systems based on mono(alkyl) complex **4**, unlike bis(alkyl) complexes **2** and **3**, afford polymeric chains composed of *cis*-1,4, *trans*-1,4 and 3,4-units (see Entries21–23, 25–27). These ternary catalytic systems (**4**/[Ph$_3$C][B(C$_6$F$_5$)$_4$],

$[PhNHMe_2][B(C_6F_5)_4]/10AliBu_3$) produce polymer samples with relatively broad molecular weight distribution (M_w/M_n = 3.2–5.9). Ternary catalytic systems based on compound **4** (**4**/$[Ph_3C][B(C_6F_5)_4]$, $[PhNHMe_2][B(C_6F_5)_4]/10AliBu_3$) demonstrate rather high *cis*-1,4 selectivity (78.3–92.3%). Polymer samples obtained with the system (**4**/$[Ph_3C][B(C_6F_5)_4]$/10 $AliBu_3$) contain up to 88.9% of *cis*-1,4 units (Entries 25–27). In the case of the catalytic system with $[PhNHMe_2][B(C_6F_5)_4]$, the content of *cis*-1,4 units is somewhat higher (92.3%) (Entries 21–23). The ternary systems containing compound **4** make it possible to obtain polyisoprenes with high molecular weights (125.6–955.9×10^3). In the case of compounds **2**–**4**, the nature of the borate also had a significant influence on the molecular weight distribution of the resulting polyisoprene. In the case of complexes **2** and **3**, switching from $[Ph_3C][B(C_6F_5)_4]$ to $[PhNHMe_2][B(C_6F_5)_4]$ leads to the increase in the polydispersity index from 2.1 to 2.6 (for **2**, Table 2, Entries 3–5, 7–9) and from 2.3 to 3.5 (for **3**, Table 2, Entries 12–14, 16–18). However, in the case of **4** we observed the opposite pattern: the replacement of $[PhNHMe_2][B(C_6F_5)_4]$ with $[Ph_3C][B(C_6F_5)_4]$ leads to the slight increase in the polydispersity index from 5.5 to 5.9 (Table 2, Entries 21–23, 25–27). Ternary catalytic systems (**2**–**4**/$[Ph_3C][B(C_6F_5)_4]$, $[PhNHMe_2][B(C_6F_5)_4]/10AliBu_3$) enable regio- and stereoselective polymerization process allowing for the formation of polyisoprenes containing predominantly *cis*-1,4-units (66.3–98.4%). In our previous studies, bis(alkyl) complexes $\{2\text{-}[Ph_2P{=}O]C_6H_4NC(tBu)N(2,6\text{-}iPr_2C_6H_3)\}Ln(CH_2SiMe_3)_2$ (Ln = Y, Lu, Er) coordinated by tridentate amidinate ligand were investigated.[9b] Ternary systems ($\{2\text{-}[Ph_2P{=}O]C_6H_4NC(tBu)N(2,6\text{-}iPr_2C_6H_3)\}Ln(CH_2SiMe_3)_2$/ $[Ph_3C][B(C_6F_5)_4]$, $[PhNHMe_2][B(C_6F_5)_4]/10AliBu_3$) allow to reach quantitative conversion of up to 10000 equiv. of monomer with higher reaction rate (2 h) compared to the systems based on complexes **2** and **3**. The catalytic systems based on complexes $\{2\text{-}[Ph_2P{=}O]C_6H_4NC(tBu)N(2,6\text{-}iPr_2C_6H_3)\}Ln(CH_2SiMe_3)_2$ produce predominantly *cis*-1,4 polyisoprene (up to 98.5 %), which is comparable to the results obtained for the systems containing bis(alkyl) complexes **2**–**3** (*cis*-1,4-units up to 98.4%).

In order to elucidate the catalytically active species forming in the ternary systems and initiating isoprene polymerization, a series of NMR-tube reactions was carried out under control of ^1H NMR. It was found that in the reaction of **3** with an equimolar amount of $[Ph_3C][B(C_6F_5)_4]$ in benzene-d_6 no elimination of Ph_3CH (δ 5.41 ppm) and 1,3,5-triazapentadiene took place. However, the appearance of cationic monoalkyl species $[\{iPr_2C_6H_3NC(Ph)NC(Ph)NC_6H_3iPr_2\}Lu(CH_2SiMe_3)(THF)_x][B(C_6F_5)_4]$ and $Ph_3CCH_2SiMe_3$ were detected in the reaction mixture (see ESI).

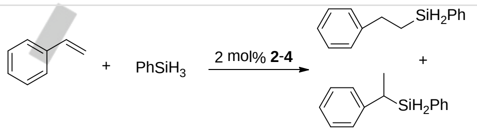
The ^1H NMR spectrum of the reaction of **3** with $[Ph_3C][B(C_6F_5)_4]$ and 5 equiv. of $AliBu_3$ in benzene-d_6 presents a complex set of signals. Overlapping of the signals of iBu_3 and 1,3,5-triazapentadiene hampers an unambiguous signal assignment. However, one can state that no transfer of *tap* ligand from Lu to Al occurs since the ^1H NMR spectrum of the product of the reaction of $AliBu_3$ with 1,3,5-triazapentadiene presents a set of signals distinct from that characteristic for **3**. The THF molecule most likely remains coordinated with Lu ion and does not migrate to Al as it is evidenced by invariability of chemical shifts of the corresponding signals. Similarly, to the system described in the paper of Cui[26c] the formation of Ph_3CH and isobutene was observed. The ^{11}B NMR spectrum of this reaction mixture presents a single singlet at δ −15.9 ppm. All these findings are in agreement with the previously proposed scheme.[25b,26c,27]

After hydrolysis of the reaction mixture the parent 1,3,5-triazapentadiene $iPr_2C_6H_3NC(Ph)NC(Ph)NHC_6H_3iPr_2$ was isolated in quantitative yield, no product of alkylation of the pendant C=N bond resulting from the addition of $AliBu_3$ was detected in the reaction mixture.

It should be noted that the ternary systems **2**–**4**/$[Ph_3C][B(C_6F_5)_4]/10AliBu_3$ were inactive in the polymerization of α-olefins.

Hydrosilylation of alkenes is an important approach for the production of organosilanes[28] and during the past three decades the possibility of application of rare-earth metal complexes for catalysis of this transformation was extensively studied.[29] Alkyl, hydrido and amido rare-earth complexes supported by a variety of cyclopentadienyl and "post-metallocene" ligands demonstrated their high potential as pre-catalysts of this useful reaction.[28e,29b]

Table 3. Hydrosilylation of styrene with $PhSiH_3$ catalyzed by complexes **2**–**4**. Optimization of the reaction conditions.[a]



Entry[a]	Cat.	t(h)	Solvent	T °C	Conv. (%)[b]	Selectivity (%)[c] 1,2- /2,1-
1	**2**	1	benzene-d_6	20	23	n.d.
2	**2**	6	benzene-d_6	20	78	n.d.
3	**2**	12	benzene-d_6	20	>99	0 / >99
4	**2**	12	pyridine	20	<5	—
5	**2**	12	THF	20	22	0 / >99
6	**2**	12	toluene	20	>99	0 / >99
7	**2**	6	toluene	60	84	0 / >99
8	**2**	6	neat	60	88	0 / >99
9	**3**	12	benzene-d_6	20	>99	0 / >99
10	**3**	12	THF	20	27	0 / >99
11	**3**	6	toluene	60	86	0 / >99
12	**3**	6	neat	60	91	0 / >99
13	**4**	12	benzene-d_6	20	91	18 / 82
14	**4**	12	pyridine	20	0	—
15	**4**	12	THF	20	<2	—
16	**4**	12	toluene	20	87	20 / 80
17	**4**	6	toluene	60	76	21 / 79

18	**4**	6	neat	60	85	26 / 74

[a]Reactions were carried out on a scale of 1 mmol of $PhSiH_3$ and 1mmol of styrene, in the presence of 2 mol % catalyst, in 1 mL of solvent. [b]Conversion was estimated based on integration of the ^1H NMR spectrum. [c]The ratio of 1,2- and 2,1-regioisomers was calculated by integration of the resonances in the ^1H NMR spectra, set according to previously published.[30]

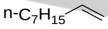
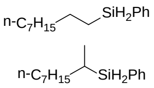
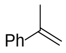
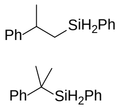
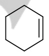
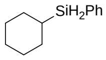
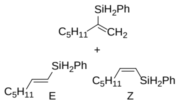
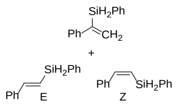
In contrast to the platinum group metals, rare-earth catalysts promote hydrosilylation of alkenes without side reactions, such as isomerization and dehydrogenative silylation.

Complexes **2**–**4** were evaluated as pre-catalysts for addition of $PhSiH_3$ to styrene. The results are summarized in Table 3. The catalytic reactions in benzene-d_6 and toluene were carried out in the presence of 2 mol % of catalyst at 20 °C and result in 87–99% conversion in 12 h (Entries 3, 6, 9, 13, 16). Catalytic activity in coordinating solvent (THF or pyridine) proved to be much lower and under analogous conditions the reactions in 12 h achieved 2–27% conversions (Entries 4, 5, 10, 14, 15). Monitoring the addition of $PhSiH_3$ to styrene under solvent-free conditions or in toluene solution at 60 °C showed that 84–91% conversions could be reached in 12 h (see Table 3, Entries 7, 8, 11, 12, 17, 18). Bis(alkyl) complexes **2** and **3** exhibit high regioselectivity and provide the formation of the Markovnikov (2,1) addition product $PhHC(SiH_2Ph)Me$[30] in >99% yield (Table 3, Entries 3, 5–12). Complex **4** leads to the formation of a mixture of products with a marked predominance of a Markovnikov addition product (74–82%, entries 13, 16–18). Such a regioselectivity in styrene hydrosilylation is normally rationalized in terms of η^n-coordination between the Lewis acidic/electrophilic metal center and π-electron system of styrene, directing the insertion reaction toward the α-phenylalkyl intermediate.[29b,30]

Complexes **2** and **3** proved to be slightly more active than mono(alkyl) Sc complex **4** (Table 3, entries 3, 9, 13). It should also be noted that the scandium compound **4** provided less regioselective formation of the Markovnikov addition product (2,1) with a yield of up to 82% compared to compounds **2**–**3** (> 99%). The related yttrium bis(alkyl) complex $[PhC(NC_6H_3iPr\text{-}2,6)_2]Y(CH_2SiMe_3)_2(THF)$ containing amidinate ligand was reported to catalyze hydrosilylation of styrene with $PhSiH_3$ (1:1 ratio) in benzene-d_6 solution. Quantitative yield was achieved in 190 min at 80 °C.[31] Complex $[PhC(NC_6H_3iPr\text{-}2,6)_2]Y(CH_2SiMe_3)_2(THF)$ provides predominantly the formation of the Markovnikov (2,1) addition product $PhHC(SiH_2Ph)Me$ in 77% yield, while in the presence of compounds **2**–**3** the reaction proceeds in a more regioselective manner affording the Markovnikov addition product (2,1) in quantitative yield (> 99%). In hydrosilylation of 1-nonene with $PhSiH_3$ in benzene-d_6 catalyzed by complexes **2**–**3** quantitative yield is achieved in 12 h at room temperature[32a]. The results are presented in the Table 4. In the case of complex **2**, mainly anti-Markovnikov (1,2) addition product is formed in 79% yield (entry 1). Lutetium complex **3** provides the formation of anti-Markovnikov (1,2) addition product even in higher yield (86%, entry 2), while Sc complex **4** performed the highest selectivity: in 12 h 87% conversion was reached with >99% regioselectivity of the formation of anti-Markovnikov (1,2) addition product (entry 3).

Complexes **2** and **3** enable addition of $PhSiH_3$ to 1,1-disubstituted C=C bond of α-methylstyrene, however, the reactions predictably turned out to be much slower than with styrene. For complex **2**, the catalytic reaction proceeded with 27% conversion within 24 h showing predominant regioselectivity (83%) of Markovnikov (2,1) addition product (entry 4). Complex **3** demonstrated similar activity, only 32% conversion was reached in 24 h with 73% of Markovnikov (2,1) regioselectivity (entry 5)[32,33]. Compound **4** was found to be inert in the case of α-methylstyrene even at 50 °C (24 h). When cyclohexene was used as a substrate, no hydrosilylation with $PhSiH_3$ in the presence of **2**–**4** was observed for all runs (20 °C, 48 h, entry 7–9)[32h].

Table 4. Hydrosilylation of alkenes and alkynes with $PhSiH_3$ catalyzed by complexes **2**–**4**.[a]

Entry[a]	substrates	Cat.	t (h)	Conv. (%)[b]	products	Selectivity (%)[c] 1,2- /2,1-
1		**2**	12	99		79 / 21
2		**3**		99		86 / 14
3		**4**		87		>99 / 0
4		**2**	24	27		17 / 83
5		**3**		32		27 / 73
6		**4**		0		—
7		**2**	48	0		—
8		**3**		0		—
9		**4**		0		—
10	$n\text{-}C_5H_{11}\!-\!\!\equiv$	**2**	24	98		88 / 12
11		**3**		95		94 / 6
12		**4**		36		83 / 17
13	$Ph\!-\!\!\equiv$	**2**	48	<7		n.d.
14		**3**		<3		n.d.
15		**4**		0		—

[a] Reaction conditions: substrates:silane (1:1), 2 mol% catalyst, 20 °C, benzene-d_6. [b]Calculated by ^1H NMR spectroscopy. [c]The ratio of 1,2- and 2,1-regioisomers was calculated by integration of the resonances in the ^1H NMR spectra or analyzed by GC−MS, set according to previously published.[10a,28e,30d,32,33]

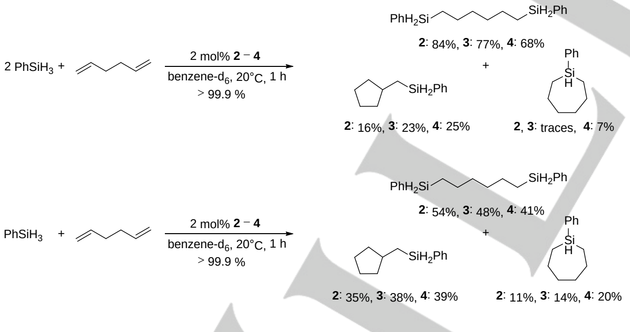
The reactions of 1-heptyne with $PhSiH_3$ in benzene-d_6 (24 h, 20 °C) in the presence of 2 mol % of catalyst result in close-to-complete (98% for **2** and 95% for **3**) conversion (Entries 10, 11). For complex **2**, regioselectivity of anti-Markovnikov (1,2) addition was 88% (entry 10). Lutetium complex **3** provided even higher selectivity (94%) in anti-Markovnikov (1,2) addition (entry 11). Complex **4** demonstrated lower activity, only 36% conversion was reached in 24 h with 83% formation of anti-Markovnikov (1,2) addition product (entry 12)[32d].

Hydrosilylation of phenylacetylene with $PhSiH_3$ catalyzed by complexes **2**–**4** has been also investigated. It was found that complexes **2**–**3** at room temperature performed low activity: 7% conversion was reached in 48 h (Entries 13–14)[32c,32i].

Compound **4** turned out to be inactive in this transformation. Thus, one can conclude that complexes **2**–**4** are more suitable for catalysis of hydrosilylation of double C=C bonds and are less active in the case of acetylenes. This is in line with previously reported observations.[29b,32c] Moreover, it is noteworthy that in the case of the hydrosilylation reaction of alkenes and alkynes (Table 4), higher selectivity of the lutetium complex compared to the yttrium counterpart is observed.

Hydrosilylation of 1,5-hexadiene with $PhSiH_3$ catalyzed by rare-earth complexes is known to be able to afford a series of products: 1,6-bis(phenylsilyl)hexane, 6-phenylsilyl-1-hexene, (phenylsilylmethyl)cyclopentane, phenylsilacycloheptane as well as oligomers.[33] The possible reaction pathways of 1,5-hexadiene hydrosilylation by rare-earth metal catalyst has been formerly proposed.[30e]

Hydrosilylation of 1,5-hexadiene with $PhSiH_3$ (1:2 ratio) in benzene-d_6 at room temperature catalyzed by complexes **2** and **3** was monitored by ^{1}H NMR spectroscopy[30c,30e] and GC−MS. In the case of complex **2**, the reaction leads to the formation of a mixture of products: 1,6-bis(phenylsilyl)hexane (84%) and (phenylsilylmethyl)cyclopentane (16%). Complex **3** also affords a mixture of 1,6-bis(phenylsilyl)hexane (77%) and (phenylsilylmethyl)cyclopentane (23%). Notably, GC–MS also allowed to determine phenylsilacycloheptane in trace amounts (<0.1%) (Scheme 4). However, when the reaction of 1,5-hexadiene with $PhSiH_3$ in the presence of complexes **2** and **3** is performed at 1:1 ratio, we also observe the formation of phenylsilacycloheptane. Hydrosilylation of 1,5-hexadiene with $PhSiH_3$ catalyzed by **2** affords a mixture of 1,6-bis(phenylsilyl)hexane (54%), phenylsilacycloheptane (11%) and (phenylsilylmethyl)cyclopentane (35%). For the complex **3**, a product mixture consisting of 1,6-bis(phenylsilyl)hexane (48%), phenylsilacycloheptane (14%) and (phenylsilylmethyl)cyclopentane (38%) is also formed. So, both compounds **2** and **3** demonstrate similar activity and selectivity in the hydrosilylation of 1,5-hexadiene with $PhSiH_3$.



Scheme 4. Hydrosilylation of 1,5-hexadiene with $PhSiH_3$ catalyzed by alkyl complexes **2**–**4**.

Hydrosilylation of 1,5-hexadiene with $PhSiH_3$ (1:2 ratio) catalyzed by **4** affords a mixture of 1,6-bis(phenylsilyl)hexane (68%), phenylsilacycloheptane (7%) and (phenylsilylmethyl)cyclopentane (25%). When the reaction of 1,5-hexadiene with $PhSiH_3$ in the presence of complex **4** is performed at the 1:1 ratio, we observe the formation of 1,6-bis(phenylsilyl)hexane (41%), phenylsilacycloheptane (20%) and (phenylsilylmethyl)cyclopentane (39%). The composition of the reaction products was determined by ^{1}H NMR[30a,34] and GC−MS.

It was interesting to compare activity and selectivity of the alkyl complexes with those of formerly reported compounds.[28b] Dimeric hydrido yttrium complex $[Y(L)(THF)(\mu\text{-}H)]_2$ (L = $(C_5Me_4CH_2SiMe_2NCMe_3)_2$)[35] with a linked amido-cyclopentadienyl ligand catalyzed hydrosilylation of 1,5-hexadiene with $PhSiH_3$ (1:1 ratio) in hexane, and quantitative yield was achieved in 120 min at 25 °C. For the complex $[Y(L)(THF)(\mu\text{-}H)]_2$, a mixture of products consisting of both linear and cyclized products as well as involatile oligomers was formed. Yttrium alkyl complex $[Y(etbmp)(CH_2SiMe_3)(THF)_n]$[30d] containing tetradentate [OSSO]-type bis(phenolato) ligand was reported to catalyze hydrosilylation of 1,5-hexadiene with $PhSiH_3$ (1:2 ratio, 50 °C, 21 h) yielding predominantly 1,6-bis(phenylsilyl)hexane (90%) and (phenylsilylmethyl)cyclopentane (10%). Compared with the data mentioned above, complexes **2**–**4** proved to be more active pre-catalysts for hydrosilylation of 1,5-hexadiene with $PhSiH_3$ (1:2 ratio, 20 °C, 1 h), however do not provide sufficient control of selectivity.

Conclusion

In summary, new bis(alkyl) complexes $[iPr_2C_6H_3NC(Ph)NC(Ph)NC_6H_3iPr_2]Ln(CH_2SiMe_3)_2(THF)$ (Ln =Y (**2**), Lu (**3**)) coordinated by 1,3,5-triazapentadienyl ligand were synthesized through alkane elimination reaction. X-ray analysis established that in complex **3** the triazapentadienyl ligand coordinates to the Lu^{3+} ion in rather unusual "amidinate" fashion resulting in the formation of a four-membered metallocycle. Surprisingly, the analogous reaction with $Sc(CH_2SiMe_3)_3(THF)_2$ resulted in the cleavage of one C−N bond of 1,3,5-triazapentadiene and afforded a dimeric mono(alkyl) complex $[\{\mu^2\text{-}iPr_2C_6H_3NC(Ph)N\}Sc(CH_2SiMe_3)(THF)]_2$ (**4**) coordinated by μ^2-bridging dianionic amidinate ligand. Complexes **2**–**4** were evaluated as components of ternary catalytic systems Ln/borate/$AliBu_3$ (borate: $[Ph_3C][B(C_6F_5)_4]$ (TB), $[PhNHMe_2][B(C_6F_5)_4]$ (HNB), [Ln]/[borate]/[$AliBu_3$] = 1/1/10) for isoprene polymerization. All obtained polymer samples feature microstructures containing predominantly *cis*–1,4-units (66.3–98.4%). The alkyl complexes **2**–**4** proved to be active in catalysis of olefin hydrosilylation and demonstrated excellent regioselective preference for terminal (1,2) addition to aliphatic olefins and favored internal (2,1) addition in the case of styrene. In hydrosilylation of 1-nonene with $PhSiH_3$ complexes **2**–**3** provide quantitative conversion in 12 h at room temperature with predominant formation of anti-Markovnikov addition product (79–86%). Complex **4** performed slightly lower activity but higher selectivity compared to those of **2**–**3**: in 12 h 87% conversion was reached with >99% regioselectivity in the formation of anti-Markovnikov (1,2) addition product. Complexes **2**–**4** were shown to catalyze efficiently the hydrosilylation of 1,5-hexadiene with $PhSiH_3$ (1:2 ratio) to give a mixture of products, predominantly 1,6-bis(phenylsilyl)hexane (68–84%). When the reaction of 1,5-hexadiene with $PhSiH_3$ in the presence of complexes **2**–**4** is performed at the 1:1 ratio, we observe a decrease in the amount of 1,6-bis(phenylsilyl)hexane (41–54%) but the yield of phenylsilacycloheptane (11–20%) and (phenylsilylmethyl)cyclopentane (35–39%) increases.

Experimental Section

All manipulations were performed in evacuated tubes using standard Schlenk-flask techniques or under purified nitrogen in a glove-box with rigorous exclusion of traces of moisture and air. After drying over KOH, THF was purified by distillation from sodium/benzophenone ketyl; hexane and toluene were dried by distillation from sodium/benzophenone ketyl prior to use. Benzene-d$_6$ was dried with sodium and condensed in vacuum into NMR tubes prior to use. Chloroform-d was used without additional purification. $\mathrm{Ln(CH_2SiMe_3)_3(THF)_2}$[36] and **1**[15] were prepared according to previously published procedures. $\mathrm{Ph_3SiH}$ was purchased from Aldrich Chemical Co. Inc. and dried over $\mathrm{CaH_2}$ before use. $\mathrm{[Ph_3C][B(C_6F_5)_4]}$ and $\mathrm{[HNMe_2Ph][B(C_6F_5)_4]}$ were purchased from Synor Ltd. All other commercially available chemicals were used after the appropriate purifications. NMR spectra were recorded with Bruker Avance DRX-400 and Bruker DRX-200 spectrometers in chloroform-d and benzene-d$_6$ at 25 °C, unless otherwise stated. Chemical shifts are reported in ppm relative to TMS and peaks are referenced to the chemical shifts of residual solvent resonances (^{1}H and ^{13}C). IR spectra were recorded as Nujol mulls with a “Bruker-Vertex 70” instrument. The C, H, N elemental analysis are conducted in the microanalytical laboratory of IMOC. Lanthanide metal analysis was carried out by complexometric titration.[37] GC-MS data were obtained with a Thermo Electron Corporation, USA & Polaris Q system. GPC was carried out using the chromatograph “KnauerSmartline” with PhenogelPhenomenex Columns 5u (300 × 7.8 mm) 104, 105 and a Security Guard Phenogel Column with RI and UV detectors (254 nm). The mobile phase used was THF, and the flow rate was 2 mL min^{-1}. Columns were calibrated with Phenomenex Medium and High Molecular Weight Polystyrene Standard Kits with peak M$_w$ from 2700 to 2 570 000 Da. The number average molecular masses (M$_n$) and polydispersity index (M$_w$/M$_n$) of the polymers were calculated with reference to a universal calibration versus polystyrene standards.

Synthesis of $\mathbf{[2,6\text{-}iPr_2C_6H_3NC(Ph)NC(Ph)NC_6H_3iPr_2\text{-}2,6]Y(CH_2SiMe_3)_2(THF)}$ (2). A solution of **1** (0.19 g, 0.35 mmol) in hexane (15 mL) was added to a solution of $\mathrm{(Me_3SiCH_2)_3Y(THF)_2}$ (0.18 g, 0.35 mmol) in hexane (15 mL) at 0 °C and the reaction mixture was stirred for 1 h. The reaction mixture was warmed up to room temperature and was stirred for additional 30 min. The solution was concentrated in vacuum and cooled to −20 °C. Complex **2** was isolated as a bright-yellow crystalline solid in 58% yield (0.18 g). ^{1}H NMR (400 MHz, $\mathrm{C_6D_6}$, 25 °C) δ: −0.20 (s, 4H, $\mathrm{C}H_2\mathrm{SiMe_3}$), 0.36 (s, 18H, $\mathrm{CH_2Si}Me_3$), 0.98 (d, $^3J_{\mathrm{H\text{-}H}}$ = 6.8 Hz, 12 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.32 (d, $^3J_{\mathrm{H\text{-}H}}$ = 6.8 Hz, 12 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.43 (m, 4 H, β-$\mathrm{C}H_2$, THF), 3.45 (sept, $^3J_{\mathrm{H\text{-}H}}$ = 6.8 Hz, 4 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.75 (m, 4 H, α-$\mathrm{C}H_2$, THF), 6.60 (m, 3 H, Ar–H), 6.67 (t, $^3J_{\mathrm{H\text{-}H}}$ = 7.5 Hz, 4 H, Ar–H), 7.00 (m, 5 H, Ar–H), 7.10 (d, $^3J_{\mathrm{H\text{-}H}}$ = 7.5 Hz, 4 H, Ar–H). ^{13}C NMR (100 MHz, 25 °C, $\mathrm{C_6D_6}$), δ 4.8 ($\mathrm{CH_2Si}Me_3$), 23.3 ($\mathrm{CH(CH_3)_2}$), 25.6 (β-$\mathrm{CH_2}$, THF), 25.7 ($\mathrm{CH(CH_3)_2}$), 37.1 (d, $^1J_{\mathrm{Y\text{-}C}}$ = 38.4 Hz, $C\mathrm{H_2SiMe_3}$), 68.9 (α-$C\mathrm{H_2}$, THF), 123.5, 124.3, 127.5, 128.4, 129.1, 137.8, 140.0, 144.1 (Ar–C); 169,2 (NCN) ppm. IR (Nujol, KBr) (υ, cm^{-1}): 1603 (m), 1580 (m), 1504 (s), 1309 (s), 1250 (s), 1236 (s), 1177 (w), 1157 (w), 1135 (m), 1095 (s), 1073 (m), 1028 (s), 859 (s), 777 (s), 766 (s), 695 (s), 670 (m). Elemental Anal. Calc. for $\mathrm{C_{50}H_{74}YN_3OSi_2}$ (878.22 g/mol): Calculated (%): C, 68.38; H, 8.49; N, 4.78; Y, 10.12. Found (%): C, 68.11; H, 8.64; N, 4.62, Y, 10.03.

Synthesis of $\mathbf{[2,6\text{-}iPr_2C_6H_3NC(Ph)NC(Ph)NC_6H_3iPr_2\text{-}2,6]Lu(CH_2SiMe_3)_2(THF)}$ (3). A solution of **1** (0.20 g, 0.37 mmol) in hexane (15 mL) was added to a solution of $\mathrm{(Me_3SiCH_2)_3Lu(THF)_2}$ (0.24 g, 0.37 mmol) in hexane (15 mL) at 0 °C and the reaction mixture was stirred for 1 h. The reaction mixture was warmed up to room temperature and was stirred for additional 30 min. The solution was concentrated in vacuum and cooled to −20 °C. Complex **3** was isolated as a bright-yellow crystalline solid in 62% yield (0.22 g). ^{1}H NMR (400 MHz, 25 °C, $\mathrm{C_6D_6}$) δ: −0.29 (s, 4H, $\mathrm{C}H_2\mathrm{SiMe_3}$), 0.37 (s, 18H, $\mathrm{CH_2Si}Me_3$), 1.01 (d, $^3J_{\mathrm{H\text{-}H}}$ = 5.6 Hz, 12 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.19 (m, 4 H, β-$\mathrm{C}H_2$, THF), 1.26 (d, $^3J_{\mathrm{H\text{-}H}}$ = 5.6 Hz, 12 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 3.37 (m, 4 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.74 (m, 4 H, α-$\mathrm{C}H_2$, THF), 6.71–7.34 (m, 16 H, Ar–H). ^{13}C NMR (100 MHz, $\mathrm{C_6D_6}$, 25 °C): δ 4.6 ($\mathrm{CH_2Si}Me_3$), 23.2 ($\mathrm{CH(CH_3)_2}$), 25.0 (β-$C\mathrm{H_2}$, THF), 25.2 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 28.6 ($C\mathrm{H(CH_3)_2}$), 46.3 ($C\mathrm{H_2SiMe_3}$), 70.4 (α-$C\mathrm{H_2}$, THF), 122.6, 123.6, 124.5, 128.9, 129.0, 137.1, 140.0, 143.8 (Ar–C); 176.9 (NCN) ppm. IR (Nujol, KBr) (υ, cm^{-1}): 1600 (s), 1577 (s), 1507 (s), 1312 (s), 1249 (s), 1239 (s), 1180 (w), 1158 (w), 1135 (m), 1095 (s), 1070 (m), 1022 (s), 853 (s), 774 (s), 765 (s), 740 (s), 698 (s), 673 (s). Elemental Anal. Calc. for $\mathrm{C_{50}H_{74}LuN_3OSi_2}$ (964.27 g/mol): Calculated (%): C, 62.28; H, 7.74; N, 4.36; Lu, 18.14. Found (%): C, 62.04; H, 7.80; N, 4.17, Lu, 18.02.

Synthesis of $\mathbf{[\{\mu^2\text{-}2,6\text{-}iPr_2C_6H_3NC(Ph)N\}Sc(CH_2SiMe_3)(THF)]_2}$ (4). A solution of **1** (0.20 g, 0.37 mmol) in toluene (20 mL) was added to a solution of $\mathrm{(Me_3SiCH_2)_3Sc(THF)_2}$ (0.17 g, 0.37 mmol) in toluene (20 mL) at 20 °C and the reaction mixture was stirred for 12 h. The toluene solution was slowly concentrated in vacuum at room temperature. Complex **4** was isolated as a light-yellow crystalline solid in 43% yield (0.08 g). ^{1}H NMR (400 MHz, 25 °C, $\mathrm{C_6D_6}$) δ: 0.35 (s, 18H, $\mathrm{CH_2Si}Me_3$), 0.50 (br s, 2H, $\mathrm{C}H_2\mathrm{SiMe_3}$), 0.55 (br s, 2 H, $\mathrm{C}H_2\mathrm{SiMe_3}$), 0.99 (d, $^3J_{\mathrm{H\text{-}H}}$ = 6.8 Hz, 12 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.24 (m, together 20 H, $\mathrm{CH(C}H_3\mathrm{)_2}$, β-$\mathrm{C}H_2$, THF), 3.40 (sept, $^3J_{\mathrm{H\text{-}H}}$ = 6.8 Hz, 4 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 3.92 (m, 8 H, α-$\mathrm{C}H_2$, THF), 6.64–6.84 (m, 7 H, Ar–H), 7.00 (m, 5 H, Ar–H), 7.35 (d, $^3J_{\mathrm{H\text{-}H}}$ = 8.2 Hz, 4 H, Ar–H). ^{13}C NMR (100 MHz, 25 °C, $\mathrm{C_6D_6}$), δ 4.0 ($\mathrm{CH_2Si}Me_3$), 23.3, 25.2 ($\mathrm{CH(CH_3)_2}$), 25.9 (β-$C\mathrm{H_2}$, THF), 28.5 ($C\mathrm{H(CH_3)_2}$), 47.0 ($C\mathrm{H_2SiMe_3}$), 70.2 (α-$C\mathrm{H_2}$, THF), 123.6, 124.3, 124.6, 125.2, 127.2, 129.0, 129.2, 130.9, 136.6, 140.0, 142.7 (Ar–C); 175,5 (NCN) ppm. IR (Nujol, KBr) (υ, cm^{-1}): 1677 (w), 1591 (m), 1549 (s), 1308 (m), 1263 (w), 1247(m), 1230 (s), 1180 (m), 1155 (m), 1116 (s), 1071 (m), 1033 (s), 971 (m), 921 (w), 860 (s), 810 (s), 777 (m), 727 (s), 699 (m), 660 (m), 635 (m), 588 (s). Elemental Anal. Calc. for $\mathrm{C_{54}H_{82}N_4O_2Sc_2Si_2}$ (965.34 g/mol): Calculated (%): C, 67.19; H, 8.56; N, 5.80; Sc, 9.31. Found (%): C, 66.97; H, 8.71; N, 5.68, Sc, 9.22.

$\mathbf{2,6\text{-}iPr_2C_6H_3N{=}C(Ph)CH_2SiMe_3}$. ^{1}H NMR (400 MHz, 25 °C, $\mathrm{C_6D_6}$) δ: 0.24 (s, 9H, $\mathrm{CH_2Si}Me_3$), 0.95 (d, $^3J_{\mathrm{H\text{-}H}}$ = 6.8 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.35 (s, 2 H, $\mathrm{C}H_2\mathrm{SiMe_3}$ overlaps with β-$\mathrm{C}H_2$, THF), 1.38 (d, $^3J_{\mathrm{H\text{-}H}}$ = 6.8 Hz, 6 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 3.64 (sept, $^3J_{\mathrm{H\text{-}H}}$ = 6.8 Hz, 2 H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 6.63–7.39 (m, 8 H, Ar–H). ^{13}C NMR (100 MHz, 25 °C, $\mathrm{C_6D_6}$), δ 3.9 ($\mathrm{CH_2Si}Me_3$), 24.1, 25.3 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 28.4 ($C\mathrm{H(CH_3)_2}$), 30.2 ($C\mathrm{H_2SiMe_3}$), 124.1, 127.2, 129.4, 129.7, 131.5, 142.4, 143.3, 145.1 (Ar–C); 184.3 (NC) ppm. MS (EI): m/z = 351.6 [M$^+$].

Reaction of $\mathbf{[2,6\text{-}iPr_2C_6H_3NC(Ph)NC(Ph)NC_6H_3iPr_2\text{-}2,6]Lu(CH_2SiMe_3)_2(THF)}$ with $\mathbf{[Ph_3C][B(C_6F_5)_4]}$. $\mathrm{[Ph_3C][B(C_6F_5)_4]}$ (19.2 mg, 20.7 µmol) in 0.3 mL of benzene-d$_6$ was added to a solution of **3** (20 mg, 20.7 µmol) in 0.3 mL of benzene-d$_6$ at 25 °C. ^{1}H NMR (200 MHz, 25 °C, $\mathrm{C_6D_6}$) $\mathrm{[\{2,6\text{-}iPr_2C_6H_3NC(Ph)NC(Ph)NC_6H_3iPr_2\text{-}2,6\}Lu(CH_2SiMe_3)(THF)][B(C_6F_5)_4]}$: δ (ppm) −0.18 (s, 2H, $\mathrm{C}H_2\mathrm{SiMe_3}$), 0.31 (s, 9 H, $\mathrm{CH_2Si}Me_3$), 0.99 (d, $^3J_{\mathrm{H\text{-}H}}$ = 6.7 Hz, 12 H, $\mathrm{CH(C}H_3\mathrm{)_2}$), 1.38 (d, $^3J_{\mathrm{H\text{-}H}}$ = 6.7 Hz, 12 H, $\mathrm{CH(C}H_3\mathrm{)_2}$ overlaps with β-$\mathrm{C}H_2$, THF), 3.64 (m, together 8 H, $\mathrm{C}H\mathrm{(CH_3)_2}$, α-$\mathrm{C}H_2$, THF), 6.95–7.07 (m, 16 H, Ar–H overlaps with $\mathrm{Ph_3CCH_2SiMe_3}$); $\mathrm{Ph_3CCH_2SiMe_3}$: δ (ppm) −0.22 (s, 9 H, $\mathrm{CH_2Si(C}H_3\mathrm{)_3}$), 2.05 (s, 2 H, $\mathrm{C}H_2\mathrm{SiMe_3}$), 6.95–7.07 (m, 9 H, *m*-Ph and *p*-Ph), 7.31 (d, $^3J_{\mathrm{H\text{-}H}}$ = 7.1 Hz, 6 H, o-Ph).

General procedure for isoprene polymerization. All polymerization tests were conducted under a nitrogen atmosphere. In a typical procedure, 10 µmol of the selected catalyst precursor (**2**–**4**) was dissolved in toluene (3 mL) and treated with a solution of the proper activator {10 µmol; $\mathrm{[CPh_3][B(C_6F_5)_4]}$ or $\mathrm{[HNMe_2Ph][B(C_6F_5)_4]}$} in toluene (2 mL). 10 equiv. of $\mathrm{AliBu_3}$ (0.1 mL, 100 µmol, 1.0 M in toluene) were added and the reaction mixture was stirred for 2 min; then 1 mL (10 mmol) of isoprene was added *via* syringe at room temperature. The reaction mixture was stirred for 0.2–48 h. Afterwards, polymerization was stopped by quenching the mixture with an excess of methanol (20 mL) and dried under vacuum at ambient temperature to a constant weight. The polymer microstructures were determined by ^{1}H and ^{13}C NMR spectroscopy in $\mathrm{CDCl_3}$ at r.t.[25b,26b,38] GPC of polyisoprenes was performed in THF at 20 °C. The average molecular weights (M$_n$) and polydispersity (M_w/M_n) of the polymers were calculated with reference to a universal calibration against polystyrene standards.

Typical procedure for hydrosilylation. All hydrosilylation tests were conducted in a glove-box under a nitrogen atmosphere. In a typical procedure, 2 mol. % (0.005 g, 0.006 mmol,) of the selected catalyst precursor **2** was placed in an NMR tube and dissolved in C_6D_6 (1 mL). To the solution, styrene (0.034 mL, 0.3 mmol) and $PhSiH_3$ (0.037 mL, 0.3 mmol) were added and the tube was vigorously shaken. The reaction proceeded at room temperature and was monitored by ^1H and ^{13}C NMR spectroscopy. The ratio of Markovnikov and anti-Markovnikov regioisomers was calculated by integration of the appropriate signals in the ^1H NMR spectra. The products of hydrosilylation reactions were identified on the basis of previously published ^1H NMR spectroscopic data for these compounds $PhHC(SiH_2Ph)Me$[30d,33], n-$C_9H_{19}SiH_2Ph$[32a], $Ph(Me)_2CSiH_2Ph$[32g, 33], (E)-hept-1-en-1-yl(phenyl)silane[32d], (Z)-phenyl(styryl)silane[32i], (E)-phenyl(styryl)silane[32c], 1,6-bis(phenylsilyl)hexane[30e,33], (phenylsilylmethyl)cyclopentane[30e,33], phenylsilacycloheptane[34a].

X-ray crystallography. The X-ray data for **3** and **4** were collected with *Bruker D8 Quest* (**3**) and *Bruker Apex II* (**4**) diffractometers ($Mo_{K\alpha}$-radiation, ω-scans technique, λ = 0.71073 Å) using APEX2[39] software packages. The structures were solved by direct methods and were refined by full-matrix least squares on F^2 for all data using SHELX.[40] XABS2[41] (**3**) and SADABS[42] (**4**) and were used to perform absorption corrections. All non-hydrogen atoms in **3** and **4** were found from Fourier syntheses of electron density (all non-hydrogen atoms were refined anisotropically). All hydrogen atoms in **3** and **4** were placed in calculated positions and were refined in the "riding" model with $U(H)_{iso} = 1.2U_{eq}$ of their parent atoms ($U(H)_{iso} = 1.5U_{eq}$ for methyl groups). *Platon*/*SQUEEZE*[43] was used to calculate the contribution of the two toluene solvent molecules per complex **4** to the final structural model. The crystallographic data and structures refinement details are given in Table S1. CCDC– 2070349 (**3**) and 2039699 (**4**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre: ccdc.cam.ac.uk/structures. The corresponding CIF files are also available as the Supporting Information.

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Keywords: Rare Earth metal•1,3,5-triazapentadiene•Hydrosilylation•Polymerization•Isoprene

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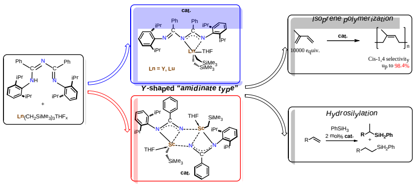
Entry for the Table of Contents



In Y^{3+}and Lu $^{3+}$bis(alkyl) complexestriazapentadienyl ligand adopts previously unknownκ^2-N,N'“amidinate” coordination mode.The attempt of synthesis of the Sc^{3+}analogue results in the cleavage of C-N bond of 1,3,5-triazapentadiene and affords a dinuclearmonoalkyl complex coordinated by dianionicamidinate ligand.Alkyl complexes were testedas catalysts for isoprene polymerization and olefin hydrosilylation.