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Bis(alkyl) rare-earth complexes supported by new tridentate amidinate ligand with a pendant diphenylphosphine oxide group. Synthesis, structures and catalytic activity in isoprene polymerization

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A new tridentate amidine 2-[$Ph_2P(O)$]C_6H_4NHC(tBu)=N(2,6-$Me_2C_6H_3$) (**1**) bearing in a side chain a pendant $Ph_2P=O$ group was synthesized and proved to be a suitable ligand for coordination to rare-earths ions. Bis(alkyl) complexes {2-[$Ph_2P(O)$]C_6H_4NC(tBu)N(2,6-$Me_2C_6H_3$)}Ln(CH_2SiMe_3)$_2$(THF)$_n$ (Ln = Y, n = 1 (**3**), Ln = Er, n = 1 (**4**), Ln = Lu, n = 0 (**5**)) were prepared using alkane elimination reactions of **1** and Ln(CH_2SiMe_3)$_3$(THF)$_2$ (Ln = Y, Er, Lu) in hexane and were isolated in 50, 70 and 75 % yields respectively. The X-ray studies revealed that complexes **2-5** feature intramolecular coordination of P=O group to the metal ion.The lutetium complex **5** proved to be rather stable: at 20 °C its half-life time is 1155 h, while for the yttrium analogue the half-life time was found to be 63 h. Complexes **3-5** were evaluated as precatalysts for isoprene polymerization. The systems Ln/borate/AliBu$_3$ (Ln = **3-5**, borate = [PhNHMe$_2$][B(C_6F_5)$_4$], [Ph$_3$C][B(C_6F_5)$_4$]) turned out to be highly efficient in isoprene polymerization and enable complete conversion of 1000-10000 equivalents of monomer into polymer at 20 °C within 0.5-2.5 h affording polyisoprenes with very high content of 1,4-cis units (up to 96.6 %) and from narrow (1.49) to moderate (3.54) polydispersities. A comparative study of catalytic performance of the related bis(alkyl) yttrium complexes supported by amidinate ligands of different denticity and structure [tBuC(N-2,6iPr$_2C_6H_4$)$_2$]$^-$, [tBuC(N-2,6-iPr$_2C_6H_4$)(N-2-MeOC_6H_4)]$^-$ and {2-[$Ph_2P(O)$]C_6H_4NC(tBu)N(2,6-$Me_2C_6H_3$)}$^-$ demonstrated that the introduction of a pendant donor group (2-MeOC_6H_4 or $Ph_2P(O)$) into a side chain of amidinate scaffold results in a significant increase of catalytic activity. The amidinate ligand bearing a $Ph_2P(O)$-group provides high isoprene polymerization rate along with excellent control of regio- and stereoselectivities and allows to obtain polyisoprenes with reasonable molecular weight distribution.

Introduction

An impressive progress has been made in the chemistry of σ-bonded rare earth metal alkyls, which proved to be highly active species that exhibit unique reactivity[1] and catalytic activity in a wide range of conversions of unsaturated substrates.[2] Bis(alkyl) rare earth complexes until recently remained poorly explored due to their limited thermal stability[1] and tendency to undergo ligand redistribution and C-H bond activation reactions.[3] Currently this class of compounds is in the focus of interest as potential precursors to cationic alkyl species that were found to be efficient catalysts of homo- and copolymerization of olefins.[4] Due to large ionic radii[5] and Lewis acidity of rare-earth metals the stability and reactivity of their organic derivatives are highly influenced by the coordination and steric saturation of the metal centre. This emphasizes the role of ligand design for the synthesis of isolable rare-earth species[6] as well as for providing the control of selectivity of metal promoted reactions. The chelating monoanionic amidinate fragment [RC(NR)$_2$]$^-$ which forms stable complexes with various metal ions across the periodic table of elements[7] presents a useful platform for "tailoring" new versatile ligand systems. Amidinate ligands have been successfully employed in organo-rare earth chemistry and have allowed for the synthesis and isolation of a series of highly reactive species.[8] Monoalkyl, bis(alkyl), cationic alkyl, and hydrido rare earth complexes coordinated by amidinate ligands have been reported and performed catalytic activity in various transformations of unsaturated substrates.[9] Hemilabile ligands[10] bearing, in addition to an inert fragment a Lewis base groups capable to coordinate to the metal attract substantial interest due to possible catalytic applications. These ligands are capable of temporarily occupying coordination sites at reactive metal centers in the absence of a substrate and thus saturating its coordination sphere. However, in the presence of

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the substrate the coordination bond between the weakly coordinating group and the metal ion can dissociate, liberating the coordination site for a substrate, while the inert part of the ligand remains permanently anchored to the metal centre. Amidinate ligands that contain a pendant coordinating group[11] in the side chain were shown to enable the synthesis of bis(alkyl) rare earth species. It has been established that P=O group forms strong coordination bonds with Ln^{3+} ions[12] and phosphine oxides $R_3P=O$ have been extensively investigated as ligands in Ln^{3+} coordination.[13] Moreover a number of multidentate ligands containing $Ph_2P=O$ moiety have been successfully used for the synthesis of rare-earth complexes.[14] Taking into account the fact that P=O group tolerates the presence of highly reactive Ln-C bonds[15] we focused on development of a new P=O functionalized amidinate ligand. Herein we report on the synthesis of new tridentate amidine bearing a $Ph_2P=O$ group in a side chain and its application for the preparation of a series of bis(alkyl) and bis(chloro) derivatives of rare earth metals. Catalytic activity of amidinate bis(alkyl) species in isoprene polymerization will be discussed.

Results and Discussion

New tridentate amidine $2-[Ph_2P(O)]C_6H_4NHC(t-Bu)=N(2,6-Me_2C_6H_3)$ (**1**) bearing a pendant Lewis base group $Ph_2P=O$ linked to the NCN fragment via conformationally rigid o-phenylene linker was synthesized by the reaction of imidoyl chloride $2,6-Me_2C_6H_3[N=C(Cl)tBu]$[16] with $2-[Ph_2P(O)]C_6H_4NH_2$[17] in the presence of triethylamine (Scheme 1). Recrystallization of the reaction product from diethyl ether after appropriate workup afforded colourless crystals of **1** in 64% yield.
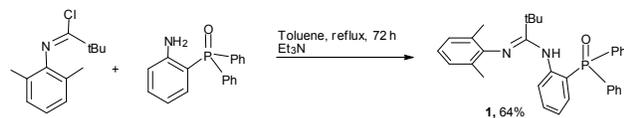
Scheme 1

In the ^1H NMR spectrum of **1** the amidinate NH proton gives rise to a broadened singlet at 9.66 ppm. The variable temperature ^1H NMR studies of **1** in d^8-toluene (-60 °C ÷ 50 °C) did not give evidences for a dynamic behaviour associated with the migration of the amidinate proton. The $^{31}P\{^1H\}$ NMR spectrum of **1** contains the only singlet at 36.5 ppm. The sole sharp absorption band at 3298 cm^{-1} in the IR spectrum of **1** corresponding to the N-H group stretching vibrations together with simplicity of its ^1H and ^{31}P NMR spectra (single sets of signals) indicate localization of the amidine proton at one nitrogen and the absence of its migration within the NCN fragment.

Transparent crystals of **1** suitable for X-ray study were obtained by slow evaporation of the diethyl ether solution at room temperature. The molecular structure of **1** is depicted in Figure 1 and the structure refinement data are listed in Table S1 (see ESI).

The molecular structure of **1** was established by the X-ray diffraction study which revealed the presence of intramolecular hydrogen bonding between the amidinate hydrogen and the oxygen atom of the diphenylphosphine

oxide fragment resulting in short contact H(1)···O(1) 2.11(2) Å. The N-C bond lengths in the NCN fragments are not equivalent: the bond length of N(2)-C(1) (1.281(2) Å) is indicative of its double character, while that of N(1)-C(1) (1.381(2) Å) corresponds to a single C-N bond.[18] The plane of the amidinate fragment adopts the orthogonal orientation relative to the plane of dimethylphenyl group (the value of dihedral angle is 89.7(9)°).
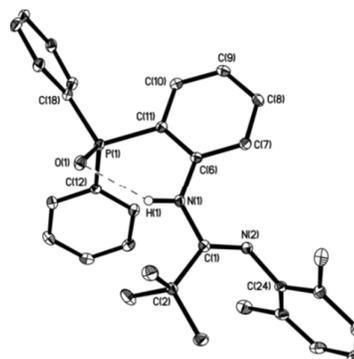
Fig. 1. ORTEP diagram (30% probability thermal ellipsoids) of **1** showing the atom numbering scheme. Hydrogen atoms except H(1) are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)-O(1) 1.4966(9), N(1)-C(1) 1.381(2), N(2)-C(1) 1.281(2), N(1)-H(1) 0.87(2), O(1)-H(1) 2.11(2), N(2)-C(1)-N(1) 118.0 (1), C(6)-N(1)-H(1) 114(1), C(1)-N(1)-H(1) 117(1).

Amidine **1** can be readily deprotonated by n-BuLi in diethyl ether-hexane mixture at 0 °C. Lithium amidinate obtained *in situ* was reacted with anhydrous YCl_3 in 1:1 molar ratio (Scheme 2). The salt metathesis reaction was carried out in THF at room temperature (12 h). After removal of THF in vacuum the remaining solid residue was extracted with toluene. Recrystallization of the reaction product from DME-hexane mixture afforded pale yellow crystals of amidinate dichloro yttrium complex $\{2-[Ph_2P(O)]C_6H_4NC(tBu)N(2,6-Me_2C_6H_3)\}YCl_2(DME)$ (**2**) in 56% yield. Complex **2** is air- and moisture sensitive, well soluble in polar (THF, DME) and aromatic (toluene) solvents but slightly soluble in hexane.
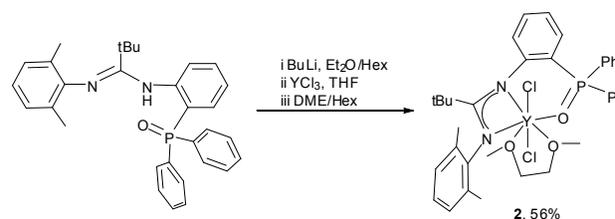
Scheme 2

The ^1H and ^{13}C NMR spectra of **2** exhibit the expected sets of signals due to the amidinate ligand and coordinated DME molecule. In the ^{31}P NMR spectrum of **2** a singlet at 35.1 ppm was observed.

The crystals of **2** suitable for X-ray diffraction study were obtained by slow condensation of hexane into concentrated DME solution. Compound **2** crystallizes as a solvate containing one DME molecule per two molecules of yttrium complex. The

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molecular structure of **2** is depicted in Figure 2 and the structure refinement data are listed in Table S1 (see ESI). According to the X-ray data complex **2** is a salt-free compound and adopts a monomeric structure. The amidinate ligand is tridentate and coordinates to the yttrium ion through two nitrogens and the oxygen atom of the $Ph_2P=O$ group. The yttrium atom is also bound with two terminal chloro ligands and is coordinated by two oxygen atoms of DME molecule, thus resulting in a formal coordination number of seven. The coordination environment of yttrium presents a distorted pentagonal bipyramid. Two nitrogen atoms, two DME oxygens and the oxygen of $Ph_2P=O$ group are located in the equatorial plane, while two chloro ligands occupy the apical positions. The Y-Cl (2.6079(7) and 2.6162(7) Å) bond lengths in **2** are significantly longer than the analogous bonds in the seven coordinate amidinate chloro yttrium complex [PhC(NC$_6$H$_3$iPr$_2$-2,6)$_2$]YCl$_2$(THF)$_3$ (Y(1)-Cl(1) 2.579 Å).[19] The C-N bonds within the amidinate fragment are somewhat different (N(1)-C(1) 1.311(3) Å and N(2)-C(1) 1.380(3) Å). The Y-N bonds are also non-equivalent. Thus the length of one of them (Y(1)-N(2) 2.376(2) Å) corresponds to the values formerly reported for the related amidinate and guanidinate ligands ([{o-MeOC$_6$H$_4$NC(Ph)N(SiMe$_3$)}YCl$_2$(THF)$_2$]$_2$ (2.375(2), 2.384(2) Å),[20] {[(Me$_3$Si)$_2$NC(NiPr)$_2$]$_2$Y(μ-Cl)}$_2$ (2.326(4)-2.388(4)Å),[21] [PhC(NC$_6$H$_3$iPr$_2$-2,6)$_2$]YCl$_2$(THF)$_3$ (2.384(3) Å),[19] while the second one is noticeably longer (Y(1)-N(1) 2.459(2) Å). Such a geometric situation of the YNCN moiety obviously reflects the effect of coordination of the $Ph_2P=O$ group to the yttrium ion. It is noteworthy that the distance between the yttrium ion and the oxygen of the $Ph_2P=O$ (2.249(2) Å) is much shorter compared to the distances to the DME oxygens (2.463(2), 2.393(2) Å). The YNCN fragment in **2** is not planar: the value of the dihedral angle between NYN and NCN planes is 162.3(4)°.
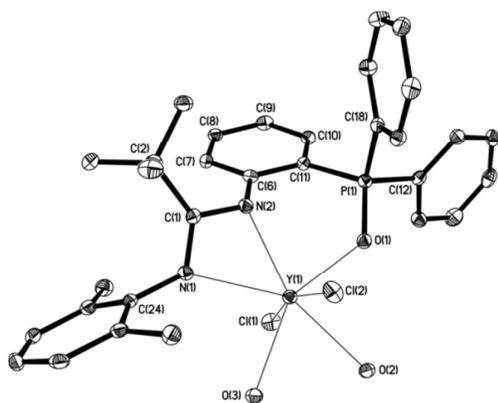
Fig. 2. ORTEP diagram (30% probability thermal ellipsoids) of **2** showing the atom numbering scheme. Solvate DME, carbon atoms of coordinated DME molecule and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Y(1)-Cl(1) 2.6162(7), Y(1)-Cl(2) 2.6079(7), Y(1)-N(1) 2.459(2), Y(1)-N(2) 2.376(2), Y(1)-O(1) 2.249(2), Y(1)-O(2) 2.463(2), Y(1)-O(3) 2.393(2), N(1)-C(1) 1.311(3), N(2)-C(1) 1.380(3), P(1)-O(1) 1.511(2), N(1)-C(1)-N(2) 112.1(2), N(1)-Y(1)-N(2) 55.0(2), Cl(1)-Y(1)-Cl(2) 165.16(2).

To synthesize bis(alkyl) rare-earth complexes supported by new tridentate amidinate ligand the alkane elimination

approach was applied. The equimolar amounts of $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Er, Lu)[22] and **1** were reacted in hexane at 0 °C (Scheme 3).
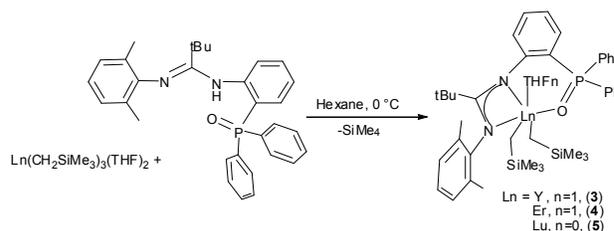
Scheme 3

Slow cooling of the reaction mixtures to -20 °C resulted in colourless microcrystalline powder of **3**, yellowish pink crystals of **4** or colourless crystals of **5** in 50, 70 and 75 % yields respectively. The NMR tube scale reactions of the diamagnetic tris(alkyl) derivatives $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Y, Lu) with the amidine **1** were carried out in C_6D_6 under ^1H NMR spectroscopy control and showed clear formation of the bis(alkyl) species in quantitative yield and the liberation of one equivalent of TMS. Decrease in the isolated yields of complexes **3**-**5** compared to those in the NMR tube scale experiment is apparently caused by the high solubility of these compounds in aliphatic and aromatic hydrocarbons. Complex **3** can be also obtained by alkylation of **2** with two equivalents of $LiCH_2SiMe_3$ in toluene mixture in 43% yield. Complexes **3**-**5** are highly air- and moisture-sensitive.

The ^1H NMR (C_6D_6, 25 °C) spectra of diamagnetic complexes **3** and **5** exhibit the single sets of signals due to the amidinate ligand. The methylene protons of the alkyl groups bound to the metal ions appear as a broad signal at -0.33 ppm for **3** and a singlet at -0.42 ppm for **5**, respectively. In the $^{13}C\{^1H\}$ NMR spectra the appropriate carbons give rise to a doublet at 33.1 ppm ($^1J_{CY}$ = 39.8 Hz) in the case of the yttrium compound **3** and a singlet at 30.1 ppm for lutetium complex **5**. Noteworthy that yttrium complex **3** contains one coordinated THF molecule while the lutetium derivative **5** is base-free. The $^{31}P\{^1H\}$ of spectrum of **3** displays a doublet at 38.3 ppm ($^2J_{PY}$ = 2.95 Hz) while in that of **5** a singlet at 41.0 ppm was observed.

The thermal stabilities of diamagnetic bis(alkyl) complexes **3** and **5** were evaluated in C_6D_6 solutions by ^1H NMR spectroscopy. The lutetium complex **5** proved to be rather stable: at 20 °C its half-life time is 1155 h, while for the yttrium analogue the half-life time was found to be 63 h.

The molecular structures of complexes **4** and **5** were established by the X-ray diffraction studies. Transparent crystals of complexes **4** and **5** suitable for X-ray diffraction studies were obtained by cooling the concentrated toluene solutions to -20 °C for **5** and THF/hexane (1:3) at -20 °C for **4**. The molecular structures of complexes **4** and **5** are shown in Figures 3 and 4 respectively. The structures refinement data are given in Table S1 (see ESI). Complex **5** crystallizes as a solvate **5**·0.5C$_7$H$_8$. The X-ray studies revealed that complexes **4** and **5** are monomeric. In both compounds the lanthanide ion is coordinated by two nitrogen and one oxygen atoms of tridentate amidinate ligand and by two alkyl groups. Erbium complex **4** featuring a larger Ln^{3+} ion size (compare ion radii Er^{3+}: 0.89, Lu^{3+}: 0.861 Å)[5] contains in the metal coordination sphere additional THF molecule. This fact is in line with the

NMR data which gave evidence for the absence of coordinated THF in **5** whereas the complex of Y^{3+} having the ionic radius similar to that of Er^{3+} (compare ion radii Er^{3+}: 0.89, Y^{3+}: 0.900 Å)[5] contains one THF molecule. Thus the Lu^{3+} ion in **5** is five-coordinate while the Er ion in **4** is six-coordinate. The Lu-C bond distances (2.325(2) and 2.365(2) Å) fall into the interval of values typical for five-coordinate lutetium alkyl complexes: [CyC(N-2,6-iPr$_2$C$_6$H$_3$)$_2$]Lu(CH$_2$SiMe$_3$)$_2$(THF) (2.328(4), 2.327(4) Å),[23] [(2,6-iPr$_2$C$_6$H$_3$)N=C(Me)C(=CH$_2$)N-(C$_6$H$_3$-2,6-iPr$_2$)]Lu(CH$_2$SiMe$_3$)$_2$(THF) (2.320(4), 2.354(4) Å),[24] {MeC$_4$H$_2$SCH$_2$NHC$_6$H$_4$(Ph)$_2$P=NC$_6$H$_2$Me$_3$-2,4,6}Lu(CH$_2$SiMe$_3$)$_2$(THF) (2.344(6), 2.366(6) Å),[25] (C$_{zx}$)Lu(CH$_2$SiMe$_3$)$_2$ (C$_{zx}$ = 1,8-bis(4,4-dimethyloxazolin-2-yl)-3,6-di-tert-butylcarbazolyl) (2.347(4) and 2.355(4) Å),[26] ((2,6-iPrC$_6$H$_3$N=C(C$_6$H$_5$)NCH$_2$CH$_2$(NCHCHN(C$_6$H$_2$Me$_3$-2,4,6)CH)Lu(CH$_2$SiMe$_3$)$_2$ (2.337(5) and 2.359(5) Å).[27] The Er-C bond distances in **4** (2.401(3), 2.453(3) Å) are slightly elongated compared to the formerly described six-coordinate bis(alkyl) erbium complex [(C$_5$Me$_4$SiMe$_3$)Er(CH$_2$SiMe$_3$)$_2$THF] (2.337(9), 2.381(1) Å).[28] The Ln-N bonds in **4** (2.413(3) and 2.417(3) Å) and in **5** (2.376(1) and 2.327(2) Å) fall into the interval of values typical for the related lutetium and erbium complexes (for Lu complexes see: ((2,6-iPrC$_6$H$_3$N=C(C$_6$H$_5$)NCH$_2$CH$_2$(NCHCHN(C$_6$H$_2$Me$_3$-2,4,6)CH)Lu(CH$_2$SiMe$_3$)$_2$ (2.352(3) and 2.260(4) Å);[27] [CyC(N-2,6-Me$_2$C$_6$H$_3$)$_2$]Lu[N(SiMe$_3$)$_2$]$_2$(μ-Cl)Li(THF)$_3$ (2.328(5) and 2.380(5) Å),[29] [(Me$_3$Si)$_2$NC(NiPr)$_2$]$_2$Lu(OtBu) (2.294(4) and 2.323(4) Å).[30] For Er complexes see: [Me$_2$NC(NiPr)$_2$]$_3$Er (2.410(7) Å),[31] [HC(N-2,6-iPr$_2$C$_6$H$_3$)$_2$]Er(CH$_2$SiMe$_3$)(THF) (2.365(6)-2.439(6) Å)[32]). The Lu-O bond distance in **5** (2.188(1) Å) is noticeably shorter than the related distance in the formerly reported five-coordinate compounds ([CyC(N-2,6-iPr$_2$C$_6$H$_3$)$_2$]Lu(CH$_2$SiMe$_3$)$_2$(THF) Lu-O (2.315(3) Å),[23] [NPN]Lu(CH$_2$SiMe$_3$)(THF) (2.303(2) Å).[33] The Er-O(1) (P=O) bond length (2.282(2)Å) is much shorter, whereas the bond length Er-O(2) (THF) (2.454 (2) Å) is significantly longer than a coordination bond Er-O (THF) in five-coordinate complex [(C$_5$Me$_4$SiMe$_3$)Er(CH$_2$SiMe$_3$)$_2$(THF)].[28] The four-membered LnNCN cycles are planar (the maximum deviation is 0.003(2) Å for **4** and 0.009(1) Å for **5**).
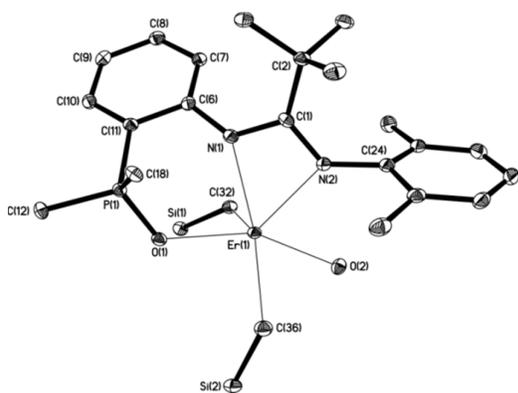
Fig.**3**. ORTEP diagram (30% probability thermal ellipsoids) of **4** showing the atom numbering scheme. Carbon atoms of Ph-fragments of Ph$_2$P=O, Me-groups of SiMe$_3$ and THF molecule and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Er(1)-O(1) 2.282(2), Er(1)-O(2)

2.454(2), Er(1)-C(32) 2.401(3), Er(1)-C(36) 2.453(3), Er(1)-N(1) 2.417(3), Er(1)-N(2) 2.413(3), N(2)-Er(1)-N(1) 54.16(8), C(32)-Er(1)-C(36) 134.6(1), O(1)-Er(1)-O(2) 154.76(8), N(2)-C(1)-N(1) 110.7(3).
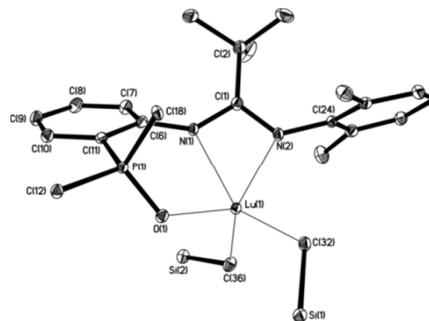
Fig. **4**. ORTEP diagram (30% probability thermal ellipsoids) of **5** showing the atom numbering scheme. Carbon atoms of Ph-fragments of Ph$_2$P=O and Me-groups of SiMe$_3$ and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Lu(1)-O(1) 2.188(1), Lu(1)-C(36) 2.325(2), Lu(1)-C(32) 2.365(2), Lu(1)-N(1) 2.376(1), Lu(1)-N(2) 2.327(2); N(2)-Lu(1)-N(1) 55.57(6), N(2)-C(1)-N(1) 109.6(2), C(36)-Lu(1)-C(32) 108.12(7).

Catalytic tests in isoprene polymerization

Bis(alkyl) rare earth species established a reputation as suitable precursors for catalytic systems performing controlled diene polymerization with high activities and selectivities.[33,34] The catalytic activity of complexes **2**-**5** in isoprene polymerization was explored in toluene under different conditions at room temperature. The results of the catalytic tests are summarized in Table 1. The systems **2**-AliBu$_3$, **2**-AliBu$_3$-borate do not initiate isoprene polymerization (Table S2, see ESI). Complexes **3**-**5** alone also turned out to be inactive in isoprene polymerization. When complexes **3**-**5** were activated with an equimolar amount of borate (B(C$_6$F$_5$)$_3$, [HNEt$_3$][BPh$_4$], [HNMe$_2$Ph][B(C$_6$F$_5$)$_4$] or [CPh$_3$][B(C$_6$F$_5$)$_4$]) no polymerization occurred. This suggests that the cationic alkyl species generated from the binary system is not an active in isoprene polymerization. Also, the binary systems **3**-**5**/AlR$_3$ (R = Me, Et, iBu; AlR$_3$/Ln = 1:10) were not suitable as polymerization initiators.

The ternary systems **3**-**5**/borate/AliBu$_3$ (1:1:10; borate = ([Et$_3$NH][BPh$_4$], B(C$_6$F$_5$)$_3$, [Ph$_3$C][B(C$_6$F$_5$)$_4$], [PhNHMe$_2$][B(C$_6$F$_5$)$_4$]) were found to be able to initiate isoprene polymerization, however their catalytic activities are dramatically influenced by the nature of borate and aluminium alkyl components. Thus the catalytic systems containing AlMe$_3$ were inactive in polymerization however polymerizations occurred for AliBu$_3$ analogues. When the ternary systems based on complexes **3**-**5** activated by [Et$_3$NH][BPh$_4$] were used no catalytic activity was detected. In the presence of the system **3**/B(C$_6$F$_5$)$_3$/AliBu$_3$ (1:1:10) and [Ln]/[monomer] ratio1:1000 in 24 h only trace amounts of polyisoprene were obtained (Table 1, entry 5).

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Table 1. Catalytic tests in isoprene polymerization initiated by systems (3-5)/borate/AliBu$_3$ (borate: [Et$_3$NH][BPh$_4$], B(C$_6$F$_5$)$_3$, [Ph$_3$C][B(C$_6$F$_5$)$_4$], [PhNHMe$_2$][B(C$_6$F$_5$)$_4$], [Ln]/[borate]/[AliBu$_3$]=1:1:10).

	comp.	borate	[IP]/[Ln]	t, h	Yield, %	Cis-1,4	Trans-1,4	3,4-	M$_n$(×10^{-3})^a	M$_n$(×10^{-3})$_{calc}$ ^{b}	M$_w$/M$_n$
1	3	HNB	1000	0.5	100	87.2	8.6	4.2	75.3	68.1	1.49
2	3	HNB	5000	0.5	61	96.3	1.2	2.5	119.9	207.8	2.15
3	3	HNB	5000	1	91	92.5	5.8	1.7	257.9	306.0	3.14
4	3	HNB	10000	2	72	96.6	1.2	2.2	271.3	490.5	2.22
5	3	B(C$_6$F$_5$)$_3$	1000	24	1	93.0	4.6	2.4	5.2	0.9	3.92
6	3	Et$_3$NB	1000	24	0	-	-	-	-	-	-
7	3	TB	1000	1	100	91.6	2.7	5.7	34.3	67.7	2.49
8	3	TB	5000	2	100	95.4	3.9	0.7	127.0	340.6	1.84
9	3	TB	10000	2	95	92.3	4.3	3.4	200.4	647.1	2.48
10	4	HNB	1000	0.5	100	76.9	18.0	5.2	48.7	68.1	1.65
11	4	HNB	5000	1.5	77	92.8	4.1	3.1	127.6	262.3	2.45
12	4	HNB	10000	2	73	93.5	3.9	2.7	484.1	497.3	2.49
13	4	TB	1000	0.5	99	73.5	21.2	5.3	28.0	67.4	1.56
14	4	TB	5000	1.5	97	74.9	19.1	6.0	88.3	330.4	4.05
15	4	TB	10000	2	51	87.7	0.7	11.6	413.4	347.4	3.54
16	4*	TB	1000	0.5	79	83.8	9.2	7.0	52.2	53.8	2.13
17	4*	HNB	1000	0.5	75	88.8	7.7	3.5	60.1	51.1	1.91
18	5	HNB	1000	0.5	99	71.7	22.5	5.8	30.0	67.4	1.72
19	5	HNB	5000	1	95	80.7	14.8	4.5	118.6	323.6	1.99
20	5	HNB	10000	1.5	91	83.9	12.00	4.10	456.9	619.9	2.40
21	5	TB	1000	2	82	85.5	10.3	4.2	41.5	55.9	1.53
22	5	TB	2000	2	80	85.7	9.7	4.6	2968.0 (5.4%) 67.5 (94.6%)	109.0	2.18 1.46
23	5	TB	3000	2.5	100	71.7	22.8	5.5	71.1	204.4	1.98
24	5	TB	4000	2.5	100	73.9	20.4	5.7	74.4	272.5	1.98
25	5	TB	5000	2.5	100	62.5	30	7.5	3220.6 (2.5%) 56.1 (97.5%)	340.6	2.52 2.75
26	6	TB	1000	6	54	59.1	9.6	31.1	63.2	36.7	2.15
27	6	HNB	1000	6	99	57.9	12.3	29.8	72.8	67.3	1.88
28	7	TB	1000	1	99	48.0	2.0	52.0	130.0	67.3	2.12
29	7	HNB	1000	1	80	72.0	12.6	15.4	55.6	54.4	1.99

Conditions: complex (10 µmol in toluene, [AlR$_3$]:[Ln]:[borate] = 10/1/1, T: 25 °C.); HNB = [PhNHMe$_2$][B(C$_6$F$_5$)$_4$], TB = [Ph$_3$C][B(C$_6$F$_5$)$_4$], Et$_3$NB = [Et$_3$NH][BPh$_4$]; a) Determined by GPC against polystyrene standard; *The catalytic tests were performed at [Ln]/[borate]/[AliBu$_3$]=1:1:1; b)M$_{calc}$=([IP]/[Ln])×68.12×(conversion).

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The ternary systems containing $[Ph_3C][B(C_6F_5)_4]$ and $[PhNHMe_2][B(C_6F_5)_4]$ demonstrated high catalytic activity at room temperature and ability to convert into polymer up to 10000 equivalents of monomer in 30-120 min achieving from high to total conversions (Table 1, entries 4, 9, 12, 20). Moreover these catalytic systems proved to be able to provide control of regio- and stereoselectivities of polymerization process enabling formation of polyisoprenes containing predominatly cis-1,4-units (62.5-96.6 %).

The system $3/[PhNHMe_2][B(C_6F_5)_4]/Al\textit{i}Bu_3$ (1:1:10) performed very high catalytic activity: 1000 equivalents of monomer were converted into polymer in 30 min. The GPC curve indicated that the polyisoprene sample produced by this ternary catalyst system is unimodal with a M_n of 75.3×10^3 and narrow polydispersity (1.49). Moreover this catalytic system provided good control of regioselectivity with predominant 1,4-regularity (95.8), albeit the content of cis-1.4 units was found to be somewhat lower - 87.2%. When [Ln]/[monomer] ratio was increased to 1:5000 in 1 h conversion reached 91% (Table 1, entry 3). The obtained polyisoprene sample had a M_n of 257.9×10^3 however molecular weight distribution became somewhat broader (3.14). Excellent regio- and stereoselectivities were detected under these polymerization conditions, cis-1,4-regularity reached 92.5 %. Even better cis-1,4-regularity (96.6%) was found for polyisoprene obtained when the monomer loading was increased to 10000. In 2 h 72% of monomer was converted into polymer featuring a M_n of 271.3×10^3 and PDI 2.22.

When $[Ph_3C][B(C_6F_5)_4]$ was used as an activator instead of $[PhNHMe_2][B(C_6F_5)_4]$ in combination with **3** under similar conditions the catalytic activity dropped, at [Ln]/[monomer] ratio 1:1000 quantitative conversion is achieved in 1 hour (Table 1, entry 7) instead of 30 minutes (Table 1, entry 1).

The catalytic systems $Ln/[PhNHMe_2][B(C_6F_5)_4]/Al\textit{i}Bu_3$ (1:1:10) based on Y and Er complexes performed similar activities (Table 1, entries 1-4 and 10-12), however cis-1,4 selectivity for Er complex was slightly lower. The PDIs of the polyisoprenes obtained with both Y and Er complexes have close values. For the Y and Er systems containing $[Ph_3C][B(C_6F_5)_4]$ activator the observed activities at monomer loading 1000 and 5000 equivalents have similar values, however when [Ln]/[monomer] ratio was increased to 1:10000 the activity of Er containing system dropped (in 2 h conversion for **3** is 95%, while for **4** – 51%). Despite the similar ionic radii of Y^{3+} and Er^{3+5} the cis-1,4 selectivities of the system based on Er complex were noticeably lower (74.9-87.7 % vs 91.6-92.3 % for Y).

The decrease of $[Er]/[Al\textit{i}Bu_3]$ ratio to 1:1 for both systems $4/[PhNHMe_2][B(C_6F_5)_4]/Al\textit{i}Bu_3$ and $4/[Ph_3C][B(C_6F_5)_4]/Al\textit{i}Bu_3$ ([Er]/[monomer] ratio 1:1000) resulted in noticeable decrease of catalytic activity $([Ph_3C][B(C_6F_5)_4]$: 79 vs 99%;

$[PhNHMe_2][B(C_6F_5)_4]$: 75 vs 100%). As it could be expected the decrease of concentration of $Al\textit{i}Bu_3$ which also acts as a chain transfer reagent[32] results in the increase of the molecular weights of the obtained polyisoprenes (entries 10, 13, 16, 17) as well as in a good agreement of values of experimental and calculated polyisoprene molecular weights (compare: $[Ph_3C][B(C_6F_5)_4]$, $M_n(\times10^{-3})_{calc} = 53.8$, $M_n(\times10^{-3}) = 52.2$; $[PhNHMe_2][B(C_6F_5)_4]$, $M_n(\times10^{-3})_{calc} = 51.1$, $M_n(\times10^{-3}) = 60.1$).

The catalytic system containing lutetium complex $5/[PhNHMe_2][B(C_6F_5)_4]/Al\textit{i}Bu_3$ (1:1:10) demonstrated activities comparable to those of the yttrium analogue $3/[PhNHMe_2][B(C_6F_5)_4]/Al\textit{i}Bu_3$. Moreover at [Ln]/[monomer] ratio 1:10000 this system performs the highest activity: in 1.5 h 91% conversion was reached. The combination of **5** with $[Ph_3C][B(C_6F_5)_4]$ afforded somewhat less active systems. The lutetium based catalytic systems proved to be less stereoselective, the content of cis-1,4-units in the obtained polyisoprenes does not exceed 86.6 %. However the increase of the presence of trans-1,4 units was observed (9.65 – 30 %). The polyisoprenes obtained with the system $5/[PhNHMe_2][B(C_6F_5)_4])/Al\textit{i}Bu_3$ (1:1:10) feature high molecular weights and relatively narrow molecular weight distributions. When $[Ph_3C][B(C_6F_5)_4]$ was used as an activator the synthesized polymers displayed bimodal molecular weights distribution and slightly broader PDIs.

To elucidate the effect of the structure and denticity of amidinate scaffold on catalytic activity, regio- and stereoselectivity of ternary systems a series of catalytic tests on isoprene polymerization with related bis(alkyl) yttrium complexes coordinated by bidentate $[tBuC(N-2,6-iPr_2C_6H_3)_2]Y(CH_2SiMe_3)_2(THF)^{35}$ (**6**) and tridentate $[tBuC(N-2,6-iPr_2C_6H_3)(N-2-MeOC_6H_4)]Y(CH_2SiMe_3)_2(THF)^{11c}$ (**7**) amidinate ligands was carried out. The comparative catalytic tests ([Y]/[borate]/[Al\textit{i}Bu_3], 1:1:10 molar ratio; borate = $[PhNHMe_2][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$; [IP]/[Ln] = 1000) revealed that the systems containing complex **6** with nonsubstituted amidinate ligand perform lowest catalytic activities in the total absence of selectivity (Table 1, entrees 26, 27). Addition to one of nitrogens of the amidinate framework of 2-MeOC_6H_4 group coordinating to the metal centre increases catalytic activity noticeably. For the system $7/[Ph_3C][B(C_6F_5)_4]/Al\textit{i}Bu_3$ in 1 h complete isoprene conversion was already reached (vs 54% for **6**), albeit no selectivity appeared (Table 1, entrees 28, 29). When **7** was used in the combination with $[PhNHMe_2][B(C_6F_5)_4]$ under the similar conditions the polymer yield in 1 h was lower - 80%, however the 1,4-cis-selectivity increased to 72%. The introduction of $2\text{-}[Ph_2P(O)]C_6H_4$ pendant into the amidinate scaffold affords catalytic systems providing both high activity and 1,4-cis-selectivity (Table 1, entrees 1, 7) in isoprene polymerization. The system $3/[PhNHMe_2][B(C_6F_5)_4]/Al\textit{i}Bu_3$ allows to achieve

complete monomer conversion in 0.5 h performing 87.2 % cis-1,4 selectivity. When [Ph₃C][B(C₆F₅)₄] was used the reaction was somewhat slower (100% in 1 h), however higher degree of 1,4-cis-selectivity was reached (91.6 %). Moreover high efficiency and switchable regioselectivity of the catalytic systems based on yttrium complex ligated by bidentate amidinate [PhC(N-2,6-*i*Pr₂C₆H₃)₂]Y(o-CH₂C₆H₄NMe₂)₂ formerly reported by Hou[30k] give evidence for importance of alkyl group in the precatalyst. Noteworthy the Lu bis(alkyl) complex coordinated by amidinate ligand bearing a pendant NHC group in a side chain ((2,6-*i*PrC₆H₃N=C(C₆H₅)NCH₂CH₂(NCHCHN(C₆H₂Me₃-2,4,6)CH)Lu(CH₂SiMe₃)₂[23] enables highly 3,4-selective polymerization of isoprene (up to 98.7% of 3,4-units), while the Lu complex **5** under similar conditions promotes the formation of cis-1,4 enriched polymer (85.5 % of cis-1,4 units). The examples listed above clearly emphasize the role of amidinate ligand tailoring for regio- and stereospecific isoprene polymerization.

Conclusions

A new amidine bearing a pendant Ph₂P=O group linked to the nitrogen via conformationally rigid o-phenylene group allowed for the synthesis of relatively stable bis(alkyl) species of Y, Er, Lu. A tridentate coordination of the amidinate ligand was detected in bis(alkyl) and the related bischloro derivatives. The ternary systems {2-[Ph₂P(O)]C₆H₄NC(*t*Bu)N(2,6-Me₂C₆H₃)}Ln(CH₂SiMe₃)₂(THF)ₙ/borate/Al*i*Bu₃ (borate = [PhNHMe₂][B(C₆F₅)₄], [Ph₃C][B(C₆F₅)₄], molar ratio, 1:1:10, toluene) demonstrated high catalytic activity in isoprene polymerization under mild conditions. They enable complete conversion of 1000-10000 equivalents of isoprene into polymer at 20 °C within 0.5-2.5 h affording polyisoprenes with very high content of 1,4-cis units (up to 96.6 %) and reasonable molecular weights distribution (1.49 - 3.54). A comparative study of catalytic performance of the ternary systems LY(CH₂SiMe₃)₂(THF)ₙ/borate/Al*i*Bu₃ based on related bis(alkyl) yttrium complexes supported by amidinate ligands of different denticity and structure [*t*BuC(N-2,6-*i*Pr₂C₆H₃)₂]Y(CH₂SiMe₃)₂(THF)(**6**), [*t*BuC(N-2,6-*i*Pr₂C₆H₃)(N-2-MeOC₆H₄)]Y(CH₂SiMe₃)₂(THF) (**7**), {2-[Ph₂P(O)]C₆H₄NC(*t*Bu)N(2,6-Me₂C₆H₃)}Y(CH₂SiMe₃)₂(THF) (**3**) revealed that complex **6** having lowest coordination number (5) of the catalytic center exhibits lowest activity and regioselectivity. Surprisingly complexes supported by tridentate amidinate ligands and featuring six-coordinate catalytic center exhibit higher activities. Application of complex **7** coordinated by [*t*BuC(N-2,6-*i*Pr₂C₆H₃)(N-2-MeOC₆H₄)] ligand provides noticeable increase of catalytic activity, however degree of control of selectivity remains rather low. The introduction of a pendant Ph₂P(O) group into the amidinate ligand allowed to reach the highest 1,4-cis selectivity (96.6 %) while maintaining very high activity. At present to increase 1,4-cis selectivity of isoprene polymerization we are working on modification of amidinate

scaffold and synthesis of the related rare earth bis(alkyl) species.

Experimental Section

General conditions: All experiments were performed in evacuated tubes by using standard Schlenk techniques, with rigorous exclusion of traces of moisture and air. After being dried over KOH, THF was purified by distillation from sodium/benzophenoneketyl; hexane, diethyl ether and toluene were dried by distillation from sodium and benzophenoneketyl prior to use. C₆D₆ was dried with sodium and condensed in vacuum into NMR tubes prior to use. CDCl₃ was used without additional purification. 2,6-Dimethylaniline was purchased from Acros. Anhydrous YCl₃[36], (Me₃SiCH₂)₃Ln(THF)₂,[22] 2,6-Me₂C₆H₃[N=C(Cl)*t*Bu],[16] 2-(P(O)Ph₂)C₆H₄NH₂[17] were prepared according to the literature procedures. 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 CDCl₃, C₆D₆ at 20 °C, unless otherwise stated. Chemical shifts for ¹H and ¹³C NMR spectra were referenced internally to the residual solvent resonances and are reported relative to TMS. IR spectra were recorded as Nujol mulls with a "Bruker-Vertex 70" instrument. GPC analysis was provided with chromatograph "Knauer Smartline" with Phenogel Phenomenex Columns 5u (300×7.8 mm) 10^4, 10^5 and Security Guard Phenogel Column with RI and UV detectors (254 nm). Mobile phase was THF, flow rate was 2 ml/min. Columns was calibrated by Phenomenex Medium and High Molecular Weight Polystyrene Standard Kits with peak Mw from 2700 to 2570000 Da. Lanthanide metal analyses were carried out by complexometric titration.[37] The C, H, N elemental analyses were performed in the microanalytical laboratory of the G. A. Razuvaev Institute of Organometallic Chemistry.

Synthesis of 2-[Ph₂P(O)]C₆H₄NHC(*t*Bu)=N(2,6-Me₂C₆H₃) (1).

A solution of 2,6-Me₂C₆H₃[N=C(Cl)*t*Bu] (1.75 g, 7.82 mmol) and Et₃N (0.79 g, 7.82 mmol) in toluene (20 ml) was added to a suspension of 2-[Ph₂P(O)]C₆H₄NH₂ (2.30 g, 7.82 mmol) in 10 mL of toluene. The reaction mixture was refluxed with stirring for 3 days then the solvent was removed in vacuum. The resulting white solid was dissolved in diethyl ether (100 mL) and was washed with water solution of Na₂CO₃ (1%, 3×100 mL). The ether layer was separated and dried with MgSO₄. After recrystallization from Et₂O **1** was isolated as colourless crystals in 64 % yield (2.40 g). M.p. 148-151 °C. Ms (EI): m/z = 480.4 [M+]. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 1.23 (s, 9 H, C(C*H*₃)₃), 1.84 (s, 6 H, C₆H₃(C*H*₃)₂), 6.58-6.81 (m, 5 H, Ar-*H*), 7.12 (t, ³*J*ₕₕ = 7.67 Hz, 1 H, Ar-*H*), 7.48 (td, ³*J*ₕₕ = 7.5, 3.0 Hz, 5 H, Ar-*H*), 7.56-7.65 (m, 6 H, Ar-*H*), 9.66 (s, 1 H, N*H*). ¹³C{¹H} NMR (50 MHz, CDCl₃, 298 K): δ 18.6 (C₆H₃(*C*H₃)₂), 28.7 (C(*C*H₃)₃), 40.5 (*C*(CH₃)₃), 116.1 (d, *J*ᴄₚ = 102.9 Hz), 119.9 (d, *J*ᴄₚ = 12.9 Hz), 120.7, 121.5 (d, *J*ᴄₚ = 7.5 Hz), 125.7, 127.51, 128.6 (d, *J*ᴄₚ = 12.3 Hz), 131.5 (d, *J*ᴄₚ = 35.9 Hz), 132.0, 132.1, 132.2, 132.8 (d, *J*ᴄₚ = 39.9 Hz), 146.2 (d, *J*ᴄₚ = 3.5 Hz), 147.6 (Ar-*C*), 156.4 (N*C*N). ³¹P{¹H} NMR (81 MHz, CDCl₃, 298 K): δ 36.5. IR (Nujol, KBr;

ν_{max}(cm^{-1})): 3298 (N-H) (s), 1669 (C=N) (s), 1604 (s), 1577 (s), 1538 (s), 1403 (w), 1311 (s), 1265 (w), 1246 (w), 1223 (w), 1203 (w)1165 (P=O) (s), 1153 (s), 1133 (m), 1121 (s), 1100 (s), 1092 (s), 1071 (s), 1029 (s), 998 (w), 947 (w).Elemental analysis requires C$_{31}$H$_{33}$N$_2$OP (480.56): C, 77.48; H, 6.92; N, 5.83. Found: C, 77.40; H, 6.81; N, 5.77.

Synthesis of {2-[Ph$_2$P(O)]C$_6$H$_4$NC(*t*Bu)N(2,6-Me$_2$C$_6$H$_3$)}YCl$_2$(DME) (2).

A solution of n-BuLi (0.83 M, 0.85 mL) in hexane was added to a solution of **1** (0.34 g, 0.70 mmol) in Et$_2$O (30 mL) at 0 °C and the reaction mixture was stirred for 1 h. The solvent was removed and the resulted yellow solid residue was dissolved in 15 mL of THF and was added to a suspension of YCl$_3$ (0.14 g, 0.70 mmol) in THF (20 mL). The reaction mixture was stirred at room temperature for 12 h, filtered and the solvent was removed in vacuum. The remaining solid was extracted with toluene (50 mL). After filtration of the toluene extracts the solvent was removed in vacuo at room temperature and the remaining solid was dissolved in DME (10 mL). Slow condensation of hexane into a DME solution afforded pale yellow crystals of **2** in 56% yield (0.28 g). ^{1}H NMR: (400 MHz, C$_6$D$_6$, 298 K): δ 1.02 (s, 9 H, C(CH$_3$)$_3$), 2.80 (s, 6 H, C$_6$H$_3$(CH$_3$)$_2$), 3.12 (s, 6 H, CH$_3$ (DME)), 3.32 (4 H, CH$_2$ (DME)), 6.47 (td, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 3.3 Hz, 1 H, Ar-H), 6.78-7.11 (m, 12 H, Ar-H), 7.61, 8.29 (br. s, both 2 H, Ar-H). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$, 298 K): δ 21.5 (C$_6$H$_3$(CH$_3$)$_2$), 29.9 (C(CH$_3$)$_3$), 43.0 (C(CH$_3$)$_3$), 58.4 (CH$_3$ (DME)), 71.9 (CH$_2$ (DME)), 115.2 (d, J= 110.0 Hz), 116.0 (d, J= 14.2 Hz), 122.6 (d, J= 7.7 Hz), 123.7, 128.2, 128.3 (d, J_{CP}= 11.9 Hz), 132.0 (d, J_{CP}= 3.0 Hz), 132.2, 132.7 (d, J_{CP}= 12.5 Hz), 133.3, 146.3, 156.5 (d, J_{CP}= 3.0 Hz) (Ar-C), 187.0 (d, J_{CY} = 2.0 Hz, NCN). ^{31}P{^{1}H} NMR (81 MHz, C$_6$D$_6$, 298 K): δ 35.1. IR (Nujol, KBr; ν_{max} (cm^{-1})):1582 (s), 1545 (s), 1503 (s), 1398 (s), 1357 (s), 1292 (m), 1264 (m), 1242 (w), 1216 (s), 1174 (m), 1162 (m), 1131 (s), 1086 (m), 1069 (m), 1038 (s), 1000 (w), 981 (s), 936 (s), 926 (s), 855 (m), 817 (m), 790 (s).Elemental analysis requires C$_{35}$H$_{42}$Cl$_2$N$_2$O$_3$PY (729.51): C, 57.62; H, 5.80; N, 3.84; Y, 12.18. Found C, 57.51; H, 5.91; N, 3.92; Y, 12.11.

Synthesis of {2-[Ph$_2$P(O)]C$_6$H$_4$NC(*t*Bu)N(2,6-Me$_2$C$_6$H$_3$)}Y(CH$_2$SiMe$_3$)$_2$THF] (3).

Method A. A solution of (Me$_3$SiCH$_2$)$_3$Y(THF)$_2$ (0.31 g, 0.62 mmol) in hexane (20 mL) was added to a suspension of **1** (0.30 g, 0.62 mmol) in hexane (20 mL) at 0 °C and the reaction mixture was stirred for 30 min. The reaction mixture was warmed up to the room temperature and was stirred for additional 30 min. The solution was concentrated and cooled to -20 °C. Complex **3** was isolated as white crystalline solid in 50% yield (0.25 g). ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ -0.33 (s, 4 H, CH$_2$Si(CH$_3$)$_3$), 0.30 (s, 18 H, CH$_2$Si(CH$_3$)$_3$), 0.75 (s, 9 H, C(CH$_3$)$_3$), 1.38 (m, 4 H, β-THF), 2.28 (s, 6 H, C$_6$H$_3$(CH$_3$)$_2$), 3.59 (m, 4 H, α-THF), 6.49 (td, $^3J_{HH}$ = 7.1 Hz, $^3J_{HH}$ = 2.9 Hz, 2 H, Ar-H), 6.86-7.06 (m, 10 H, Ar-H), 7.79-7.85 (m, 5 H, Ar-H). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$, 298 K): δ 4.6 (CH$_2$Si(CH$_3$)$_3$), 20.6 (C$_6$H$_3$(CH$_3$)$_2$), 25.6 (β-THF), 30.0 (C(CH$_3$)$_3$), 33.1 (d, $^1J_{CY}$ = 39.81 Hz, CH$_2$Si(CH$_3$)$_3$), 42.3 (d, $^3J_{CY}$ = 1.75 Hz, C(CH$_3$)$_3$), 68.3 (α-THF), 118.1 (d, J_{CP} = 108.8 Hz), 118.4 (d, J_{CP} = 14.1 Hz), 123.7, 125.0

(d, J_{CP} = 7.4 Hz), 128.4, 129.0 (d, J_{CP} = 12.7 Hz), 131.2, 132.3 (d, J_{CP} = 6.9 Hz), 132.6 (d, J_{CP} = 1.8 Hz), 133.6 (d, J_{CP} = 15.5 Hz), 134.0 (d, J_{CP} = 2.3 Hz), 146.5, 155.3 (d, J_{CP} = 3.0 Hz) (Ar-C), 180.2 (NCN). ^{31}P{^{1}H} NMR (81 MHz, C$_6$D$_6$, 298 K): δ 38.28 ($^2J_{PY}$ = 2.95 Hz). Elemental analysis requires C$_{43}$H$_{62}$N$_2$O$_2$PSi$_2$Y (815.02): C, 63.37; H, 7.67; N, 3.44; Y, 10.91. Found: C, 63.28; H, 7.53; N, 3.29; Y, 11.00.

Method B. A solution of **2** (0.12 g, 0.16 mmol) in 30 ml of THF was refluxed for 15 min, after then the volatiles were removed in vacuum. The solid residue was dispersed in toluene (30 ml) and LiCH$_2$SiMe$_3$ (0.03 g, 0.32 mmol) was added at 0 °C. The reaction mixture was stirred at 0 °C for 60 min, filtered, concentrated and cooled at -20 °C overnight. Complex **3** was obtained in 43% yield (0.056 g).

Synthesis of {2-[Ph$_2$P(O)]C$_6$H$_4$NC(*t*Bu)N(2,6-Me$_2$C$_6$H$_3$)}Er(CH$_2$SiMe$_3$)$_2$THF] (4).

A synthetic procedure similar to that for **3** was used. **1** (0.20 g, 0.42 mmol) in hexane (20 mL), (Me$_3$SiCH$_2$)$_3$Er(THF)$_2$ (0.24 g, 0.42 mmol) in hexane (20 mL). Complex **4** was recrystallized from THF/hexane mixture at -20°C and was isolated as yellow-pink crystals in 70% yield (0.26 g). Elemental analysis requires C$_{43}$H$_{62}$ErN$_2$O$_2$PSi$_2$ (893.35): C, 57.81; H, 7.00; Er, 18.72; N, 3.14. Found: C, 57.89; H, 7.11; Er, 18.80; N, 3.02.

Synthesis of {2-[Ph$_2$P(O)]C$_6$H$_4$NC(*t*Bu)N(2,6-Me$_2$C$_6$H$_3$)}Lu(CH$_2$SiMe$_3$)$_2$] (5).

A synthetic procedure similar to that for **3** was used. **1** (0.20 g, 0.42 mmol) in hexane (20 mL), (Me$_3$SiCH$_2$)$_3$Lu(THF)$_2$ (0.24 g, 0.42 mmol) in hexane (20 mL). Complex **3** was recrystallized from toluene at -20 °C and was isolated as colourless crystals in 75% yield (0.26 g). ^{1}H NMR (400 MHz, C$_6$D$_6$, 298 K): δ -0.42 (s, 4 H, CH$_2$Si(CH$_3$)$_3$), 0.27 (s, 18 H, CH$_2$Si(CH$_3$)$_3$), 0.80 (s, 9 H, C(CH$_3$)$_3$), 2.26 (br.s, 6 H, C$_6$H$_3$(CH$_3$)$_2$), 6.46 (td, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 3.3 Hz, 1 H, Ar-H), 6.81-7.10 (m, 12 H, Ar-H), 7.66-7.76 (m, 4 H, Ar-H). ^{13}C{^{1}H} NMR (100 MHz, C$_6$D$_6$, 298 K): δ 4.0 (CH$_2$Si(CH$_3$)$_3$), 20.1 (C$_6$H$_3$(CH$_3$)$_2$), 29.3 (C(CH$_3$)$_3$), 30.6 (CH$_2$Si(CH$_3$)$_3$), 42.1 (C(CH$_3$)$_3$), 117.4 (d, J_{CP} = 109.3 Hz), 118.2 (d, J_{CP} = 14.2 Hz), 124.0, 124.5 (d, J_{CP} = 7.2 Hz), 128.1, 128.8 (d, J_{CP} = 12.8 Hz), 130.9, 131.6 (d, J_{CP} = 10.0 Hz), 132.4 (d, J_{CP} = 2.4 Hz), 133.2 (d, J_{CP} = 12.8 Hz), 133.7 (d, J_{CP} = 1.6 Hz), 144.8, 153.8 (d, J_{CP} = 3.0 Hz) (Ar-C), 180.1 (NCN). ^{31}P{^{1}H} NMR (81 MHz, C$_6$D$_6$, 298 K): δ 41.04.Elemental analysis requires C$_{39}$H$_{54}$LuN$_2$OPSi$_2$ (828.97): C, 56.51; H, 6.57; Lu, 21.11; N, 3.38. Found: C, 56.43; H, 6.61; Lu, 21.00; N, 3.43.

Isoprene polymerization. A typical polymerization procedure was carried out as following. Under a nitrogen atmosphere and room temperature borate (0.01 mmol) was added to a solution of (**3-5**) (0.01 mmol) in toluene (volume of toluene (in milliliters) is equal to the mass of isoprene (in grams)). After which to the reaction mixture was added a mixture of isoprene (1000-10000 equiv.) and 10 equivalents of Al*i*Bu$_3$ (0.1 mmol). Polymerization was initiated and carried out for 30–150 min. The reaction mixture was quenched by the addition of ethanol, and then poured into a large amount of ethanol to precipitate the polymer, which was dried under vacuum at 60 °C to a

constant weight. Then, 1,4- 3,4-regioselectivity was determined by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. GPC of polyisoprenes was performed in THF at 20 °C. The number average molecular masses (M_n) and polydispersity indexes (M_w/M_n) of the polymers were calculated with reference to a universal calibration against polystyrene standards.

X-Ray Crystallography

The X-Ray data for **1**, **2**, **4** and **5** were collected on Bruker Smart APEX (**2**), Bruker D8 Quest (**4**) and Agilent Xcalibur E (**1**, **5**) diffractometers (graphite-monochromated, MoK$_\alpha$ radiation, ω-scans technique, λ = 0.71073 Å, T = 100(2) K). The structures were solved by direct methods and were refined on F^2 using SHELX / SHELXTL[38] and CrysAlis Pro[39] packages. All non-hydrogen atoms and H(1) atom in **1** were found from Fourier syntheses of electron density and were refined anisotropically. All other hydrogen atoms in **1**, **2**, **4**, **5** were placed in calculated positions and were refined in the riding model. SADABS[40] and ABSPACK[34] were used to perform area-detector scaling and absorption corrections. CCDC-1041025 (**1**), 1041026 (**2**), 1041027 (**4**), 1041028 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via ccdc.cam.ac.uk/getstructures.

Acknowledgements

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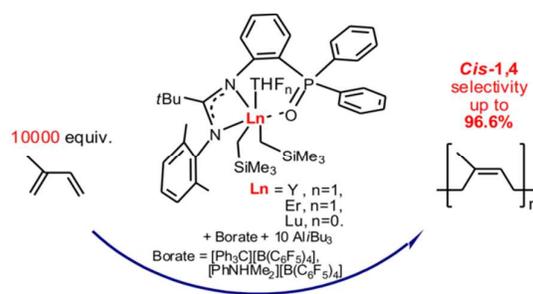
Table of contents entry

The introduction of a pendant $Ph_2P(O)$ group into the amidinate ligand allowed to reach high 1,4-cis selectivity (96.6 %) while maintaining very high activity.