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Sc and Y Hetero-alkyl Complexes with $NC_{sp3}N$ Pincer Type Diphenylmethanido Ligand: Synthesis, Structure and Reactivity.

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Abstract: New diphenylmethane $[4\text{-tBu-2-}(C_3H_2N_2Me\text{-}1)C_6H_3]_2CH_2$ (**1**) bearing pendant imidazolyl groups in *ortho*-positions of aromatic rings of diphenylmethane skeleton was synthesized using Stille cross-coupling reaction between bis(4-(tert-butyl)-2-iodophenyl)methane and $Bu_3Sn(C_3H_2N_2Me)$ in the presence of $Pd(PPh_3)_4$. Potassium diphenylmethanide $[\{[4\text{-tBu-2-}(C_3H_2N_2Me\text{-}1)C_6H_3]_2CH\}K(OEt_2)]_2$ (**2**^{K}) was prepared by treatment of **1** with an equimolar amount of Lochmann-Schlosser super base. Rare-earth metal hetero-alkyl complexes $\{[4\text{-tBu-2-}(C_3H_2N_2Me\text{-}1)C_6H_3]_2CH\}Ln(CH_2SiMe_3)_2(THF)_n$ (Ln = Sc, n = 0 (**2**^{Sc}); Y, n = 1 (**2**^{Y})) with $NC_{sp3}N$ pincer type diphenylmethanido ligand were synthesized by the selective sp^3 CH-bond activation of the central CH_2 group in **1** by $Ln(CH_2SiMe_3)_3(THF)_2$. According to the X-ray data the diphenylmethanido ligands in **2**^{K} and **2**^{Sc} perform a tridentate pincer-type κ^3-N,C,N coordination. Complexes **2**^{Ln} were evaluated as catalysts for isoprene polymerization and hydrosilylation of alkenes and alkynes.

Introduction

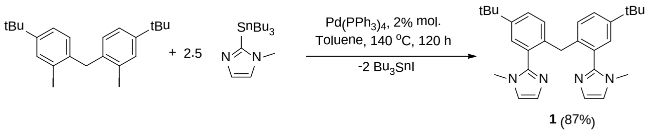
Pincer ligands have found a vast application in coordination and organometallic chemistry of d-transition metals[1] due to their robust tridentate coordination to the metal centres which provides high thermal and kinetic stability of their derivatives along with high activity in a variety of catalytic transformations.[2] One of the advantages of the pincer ligands is the simplicity of modification of their electronic and steric properties via variation of the nature of the central atom, covalently bounding the metal ion, the nature of the pendant donor groups, and the nature and size of the linker between the coordination sites of the ligand, what allows for tailoring geometry and tuning electronic structure of metal complex, thereby providing control of its reactivity. The progress in chemistry and catalytic application of d-transition metals complexes with pincer ligands have been summarized in several reviews,[3] and books[4] published over recent years.

In contrast pincer-type alkyl complexes of rare-earth metals still remain poorly explored. To date only few examples of carbon centred pincer-type rare-earth metal complexes are described and most of them are derived from 1,3-disubstituted benzenes and feature covalent $Ln{-}C_{sp2}$ bond. Coordination bonds between Ln ions and donor atoms of the side arms of the pincer ligands, such as nitrogen,[5] oxygen,[6] sulphur,[6b] or carbon atoms of NHC pendant[7] provides robust linkage with the rare earth metal ions. The $Ln{-}C_{sp3}$ pincer complexes are less investigated and to date bis(iminophosphorano)methanido $[CH(PPh_2NR)_2]^-$ (R = $SiMe_3$, iPr, Ad, Ph, $C_6H_2Me_3$-2,4,6),[8] bis(thiophosphinoyl)methanido $[CH(PPH_2S)_2]^-$ [9] and bis(pyrazolyl)methanido $[CH(C_3HN_2Me_2\text{-}3,5)_2]^-$ [10] derivatives are known. Recently tridentate diarylmethanido ligand $[2,2'\text{-}(4\text{-}MeC_6H_3NMe_2)_2CH]^-$ was used for the preparation of Ln(II) $NC_{sp3}N$ pincer type complexes.[11] C_{sp3} centred pincer type ligands were successfully applied for the synthesis of alkylidene complexes *via* double deprotonation of bis(iminophosphorano)methane ligands by amido or alkyl precursors.[12] Bis(thiophosphinoyl)methane also gives an opportunity for the preparation of rare-earths alkylidenes.[9,13]

Herein we report on the synthesis of new imidazolyl substituted diphenylmethane which due to the presence of N-donor centres proved to be suitable for tridentate coordination with hard Lewis acids as Ln(III) ions. The synthetic approaches to the deprotonation of the central methylene fragment as well as the synthesis of the $NC_{sp3}N$ pincer-type rare earth alkyl complexes will be considered as well.

Results and Discussion

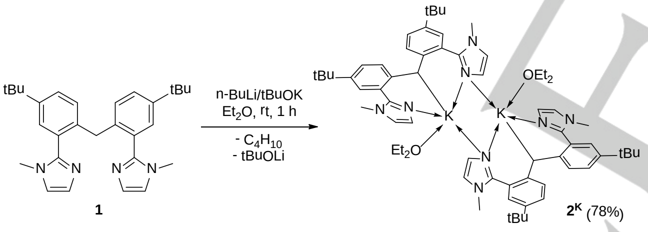
Bis(4-(*tert*-butyl)-2-(1-methyl-1H-imidazol-2-yl)phenyl)methane $[4\text{-tBu-2-}(C_3H_2N_2Me\text{-}1)C_6H_3]_2CH_2$ (**1**) was prepared by Stille cross-coupling reaction between bis(4-(tert-butyl)-2-iodophenyl)methane[14] and excess (2.5 equiv.) of 1-methyl-2-(tributylstannyl)-1H-imidazole[15] catalysed by $Pd(PPh_3)_4$[16] in toluene solution (Scheme 1). Compound **1** was purified by column chromatography (silica gel, EtOAc) and was isolated as amorphous colourless solid in 87% yield. Compound **1** is well soluble in chloroform, THF, aromatic solvents (toluene, benzene), moderately soluble in Et_2O and almost insoluble in hexane.



Scheme 1. Synthesis of imidazolyl substituted diphenylmethane **1**.

In the ^{1}H NMR spectrum of **1** the central methylene protons appear as a sharp singlet at 3.97 ppm, while in the ^{13}C{^{1}H} spectrum the related carbon gives rise to the signal at 36.2 ppm ($CDCl_3$, 298 K). The protons of t-Bu groups appear as a sharp singlet at 1.25 ppm and the aromatic protons of the diphenylmethane fragment give two doublets 6.56 (d, $^3J_{HH}$ = 8.1 Hz), 7.14 (d, $^4J_{HH}$ = 2.1 Hz) and one doublet of doublets 7.20 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.1 Hz). Imidazolyl substituents in *ortho*-positions of the diphenylmethane fragment give singlet at 3.05 ppm attributed to methyl group, and two doublets at 6.88 and 7.11 ppm with small coupling constant ($^3J_{HH}$ = 1.2 Hz), what is characteristic for aromatic protons of imidazolyl ring. Long range ^{15}N−^{1}H correlation allowed to determine the chemical shifts of ^{15}N atoms in compound **1**, where two non-equal nitrogen atoms appear at 158.2 (NMe) and 256.8 (N) ppm respectively. **1** was also characterized by IR-spectroscopy, GC-MS and elemental analysis (See Experimental Section and ESI).

Diphenylmethanido ligand can be bound to rare earth ion by the salt metathesis protocol starting from anhydrous $LnCl_3$ and alkali metal diphenylmethanides.[17] It was found that **1** does not react with n-BuLi, however can be readily deprotonated by Lochmann-Schlosser super base n-BuLi/t-BuOK affording the potassium diphenylmethanide [{[4-tBu-2-($C_3H_2N_2$Me-1)C_6H_3]$_2$CH}K(OEt_2)]$_2$ (**2^K**, Scheme 2). Similarly the phosphino substituted diphenyl methane [4-tBu-2-(PPh_2)C_6H_3]$_2$$CH_2$ also was inert toward alkyl lithium reagents but metalation was successful when *n*-BuLi/*t*-BuOK mixture was used.[18] On the contrary the NMe_2 substituted analogue 2,2'-(4-Me$C_6H_3$$NMe_2$)$_2$$CH_2$ readily reacts with both n-BuLi and Lochmann-Schlosser super bases (n-BuLi/t-BuOM, M = Na, K).[19]



Scheme 2. Synthesis of potassium dihpenylmethanide **2^K**.

Potassium diphenylmethanide **2^K** was isolated as bright orange crystals after crystallization from Et_2O solution by slow concentration at ambient temperature. Complex **2^K** is well soluble in THF, moderately soluble in Et_2O and almost insoluble in aromatic (benzene, toluene) and aliphatic (hexane) solvents. It is extremely air and moister sensitive, but can be stored in inert atmosphere or vacuum without any traces of decomposition for several weeks.

2^K crystallizes in monoclinic *P2$_1$/c* space group with one centrosymmetric dimeric molecule lying on the inversion centre per asymmetric unit. The single crystal X-ray diffraction study revealed that each potassium ion in **2^K** is bound with tridentate diphenylmethanido ligand *via* central carbon and two nitrogen atoms of imidazolyl substituents, while the formation of a dimer realizes due to coordination of one nitrogen atom of imidazolyl fragment of each diphenylmethanido ligand to both potassium ions (Figure 1). Moreover, each K ion is additionally bonded with one oxygen atom of coordinated Et_2O molecule. Diphenylmethanido fragment in **2^K** is nearly planar, the dihedral angle between two phenyl rings is 10.12(9)°. Both imidazolyl fragments in tridentate diphenylmethanido ligand are nearly orthogonal to the phenyl rings (the angles between planes of imidazolyl and aryl rings are 72.92(5) and 74.26(6)°). The K−C distance in **2^K** is 3.007(2) Å, what is very close to the related distances measured in potassium diphenylmethanido complexes with unsubstituted benzhydryl ligand [(Ph_2CH)K(THF)]$_\infty$ (K−C: 3.003 Å)[17] and substituted tridentate diphenylmethanide containing NMe_2 groups in *ortho*-positions of Ph rings {[2,2'-(4-Me$C_6H_3$$NMe_2$)$_2$CH]K(THF)}$_2$ (K−C: 3.044(3) Å).[19] The K−N distances in **2^K** (K−N: 2.846(2)–2.899(2) Å) are somewhat shorter compared to the NMe_2-substituted analogue {[2,2'-(4-Me$C_6H_3$$NMe_2$)$_2$CH]K(THF)}$_2$. In the latter compound η^5-pentadienyl type of coordination was realized due to the interactions between K ion, central benzhydryl and *ispo*- and *ortho*-carbons of both aromatic rings (K−C$_{Ar}$: 3.059(3)−3.184(3) Å). In contrast in **2^K** no K−C$_{Ar}$ interactions were detected. The shortest distances between K ion and carbon atoms of phenyl and imidazolyl rings are significantly longer (K−C$_{ipso}$ 3.328(2) Å; K−C$_{ortho}$ 3.520(2) Å; K−C$_{Im}$ 3.299(2) Å). Thus coordination mode of the tridentate diphenylmethanido ligand varies depending on the substituents in the phenyl rings: κ^3-[N,C,N] in **2^K** *vs* μ-η^5-pentadienyl:κ^3-CNN in NMe_2 substituted analogue. Despite the different coordination modes of tridentate diphenylmethanido ligands in **2^K** and {[2,2'-(4-Me$C_6H_3$$NMe_2$)$_2$CH]K(THF)}$_2$ the central benzhydryl carbon retains sp^2-configuration in the solid state with the sum of the bond angles around 360.0(2)°.

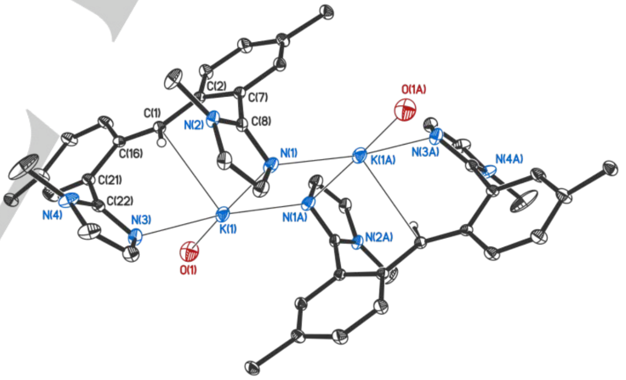


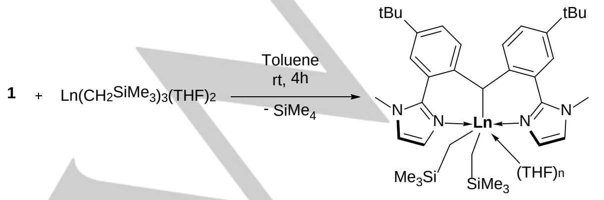
Figure 1. Molecular structure of [{[4-tBu-2-($C_3H_2N_2$Me-1)C_6H_3]$_2$CH}K(OEt_2)]$_2$ (**2^K**). The Et groups of coordinated Et_2O molecules, CH_3 groups of tBu substituents and all hydrogen atoms except H(1A) are omitted for clarity. Bond lengths (Å) and angles (°): K(1)−C(1) 3.007(2), K(1)−N(1) 2.899(2), K(1)−N(3) 2.860(2), K(1)−N(1A) 2.846(2), K(1)−O(1) 2.700(3); C(1)−K(1)−N(1) 77.57(4), C(1)−K(1)−N(3) 67.42(4), C(1)−K(1)−O(1) 103.66(7), N(1)−K(1)−N(3) 92.69(4), K(1)−N(1)−K(1A) 93.91(4), N(1)−K(1)−O(1) 173.80(7), N(3)−K(1)−O(1) 93.38(7).

In the ^{1}H and ^{13}C{^{1}H} NMR spectra of **2^K** recorded in THF-d$_8$ solution at 298 K the diphenylmethanido ligand gives a single set of signals. The protons of the central benzhydryl CH fragment linked with the K ion appear as a sharp singlet at 3.02 ppm. It should be noted that for the previously reported NMe_2-substituted analogue {[2,2'-(4-Me$C_6H_3$$NMe_2$)$_2$CH]K(THF)}$_2$ the chemical shift of the signal corresponding to the diphenylmethanido protons CH was 4.12 ppm (THF-d$_8$).[19] Such a shift can be associated with strong shielding of the central proton by aromatic systems of imidazolyl substituents in the case of **2^K**. The value of $^1J_{CH}$ coupling constant is known to correlate with the type of hybridization of the C−H bonding orbital.[20] The values are roughly proportional to the contribution of s-character and can be evaluated from the empirical formula $^1J_{CH} = 500*\%s$ (%s = 0.25 for sp^3, 0.33 for sp^2).[21] The $^1J_{CH}$ coupling constant measured for **2^K** (144 Hz; %s = 0.29) is comparable to the NMe_2 substituted analogue {[2,2'-(4-$MeC_6H_3NMe_2)_2CH]K(THF)\}_2$ (149 Hz; %s = 0.30) and corresponds to intermediate hybridization between sp^2 and sp^3 types.

Unfortunately, the attempts of synthesis of rare-earth complexes applying a salt metathesis approach by the reactions of **2^K** with anhydrous $LnCl_3$ (Ln = Sc, Y, Nd) did not allow for the isolation of the targeted diphenylmethanido complex. The reactions in THF solution at ambient temperature resulted in KCl precipitation thus indicating that the reaction took place. However, the trials to isolate any individual metal containing product failed.

Alkane elimination reaction between rare-earth metals tris(alkyl) complexes and ligands is a commonly used simple and efficient synthetic procedure for preparation of bis- and monoalkyl complexes.[22] In a number of publication it was demonstrated that intramolecular activation of sp^3 or sp^2 CH bonds of the proligand by alkyl group at the rare-earth metal centre results in the formation of heteroalkyl complexes containing two different Ln−C bonds.[23] Recently selective intermolecular CH bond activation was applied as a straightforward synthetic approach to heteroalky complexes containing CH_2SiMe_3 and bis(pyrazolyl)methyl ligands covalently bonded to one yttrium centre.[10]

In order to prepare rare-earth metal derivatives via CH-bond activation of the central methylene group of **1** its reactions with rare-earth metal tris(alkyl) precursors $Ln(CH_2SiMe_3)_2(THF)_2$ and $Ln(CH_2C_6H_4NMe_2\text{-}o)_3$, (Ln = Sc, Y) were investigated. Complexes $Ln(CH_2C_6H_4NMe_2\text{-}o)_3$ proved to be absolutely inert toward diphenylmethane **1**, no interactions were detected by ^1H NMR spectroscopy even at high temperature (C_6D_6, 80 °C). On the other hand $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Y) complexes readily activate the central CH_2 group of **1** affording heteroleptic alkyl complexes {[4-tBu-2-($C_3H_2N_2$Me-1)$C_6H_3]_2CH\}Ln(CH_2SiMe_3)_2$ $(THF)_n$ (Ln = Sc, n = 0 (**2^{Sc}**); Y, n = 1 (**2^Y**); Scheme 3) at room temperature. The ^1H NMR monitoring of the reactions (C_6D_6, 20 °C) indicates quantitative release of $SiMe_4$ and formation of **2^{Ln}** in 2 h. The preparative scale reactions were performed in toluene solution at ambient temperature (4 h). Recrystallization of the reaction products by slow diffusion of hexane into concentrated toluene solutions of complexes **2^{Sc}** and **2^Y** resulted in the formation of bright orange microcrystalline solids in 85 and 73% yield respectively.



2^{Sc} (n = 0), 85%
2^Y (n = 1), 73%

Scheme 3. Synthesis of heteroleptic Ln^{3+} alkyl complexes **2^{Sc}** and **2^Y**.

Different size of the metal ions (Sc^{3+} 0.745 Å *vs* Y^{3+} 0.900 Å)[24] lead to the formation of complexes with different coordination numbers. Thus, **2^{Sc}** is a THF-free complex, while yttrium analogue **2^Y** was isolated as an adduct with one THF molecule. The composition of **2^{Sc}** and **2^Y** was proved by NMR spectroscopy and by microanalysis data.

The structure of **2^{Sc}** was also unambiguously established by X-ray analysis. The molecular structure of **2^{Sc}** is depicted in Figure 2. Complex **2^{Sc}** crystallizes in triclinic *P-1* space group with one molecule in the asymmetric unit. The diphenylmethanido ligand in **2^{Sc}** is tridentate and is linked with the Sc^{3+} ion by covalent Sc−C and two coordination Sc−N bonds resulting in $NC_{sp3}N$ pincer type bonding. Moreover, two remaining CH_2SiMe_3 groups are covalently bound with Sc^{3+} ion, thus increasing its coordination number to 5. The geometry of coordination environment of Sc^{3+} ion in **2^{Sc}** can be described as a distorted tetragonal pyramid with C(34) carbon atom of the alkyl CH_2SiMe_3 group in the apical position.

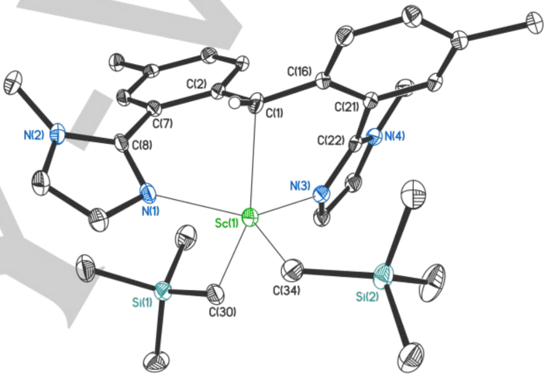


Figure 2. Molecular structure of {[4-tBu-2-($C_3H_2N_2$Me-1)$C_6H_3]_2CH\}Sc(CH_2SiMe_3)_2$ (**2^{Sc}**). The CH_3 groups of tBu substituents and all hydrogen atoms except H(1A) are omitted for clarity. Bond lengths (Å) and angles (°): Sc(1)−C(1) 2.387(4), Sc(1)−C(30) 2.242(4), Sc(1)−C(34) 2.211(3), Sc(1)−N(1) 2.250(3), Sc(1)−N(3) 2.266(3); C(34)−Sc(1)−C(30) 103.2(2), C(34)−Sc(1)−N(1) 101.9(2), C(30)−Sc(1)−N(1) 91.5(2), C(34)−Sc(1)−N(3) 112.9(2), C(30)−Sc(1)−N(3) 90.7(2), N(1)−Sc(1)−N(3) 143.7(2), C(34)−Sc(1)−C(1) 109.9(2), C(30)−Sc(1)−C(1) 146.7(2), N(1)−Sc(1)−C(1) 77.9(2), N(3)−Sc(1)−C(1) 80.5(2).

Diphenylmethanido moiety in **2^{Sc}** is not planar. The dihedral angle between two phenyl rings of the diphenylmethanido skeleton is 57.21(6)°. Imidazolyl fragments are also twisted with respect to the phenyl rings of dihpenylmethanido fragment (angles between planes of imidazolyl and phenyl rings are 43.76(5) and 46.11(5)°). It should be noted that, in contrast to **2^K**, the imidazolyl fragments in **2^{Sc}** are oriented in the opposite directions relative to each other. The geometry of the central diphenylmethanido carbon in **2^{Sc}** is indicative of its intermediate hybridization state between sp^2 and sp^3: the sum of the bond angles C(2)−C(1)−C(16), C(2)−C(1)−H(1A) and C(16)−C(1)−H(1A) is 351(2)° and is noticeably larger compared to the related heteroalkyl complex containing a σ-bonded diphenylmethanido ligand $[Ph_2CH]Lu(CH_2SiMe_3)_2(THF)_2$ (338.5°).[17] The measured value is close to the sum of the angles around benzhydryl carbon atom in the parent potassium complex $\mathbf{2}^{\mathbf{K}}$ and for recently published Ln(II) complexes with bulky benzhydryl ligands.[25]

The Sc−C bonds bond lengths in $\mathbf{2}^{\mathbf{Sc}}$ are slightly different (2.211(3) and 2.242(4) Å), while the Sc−CH bond is significantly longer (2.378(4) Å). The Sc−CH_2SiMe_3 bond lengths are close to those in pentacoordinated Sc^{3+} tris(alkyl) [26] as well as in mono- and bis(alkyl) complexes coordinated by dianionic (N^-,N,N^-)[27] and monoanionic (N,N^-,N),[28] (N,N,N^-),[29] (O,N^-,O),[30] and (P,N^-,P)[31] pincer type ligands. The distance between Sc^{3+} ion and diphenylmethanido carbon is so long that can be compared with coordination Sc−C bonds in the pentacoordinated complex with N-heterocyclic carbene ligand {[Me-NHC-CH_2CH(n-Bu)OSc$(CH_2SiMe_3)_2$]$_2$ (Sc−C 2.385(2) Å).[32] The Sc−N bond distances in $\mathbf{2}^{\mathbf{Sc}}$ (2.250(3) and 2.266(3) Å) are slightly shorter than the values measured in Sc complexes with coordinated imidazolyl fragments (2.270–2.303 Å).[33]

At ambient temperature in the ^1H NMR spectrum of $\mathbf{2}^{\mathbf{Sc}}$ the central diphenylmethanido protons appear as a singlet at 4.09 ppm, while the appropriate carbons in the ^{13}C NMR spectrum give rise to a singlet at 69.5 ppm. Two alkyl CH_2SiMe_3 groups in case of $\mathbf{2}^{\mathbf{Sc}}$ are non-equivalent and give rise to two sets of signals both in ^1H ($ScCH_2$: δ_H = 0.03 and 0.45 ppm; $SiMe_3$: δ_H = −0.09 and 0.05 ppm) and ^{13}C ($ScCH_2$: δ_C = 39.3 and 46.2 ppm; $SiMe_3$: δ_C = 3.5 and 3.8 ppm) spectra. The methyl protons of the imidazolyl fragments in the ^1H NMR spectrum of $\mathbf{2}^{\mathbf{Sc}}$ are also not equivalent and are presented by two very broad singlets at 2.87 and 3.08 ppm, while only one signal at 1.26 ppm is attributed to the protons of tBu-groups. Cooling the solution of $\mathbf{2}^{\mathbf{Sc}}$ to 243 K resulted in sharpening of all signals in ^1H and ^{13}C NMR spectra. More over at this temperature the tBu and aromatic protons of two parts of diphenylmethanido skeleton become non-equivalent both in ^1H and ^{13}C NMR spectra (See ESI Fig. S10 and S11). For the imidazolyl substituents also two sets of signals appear. At high temperature (333 K) in the ^1H NMR spectrum of $\mathbf{2}^{\mathbf{Sc}}$ a single set of signals corresponding to the protons of tBu-substituents (1.25 ppm) and imidazolyl fragments (3.08 ppm) appears, while two CH_2SiMe_3 groups remain non-equivalent. Such a behaviour of $\mathbf{2}^{\mathbf{Sc}}$ in solution at various temperatures can be associated with dynamic processes in the metal coordination sphere probably due to fast in NMR time-scale formation/dissociation of Sc−N coordination bonds.

In case of $\mathbf{2}^{\mathbf{Y}}$ the central diphenylmethanido protons appear in the ^1H NMR spectrum (C_6D_6, 293 K) as a singlet at 4.03 ($\mathbf{2}^{\mathbf{Y}}$), while the appropriate carbon in the ^{13}C NMR spectrum gives rise to a doublet at 67.2 ppm ($^1J_{YC}$ = 8.2 Hz) due to splitting with ^{89}Y nuclei (I = ½, 100%). Unlike $\mathbf{2}^{\mathbf{Sc}}$ in the ^1H and ^{13}C NMR spectra of $\mathbf{2}^{\mathbf{Y}}$ two alkyl CH_2SiMe_3 groups are equivalent and give a single set of signals (YCH_2: δ_H = –0.28 ppm; δ_C = 34.1 ppm; $SiMe_3$: δ_H = 0.30 ppm; δ_C = 4.6 ppm). Both of them are rather broad and no ^{89}Y−^1H or ^{89}Y−^{13}C coupling was observed. tBu and Me groups of the diphenylmethanido ligand in the case of $\mathbf{2}^{\mathbf{Y}}$ are also equivalent and give a sharp singlet at 1.26 ppm (tBu) and a broad singlet at 2.82 ppm (CH_3). The values of ^{13}C−^1H coupling constants of the central diphenylmethanido CH groups for $\mathbf{2}^{\mathbf{Sc}}$ (133.6 Hz) and $\mathbf{2}^{\mathbf{Y}}$ (135.8 Hz) are indicative of the hybridization state intermediate between sp^3 and sp^2.

Both heteroleptic alkyl complexes $\mathbf{2}^{\mathbf{Ln}}$ turned out to be rather stable. No decomposition was detected after heating in solution at 80 °C (C_7D_8, 3 days); noticeable decomposition of $\mathbf{2}^{\mathbf{Ln}}$ starts only after heating at 100 °C for 6 h. Decomposition is accompanied by $SiMe_4$ elimination along with the formation of complex mixture of the metal containing products.

Stereospecific diene polymerization is perhaps an area of catalysis where organolanthanides have largely been employed with success demonstrating all their inherent potentialities.[34] In this regard, heteroleptic alkyl complexes $\mathbf{2}^{\mathbf{Sc}}$ and $\mathbf{2}^{\mathbf{Y}}$ have been used as catalyst precursors for the isoprene (IP) polymerization under variable reaction conditions. The choice of metal ion and the catalyst activator(s) play a fundamental role in the control of the ultimate catalyst performance. Catalytic activity of complexes $\mathbf{2}^{\mathbf{Ln}}$ in isoprene polymerization was evaluated in toluene at room temperature. The results of the catalytic tests are summarized in Table 1.

Complexes $\mathbf{2}^{\mathbf{Ln}}$ as well as the binary systems $\mathbf{2}^{\mathbf{Ln}}$/borate (Borate = $[Ph_3C][B(C_6F_5)_4]$ (TB) or $[PhNHMe_2][B(C_6F_5)_4]$ (HNB)) or $\mathbf{2}^{\mathbf{Ln}}$/$AliBu_3$ did not perform any appreciable activity in the process (Table 1, entries 1–6). On the other hand, ternary systems $\mathbf{2}^{\mathbf{Ln}}$/Borate/$AliBu_3$ (1:1:10 molar ratio) trigger isoprene polymerization with moderate catalytic activity. Complex $\mathbf{2}^{\mathbf{Y}}$ demonstrated higher activity in comparison with scandium analogue $\mathbf{2}^{\mathbf{Sc}}$. in the combination with TB and $AliBu_3$, it allowed to achieve 98% polymer yield ([IP]/[Cat] = 1000) in 6 h at ambient temperature (Table 1, Entry 3). Activity of the catalytic system based on scandium complex $\mathbf{2}^{\mathbf{Sc}}$/TB/$AliBu_3$ was somewhat lower and under similar conditions ([IP]/[Cat] = 1000) the polymer yield was 75%. It was found that the nature of activator (TB *vs* HNB) affects the molecular weights and PDI of the resulted polymers. Thus, the polymers obtained in the presence of TB were characterized by moderate molecular masses ($36.3{\cdot}10^3$ and $22.8{\cdot}10^3$) and rather broadened monomodal PDI (1.95 and 2.90). In the case of HNB the polymer samples were characterized by bimodal molecular mass distribution with predominant content of rather high molecular weights fractions ($93.3{\cdot}10^3$ (94.4%) for $\mathbf{2}^{\mathbf{Sc}}$ and $135.9{\cdot}10^3$ (93.5%) for $\mathbf{2}^{\mathbf{Y}}$). This effect can be rationalized by the difference in pathways of the reactions of TB and HNB with alkyl complexes as well as by the different nature of the reaction products. Thus, the reaction of TB results in an alkyl group abstraction, the formation of cationic alkyl species and $Ph_3CCH_2SiMe_3$. The protonolysis of Ln−CH_2SiMe_3 bond by HNB along with the formation of cationic alkyl species affords $PhNMe_2$. $PhNMe_2$ is able to coordinate to the rare-earth ions during the catalytic reaction and most likely this leads to the appearance of two types of catalytically active species.[35] Despite these differences in M_n and PDI of the resulted polymers in all cases the catalytic systems $\mathbf{2}^{\mathbf{Ln}}$/TB/$AliBu_3$ demonstrated similar stereoselectivities affording predominantly 1,4-cis polyisoprenes (68.5–83.4%) with close content of 1,4-trans (9.2–13.6%) and 3,4 (3.9–19.2%) units.

It should be noted that incorporation of the tridentate $[NC_{sp3}N]$ pincer type ligand in the rare-earth metals coordination sphere in complexes $\mathbf{2}^{\mathbf{Ln}}$ does not allow to achieve high activity and selectivity of the catalytic system in isoprene polymerization. For example, ternary catalytic systems [Ln]/borate/$AliBu_3$ (1:1:10 molar ratio) based on tris(alkyl) complexes $Ln(CH_2SiMe_3)_3(THF)_2$ in identical conditions proved to be more active compared to $\mathbf{2}^{\mathbf{Ln}}$ and complete conversion of 1000 equivalents of monomer was achieved in few seconds (Table 1, Entries 5–8). At the same time the ternary catalytic systems $Ln(CH_2SiMe_3)_3(THF)_2$/borate/$AliBu_3$ demonstrated selectivity similar to that of **2^{Ln}** yielding the polyisoprenes featuring the content of 1,4-cis units from 69.1% up to 81.1%. On the other hand the related rare-earth metal complexes coordinated by $[NC_{sp2}N]$,[5a,d,36] $[NC_{sp2}O]$,[6b] $[NC_{sp2}S]$,[6b] and $[CC_{sp2}C]$[37] pincer type ligands derived from 1,3-disubstituted benzene in the combination with borates (HNB, TB or $B(C_6F_5)_4$) and AlR_3 ($AliBu_3$, $AlEt_3$, $AlMe_3$) provided comparable or higher activities, but significantly higher 1,4-cis selectivity.

Table 1. Isoprene polymerization initiated by systems **2^{Ln}**/borate/Al*i*Bu$_3$ (borate: $[Ph_3C][B(C_6F_5)_4]$ (TB), $[PhNHMe_2][B(C_6F_5)_4]$ (HNB), [Ln]/[borate]/[Al*i*Bu$_3$] = 1:1:10).

Entry[a]	Cat.	Activ./Al*i*Bu$_3$ (eq.)	t	Yield, %[b]	Microstructure, %[c]			M_n $[10^{-3}]$[d]	M_w/M_n[d]
					cis-1,4	*trans*-1,4	3,4		
1	**2^{Sc}**	TB / (10)	6 h	75	82.5	13.6	3.9	36.3	1.95
2	**2^{Sc}**	HNB / (10)	6 h	68	68.5	12.3	19.2	93.3 (94.4%) 20.3 (5.6%)	3.11 1.66
3	**2^{Y}**	TB / (10)	6 h	98	79.9	10.5	9.6	22.8	2.90
4	**2^{Y}**	HNB / (10)	6 h	86	83.4	9.2	7.4	135.9 (93.5%) 5.1 (6.5%)	2.01 1.17
5	$Sc(CH_2SiMe_3)_3(THF)_2$	TB / (10)	30 s	>99	69.1	7.8	23.1	2.7 (83.7%) 588.7 (16.3%)	5.84 2.26
6	$Sc(CH_2SiMe_3)_3(THF)_2$	HNB / (10)	45 s	>99	69.6	22.9	7.5	19.6 (93.3%) 926.9 (6.7%)	4.15 1.83
7	$Y(CH_2SiMe_3)_3(THF)_2$	TB / (10)	10 s	>99	81.1	1.0	17.9	71.8	1.50
8	$Y(CH_2SiMe_3)_3(THF)_2$	HNB / (10)	10 s	>99	79.7	3.5	16.8	36.3	1.99

[a] Polymerization conditions: temp = rt (20−22 °C); toluene (3.5 mL); 10 mmol of IP [IP]; 10 µmol of catalyst [cat.] (**2^{Ln}** or $Ln(CH_2SiMe_3)_3(THF)_2$); [cat.]:[IP] = 1:1000; activators: TB, $[Ph_3C][B(C_6F_5)_4]$; HNB, $[PhNHMe_2][B(C_6F_5)_4]$; [cat.]:[activator] = 1:1.05. [b] Average value calculated over three independent runs. [c] Determined by ^{1}H NMR and ^{13}C NMR spectroscopy in $CDCl_3$ at rt. [d] Determined by GPC in THF at 40 °C against a polystyrene standard.

Such differences in selectivity of catalytic systems based on **2^{Ln}** and rare-earth metal $[NC_{sp2}N]$, $[NC_{sp2}O]$, $[NC_{sp2}S]$, and $[CC_{sp2}C]$ pincer type complexes most likely results from the different metal-ligand bonding and the structure of the real catalytically active species. Thus in **2^{Ln}** the $[NC_{sp3}N]$ pincer ligand is strongly distorted while in the $[NC_{sp2}N]$, $[NC_{sp2}O]$ and $[CC_{sp2}C]$ pincer complexes derived from 1,3-disubstituted benzene metal-ligand fragments adopt nearly planar configuration.

In order to elucidate the nature of the catalytically active species the reactivity of **2^{Ln}** towards TB and HNB in THF-d$_8$ was investigated. According to the NMR spectroscopy the reaction of **2^{Ln}** with TB expectedly affords $Ph_3CCH_2SiMe_3$ while in the case of HNB $SiMe_4$ and $PhNMe_2$ were formed. No evidences for the abstraction of diphenylmethanido ligand by trityl cation or its release due to protonolysis of the metal-ligand bond were detected. Unfortunately, the ^{1}H NMR spectra of the cationic alkyl species generated in-situ from **2^{Ln}** and TB or HNB in THF-d$_8$ solution were rather broad and do not allow to get additional information about their structure. Moreover, the cationic alkyl species proved to be unstable in THF-d$_8$ solution and decomposed within 2 h affording $SiMe_4$ and a complex mixture of metal containing products.

Rare-earth alkyl complexes are known to be efficient catalysts for hydrosilylation of multiple C−C bonds.[38] Complexes **2^{Ln}** were evaluated as catalyst for hydrosilylation of alkenes and alkynes with $PhSiH_3$. Catalytic tests were carried out in benzene-d$_6$ under NMR control in the presence of 2 mol % of catalyst ([Alkene]:[$PhSiH_3$]:[Cat] = 50:50:1). Complexes **2^{Ln}** demonstrate high activity in catalysis of $PhSiH_3$ addition to nonene-1. At ambient temperature in 12 h **2^{Ln}** allowed to achieve 97 and 90% conversions affording exclusively linier anti-Markovnikov addition product $CH_3(CH_2)_8SiH_2Ph$ (Table 2, Entries 1 and 2). Activity of **2^{Y}** in styrene hydrosilylation was significantly lower than for nonene-1, at ambient temperature it allows to achieve 43% conversion only in 48 h giving predominantly Markovnikov

Table 2. Alkene and acetylene hydrosililation catalyzed by **2^{Ln}**

Entry[a]	Substrate	Cat	T, °C	t, h	Conv., %[b]	Selectivity[b]
						Markovnikov / anti-Markovnikov
1	Nonene-1	**2^{Sc}**	20	12	97	- / **>99**
2		**2^{Y}**			90	- / **>99**
3	Styrene	**2^{Sc}**	20	48	<2	- / -
4		**2^{Y}**			43	**83** / 17
5	Styrene	**2^{Sc}**	70	24	15	**95** / 5
6		**2^{Y}**			95	**72** / 28
						E / *Z*
7	Hexyne-1	**2^{Sc}**	70	24	84	58 / 42
8		**2^{Y}**			92	55 / 45
9	PhC≡CH	**2^{Sc}**	70	24	71	56 / 44
10		**2^{Y}**			90	53 / 47

[a] Reaction conditions: C_6D_6 (0.6 mL); 10 μmol of $\mathbf{2}^{\mathbf{Ln}}$ (2% mol); [alkene]:[Cat.] = 50:1; [$PhSiH_3$]:[Cat.] = 50:1; [b] Determined by ^1H NMR and $^{29}Si\{^1H\}$ NMR spectroscopy and by GC-MS according to previously published data.[38f,39]

addition product $PhCH(Me)SiH_2Ph$ with 83% selectivity (Table 2, Entry 4). Increasing the reaction temperature up to 70 °C allowed to achieve almost quantitative conversion (95%) in 24 h (Table 2, Entry 4), but as it could be expected at this temperature the selectivity decreases giving Markovnikov addition product in 72% (Table 2, Entry 6). Surprisingly, scandium analogue $\mathbf{2}^{\mathbf{Sc}}$ was found to be almost inactive in styrene hydrosilylation at ambient temperature giving only traces of hydrosilylation products (<2%; Table 2, Entry 3). However, when temperature was increased to 70 °C in 24 h the product yield was 15%. Internal alkenes (*cyclo*-hexene, *cis*- or *trans*-stilbenes) were absolutely inactive even at high temperature (70 °C, 24 h) in the presence of $\mathbf{2}^{\mathbf{Ln}}$.

Complexes $\mathbf{2}^{\mathbf{Ln}}$ also enable $PhSiH_3$ addition to terminal triple C≡C bonds of hexyne-1 and phenylacetylene at 70 °C, while at 20 °C no reaction takes place. After 24 h at 70 °C hydrosilylation of hexyne-1 and phenylacetylene in the presence of 2 mol % of $\mathbf{2}^{\mathbf{Ln}}$ resulted in the formation of hydrosilylation products in 71–92% yield respectively (Table 2, Entries 7–10). In all cases the formation of mixtures of *E*- and *Z*-isomers almost in equal amounts was observed. In contrast to terminal triple C≡C bonds complexes $\mathbf{2}^{\mathbf{Ln}}$ were inactive in hydrosilylation of internal phenylmethyl and diphenyl acetylenes even in harsh conditions (70 °C, 24 h).

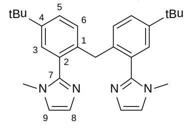
Conclusion

New diphenylmethane $[4\text{-}tBu\text{-}2\text{-}(C_3H_2N_2Me\text{-}1)C_6H_3]_2CH_2$ bearing pendant imidazolyl groups was synthesized and successfully employed as a tridentate pincer type $NC_{sp3}N$ alkyl ligand for the synthesis of heteroleptic rare-earth alkyl complexes containing two different types of Ln−C bond. It was demonstrated that tridentate diphenylmethanido ligand allows to provide high thermal stability of heteroleptic rare-earth metal alkyl species. Heteroalkyl Sc and Y complexes demonstrate moderate activity in intermolecular hydrosilylation of terminal alkenes and acetylenes. Combined with borates and $AliBu_3$ complexes $\mathbf{2}^{\mathbf{Ln}}$ catalyse isoprene polymerization. Further investigation of reactivity of heteroleptic rare-earth metal alkyl complexes containing simultaneously two different Ln−C bonds is in progress.

Experimental Section

All experiments were performed by using standard Schlenk or glove-box techniques, with rigorous exclusion of traces of moisture and air. After being dried over CaH_2 THF was purified by distillation from sodium/benzophenoneketyl; hexane and toluene were dried by distillation from sodium/triglyme and benzophenoneketyl prior to use. Benzene-d_6, toluene-d_8 and THF-d_8 were dried with sodium and were condensed in vacuum into NMR tubes prior to use. $CDCl_3$ was used without additional purification. Bis(4-(tert-butyl)-2-iodophenyl)methane,[14] 1-methyl-2-(tributylstannyl)-1H-imidazole,[15] $Pd(PPh_3)_4$,[16] $Ln(CH_2SiMe_3)_3(THF)_2$,[40] and $Ln(CH_2C_6H_4NMe_2\text{-}2)_3$[41] were prepared according to literature procedures. NMR spectra were recorded using a Bruker DPX 200 or Bruker Avance III 400 MHz spectrometer. Chemical shifts for ^1H, $^{13}C\{^1H\}$ NMR spectra were referenced internally to the residual solvent resonances and are reported relative to $SiMe_4$. Lanthanide metal analyses were carried out by complexometric titration.[42] The C, H, and N elemental analyses were performed in the microanalytical laboratory of the G. A. Razuvaev Institute of Organometallic Chemistry.

Synthesis of $[4\text{-}tBu\text{-}2\text{-}(C_3H_2N_2Me\text{-}1)C_6H_3]_2CH_2$ (1). In a glove-box to a solution of bis(4-(tert-butyl)-2-iodophenyl)methane (1.50 g, 2.87 mmol) and 1-methyl-2-(tributylstannyl)-1H-imidazole (2.62 g, 7.05 mmol) in toluene (50 mL) $Pd(PPh_3)_4$ (0.065 g, 0.06 mmol; 2% mol) was added. The reaction mixture was heated in oil bath at 140 °C for 120 h, hydrolysed with water and organic compounds were extracted with ethyl acetate. **1** was purified by column chromatography (silicagel, EtOAc) and was isolated as amorphous solid in 87% yield (1.08 g, 2.45 mmol). ^1H NMR (400 MHz, $CDCl_3$, 293 K): 1.26 (s, 18H, CH_3tBu), 3.06 (s, 6H, NCH_3), 3.98 (s, 2H, CH_2), 6.57 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H^6), 6.89 (d, $^3J_{HH}$ = 1.2 Hz, 2H, $H^{8,9}$), 7.12 (d, $^3J_{HH}$ = 1.2 Hz, 2H, $H^{8,9}$), 7.15 (d, $^4J_{HH}$ = 2.1 Hz, 2H, H^3), 7.21 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 2.1 Hz, 2H, H^5) ppm. $^{13}C\{^1H\}$ (100 MHz, $CDCl_3$, 293 K): 31.3 (s, CH_3 tBu), 32.9 (s, NCH_3), 34.4 (s, *C* tBu), 36.2 (s, CH_2), 120.3 (s, *C*H, $C^{8,9}$), 126.0 (s, *C*H, C^5), 127.4 (s, *C*H, C^3), 127.7 (s, *C*H, $C^{8,9}$), 129.5 (s, C^2), 129.9 (s, *C*H, C^6), 138.6 (s, C^1), 147.7 (s, C^7), 148.8 (s, C^4) ppm. $^{15}N{-}^1H$ correlation: 158.2 (NMe), 256.8 (N). ^1H NMR of **1** (400 MHz, C_6D_6, 293 K): 1.11 (s, 18H, CH_3 tBu), 2.64 (s, 6H, NCH_3), 4.30 (s, 2H, CH_2), 6.47 (d, $^3J_{HH}$ = 1.0 Hz, 2H, $H^{8,9}$), 7.08 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 2.1 Hz, 2H, H^5), 7.12 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H^6), 7.21 (d, $^4J_{HH}$ = 2.1 Hz, 2H, H^3), 7.33 (d, $^3J_{HH}$ = 1.0 Hz, 2H, $H^{8,9}$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, C_6D_6, 293 K): 31.0 (s, CH_3 tBu), 32.2 (s, NCH_3), 34.0 (s, *C* tBu), 35.4 (s, CH_2), 120.0 (s, *C*H, $C^{8,9}$), 125.8 (s, *C*H, C^5), 127.1 (s, *C*H, C^3), 128.4 (s, *C*H, $C^{8,9}$), 130.5 (s, C^2), 130.7 (s, *C*H, C^6), 139.5 (s, C^1), 148.0 (s, C^7), 148.1 (s, C^4) ppm. Elemental analysis calculated for $C_{29}H_{36}N_4$ (440.62 g/mol): C, 79.05; H, 8.24; N, 12.72. Found: C, 79.15; H, 8.08; N, 12.77. MS: [M^+] 440.2. IR (Nujol, KBr): 1740 (w), 1650 (m), 1610 (m), 1570 (m), 1525 (m), 1485 (s), 1405 (s), 1360 (s), 1340 (m), 1280 (s), 1260 (s), 1230 (w), 1200 (m), 1130 (s), 1105 (m), 1080 (m), 1050 (w), 1030 (s), 920 (m), 895 (m), 870 (w), 850 (w) 835 (m), 810 (s), 680 (s), 635 (m) cm^{-1}.



Synthesis of $[\{[4\text{-}tBu\text{-}2\text{-}(C_3H_2N_2Me\text{-}1)C_6H_3]_2CH\}K(OEt_2)\}_2$ ($\mathbf{2}^{\mathbf{K}}$). To a mixture of **1** (0.400 g, 0.91 mmol) and tBuOK (0.100 g, 0.91 mmol) in Et_2O (20 mL) a hexane solution of n-BuLi (1.5 M, 0.6 mL, 0.91 mmol) was added. The solution immediately became bright orange and the orange precipitate formed. The reaction mixture was stirred at ambient temperature for 1 h, then the solvent was removed in vacuum and the solid residue was washed 3 times with hexane (15 mL) to remove LiOtBu. Crystallization of the reaction product by slow concentration of the solution in Et_2O at ambient temperature resulted in the formation of bright orange crystals of $\mathbf{2}^{\mathbf{K}}$. Complex $\mathbf{2}^{\mathbf{K}}$ was isolated in 78% yield (0.390 g, 0.35 mmol). ^1H NMR (400 MHz, THF-D_8, 293 K): 1.13 (t, $^3J_{HH}$ = 7.0 Hz, 12H, CH_3 Et_2O), 1.19 (s, 36H, CH_3 tBu), 3.02 (s, 2H, KC*H*), 3.31 (s, 12H, NCH_3), 3.40 (q, $^3J_{HH}$ = 7.0 Hz, 8H, CH_2 Et_2O), 6.55 (d, $^4J_{HH}$ = 2.5 Hz, 4H, H^3), 6.72 (d, $^3J_{HH}$ = 1.2 Hz, 4H, $H^{8,9}$), 6.77 (d, $^3J_{HH}$ = 1.2 Hz, 4H, $H^{8,9}$), 6.85 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 2.5 Hz, 4H, H^5),7.18 (d, $^3J_{HH}$ = 8.8 Hz, 4H, H^6) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, THF-D_8, 293 K): 14.7 (s, CH_3 Et_2O), 31.2 (s, CH_3 tBu), 31.9 (s, NCH_3), 65.3 (s, CH_2 Et_2O), 72.7 (s, K*C*H), 114.4 (s, *C*H, C^6), 118.9 (s, *C*H, $C^{8,9}$), 125.7 (s, *C*H, C^5), 126.3 (s, *C*H, $C^{8,9}$), 126.6 (s, *C*H, C^3),126.9 (s, C^4), 128.1 (s, C^1), 142.4 (s, C^2), 152.1 (s, C^7) ppm. Elemental analysis calculated for $C_{66}H_{90}K_2N_8O_2$ (1105.67 g/mol): C, 71.69; H, 8.20; N, 10.13. Found: C, 71.50; H, 8.15; N, 10.30.

Synthesis of $\{[4\text{-}tBu\text{-}2\text{-}(C_3H_2N_2Me\text{-}1)C_6H_3]_2CH\}Sc(CH_2SiMe_3)_2$ ($\mathbf{2}^{\mathbf{Sc}}$). A toluene solution (10 mL) of **1** (0.410 g, 0.94 mmol) was added to a solution of $Sc(CH_2SiMe_3)_3(THF)_2$ (0.425 g, 0.94 mmol) in toluene (10 mL). The orange reaction mixture was stirred at ambient temperature for 4 h and the volatiles were removed in vacuum. The solid residue was dissolved in small amount of fresh toluene (3 mL) and to the resulted solution hexane was layered to give bright orange crystals of **2$^{\mathrm{Sc}}$**. The mother liquid was decanted and the crystals were washed with hexane and dried in vacuum. Complex **2$^{\mathrm{Sc}}$** was isolated in 85% yield (0.525 g, 0.80 mmol). ^{1}H NMR (400 MHz, toluene-d$_8$, 293 K): −0.09 (s, 9H, SiMe$_3$), 0.03 (s, 2H, ScCH_2), 0.05 (s, 9H, SiMe$_3$), 0.49 (brs, 1H, ScCH_2),0.58 (br s, 1H, ScCH_2), 1.26 (s, 18H, CH_3 tBu), 2.87 (br s, 3H, NCH_3), 3.08(br s, 3H, NCH_3), 4.09 (s, 1H, ScCH), 6.12 (br s, 2H, CH), 6.33 (br s, 1H, CH),6.84 (br s, 3H, CH), 7.26 (br s, 2H, CH) ppm. ^{13}C{^{1}H} NMR (100 MHz, toluene-d$_8$, 293 K): 3.5 (s, SiMe$_3$), 3.8 (s, SiMe$_3$), 31.5 (s, CH$_3$ tBu), 34.0 (s, C tBu), 34.3 (br s, NCH$_3$), 39.3 (br s, ScCH$_2$), 46.2(br s, ScCH$_2$), 69.5(s, ScCH), 117.2 (very br, CH Ar), 120.6 (br s, CH Ar), 125.7 (s, CH Ar),126.5 (s, CH Ar), 129.2 (s, CH Ar), 130.4 (s, CH Ar), 139.2 (s, C Ar), 142.5 (br s, C Ar), 144.5 (br s, C Ar), 148.4 (br s, C Ar) ppm. ^{1}H NMR (400 MHz, toluene-d$_8$, 243 K): −0.04 (s, 9H, SiMe$_3$), 0.03 (d, $^2J_{\mathrm{HH}}$ = 10.4 Hz, 1H, ScCH_2), 0.05 (d, $^2J_{\mathrm{HH}}$ = 10.4 Hz, 1H, ScCH_2), 0.15 (s, 9H, SiMe$_3$), 0.54 (d, $^2J_{\mathrm{HH}}$ = 11.0 Hz, 1H, ScCH_2), 0.79 (d, $^2J_{\mathrm{HH}}$ = 11.0 Hz, 1H, ScCH_2), 1.28 (s, 9H, CH_3 tBu), 1.29 (s, 9H, CH_3 tBu), 2.67 (s, 3H, NCH_3), 2.95 (s, 3H, NCH_3), 4.22 (s, 1H, ScCH), 5.94 (s, 1H, H^{8,9}), 6.08 (s, 1H, H^{8,9}), 6.36 (d,$^3J_{\mathrm{HH}}$ = 8.5 Hz, 1H, H^6), 6.88 (dd,$^3J_{\mathrm{HH}}$ = 8.5 Hz, $^4J_{\mathrm{HH}}$ = 1.5 Hz, 1H, H^5), 6.94 (d, $^4J_{\mathrm{HH}}$ = 1.5 Hz, 1H, H^3), 7.00 (d, $^4J_{\mathrm{HH}}$ = 1.5 Hz, 1H, H^3), 7.14 (m, 3H, H^{5,6,8,9}), 7.35 (s, 1H, H^{8,9}) ppm. ^{13}C{^{1}H} NMR (100 MHz, toluene-d$_8$, 243 K): 3.3 (s, SiMe$_3$), 3.6 (s, SiMe$_3$), 31.2 (s, CH$_3$ tBu), 31.3 (s, CH$_3$ tBu), 33.1 (s, NCH$_3$), 33.7 (s, C tBu), 34.0 (s, NCH$_3$), 34.1 (s, C tBu), 39.0 (br s, ScCH$_2$), 45.3 (br s, ScCH$_2$), 69.3 (s, ScCH), 116.5 (s, CH, C^6), 118.4 (s, CH, C^6), 120.1 (s, CH, C^{8,9}), 120.9 (s, CH, C^{8,9}), 122.3 (s, CH, C^5), 126.1 (s, CH, C^3), 126.4 (s, CH, C^3), 127.4 (s, CH, C^5), 128.2 (s, CH, C^{8,9}), 130.0 (s, CH, C^{8,9}), 135.0 (s, C^4), 135.8 (s, C^1), 138.6 (s, C^4), 141.9 (s, C^2), 142.6 (s, C^1), 144.1 (s, C^2), 147.8 (s, C^7), 150.8 (s, C^7) ppm. Elemental analysis calculated for $C_{37}H_{57}N_4ScSi_2$ (659.00 g/mol): C, 67.43; H, 8.72; N, 8.50; Sc, 6.82. Found: C, 67.24; H, 8.92; N, 8.33; Sc, 6.75.

Synthesis of {[4-tBu-2-($C_3H_2N_2$Me-1)C_6H_3]$_2$CH}Y(CH_2SiMe_3)$_2$(THF) (2$^{\mathrm{Y}}$). Complex **2$^{\mathrm{Y}}$** was synthesized and isolated similarly to **2$^{\mathrm{Sc}}$** starting from Y(CH_2SiMe_3)$_3$(THF)$_2$ (0.640 g, 1.29 mmol) and **1** (0.560 g, 1.29 mmol). Complex **2$^{\mathrm{Y}}$** was isolated as bright orange microcrystalline solid in 73% yield (0.730 g, 0.94 mmol). ^{1}H NMR (400 MHz, C_6D_6, 298 K): –0.28 (br s, 4H, YCH_2), 0.30 (s, 18H, SiMe$_3$), 1.26 (s, 18H, CH_3 tBu), 1.39 (br s, 4H, β-CH_2 THF), 2.82 (br s, 6H, NCH_3), 3.57 (br s, 4H, α-CH_2 THF), 4.03 (br s, 1H, YCH), 6.11 (s, 2H, CH Ar), 6.82 (s, 2H, CH Ar), 6.96 (br m, 4H, CH Ar), 7.26 (br m, 2H, CH Ar) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, 293 K): 4.6 (s, SiMe$_3$), 25.7 (s, β-CH$_2$ THF), 31.6 (s, CH$_3$ tBu), 33.6 (s, NCH$_3$), 33.9 (s, C tBu), 34.1 (br s, YCH$_2$), 67.2 (d, $^1J_{\mathrm{YC}}$ = 8.1 Hz, YCH), 68.4 (s, α-CH$_2$ THF), 117.6 (very br, CH Ar), 120.5 (br s, CH, CH Ar), 126.8 (s, CH Ar), 127.2 (s, CH Ar), 127.5 (s, CH Ar), 128.6 (s, CH Ar), 139.9 (br s, C Ar), 143.9 (br s, C Ar), 150.5 (br s, C Ar) ppm. Y-HMBC (400 MHz, C_6D_6, 293 K): {–0.28;832}, {4.03;832}. Elemental analysis calculated for $C_{41}H_{65}N_4OSi_2Y$ (775.06 g/mol): C, 63.54; H, 8.45; N, 7.23; Y, 11.47. Found: C, 63.70; H, 8.58; N, 7.20; Y, 11.39.

Polymerization of Isoprene. A typical polymerization procedure was carried out as following. Under a nitrogen atmosphere and room temperature, a toluene solution (2 mL) of [HNMe$_2$Ph][B(C_6F_5)$_4$] (8.0 mg, 10 μmol) or [Ph$_3$C][B(C_6F_5)$_4$] (9.2 mg, 10 μmol) was added to a toluene solution (3 mL) of complexes **2$^{\mathrm{Ln}}$** (10 μmol) in a 25 mL flask. Then 10 equiv. of AliBu$_3$ (0.1 mL, 100 μmol, 1.0 M in toluene) were added under stirring after a few minutes. Upon the addition of 1000 equiv of isoprene (1 mL, 0.01 mol), polymerization was initiated and carried out for 2–4 h. The reaction mixture was poured into methanol and then dried under vacuum at ambient temperature to a constant weight. Then, 1,4- and 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 ($M_{\mathrm{w}}/M_{\mathrm{n}}$) of the polymers were calculated with reference to a universal calibration against polystyrene standards.

General procedure for hydrosilylation reactions. To a solution of complexes **2$^{\mathrm{Ln}}$** (10 μmol) in C_6D_6 (0.6 mL) were added PhSiH$_3$ (0.5 mmol) and alkene or acetylene (0.5 mmol). The reaction course was controlled by ^{1}H NMR spectroscopy. Conversion and selectivity were determined by integrating the remaining substrates and the newly formed hydrosilylation products in the ^{1}H, ^{13}C{^{1}H} and ^{29}Si{^{1}H} NMR spectra according to previously known data.

X-ray crystallography. The X-ray data for **2$^{\mathrm{K}}$** and **2$^{\mathrm{Sc}}$** were collected with *Bruker D8 Quest* and *Rigaku OD Xcalibur* diffractometers (Mo$_{K\alpha}$-radiation, *ω*-scans technique, λ = 0.71073 Å, T = 100 K) using *APEX3*[43] and *CrysAlis Pro*[44] software packages. *SADABS*[45] and *CrysAlis Pro* was used to perform absorption corrections. The structures were solved by direct methods and were refined by full-matrix least squares on F^2 for all data using *SHELX*.[46] All non-hydrogen atoms and H(1A) atoms in **2$^{\mathrm{K}}$** and **2$^{\mathrm{Sc}}$** were found from Fourier syntheses of electron density (all non-hydrogen atoms were refined anisotropically). All other hydrogen atoms 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). The crystallographic data and structures refinement details are given in Table S1 (See ESI). CCDC–1980060 (**2$^{\mathrm{K}}$**) and 1980061 (**2$^{\mathrm{Sc}}$**) 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 in the Supporting Information.

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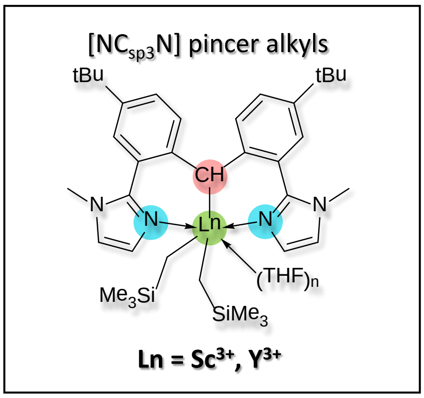

Thermally stable heteroleptic tri(alkyl) rare-earth metal complexes [NC$_{sp3}$N]Ln(CH$_2$SiMe$_3$)$_2$(THF)$_n$ (Ln = Sc, Y) containing NC$_{sp3}$N pincer dyphenylmethanido ligand were synthesized through selective C$_{sp3}$−H bond activation of the central CH$_2$ group of imidazolyl substituted diphenylmethane. Incorporation of NC$_{sp3}$N pincer dyphenylmethanido ligand provides stability and at the same time maintains high reactivity of these heteroleptic tri(alkyl)s.