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Bis(imidazolin-2-iminato) Rare Earth Metal Complexes: Synthesis, Structural Characterization, and Catalytic Application

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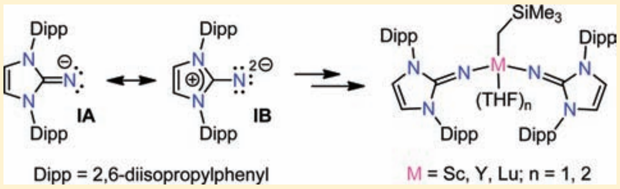
Supporting Information

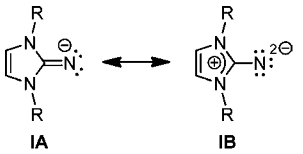


ABSTRACT: Reaction of anhydrous rare earth metal halides MCl_3 with 2 equiv of 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-imine ($Im^{Dipp}NH$) and 2 equiv of trimethylsilylmethyl lithium (Me_3SiCH_2Li) in THF furnished the complexes $[(Im^{Dipp}N)_2MCl(THF)_n]$ (M = Sc, Y, Lu). The molecular structures of all three compounds were established by single-crystal X-ray diffraction analyses. The coordination spheres around the pentacoordinate metal atoms are best described as trigonal bipyramids. Reaction of YbI_2 with 2 equiv of $LiCH_2SiMe_3$ and 2 equiv of the imino ligand $Im^{Dipp}NH$ in tetrahydrofuran did not result in a divalent complex, but instead the Yb(III) complex $[(Im^{Dipp}N)_2YbI(THF)_2]$ was obtained and structurally characterized. Treatment of $[(Im^{Dipp}N)_2MCl(THF)_n]$ with 1 equiv of $LiCH_2SiMe_3$ resulted in the formation of $[(Im^{Dipp}N)_2M(CH_2SiMe_3)(THF)_n]$. The coordination arrangement of these compounds in the solid state at the metal atoms is similar to that found for the starting materials, although the introduction of the neosilyl ligand induces a significantly greater distortion from the ideal trigonal-bipyramidal geometry. $[(Im^{Dipp}N)_2Y(CH_2SiMe_3)(THF)_2]$ was used as precatalyst in the intramolecular hydroamination/cyclization reaction of various terminal aminoalkenes and of one aminoalkyne. The complex showed high catalytic activity and selectivity. A comparison with the previously reported dialkyl yttrium complex $[(Im^{Dipp}N)Y(CH_2SiMe_3)_2(THF)_3]$ showed no clear tendency in terms of activity.

INTRODUCTION

Imidazolin-2-iminato ligands (Im^RN) were recently introduced to rare earth metal chemistry as suitable noncyclopentadienyl ancillary ligands and were shown to form particularly short and strong metal−nitrogen bonds.[1,2] The pronounced electron-donating capacity of these monanionic ligands arises from the ability of the imidazolium ring to efficiently stabilize a positive charge, as indicated by the two limiting resonance structures **IA** and **IB** shown in Scheme 1.[3] The contribution of the more strongly polarized form **1B** usually increases upon metal coordination, which means that imidazolin-2-iminato ligands are able to act as 2σ,4π-electron donors toward early transition metals or metals in a higher oxidation state.[4,5] Therefore, similarly to phosphoraneiminato ligands,[6] these ligands can be regarded as monodentate analogues of the ubiquitous cyclopentadienyl ligands.[7−10] Furthermore, these monoanionic ligands share an isolobal relationship with dianionic imido ligands,[11] and consequently, imidazolin-2-iminato complexes could be regarded as models for mononuclear rare earth metal imido complexes;[12] these were unknown until fairly recently, since the imido (RN) group was generally found to bind in a capping or bridging fashion.[13,14] By using a diamine-functionalized nacnac ligand, however, Chen and co-workers recently succeeded in the isolation and structural characterization of the first scandium terminal imido complex and reported its reactivity along the scandium−nitrogen bond.[15]

Scheme 1. Mesomeric Structures for Imidazolin-2-iminato Ligands (Im^RN)



In view of the large number of mono-, bis-, and tris(cyclopentadienyl) rare earth metal complexes of the types **II−IV** that have been prepared since the first report of $[(\eta\text{-}C_5H_5)_3M]$ (M = Sc, Y, La, Ce, Pr, Nd, Sm, Gd) by Wilkinson and Birmingham in 1954,[16] we set out to synthesize a similar series of noncyclopentadienyl mono-, bis-, and tris(imidazolin-2-iminato) complexes of the types **V−VIII** with isolobal, Cp-analogous Im^RN ligands (Figure 1).[1] Our initial studies involved the preparation of mono(imidazolin-2-iminato) complexes of type **V**, and the dichlorides $[(Im^RN)MCl_2(THF)_3]$ (R = Dipp =2,6-diisopropylphenyl, M = Sc, Y, Lu, Gd; R = *t*Bu, M = Y) were obtained,[12,17] which proved to be excellent starting materials for the preparation of

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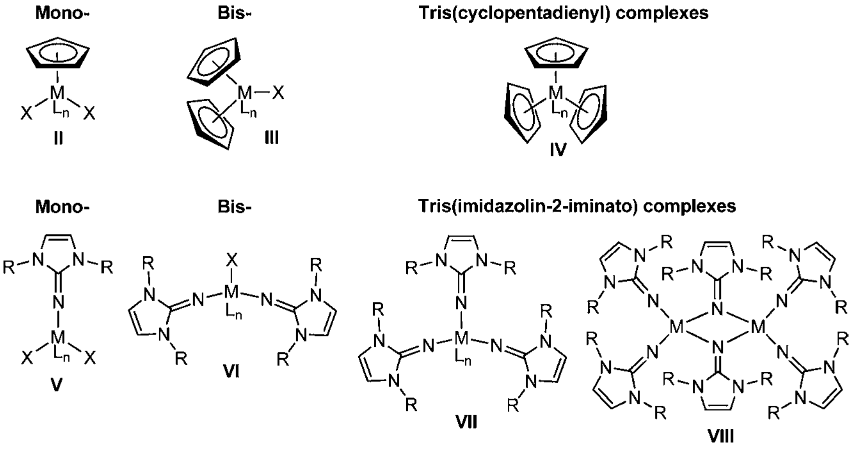


Figure 1. Relationship between cyclopentadienyl and imidazolin-2-iminato rare earth metal complexes.

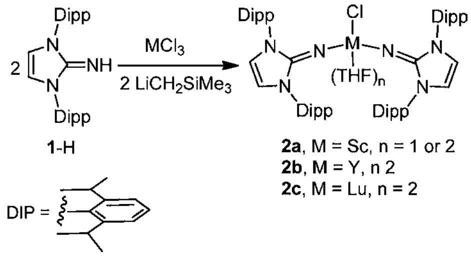
mononuclear alkyl, amido, cyclopentadienyl, cyclooctatetraenyl, and carboranyl complexes by salt metathesis reactions.[12,18,19] It was also shown that the resulting bis(neosilyl) complexes $[(\mathrm{Im^{Dipp}N})\mathrm{M}(\mathrm{CH_2SiMe_3})_2(\mathrm{THF})_3]$ (M = Y, Lu) act as efficient catalysts for hydroamination and hydrosilylation reactions.[18] Several homoleptic tris(imidazolin-2-iminato) complexes were also already prepared and structurally characterized as mono- or binuclear complexes of the types **VII** or **VIII**, depending on the steric demand of the imidazole substituents.[20]

In contrast, the preparation of bis(imidazolin-2-iminato) complexes of type **VI**, which might be regarded as long overdue given the ubiquity of bis(cyclopentadienyl) ligand frameworks in rare earth metal chemistry and the prevalent use of the corresponding lanthanocenes and group 3 metallocenes as catalysts for a large variety of organic transformations and polymerizations,[7,9,21] had never been reported. With this contribution, we would like to close this gap by reporting the synthesis and structural characterization of the complexes $[(\mathrm{Im^{Dipp}N})_2\mathrm{MX}(\mathrm{THF})_n]$ (M = Sc, Y, Lu, X = Cl, $\mathrm{CH_2SiMe_3}$, n = 1 or 2). In these neosilyl complexes, the presence of one metal−carbon σ bond suggests that the systems might be catalytically active species, which is indeed confirmed by studying the yttrium complex $[(\mathrm{Im^{Dipp}N})_2\mathrm{Y}(\mathrm{CH_2SiMe_3})(\mathrm{THF})_2]$ as a catalyst for intramolecular hydroamination/cyclization reactions.

■ RESULTS AND DISCUSSION

Preparation and Structural Characterization of Bis(imidazolin-2-iminato) Mono(chloride) Complexes. Following the same strategy as described for the preparation of mono(imidazolin-2-iminato) dichloro complexes of the type $[(\mathrm{Im^{Dipp}N})\mathrm{MCl_2}(\mathrm{THF})_3]$,[12,18] the reaction of 1 equiv of the anhydrous rare earth metal halides $\mathrm{MCl_3}$ (M = Sc, Y, Lu) with 2 equiv of 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-imine ($\mathrm{Im^{Dipp}NH}$, **1**-H) and 2 equiv of trimethylsilylmethyl lithium ($\mathrm{Me_3SiCH_2Li}$) in THF furnished the imidazolin-2-iminato complexes $[(\mathrm{Im^{Dipp}N})_2\mathrm{MCl}(\mathrm{THF})_n]$ (M = Sc (**2a**), Y (**2b**), Lu (**2c**)) as white solids after extraction with toluene (Scheme 2).[22] Characterization of complexes **2** at this stage by NMR spectroscopy and elemental analysis indicates the formation of a mono(tetrahydrofuran) complex for scandium, whereas bis(tetrahydrofuran) complexes are obtained for the larger yttrium and lutetium ions (Scheme 2).[23] In agreement with the formation of a C_s-symmetric complex, the ^{1}H and ^{13}C{^{1}H} NMR spectra of **2a** (in $\mathrm{C_6D_6}$) show signals that indicate the presence of two sets of chemically inequivalent isopropyl groups. In contrast, the spectra of **2b** and **2c** confirm time-averaged C_{2v}-symmetry in solution, and for instance, only one septet or, more precisely, one quartet of quartets together with two doublets are observed, as expected for eight equivalent isopropyl substituents featuring diastereotopic methyl groups (see Supporting Information for selected NMR spectra).

Scheme 2. Syntheses of the Bis(imidazolin-2-iminato) Complexes $[(\mathrm{Im^{Dipp}N})_2\mathrm{MCl}(\mathrm{THF})_n]$ (2a−2c)



Single crystals of complexes **2** were obtained from THF-pentane solutions (3:1) at −30 °C, and the molecular structures of **2a**−**2c** were established by X-ray diffraction analyses, revealing in all three cases the formation of bis(tetrahydrofuran) complexes of the type $[(\mathrm{Im^{Dipp}N})_2\mathrm{LnCl}(\mathrm{THF})_2]$ (Scheme 2). The scandium and lutetium complexes are isostructural and crystallize as THF solvates **2a**·2THF and **2c**·2THF (a total of 4 THF per metal atom) in the monoclinic space group $C2/c$ (Figure 2), whereas the yttrium complex **2b** crystallizes with disordered pentane in the triclinic space group $P\bar{1}$ (Figure 3). The coordination spheres around the pentacoordinate metal atoms in **2a**−**2c** are best described as trigonal bipyramids with the THF ligands adopting the axial positions, despite a pronounced deviation of the O1−M−O2 angles from 180° [162.67(7)° for **2a**, 164.50(7)° for **2b**, and 161.98(14)° for **2c**]. The orientation of the three anionic equatorial ligands, the two imidazolin-2-iminato ligands, and the chlorine atom, however, is nearly perfectly planar, with the sum of the N−M−N and N−M−Cl angles being almost exactly 360°. For quantifying the structural distortion in pentacoordinate metal complexes, which are usually intermediate between the idealized trigonal bipyramidal and square pyramidal extremes, Addison and Reedijk have introduced the structural index parameter $\tau = (\alpha - \beta)/60$, in which α and β are the two largest angles around the metal atom.[24] Accordingly, a τ value of zero is obtained for perfect tetragonal geometry, while it

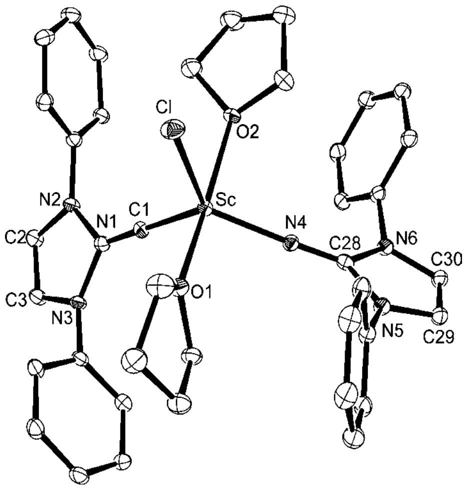


Figure 2. ORTEP diagram of **2a** in **2a**·2THF with thermal displacement parameters drawn at 30% probability. The isopropyl groups have been omitted for clarity.

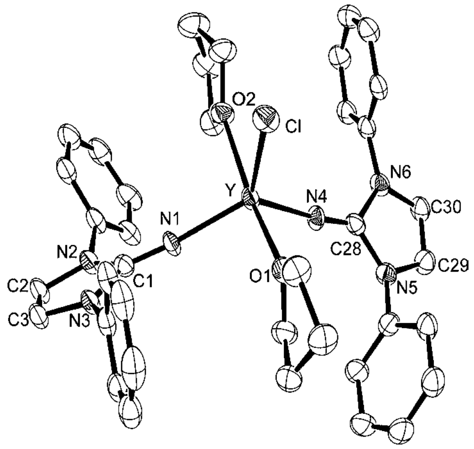


Figure 3. ORTEP diagram of **2b** in **2b**·*n*-pentane with thermal displacement parameters drawn at 50% probability. The isopropyl groups were omitted for clarity.

becomes unity for a perfect trigonal bipyramid. The largest angles in complexes **2** are O1−M−O2 and Cl−M−N4 (Table 1), and the resulting τ values of 0.67 (**2a**), 0.71 (**2b**), and 0.67 (**2c**) support the assignment of distorted trigonal bipyramidal geometries.

The imidazolin-2-iminato ligands in **2a**−**2c** coordinate in almost perfectly linear fashion, indicating that two $\mathrm{Im^{Dipp}N}$ ligands are conveniently accommodated at the metal atoms. Comparison with the structures of the dichlorides $[(\mathrm{Im^{Dipp}N})\mathrm{MCl_2(THF)_3}]$ (M = Sc, Y, Lu) shows, however, that the introduction of a second $\mathrm{Im^{Dipp}N}$ is accompanied by an elongation of the metal−nitrogen bonds, in particular for the scandium system, which shows an increase from 1.963(2) to 2.003(2) Å (M−N1) and 2.014(2) Å (M−N4) in **2a.**[12b] Close inspection of the structures reveals that the two THF ligands in the yttrium complex **2b** are oriented in a mutually parallel fashion, whereas a perpendicular orientation is found in the isostructural complexes **2a** and **2c**, since the β-$\mathrm{CH_2}$ group of the twisted THF ligand develops an intermolecular C−H···Cl contact with the chlorine atom of a neighboring molecule. As a result, hydrogen-bonded dimers are formed in the solid state as shown in Figure 4 for the lutetium complex **2c**.

Attempted Preparation of a Bis(imidazolin-2-iminato) Ytterbium(II) Complex. With a successful synthetic route at hand for the preparation of bis(imidazolin-2-iminato) complexes containing trivalent rare earth metals (*vide supra*), we intended to prepare the corresponding divalent lanthanide complexes $[(\mathrm{Im^{Dipp}N})_2\mathrm{M}]$, e.g., with M = Eu and M = Yb, since a similarly rich chemistry could be expected from these species as reported for related divalent lanthanocenes.[7,25] Hence, the reaction of 1 equiv of $\mathrm{YbI_2}$ with 2 equiv of $\mathrm{LiCH_2SiMe_3}$ and 2 equiv of the imino ligand $\mathrm{Im^{Dipp}NH}$ (**1**-H) in tetrahydrofuran was expected to generate $[(\mathrm{Im^{Dipp}N})_2\mathrm{Yb}]$, but instead the Yb(III) complex $[(\mathrm{Im^{Dipp}N})_2\mathrm{YbI(THF)_2}]$ (**3**) was isolated as a yellow crystalline material. The reaction is accompanied by the formation of a gray precipitate, presumably ytterbium metal, indicating that **3** had been formed by disproportionation (Scheme 3). We assume that the electron-richness of the imidazolin-2-iminato ligands prevents the isolation of a stable divalent lanthanide complex, and future work will be directed at

Table 1. Selected Bond Lengths [Å] and Angles [deg] in the Complexes 2a−2c, 3, 4b, and 4c

	2a·2THF (M = Sc)	**2b**·*n*-pentane (M = Y)	**2c**·2THF (M = Lu)	**3**·toluene (M = Yb)	**4b**·*n*-pentane (M = Y)	**4c**·*n*-pentane (M = Lu)
M−N1	2.003(2)	2.166(2)	2.124(4)	2.109(3)	2.1701(15)	2.1333(17)
M−N4	2.014(2)	2.168(2)	2.137(4)	2.104(3)	2.1993(15)	2.1636(16)
M−O1	2.2241(18)	2.3432(17)	2.311(3)	2.332(2)	2.3766(13)	2.3144(16)
M−O2	2.2336(17)	2.3607(18)	2.310(3)	2.320(2)	2.314(13)	2.3261(16)
M−Cl/I	2.4569(9)	2.6028(7)	2.5471(13)	3.0132(3)		
M−C55					2.4510(19)	2.393(2)
M−N1−C1	178.2(2)	172.6(2)	178.1(4)	179.1(3)	179.55(14)	179.24(17)
M−N4−C28	176.9(2)	172.5(2)	175.8(4)	177.6(3)	169.35(14)	169.30(16)
N1−M−N4	121.70(9)	116.89(8)	120.47(16)	118.49(10)	126.63(6)	125.89(7)
O1−M−O2	162.67(7)	164.50(7)	161.98(14)	163.95(8)	166.33(5)	167.07(6)
Cl/I−M−N1	115.51(7)	120.97(6)	117.51(12)	123.90(7)		
Cl/I−M−N4	122.76(7)	122.14(6)	122.00(11)	117.53(7)		
C55−M−N1					128.71(6)	105.17(7)
C55−M−N4					104.64(6)	128.92(8)
Cl/I−M−O1	81.38(6)	81.93(5)	81.95(10)	80.32(6)	84.78(6)	85.21(7)
Cl/I−M−O2	82.49(5)	82.58(5)	80.70(10)	84.26(6)	84.70(6)	85.11(7)
τ[a]	0.67	0.71	0.67	0.67	0.63	0.64

[a] τ = (α − β)/60° with α and β being the two largest angles around the metal atom.

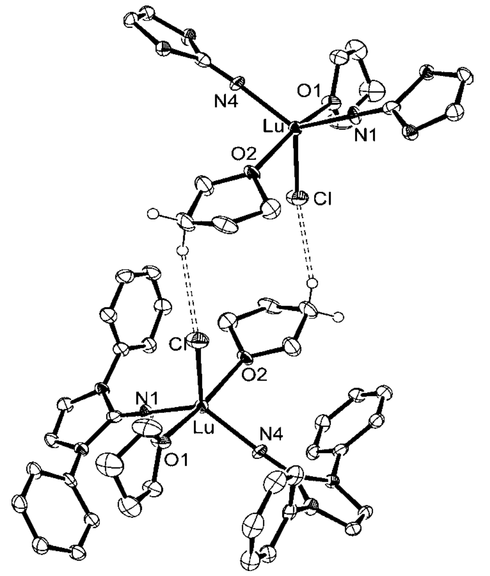
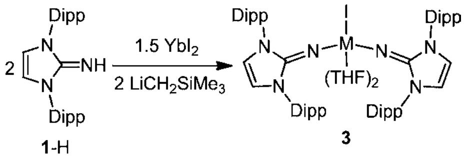


Figure 4. ORTEP diagram of two molecules of **2c** showing short H···Cl intermolecular contacts of 2.78 Å; thermal displacement parameters are drawn at 50% probability. The isopropyl and the Dipp groups are partially omitted for clarity.

Scheme 3. Syntheses of the Bis(imidazolin-2-iminato) Ytterbium(III) Complex 3



trapping the Yb(II) intermediate, e.g., by reaction with dinitrogen.[25]

Complex **3** crystallizes as a toluene solvate in the triclinic space group $P\bar{1}$, and the resulting single crystal X-ray structure is shown in Figure 5. The ionic radius of $\mathrm{Yb^{III}}$ (0.868 Å) is almost identical to that of $\mathrm{Lu^{III}}$ (0.861 Å),[23] and accordingly, the structural parameters of **3** are very similar to those in complexes **2**. The pentacoordinated ytterbium atom resides in a distorted trigonal bipyramidal environment, as indicated by a τ value of 0.67. As expected, the Yb–N bond lengths are short [2.109(3), 2.104(3) Å] and are indeed among the shortest ever observed for ytterbium–nitrogen systems; the only shorter Yb–N bond length of 2.089(4) Å was reported for a dimeric Yb–nacnac complex containing a tightly bound piperidyl ligand.[26] In contrast, the Yb–I distance of 3.0132(3) Å falls in the conventional range in comparison with related ytterbium–iodine systems; it is for instance slightly longer than the values of 2.916(2) and 2.9316(7) Å reported for the bis(aryloxide) complex [$(t\mathrm{Bu_3C_6H_2O})_2\mathrm{YbI(THF)_2}$] and the ytterbocene [$\mathrm{Cp_2YbI(THF)}$], respectively.[27,28]

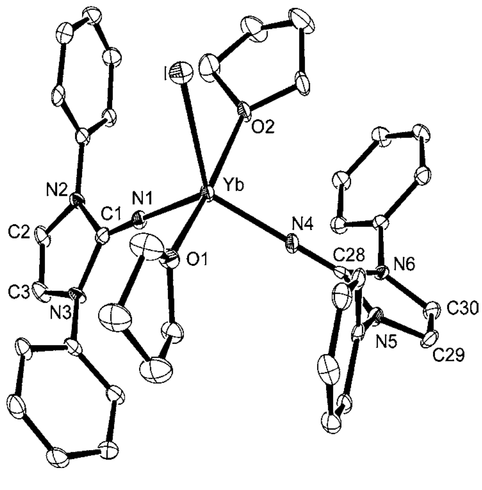
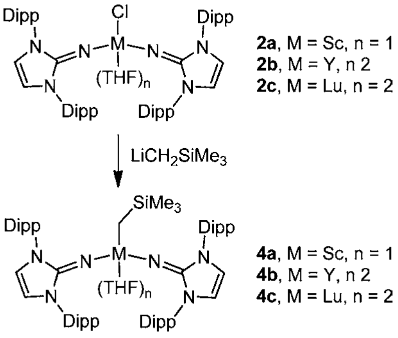


Figure 5. ORTEP diagram of **3** in **3**·toluene with thermal displacement parameters drawn at 50% probability. The isopropyl groups have been omitted for clarity.

Preparation and Structural Characterization of Bis(imidazolin-2-iminato) Neosilyl Complexes. Catalytically active lanthanide complexes for olefin transformations should contain at least one kinetically labile σ-bonded ligand. Accordingly, substitution of the chlorine atoms from the complexes **2** by an alkyl group could afford useful homogeneous catalysts. Therefore, the reaction of **2a**–**2c** with 1 equiv of $\mathrm{LiCH_2SiMe_3}$ was carried out in THF (Scheme 4), leading to the formation of [$(\mathrm{Im^{Dipp}N})_2\mathrm{M(CH_2SiMe_3)(THF)}_n$] (**4a**–**4c**). NMR spectroscopy indicates that the scandium complex **4a** contains only one additional THF ligand bound to the metal atom (n = 1), whereas the yttrium and lutetium congeners contain two THF molecules. Accordingly, the ^{1}H NMR spectrum of **4a** recorded in $\mathrm{C_6D_6}$ is similar to that of **2a** (*vide supra*) and exhibits the number of resonances (two septets and four doublets) expected for the isopropyl groups in a C_s-symmetric complex. Consequently, the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum displays two different signals for the *ortho* and *meta* carbon atoms of the phenyl rings together with two and four resonances for the *i*Pr CH and $\mathrm{CH_3}$ groups, respectively. In contrast, the lutetium complex **4c** shows rather broad ^{1}H and $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR resonances, which is presumably a result of hindered rotation around the metal–nitrogen bonds, whereas the spectra of **4b** containing the larger yttrium ion are in agreement with time-averaged C_{2v}-symmetry (see Supporting Information for selected NMR spectra). The methylene groups of the neosilyl ligands give rise to $^1\mathrm{H}/^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR resonances at −0.56/34.1 (**4a**), −0.92/25.5 (**4b**), and −0.97/30.9 ppm (**4c**), which fall in the expected ranges.[29]

Scheme 4. Syntheses of the Bis(imidazolin-2-iminato) Complexes [$(\mathrm{Im^{Dipp}N})_2\mathrm{M(CH_2SiMe_3)(THF)}_n$] (4a–4c)



For complexes **4b** and **4c**, the composition was additionally confirmed by X-ray diffraction analysis of the colorless crystals obtained from THF/*n*-pentane solution at −30 °C (Figure 6). The two complexes are isostructural and crystallize as *n*-pentane solvates in the triclinic space group $P\bar{1}$. The coordination arrangement at the metal atoms is similar to

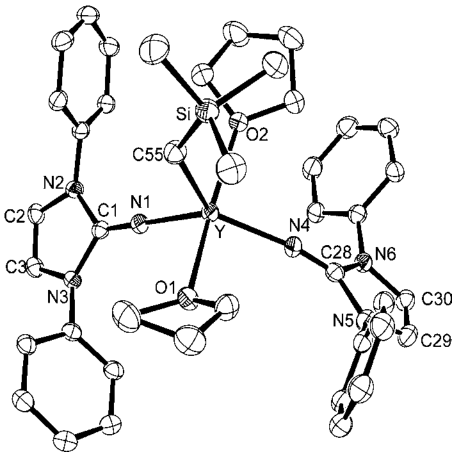
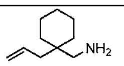
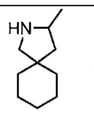
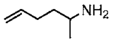
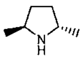
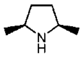
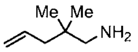
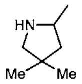
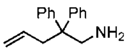
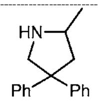
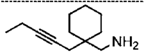
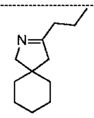
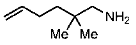
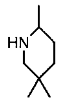


Figure 6. ORTEP diagram of **4b** in **4b**·*n*-pentane with thermal displacement parameters drawn at 50% probability. The isopropyl groups have been omitted for clarity.

that found for the starting materials **2**, although the introduction of the neosilyl ligand induces a significantly stronger distortion from an ideal trigonal bipyramidal orientation, and thus, smaller τ values of 0.63 (**4b**) and 0.64 (**4c**) are observed (Table 1). The equatorial ligands, the two $\mathrm{Im^{Dipp}N}$ ligands and the neosilyl group, are coplanar with the metal atoms as indicated by angle sums of 360°. However, they strongly deviate from a trigonal-planar arrangement, since the N−M−C55 angles are markedly different [128.71(6)° versus 104.64(6)° in **4b**, 128.92(8)° versus 105.17(7)° in **4c**] because of the steric impact of the $\mathrm{SiMe_3}$ moiety, which is tilted toward one of the $\mathrm{Im^{Dipp}N}$ ligands. As a consequence, this ligand exhibits in both complexes a more pronounced deviation of the corresponding M−N4−C28 axis [169.35(14)° in **4b**, 169.30(16)° in **4c**] from linearity than observed for the second ligand [Y−N1−C1 = 179.55(14)° (**4b**), Lu−N1−C1 = 179.24(17)° (**4c**)], and this bending is also accompanied by an elongation of the M−N4 bonds [2.1993(15) Å in **4b**, 2.1636(16) Å in **4c**] compared to M−N1 [2.1701(15) Å in **4b**, 2.1333(17) Å in **4c**]. These values are also larger than those observed for the chloro complexes **2** (Table 1). Finally, the M−C55 bond lengths in **4b** and **4c** lie in the range found for related mono(neosilyl) rare earth yttrium and lutetium complexes.[30]

Catalytic Hydroamination Studies. Catalytic hydroamination is the addition of an organic amine N−H bond to a carbon−carbon double or triple bond in one step. It is attractive for academic and industrial researchers because most of the classical amine syntheses involve multistep reactions and thus involve byproducts and large amounts of chemical waste. Hydroamination can be catalyzed by a large number of s-, d-,

Table 2. Catalytic Hydroamination Reactions with Catalyst 4b and 5[a,b,c]

Entry	Substrate	Product		[Cat.]	T [°C]	t [min]	Yield[c] [%]
1			**4b**	5 mol%	RT	8	98
			5[18]	5 mol%	RT	5	quant.
2			**4b**	3 mol%	120	120	99 cis:trans 1:5
			**5**[18]	5 mol%	120	180	quant. cis:trans 1:3
3			**4b**	3 mol%	RT	330	90
			4b	3 mol%	60	60	96
			5[18]	5 mol%	60	60	92
4			**4b**	5 mol%	RT	5	quant.
			5[18]	5 mol%	RT	5	98
5			quant.	5 mol%	RT	50	quant.
			5[18]	5 mol%	RT	5	quant.
6			**4b**	5 mol%	120	30	quant.

[a]Conditions: cat. 15−20 mg, C_6D_6. [b]Data taken of compound $[(\mathrm{Im^{Dipp}N})\mathrm{Y}(\mathrm{CH_2SiMe_3})_2(\mathrm{THF})_3]$ (**5**) were taken from ref 18. [c]Yields calculated by ^{1}H NMR; ferrocene as internal standard.

and f-block metal complexes. Progress in this area over the past decade has been reviewed extensively.[21a,31] Hydroamination catalyzed by rare earth element complexes was pioneered in the 1990s by T. J. Marks et al.[21a,32] The early work, in which the mechanism was also studied in detail, was based on cyclopentadienyl complexes. In the past decade a number of cyclopentadienyl-free complexes containing amido and alkoxide ligands have been developed.[31d,j,t,y,33−36] Since the related imidazolin-iminato complexes $[(\mathrm{Im^{Dipp}N})\mathrm{M}(\mathrm{CH_2SiMe_3})_2(\mathrm{THF})_3]$ (M = Y, Lu) were reported to act as efficient catalysts for hydroamination, we were also interested in the catalytic activity of the compounds **4** reported herein; these complexes also fulfill the requirement that at least one kinetically labile, σ-bonded ligand, e.g., H, $\mathrm{CH(SiMe_3)_2}$, $\mathrm{CH_2SiMe_3}$, $\mathrm{CH_2Ph}$, $\mathrm{N(SiMe_3)_2}$, must be present as a leaving group. By using similarly coordinated rare earth element complexes as catalysts for the hydroamination reactions, the rate usually increases with increasing ion radius of the central metal. This was observed for example for the imidazolin-2-iminato complexes $[(\mathrm{Im^{Dipp}N})\mathrm{M}(\mathrm{CH_2SiMe_3})_2(\mathrm{THF})_3]$ (M = Y, Lu).[18] On the basis of these considerations, we focused our catalytic studies (shown in Table 2) on the yttrium compound **4b** and compared the results with the related imidazolin-2-iminato dialkyl yttrium complex $[(\mathrm{Im^{Dipp}N})\mathrm{Y}(\mathrm{CH_2SiMe_3})_2(\mathrm{THF})_3]$ (**5**).[18] We studied the intramolecular hydroamination/cyclization reaction of various terminal aminoalkenes and of one aminoalkyne using a catalyst loading of 3−5 mol %. All experiments were carried out under rigorously anaerobic reaction conditions by using dry, degassed substrates. The reactions, which proceeded regiospecifically, were monitored by ^{1}H NMR spectroscopy by using ferrocene as an internal standard. All substrates were converted to the cyclic product in high yields.

As expected, the reaction time is strongly substrate dependent. On the basis of the Thorpe−Ingold effect,[37] the reaction rate increases with growing steric bulk of the substituents in β-position to the amino group. Thus, the aminoalkenes shown in the Table 2 entries 1 and 4 were converted rapidly to the corresponding pyrrolidines at room temperature. These two substrates were cyclized by precatalysts **4b** and **5** in a comparable time. In contrast, a much higher reaction temperature (120 °C) is needed for the cyclization of 2-amino-5-hexene (entry 2). In this reaction, the *trans* isomer was preferentially formed, which is probably a result of some steric strain in the transition state. A comparison of compounds **4b** and **5** does not show a clear tendency. Whereas compound **4b** transformed 2-amino-5-hexene (entry 2) much faster, the alkyne [1-(pent-2-ynyl)cyclohexyl]methanamine was more easily cyclized by using compound **5** as catalyst (entry 5). This aminoalkyne cyclized at room temperature. The transformation of the olefins 2,2-dimethyl-pent-4-enylamine (entry 3) and 2,2-diphenyl-pent-4-enylamine (entry 4) proceeded in about the same time with similar yields at 60 °C. The cyclization of 2,2-dimethyl-pent-4-enylamine (entry 3) was also followed at room temperature by using compound **4b** as a catalyst. As expected, a significantly longer reaction time was necessary to complete the reaction. Formation of the six-membered ring starting from 2,2-dimethylhex-5-en-1-amine (entry 6) was achieved, but a higher reaction temperature was needed compared to the formation of the corresponding five-membered ring. It can be concluded that the rate of cyclization for aminoalkenes follows the order 5 > 6, which is consistent with the stereoelectronically controlled cyclization processes observed for example for the lanthanocene catalysts.[32,38]

Attempts to add propan-1-amine to prop-1-yn-1-ylbenzene and [2-(trimethylsilyl)ethynyl]benzene by using 5 mol % of compound **4b** as precatalyst failed even at elevated temperatures. These results are in contrast to the observations made for $[\mathrm{Me_2Si(C_5Me_4)_2NdCH(SiMe_3)_2}]$ which is an active catalyst in the intermolecular hydroamination reaction.[39]

■ CONCLUSIONS

During our ongoing research on complexes of the rare earth elements with strong nitrogen-donor ligands, we obtained bis(imidazolin-2-iminato) complexes of the smaller rare earth elements.[22] In a straightforward synthetic approach, the halide and the alkyl complexes, $[(\mathrm{Im^{Dipp}N})_2\mathrm{MCl}(\mathrm{THF})_n]$ and $[(\mathrm{Im^{Dipp}N})_2\mathrm{M}(\mathrm{CH_2SiMe_3})(\mathrm{THF})_2]$ (M = Sc, Y, Lu), were obtained and fully characterized. In the solid state the coordination spheres around the pentacoordinate metal atoms in all compounds are best described as distorted trigonal bipyramids. The yttrium alkyl complex $[(\mathrm{Im^{Dipp}N})_2\mathrm{Y}(\mathrm{CH_2SiMe_3})(\mathrm{THF})_2]$ was used as precatalyst in the intramolecular hydroamination/cyclization reaction of various terminal aminoalkenes and of one aminoalkyne. The complex showed high catalytic activity and selectivity. A comparison with the previously reported dialkyl yttrium complex $[(\mathrm{Im^{Dipp}N})\mathrm{Y}(\mathrm{CH_2SiMe_3})_2(\mathrm{THF})_3]$ showed a substrate-dependent activity. Although the monoalkyl complex $[(\mathrm{Im^{Dipp}N})_2\mathrm{Y}(\mathrm{CH_2SiMe_3})(\mathrm{THF})_2]$ mostly showed a higher activity, no general trend was observed.

■ EXPERIMENTAL SECTION

General Information. All manipulations of air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-4} Torr) line, or in an argon-filled glovebox (MBraun 200B). All solvents were purified by a solvent purification system from MBraun and stored over molecular sieve (4 Å) prior to use. Deuterated solvents were obtained from Sigma Aldrich (all ≥99 atom % D) and were degassed, dried, and stored in the argon-filled glovebox. NMR spectra were recorded on Bruker DPX 200, Bruker DRX 400, Bruker Avance 400 MHz, and Bruker Avance II 300 MHz NMR devices. The chemical shifts are expressed in parts per million (ppm) using tetramethylsilane (TMS) as internal standard (^{1}H, ^{13}C). Elemental analyses (C, H, N) were carried out by combustion and gas chromatographic analysis with an Elementar vario ICRO. Some results gave low values for the carbon content, despite acceptable H and N measurements. This might be ascribed to the extreme sensitivity of the complexes and to the possibility of metal carbide formation during combustion. 1,3-Bis(2,6-diisopropylphenyl)-imidazolin-2-imine and $[\mathrm{LiCH_2SiMe_3}]$ were prepared according to published procedures.[3c,40]

Preparation of the Scandium Complex $[(\mathrm{Im^{Dipp}N})_2\mathrm{ScCl}(\mathrm{THF})]$ (2a). A solution of anhydrous $\mathrm{ScCl_3}$ (76 mg, 0.50 mmol) in THF/*n*-pentane solution (10/10 mL) was treated with $\mathrm{LiCH_2SiMe_3}$ (94 mg, 1.00 mmol). After stirring for 12 h, a solution of **1**-H (404 mg, 1.00 mmol) in THF (5 mL) was added. The reaction mixture was stirred for another 12 h. The solvent was evaporated, and the compound was extracted with 3 × 10 mL of toluene and then dried in vacuo. Yield: 82% (391 mg, 0.408 mmol). The complex was crystallized from THF/*n*-pentane (1:3) at −30 °C to obtain colorless crystals. Elemental analysis was performed before recrystallization from THF/*n*-pentane. Anal. Calcd for $[\mathrm{C_{58}H_{80}ClN_6OSc}]$: C, 72.74; H, 8.42; N, 8.78. Found: C, 72.79; H, 8.44; N, 8.81. ^{1}H ($\mathrm{C_6D_6}$, 200 MHz, 25 °C): δ 7.22−7.06 (m, 12 H, *p*-H, *m*-H), 5.81 (s, 4 H, NCH), 3.36 (sept, 4 H, C*H*Me$_2$), 3.31 (sept, 4 H, C*H*Me$_2$), 3.22 (br, 4 H, THF), 1.40 (d, 12 H, CHC*H*$_3$), 1.22 (d, 24 H, CHC*H*$_3$), 1.20 (d, 12 H, CHC*H*$_3$), 1.03 (br,

Table 3. Crystallographic Data

	2a·2THF	**2b**·*n*-pentane	**2c**·2THF	**3**·toluene	**4b**·*n*-pentane	**4c**·*n*-pentane
empirical formula	$C_{70}H_{104}ClN_6O_4Sc$	$C_{67}H_{100}ClN_6O_2Y$	$C_{70}H_{104}ClN_6O_4Lu$	$C_{69}H_{96}IN_6O_2Yb$	$C_{71}H_{111}N_6O_2SiY$	$C_{71}H_{111}N_6O_2SiLu$
a (Å)	39.1283(18)	12.5879(6)	39.0752(14)	12.6034(4)	14.2317(4)	14.1874(4)
b (Å)	12.5508(3)	13.6024(8)	12.5876(2)	14.0206(4)	14.8154(6)	14.8204(4)
c (Å)	27.2569(11)	19.3331(9)	27.4730(8)	19.4205(6)	17.4390(6)	17.3985(6)
α (deg)	90	77.231(4)	90	74.501(2)	83.903(4)	84.290(2)
β (deg)	99.461(4)	86.272(4)	99.398(4)	78.931(2)	79.481(4)	79.636(2)
γ (deg)	90	82.362(4)	90	83.188(2)	74.332(4)	74.497(2)
V (Å^3)	13 203.6(9)	3197.6(3)	13331.6(7)	3237.20(17)	3474.6(2)	3462.54(18)
Z	8	2	8	2	2	2
fw	1174.00	1145.89	1304.01	1341.46	1197.66	1283.72
space group	$C2/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
T (K)	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)
λ (Å)	1.541 84	1.541 84	1.541 84	0.710 73	1.541 84	1.541 84
D_{calcd} (g cm^{-3})	1.181	1.190	1.299	1.376	1.145	1.231
μ (mm^{-1})	1.718	2.019	3.592	1.969	1.691	3.239
reflns collected	96 180	45 681	67 756	117 954	49 555	49 482
indep reflns	13 669	13 215	13 789	14 247	14 338	14 320
	$R_{int} = 0.1143$	$R_{int} = 0.0688$	$R_{int} = 0.1119$	$R_{int} = 0.0732$	$R_{int} = 0.0320$	$R_{int} = 0.0264$
GOF on F^2	0.876	1.049	0.874	0.858	1.090	1.082
$R(F_o)$ [$I > 2\sigma(I)$]	0.0537	0.0617	0.0476	0.0313	0.0377	0.0311
$R_w(F_o^2)$	0.1294	0.1738	0.1201	0.0605	0.1019	0.0826
$\Delta\rho$ [e Å^{-3}]	0.504/−0.405	1.659/−1.083	1.092/−1.177	2.036/−0.810	0.530/−0.588	0.867/−1.230

4 H, THF) ppm. $^{13}C\{^1H\}$ (C_6D_6, 50.3 MHz, 25 °C): δ 148.8 (*o*-C), 147.9 (*o*-C), 137.0 (NCN), 136.6 (*ipso*-C), 128.0 (*p*-C), 123.9 (*m*-C), 123.7 (*m*-C), 112.6 (NCH), 70.8 (THF), 28.4 ($CHMe_2$), 28.3 ($CHMe_2$), 24.80 (THF), 24.3 ($CHCH_3$), 24.1 ($CHCH_3$), 23.4 ($CHCH_3$), 23.1 ($CHCH_3$) ppm.

Preparation of the Yttrium Complex [(Im^{Dipp}N)$_2$YCl(THF)$_2$] (2b). A solution of anhydrous YCl_3 (98 mg, 0.50 mmol) in THF/*n*-pentane solution (10/10 mL) was treated with $LiCH_2SiMe_3$ (94 mg, 1.00 mmol). After stirring for 12 h, a solution of **1**-H (404 mg, 1.00 mmol) in THF (5 mL) was added. The reaction mixture was stirred for another 12 h. The solvent was evaporated, and the compound was extracted with 3 × 10 mL of toluene and then dried in vacuo. Yield: 69% (372 mg, 0.346 mmol). The complex was crystallized from THF/*n*-pentane (1:3) at −30 °C to obtain colorless crystals. Elemental analysis was performed before recrystallization from THF/*n*-pentane. Anal. Calcd for [$C_{62}H_{88}ClN_6O_2Y$]: C, 69.35; H, 8.26; N, 7.83. Found: C, 68.85; H, 8.29; N, 7.93. ^1H (C_6D_6, 200 MHz, 25 °C): δ 7.24−7.16 (m, 12 H, *p*-H, *m*-H), 5.90 (s, 4 H, NC*H*), 3.43 (sept, 8 H, C*H*Me$_2$), 3.27 (br, 8 H, THF), 1.42 (d, 24 H, CHC*H*$_3$), 1.22 (d, 24 H, CHC*H*$_3$), 1.12 (br, 8 H, THF) ppm. $^{13}C\{^1H\}$ (C_6D_6, 50.3 MHz, 25 °C): δ 148.7 (*o*-C), 137.7 (*ipso*-C), 128.3 (*p*-C), 123.9 (*m*-C), 113.2 (NCH), 69.7 (THF), 28.6 ($CHMe_2$), 25.4 (THF), 24.9 ($CHCH_3$), 23.9 ($CHCH_3$) ppm.

Preparation of the Lutetium Complex [(Im^{Dipp}N)$_2$LuCl(THF)$_2$] (2c). A solution of anhydrous $LuCl_3$ (141 mg, 0.50 mmol) in THF/*n*-pentane solution (10/10 mL) was treated with $LiCH_2SiMe_3$ (94 mg, 1.00 mmol). After stirring for 12 h, a solution of **1**-H (404 mg, 1.00 mmol) in THF (5 mL) was added. The reaction mixture was stirred for another 12 h. The solvent was evaporated, and the compound was extracted with 3 × 10 mL of toluene and then dried in vacuo. Yield: 60% (350 mg, 0.302 mmol). The complex was crystallized from THF/*n*-pentane (1:3) at −30 °C to obtain colorless crystals. Elemental analysis was performed before recrystallization from THF/*n*-pentane. Anal. Calcd for [$C_{62}H_{88}ClLuN_6O_2$]: C, 64.21; H, 7.65; N, 7.25. Found: C, 62.45; H, 7.37; N, 8.08. ^1H (C_6D_6, 400 MHz, 25 °C): δ 7.27−7.08 (m, 12 H, *p*-H, *m*-H), 5.91 (s, 4 H, NC*H*), 3.43 (br, 4 H, C*H*Me$_2$), 3.13 (br, 8 H, THF), 1.40 (d, 24 H, CHC*H*$_3$), 1.21 (d, 24 H, CHC*H*$_3$), 1.19 (br, 4 H, THF) ppm. $^{13}C\{^1H\}$ (C_6D_6, 100 MHz, 25 °C): δ 148.6 (*o*-C), 137.7 (*ipso*-C), 128.3 (*p*-C), 123.9 (*m*-C), 113.2 (NCH), 69.8 (THF), 28.8 ($CHMe_2$), 25.4 (THF), 23.9 ($CHCH_3$), 23.6 ($CHCH_3$) ppm.

Preparation of Bis(imidazolin-2-iminato) Ytterbium Complex [(Im^{Dipp}N)$_2$YbI(THF)$_2$] (3). To a solution of anhydrous YbI_2 (264 mg, 0.62 mmol) in toluene, 2 equiv of $LiCH_2SiMe_3$ (116 mg, 1.24 mmol) was added. After stirring for 12 h, a solution of **1**-H (500 mg, 1.24 mmol) in toluene (5 mL) was added. The reaction mixture was stirred for another 12 h. After 2 h the solution turned from green to brown. The solvent was evaporated, and the compound was extracted with 3 × 10 mL of toluene. The complex was crystallized from THF/*n*-pentane (1:3) at −30 °C to obtain yellow crystals. The yield could not be calculated since lithium iodide could not be removed from the reaction mixture, and we were unable to isolate pure material.

Preparation of the Scandium Neosilyl Complex [(Im^{Dipp}N)$_2$Sc(CH$_2$SiMe$_3$)(THF)] (4a). To a THF (10 mL) solution of [(Im^{Dipp}N)$_2$ScCl(THF)$_2$] (**2a**) (262 mg, 0.255 mmol) was added 24 mg (0.26 mmol) of $LiCH_2SiMe_3$ in THF (5 mL) dropwise at ambient temperature, and then the reaction mixture was stirred for 12 h. The solvent was evaporated and subsequently the compound was extracted with *n*-pentane. The *n*-pentane was removed in vacuo. The compound was crystallized from THF/*n*-pentane at −30 °C. Yield: 90% (232 mg, 0.230 mmol). Anal. Calcd for [$C_{62}H_{91}N_6OScSi$]: C, 73.77; H, 9.09; N, 8.33. Found: C, 72.74; H, 8.92; N, 8.29. ^1H (C_6D_6, 400 MHz, 25 °C): δ 7.21−7.06 (m, 12 H, *p*-H, *m*-H), 5.82 (s, 4 H, NC*H*), 3.45 (sept, 4 H, C*H*Me$_2$), 3.18 (sept, 4 H, C*H*Me$_2$), 2.81 (br, 4 H, THF), 1.32 (d, 12 H, CHC*H*$_3$), 1.22 (d, 12 H, CHC*H*$_3$), 1.20 (d, 12 H, CHC*H*$_3$), 1.18 (d, 12 H, CHC*H*$_3$), 0.87 (br, 4 H, THF), 0.21 (s, 9H, SiMe$_3$), −0.56 (s, 2H, C*H*$_2$SiMe$_3$) ppm. $^{13}C\{^1H\}$ (C_6D_6, 100 MHz, 25 °C): δ 148.6 (*o*-C), 148.1 (*o*-C), 137.2 (*ipso*-C), 135.5 (NCN), 128.4 (*p*-C), 124.2 (*m*-C), 123.8 (*m*-C), 113.4 (NCH), 70.9 (THF), 34.1 (CH_2SiMe_3) 28.5 ($CHMe_2$), 28.4 ($CHMe_2$), 25.1 (THF), 24.54 ($CHCH_3$), 24.51 ($CHCH_3$), 23.64 ($CHCH_3$), 23.46 ($CHCH_3$), 4.7 ($SiMe_3$) ppm.

Preparation of the Yttrium Neosilyl Complex [(Im^{Dipp}N)$_2$Y(CH$_2$SiMe$_3$)(THF)$_2$] (4b). To a THF (10 mL) solution of [(Im^{Dipp}N)$_2$YCl(THF)$_2$] (**2b**) (288 mg, 0.268 mmol) was added 26 mg (0.28 mmol) of $LiCH_2SiMe_3$ in THF (5 mL) dropwise at ambient temperature, and then the reaction mixture was stirred for 12 h. The solvent was evaporated, and the compound was subsequently extracted with *n*-pentane. The *n*-pentane was removed under *in vacuo*. The compound was crystallized from THF/*n*-pentane at −30 °C. Yield: 87% (263 mg, 0.234 mmol). Anal. Calcd for [$C_{66}H_{99}N_6O_2SiY$]: C, 70.43; H, 8.87; N, 7.47. Found: C, 69.88; H, 8.83; N, 8.08. ^1H (C_6D_6, 400 MHz, 25 °C): δ 7.19–7.08 (m, 12H, *m*-H, *p*-H), 5.86 (s, 4H, NC*H*), 3.43–3.39 (m, 8H, THF), 3.12 (br, 8H, C*H*Me$_2$), 1.26 (d, 24H, CHC*H*$_3$), 1.24 (br, 8H, THF), 1.22 (d, 24H, CHC*H*$_3$), 0.19 (s, 9H, Si*Me*$_3$), −0.92 (d, 2H, C*H*$_2$SiMe$_3$, $^2J_{89Y,H}$ = 3.14 Hz) ppm. $^{13}C\{^1H\}$ (C$_6$D$_6$, 100 MHz, 25 °C): δ 148.64 (*o*-*C*), 137.4 (*ipso*-*C*), 128.0 (*p*-*C*), 123.8 (*m*-*C*), 112.9 (NCH), 69.4 (THF), 28.87 (CHMe$_2$), 25.8 (THF), 25.5 (br, CH$_2$SiMe$_3$), 24.5 (CHCH$_3$), 23.3 (CHCH$_3$), 4.85 (Si*Me*$_3$) ppm; the NCN and resonances were not observed.

Preparation of the Lutetium Neosilyl Complex [(Im^{Dipp}N)$_2$Lu(CH$_2$SiMe$_3$)(THF)$_2$] (4c). To a THF (10 mL) solution of [(Im^{Dipp}N)$_2$LuCl(THF)$_2$] (**2c**) (280 mg, 0.241 mmol) was added 23 mg (0.24 mmol) of LiCH$_2$SiMe$_3$ in THF (5 mL) dropwise at ambient temperature, and then the reaction mixture was stirred for 12 h. The solvent was evaporated, and the compound was subsequently extracted with *n*-pentane. The *n*-pentane was removed *in vacuo*. The compound was crystallized from THF/*n*-pentane at −30 °C. Yield: 87% (253 mg, 0.209 mmol). Anal. Calcd for [C$_{66}$H$_{99}$LuN$_6$O$_2$Si]: C, 65.43; H, 8.24; N, 6.94. Found: C, 62.25; H, 7.50; N, 6.64. ^{1}H (C$_6$D$_6$, 400 MHz, 25 °C): δ 7.19–7.08 (m, 12 H, *p*-H, *m*-H), 5.86 (s, 4 H, NC*H*), 3.59 (br, 4 H, THF), 3.43 (br, 4 H, C*H*Me$_2$), 3.21 (br, 4 H, C*H*Me$_2$), 2.75 (br, 4 H, THF), 1.28 (br, 24 H, CHC*H*$_3$), 1.26 (br, 8 H, THF), 1.23 (d, 24 H, CHC*H*$_3$), 0.21 (s, 9H, Si*Me*$_3$), −0.97 (s, 2H, C*H*$_2$SiMe$_3$) ppm. $^{13}C\{^1H\}$ (C$_6$D$_6$, 100 MHz, 25 °C): δ 148.7 (*o*-*C*), 148.3 (*o*-*C*), 140.6 (br, NCN), 137.5 (br, *ipso*-*C*), 128.0 (*p*-*C*), 123.9 (br, *m*-*C*), 123.7 (br, *m*-*C*), 113.0 (NCH), 71. (br, THF), 67.8 (br, THF), 30.91 (CH$_2$SiMe$_3$), 28.4 (CHMe$_2$), 28.4 (CHMe$_2$), 25.5 (THF), 24.8 (br, CHCH$_3$), 24.5 (br, CHCH$_3$), 23.8 (br, CHCH$_3$), 23.5 (br, CHCH$_3$), 4.94 (Si*Me*$_3$) ppm.

General Procedure for Catalytic Hydroamination of Alkenes. The catalyst was weighed under argon gas into an NMR tube. C$_6$D$_6$ (≈0.5 mL) was condensed into the NMR tube, and the mixture was frozen to −196 °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before insertion into the core of the NMR machine (t_0). The ratio between the reactant and the product was calculated by comparison of the integrations of the corresponding signals. Ferrocene was used as an internal standard for the kinetic measurements. The substrates *C*-(1-allyl-cyclohexyl)-methylamine,[42] 2-amino-5-hexene (*via* hex-5-en-2-one oxime[41]),[36c] 2,2-dimethyl-pent-4-enylamine,[42] 2,2-diphenyl-pent-4-enylamine,[42] [1-(pent-2-ynyl)cyclohexyl]methanamine,[43] and 2,2-dimethylhex-5-en-1-amine[35e] were synthesized according to the literature procedures. ^{1}H NMR spectra of 3-methyl-2-aza-spiro[4.5]decane,[42] 2,5-dimethylpyrrolidine,[36c] 2,4,4-trimethylpyrrolidine,[42] 2-methyl-4,4-diphenylpyrrolidine,[42] 3-propyl-2-azaspiro[4.5]dec-2-ene,[43] and 2,5,5-trimethylpiperidine[44] conform with the literature.

X-ray Crystal Structure Determinations. Data were recorded on Oxford Diffraction diffractometers at low temperature using mirror-focused Cu K*α* or monochromated Mo K*α* radiation (Table 3). Absorption corrections were based on multiscans. Structures were refined anisotropically on F^2 using the program SHELXL-97.[45] Hydrogen atoms were included using a riding model starting from calculated positions, except for methyl groups, which were refined as idealized rigid groups allowed to rotate but not tip. All structures contained solvent of crystallization; this was ordered except for the pentane of **2b**, which was mathematically removed using the program SQUEEZE.[46]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data in CIF format. Additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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