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Bis(phosphinimino)methanide Rare Earth Amides: Synthesis, Structure, and Catalysis of Hydroamination/Cyclization, Hydrosilylation, and Sequential Hydroamination/Hydrosilylation

Marcus Rastätter, Agustino Zulys, and Peter W. Roesky*[a]

Abstract: A series of yttrium and lanthanide amido complexes [Ln{N(SiHMe$_2$)$_2$}$_2${CH(PPh$_2$NSiMe$_3$)$_2$}] (Ln = Y, La, Sm, Ho, Lu) were synthesized by three different pathways. The title compounds can be obtained either from [Ln{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] and [CH$_2$(PPh$_2$NSiMe$_3$)$_2$] or from KN(SiHMe$_2$)$_2$ and [Ln{CH(PPh$_2$NSiMe$_3$)$_2$}Cl$_2$]$_2$, while in a third approach the lanthanum compound was synthesized in a one-pot reaction starting from K{CH(PPh$_2$NSiMe$_3$)$_2$}, LaCl$_3$, and KN(SiHMe$_2$)$_2$. All the complexes have been characterized by single-crystal X-ray diffraction. The new complexes, [Ln{N(SiHMe$_2$)$_2$}$_2${CH(PPh$_2$NSiMe$_3$)$_2$}], were used as catalysts for hydroamination/cyclization and hydrosilylation reactions. A clear dependence of the reaction rate on the ionic radius of the center metal was observed, showing the lanthanum compound to be the most active one in both reactions. Furthermore, a combination of both reactions—a sequential hydroamination/hydrosilylation reaction—was also investigated.

Keywords: catalysis · hydroamination · hydrosilylation · N,P ligands · rare earth metals

Introduction

In lanthanide chemistry, alkyl, amido, and hydrido cyclopentadienyl complexes, especially metallocenes such as [Ln(C$_5$Me$_5$)$_2$R] (R = CH(SiMe$_3$)$_2$, N(SiMe$_3$)$_2$, H), have proven to be highly efficient catalysts[1] for a variety of olefin transformations including hydrogenation,[2–5] polymerization,[6–8] hydroamination,[4,9] hydrosilylation,[10,11] hydroboration,[12] and hydrophosphination.[13] In addition to the well established cyclopentadienyl complexes, a number of non-cyclopentadienyl lanthanide complexes based on amido and alkoxide ligands are today also known to be active in hydroamination/cyclization catalysis.[14–18] The first non-cyclopentadienyl lanthanide catalyst for the hydroamination/cyclization reaction was developed by us,[14] while recently we have introduced the use of the bis(phosphinimino)methanide {CH(PPh$_2$NSiMe$_3$)$_2$}$^-$, previously employed by a number of research groups in main group and transition metal chemistry,[19–27] into yttrium and lanthanide chemistry as a cyclopentadienyl replacement.[28–30] The obtained complexes were used as homogenous catalysts for a number of different catalytic applications. Thus, [Ln{CH(PPh$_2$NSiMe$_3$)$_2$}{N(PPh$_2$)$_2$}Cl] species are active catalysts for the ring-opening polymerization of ε-caprolactone and the polymerization of methyl methacrylate,[30] whereas [Ln{CH(PPh$_2$NSiMe$_3$)$_2$}(η^8-C$_8$H$_8$)] was used as catalyst for the hydroamination/cyclization reaction.[28]

Very recently, Doye et al. have reported on Ti-based catalysts for sequential hydroamination/hydrosilylation,[31] while we have recently communicated the synthesis—based on these results—of [La{N(SiHMe$_2$)$_2$}$_2${CH(PPh$_2$NSiMe$_3$)$_2$}] as a non-cyclopentadienyl lanthanide catalyst useable for the hydroamination/cyclization and the hydrosilylation reactions.[32] Furthermore, we also studied this system for sequential hydroamination/hydrosilylation catalysis, and our catalyst turned out to be significantly more active than the previously reported systems.[31] In this contribution we now present a full account of the reaction scope, substrate selectivity, lanthanide ion size effect, and kinetic/mechanistic aspects of hydroamination/cyclization, hydrosilylation, and sequential hydroamination/hydrosilylation reactions catalyzed by [Ln{N(SiHMe$_2$)$_2$}$_2${CH(PPh$_2$NSiMe$_3$)$_2$}]. As well as the easy preparation of a sophisticated catalyst, the main focus of this contribution is to study the catalytic activity of a

[a] Dipl.-Chem. M. Rastätter, M.Sc. A. Zulys, Prof. Dr. P. W. Roesky
Institut für Chemie und Biochemie
Freie Universität Berlin
Fabeckstrasse 34–36, 14195 Berlin (Germany)
Fax: (+49) 30-838-52440
E-mail: roesky@chemie.fu-berlin.de

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robust and extremely efficient complex that may find broad application in organic synthesis

Results and Discussion

Metal complex synthesis: The starting materials [Ln{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] [Ln = Y (**1a**), La (**1b**), Sm (**1c**), Ho (**1d**), Lu (**1e**)] (Anwander amides)[33] were prepared in a modified synthesis similar to that published by Anwander et al., although in a one-pot synthesis, in contrast to the published two-step procedure, which first required the preparation of the THF solvates [LnCl$_3$(thf)$_x$]. Treatment of LnCl$_3$ (Ln = Y, La, Sm, Lu) with KN(SiHMe$_2$)$_2$ (2.9 equiv) gave **1a–e** in high yields. Compounds **1a–c** and **1e** have been described previously,[33–35] while the new compound **1d** was characterized by Raman spectroscopy and elemental analysis. The characteristic Si–H vibrations of **1d** were observed in the Raman spectrum at 2013 and 2076 cm^{-1}, while its solid-state structure was established by single-crystal X-ray diffraction. Compound **1d**, which in the solid state adopts a distorted trigonal bipyramidal geometry (Figure 1), crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell and is thus isostructural to the previously reported compounds **1a–c** and **1e**.[33–35]

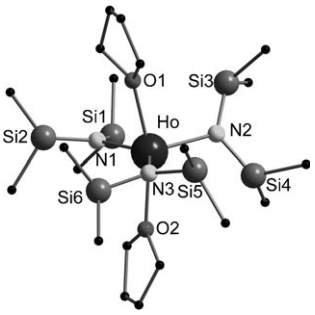
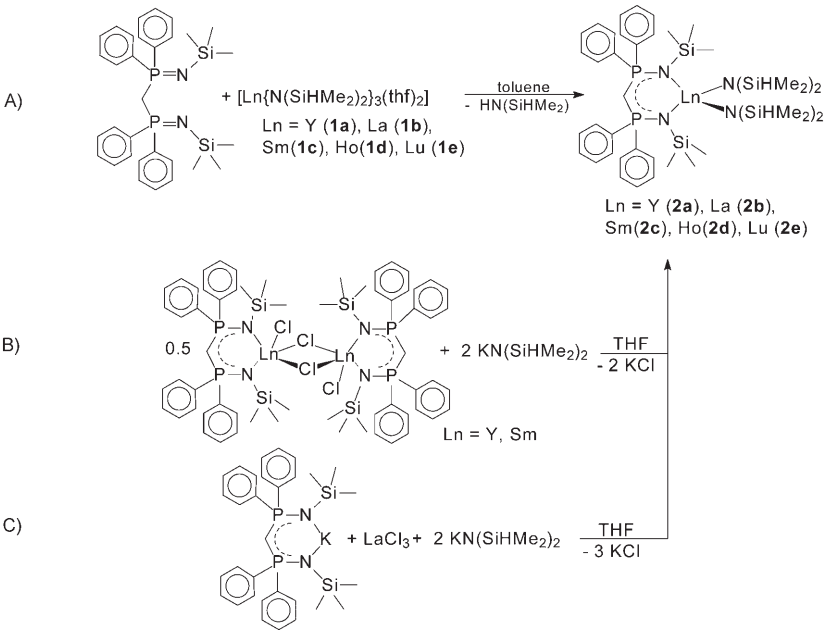


Figure 1. Solid-state structure of **1d**, showing the atom labeling scheme and omitting hydrogen atoms. Selected bond lengths [Å] or angles [°]: Ho–N1 2.270(2), Ho–N2 2.235(2), Ho–N3 2.278(2), Ho–O1 2.385(2), Ho–O2 2.404(2), Ho–Si4 3.2960(9), Ho–Si6 3.3050(10); N1-Ho-N2 110.69(10), N1-Ho-N3 135.14(10), N2-Ho-N3 114.05(10), N1-Ho-O1 88.00(7), N2-Ho-O1 95.32(8), N3-Ho-O1 84.81(8), N1-Ho-O2 87.32(8), N2-Ho-O2 101.70(8), N3-Ho-O2 86.96(8), O1-Ho-O2 162.92(8).



Scheme 1.

The title compounds [Ln{N(SiHMe$_2$)$_2$}$_2${CH(PPh$_2$NSiMe$_3$)$_2$}] [Ln = Y (**2a**), La (**2b**), Sm (**2c**), Ho (**2d**), Lu (**2e**)] can be obtained by three different synthetic approaches. To study the lanthanide ion size effect, the complexes of the smallest (Lu) and the largest (La) lanthanide ion, as well as those of some selected elements in between, were synthesized. The first approach starts from compounds **1a–e**, which were treated with [CH$_2$(PPh$_2$NSiMe$_3$)$_2$] in boiling toluene to give **2a–e** through amine eliminations (Scheme 1A). This method gave the highest yields and pure products and so was applied for the synthesis of all five complexes. In contrast with the previously described reactions between samarium tris(dicyclohexylamide) and [CH$_2$(PPh$_2$NSiMe$_3$)$_2$],[51] which under similar reaction conditions afford [Sm{C(Ph$_2$P=NSiMe$_3$)$_2$}(NCy$_2$)(thf)],[36] no carbene-type complex was observed when **1a–e** were used as starting materials.

Compounds **2a** and **2c** were also obtained by treatment of [Ln{(Me$_3$SiNPPh$_2$)$_2$CH}Cl$_2$]$_2$ (Ln = Y, Sm, 1 equiv) with KN(SiHMe$_2$)$_2$ (2 equiv, Scheme 1B).

The most convenient approach would seem to be a one-pot reaction sequence in which the potassium methanide complex K{CH(PPh$_2$NSiMe$_3$)$_2$} is treated with anhydrous lanthanum trichloride and KN(SiHMe$_2$)$_2$ in a 1:1:2 molar ratio in THF. Unfortunately, the yields are lower than those obtained in the other methods and the product has to be purified (Scheme 1C).

Compounds **2a–e** were characterized by standard analytical/spectroscopic techniques and the solid-state structures of all five compounds were established by single-crystal X-ray diffraction. The ^{1}H NMR spectra of **2a**, **2b**, and **2e** show the characteristic signals for the two different substituents. Singlets for the SiMe$_3$ groups [δ = 0.12 (**2a**), 0.13 (**2b**), or 0.12 ppm (**2e**)] and triplets for the PCHP groups [δ = 2.36

(**2a**), 2.65 (**2b**), or 2.77 ppm (**2e**)] are thus observed for the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligands, whereas doublets [$\delta = 0.60$ (**2a**), 0.56 (**2b**), or 0.64 ppm (**2e**)] and septets [$\delta = 5.50$ (**2a**), 5.44 (**2b**), or 5.45 ppm (**2e**)] are seen for the $\{N(SiHMe_2)_2\}^-$ ligands. In the $^{31}P\{^1H\}$ NMR spectra the characteristic signals of the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligands are observed. As a result of the influence of the paramagnetic samarium center, the observed chemical shift in the $^{31}P\{^1H\}$ NMR spectrum of **2c** ($\delta = 26.3$ ppm) differs from those in the diamagnetic compounds **2a**, **2b**, and **2e** [$\delta = 20.1$ (**2a**), 17.1 (**2b**), 20.6 ppm (**2e**)].

The solid-state structures of complexes **2a–e** were established by single-crystal X-ray diffraction (Figure 2). The coordination polyhedra are formed by the $\{N(SiHMe_2)_2\}^-$ groups and the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligands. Six-membered metallacycles (N1-P1-C1-P2-N2-Ln) are formed by chelation of the two trimethlysilylimine groups to the lanthanide atom. The rings all adopt twist boat conformations, in which the central carbon atoms and the lanthanide atoms are displaced from the N_2P_2 least-squares planes. The distances between the central carbon atom (C1) and the lanthanide atom [2.697(4) (**2a**), 2.875(4) (**2b**), 2.771(3) (**2c**), 2.685(3) (**2d**), 2.647(4) Å (**2e**)] are longer than average Ln–C distances; however, a resultant tridentate coordination of the ligand is observed as previously.[28–30] In contrast with the results obtained by ^1H NMR for the diamagnetic compounds **2a**, **2b**, and **2e**, the two $\{N(SiHMe_2)_2\}^-$ groups are not equivalent in the solid state. The $\{N(SiHMe_2)_2\}^-$ groups attached to the sterically more hindered side (*cis* to C1) are symmetrically oriented, whereas the other $\{N(SiHMe_2)_2\}^-$ groups (*trans* to C1) are asymmetric and their geometries can best be compared to that found in $[(C_5HPh_4)_2La\{N(SiHMe_2)_2\}]$.[37] One of the silicon atoms in this kind of groups (Si6) approaches more closely to the metal center than the others [Ln–Si6 3.1331(13) (**2a**), 3.2848(12) (**2b**), 3.1935(11) (**2c**), 3.1342(9) (**2d**), 3.1034(14) Å (**2e**), vs Ln–Si3 3.2922(15) (**2a**), 3.4440(12) (**2b**), 3.3271(11) (**2c**), 3.3011(11) (**2d**), 3.3042(13) Å (**2e**) and Ln–Si4 3.4610(14) (**2a**), 3.4768(13) (**2b**), 3.4828(11) (**2c**), 3.4381(11) (**2d**), 3.3953(13) Å (**2e**)]. A similar effect is observed in $[(C_5HPh_4)_2La\{N(SiHMe_2)_2\}]$ (3.261(2) vs 3.472(2) Å for one of the two independent molecules in the unit cell).[37] Concomitant with this effect, a decrease in the Ln-N-Si angle [Ln-N4-Si6 103.5(2) (**2a**), 105.6(2) (**2b**), 104.49(13) (**2c**), 103.59(13) (**2d**), 103.8(2)° (**2e**), vs 134.6(2) (**2a**), 130.7(2) (**2b**), 132.5(2) (**2c**), 134.69(15) (**2d**), 135.0(2)° (**2e**) for Ln-N4-Si5] is observed in **2a–e**. This is indicative of a weak β-Si–H monoagostic interaction, as has been discussed for other dimethylsilylamido rare earth metal complexes.[37,38] The metal–nitrogen bond lengths in the $\{N(SiHMe_2)_2\}^-$ groups [Ln–N3 2.250(4) (**2a**), 2.415(3) (**2b**), 2.309(3) (**2c**), 2.252(3) (**2d**), 2.207(4) (**2e**) and Ln–N4 2.260(3) (**2a**), 2.397(3) (**2b**), 2.318(3) (**2c**), 2.257(3) (**2d**), 2.220(4) Å (**2e**)] are close to those found in the starting material $[Ln\{N(SiHMe_2)_2\}_3(thf)_2]$,[33,34,35] but they are shorter than the Ln–N distance in the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand [Ln–N1 2.403(3) (**2a**), 2.536(2) (**2b**), 2.456(2) (**2c**), 2.392(3) (**2d**), 2.356(3) (**2e**) and Ln–N2 2.393(3) (**2a**), 2.536(3) (**2b**), Å 2.443(2) (**2c**), 2.386(2) (**2d**), 2.342(4) Å (**2e**)].

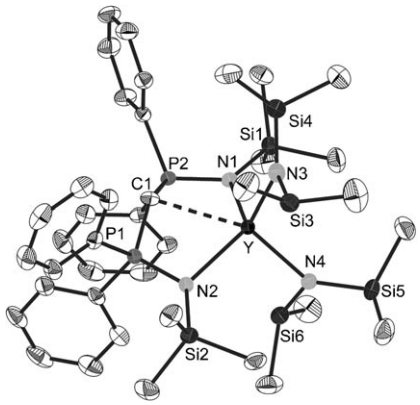
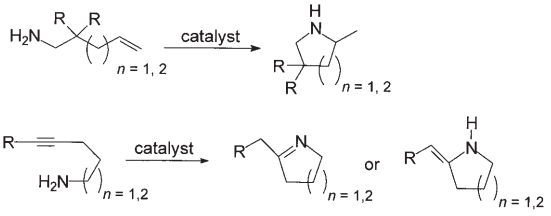


Figure 2. Perspective ORTEP view of the molecular structure of **2a**. Thermal ellipsoids are drawn to encompass 50% probability. Selected bond lengths [Å] or angles [°] (also given for isostructural **2b–2e**): **2a**: Y–C1 2.697(4), Y–N1 2.403(3), Y–N2 2.393(3), Y–N3 2.250(4), Y–N4 2.260(3), Y–Si3 3.2922(15), Y–Si4 3.4610(14), Y–Si6 3.1331(13); N1-Y-N2 119.91(12), N1-Y-C1 64.42(12), N2-Y-C1 64.56(12), Y-N4-Si5 134.6(2), Y-N4-Si6 103.5(2). **2b**: La–C1 2.875(4), La–N1 2.536(2), La–N2 2.536(3), La–N3 2.415(3), La–N4 2.397(3), La–Si3 3.4440(12), La–Si4 3.4768(13), La–Si6 3.2848(12); N1-La-N2 112.05(9), N1-La-C1 60.75(9), N2-La-C1 60.49(9), La-N4-Si5 130.7(2), La-N4-Si6 105.6(2). **2c**: Sm–C1 2.771(3), Sm–N1 2.456(2), Sm–N2 2.443(2), Sm–N3 2.309(3), Sm–N4 2.318(3), Sm–Si3 3.3271(11), Sm–Si4 3.4828(11), Sm–Si6 3.1935(11); N1-Sm-N2 116.50(8), N1-Sm-C1 62.69(8), N2-Sm-C1 62.63(8), Sm-N4-Si5 132.5(2), Sm-N4-Si6 104.49(13). **2d**: Ho–C1 2.685(3), Ho–N1 2.392(3), Ho–N2 2.386(2), Ho–N3 2.252(3), Ho–N4 2.257(3), Ho–Si3 3.3011(11), Ho–Si4 3.4381(11), Ho–Si6 3.1342(9); N1-Ho-N2 119.43(9), N1-Ho-C1 64.21(9), N2-Ho-C1 64.57(9), Ho-N4-Si5 134.69(15), Ho-N4-Si6 103.59(13). **2e**: Lu–C1 2.647(4), Lu–N1 2.356(3), Lu–N2 2.342(4), Lu–N3 2.207(4), Lu–N4 2.220(4), Lu–Si3 3.3042(13), Lu–Si4 3.3953(13), Lu–Si6 3.1034(14); N1-Lu-N2 121.25(12), N1-Lu-C1 65.11(12), N2-Lu-C1 65.64(13), Lu-N4-Si5 135.0(2), Lu-N4-Si6-Lu 103.8(2).

Catalysis: Since we were interested in studying sequential hydroamination/hydrosilylation we first tested the two reactions separately. The mechanism of the lanthanide metallocene-catalyzed hydroamination/cyclization reaction was established some years ago by Marks et al.[9] The scope and the limitations of using **2a–e** as catalysts in the intramolecular hydroamination/cyclization reaction were tested with different non-activated terminal aminoalkynes and aminoalkenes (Scheme 2). We first investigated the dependence of the rate on the ion radius of the center metal (Ln^{3+}, coordination number 6)[39] by using 1-(prop-2-enyl)-cyclohexane-



Scheme 2.

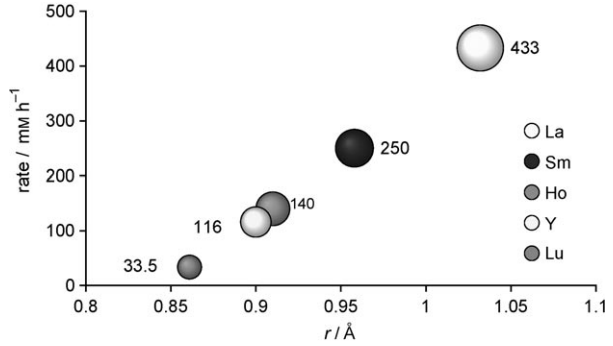


Figure 3. Plot of reaction rates for the hydroamination/cyclization of 1-(prop-2-enyl)-cyclohexanemethanamine (**8a**) with compounds **2a–e** as catalysts vs ionic radii of the center metals (Ln^{3+}, C.N. 6).[39]

methanamine (**8a**) as test substrate (Figure 3). As observed for the metallocene catalysts[9] of the lanthanides, the rates increase with increasing ion radius, showing the lanthanum compound **2b** to be the most active one.

Kinetic studies were undertaken by in situ ^{1}H NMR spectroscopy. The reaction behavior of a 50-fold molar excess of the substrate with constant catalyst concentration was monitored until complete substrate consumption and the decrease in the substrate peak was integrated in relation to the product signals. Figure 4 presents kinetics data for the cyclization of 1-(prop-2-enyl)-cyclohexanemethanamine (**8a**) as substrate with **2a** as catalyst, which indicates zero-order kinetics in substrate concentration, in analogy to the results for the metallocene catalysts. When the initial concentration of the aminoalkene was held constant and the concentration of the catalyst was varied over a fivefold range, a plot of ln(rate) versus ln[catalyst] indicates the reaction to be first order in catalyst concentration (Figure 5). The rate law can be expressed as in [Eq. (1)] and is identical to that for the lanthanide metallocene-catalyzed hydroamination/cyclization reactions.[5]

$$\upsilon = k\,[\text{substrate}]^0[\text{catalyst}]^1 \quad (1)$$

The catalytic reaction was also monitored by ^{31}P{^{1}H} NMR spectroscopy. The observed NMR signal for the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand remains in the region of the starting material ($\delta = 17.1$ ppm) and does not shift to the range of the free ligand $\{CH_2(PPh_2NSiMe_3)_2\}$ ($\delta = 3.39$ ppm),[40] which clearly indicates that the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand stays attached to the metal center during the catalytic conversions.

In our substrate screening we focused on non-activated aminoalkenes and aminoalkynes (Tables 1 and 2). The rigorously anaerobic reaction between the catalyst and dry, degassed aminoalkene and aminoalkyne proceeded regiospecifically (Tables 1 and 2) and it turned out that all substrates were converted into the cyclic products under moderate reaction conditions. The aminoalkynes could be cyclized in high yields at room temperature (Table 1, entries 1, 4, and 5), at 60 °C (Table 1, entry 3), or at 100 °C (Table 1, entry 2). Substrates bearing bulky geminal substituents in the β-position to the amino group (Thorpe–Ingold effect)[41] could be cyclized with reasonable catalyst/activator loadings of

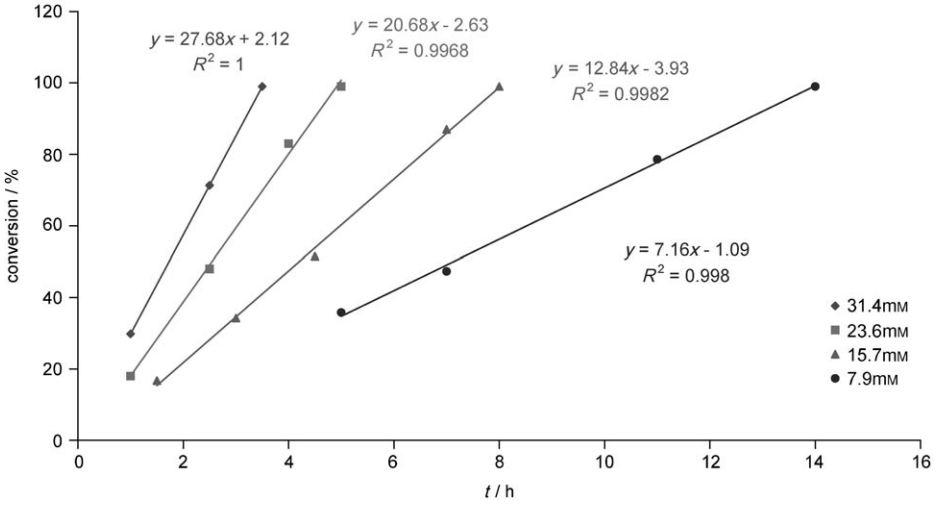


Figure 4. Ratio of conversion to lanthanide concentration as a function of time for the hydroamination/cyclization of 1-(prop-2-enyl)-cyclohexanemethanamine (**8a**) with compound **2a** as catalyst in benzene.

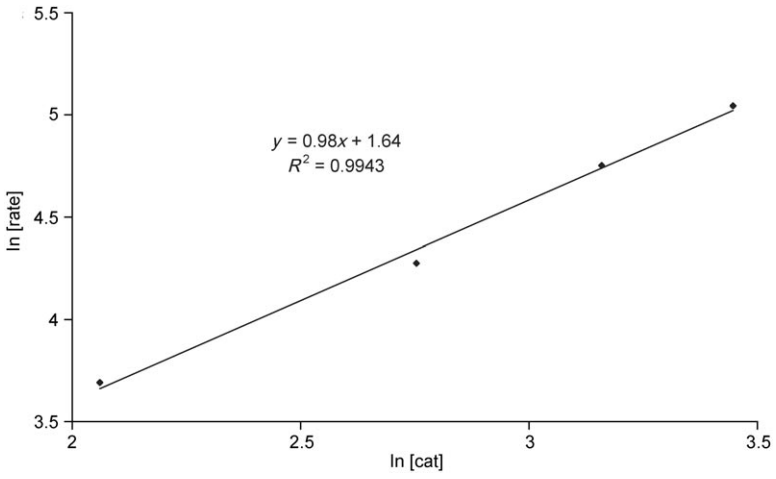
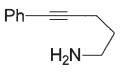
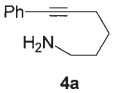
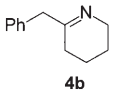
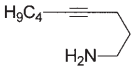
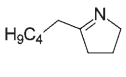
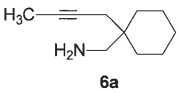
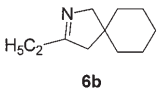
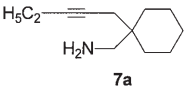
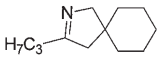


Figure 5. Determination of the reaction order in catalyst concentration for the hydroamination/cyclization of 1-(prop-2-enyl)-cyclohexanemethanamine **8a** using compound **2a** as catalysts in benzene.

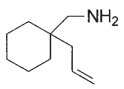
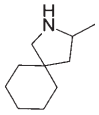
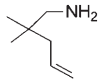
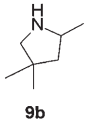
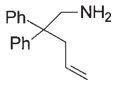
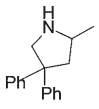
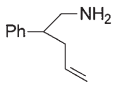
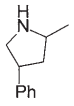
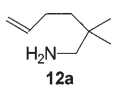
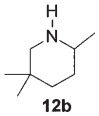
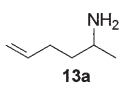
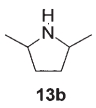
Table 1. Hydroamination/cyclization of terminal aminoalkynes catalyzed by **2b**.

Entry	Substrate	Product	Cat. [mol%]	*T* [°C]	*t* [h]	Yield [%][a]
1	 **3a**	 **3b**	1.0 1.0	RT 60	120 1	quant quant
2	 **4a**	 **4b**	2.0	100	4	95
3	 **5a**	 **5b**	2.0	60	4	99
4	 **6a**	 **6b**	2.0	RT	30	99[b]
5	 **7a**	 **7b**	2.0	RT	40	99

[a] Calculated by ^{1}H NMR, with $HN(SiHMe_2)_2$ as internal standard. [b] Ferrocene as additional internal standard.

1–2 mol% in good reaction times at room temperature (Table 1, entries 4 and 5). As already reported earlier, hydroamination of aminoalkenes shows significantly lower turnover frequencies than that of aminoalkynes (Table 2).[9] Most of the substrates could be cyclized at 60°C reaction temperature. As observed for the aminoalkynes, the Thorpe–Ingold effect also has a significant influence on to the reactivity: compounds **8a**, **9a**, and **10a** are thus rapidly converted into the pyrrolidines with reasonable catalyst loadings of 1–2 mol% (Table 2, entries 1–3). Substrate **10a** was the most reactive of the aminoalkenes, giving the corresponding pyrrolidine within 1.5 h. Compound **13a**, which is known to be a difficult substrate for this reaction, could be converted into 2,5-dimethylpyrrolidine (**13b**) in good yield and in a 4:1 *trans*/*cis* ratio. The formation of a six-membered ring by use of our catalyst represents a very promising result (Table 2, entry 5). It can be concluded that the rate of cyclization for aminoalkenes follows the order 5 > 6 (Table 2, entries 2 and 5), consistently with classical, stereoelectronically controlled, cyclization processes. In earlier studies we had investigated the homoleptic amides $[Ln\{N(SiMe_3)_2\}_3]$ as catalysts for hydroamination catalysis.[14b] A comparison of $[La\{N(SiMe_3)_2\}_3]$ with catalyst **2b** for substrate **3a** shows a higher activity for the latter catalyst. Obviously, the rates for the hydroamination are slower than those observed for the metallocene catalyst compounds, yet the current catalytic system has the advantage of being a very easily synthesized and robust catalyst. Indeed, compounds **2a–e** are far more easily accessible than metallocene catalysts. The $CH_2(PPh_2NSiMe_3)_2$ can be made in few hours without solvent from commercial available educts. The title complexes are also accessible in a one-step procedure. Moreover, compounds **2a–e** are much more robust towards moisture and air than the corresponding metallocenes. It is well established that leaving groups other than $HN(SiHMe_2)_2$ may give higher activities for hydroamination,[17b,42] but attaching these groups would result in

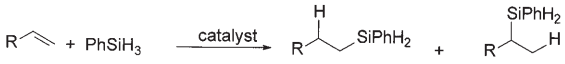
Table 2. Hydroamination/cyclization of terminal aminoalkenes catalyzed by **2b**.

Entry	Substrate	Product	Cat [mol%]	*T* [°C]	*t* [h]	Yield [%][a]
1	 **8a**	 **8b**	1.1 1.1	RT 60	150 3	91[b] quant
2	 **9a**	 **9b**	1.3	60	6	quant
3	 **10a**	 **10b**	2.0	60	1.5	quant
4	 **11a**	 **11b**	1.7	60	36	82 (*trans*/*cis* 79:21)
5	 **12a**	 **12b**	2.2	60	22	quant
6	 **13a**	 **13b**	3.0 3.0	60 100	50 35	– 81 (*trans*/*cis* 80:20)

[a] Calculated by ^{1}H NMR, with $HN(SiHMe_2)_2$ as internal standard. [b] Ferrocene as additional internal standard.

other disadvantages. In general, lanthanide alkyls are much more sensitive towards moisture and air and much less readily accessible, while other amido groups give carbene-type complexes (e.g., NCy_2)[36] or are catalytically inactive (e.g., NPh_2).[28]

As well as hydroamination, intermolecular hydrosilylation catalyzed by **2a–e** was also investigated (Scheme 3, Tables 3 and 4). Hydrosilylation of alkenes is one of the most versatile and efficient methods for the synthesis of alkylsilanes and their derivatives.[43] Usually, the highly air- and moisture-sensitive lanthanide alkyl and hydride complexes have been used as catalysts for hydrosilylation,[44] and there is only one example in which the more stable lanthanide amido catalyst [La{N(SiMe$_3$)$_2$}$_3$] has been used as a hydrosilylation catalyst (see also Table 3, entry 6).[45] Again we focused on the dependence of the rate on the ionic radius of the center metal, using hex-1-ene and $PhSiH_3$ as substrates (Table 3). As observed in the hydroamination, the rates increase with increasing ionic radius, showing the lanthanum compound **2b** to be the most active one (Table 3, entry 2). Compound **2b** can be used at room temperature to give quantitative yields, reacting approximately twice as fast as [La{N(SiMe$_3$)$_2$}$_3$] with use of half of the catalyst loading (Table 3, entry 6). In this context, we also used compound **1b** as a catalyst for the hydrosilylation reaction. Compound **1b** is less active than compound **2b**, but we did not investigate the catalytic activity of **1b** in more detail, because we and others had shown previously that the homoleptic amides of the lanthanides have only limited application as catalysts for the hydroamination reaction,[14b,15b] so compound **1b** is obviously not a good catalyst in the desired sequential hydroamination/hydrosilylation.



Scheme 3.

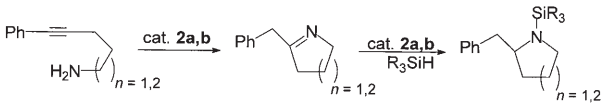
Table 3. Hydrosilylation of hex-1-ene (**15a**) with phenylsilane catalyzed by **2a–c**, **2e**, and [La{N(SiMe$_3$)$_2$}$_3$].[a]

Entry	Catalyst	Cat. [mol %]	T [°C]	t [h]	Yield [%][b] (ratio *n*/iso)
1	**2a**	1.5	100	26	99 (99:1)
2	**2b**	1.5	RT	16	99 (99:1)
3	**2c**	1.5	100	6	99 (99:1)
4	**2e**	1.5	100	32	99 (99:1)
5	**1b**	3	RT	20	99 (99:1)
6	[La{N(SiMe$_3$)$_2$}$_3$]	3	RT	40	98[a] (96:4)

[a] Ref. [45]. [b] Calculated by ^{1}H NMR.

As substrates for a full screening of compound **2b** we used terminal olefins and dienes that had been employed as "benchmark" substrates earlier (Table 4).[45] All substrates were treated with $PhSiH_3$ at room temperature, together with 1.5 mol % catalyst, to give the corresponding silanes quantitatively. With regard to reaction temperature, catalyst loading, and yields, the activity of compound **2b** is comparable to that reported for metallocene catalysts.[9] The aliphatic substrates (Table 4, entries 1–3) were converted into the corresponding anti-Markovnikov products with very high regioselectivity. In contrast, with styrene as substrate a product mixture was obtained (Table 4, entry 4). Additionally, the cyclization/silylation of hexa-1,5-diene (**18a**) to afford the corresponding cyclopentane **18b** (Table 4, entry 5) was investigated. Quantitative yields and high regioselectivity were observed.

Finally, we were interested in combining the hydroamination/cyclization and the hydrosilylation reactions to provide a sequential hydroamination/hydrosilylation reaction catalyzed by the diamagnetic complexes **2a** and **2b** (Scheme 4). Since no mechanistic studies involving sequential hydroami-



Scheme 4.

Table 4. Hydrosilylation reaction of terminal olefins and dienes catalyzed by **2b**.

Entry	Substrate	Product	Cat. [mol %]	T [°C]	t [h]	Yield [%][a] (ratio *n*/iso)
1	H_9C_4 **14a**	H_9C_4 SiH_2Ph **14b**	1.5	RT	16	99 (99:1)
2	$H_{13}C_6$ **15a**	$H_{13}C_6$ SiH_2Ph **15b**	1.5	RT	24	99[b] (99:1)
3	**16a**	SiH_2Ph **16b**	1.5	RT	22	99 (99:1)
4	Ph **17a**	SiH_2Ph Ph **17b**	1.5	RT	30	99 (35:65)
5	**18a**	SiH_2Ph **18b**	1.5	RT	36	99 (99:1)

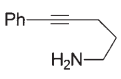
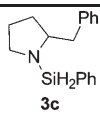
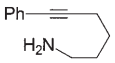
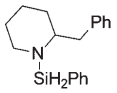
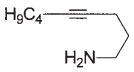
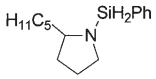
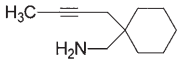
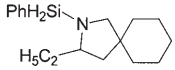
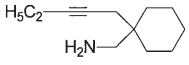
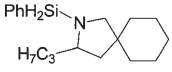
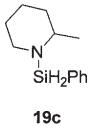
[a] Calculated by ^{1}H NMR, with $HN(SiHMe_2)_2$ as internal standard. [b] Ferrocene as additional internal standard.

nation/hydrosilylation reactions have been reported in lanthanide chemistry we were interested in studying the reaction by multinuclear NMR, which is perfectly possible with the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand. Unlike Doye et al., who did not isolate the hydrosilylation product but instead performed a hydrolytic workup to isolate the corresponding secondary amine, we were interested in obtaining the silicon species.[31] The hydrogenation[46] and hydrosilylation[47] of imines had been reported previously, but not in sequential reactions. As substrates, six different phenyl- and alkylalkynes and $PhSiH_3$ were used. The reactions occurred with complete selectivity with catalyst loadings of 2 mol% (Table 5). As also observed in the other reactions, the lanthanum compound **2b** was more active than the yttrium complex **2a**, and, as observed in the non-sequential reactions, the hydroamination is always the slower reaction. The hydrosilylation reaction was thus always complete within 4 h at room temperature with the use of **2b** as catalyst, while quantitative conversions in the slower hydroamination reaction in the presence of **2b** in short reaction times were observed at room temperature with the substrates **6a** and **7a**, at 60 °C with the substrates **3a** and **5a**, and at 100 °C with the substrates **4a** and **19a**. As described above, the Thorpe–Ingold effect has a significant influence on to the reactivity of the substrates. As products, both five-membered (**3c**, **5c**, **6c**, and **7c**) and six-membered rings (**4c**, **19c**) were formed. The silylamides shown in Table 5 are viscous oils that could only be characterized by NMR techniques. For full characterization we hydrolyzed these products by exposure to air to give the corresponding amines and then characterized these amines.

To the best of our knowledge, compounds **2a** and **2b** are the first rare earth catalysts for sequential hydroamination/hydrosilylation reactions to be reported. Moreover, compound **2b** is more active than any other catalyst reported so far for this reaction. Whereas for the titanium-based systems a 10 mol% loading of catalyst was reported, we used only 2 mol%.[31] Moreover, the second step, the hydrosilylation, involves working at room temperature with **2b** whereas a reaction temperature of 105 °C was reported for the titanium catalysts. To the best of our knowledge only two more complexes have been reported as catalysts for sequential hydroamination/hydrosilylation reactions,[48] and those catalysts, which are iridium complexes, were used for one reaction only. The catalyst loadings were compared to those used by us in a similar range, but the reaction temperature for the second step was reported to be 60 °C.

The general advantage of the reported reactions is that cyclic amines can be obtained either by direct hydroamination of the corresponding aminoalkene or by a stepwise hydroamination/hydrosilylation reaction sequence involving the corresponding aminoalkynes. Since the hydroamination of aminoalkenes is significantly slower than the hydroamination of aminoalkynes, the reported sequential hydroamination/hydrosilylation is an attractive alternative pathway for the synthesis of cyclic amines. The products shown in Table 5 are silylamides and can be easily hydrolyzed by exposure to air to provide the corresponding amines.

Table 5. Hydroamination/hydrosilylation of aminoalkynes catalyzed by **2a** and by **2b**.[a]

Entry	Substrate	Product	Cat.[a]	T [°C]	t [h]	Yield [%][b]
1	 **3a**	 **3c**	**2a**	60	4	99
				60	4	99
			2b	60	4	99
				RT	4	70[c]
2	 **4a**	 **4c**	**2a**	100	16	99
				RT	4	99
			2b	100	4	99
				RT	4	99
3	 **5a**	 **5c**	**2a**	60	16	99
				60	4	99
			2b	60	16	99
				RT	4	99
4	 **6a**	 **6c**	**2a**	RT	30	99
				RT	4	99
			2b	RT	16	99
				RT	4	99
5	 **7a**	 **7c**	**2a**	RT	40	99
				RT	4	99
			2b	RT	16	99
				RT	4	99
6	 **19a**	 **19c**	**2a**	100	24	96
				60	12	95
			2b	100	4	99
				RT	4	99

[a] Conditions: 2 mol% of catalyst in C_6D_6, first step hydroamination, second step hydrosilylation. [b] Calculated by ^1H NMR. [c] Isolated yield; reaction was performed on a 2 mmol scale.

Conclusions

In summary, it should be emphasized that a series of yttrium and lanthanide amido complexes $[Ln\{N(SiHMe_2)_2\}_2\{CH(PPh_2NSiMe_3)_2\}]$ [Ln = Y (**2a**), La (**2b**), Sm (**2c**), Ho (**2d**), Lu (**2e**)] have been synthesized by three different pathways. These $[Ln\{N(SiHMe_2)_2\}_2\{CH(PPh_2NSiMe_3)_2\}]$ complexes were used as catalysts for the hydroamination/cyclization and the hydrosilylation reactions. A clear dependence of the reaction rates on the ionic radii of the center metals was observed, showing the lanthanum compound to be the more active one in both re-

actions. Furthermore, a combination of both reactions—a sequential hydroamination/hydrosilylation reaction—was also investigated. Compound **2b** is the first lanthanide catalyst studied for the sequential hydroamination/hydrosilylation reaction. Even the rates for the hydroamination are slower than the ones observed for the metallocene catalyst compounds **2a–e**, which are far more easily accessible than the metallocene catalysts. Compound $CH_2(PPh_2NSiMe_3)_2$ can be made in a few hours without solvent from commercial available educts and the title complexes are also accessible in a one-step procedure. Moreover, compounds **2a–e** are much more robust than the corresponding metallocenes towards moisture and air. Since no mechanistic studies involving sequential hydroamination/hydrosilylation reactions in lanthanide chemistry have been reported, we were interested in studying the reaction by multinuclear NMR, which is perfectly possible with the $\{CH(PPh_2NSiMe_3)_2\}^-$ ligand.

Experimental Section

General considerations: 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 glove box (M. Braun). THF was predried over Na wire and distilled under nitrogen from K and benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled under nitrogen from $LiAlH_4$. All solvents for vacuum line manipulations were stored in vacuo over $LiAlH_4$ in resealable flasks. Deuterated solvents were obtained from Chemotrade Chemiehandelsgesellschaft mbH (all $\geq$99 atom % D) and were degassed, dried, and stored in vacuo over Na/K alloy in resealable flasks. NMR spectra were recorded with a JNM-LA 400 FT-NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane and 85% phosphoric acid (^{31}P NMR). Elemental analyses were carried out with an Elementar vario EL instrument. $KN(SiHMe_2)_2$,[49] $LnCl_3$,[50] $\{CH_2(PPh_2NSiMe_3)_2\}$,[51] $[K\{CH(PPh_2NSiMe_3)_2\}]$,[28] and $[LnCl_2\{CH(PPh_2NSiMe_3)_2\}]_2$[28] were prepared by literature procedures.

[Ln{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] [Ln = Y (1a), La (1b), Sm (1c), Ho (1d), Lu (1e)]: The compounds were prepared in a modified synthesis similar to that published by Anwander et al.[33] $LnCl_3$ (Ln = Y, La, Sm, Lu, Ho) and $KN(SiHMe_2)_2$ (2.9 equiv) were placed in a flask. THF was then condensed onto the mixture at −196 °C and the suspension was stirred overnight (20 h) at ambient temperature. The solvent was then evaporated in vacuo and the residue was extracted with toluene (Ln = Y, Lu) or pentane (Ln = La, Sm, Ho). The extract was filtered, and the solvent was taken off in vacuo. The remaining microcrystalline powder was washed with a small amount of pentane at −78 °C.

[Y{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (1a): This complex was prepared from YCl_3 (0.500 g, 2.56 mmol) and $KN(SiHMe_2)_2$ (1.272 g, 7.42 mmol). Yield: 1.033 g, 66%; ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): δ = 0.38 (d, ^3J(H,H) = 2.92 Hz, 36H; SiH(CH_3)$_2$), 1.30 (m, 8H; O-CH_2), 3.84 (m, 8H; CH_2), 4.98 ppm (sept, ^3J(H,H) = 2.94 Hz, 6H; SiH(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6, 100.4 MHz, 20 °C): δ = 3.3 (SiH(*C*H$_3$)$_2$), 25.3 (O-*C*H$_2$), 71.15 ppm (*C*H$_2$).

[La{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (1b): This complex was prepared from $LaCl_3$ (0.400 g, 0.82 mmol) and $KN(SiHMe_2)_2$ (0.810 g, 2.37 mmol). Yield: 0.789 g. A second extraction with pentane gave an additional yield of 0.240 g. Overall yield 1.029 g, 93%; ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): δ = 0.38 (d, ^3J(H,H) = 2.92 Hz, 36H; SiH(CH_3)$_2$), 1.35 (m, 8H; O-CH_2), 3.91 (m, 8H; CH_2), 5.03 ppm (sept, ^3J(H,H) = 2.95 Hz, 6H; SiH(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6, 100.4 MHz, 20 °C): δ = 3.2 (SiH(*C*H$_3$)$_2$), 25.3 (O-*C*H$_2$), 70.8 ppm (*C*H$_2$).

[Sm{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (1c): This complex was prepared from $SmCl_3$ (0.2 g, 0.78 mmol) and $KN(SiHMe_2)_2$ (0.387 g, 2.26 mmol). Yield: 0.473 g, 88%; FT Raman (single crystal): 399 (w), 615 (s), 681 (m), 760 (w), 926 (w), 1240 (w), 1427 (w), 2013 (w, νSi-H), 2075 (w, νSi-H), 2896 (s), 2951 cm^{-1} (s, νCH); elemental analysis calcd (%) for $C_{20}H_{58}N_3O_2Si_6Sm$ (691.57): C 34.73, H 8.45, N 6.08; found: C 34.04, H 8.87, N 5.70.

[Ho{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (1d): This complex was prepared from $HoCl_3$ (0.400 g, 1.47 mmol) and $KN(SiHMe_2)_2$ (0.733 g, 4.28 mmol). Yield: 1.360 g, 97%. Crystals suitable for X-ray crystallography were obtained from a concentrated THF solution of **1d**. FT Raman (single crystal): $\tilde{\nu}$ = 400 (w), 625 (s), 681 (m), 761 (w), 926 (w), 1240 (w), 1427 (w), 2013 (w, νSi-H), 2076 (w, νSi-H), 2896 (s), 2895 (m), 2952 cm^{-1} (s, νCH); elemental analysis calcd (%) for $C_{20}H_{58}N_3OSi_6Ho$ (706.14): C 34.02, H 8.28, N 5.95; found: C 33.89, H 8.92; N 5.86.

[Lu{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (1e): This complex was prepared from $LuCl_3$ (0.500 g, 1.78 mmol) and $KN(SiHMe_2)_2$ (0.914 g, 5.16 mmol). Yield: 0.808 g, 63%; ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): δ = 0.39 (d, ^3J(H,H) = 3.04 Hz, 36H; SiH(CH_3)$_2$), 1.25 (m, 8H; O-CH_2), 3.85 (m, 8H; CH_2), 4.94 ppm (sept, ^3J(H,H) = 2.98 Hz, 6H; SiH(CH$_3$)$_2$); ^{13}C{^{1}H} NMR (C_6D_6, 100.4 MHz, 20 °C): δ = 3.2 (SiH(*C*H$_3$)$_2$), 25.3 (O-*C*H$_2$), 72.1 ppm (*C*H$_2$).

[Ln{N(SiHMe$_2$)$_2$}$_2${CH(PPh$_2$NSiMe$_3$)$_2$}] [Ln = Y (2a), La (2b), Sm (2c), Ho (2d), Lu (2e)]

Method A: In a general procedure, **1a–e** (1 equiv) and $[CH_2(PPh_2NSiMe_3)_2]$ (1 equiv) were dissolved in toluene (20 mL). The clear solution was heated at reflux for 36 h and was then reduced to dryness, extracted with pentane, and filtered. The filtrate was concentrated and cooled to −78 °C, and a white (**2a**, **2b**, **2e**) to slightly yellow (**2c**) or yellow/pink (**2d**) precipitate was formed.

Method B: In a salt elimination reaction, $[Ln\{(Me_3SiNPPh_2)_2CH\}Cl_2]_2$ (Ln = Y, Sm) (1 equiv) and $KN(SiHMe_2)_2$ (2 equiv) were dissolved in THF and stirred for 24 h. The solution was then reduced to dryness, extracted with pentane, and filtered. The filtrate was concentrated and cooled to −78 °C, and a white precipitate was formed.

Method C: In a one-pot reaction, $LaCl_3$ (equiv), $[K\{CH(PPh_2NSiMe_3)_2\}]$ (1 equiv), and $KN(SiHMe_2)_2$ (2 equiv) were dissolved in THF and stirred for 48 h. The solution was then reduced to dryness, extracted with pentane, and filtered. The filtrate was concentrated and cooled to −78 °C, and a white precipitate was formed.

[Y{N(SiHMe$_2$)$_2$}$_2${CH(PPh$_2$NSiMe$_3$)$_2$}] (2a)

Method A: This complex was prepared from $Y\{N(SiHMe_2)_2\}_3(thf)_2]$ (0.150 g, 0.24 mmol) and $[CH_2(PPh_2NSiMe_3)_2]$ (0.134 g, 0.24 mmol). Yield: 0.102 g, 79%.

Method B: This complex was prepared from $[YCl_2\{CH(PPh_2NSiMe_3)_2\}]_2$ (0.331 g, 0.23 mmol) and $KN(SiHMe_2)_2$ (0.158 g, 0.92 mmol). Yield: 0.371 g, 88%. Crystals suitable for X-ray crystallography were obtained from a hot pentane solution of **2a**. ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): δ = 0.12 (s, 18H; Si(CH_3)$_3$), 0.60 (d, ^3J(H,H) = 2.80 Hz, 24H; SiH(CH_3)$_2$), 2.63 (t, ^3J(H,P) = 6.83 Hz, 1H; CH), 5.50 (sept, ^3J(H,H) = 2.76 Hz, 4H; SiH(CH$_3$)$_2$), 6.8–7.5 ppm (m, 20H; Ph); ^{31}P{^{1}H} NMR (C_6D_6, 161.7 MHz, 20 °C): δ = 20.1 ppm (d, ^2J(P,Y) = 6.00 Hz); FT Raman (single crystal): $\tilde{\nu}$ = 406 (w), 622 (s), 661 (w), 679 (w), 999 (s, νPC), 1027 (m), 1109 (w), 1159 (w), 1575 (w), 1590 (m, νC=C), 2044 (w, νSi-H), 2140 (w, νSi-H), 2896 (m), 2950 (s, νCH), 3061 cm^{-1} (m, νC=C-H); elemental analysis calcd (%) for $C_{39}H_{67}N_4P_2Si_6Y$ (961.34): C 51.40, H 7.41, N 6.15; found: C 51.15, H 7.18, N 5.43.

[La{N(SiHMe$_2$)$_2$}$_2${CH(PPh$_2$NSiMe$_3$)$_2$}] (2b)

Method A: This complex was prepared from $[La\{N(SiHMe_2)_2\}_3(thf)_2]$ (0.100 g, 0.15 mmol) and $[CH_2(PPh_2NSiMe_3)_2]$ (0.082 g, 0.15 mmol). Yield: 0.133 g, 94%.

Method C: This complex was prepared from $LaCl_3$ (0.123 g, 0.5 mmol), $[K\{CH(PPh_2NSiMe_3)_2\}]$ (0.300 g, 0.5 mmol) and $KN(SiHMe_2)_2$ (0.171 g, 1 mmol). Yield: 0.390 g, 66%. Crystals suitable for X-ray crystallography were obtained from a concentrated pentane solution of **2b**. ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): δ = 0.13 (s, 18H; Si(CH_3)$_3$), 0.56 (d, ^3J(H,H) = 2.92 Hz, 24H; SiH(CH_3)$_2$), 2.35 (t, ^3J(H,P) = 6.33 Hz, 1H; CH), 5.44 (sept, ^3J(H,H) = 2.92 Hz, 4H; SiH(CH$_3$)$_2$), 6.8–7.5 ppm (m, 20H; Ph);

$^{31}P\{^1H\}$ NMR (C_6D_6, 161.7 MHz, 20 °C): $\delta = 17.1$ ppm; FT Raman (single crystal): $\tilde{\nu} = 407$ (w), 626 (s), 662 (w), 678 (w), 999 (s, νPC), 1027 (m), 1107 (w), 1159 (w), 1578 (w), 1590 (m, νC=C), 2044 (w, νSi-H), 2147 (w, νSi-H), 2895 (m), 2949 (s, νCH), 3062 cm^{-1} (m, νC=C-H); elemental analysis calcd (%) for $C_{39}H_{67}LaN_4P_2Si_6$ (961.34): C 48.73, H 7.02, N 5.83; found: C 48.72, H 7.33, N 5.34.

[Sm{N(SiHMe$_2$)$_2$}$_2${CH(PPh$_2$NSiMe$_3$)$_2$}] (2c)

Method A: This complex was prepared from [Sm{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (0.100 g, 0.15 mmol) and [CH$_2$(PPh$_2$NSiMe$_3$)$_2$] (0.082 g, 0.15 mmol). Yield: 0.133 g, 94%. Crystals suitable for X-ray crystallography were obtained from a concentrated pentane solution of **2c**.

Method B: This complex was prepared from [SmCl$_2${CH(PPh$_2$NSiMe$_3$)$_2$}]$_2$ (0.331 g, 0.21 mmol) and KN(SiHMe$_2$)$_2$ (0.145 g, 0.85 mmol). Yield: 0.335 g, 80%. Crystals suitable for X-ray crystallography were obtained from a hot pentane solution of **2c**. $^{31}P\{^1H\}$ NMR (C_6D_6, 161.7 MHz, 20 °C): $\delta = 26.3$ ppm (br); FT Raman (single crystal): $\tilde{\nu} = 402$ (w), 618 (s), 659 (w), 680 (w), 999 (s, νPC), 1027 (m), 1108 (w), 1159 (w), 1575 (w), 1590 (m, νC=C), 2047 (w, νSi-H), 2122 (w, νSi-H), 2895 (m), 2948 (s, νCH), 3060 cm^{-1} (m, νC=C-H); elemental analysis calcd (%) for $C_{39}H_{67}N_4P_2Si_6Sm$ (972.80): C 48.15, H 6.94, N 5.76; found: C 49.80, H 6.83, N 5.13.

[Ho{N(SiHMe$_2$)$_2$}$_2${CH(PPh$_2$NSiMe$_3$)$_2$}] (2d)

Method A: This complex was prepared from [Ho{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (0.500 g, 0.71 mmol) and [CH$_2$(PPh$_2$NSiMe$_3$)$_2$] (0.396 g, 0.71 mmol). Yield: 0.404 g, 58%. Crystals suitable for X-ray crystallography were obtained from a concentrated pentane solution of **2d**; FT Raman (single crystal): $\tilde{\nu} = 405$ (w), 623 (s), 661 (w), 679 (w), 999 (s, νPC), 1027 (m), 1108 (w), 1159 (w), 1575 (w), 1590 (m, νC=C), 2045 (w, νSi-H), 2137 (w, νSi-H), 2895 (m), 2950 (s, νCH), 3061 cm^{-1} (m, νC=C-H); elemental analysis calcd (%) for $C_{39}H_{67}HoN_4P_2Si_6$ (987.37): C 47.44, H 6.84, N 5.67; found: C 47.56, H 6.89, N 5.28.

[Lu{N(SiHMe$_2$)$_2$}$_2${CH(PPh$_2$NSiMe$_3$)$_2$}] (2e)

Method A: This complex was prepared from [Lu{N(SiHMe$_2$)$_2$}$_3$(thf)$_2$] (0.150 g, 0.24 mmol) and [CH$_2$(PPh$_2$NSiMe$_3$)$_2$] (0.134 g, 0.24 mmol). Yield: 0.102 g, 79%. Crystals suitable for X-ray crystallography were obtained from a concentrated pentane solution of **2e**. ^1H NMR (C_6D_6, 400 MHz, 20 °C): $\delta = 0.12$ (s, 18H; SiH(CH_3)$_2$), 0.64 (d, ^3J(H,H) = 2.92 Hz, 24H; Si(CH_3)$_3$), 2.77 (t, ^3J(H,P) = 6.65 Hz, 1H; C*H*), 5.45 (sept, ^3J(H,H) = 2.90 Hz, 4H; Si*H*(CH_3)$_2$), 6.8–7.5 ppm (m, 20H; Ph); $^{31}P\{^1H\}$ NMR (C_6D_6, 161.7 MHz, 20 °C): $\delta = 20.6$ ppm; FT Raman (single crystal): $\tilde{\nu} = 407$ (w), 626 (s), 662 (w), 677 (w), 999 (s, νPC), 1027 (m), 1108 (w), 1159 (w), 1575 (w), 1590 (m, νC=C), 2044 (w, νSi-H), 2150 (w, νSi-H), 2895 (m), 2949 (s, νCH), 3062 cm^{-1} (m, νC=C-H); elemental analysis calcd (%) for $C_{39}H_{67}LuN_4P_2Si_6$ (997.40): C 46.96, H 6.77, N 5.62; found: C 47.26, H 6.65, N 4.62.

General for the hydroamination and hydrosilylation reactions (NMR scale reaction): The catalyst was weighed into an NMR tube under argon gas. C_6D_6 (≈0.7 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 the insertion into the NMR probe (t_0). The ratio of reactant to product was exactly calculated by comparison of the integrations of the corresponding signals. The N(Si*HMe*$_2$)$_2$ groups were used as an internal standard for the kinetic measurements. By use of ferrrocene as an independent standard in some reactions it was shown that HN(SiHMe$_2$)$_2$ is formed in stoichiometric ratios. The sequential hydroamination/hydrosilylation reaction was performed in a one-pot sequence. After completion of a hydroamination reaction, $PhSiH_3$ was just added to the reaction mixture.

For the intramolecular hydroamination/cyclization reactions, the substrates 5-phenylpent-4-yn-1-amine[9c] (**3a**), 6-phenylhex-5-yn-1-amine[9c] (**4a**), non-4-yn-1-amine[9h] (**5a**), (1-allylcyclohexyl)methanamine[9i] (**8a**), 2,2-dimethylpent-4-en-1-amine[9b] (**9a**), 2,2-diphenylpent-4-en-1-amine[9i] (**10a**), 2-phenylpent-4-en-1-amine[9b] (**11a**), 2,2-dimethylhex-5-en-1-amine[9b] (**12a**), hex-5-en-2-amine[9b] (**13a**), and hex-5-yn-1-amine[9h] (**19a**) were synthesized by literature procedures. The new compounds [1-(but-2-ynyl)cyclohexyl]methanamine (**6a**) and [1-(pent-2-ynyl)cyclohexyl]methanamine (**7a**) were synthesized by modifications of literature methods as described below. All substrates were dried by stirring over $LiAlH_4$. The substrates for the hydrosilylation (**14a**–**18a**) are commercially available.

Substrate synthesis

[1-(But-2-ynyl)cyclohexyl]methanamine (6a): Cyclohexanecarbonitrile (7.5 mL, 64 mmol) was added dropwise at 0 °C to a solution of lithium diisopropylamide (65 mmol) in THF (200 mL), followed by stirring at 0 °C for 2 h. 1-Bromobut-2-yne (65 mmol) was then added and the mixture was stirred for 3 h at 0 °C. The prepared 1-(but-2-ynyl)cyclohexanecarbonitrile was purified by distillation under reduced pressure. An unsaturated nitrile (40 mmol) was added under nitrogen at room temperature with stirring to a suspension of $LiAlH_4$ (2.28 g, 60 mmol) in dry ether (200 mL). The mixture was stirred, heated at reflux for 2 h, and then cooled in an ice bath. A THF/water mixture 5:1 (9.2 mL) and then aqueous NaOH (15%, 10 mL) were added dropwise to the reaction mixture with vigorous stirring and cooling. After filtration of the dry granular precipitate and washing with THF, the filtrate was condensed to leave a colorless oil **6a**, which was purified by distillation. Yield 67%; ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 0.64$ (br s, 2H; (NH_2)), 1.20–1.32 (m, 10H), 1.55 (t, $J(^1H,^1H) = 2.56$ Hz, 3H), 2.14 (q, $J(^1H,^1H) = 2.56$ Hz, 2H), 2.55 ppm (s, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 25 °C): $\delta = 3.4$, 22.0, 25.4, 26.7, 33.0, 37.5, 49.1, 77.0, 86.8 ppm; MS (EI): *m*/*z* (%): 165 $[M]^+$ (34), 150 $[M-CH_3]^+$ (19), 30 $[CH_2NH_2]^+$ (100).

[1-(Pent-2-ynyl)cyclohexyl]methanamine (7a): Compound **7a** was synthesized in a manner analogous to that used for **6a** with 1-bromopent-2-yne in place of 1-bromobut-2-yne. Yield 67%; ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 0.64$ (br s, 2H; (NH_2)), 0.98 (t, $J(^1H,^1H) = 7.44$ Hz, 3H), 1.20–1.32 (m, 10H), 2.00 (q, $J(^1H,^1H) = 7.44$ Hz, 2H), 2.16 (m, 2H), 2.56 ppm (s, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 25 °C): $\delta = 12.8$, 14.6, 22.0, 22.3, 26.7, 33.0, 37.5, 49.1, 77.3, 88.4 ppm; MS (EI): *m*/*z* (%): 179 $[M]^+$ (14), 164 $[M-CH_3]^+$ (11), 30 $[CH_2NH_2^+]$ (100).

Products: The spectra of compounds **3b**,[9c] **4b**,[9c] **5b**,[9h] **8b**,[9i] **9b**,[9b] **10b**,[9i] **11b**,[9b] **12b**,[9b] **13b**,[9b] **14b**,[11] **15b**,[11] **16b**,[11] **17b**,[11] and **18b**[10c] were consistent with the literature. As a result of their high air sensitivities the silyamides were not obtained analytically pure and so were only characterized by NMR. For better characterization they were then hydrolyzed to afford the corresponding amines. The silyamides **3c**, **4c**, **5c**, **6c**, **7c**, and **19c** in air gave the corresponding amines 2-benzylpyrrolidine (**3d**),[9i] 2-benzylpiperidine (**4d**),[9i] 2-pentylpyrrolidine (**5d**),[11] **6d**, **7d**, and 2-methylpiperidine (**19d**),[9i] which were characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and MS.

2-Benzyl-1-(phenylsilyl)pyrrolidine (3c): ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 1.34$–1.47 (m, 4H), 2.32 (m, 1H), 2.72 (m, 1H), 2.92 (m, 2H), 3.51 (m, 1H), 5.05 (m, 2H), 6.92–7.55 ppm (m, 10H; 2×Ph); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 25 °C): $\delta = 26.0$, 32.1, 44.1, 48.9, 62.4, 126.2, 128.3, 128.4, 128.5, 129.7, 135.1, 136.0, 140.2 ppm.

2-Benzyl-1-(phenylsilyl)piperidine (4c): ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 1.07$–1.25 (m, 6H), 2.37 (m, 1H), 2.55 (m, 1H), 2.70–2.76 (m, 2H), 3.05 (m, 1H), 4.70 (m, 2H), 6.76–7.30 ppm (m, 10H; 2×Ph); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 25 °C): $\delta = 20.8$, 27.5, 30.0, 38.3, 43.3, 56.8, 126.2, 128.3, 128.5, 129.6, 130.2, 135.1, 136.1, 140.7 ppm.

2-Pentyl-1-(phenylsilyl)pyrrolidine (5c): ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 0.82$ (t, $J(^1H,^1H) = 7.2$ Hz, 3H), 1.13–1.29 (m, 8H), 1.41–1.55 (m, 4H), 1.56–1.71 (m, 1H), 2.97 (m, 2H), 3.25 (m, 1H), 5.16 (q, $J(^1H,^1H) = 10$ Hz, 2H), 7.31–7.60 ppm (m, 5H; Ph); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 25 °C): $\delta = 14.4$, 23.0, 26.6, 26.7, 32.3, 32.9, 37.9, 49.0, 60.6, 128.3, 130.0, 135.2, 136.0 ppm.

3-Ethyl-2-azaspiro[4.5]dec-2-ene (6b): ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 1.10$ (t, $J(^1H,^1H) = 7.44$ Hz, 3H), 1.21–1.31 (m, 10H), 1.97 (s, 2H), 2.10 (q, $J(^1H,^1H) = 7.44$ Hz, 2H), 3.58 ppm (s, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 25 °C): $\delta = 10.7$, 24.0, 26.2, 27.4, 33.5, 37.4, 42.5, 73.1, 176.0 ppm; MS (EI): *m*/*z* (%): 166 $[M+H]^+$ (100).

3-Ethyl-2-(phenylsilyl)-2-azaspiro[4.5]decane (6c): ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 0.72$ (t, $J(^1H,^1H) = 7.44$ Hz, 3H), 0.98 (m, 1H), 1.27–1.21 (m, 10H), 1.62 (m, 3H), 2.72 (d, $J(^1H,^1H) = 9.6$ Hz, 1H), 2.85 (d, $J(^1H,^1H) = 9.6$ Hz, 1H), 3.20–3.25 (m, 1H), 5.14 (s, 2H), 7.60–7.31 ppm

(m, 5H; Ph); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 25 °C): $\delta = 10.6$, 23.5, 24.5, 26.6, 31.0, 35.4, 37.2, 44.1, 60.9, 128.3, 130.0, 135.1, 135.4 ppm.

3-Ethyl-2-azaspiro[4.5]decane (6d): ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 0.76$ (t, $J(^1H,^1H) = 7.08$ Hz, 3H), 0.87 (m, 1H), 1.14–1.31 (m, 12H), 1.57 (m, 1H), 2.44 (d, $J(^1H,^1H) = 9.6$ Hz, 1H), 2.59 (d, $J(^1H,^1H) = 10.8$ Hz, 1H), 2.75–2.82 ppm (m, 1H); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 25 °C): $\delta =$ 11.4, 23.4, 23.6, 25.9, 29.0, 36.7, 38.0, 42.9, 59.9 ppm; MS (EI): *m*/*z* (%): 167 $[M]^+$ (14), 138 $[M-C_2H_5]^+$ (100).

3-Propyl-2-azaspiro[4.5]dec-2-ene (7b): ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 0.89$ (t, $J(^1H,^1H) = 7.44$ Hz, 3H), 1.10–1.31 (m, 10H), 1.60 (dt, 2H), 1.98 (s, 2H), 2.12 (t, $J(^1H,^1H) = 7.44$ Hz, 2H), 3.61 ppm (t, $J(^1H,^1H) = 1.72$ Hz, 2H); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 25 °C): $\delta = 14.2$, 19.9, 24.0, 26.2, 36.2, 37.4, 42.4, 50.0, 73.0, 175.1 ppm; MS (EI): *m*/*z* (%): 179 $[M]^+$ (44), 151 $[M-C_2H_4]^+$ (100), 136 $[M-C_3H_7]^+$ (15).

2-(Phenylsilyl)-3-propyl-2-azaspiro[4.5]decane (7c): ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 0.79$ (t, $J(^1H,^1H) = 7.2$ Hz, 3H), 0.98 (m, 1H), 1.11–1.31 (m, 12H), 1.62 (m, 3H), 2.73 (d, $J(^1H,^1H) = 9.6$ Hz, 1H), 2.85 (d, $J(^1H,^1H) = 9.6$ Hz, 1H), 3.28–3.35 (m, 1H), 5.17 (s, 2H), 7.60–7.31 ppm (m, 5H; Ph); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 25 °C): $\delta = 14.5$, 19.9, 23.5, 24.5, 26.7, 35.4, 37.3, 40.8, 44.2, 59.3, 128.3, 130.0, 135.1, 136.0 ppm.

3-Propyl-2-azaspiro[4.5]decane (7d): ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 0.87$ (t, $J(^1H,^1H) = 7.2$ Hz, 3H), 1.18–1.31 (m, 13H), 1.43 (m, 4H), 1.50 (m, 1H), 2.48 (d, $J(^1H,^1H) = 10.72$ Hz, 1H), 2.67 (d, $J(^1H,^1H) =$ 10.72 Hz, 1H), 2.84–2.91 ppm (m, 1H); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 25 °C): $\delta = 14.5$, 20.8, 23.9, 24.2, 26.4, 37.1, 38.4, 38.7, 43.1, 58.4 ppm; MS (EI): *m*/*z* (%): 181 $[M]^+$ (12), 138 $[M-C_3H_7]^+$ (100).

2-Methyl-1-(phenylsilyl)piperidine (19c): ^1H NMR (C_6D_6, 400 MHz, 25 °C): $\delta = 1.05$ (d, $J(^1H,^1H) = 6.84$ Hz, 3H), 1.23 (m, 2H), 1.34 (m, 2H), 1.48 (m, 2H), 2.70 (m, 1H), 2.94 (m, 1H), 3.08 (m, 1H), 5.09 (d, $J(^1H,^1H) = 2.80$ Hz, 2H; PhSiH_2), 7.10–7.58 ppm (m, 5H; Ph); $^{13}C\{^1H\}$ NMR (C_6D_6, 100 MHz, 25 °C): $\delta = 20.4$, 23.1, 27.6, 34.3, 47.0, 51.9, 128.3, 129.9, 134.7, 136.0 ppm.

X-ray crystallographic studies of 1d and 2a–e: Crystals of **1d** suitable for X-ray crystallography were obtained from a concentrated THF solution. Crystals of **2a–e** were grown from saturated pentane solutions. A suitable crystal was in each case covered in mineral oil (Aldrich) and mounted onto a glass fiber. The crystal was transferred directly to the −73 °C cold N_2 stream of a Stoe IPDS 2T or a Bruker CCD Apex 1000 diffractometer. Subsequent computations were carried out on an Intel Pentium IV PC. CCDC-624685 (**1d**), -286336 (**2b**), -624686 (**2a**), -624687 (**2c**), -624688 (**2d**), and -624689 (**2e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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