A bis(phosphinimino)methanide lanthanum amide as catalyst for the hydroamination/cyclisation, hydrosilylation and sequential hydroamination/hydrosilylation catalysis†

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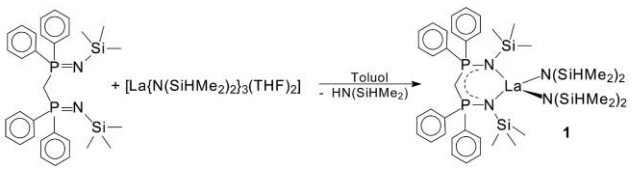
[La{N(SiHMe$_2$)$_2$}$_2${CH(PPh$_2$NSiMe$_3$)$_2$}], which was obtained *via* an amine elimination starting from [CH$_2$(PPh$_2$NSiMe$_3$)$_2$] and [La{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$], was used as catalyst for the hydroamination/cyclisation, the hydrosilylation and the sequential hydroamination/hydrosilylation reaction.

In lanthanide chemistry alkyl, amido and hydrido cyclopentadienyl complexes and especially metallocenes such as [(C$_5$Me$_5$)$_2$LnR] (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] polymerization,[3] hydroamination,[4] hydrosilylation,[5] hydroboration,[6] and hydrophosphination.[7] Besides the well established cyclopentadienyl complexes today a number of non-cyclopentadienyl lanthanide complexes, which are based on amido and alkoxide ligands are known to be active in the hydroamination/cyclisation catalysis.[8–10] Recently, we introduced the bis(phosphinimino)methanide {CH(PPh$_2$NSiMe$_3$)$_2$}$^-$, into yttrium and lanthanide chemistry as a cyclopentadienyl replacement.[11–13] We have previously reported the synthesis of a series of lanthanide bis(phosphinimino)methanide complexes including yttrium, which were used as homogenous catalysts for a number of different catalytic applications. Very recently, Doye *et al.* reported on a Ti based catalyst for a sequential hydroamination/hydrosilylation.[14] Based on these results we desired to synthesise a non-cyclopentadienyl lanthanide catalyst which is useable as catalyst for hydroamination/cyclisation and the hydrosilylation reaction. Furthermore, we wanted to study this system for a sequential hydroamination/hydrosilylation catalysis. In contrast to the work of 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 for obtaining the silicon species.

The title compound [La{N(SiHMe$_2$)$_2$}$_2${CH(PPh$_2$NSiMe$_3$)$_2$}] (**1**) was obtained *via* an amine elimination in boiling toluene starting from [CH$_2$(PPh$_2$NSiMe$_3$)$_2$] and [La{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] (Anwander Amide).[15] (Scheme 1).‡ The ^{1}H NMR spectrum of **1** shows the characteristic signals for the two different substituents. Thus, a singlet at δ 0.13 ppm and a triplet at 2.35 ppm are observed for the {CH(PPh$_2$NSiMe$_3$)$_2$}$^-$ ligand, whereas a doublet at δ 0.56 ppm and a septet at δ 5.44 are observed for the {N(SiHMe$_2$)$_2$}$^-$ groups. In the ^{31}P{^{1}H} NMR spectrum the characteristic signal of the {CH(PPh$_2$NSiMe$_3$)$_2$}$^-$ ligand is observed at δ 17.1 ppm.

The solid state structure of complex **1** was established by single crystal X-ray diffraction (Fig. 1). The co-ordination polyhedron is formed by the {N(SiHMe$_2$)$_2$}$^-$ groups and the {CH(PPh$_2$NSiMe$_3$)$_2$}$^-$ ligand. A six-membered metallacycle (N1-P1-C1-P2-N2-La) is formed by chelation of the two trimethlysilylimine groups to the lanthanide atom. The ring adopts a twist boat conformation, in which the central carbon atom and the lanthanum atom are displaced from the N$_2$P$_2$ least-squares plane. The distance between the central carbon atom (C1) and the lanthanum atom (287.5(4) pm) is longer than the average La–C distances; however a resultant tridentate coordination of the ligand is observed as before.[12,13] In contrast to the results obtained by ^{1}H NMR the two {N(SiHMe$_2$)$_2$}$^-$ groups are not equivalent in the solid state. The {N(SiHMe$_2$)$_2$}$^-$ group, which is attached to the sterically more hindered side (*cis* to C1) is symmetrically oriented, whereas the other {N(SiHMe$_2$)$_2$}$^-$ group (*trans* to C1) is asymmetric and can best be compared to the geometry found in [(C$_5$HPh$_4$)$_2$La{N(SiHMe$_2$)$_2$}].[16] One of the silicon atoms in this group (Si6) is getting closer to the metal centre than the others (La–Si6 328.48(12) pm *vs.* La–Si3 344.40(12) pm and La–Si4 347.68(13) pm). A similar effect is observed in [(C$_5$HPh$_4$)$_2$La{N(SiHMe$_2$)$_2$}] (326.1(2) pm *vs.* 347.2(2) pm for



Scheme 1

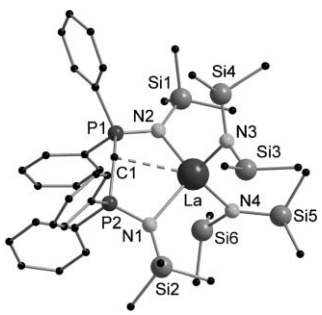


Fig. 1 Solid-state structure of **1**, omitting hydrogen atoms.

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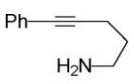
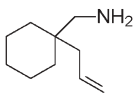
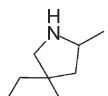
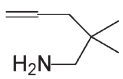
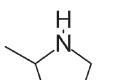
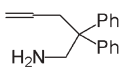
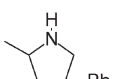
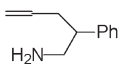
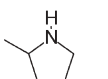
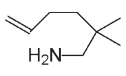
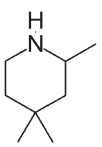
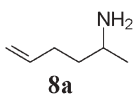
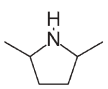
one of the two independent molecules).[16] Concomitant with this effect a decrease in the La–N–Si angle (La–N4–Si6 105.6(2)° *vs.* 130.7(2)° for La–N4–Si5) is observed in **1**. This is indicative of a weak β-SiH monoagostic interaction as has been discussed for other dimethylsilylamido rare-earth-metal complexes.[15–17]

Since we were interested in studying the sequential hydroamination/hydrosilylation first we tested both reactions separately. Compound **1** was used as the catalyst in the intramolecular hydroamination/cyclisation reaction of non-activated terminal aminoolefines and one aminoalkynes first (Table 1).§ Here we focused on aminoalkenes because it is well known that compared to the hydroamination of aminoalkynes, aminoalkenes exhibit significantly lower turnover frequencies. It turned out that the substrates are converted to the cyclic product at 60 °C in high yield. Some compounds could be converted even at room temperature (entry 1-2). The rigorously anaerobic reaction of the catalyst with dry, degassed aminoolefin and aminoalkyne proceeds regiospecifically. Kinetic studies indicate zero-order behaviour in substrate over a ten fold concentration range. Substrates bearing bulky geminal substituents in the β-position to the amino group (Thorpe–Ingold effect)[18] could be cyclised with reasonable catalyst/activator loadings of 1–3 mol% within good reaction times. Substrate **5a** was the most reactive of the aminoolefins, giving the corresponding pyrrolidine within 1.5 h. Compound **8a** which is known to be a difficult substrate for this reaction, could be converted to 2,5-dimethyl-pyrrolidine (**8b**) in good yield. We were pleased to find that the formation of six membered rings can also be performed with our catalyst (entry 6). It can be concluded that the rate of cyclisation for aminoalkynes follows the order 5 > 6, consistent with classical, stereoelectronically controlled, cyclisation processes.

Table 1 Hydroamination/cyclisation reaction of terminal aminoolefines and alkynes catalyzed by **1**

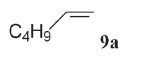
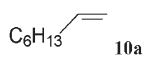
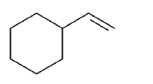
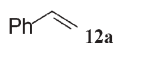
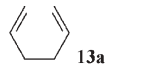
Entry	Substrate	Product	*T*/°C	mol% cat	Yield (%)[a]	*t*/h
1	 **2a**	 **2b**	RT 60	1.0 1.0	Quant Quant	120 1
2	 **3a**	 **3b**	RT 60	1.1 1.1	91 Quant	150 3
3	 **4a**	 **4b**	60	1.3	Quant	6
4	 **5a**	 **5b**	60	2.0	Quant	1.5
5	 **6a**	 **6b**	60	1.7	82	36
6	 **7a**	 **7b**	60	2.2	Quant	22
7	 **8a**	 **8b**	60 100	3.0 3.0	— 81 (80 : 20) (*trans*/*cis*)	50 35

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

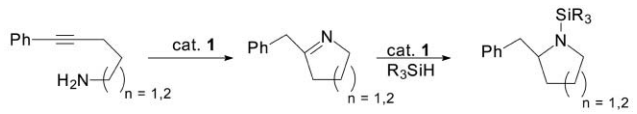
Beside the hydroamination, also the hydrosilylation catalysed by **1** was also investigated. The hydrosilylation of alkenes is one of the most versatile and efficient methods for the synthesis of alkylsilanes and their derivatives. Usually, the very air and moisture sensitive lanthanide alkyl and hydride complexes were used as catalysts for the hydrosilylation.[19] Recently, the more stable lanthanide amido catalyst, $[La\{N(SiMe_3)_2\}_3]$, has been introduced as a hydrosilylation catalyst.[20]

As substrates, we used terminal olefins and dienes, which were used as "benchmark" substrates earlier (Table 2).[20] All substrates were reacted at room temperature with $PhSiH_3$ in quantitative yields with 1.5 mol% catalyst quantitatively to the corresponding silanes. The catalyst loading is half of the amount used with the $[La\{N(SiMe_3)_2\}_3]$ system. In regard of reaction temperature, catalyst loading and yields, the activity of compound **1** is comparable to that reported for metallocene catalysts.[5] The aliphatic substrates (entry 1-3) were converted in very high regioselectivity to the corresponding anti-Markovnikov products. In contrast using styrene as substrate a product mixture is

Table 2 Hydrosilylation reaction of terminal olefins and dienes catalyzed by **1**[a]

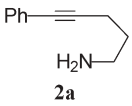
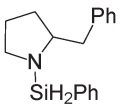
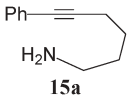
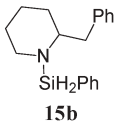
Entry	Substrate	Product	*T*/h	Yield (%)[b] (ratio)
1	 **9a**	**9b**	16	99 (99 : 1)
2	 **10a**	**10b**	24	99 (99 : 1)
3	 **11a**	**11b**	22	99 (99 : 1)
4	 **12a**	**12b**	30	99 (65 : 35)
5	 **13a**	**13b**	36	99 (99 : 1)

[a] Condition, 1.5 mol% of **1** in C_6D_6 at room temperature. [b] Calculated by ^{1}H NMR.



Scheme 2

Table 3 Hydroamination/hydrosilylation of aminoalkynes catalyzed by **1**[a]

Entry	Substrate	Product	Conditions[a]	Yield (%)
1	 **2a**	 **14b**	1) 60 °C, 4 h 2) RT, 4 h	99 70[b]
2	 **15a**	 **15b**	1) 100 °C, 4 h 2) RT, 4 h	99

[a] Condition, 2 mol% of **1** in C_6D_6 at room temperature. [b] Calculated by ^{1}H NMR. [b] Isolated yield, reaction was performed on a 2 mmol scale.

obtained. Additionally, the cyclisation/silylation of 1,5-hexadiene (**13a**) to the corresponding cyclopentane (**13b**) (entry 5) was investigated. Quantitative yields and high regioselectivity were observed.

Finally, we were interested to combine the hydroamination/cyclisation and the hydrosilylation reaction to a sequential hydroamination/hydrosilylation reaction catalyzed by **1** (Scheme 2). Phenylalkynes and $PhSiH_3$ were used as substrates. The reactions occur in quantitative selectivity with catalysts loadings of 2 mol% (Table 3). Quantitative conversions are observed in short reaction times at 60 °C (**2a**) and 100 °C (**15a**), respectively, for the hydroamination and at room temperature for the hydrosilylation step. A five membered (**14b**) and a six membered ring (**15b**) were formed as products. To the best of our knowledge, compound **1** is the first rare-earth catalyst to be reported for the sequential hydroamination/hydrosilylation reaction. Thus cyclic amines can now be either obtained by a direct hydroamination of the corresponding aminoalkene or by a stepwise hydroamination/hydrosilylation reaction of 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.

We thank the Deutsche Forschungsgemeinschaft for financial support.

Notes and references

‡ Preparation of **1**: 0.100 g (0.15 mmol) of $[La\{N(SiHMe_2)_2\}_3(THF)_2]$ and 0.082 g (0.15 mmol) $[CH_2(PPh_2NSiMe_3)_2]$ were dissolved in 20 ml toluene. The clear solution was refluxed for 36 h. Afterwards the solution was reduced to dryness, extracted with pentane and filtered. The filtrate was concentrated, cooled to −78 °C and a white precipitate was formed. Yield: 0.133 g, 94%. Crystals suitable for X-ray crystallography were obtained from a concentrated pentane solution. ^{1}H NMR (C_6D_6, 400 MHz, 20 °C): δ = 0.13 (s, 18H, $SiH(CH_3)_2$); 0.56 (d, 24H, $Si(CH_3)_3$, ^3J(H,H) = 2.92 Hz); 2.35 (t, 1H, C**H**, ^3J = 6.33 Hz); 5.44 (sp, 4HSi**H**$(CH_3)_2$, ^3J(H,H) = 2.92 Hz); 6.8–7.5 (m, 20H Ph). ^{31}P-NMR{^{1}H} (C_6D_6, 161.7 MHz, 20 °C): δ = 17.1 (s). for $C_{39}H_{67}LaN_4P_2Si_6$ (961.34): calcd: C 48.73, H 7.02, N 5.83; found: C 48.7 H 7.3 N 5.3.

§ For the general procedure of the hydroamination and hydrosilyation reaction see ESI.† Crystal data for **1**: $C_{39}H_{67}LaN_4P_2Si_6$, M = 961.36, monoclinic space group $P2_1/n$, a = 1177.80(7) pm, b = 2170.67(10) pm, c = 1976.88(15) pm, β = 92.381(6)°, V = 5049.8(5) × 10^6 pm^3, T = 200(2) K, Z = 4, μ = 1.081 mm^{-1}, 23698 reflections collected, $R1$ = 0.0323 for 5997 $F > 2(F)$, $wR2$ = 0.0542 for all 8793 data, 483 parameters, all non hydrogen atoms calculated anisotropic; the positions of the H atoms were calculated for idealised positions. The structure was solved and refined using SHELXS-97[21a] and SHELXL-97[21b]. CCDC 286336. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514242c

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