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Ln(II) amido complexes coordinated by ring-expanded N-heterocyclic carbenes – promising catalysts for olefin hydrophosphination†

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First Ln(II) ring-expanded NHC complexes (er-NHC)Ln[N(SiMe$_3$)$_2$]$_2$ (Ln = Sm, Yb) are synthesized and proved to be highly efficient pre-catalysts for the intermolecular hydrophosphination of such indolent substrates as 1-alkenes, cyclohexene and norbornene.

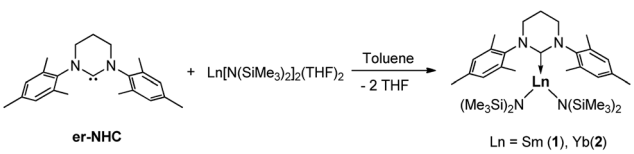
N-heterocyclic carbenes (NHCs) constitute an important class of ligands in coordination chemistry[1–6] and their complexes have multiple catalytic applications including olefin metathesis,[7–9] cross-coupling[10] and hydrofunctionalization[11,12] reactions. A remarkable impact of the σ-donor character of NHC ligands on the catalytic activity and selectivity of transition-metal catalyzed reactions has been highlighted in a series of reviews.[13–15] Variation of an NHC ring size may be exploited as one of the tools for tuning NHC basicity and ring expansion was shown to provide improved σ-donor properties.[16–18] Despite the long lasting excitement around the NHC complexes of d-metals, the lanthanide-NHC chemistry still remains poorly explored.[19,20] However, a series of reports revealing the great promise of these complexes in catalysis have been published recently.[21–25]

Hydrophosphination, that is, the addition of P–H functionality across C–C multiple bonds, is an atom-economic approach for the synthesis of valuable compounds that may be one of the prospective fields of application of Ln complexes.[26–28] Great progress has been made recently in this area; however, success is somewhat elusive for non-activated substrates. Hydrophosphination of 1-alkenes and internal C=C bonds still remains a challenging transformation.[26] A substantial breakthrough was Waterman and co-workers' account of a Zr precatalyst for the hydrophosphination of non-activated alkenes such as 1-hexene and ethylene.[29,30] Ionic yttrium alkyl[31] and Yb(II) and Ca(II) amido[32] complexes were also shown to enable the hydrophosphination of such a reluctant substrate as 1-nonene, however, with noticeably lower activity.

Recently the role of NHC ligands was shown to be crucial for the ability of complexes (NHC)$_2$M[N(SiMe$_3$)$_2$]$_2$ (M = Ca, Sm, Yb) to catalyze the hydrophosphination of C=C and C≡C bonds with PH$_3$ and the complexes coordinated by 5-membered NHCs proved to be highly efficient catalysts for this transformation.[22] However, complexes (NHC)$_n$M[N(SiMe$_3$)$_2$]$_2$ (NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, n = 2; 1,3-bis(2,6-dimethylphenyl)imidazolin-2-ylidene, n = 1) were inert in the addition of PhPH$_2$ and Ph$_2$PH to 1-nonene. Bearing in mind the stronger electron donating character of ring-expanded NHCs (er-NHCs)[33,34] we focused our attention on these ligands. Herein we report the preparation of Sm(II) and Yb(II) bis(amido) complexes coordinated by a 6-membered ring NHC ligand and their catalytic performance in hydrophosphination reactions.

Complexes (er-NHC)Ln[N(SiMe$_3$)$_2$]$_2$ (Ln = Sm (**1**), Yb(**2**)) coordinated by a 6-membered NHC ligand were synthesized by the reactions of (THF)$_2$Ln[N(SiMe$_3$)$_2$]$_2$ with equimolar amounts of 1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene at room temperature in toluene. Recrystallization from toluene at −30 °C affords **1** and **2** as black or red crystals in 78 and 81% yields, respectively (Scheme 1).

Complexes **1** and **2** are both stable in solid state and in solution under conditions excluding contact with oxygen and



Scheme 1 Synthesis of **1** and **2**.

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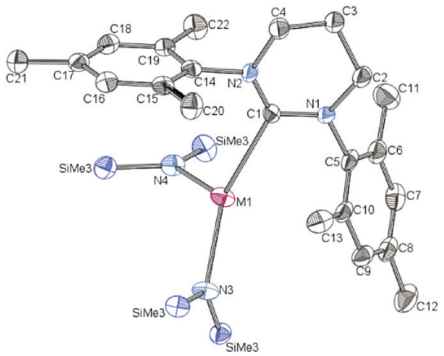
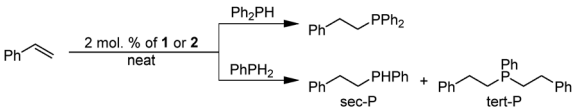


Fig. 1 Molecular structures of **1** and **2** (M = Sm (**1**), Yb (**2**)). The thermal ellipsoids are given at the 75% probability level. H atoms are omitted for clarity. The selected bond lengths (Å) and angles (deg) are as follows: **1**: Sm(1)–C(1) 2.807(3), Sm(1)–N(3) 2.466(3), Sm(1)–N(4) 2.448(3), C(1)–Sm(1)–N(3) 128.18(9), C(1)–Sm(1)–N(4) 113.1(2), N(3)–Sm(1)–N(4) 116.9(2); **2**: Yb(1)–C(1) 2.664(2), Yb(1)–N(3) 2.344(2), Yb(1)–N(4) 2.342(2), C(1)–Sm(1)–N(3) 126.02(7), C(1)–Yb(1)–N(4) 113.72(7), N(3)–Yb(1)–N(4) 119.51(7).

Table 1 Hydrophosphination of styrene with $PhPH_2$ and Ph_2PH catalyzed by **1** and **2**[a]



No.	Pre-cat	Phosphine	Styrene : phosphine	Time (h)	Conv.[c] (%)	*sec*-P/*tert*-P[d,e]
1	**1**	$PhPH_2$	1 : 1	1	96	97/3
2[b]	**1**		2 : 1	2	98	4/96
3	**1**	Ph_2PH	1 : 1	1	98	—
4	**2**	$PhPH_2$	1 : 1	2	73	98/2
5[b]	**2**		2 : 1	8	92	10/90
6	**2**	Ph_2PH	1 : 1	2	87	—

[a] Reaction in neat substrates $[phosphine]_0 : [styrene]_0 : [precat]_0 = 50 : 50 : 1$, $[precat]_0$ = 87.0 mM, T [°C] = 40. [b] $[phosphine]_0 : [styrene]_0 : [precat]_0 = 50 : 100 : 1$ $[precat]_0$ = 60.0 mM. [c] Conversion of styrene, determined by NMR spectroscopy. [d] Chemoselectivity was determined by $^{31}P\{^1H\}$ NMR spectroscopy. [e] Regioselectivity was determined by ^1H, $^{31}P\{^1H\}$ NMR spectroscopy.

moisture. The crystal structures of **1** and **2** were established *via* single-crystal X-ray diffraction studies (Fig. 1). The crystal data and structural refinement details are listed in Table S1 (ESI†).

Complexes **1** and **2** are isomorphous, crystallize in the monoclinic $P2_1/c$ space group and adopt the trigonal-planar geometry of three-coordinate metal centers (N_{amido}–Sm(II)–N_{amido} 116.9(2)°, N_{amido}–Yb(II)–N_{amido} 119.51(7)°), similarly to the related Ln(II)-NHC adducts $[(Me_3Si)_2N]_2Ln(NHC)$ (NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, 1,3-diisopropyl-4,5-dimethyl-imidazol-2-ylidene)[21] and $(NHC)Ln[C(SiHMe_2)_3]_2$ (NHC = 1,3-di-*tert*-butylimidazol-2-ylidene, Ln = Yb, Sm).[25] Ln(II) ions in **1** and **2** deviate from the C(1)N(3)N(4) planes by 0.20 and 0.12 Å, respectively. The Ln–C_{NHC} bond lengths in **1** (2.807(3) Å) and **2** (2.664(2) Å) are somewhat longer than those observed in the related alkyl complexes $(NHC)Ln\{C(SiHMe_2)_3\}_2$ (Sm, 2.780(2); Yb, 2.605(2) Å). Also, the Yb–C_{NHC} distance in **2** is slightly longer compared to that measured in the 5-membered NHC analogue (2.600(3) Å),[21] reflecting the greater steric demand of the 6-membered NHC ligand. The dihedral angles between the planes of the mesityl rings of the NHC ligand are 107.1(2)° (**1**) and 112.94(7)° (**2**). The M–N_{amido} distances in **1** (2.448(3), 2.466(3) Å) and **2** (2.342(2), 2.344(2) Å) are close to those in the parent four-coordinate amides $(THF)_2Ln[N(SiMe_3)_2]_2$ (Sm, 2.423(8), 2.44(1);[35] Yb, 2.333(4), 2.347(4) Å[36]) and the three-coordinate complex $[(Me_3Si)_2N]_2Yb(NHC)$ (Yb, 2.317(3), 2.323(2) Å).[21] The Ln···C_{Me} distances between metal ions and a couple of Me groups of the silylamido ligands are noticeably shorter (**1**: 3.179(4), 3.230(4) Å; **2**: 3.095(3), 3.114(3) Å) than the others (**1**: 3.622(4), 3.695(4) Å; **2**: 3.680(3), 3.716(5) Å).

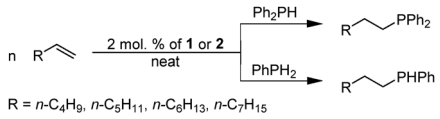
Complexes **1** and **2** were evaluated as pre-catalysts for the intermolecular hydrophosphination of alkene substrates (styrene, 1-hexene, 1-heptene, 1-octene, 1-nonene, cyclohexene, norbornene) with $PhPH_2$ or Ph_2PH.

Complexes **1** and **2** proved to be highly efficient catalysts for styrene hydrophosphination with $PhPH_2$ and Ph_2PH. The catalytic runs were carried out in the presence of 2 mol. % of the catalyst in neat substrates at 40 °C. Quantitative conversions were reached within 1–8 h. The representative data are gathered in Table 1. All reactions proceeded in a highly regioselective manner to afford exclusively anti-Markovnikov addition products. Moreover, for primary $PhPH_2$ the reactions catalyzed by **1** and **2** proved to be highly chemoselective, leading to the formation of the secondary phosphine (*sec*-P) with >96% selectivity when the reaction was carried out in a 1 : 1 molar ratio of substrates. To investigate the possibility of double alkylation of $PhPH_2$ catalyzed by complexes **1** and **2**, hydrophosphination reactions were carried out at a substrate molar ratio of $[styrene]_0 : [PhPH_2]_0 = 2 : 1$. Complexes **1** and **2** enable the formation of the tertiary phosphine $PhP(CH_2CH_2Ph)_2$ in quantitative yields with excellent chemoselectivity (Table 1, entries 2 and 5). Complex **1** displays noticeably higher catalytic activity: quantitative conversion was reached in 2 h *vs.* 8 h for **2**. This observation is in line with the larger ion size of Sm(II).[37]

Hydrophosphination of non-activated substrates still remains a challenge, and only a few catalysts enable this transformation.[26,27,38] The addition of $PhPH_2$ or Ph_2PH to non-activated 1-alkenes usually requires prolonged reaction times and harsher conditions compared to those for styrenic substrates and provides secondary and tertiary phosphines in lower yields. We suggested that the combination of a metal center featuring a large ion size with a strong σ-donor NHC ligand in the complex would be a promising solution. On the other hand, the sterically demanding ring-expanded N-heterocyclic carbene can reduce catalyst deactivation due to the stabilization of the low-coordinate Ln(II) metal center and providing solubility of the catalytically active species. Indeed, complex **1** demonstrated the best results among the rare-earth based complexes in the catalysis of the addition of $PhPH_2$ or Ph_2PH to normally inert 1-alkenes.

Hydrophosphination of 1-hexene, 1-heptene, 1-octene and 1-nonene with an equimolar amount of $PhPH_2$ or Ph_2PH in the presence of 5 mol% of **1** in neat substrates at 80 °C affords the corresponding anti-Markovnikov addition products in moderate yields (35–50%) (Table 2).

Table 2 Hydrophosphination of 1-alkenes with $PhPH_2$ and Ph_2PH catalyzed by **1** and **2**[a]



No.	Pre-cat	R	Phosphine	Product	Time (h)	Conv.[c,d,e] (%)
1	**1**	n-C_4H_9	$PhPH_2$	n-C_4H_9-CH(Ph)-PHPh	72	50
2	**1**				120	81[b]
3	**1**		Ph_2PH	n-C_4H_9-CH(Ph)-PPh_2	72	49
4	**1**	n-C_5H_{11}	$PhPH_2$	n-C_5H_{11}-CH(Ph)-PHPh	72	47
5	**1**		Ph_2PH	n-C_5H_{11}-CH(Ph)-PPh_2	72	40
6	**1**	n-C_6H_{13}	$PhPH_2$	n-C_6H_{13}-CH(Ph)-PHPh	72	43
7	**1**				120	76[b]
8	**1**		Ph_2PH	n-C_6H_{13}-CH(Ph)-PPh_2	72	39
9	**1**	n-C_7H_{15}	$PhPH_2$	n-C_7H_{15}-CH(Ph)-PHPh	72	40
10	**1**		Ph_2PH	n-C_7H_{15}-CH(Ph)-PPh_2	72	35
11	**2**	n-C_4H_9	$PhPH_2$	n-C_4H_9-CH(Ph)-PHPh	96	15
12	**2**		Ph_2PH	n-C_4H_9-CH(Ph)-PPh_2	96	12
13	**2**	n-C_7H_{15}	$PhPH_2$	n-C_7H_{15}-CH(Ph)-PHPh	96	11
14	**2**		Ph_2PH	n-C_7H_{15}-CH(Ph)-PPh_2	96	10

[a] Reaction in neat substrates $[phosphine]_0:[1\text{-alkene}]_0:[precat]_0 = 20:20:1$, $[precat]_0$ = 200.0 mM, T [°C] = 80. [b] $[phosphine]_0:[1\text{-alkene}]_0:[precat]_0 = 20:80:1$ $[precat]_0$ = 80.0 mM. [c] Conversion of phosphine, determined by NMR spectroscopy. [d] Chemoselectivity was determined by $^{31}P\{^1H\}$ NMR spectroscopy. [e] Regioselectivity was determined by ^1H, $^{31}P\{^1H\}$ NMR spectroscopy.

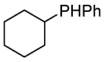
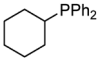
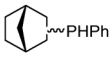
In the case of $PhPH_2$ an increase in olefin concentration ($[phosphine]_0:[1\text{-alkene}]_0 = 1:4$) allows 76–81% conversions to be reached (Table 2, entries 2 and 7). However, despite the use of an excess of 1-alkene and rather harsh conditions (90 °C, 120 h), quantitative conversion was not achieved. A further increase in the reaction time and temperature (>100 °C) results only in the formation of the products of dehydrogenative coupling of phosphines (PhHPPHPh and Ph_2PPPh_2).[39,40] Furthermore, despite the presence of a four-fold molar excess of 1-alkenes, hydrophosphination with $PhPH_2$ affords exclusively secondary phosphines with no traces of the double addition product. Similarly to the previously reported examples of Ln-catalyzed hydrofunctionalization reactions[41,42] Sm(II) complexes showed higher catalytic activity compared to the Yb(II) analogues, which can be explained by the larger ionic radius of Sm(II). The reaction rate decreases slightly with the growth of the chain length of 1-alkene. Most likely this is associated with the fact that olefin insertion into an M–P bond is a rate-limiting stage of hydrophosphination[43,44] and the steric and electronic properties of the olefinic substrate have a noticeable effect on the reaction rate. Notably, under the same reaction conditions, rare- and alkaline earth 5-membered NHC adducts $(NHC)_2M[N(SiMe_3)_2]_2$ (M = Ca, Yb(II), Sm(II); NHC = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, 1,3-diisopropylimidazol-2-ylidene) were totally inactive in the hydrophosphination of 1-hexene and 1-nonene with $PhPH_2$ and Ph_2PH.

Moreover, complex **1** enables the hydrophosphination of normally inert internal double bonds of cyclohexene and norbornene with $PhPH_2$ and Ph_2PH. The catalytic tests were carried out in neat substrates at 70 °C. The addition of $PhPH_2$ and Ph_2PH to cyclohexene at an equimolar ratio of substrates in 96 h reaches 53% and 69%, respectively (Table 3, entries 1 and 3). A simultaneous increase in the reaction time to 168 h, an increase in temperature to 90 °C and the application of a four-fold molar excess of cyclohexene allow the increase in conversion, but just slightly (62%). Increases in the reaction time and temperature promote $PhPH_2$ dehydrogenative coupling, while no double $PhPH_2$ alkylation was detected. Ph_2PH proved to be more reactive and under analogous conditions the conversion reaches 69 and 73%, respectively (Table 3, entries 3 and 4). This observation is in line with the previously described tendency.[27,28] For norbornene featuring a more strained cycle the reactions with $PhPH_2$ and Ph_2PH proceed noticeably faster and at 70 °C within 48 h the conversion rates reach 84 and 89%, respectively. The addition of $PhPH_2$ and Ph_2PH to norbornene occurs chemoselectively to afford mixtures of endo and exo isomers: 2-phenylphosphinonorbonane and 2-diphenylphosphinonorbornane, respectively.[30,45]

The mechanism of olefin hydrophosphination catalyzed by amido and alkyl Ln(II) complexes was previously established[23,43,44,46] and we assume that **1** and **2** exhibit a similar catalytic cycle. Preliminary mechanistic studies revealed that the catalytic reactions are not associated with the oxidation of Ln(II) centers in the presence of an excess of Ph_2PH and 1-nonene (ESI,† Fig. S9). The reaction of **2** with 2 equivalents of Ph_2PH (C_6D_6, 25 °C) results in a gradual release of $HN(SiMe_3)_2$ and the formation of soluble transient amido-phosphido species coordinated by the NHC ligand (ESI,† Fig. S11 and S12; ^{31}P NMR δ 9.6 ppm). In ~24 h the yield of $HN(SiMe_3)_2$ reaches 2 equivalents and the precipitate of the putative $(NHC)Yb(PPh_2)_2$ complex forms. The ^1H NMR spectrum of the natant solution contains only $HN(SiMe_3)_2$ signals, and no release of free NHC was detected. It is noteworthy that in neat substrates no precipitate forms. $(NHC)Yb(PPh_2)_2$ does not enable the Ph_2PH addition to 1-nonene. Therefore, the question about active species formed under catalytic conditions remains open.

In summary, first examples of Ln(II) complexes coordinated by the 6-membered NHC ligand (er-NHC)Ln$[N(SiMe_3)_2]_2$ were synthesized. Complexes **1** and **2** constitute very competent pre-catalysts for the intermolecular hydrophosphination of styrene and enable the highly regio- and chemoselective formation of secondary and tertiary phosphines in close-to-quantitative yields under mild conditions. Their catalytic performance in styrene hydrophosphination is comparable to that of 5-membered NHC-containing analogues $(NHC)_2Ln[N(SiMe_3)_2]_2$ and significantly superior to that of most catalysts published so far. The most important finding of this study is that the application of a more σ-donor ring-expanded carbene provides

Table 3 Hydrophosphination of cyclohexene and norbornene with $PhPH_2$ and Ph_2PH catalyzed by **1**[a]

No.	Alkene	Phosphine	Product	Time (h)	Conv.[c,d,e] (%)
1		$PhPH_2$		96	53
2				168	62[b]
3		Ph_2PH		96	69
4				168	73[b]
5		$PhPH_2$		48	84
6		Ph_2PH		48	89

[a] Reaction in neat substrates $[phosphine]_0:[olefin]_0:[\mathbf{1}]_0 = 20:20:1$, $[precat]_0 = 190.0$ mM, T [°C] = 70. [b] $[phosphine]_0:[cyclohexene]_0:[\mathbf{1}]_0 = 20:80:1$ $[\mathbf{1}]_0 = 70.0$ mM; T [°C] = 90. [c] Conversion of phosphine, determined by NMR spectroscopy. [d] Chemoselectivity was determined by $^{31}P\{^1H\}$ NMR spectroscopy. [e] Regioselectivity was determined by ^1H, $^{31}P\{^1H\}$ NMR spectroscopy.

a catalyst enabling a highly challenging transformation – hydrophosphination of normally inert 1-alkenes. The most promising results were obtained for **1** which provides excellent conversion: up to 81% for 1-alkene, 73% for cyclohexene and 89% for norbornene. Moreover, for the hydrophosphination of 1-alkenes with $PhPH_2$ excellent regio- and chemoselectivities are observed. The possibility of a rare-earth mediated hydrophosphination of cyclohexene and norbornene with both $PhPH_2$ and Ph_2PH was demonstrated for the first time. Studies aimed at enlarging the reaction scope to various types of substrates as well as mechanistic and kinetic studies are currently underway.

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Conflicts of interest

There are no conflicts to declare.

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