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Ca(II), Yb(II) and Sm(II) bis(Amido) Complexes Coordinated by NHC Ligands – Efficient Catalysts for Highly Regio- and Chemoselective Consecutive Hydrophosphinations with PH₃

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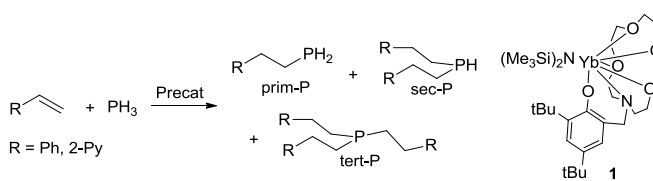
Abstract: The first example of intermolecular hydrophosphination of styrene, 2-vinylpyridine and phenylacetylene with PH₃ catalyzed by bis-(amido) complexes [(Me₃Si)₂N]₂M(NHC)₂ (M = Ca, Yb, Sm) coordinated by NHC ligands is described. The reactions of styrene with PH₃ proceed under mild conditions in quantitative yields to afford only anti-Markovnikov product and allow for the chemoselective synthesis of primary, secondary and tertiary phosphines. Addition of phenylacetylene to PH₃ regardless the initial molar substrates ratio results in the exclusive formation of a tertiary tris-(Z-styryl)-phosphine. Crucial effect of the Lewis base coordinated to the metal ion in precatalyst on catalytic activity in styrene hydrophosphination with PH₃ was demonstrated. Free NHCs were also found to be able to promote addition of PH₃ to styrene, however they provide much lower reaction rates compared to the metal complexes.

The formation of C–P bonds via single step intermolecular hydrophosphination reactions of unsaturated substrates is a promising, atom-efficient route to a variety of phosphorus-containing compounds. To date, a number of examples of this transformation realized due to acid^[1], base^[2], d-transition^[3], alkaline-earth^[4], and rare-earth^[4a, 5] metals catalysis or radical initiation^[2a, c, 6] was reported and is covered in several reviews^[2c, 5e, 7]. Despite the progress achieved in this area a substrate scope of this reaction remains limited and mainly involves activated olefins and ubiquitous phenyl- and diphenylphosphine. Meanwhile, PH₃ addition to alkenes and alkynes which is a progressive and convenient synthetic route to a variety of primary, secondary and tertiary phosphines still remains poorly explored. Ease of synthesis of PH₃, its low cost (vs PhPH₂) and availability make it commercially attractive starting compound for the synthesis of phosphines. Hydrophosphination of multiple C–C bonds with PH₃ becomes feasible under free radical initiation^[8], acid^[1] and superbasic^[9] conditions, or UV-irradiation^[10], however, suffers from a lack of selectivity. The only example of application of late transition metal complexes for catalytic hydrophosphination of activated substrates (acrylonitrile^[11], ethyl

acrylate^[12], formaldehyde^[13]) with PH₃ was published by Pringle and co-workers. No examples of PH₃ addition to non-activated olefins, vinyl arenes and alkynes catalyzed by rare- and alkaline-earth metals complexes have been published so far. Moreover, the examples of hydrophosphination reactions catalyzed by free carbenes also still remain unknown despite the immense progress in organocatalysis achieved through their use^[14].

We found that homo- and heteroleptic Yb(II), Sm(II) and Ca(II) amido complexes^{[4a], [4c], [5b]} performing high catalytic activity in styrene hydrophosphination with Ph₂PH and PhPH₂ proved to be completely inert in the case of PH₃. Complex {LO^{NO4}}YbN(SiMe₃)₂ (**1**)^[4a] was the only exception which enabled transformation of PH₃ into phenethylphosphines with high conversions, reaction rates and perfect anti-Markovnikov regioselectivity at 60°C, albeit with moderate chemoselectivity at molar ratios [styrene]₀: [PH₃]₀ < 3 (Table 1, entries 1,2). Whereas at [styrene]₀: [PH₃]₀ = 3 (PhCH₂CH₂)₃P was obtained in 99% yield. In the case of 2-vinylpyridine **1** demonstrated noticeably lower catalytic activity and did not enable insertion of olefin molecule towards third P–H bond even at [2-vinylpyridine]₀: [PH₃]₀ = 3 (Table 1, entry 4). No reaction of PH₃ with toluene and phenylacetylene was detected in the presence of **1**.

Table 1. Hydrophosphination of styrene and 2-vinylpyridine with PH₃, catalyzed by complex **1**.



No	[Alkene] ₀ : [PH ₃] ₀	Time, h	Conv., % ^[e]	prim-P / sec-P / tert-P ^[f]
1 ^[a]	1:1	2	99	70:25:5
2 ^[b]	2:1	3	99	10:74:16
3 ^[c]	3:1	10	99	0:1:99
4 ^[d]	3:1	24	40	80:20:0

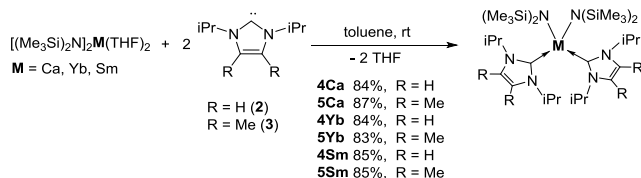
[a] [PH₃]₀: [styrene]₀: [cat]₀ = 50:50:1, [cat]₀ = 21.0 mM, T[°C] = 60, C₆D₆. [b] [PH₃]₀: [styrene]₀: [cat]₀ = 50:100:1, [cat]₀ = 21.0 mM, T[°C] = 60, C₆D₆. [c] [PH₃]₀: [styrene]₀: [cat]₀ = 50:150:1, [cat]₀ = 21.0 mM, T[°C] = 60, C₆D₆. [d] [PH₃]₀: [2-vinylpyridine]₀: [cat]₀ = 50:150:1, [cat]₀ = 21.0 mM, T[°C] = 60, C₆D₆. [e] Conversion determined by ¹H NMR spectroscopy. [f] Chemoselectivity was determined by ³¹P NMR spectroscopy.

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Despite high activity complex **1** features a considerable drawback: low stability. According to ^1H NMR spectroscopy monitoring **1** decomposes completely in C_6D_6 solution in vacuum in 4 days with liberation of ethylene most likely due to cleavage of aza-crown moiety. We focused on elaboration of simple in preparation, accessible catalysts efficient in intermolecular hydrophosphination of multiple C-C bonds with PH_3 . The analysis of the state of the art suggests that electron-donating properties, denticity of the Lewis base coordinated to a metal in pre-catalyst as well as its ability to provide stabilization of the catalytic centre and solubility of a real catalytic species are among the factors that strongly affect catalytic activity of complexes in intermolecular olefin hydrophosphination.^{[4a], [5b], [5e]} Bis(amido) complexes $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{M}(\text{NHC})_2$ ($\text{M} = \text{Ca}, \text{Yb}, \text{Sm}$) coordinated by NHC-ligands were obtained in high yields by the reactions of $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{M}(\text{THF})_2$ with two equivalents of **2** and **3** in toluene (Scheme 1). The synthesis of **5Yb** was previously reported by Cui and co-workers.^[15]



Complexes **4-5M** ($\text{M} = \text{Ca}, \text{Yb}, \text{Sm}$) were isolated in 83-87% yields. All complexes are stable in both solid state and in hexane or toluene solutions under conditions excluding contact with oxygen and moisture. Crystal structures of **4-5M** were established by X-ray analysis and are depicted in Figure 1. The crystal and structural refinement data are listed in the Tables S1-3 (ESI). The isostructural complexes **4Ca**, **4Yb**, **4Sm** crystallize as solvates **4M**· $\frac{1}{2}\text{C}_7\text{H}_8$, while **5Ca**, **5Yb**, **5Sm** form solvates with one toluene molecule **5M**· C_7H_8 . The substitution of THF molecules with the NHC ligands in the coordination sphere of the metal ion in bis(amido) complexes results in some (0.04-0.07 Å) increase in the M-N bond lengths compared to the parent amide $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{M}(\text{THF})_2$ most likely due to greater steric demand of NHC-ligands (See Table S4 in ESI). No significant difference in M-C bonds lengths in the couples **4,5Ca**, **4,5Yb** and **4,5Sm** was observed. The N-M-N bond angles in complexes **4,5M** and the parent $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{M}(\text{THF})_2$ are almost indistinguishable. The C-M-C bond angles in complexes **4,5M** (81.3(5)-85.4(2)°) have values close to the O-M-O bond angles in $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{M}(\text{THF})_2$ complexes (81.4(1)-85.4(4)°).^[16]

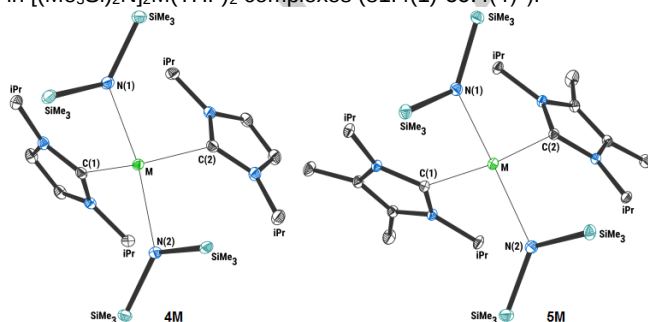


Figure 1. Molecular structures of complexes **4** ($\text{M} = \text{Ca}$ (**4Ca**), Yb (**4Yb**), Sm (**4Sm**)) and **5** ($\text{M} = \text{Ca}$ (**5Ca**), Yb (**5Yb**), Sm (**5Sm**)). Hydrogen atoms and methyl substituents of *i*Pr groups are omitted for clarity; thermal ellipsoids drawn at the 30% probability level.

Complexes **4,5M** proved to be highly efficient catalysts for styrene hydrophosphination with PH_3 in neat substrates at 70°C. They enable addition of one equivalent of styrene to PH_3 with excellent anti-Markovnikov regioselectivity and chemo-selectivity over 95% of formation of the target primary phenethylphosphine (*prim*-P) (Table 2). The reaction proceeds with high rates even at low catalyst loading (0.4 molar %). The overall turnover number $\text{TON} = 247$ and apparent turnover frequency $\text{TOF} = 15 \text{ h}^{-1}$ were reached in 16 h. Interestingly despite the difference in ion size and M(II) redox properties in the PH_3 monoalkylation step, all compounds exhibit similar activity. No noticeable influence of the nature of NHC-ligand on catalytic activity was also observed.

Table 2. Hydrophosphination of styrene with PH_3 ($[\text{PH}_3]_0 : [\text{styrene}]_0 = 1:1$), catalyzed by complexes **4-5**.

		$\text{Ph-CH=CH}_2 + \text{PH}_3 \xrightarrow{\text{Pecat}} \text{Ph-CH}_2\text{-CH}_2\text{-PH}_2 \text{ (prim-P)} + \text{Ph-CH=CH-CH}_2\text{-PH}_2 \text{ (sec-P)}$				
№	Cat.	Loading, mol. %	Time, h	Conv., % ^[b]	<i>prim</i> -P / <i>sec</i> -P / <i>tert</i> -P ^[c]	
1	4Ca	2	2	99	2:95:3	
2 ^[a]		0.4	16	97(95 ^[d])	0:1:99	
3	5Ca	2	2	99	3:95:2	
4 ^[a]		0.4	16	95(93 ^[d])	0:2:98	
5	4Yb	2	3	99	5:92:3	
6 ^[a]		0.4	24	97(95 ^[d])	0:15:85	
7	5Yb	2	3	99	6:92:2	
8 ^[a]		0.4	24	98(96 ^[d])	0:18:82	
9	4Sm	2	2	99	0:94:6	
10 ^[a]		0.4	16	96(94 ^[d])	0:1:99	
11	5Sm	2	2	99	2:93:5	
12 ^[a]		0.4	16	98(96 ^[d])	0:1:99	

Reaction in neat substrates $[\text{PH}_3]_0 : [\text{styrene}]_0 : [\text{cat}]_0 = 50:50:1$, $[\text{cat}]_0 = 140.0 \text{ mM}$, $T[^\circ\text{C}] = 70$. [a] $[\text{PH}_3]_0 : [\text{styrene}]_0 : [\text{cat}]_0 = 250:250:1$, $[\text{cat}]_0 = 28.0 \text{ mM}$, $T[^\circ\text{C}] = 70$. [b] Conversion determined by ^1H and ^{31}P NMR spectroscopy. [c] Chemoselectivity determined by ^{31}P NMR spectroscopy. [d] Yield of isolated product.

Moreover complexes **4,5M** allow for the addition of two and three equivalents of styrene to PH_3 leading to the selective formation of secondary and tertiary phosphines. At 70°C and 2 mol.% of catalyst loading complexes **4,5M** enable the formation of secondary or tertiary phosphines with quantitative conversion, chemoselectivity over 95% and absolute anti-Markovnikov regioselectivity (Table 3). Surprisingly unlike the monoalkylation step in the double and triple olefin addition to PH_3 complexes

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4,5Yb proved to be noticeably less catalytically active and chemoselective compared to the Ca and Sm congeners. Thus, for the complexes of Ca and Sm quantitative conversions in the formation of secondary and tertiary phosphines were reached in 16 and 48 h respectively, for the Yb analogues the completion of the same reactions required 24 and 60 h.

Table 3. Hydrophosphination of styrene with PH_3 at different $[\text{PH}_3]_0:[\text{Styrene}]_0$ ratios, catalyzed by complexes **4-5M** and free carbenes **2-3**.

$\text{Ph-CH=CH}_2 + \text{PH}_3 \xrightarrow{\text{Pecat}} \text{Ph-CH}_2\text{CH}_2\text{PH}_2 + \text{Ph-CH}_2\text{CH}_2\text{CH}_2\text{PH} + \text{Ph-CH}_2\text{CH}_2\text{CH}_2\text{P(Ph)}_2$				
prim-P sec-P tert-P				
No	Cat.	$[\text{styrene}]_0:[\text{PH}_3]_0$	Time, h	prim-P / sec-P / tert-P ^[c]
1 ^[a]	4Ca	2:1	16	2:95:3
2 ^[b]		3:1	48	0:1:99
3 ^[a]	5Ca	2:1	16	3:95:2
4 ^[b]		3:1	48	0:2:98
5 ^[a]	4Yb	2:1	24	5:92:3
6 ^[b]		3:1	60	0:15:85
7 ^[a]	5Yb	2:1	24	6:92:2
8 ^[b]		3:1	60	0:18:82
9 ^[a]	4Sm	2:1	16	0:94:6
10 ^[b]		3:1	48	0:1:99
11 ^[a]	5Sm	2:1	16	2:93:5
12 ^[b]		3:1	48	0:1:99
13 ^[a]	2	2:1	48	4:93:3
14 ^[b]		3:1	72	0:31:69
15 ^[a]	3	2:1	48	4:94:2
16 ^[b]		3:1	72	0:23:73

[a] Reaction in neat substrates $[\text{PH}_3]_0:[\text{styrene}]_0:[\text{precat}]_0 = 50:100:1$, $[\text{cat}]_0 = 75.0 \text{ mM}$, $T[^\circ\text{C}] = 70$. [b] Reaction in neat substrates $[\text{PH}_3]_0:[\text{styrene}]_0:[\text{precat}]_0 = 50:150:1$, $[\text{cat}]_0 = 50.0 \text{ mM}$, $T[^\circ\text{C}] = 70$. [c] Chemoselectivity, determined by ^1H , ^{31}P NMR spectroscopy, at styrene conversion > 95%.

To follow the formation of primary, secondary and tertiary phosphines in the course of stepwise PH_3 hydrophosphination and to evaluate chemospecificity of the reaction stages kinetic monitoring of the reaction of styrene with PH_3 catalyzed by **4Sm** (25 °C, benzene- d_6 , $[\text{styrene}]_0:[\text{PH}_3]_0 = 8$) was carried out. The kinetic profile for the concentrations (Figure 2) in the various phosphines is not typical of consecutive reactions.

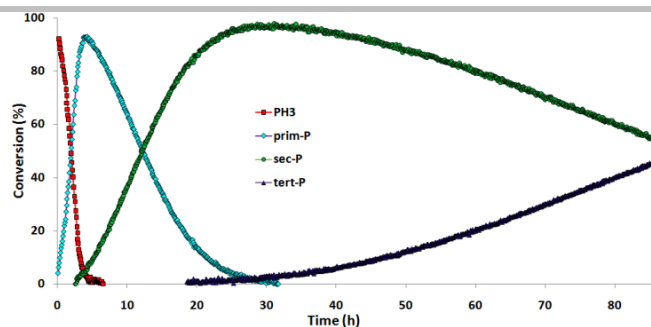


Figure 2. Plot of the reagents conversion vs reaction time for the hydrophosphination of styrene with PH_3 catalyzed by **4Sm** in benzene- d_6 at 25 °C. Reaction conditions: $[\text{PH}_3]_0:[\text{styrene}]_0:[\text{4Sm}]_0 = 20:160:1$; total volume 0.67 mL; $[\text{4Sm}]_0 = 30.0 \text{ mM}$.

The kinetic profile reflects chemospecific formation of primary, secondary and tertiary phosphines. First, PH_3 is selectively converted into $\text{PhCH}_2\text{CH}_2\text{PH}_2$ and the latter started to react only when PH_3 was consumed completely. The formation of secondary phosphine ($\text{PhCH}_2\text{CH}_2\text{CH}_2\text{PH}$) was detected only in ~4 h after the start of the reaction. Similarly, tertiary phosphine ($\text{PhCH}_2\text{CH}_2\text{CH}_2\text{P}$) began to appear only after full consumption of $\text{PhCH}_2\text{CH}_2\text{PH}_2$ nearly in 28 h after the reaction start. The plots of the concentration of PH_3 , $\text{PhCH}_2\text{CH}_2\text{PH}_2$ and ($\text{PhCH}_2\text{CH}_2\text{CH}_2\text{P}$) vs time in the presence of the excess of styrene obtained in the kinetic experiment are linear and are indicative of the zeroth order of the reaction in phosphines. Remarkably, the observed rate constants of the subsequent stages of the reaction $k_{\text{obs}1} = 3.50(1) \cdot 10^{-2} \text{ h}^{-1}$, $k_{\text{obs}2} = 8.32(1) \cdot 10^{-3} \text{ h}^{-1}$, $k_{\text{obs}3} = 1.65(1) \cdot 10^{-3} \text{ h}^{-1}$ differ noticeably. The similar tendency was observed for the rates of consumption of PH_3 , $\text{PhCH}_2\text{CH}_2\text{PH}_2$ and ($\text{PhCH}_2\text{CH}_2\text{CH}_2\text{P}$) $k_1 = 1.6812(1) \cdot 10^{-1} \text{ mol L}^{-1} \text{ h}^{-1}$, $k_2 = 3.4980(1) \cdot 10^{-2} \text{ mol L}^{-1} \text{ h}^{-1}$, $k_3 = 5.9400(1) \cdot 10^{-3} \text{ mol L}^{-1} \text{ h}^{-1}$ thus giving a plausible explanation of the observed chemoselectivity. On the other hand the difference of the reaction rates of the σ -bond metathesis of the reaction intermediate with PH_3 , primary and secondary phosphines can also contribute into the chemoselectivity control.^[4a] This suggestion is consistent with the difference of pK_a values of PH_3 , primary, secondary phosphines.^[17] We assume that the catalytic cycle of olefin hydrophosphination with PH_3 is similar to that previously established for the reactions involving Ph_2PH and PhPH_2 .^[4a,15]

Complexes **4,5M** proved to be inactive in catalysis of PH_3 addition towards double $\text{C}=\text{C}$ bonds of 1-nonene, 2,3-dimethylbutadiene, cyclohexene and norbornene.

In order to evaluate the effect of the nature of the Lewis base coordinated to the metal ion on activity in catalysis of PH_3 addition to styrene, the catalytic tests with $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{M}(\text{L})_2$ ($\text{M} = \text{Ca}, \text{Yb}, \text{Sm}$; $\text{L} = \text{THF}, \text{Et}_2\text{O}$) were performed under analogous conditions. It is noteworthy that unlike **4,5M** the bis(amides) coordinated by THF or Et_2O turned out absolutely catalytically inactive in this transformation thus giving an evidence for a decisive role of the Lewis base coordinated to the metal in the stabilization of the real catalytic species. As evidenced by the stoichiometric reactions of PH_3 with $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{M}(\text{L})_2$ (2:1 molar ratio, benzene- d_6) affording the black precipitates regardless of the presence or absence of styrene in the reaction mixture insolubility of the resulting species in hydrocarbon solvents is the most likely reason of their catalytic inertness. Moreover, ability of free carbenes **2** and **3** to promote addition of PH_3 to

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styrene was verified. Surprisingly **2** and **3** were found to enable this reaction under the same conditions as **4,5M** affording selectively primary, secondary and tertiary phosphines (Table 2, entries 13-14; Table 3, entries 13-16). However at the stage of addition of third equivalent of styrene to PH_3 the reaction catalyzed by **2** and **3** is somewhat less selective compared to the results obtained with **4,5M**. The kinetic monitoring of the reaction of PH_3 with styrene (Figure 3) revealed that in the presence of **2, 3** the reaction proceeds selectively and follows the same kinetic law as in the case of **4,5M**. However, free NHCs **2, 3** provide much lower reaction rates compared to metal complexes **4,5M** ($k_{\text{obs1}}(\mathbf{4Sm})/k_{\text{obs1}}(\mathbf{3}) = 4.67$) (Figure 3).

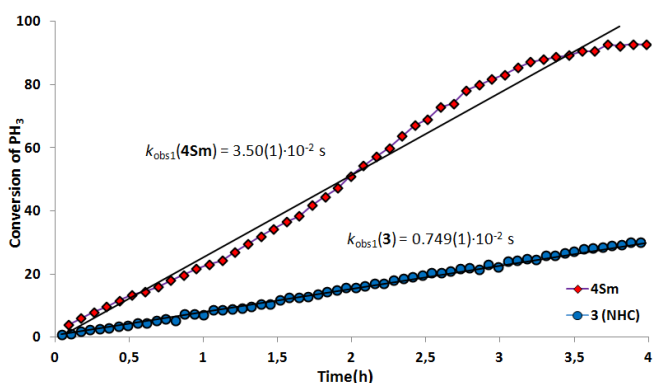
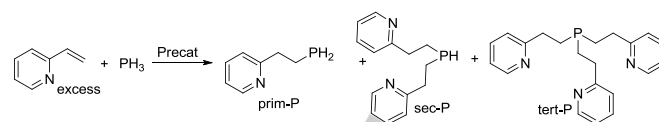


Figure 3. Comparative plot of the reagents conversion vs reaction time for the hydrophosphination of styrene with PH_3 catalyzed by **4Sm** and **3** (free NHC) in benzene- d_6 at 25 °C. Reaction conditions: $[\text{PH}_3]_0:[\text{styrene}]_0:[\text{Cat}]_0 = 20:160:1$; total volume 0.67 mL; $[\text{Cat}]_0 = 30.0$ mM.

To the best of our knowledge this is the first example of intermolecular hydrophosphination catalyzed by NHCs reported so far. NHCs being rather strong bases^[18] are known to be able to activate small molecules like H_2 , NH_3 ^[19] and PH_3 ^[20] via their addition towards carbene C atom. We assume that the formation of organophosphines in the reactions catalyzed by free carbenes proceeds via transient carbene- PH_3 adduct.^[19] Currently, detailed mechanistic and kinetic studies of styrene hydrophosphination with PH_3 , catalyzed by both free carbenes and their $\text{Ln}(\text{II})$ complexes, are underway. When 2-vinylpyridine was used as an olefinic substrate hydrophosphination with PH_3 proved to be less chemoselective and the reaction course was complicated by the simultaneous sluggish substrate polymerization. Nevertheless complexes **5Ca** and **4,5Sm** enable formation of tertiary tris(2-(pyridin-2-yl)ethyl)phosphine with high conversion and chemoselectivity up to 90%. Surprisingly Yb complexes were less active in the case of 2-vinylpyridine; the reactions with PH_3 afforded only mono- and double addition products. No formation of tertiary phosphine was detected. Hydrophosphination of 2-vinylpyridine with PH_3 can be applied as a convenient one-pot synthetic approach to tris(2-(pyridin-2-yl)ethyl)phosphine, a useful ligand for coordination chemistry.^[21]

Table 4. Hydrophosphination of 2-vinylpyridine with PH_3 , catalyzed by complexes **4-5**.

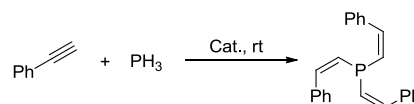


No	Cat.	[2-vinylpyridine] ₀ :[PH ₃] ₀	Time, h	prim-P / sec-P / tert-P [a][b]
1	4Ca	6:1	10	0:50:50
2	5Ca	6:1	10	0:10:90
3	4Yb	6:1	10	40:60:0
4	5Yb	6:1	10	50:50:0
5	4Sm	6:1	10	0:25:75
6	5Sm	6:1	10	0:20:80

Reaction in neat substrates $[\text{PH}_3]_0:[\text{2-vinylpyridine}]_0:[\text{precat}]_0 = 50:300:1$, $[\text{precat}]_0 = 30.0$ mM, $T[^\circ\text{C}] = 70^\circ\text{C}$. [a] Conversion determined by NMR spectroscopy. [b] Chemoselectivity was determined by ^{31}P NMR spectroscopy.

Surprisingly unlike olefin hydrophosphination the addition of PH_3 towards terminal $\text{C}\equiv\text{C}$ triple bond of phenylacetylene regardless the initial molar ratio of substrates affords exclusively tertiary tris-(Z-styryl)-phosphine (Table 5). The kinetic monitoring of the reaction by ^{31}P NMR spectroscopy did not give any evidence for the formation of primary and secondary styrylphosphines even at low consumption of PH_3 , only tris-(Z-styryl)-phosphine was detected in the reaction mixture (Figure 4).

Table 5. Hydrophosphination of phenylacetylene with PH_3 ($[\text{PH}_3]_0:[\text{phenylacetylene}]_0 = 1:4$), catalyzed by complexes **4-5**.



No	Cat.	Time, h	Conv., % ^[a]
1	4Ca	16	99
2	5Ca	16	99
3	4Yb	24	99
4	5Yb	24	98
5	4Sm	16	99
6	5Sm	16	99
7	2	48	91
8	3	48	93

Reaction in neat substrates $[\text{PH}_3]_0:[\text{phenylacetylene}]_0:[\text{precat}]_0 = 50:200:1$, $[\text{precat}]_0 = 50.0$ mM, RT. [a] Conversion determined by NMR spectroscopy.

It should be noted that the same reaction can be also promoted by free NHC, however this reaction was found to be much slower than those catalyzed by their $\text{M}(\text{II})$ complexes.

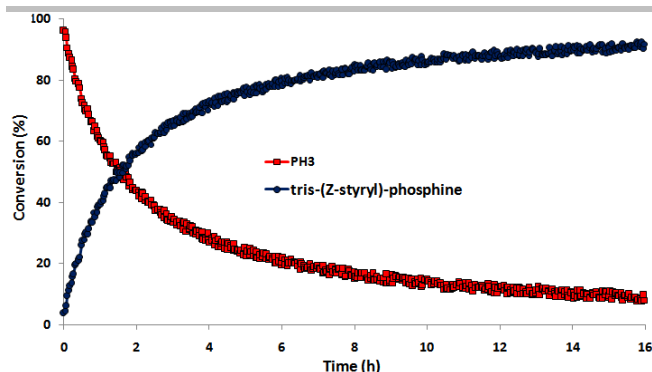


Figure 4. Plot of reagent concentration vs reaction time for the hydrophosphination of phenylacetylene with PH_3 catalyzed by **4Sm** in benzene- d_6 at 25 °C. Reaction conditions: $[\text{PH}_3]_0/[\text{phenylacetylene}]_0/[\text{4Sm}]_0 = 20/200/1$; total volume 0.67 mL; $[\text{4Sm}]_0 = 30.0$ mM.

In conclusion, we demonstrated that M(II) ($\text{M} = \text{Ca}, \text{Yb}, \text{Sm}$) bis(amides) coordinated by NHC ligands enable addition of PH_3 to double and triple C-C bonds under mild conditions and with high reaction rates. In styrene hydrophosphination complexes **4,5M** perform exceptional regio- and chemoselectivities, thus allowing for a selective synthesis of the whole range of primary, secondary and tertiary phosphines in excellent yields. The analysis of catalytic activity of bis(amido) complexes $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{M}(\text{NHC})_2$ and $[(\text{Me}_3\text{Si})_2\text{N}]_2\text{M}(\text{THF})_2$ ($\text{M} = \text{Ca}, \text{Yb}, \text{Sm}$) revealed a determining effect of Lewis base coordinated to the metal ion in precatalyst on its catalytic activity in hydrophosphination of double and triple C-C bonds with PH_3 . We also demonstrated the first example of catalytic activity of free NHCs in intermolecular hydrophosphination. Hydrophosphination of 2-vinylpyridine with PH_3 catalyzed by **4,5M** was shown to be a convenient one-pot synthetic approach to a tetradentate tris(2-(pyridin-2-yl)ethyl)phosphine. Hydrophosphination of phenylacetylene with PH_3 regardless the initial molar ratio of substrates affords exclusively tertiary tris-(Z-styryl)-phosphine. Further investigations of the reaction scope and mechanism are now in progress in our laboratory.

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Keywords: homogeneous catalysis • phosphanes • lanthanides • carbene ligands • calcium

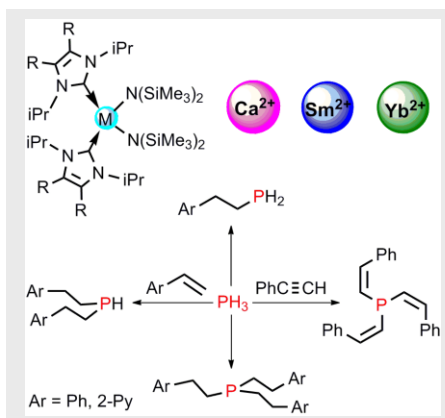
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The first example of intermolecular hydrophosphination of styrene, 2-vinylpyridine and phenylacetylene with PH_3 catalyzed by Ca(II) , Yb(II) and Sm(II) bis-(amido) complexes coordinated by NHC ligands is described. The reactions of styrene with PH_3 proceed under mild conditions in quantitative yields to afford only anti-Markovnikov product and allow for the chemoselective synthesis of primary, secondary and tertiary phosphines.



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Cherkasov, Alexander A. Trifonov*

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**Highly Regio- and Chemoselective
 PH_3 Addition to Double and Triple C-
C Bonds Catalyzed by Ca(II) , Yb(II)
and Sm(II) bis(Amido) Complexes
Coordinated by NHC Ligands**