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Amido Ca and Yb(II) Complexes Coordinated by Amidine-Amidopyridinate Ligands for Catalytic Intermolecular Olefin Hydrophosphination

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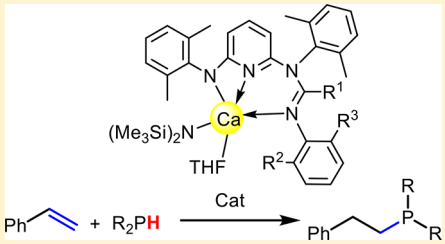
Supporting Information

ABSTRACT: A series of amido Ca and Yb(II) complexes LM[N(SiMe$_3$)$_2$](THF) (**1Yb**, **1**−**4Ca**) coordinated by amidine-amidopyridinate ligands **L**$^{1-4}$ were synthesized via a transamination reaction between proligands **L**$^{1-4}$**H** and bisamido complexes M[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (M = Yb, Ca). The reactions of Yb[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ with proligands **L**^{2}**H**-**L**^{4}**H** containing CF_3 and C_6H_4F fragments do not allow for preparing the target Yb(II) complexes, while the Ca analogues were synthesized in good yields. Complexes **1Yb** and **1**−**4Ca** were evaluated as precatalysts for hydrophosphination of styrene, *p*-substituted styrenes, α-Me-styrene, and 2,3-dimethylbutadiene with various primary and secondary phosphines (PhPH$_2$, 2,4,6-Me$_3$C$_6$H$_2$PH$_2$, 2-C$_5$NH$_4$PH$_2$, Ph$_2$PH, Cy$_2$PH). Complexes **1Yb**, **1**−**4Ca** performed high catalytic activities in styrene hydrophosphination with PhPH$_2$ and Ph$_2$PH and demonstrated high regioselectivity affording exclusively the anti-Markovnikov addition products. For primary PhPH$_2$ the reactions (1:1 molar ratio of substrates) catalyzed by **1Yb**, **1Ca**, and **2Ca** proved to be highly chemoselective affording the secondary phosphine Ph(PhCH$_2$CH$_2$)PH; however, complexes **3Ca** and **4Ca** led to the formation of both secondary and tertiary phosphines in 80:20 and 86:14 ratios. Styrene hydrophosphinations with 2,4,6-Me$_3$C$_6$H$_2$PH$_2$ and 2-pyridylphosphine for all complexes **1Yb** and **1**−**4Ca** proceeded much more slowly compared to PhPH$_2$. Addition of 2-C$_5$NH$_4$PH$_2$ to styrene catalyzed by complex **1Yb** turned out to be non-regioselective and led to the formation of a mixture of Markovnikov and anti-Markovnikov addition products, while all Ca complexes enabled regioselective anti-Markovnikov addition. Complexes **1Ca** and **1Yb** containing catalytic centers featuring similar ionic radii performed different catalytic activity: the ytterbium analogue proved to be a more active catalyst for intermolecular hydrophosphination of styrene with Cy$_2$PH, 2-C$_5$NH$_4$PH$_2$, and PhPH$_2$, but less active with sterically demanding 2,4,6-Me$_3$C$_6$H$_2$PH$_2$. Styrenes containing in *p*-position electron-donating groups (Me, tBu, OMe) performed with noticeably lower rates in the reactions with PhPH$_2$ compared to styrene. Complexes **1Yb**, **1Ca**, **2Ca**, **3Ca**, and **4Ca** enabled addition of PhPH$_2$ toward the double C═C bond of α-Me-styrene, and the reaction rate for this substrate is noticeably lower; however quantitative conversions were reached in ∼40 h. Complexes **1Ca** and **2Ca** promoted 1,2-addition of PhPH$_2$ to 2,3-dimethyl butadiene with excellent regio- and chemoselectivity to afford linear secondary phosphines. Hydrophosphination of inert 1-nonene with Ph$_2$PH with 40% conversion becomes possible due to the application of complex **2Ca** (40 h, 70 °C). The rate law for the hydrophosphination of styrene with Ph$_2$PH catalyzed by **1Ca** was found to agree with the idealized equation: $v = k[\text{styrene}]^1[\mathbf{1Ca}]^1$.



INTRODUCTION

Unlike transition metals catalytic properties of complexes of main group metals have not attracted considerable attention until very recently, and the examples of their application have been mainly limited to Lewis-acidic catalysis.[1] Calcium combines a number of very important advantages which makes this metal an extremely attractive candidate for investigation of its catalytic potential. Wide abundance of this element in the Earth's crust (∼5 wt %)[2] with nearly endless resources and low production price ensures its availability. Moreover, being a biogenic, environmentally friendly element, calcium fits the current trend to develop new synthetic approaches promoted by nontoxic metals and perfectly meets all the requirements of the concept of "green" chemistry.[3]

However, the development of organocalcium chemistry for a long time was constrained by limited accessibility of this compound due to synthetic difficulties caused by enhanced

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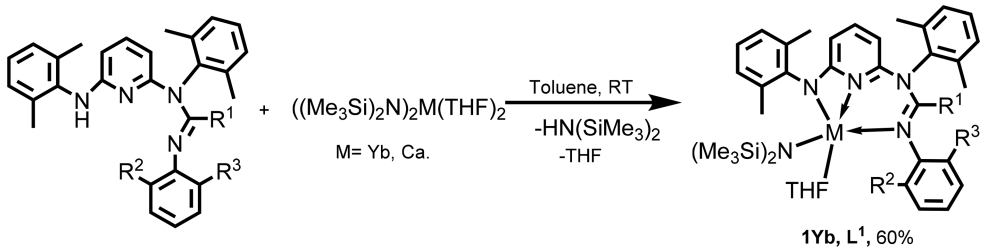
Scheme 1. Synthesis of Complexes 1Yb,1-4Ca



L¹H: R^1 = Me, R^2, R^3 = *i*Pr
L²H: R^1 = CF_3, R^2 = OMe, R^3 = H
L³H: R^1 = CF_3, R^2 = F, R^3 = H
L⁴H: R^1 = CF_3, R^2 = H, R^3 = H

1Yb, L¹, 60%
1Ca, L¹, 83%
2Ca, L², 95%
3Ca, L³, 90%
4Ca, L⁴, 84%

reactivity and low kinetic stability.[4] The high electropositive character and large ionic radii[5] of the heavy alkaline earth metals result in a chemistry that is mostly governed by electrostatic and steric requirements and make it related to that of rare earth metals. Indeed, the heavy alkaline earth and rare earth Ln^{2+} (Ln = Eu, Sm, Yb) ions due to hard Lewis acidity, oxophilicity, low polarizability[4a,c,6] and close values of ionic radii[5] exhibit strong similarities in their structures and reactivity (besides the redox reactions typical for Ln^{2+} complexes). Importantly, both families of complexes feature a typical reaction behavior, such as the ability to add to multiple C−C bonds and facile σ-bond metathesis, which makes them promising candidates for catalysis of hydroelementation of unsaturated substrates.[7]

During the past two decades, enormous progress has been reached in the synthesis and characterization of well-defined calcium complexes and their application in homogeneous catalysis.[8] They have been successfully used for olefin polymerization,[9] hydroamination,[10] and hydrosilylation.[11] The report of Hill and co-workers in 2007 on hydrophosphination of unhindered activated alkenes and diphenylacetylene[8c] enabled by Ca compounds gave a strong impetus to the development of the sphere of catalytic application of alkaline earth metals.[8b,d,9c,10b,12]

Moreover organocalcium mediated reactions present special interest from an academic point of view since they allow deeper insight into different ways of activation of C−C multiple bonds in coordination spheres of transition and main group metals.[13]

Herein we report on the synthesis of a series of new heteroleptic amido complexes of Ca(II) and Yb(II) supported by multidentate amidine-amidopyridinate ligands and their application in catalytic intermolecular hydrophosphination of various olefins and dienes. The influence of electronic and steric properties of both olefin and phosphine substrates will be considered. The detailed kinetic studies of addition of Ph_2PH to styrene catalyzed by **1Ca** will be described.

RESULTS AND DISCUSSION

As it was mentioned above due to the large ionic radii and predominantly ionic nature of metal−ligand bonding Ca(II) and Ln(II) complexes easily undergo ligand redistribution reactions (Schlenk equilibrium).[8a,14] Since application of bulky and multidentate ligands can circumvent this kinetic instability issue,[15] we focused our attention on recently designed amidine-amidopyridinate ligands.[16]

The heteroleptic amido complexes $LM[N(SiMe_3)_2](THF)$ (M = Yb, Ca) coordinated by polydentate nitrogen-based donor amidine-amidopyridinate ligands L were synthesized via a one-step transamination reaction between proligands LH[16] and bisamido complexes $M[N(SiMe_3)_2]_2(THF)_2$ (M = Yb, Ca) (Scheme 1).

In the case of Yb, the reactions smoothly proceed at room temperature, while for Ca high product yields can be achieved when the reaction mixtures are heated at 50 °C for 50 h. Complexes **1Yb** and **1Ca** were isolated after recrystallization from toluene and THF/hexane solutions in high yields as black and yellow crystals, respectively. Complex **2Ca** was obtained from toluene as orange crystals. Crystallization of complexes **3Ca** and **4Ca** from hexane afforded orange microcrystalline powders. It is noteworthy that unlike **L¹H** the reactions of $Yb[N(SiMe_3)_2]_2(THF)_2$ with proligands **L²H-L⁴H** containing CF_3 and C_6H_4F fragments did not allow for preparing the target Yb(II) complexes. The NMR-tube reactions monitored by ^1H NMR spectroscopy detected evolution of $HN(SiMe_3)_2$ and formation of paramagnetic Yb(III) species featuring low solubility in C_6D_6 and common organic solvents. All the attempts of isolation of tractable reaction products failed. Most likely such a difference of reactivity of proligands **L²H-L⁴H** with $Yb[N(SiMe_3)_2]_2(THF)_2$ and $Ca[N(SiMe_3)_2]_2(THF)_2$ is due to the redox character of the Yb(II) center which makes possible C−F bond activation.[17]

Complexes **1Yb**, **2Ca**, **3Ca**, and **4Ca** are stable both in the solid state and in hexane or toluene solutions under conditions excluding contact with oxygen and moisture, whereas complex **1Ca** is stable in solid state in solution undergoes ligand redistribution reaction affording in 1 week an equimolar mixture of homoligand compounds $[(L^1)_2Ca]$ and $Ca[N(SiMe_3)_2]_2(THF)_2$ which were isolated from the reaction mixture in 31 and 33% yields, respectively. The ^1H and $^{13}C\{^1H\}$ NMR spectra of all complexes display single sets of resonances in the −20 to +70 °C temperature range, consistent with the presence of a single C_1-symmetric species in solution. The $^{19}F\{^1H\}$ NMR spectrum of **3Ca** displayed two resonances due to CF_3 and C_6H_4F groups, and spectrum of complexes **2Ca** and **4Ca** displayed only one resonances due to the CF_3 group. In the $^{19}F\{^1H\}$ NMR spectrum of **L³H** (C_7D_8, 20 °C), the singlet due to the F atoms of the C_6H_4F ring appears at −58.8 ppm, while in the spectrum of **3Ca** these F atoms give rise to a strong field shifted signal (−127.2 ppm), thus giving evidence for Ca−F interaction. Compound **3Ca** turned out to be thermally stable in toluene solution at 70 °C: no decomposition was observed within 5 days. No fluxional behavior was detected by $^{19}F\{^1H\}$ NMR spectroscopy in the temperature region −50−70 °C.

The single crystals of **1Yb** and **1Ca** suitable for X-ray study were obtained by slow concentration of toluene and THF/

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hexane solutions respectively at room temperature. The molecular structure of complexes **1Yb** and **1Ca** are depicted in Figure 1, and the crystal and structural refinement data are

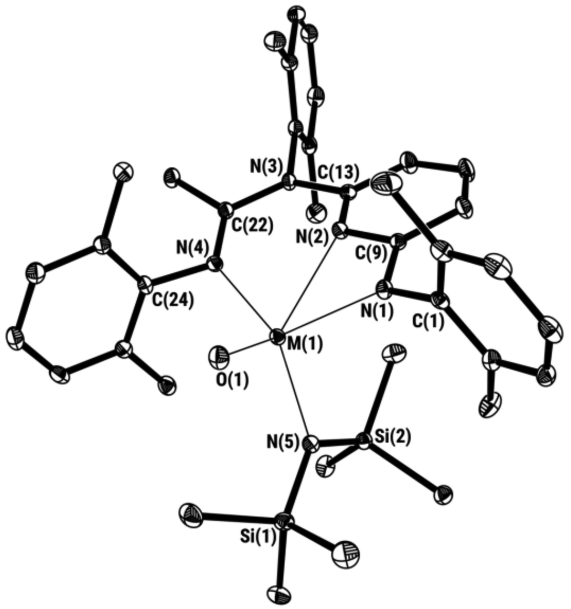

Figure 1. Molecular structure of **1** (M = Yb (**1Yb**), Ca (**1Ca**)). Hydrogen atoms, methylene fragments of the THF molecule, and methyl substituents of iPr groups are omitted for clarity; thermal ellipsoids drawn at the 30% probability level. Bond lengths (Å) and angles (deg):**1Yb**: Yb(1)−N(5) 2.365(3), Yb(1)−N(2) 2.422(3), Yb(1)−O(1) 2.436(3), Yb(1)−N(1) 2.444(3), Yb(1)−N(4) 2.499(3), N(1)−C(1) 1.415(5), N(2)−C(13) 1.331(5), N(2)−C(9) 1.375(5), N(3)−C(22) 1.390(5), N(4)−C(22) 1.296(5), N(2)−Yb(1)−N(1) 55.3(2), N(1)−C(9)−N(2) 112.7(3), N(1)−Yb(1)−N(4) 120.8(2), N(4)−C(22)−N(3) 122.2(3), N(5)−Yb(1)−N(4) 111.0(2); **1Ca**: Ca(1)−N(5) 2.330(3), Ca(1)−O(1) 2.353(2), Ca(1)−N(2) 2.371(3), Ca(1)−N(1) 2.394(3), Ca(1)−N(4) 2.557(3), N(1)−C(9) 1.332(4), N(2)−C(9) 1.382(4), N(2)−C(13) 1.319(4), N(3)−C(22) 1.391(4), N(4)−C(22) 1.298(4), N(2)−Ca(1)−N(1) 56.65(9), N(1)−C(9)−N(2) 112.8(3), N(4)−C(22)−N(3) 123.6(3), N(1)−Ca(1)−N(4) 118.8(2).

listed in Table S1 (Supporting Information). Complex **1Yb** crystallizes as a solvate **1Yb**·1/2C_7H_8, while **1Ca** forms a solvate with one toluene molecule **1Ca**·C_7H_8. According to the X-ray data, complexes **1Yb** and **1Ca** have similar structures but they are not isomorphous. They crystallize in the monoclinic crystal system but in different space groups $P2_1/n$ and $P2_1/c$. The five-coordinate metal center in **1Yb** and **1Ca** adopts a distorted square-pyramidal geometry with three of the nitrogen atoms of the amidine-amidopyridinate ligand and one oxygen atom of THF molecule in the base and the nitrogen atom of amido group in the axial vertex. The X-ray diffraction studies revealed a rather unusual geometric situation within the M-amidine-amidopyridinate fragment: surprisingly the covalent bonds Yb−$N(1)_{amido}$ (2.444(3) Å) and Ca−$N(1)_{amido}$ (2.394(3) Å) turned out slightly longer than the coordination bonds Yb−$N(2)_{pyridinato}$ (2.422(3) Å) and Ca−$N(2)_{pyridinato}$ (2.371(3) Å). Similar bonding situation has been described previously for aminopyridinato Ln(III) complexes.[18] The M−$N(5)_{silylamido}$ bond lengths in **1Yb** and **1Ca** (2.365(3) and 2.330(3) Å, respectively) fall into the range of values normally measured in five-coordinate Yb(II) and Ca complexes with terminal $N(SiMe_3)_2$ ligands.[8d,10b,19] Among the M−N bonds in **1Yb** and **1Ca**, those involving the amidinate nitrogen N(4) are the longest (Yb(1)−N(4) 2.499(3) Å; Ca(1)−N(4) 2.557(3) Å). No delocalization of negative charge was detected in the amidinate units of the ligands: the length of N(3)−C(22) bond (**1Yb**:1.390(5); **1Ca**:1.391(4) Å) corresponds to a single one, while the length of the second bond N(4)−C(22) is indicative of its double character (**1Yb**: 1.296(5); **1Ca**: N(4)−C(6) 1.298(4) Å).

The crystals of **2Ca** suitable for X-ray study were obtained by slow concentration of the toluene solution at room temperature. Complex **2Ca** crystallizes as a solvate with one toluene molecule **2Ca**·C_7H_8. The molecular structure of complex **2Ca** is depicted in Figure 2. Complex **2Ca** crystallizes in

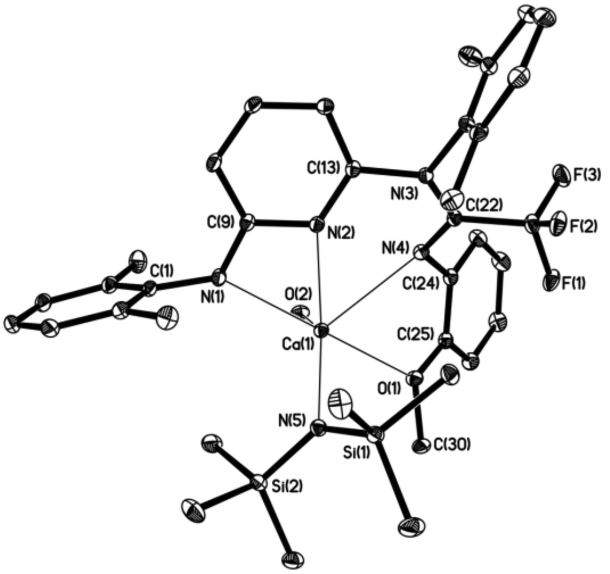

Figure 2. Molecular structure of **2Ca**. Hydrogen atoms, methylene fragments of the THF molecule and methyl substituents of iPr groups are omitted for clarity; thermal ellipsoids drawn at the 30% probability level. Bond lengths (Å) and angles (deg): Ca(1)−N(1) 2.415(2), Ca(1)−N(2) 2.391(2), Ca(1)−N(4) 2.665(2), Ca(1)−N(5) 2.320(2), Ca(1)−O(1) 2.463(2), Ca(1)−O(2) 2.375(2), N(3)−C(22) 1.374(2), N(4)−C(22) 1.284(2), N(2)−C(13) 1.323(2), N(2)−C(9) 1.371(2), N(2)−Ca(1)−N(1) 55.98(2), N(5)−Ca(1)−N(4) 128.59(6), N(2)−Ca(1)−N(4) 65.45(5), N(1)−Ca(1)−N(4) 116.38(5).

orthorhombic crystal system in the $Pna2_1$ space group. Unlike **1Yb** and **1Ca** complex **2Ca** contains tetradentate amidine-amidopyridinate ligand bearing a pendant methoxy group in the amidinate phenyl ring. The six-coordinate metal center in **2Ca** adopts a distorted octahedral geometry with three of the nitrogen and one oxygen atoms of the amidine-amidopyridinate ligand in the base and the nitrogen atom of amido group and one oxygen atom of THF molecule in the axial vertex. However, the difference of the formal coordination numbers of the metal centers in **1Ca**, **1Yb**, and **2Ca** does not affect the bonding situation within the M-amidine-amidopyridinate fragment: the covalent bond Ca−$N(1)_{amido}$ (2.415(2) Å) is longer than the coordination bond distance Ca−$N(2)_{pyridinato}$ (2.391(2) Å). Despite the different coordination numbers of the metal centers the M−$N(5)_{silylamido}$ bond lengths in **1Yb** (2.365(3) Å), **1Ca** (2.330(3) Å) and **2Ca** (2.320(2) Å) have rather similar values and fall into the region typical for five- and six-coordinate Yb(II) and Ca(II) heteroleptic amido complex-

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Table 1. Hydrophosphination of Styrene with Phosphines Catalyzed by Complexes 1Yb, 1Ca, 2Ca, 3Ca, and 4Ca[a]

no.	precatalyst [mM]	phosphine	time, h	conversion[b]	*sec*-P/*tert*-P[c]	regioselectivity Markovnikov/*anti*- Markovnikov[d]
1	**1Yb**	Ph_2PH	3	100		0/100
2		Cy_2PH	40	40		0/100
3		$PhPH_2$	3	100	95/5	0/100
4		2,4,6-$Me_3C_6H_2PH_2$	16	30	100/0	0/100
5		2,4,6-$Me_3C_6H_2PH_2$	70	43	100/0	0/100
6		2-$C_5NH_4PH_2$	70	100	100/0	44/56
7	**1Ca**	Ph_2PH	3	100		0/100
8		Cy_2PH	72	25		0/100
9		$PhPH_2$	3	33	99/1	0/100
10		$PhPH_2$	10	100	97/3	0/100
11		2,4,6-$Me_3C_6H_2PH_2$	72	84	100/0	0/100
12		2-$C_5NH_4PH_2$	72	12	100/0	0/100
13	**2Ca**	Ph_2PH	3	100		0/100
14		Cy_2PH	72	31		0/100
15		$PhPH_2$	3	55	95/5	0/100
16		2,4,6-$Me_3C_6H_2PH_2$	72	93	100/0	0/100
17		2-$C_5NH_4PH_2$	72	47	76/24[d]	0/100
18	**3Ca**	Ph_2PH	3	100		0/100
19		Cy_2PH	72	30		0/100
20		$PhPH_2$	3	100	80/20	0/100
21		2,4,6-$Me_3C_6H_2PH_2$	72	99	100/0	0/100
22		2-$C_5NH_4PH_2$	72	24	100/0[d]	0/100
23	**4Ca**	Ph_2PH	3	100		0/100
24		Cy_2PH	72	30		0/100
25		$PhPH_2$	3	76	86/14	0/100
26		2,4,6-$Me_3C_6H_2PH_2$	72	100	100/0	0/100
27		2-$C_5NH_4PH_2$	72	100	84/16[d]	0/100

[a]Reaction in neat substrates $[phosphine]_0:[styrene]_0:[precat]_0 = 50:50:1$, $[precat]_0 = 87.0$ mM, T [°C] = 70. [b]Conversion of styrene, determined by NMR spectroscopy. [c]Chemoselectivity was determined by ^{31}P NMR spectroscopy. [d]Regioselectivity was determined by ^{1}H, ^{31}P NMR spectroscopy.

es.[8d,10b,12c,19,20] The geometric parameters of the amidinate fragment in **2Ca** are similar to those in **1Ca** and **1Yb**. The noticeable difference in the C(22)−N(3) and C(22)−N(4) bond lengths (1.374(2) vs 1.284(2) Å) is indicative of the absence of negative charge delocalization within the amidinate fragment.[21]

Hydrophosphination Catalysis. Complexes **1Yb**, **1Ca**, **2Ca**, **3Ca**,and **4Ca** were evaluated as precatalysts for styrene hydrophosphination with various phosphines. The catalytic tests were performed in the presence of 2 mol % of the catalyst in neat substrates at 70 °C. The representative data are collected in Table 1.

All complexes performed high catalytic activity in styrene hydrophosphination with $PhPH_2$ and Ph_2PH: quantitative conversions were reached in 3−10 h. The reactions were found to be highly regioselective affording exclusively the anti-Markovnikov addition products for both $PhPH_2$ and Ph_2PH with no indication for the formation of other regioisomers. Moreover, for primary $PhPH_2$ the reactions catalyzed by **1Yb**, **1Ca**, and **2Ca** proved to be highly chemoselective, leading to the formation of the secondary phosphine (*sec*-P) in >95% selectivity; that is, less than 5% of tertiary phosphine formed upon double (stepwise) hydrophosphination. However, complexes **3Ca** and **4Ca** turned out to be less chemoselective; the formation of both secondary and tertiary phosphines was detected in 80/20 (**3Ca**) and 86/14 (**4Ca**) ratios. The results of styrene hydrophosphination with $PhPH_2$ catalyzed by a series of heteroleptic amido complexes **1Ca**−**4Ca** unambiguously imply a dramatic effect of the ancillary ligand on both catalytic activity and selectivity of metal promoted reactions. It is noteworthy that the transition from L^4 to L^3 featuring a similar structure and steric demand but bearing in the ortho-position of amidinate phenyl substituent a fluorine atom capable of weak coordination to metal ions[17] leads to a noticeable increase of catalytic activity (**4Ca**: 3 h, 76% vs **3Ca**: 3 h, 100%); however it does not affect the chemoselectivity. Complex **1Ca** which does not contain CF_3 or C_6H_4F groups in the ancillary ligand framework but bears sterically demanding $iPr_2C_6H_3$ substituent at the amidinate nitrogen proved to be the least active but the most chemoselective in this series of complexes.

Addition of more sterically demanding and more donor primary phosphine $MesPH_2$ to styrene proceeds much more slowly compared to $PhPH_2$. For the reactions catalyzed by **1**−**4Ca** complete conversion requires >72 h at 70 °C, while complex **1Yb** demonstrated the lowest activity: even after 70 h the conversion did not exceed 43%. However, all precatalysts provided excellent regio- and chemoselectivities. The nature of phosphine was found to affect the hydrophosphination rate dramatically. Thus, Cy_2PH proved to be much less reactive than Ph_2PH in all catalytic tests. The reactions with styrene proceed slower; the highest conversion was provided by ytterbium compound **1Yb** and reached 40% in 40 h. Ca complexes displayed lower catalytic activity, in 72 h conversion did not exceed 31%. Lower reactivity of Cy_2PH vs Ph_2PH can be rationalized by both greater steric demand of the former (compare the Tolman cone angles: Cy_2PH, $\theta = 143°$; Ph_2PH, $\theta = 128°$)[22] and its lower acidity (compare: Cy_2PH, $pK_a = 34.6$ (35.7); Ph_2PH, $pK_a = 22.9$ (21.7),)[23] which affects phospine deprotonation and σ-bond metathesis steps of the catalytic

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cycle of intermolecular olefin hydrophosphination.[8d] Styrene hydrophosphination with 2-$C_5NH_4PH_2$ for all complexes **1Yb** and **1**−**4Ca** proceeds much more slowly compared to $PhPH_2$. Surprisingly hydrophosphination of styrene with 2-$C_5NH_4PH_2$ catalyzed by complex **1Yb** turned out to be non-regioselective and led to the formation of a mixture of Markovnikov and anti-Markovnikov addition products in a 44:56 ratio (entry 7). In contrast all Ca complexes enable regioselective reaction affording exclusively anti-Markovnikov addition products. However, complexes **2Ca** and **4Ca** demonstrate lower chemoselectivity, and the formation of both secondary and tertiary phosphines was detected in 76:24 and 84:16 ratios, respectively. It is noteworthy that complexes **1Ca** and **1Yb** containing catalytic centers with very similar ionic radii performed different catalytic activity: the ytterbium analogue proved to be a more active catalyst for intermolecular hydrophosphination of styrene with Cy_2PH, 2-$C_5NH_4PH_2$, and $PhPH_2$, but less active with sterically demanding $MesPH_2$. To elucidate the possibility of double sequential alkylation of $PhPH_2$ catalyzed by complexes **1Yb** and **1**−**4Ca** hydrophosphination reactions were carried out at a molar substrates ratio $[styrene]_0:[PhPH_2]_0$ = 2:1. Complexes **1Ca** and **2Ca** enable the formation of the tertiary phosphine $PhP(CH_2CH_2Ph)_2$ in quantitative yields and excellent chemoselectivity (Table 2, entry 2 and 4); however **2Ca** shows noticeably higher catalytic activity. Quantitative conversion was reached in 48 h vs 70 h for **1Ca**. Complexes **1Yb**, **3Ca**, and **4Ca** proved to be somewhat less active: in 70 h the conversion did not exceed 75%. Surprisingly the reactions catalyzed by complexes **1Yb**, **3Ca**, and **4Ca** under the same reaction conditions were nonselective and led to the formation of mixtures of the secondary and tertiary phosphines. It is noteworthy that heteroleptic amido complexes **1Yb**, **1**−**4Ca** coordinated by amidine-amidopyridinate ligands provide lower chemoselectivity compared to the related amido complexes supported by amidinate[24] and phenolate[8d,25] ligands.

Table 2. Double Sequential Hydrophosphination of Styrene with $PhPH_2$ ($[PhPH_2]_0:[styrene]_0$ = 1:2) Catalyzed by Complexes 1Yb, 1Ca, 2Ca, 3Ca, 4Ca[a]

no.	precatalyst	substrates	time, h	conversion[b]	*sec*-P/*tert*-P[c]
1	**1Yb**	styrene	70	75	50/50
2	**1Ca**		70	100	0/100
3	**2Ca**		16	67	67/33
4	**2Ca**	$PhPH_2$	48	100	0/100
5	**3Ca**		70	75	50/50
6	**4Ca**		70	74	52/48

[a]Reaction in neat substrates $[PhPH_2]_0:[styrene]_0:[precat]_0$ = 50:100:1, $[precat]_0$ = 87.0 mM, T [°C] = 70. [b]Conversion of styrene, determined by NMR spectroscopy. [c]Chemoselectivity was determined by ^{31}P NMR spectroscopy.

To assess the influence of the electronic properties of styrenic substrate on reaction rate, a series of catalytic tests of hydrophosphination of styrenes bearing various substituents in the para position of the aromatic ring with $PhPH_2$ was carried out. The catalytic tests were performed in the presence of 2 mol % of **1Yb**, **1Ca**, **2Ca**, **3Ca**, and **4Ca** as the precatalyst. The representative results are listed in Table 3. A number of functional groups were found to be tolerated for the hydrphosphination of styrene. Similar to our previous observations[8d] for styrenes containing in *p*-position electron-donating groups (Me, tBu, OMe), a noticeable decrease of the reaction rate was detected compared to that for unsubstituted styrene (entry 11−25). Addition of $PhPH_2$ to p-MeO-styrene proceeded at the lowest rate, most likely due to blocking the oxophilic catalytic center and competition between MeO, C═C, and phosphine for coordination site. For *p*-Cl-styrene no strong deviation from the reaction rate measured for styrene was observed (entry 6−10) with the exception of complex **1Ca** which performs noticeably higher catalytic activity in the case of the former substrate. In the case of *p*-F-styrene an essential drop of activity took place when **1Yb** was used as a precatalyst (entry 1), whereas activities of other complexes did not differ much from those measured for styrene. Such a decrease of activity can be rationalized either by competing coordination between fluoride[24,25] and olefinic units on catalytic center or by C−F bond activation mediated by Yb(II) complex[26] leading to partial deactivation of the catalyst. All of the above-mentioned complexes proved to be unable to mediate addition of $PhPH_2$ and Ph_2PH to internal double C═C bonds of cyclohexene and *trans*-stilbene. As it was exemplified by α-Me-styrene complexes **1Yb**, **1Ca**, **2Ca**, **3Ca**, and **4Ca** enable addition of $PhPH_2$ toward double C═C bond of 1,1-disubstituted terminal olefin. The reaction rate for this substrate is noticeably lower; however quantitative conversions can be reached in ∼40 h. It is noteworthy that regio- and chemoselectivities remain excellent for this substrate (entry 26−30). Catalytic addition of $PhPH_2$ to conjugated 2,3-dimethyl butadiene was tested as a prospective synthetic approach to the formation of the phosphole ring; however no formation of a heterocyclic product was detected. Complexes **1**−**4Ca** allow for the transformation of 2,3-dimethyl butadiene into the linear phosphorus containing 1,2-addition products in good yields and excellent regioselectivity, albeit only **1Ca** and **2Ca** provide a high degree of chemoselectivity control and afford secondary phosphines. For complexes **3Ca** and **4Ca** the reactions lead to the formation of mixtures of secondary and tertiary phosphines (entries 34 and 35).

Hydroelementation of inert 1-alkenes still remains a challenging and hardly realizable transformation.[7b,27] Nevertheless, complexes **3Ca** and **4Ca** enable addition of $PhPH_2$ to 1-nonene and provide ∼25% conversion in 40 h at 70 °C. For Ph_2PH within the same reaction time even higher conversions were measured and reached maximum 40% in the case of **2Ca**. Unexpectedly complex **1Yb** appeared completely inert in hydrophosphination of 1-nonene with both Ph_2Ph and $PhPH_2$.

Interestingly complexes **1Ca** and **1Yb**, although having similar structures and containing catalytic centers with very similar ionic radii, performed different catalytic activity. Ytterbium analogue proved to be more active catalyst for intermolecular hydrophosphination of styrene with Cy_2PH, 2-$C_5NH_4PH_2$, and $PhPH_2$. This fact is in line with the previous observation of higher catalytic activity of (o-$Me_2NC_6H_4$-$CHSiMe_3)_2Yb(THF)_2$ in styrene polymerization vs that of Ca congener.[9d] A higher insertion rate was explained by the authors as a result of a weaker Yb-ligand bond caused by electron−electron repulsion of the completely filled f shell. At this stage it is unclear which factors are responsible for the different selectivity in styrene hydrophosphination with $PhPH_2$ promoted by Yb and Ca complexes.

Kinetic Analysis. In order to get a deeper insight into the mechanism of intermolecular olefin hydrophosphination catalyzed by Ca compounds, more detailed kinetic studies were performed for reaction of styrene with Ph_2PH in the presence of **1Ca**. The reactions were carried out in C_6D_6, and

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Table 3. Olefin Hydrophosphination with $PhPH_2$ and Ph_2PH Catalyzed by Complexes 1Yb, 1-4Ca[a]

no.	precatalyst	substrates	time, h	conversion[b]	selectivity[c]
1	**1Yb**	styrene	3	100	94/6
2	**1Ca**		3	33	91/9
3	**1Ca**	$PhPH_2$	10	100	97/3
4	**2Ca**		3	55	95/5
5	**3Ca**		3	100	80/20
6	**4Ca**		3	76	86/14
7	**1Yb**		16	72	94/6
8	**1Ca**	p-F-styrene	3	82	91/9
9	**2Ca**		3	61	92/8
10	**3Ca**	$PhPH_2$	3	100	85/15
11	**4Ca**		3	67	86/14
12	**1Yb**		3	80	90/10
13	**1Ca**	p-Cl-styrene	3	86	96/4
14	**2Ca**		3	71	88/12
15	**3Ca**	$PhPH_2$	3	79	90/10
16	**4Ca**		3	80	91/9
17	**1Yb**		16	96	98/2
18	**1Ca**	p-Me-styrene	16	96	90/10
19	**2Ca**		16	100	68/32
20	**3Ca**	$PhPH_2$	16	100	83/17
21	**4Ca**		16	88	84/16
22	**1Yb**		16	28	100/0
23	**1Ca**	p-tBu-styrene	16	96	91/9
24	**2Ca**		16	100	83/17
25	**3Ca**	$PhPH_2$	16	100	83/17
26	**4Ca**		16	85	87/13
27	**1Yb**	p-OMe-styrene	70	55	95/5
28	**1Ca**		40	100	89/11
29	**2Ca**	$PhPH_2$	40	100	77/23
30	**3Ca**		40	100	83/17
31	**4Ca**		40	100	90/10
32	**1Yb**		40	62	100/0
33	**1Ca**	α-Me-styrene	40	82	100/0
34	**2Ca**		40	90	100/0
35	**3Ca**	$PhPH_2$	40	100	100/0
36	**4Ca**		40	88	100/0
37	**1Yb**	2,3-dimethyl-1,3-butadiene	40	40	100/0
38	**1Ca**		40	100	100/0
39	**2Ca**		40	100	100/0
40	**3Ca**	$PhPH_2$	40	90	40/60
41	**4Ca**		40	95	82/18
42	**1Yb**		96	0	
43	**1Ca**	nonene-1	72	12	100/0
44	**1Ca**		96	28	100/0
45	**2Ca**	$PhPH_2$	40	3	100/0
46	**3Ca**		40	23	100/0
47	**4Ca**		40	25	100/0
48	**1Yb**		96	0	
49	**1Ca**	nonene-1	40	4	100/0
50	**2Ca**		40	40	100/0
51	**3Ca**	Ph_2PH	40	34	100/0
52	**4Ca**		40	13	100/0
53	**1Yb**	cyclohexene	40	0	
54	**1Ca**		40	0	
55	**2Ca**	$PhPH_2$	40	0	
56	**3Ca**		40	0	
57	**4Ca**		40	0	
58	**1Yb**		40	0	
59	**1Ca**	*trans*-stilbene	40	0	
60	**2Ca**		40	0	
61	**3Ca**	$PhPH_2$	40	0	
62	**4Ca**		40	0	

[a]Reaction in neat substrates $[phosphine]_0$:$[styrene]_0$:$[precat]_0$ = 50:50:1, $[precat]_0$ = 87.0 mM, T [°C] = 70. [b]Conversion of styrene, determined by NMR spectroscopy. [c]Product chemoselectivity"Anti-Markovnikov monoaddition/double addition" determined by ^{31}P NMR spectroscopy.

kinetic monitoring was performed by ^1H NMR spectroscopy. The plot of conversion of Ph_2PH vs reaction time at 25 °C in the presence of an 8-fold molar excess of styrene proved to be linear (Figure 3), indicating a zeroth-order dependence of the reaction rate in concentration of Ph_2PH. Conversion of Ph_2PH over time was studied at two different [phosphine]/[**1Ca**] ratios (see the Supporting Information, Figure S11). In both cases, similar values of k_{app} were calculated (23.21 and 25.53 h^{-1}).

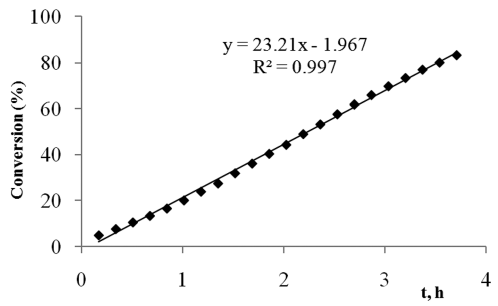

Figure 3. Plot of Ph_2PH conversion vs time for styrene hydrophosphination with Ph_2PH, catalyzed by **1Ca**. Reaction conditions: 25 °C, $[\mathbf{1Ca}]_0$ = 28 mM, $[PPh_2H]_0$:$[styrene]_0$:$[\mathbf{1Ca}]_0$ = 26:220:1, total volume 0.575 mL.

A series of experiments was conducted to determine the partial order in styrene, using a constant concentration of the catalyst and the phosphine and varying the concentration of styrene in the reaction mixture (0.96−1.67 mol/L). The plot of $\ln(k_{app})$ vs $\ln([styrene]_0)$ gave a straight line (R^2 = 0.974) with a slope of 0.9 corresponding to the apparent kinetic order for styrene (Figure 4; see also Figure S12).

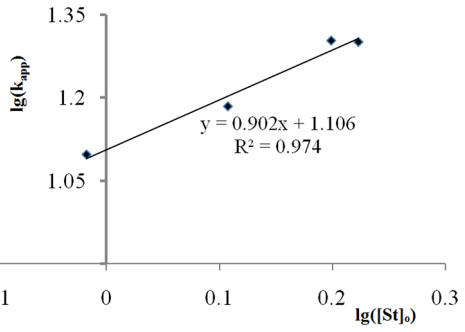

Figure 4. Plot of $\lg(k_{app})$ vs $\lg([styrene]_0)$ for hydrophosphination of styrene with Ph_2PH, catalyzed by **1Ca** at different styrene concentrations (0.96; 1.28; 1.58; 1.67 mol/L). Reaction conditions: 25 °C, $[\mathbf{1Ca}]_0$ = 48 mM, $[\mathbf{1Ca}]_0/[Ph_2PH]_0$ = 1:77, total volume 0.6 mL.

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In order to determine the partial order in the catalyst, the conversion of phosphine was monitored at constant molar ratio of substrates and at different catalyst concentrations (54.1−161.9 mmol/L) while maintaining the total volume of reactants and solvent constant (Figure 5).

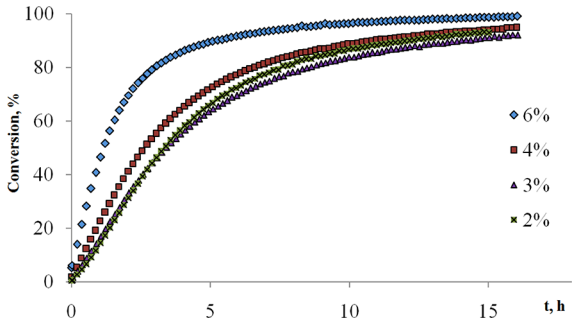

Figure 5. Kinetic curves of accumulation of tertiary phosphine at different concentrations of **1Ca** (54.1; 80.9; 107.9; 161.9 mmol/L). Reaction conditions: 25 °C, $[\text{styrene}]_0 = [Ph_2PH]_0 = 2.9$ mol/L, total volume 0.6 mL.

The initial reaction rates (k_{app}) are determined for various initial concentrations of the catalyst below 70%. A plot of $\lg(k_{app})$ vs $\lg([\mathbf{1Ca}]_0)$ gave a straight line with a slope indicating a first order in the precatalyst (Figure 6, see also Figure S13).

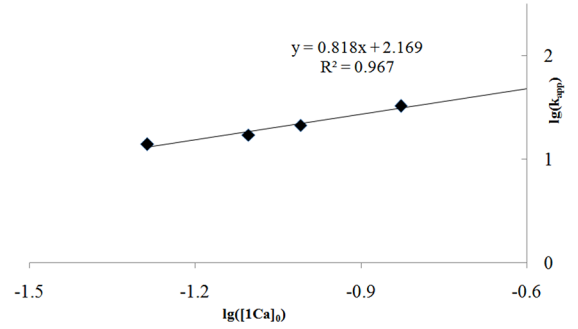

Figure 6. Plot of $\lg(k_{app})$ vs $\lg([\mathbf{1Ca}]_0)$ for hydrophosphination of styrene with Ph_2PH, catalyzed by **1Ca** at the different catalyst concentrations (54.1; 80.9; 107.9; 161.9 mmol/L). Reaction conditions: 25 °C, $[\text{styrene}]_0 = [Ph_2PH]_0 = 2.9$ mol/L, $[\text{styrene}]_0/[Ph_2PH]_0 = 1{:}1$, total volume 0.6 mL.

Thereby the rate law for the hydrophosphination of styrene with Ph_2PH catalyzed by **1Ca** agrees with the idealized equation: $v = k[\text{styrene}]^1[\mathbf{1Ca}]^1$ and is consistent with the previously reported observations.[7b,8d,12d,e,28]

CONCLUSION

The reactions of bisamido complexes $M[N(SiMe_3)_2]_2(THF)_2$ (M = Yb, Ca) and amidine-aminopyridines LH was used as a synthetic approach to the synthesis of the heteroleptic amido complexes $LM[N(SiMe_3)_2](THF)$. The reactions of $Yb[N(SiMe_3)_2]_2(THF)_2$ with proligands **L²H**-**L⁴H** bearing CF_3 and C_6H_4F groups did not result in the formation of the target Yb(II) complexes, while in the case of $Ca[N(SiMe_3)_2]_2(THF)_2$ under the similar conditions afforded analogues **2**−**4Ca** in good yields. Taking into account the fact that in the case of **L¹H** which does not contain C−F bonds the transamination reaction allows for preparing the heteroleptic amido complexes of both Ca and Yb it is logical to assume that in the reactions of **L²H**-**L⁴H** due to redox character of Yb(II) center C−F bond activation occurs and hampers the formation of $LYb[N(SiMe_3)_2](THF)$ complexes. The X-ray analysis revealed that in **1Yb** and **1Ca** the metal centers are five-coordinate, while in **2Ca** it adopts a coordination number of six because of the additional coordination of a pendant methoxy group in the amidinate phenyl ring.

The systematic study of styrene hydrophosphination with $PhPH_2$ catalyzed by a series of amido complexes **1Ca**-**4Ca** coordinated by amidine-amidopyridinate ligands unambiguously imply a dramatic effect of the steric and electronic properties of the ancillary ligand on both catalytic activity and selectivity of metal promoted reactions. It is noteworthy, that the transition from L^4 to L^3 featuring similar structure and steric demand but bearing in ortho-position of amidinate phenyl substituent a fluorine atom capable to weak coordination to metal ions[17] leads to a noticeable increase of catalytic activity (**4Ca**: 3h, 76% vs **3Ca**: 3h, 100%) however does not affect chemoselectivity. Complex **1Ca** which does not contain CF_3 or C_6H_4F groups in the ancillary ligand framework but bears sterically demanding $iPr_2C_6H_3$ substituent at the amidinate nitrogen proved to be the least active but the most chemoselective in this series of complexes.

Complexes **1Yb**, **1**−**4Ca** demonstrated high catalytic activity and regioselectivity in styrene hydrophosphination with $PhPH_2$ and Ph_2PH. For primary $PhPH_2$ the addition to styrene catalyzed by **1Yb**, **1Ca**, and **2Ca** is chemoselective and affords the secondary phosphine $Ph(PhCH_2CH_2)PH$, while when **3Ca** and **4Ca** were used as precatalysts mixtures of secondary and tertiary phosphines were formed. Complexes **1Yb** and **1**−**4Ca** enable styrene hydrophosphination with 2,4,6-$Me_3C_6H_2PH_2$ and 2-pyridylphosphine. Surprisingly despite the similar ionic radii of the catalytic centers the reaction of 2-$C_5NH_4PH_2$ with styrene catalyzed by **1Yb** proceeds non-regioselectively, while all Ca complexes enable regioselective anti-Markovnikov addition. Complexes **1Ca** and **1Yb** containing catalytic centers featuring similar ionic radii performed different catalytic activity: ytterbium analogue proved to be more active catalyst for intermolecular hydrophosphination of styrene with Cy_2PH, 2-$C_5NH_4PH_2$ and $PhPH_2$, but less active with sterically demanding 2,4,6-$Me_3C_6H_2PH_2$. Complexes **1Yb** and **1**-**4Ca** provide quantitative conversion in the addition of $PhPH_2$ toward 1,1-disubstituted C═C bond of α-Me-styrene. Ca-catalyzed hydrophosphination of inert 1-nonene with Ph_2PH achieving 40% conversion is the most impressive result reported in this paper.

EXPERIMENTAL SECTION

General Considerations. All experiments were performed in evacuated tubes or in inert atmosphere, using standard Schlenk-flask or glovebox techniques, with rigorous exclusion of traces of moisture and air. After being dried over KOH, THF and DME were purified by distillation from sodium/benzophenone ketyl, hexane, and toluene by distillation from sodium/triglyme benzophenone ketyl prior to use. Benzene-d_6, toluene-d_8, and THF-d_8 were dried with sodium/benzophenone ketyl and condensed in a vacuum prior to use. $[(Me_3Si)_2N]_2M(THF)_2$ (M = Yb,[29] Ca,[30] $L^{1-4}H$[16b] were prepared according to literature procedures. Diphenylphosphine, dicyclohexylphosphine, and phenylphosphine were donated by Synor Ltd. and were vacuum-distilled over CaH_2 and then were degassed by freeze−pump−thaw methods.

Instruments and Measurements. NMR spectra were recorded on a Bruker DPX 200 or Bruker Avance DRX-400 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were referenced internally

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using the residual solvent resonances and are reported relative to TMS. Lanthanide metal analysis was carried out by complexometric titration.[31] C, H, N elemental combustion analysis was performed in the microanalytical laboratory of IOMC.

Synthesis of [L^{1}YbN(SiMe$_3$)$_2$(THF)] (1Yb). A solution of L^{1}H (0.165 g, 0.317 mmol) in toluene (10 mL) was added to a solution of Yb[N(SiMe$_3$)$_2$](THF)$_2$ (0.202 g, 0.317 mmol) in toluene (10 mL) at room temperature. The color of the reaction mixture changed immediately from red to brownish-black. Reaction mixture was stirred for 1 h at room temperature. The volatiles were then removed under reduced pressure, and the solid residue was dissolved in a toluene/hexane mixture (1:1). Slow concentration of the solution at −20 °C resulted in the formation of **1Yb** as black crystals. The mother liquid was decanted, and the crystals were washed with cold hexane and dried in a vacuum for 30 min. Complex **1Yb** was isolated in 60% yield (0.180 g).^{1}H NMR (400 MHz, C$_6$D$_6$) δ = 0.08, 0.36 (s, together 18H, SiMe$_3$), 1.38 (compl. m, 12H, C*H*$_3$CH and 4H, β-CH$_2$ THF), 2.10 (s, 6H, CH$_3$), 2.14 (s, 3H, CH$_3$ toluene), 2.55 (s, 6H, CH$_3$), 3.44 (m, 2H, CH*i*Pr), 3.50 (m, 4H, α-CH$_2$ THF), 4.82 (d, $^3J_{HH}$ = 7.8 Hz, 1H, m-Py), 5.53 (d, $^3J_{HH}$ = 8.5 Hz,1H, m-Py), 6.66 (m, 1H, p-Py), 6.77 (d, $^3J_{HH}$ = 7.2 Hz, 1H, p-CH, NC$_6$*H*$_3$iPr$_2$), 6.83 (d, $^3J_{HH}$ Hz, 1H, p-CH, NC$_6$*H*$_3$Me$_2$), 7.00−7.16 (m, 5H, toluene+7H, NC$_6$*H*$_3$Me$_2$ and NC$_6$*H*$_3$iPr$_2$). ^{13}CNMR (101 MHz, C$_6$D$_6$) δ= 2.3, 5.9 (SiCH$_3$), 18.0 (CH$_3$), 19.6 (CH$_3$), 21.0 (CH$_3$), 21.05 (β-CH$_2$ THF), 25.4 (CHCH$_3$), 28.0 (CHCH$_3$), 67.5 (α-CH$_2$ THF), 91.9 (m-Py), 101.8(m-Py), 124.6, 125.3, 128.9, 129.3 (C toluene), 128.0 (p-C, NC$_6$H$_3$iPr$_2$), 137.5 (m-C, C$_6$H$_3$Me$_2$ and NC$_6$H$_3$iPr$_2$), 139.9 (p-Py), 149.2(i-C, C$_6$H$_3$Me$_2$), 151.5 (C, o-Py), 159.2 (o-C, py), 165.3 (N═C). IR (Nujol, KBr, ν/cm^{-1}): 1938 (w), 1784 (w), 1653 (w), 1614 (s), 1580 (m), 1459 (s), 1377 (s), 1285 (s), 1253 (m), 1221 (s), 1176 (s), 1159 (s), 1128 (s), 971 (m), 928 (m), 837 (m), 826 (m), 767 (s), 747 (s), 721 (s), 671 (w), 656 (w), 608 (w), 580 (w), 560 (w), 491 (w). Elem. Anal. Calc. for C$_{45}$H$_{67}$N$_5$OSi$_2$Yb•1/2C$_7$H$_8$ (969.32 g/mol): C 60.04; H 7.32; N 7.22; Yb 17.84. Found: C 60.45; H 7.40; N 7.34; Yb 17.95.

Synthesis of [L^{1}CaN(SiMe$_3$)$_2$(THF)] (1Ca). A solution of L^{1}H (0.300 g, 0.579 mmol) in toluene (10 mL) was added to a solution of Ca[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (0.292 g, 0.579 mmol) in toluene (10 mL). The reaction mixture was stirred for 50 h at 50 °C. The volatiles were then removed under reduced pressure, and the solid residue was dissolved in mixture of solvents THF/hexane (1:3). Slow concentration of THF/hexane solution at room temperature resulted in the formation of yellowish-green crystals of **1Ca**. The mother liquid was decanted and the crystals were washed with cold hexane and dried in a vacuum for 30 min. Complex **1Ca** was isolated in 83% yield (0.345 g). ^{1}H NMR (400 MHz, C$_6$D$_6$) δ = 0.09, 0.28 (s,18H, SiMe$_3$), 1.26 (d, $^3J_{HH}$ = 7.0 Hz, 12H, CHC*H*$_3$), 1.40 (m, 4H, β-CH$_2$ THF), 1.93 (s, 3H, CH$_3$), 1.99 (s, 6H, CH$_3$), 2.14 (s, 3H, CH$_3$ toluene), 2.29 (s, 6H, CH$_3$), 3.15 (sept, $^3J_{HH}$ = 6.9 Hz, 2H, C*H*CH$_3$), 3.56 (m, 4H, α-CH$_2$ THF), 5.56 (d, $^3J_{HH}$ = 7.9 Hz, 1H, m-Py), 6.38 (d, $^3J_{HH}$ = 7.6 Hz,1H, m-Py), 6.92 (complex m, 4H, NC$_6$H$_3$), 7.02 (complex m, 5H, toluene +4H, NC$_6$H$_3$), 7.10 (m, 2H, NC$_6$H$_3$). ^{13}C NMR (101 MHz, C$_6$D$_6$) δ = 2.3, (CH$_3$, SiMe$_3$), 17.9 (CH$_3$), 18.0 (CH$_3$), 19.0 (CH$_3$), 23.1 (CH$_3$ *i*Pr), 23.4 (CH$_3$ *i*Pr), 25.8 (CH$_3$, *i*Pr), 25.5 (β-CH$_2$ THF), 28.1 (CH, *i*Pr), 67.5 (α −CH$_2$ THF), 99.5 (m-Py), 104.5 (m-Py), 122.9, 126.4, 127.3, 128.2, 128.4, 136.5,137.2, 137.3, 137.4, 138.8 (C, C$_6$H$_3$Me$_2$ and NC$_6$H$_3$iPr$_2$), 142.4 (C, p-Py), 145.8 (i-C, C$_6$H$_3$Me$_2$), 155.1 (o-C, py), 156.0 (o-C, py), 156.4 (N═C). IR (Nujol, KBr, ν/cm^{-1}): 1940 (w), 1782 (w), 1649 (w), 1614 (s), 1580 (m), 1455 (s), 1377 (s), 1282 (s), 1259 (m), 1221 (s), 1171(s), 1155 (s), 1108 (s), 971 (m), 926 (m), 837 (m), 825 (m), 767 (s), 747 (s), 721 (s), 671 (w), 653 (w), 610 (w), 580 (w), 560 (w), 490 (w). Elem. Anal. Calc. for C$_{45}$H$_{67}$CaN$_5$OSi$_2$·C$_7$H$_8$ (882.43 g/mol): C 70.07; H 8.49; Ca 4.53; N 7.93. Found: C 69.79; H 8.61; Ca 4.57; N 8.02.

Synthesis of [L^{2}Ca(N(SiMe$_3$)$_2$)(THF)] (2Ca). A solution of L^{2}H (0.182 g, 0.360 mmol) in toluene (10 mL) was added to a solution of Ca[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (0.185 g, 0.360 mmol) in toluene (10 mL). The color of the reaction mixture changed immediately from pale-yellow to bright-red. Reaction mixture was stirred for 1 h at room temperature. The volatiles were then removed under reduced pressure, and the solid residue was redissolved in fresh toluene. Slow concentration of the toluene solution at room temperature resulted in the formation of red crystals. The mother liquid was decanted, and the crystals were washed with cold hexane and dried in a vacuum for 30 min. Complex **2Ca** was isolated in 95% yield (0.299 g).^{1}H NMR (400 MHz, C$_6$D$_6$) δ = 0.09 (s, 18H, SiMe$_3$), 1.40 (m, 4H, β-CH$_2$ THF), 1.71 (s, 3H, CH$_3$), 2.10 (s, 3H, CH$_3$ toluene), 2.27 (s, 3H, CH$_3$), 2.38 (s, 3H, CH$_3$), 2.59 (s, 3H, CH$_3$), 3.38 (s, 3H, OMe), 3.56 (m, 4H, α-CH$_2$ THF), 4.74 (d, $^3J_{HH}$ = 7.5 Hz, 1H m-Py), 5.58 (d, $^3J_{HH}$ = 8.5 Hz, 1H m-Py), 5.75 (d, $^3J_{HH}$ = 8.2 Hz, 1H p-Py), 6.53 (dd, $^3J_{HH}$ = 16.9, 8.4 Hz, 2H Ar), 6.61 (s, 2H Ar), 6.64 (t, $^3J_{HH}$ = 6.7 Hz, 2H Ar), 6.81 (d, $^3J_{HH}$ = 7.4 Hz, 1H Ar), 6.87 (d, $^3J_{HH}$ = 7.0 Hz, 1H Ar), 7.03−6.97 (complex m, 5H Ar), 7.05 (d, $^3J_{HH}$ = 7.2 Hz, 2H). ^{13}C NMR (101 MHz, C$_6$D$_6$) δ = 2.2 (CH$_3$, SiMe$_3$), 17.7 (CH$_3$), 18.0 (CH$_3$), 18.1 (CH$_3$), 20.4 (CH$_3$), 21.1 (CH$_3$ toluene), 25.5 (β-CH$_2$ THF), 56.8 (OMe), 67.5 (α −CH$_2$ THF), 92.9 (m-Py), 103.0 (m-Py), 111.2 (p-Py), 121.4, 121.5, 124.5, 125.3, 128.2, 128.6, 128.9, (C Ar), 132.2 (o-C C$_6$H$_3$Me$_2$), 133.6 (o-C C$_6$H$_3$Me$_2$), 137.3 (o-C C$_6$H$_3$Me$_2$), 138.2 (o-C Py), 138.9 (o-C Py), 140.8 (o-C C$_6$H$_3$Me$_2$), 149.9 (o-C, C$_6$H$_4$OMe), 150.5 (i-C, C$_6$H$_3$Me$_2$), 150.8 (i-C, C$_6$H$_3$Me$_2$), 165.1 (o-C, Py). ^{19}F{^{1}H} NMRδ = −58.2. IR (Nujol, KBr, ν/cm^{-1}): 1927 (w), 1783(w), 1660 (m), 1616 (s), 1603 (s), 1587 (s), 1574 (s), 1530 (s), 1495 (s), 1460 (s), 1377 (s), 1350 (s), 1288 (s), 1250 (s),1225 (s), 1188 (s), 1148 (s), 1113 (s), 1095 (s), 1049 (s), 1030 (s), 1005 (s), 977 (s), 926 (s), 881 (s), 821 (s), 772 (s), 746 (s), 716 (s), 692 (w), 662 (w), 619 (w), 608 (w), 590 (w), 565 (w), 510(w). Elem. Anal. Calc. for C$_{47}$H$_{62}$CaF$_3$N$_5$O$_2$Si$_2$ (882,27 g/mol): C 63.98; H 7.08; Ca 4.54; N 7.94. Found: C 63.88; H 7.13; Ca 4.50; N 7.99.

Synthesis of [L^{3}Ca(N(SiMe$_3$)$_2$)(THF)] (3Ca). A solution of L^{3}H (0.164 g, 0.324 mmol) in toluene (10 mL) was added to a solution of Ca(N(SiMe$_3$)$_2$)(THF)$_2$ (0.164 g, 0.324 mmol) in toluene. The color of the reaction mixture changed immediately from pale-yellow to bright-red. Reaction mixture was stirred for 1 h at room temperature. The solvent was then removed under reduced pressure, and residue was dissolved in fresh toluene. Slow concentration of the toluene solution at room temperature resulted in the formation of red powder. The mother liquid was decanted and the powder was washed with cold hexane and dried in a vacuum for 30 min. Complex L^{3}Ca(N(SiMe$_3$)$_2$)(THF) was isolated in 90% yield (0.270 g, 0.275 mmol). ^{1}H NMR (400 MHz, C$_6$D$_6$) 0.09 (s, 18H, SiMe$_3$), 1.83 (s, 3H, CH$_3$), 2.10 (s, 9H, CH$_3$ toluene), 2.19 (s, 3H, CH$_3$), 2.30 (s, 3H, CH$_3$), 2.59 (s, 3H, CH$_3$), 4.83 (d, $^3J_{HH}$ = 7.5 Hz, 1H m-Py), 5.64 (d, $^3J_{HH}$ = 8.5 Hz, 1H m-Py), 5.75 (d, *J* = 8.2 Hz, 1H m-Py), 6.53 (dd, $^3J_{HH}$ = 16.9, 8.4 Hz, 2H Ar), 6.54−7.14 (complex m, 23H Ar). ^{13}C NMR (101 MHz, C$_6$D$_6$) δ = 1.1, 2.3 (CH$_3$, SiMe$_3$), 17.9 (CH$_3$), 21.1 (CH$_3$ toluene), 25.4 (β-CH$_2$ THF), 67.7 (α-CH$_2$ THF), 94.9 (C, p-Py), 103.6 (C, m-Py), 114.8, 115.0, 125.1, 125.3, 128.2, 128.4, 128.8, 128.9, 137.5, 138.1, 139.0, 139.5, 140.1(C Ar), 150.7 (i-C, Py), 165.1 (o-C, Py). ^{19}F{^{1}H} NMR δ = 57.8, 127.2. IR (Nujol, KBr, ν/cm^{-1}): 1956 (w), 1786 (w), 1655 (w), 1613 (s), 1530 (m), 1460 (s), 1377 (s), 1287 (s), 1250 (m), 1221 (s), 1188 (s), 1163 (s), 1144 (s), 1095 (s), 1032 (m), 977 (m), 932 (m), 923 (m), 862 (m), 850 (m), 837 (m), 825 (m), 778 (m), 768 (s), 748 (s), 732 (s), 721 (s), 696 (m), 671 (w), 651 (w), 620 (w), 606 (w), 586 (w), 560 (w), 497 (w), 465(m). Elem. Anal. Calc. for C$_{56}$H$_{67}$CaF$_4$N$_5$Si$_2$ (982,41 g/mol): C 68.46; H 6.87; Ca 4.08; N 7.13;.Found: C 68.50; H 6.90; Ca 4.03; N 7.08.

Synthesis of [L^{4}Ca(N(SiMe$_3$)$_2$)(THF)] (4Ca). A solution of L^4(0.115g, 0.236 mmol) in toluene (10 mL) was added to a solution of Ca(N(SiMe$_3$)$_2$)(THF)$_2$ (0.119 g, 0.236 mmol) in toluene. The color of the reaction mixture changed immediately from pale-yellow to bright-red. Reaction mixture was stirred for 1 h at room temperature. The solvent was then removed under reduced pressure, and residue was dissolved in fresh hexane. Slow concentration of the hexane solution at room temperature resulted in the formation of red powder. The mother liquid was decanted and the powder was washed with cold hexane and dried in a vacuum for 30 min. Complex L^{4}Ca(N(SiMe$_3$)$_2$)(THF) was isolated in 84% yield (0.168g, 0.198 mmol).^{1}H NMR (400 MHz, C$_6$D$_6$) 0.09 (s, 18H, SiMe$_3$), 2.03 (m, 4H, β-CH$_2$ THF), 1.95 (s, 3H, CH$_3$), 2.10 (s, 3H, CH$_3$ toluene), 2.31 (s, 6H, CH$_3$), 2.40 (s, 3H, CH$_3$), 3.82 (m, 4H, α-CH$_2$ THF), 4.76 (d, $^3J_{HH}$ = 7.5 Hz, 1H, m-Py), 5.50 (d, $^3J_{HH}$ = 8.5 Hz, 1H, m-Py), 5.69 (d, $^3J_{HH}$ =

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8.2 Hz, 1H, m-Py), 6.56−7.15 (complex m, 16H,Ar).^{13}C NMR (101 MHz, C_6D_6) δ = 2.3 (CH_3, $SiMe_3$), 18.8 (CH_3), 21.1 (CH_3 toluene), 25.2 (β-CH_2 THF), 68.2 (α-CH_2 THF), 96.6 (p-Py), 103.2 (m-Py), 119.3, 120.3, 120.4, 121.0, 126.4, 128.7, 129.6, 132.0, 134.2, 137.8, 138.3, 141.1, 141.2, 146.1(CAr), 151.2 (i-C, Py), 164.75 (o-C, Py). ^{19}F{^{1}H} NMRδ = 56.8. IR (Nujol, KBr, ν/cm^{-1}): 1934(w) 1788(w) 1650 (s), 1606 (s), 1591 (s), 1573 (s), 1506 (s), 1451 (s), 1377 (s), 1343 (s), 1291 (s), 1262 (s), 1232 (s), 1217 (s), 1186 (s), 1148 (s), 1120 (s), 1097 (s), 1084 (s), 1027 (s), 977 (s), 948(m), 928 (s), 910 (s), 880(m), 823(m), 788 (s), 768 (s), 760 (s), 735 (s), 719 (s), 692 (s), 669(w), 625(w), 581(w), 564(w), 532(w), 508(w). Elem. Anal. Calc. for $C_{46}H_{60}CaF_3N_5OSi_2$ (852.25,41 g/mol): C 64.83; H 7.10; Ca 4.70; N 8.22. Found: C 64.50; H 6.95; Ca 4.63; N 8.08.

Disproportionation Reaction of Complex 1Ca. A solution of **1Ca** (0.100 g, 0.115 mmol) in 10 mL of hexane was stirred at room temperature for 1 week. Freezing of the resulting solution to −15 °C led to the formation of two types of crystals: [{L^1}$_2$Ca] as bright-yellow crystals and Ca(N($SiMe_3$)$_2$)(THF)$_2$ as white crystals. The mother liquid was decanted and the crystals were obtained by drop crystallization from hexane at room temperature then washed with cold hexane (3 × 2 mL) and dried in a vacuum for 30 min. Complex [{L$^1_2$Ca] was isolated in 31% yield (0.039 g, 0.036 mmol). ^{1}HNMR (400 MHz, C_6D_6) δ = 1.09 (d, $^3J_{HH}$ = 7.0 Hz,12H, CH_3,iPr), 1.27 (d, $^3J_{HH}$ = 7.0 Hz,12H, CH_3,iPr), 1.95(s, 6H, CH_3), 2.00 (s, 12H, CH_3), 2.25 (s, 12H, CH_3), 3.16 (sept, $^3J_{HH}$ = 6.9 Hz,4H, CH,*i*Pr), 5.07 (d, $^3J_{HH}$ = 7.6 Hz, 2H, m-Py), 5.61 (d, $^3J_{HH}$ = 7.9 Hz, 2H, m-Py), 6.94−7.11 (complex m, 20H, Ar). ^{13}CNMR (101 MHz, C_6D_6) δ = 13.9 (s, CH_3),17.9 (s, CH_3, $C_6H_3(CH_3)$), 19.6 (s, CH_3), 23.2 (s,CH_3, *i*Pr), 31.6 (s, 4C, CH, *i*Pr), 155.4; 156.0; 155.1 (s, i-C, C_6H_3(iPr)), 122.9, 125.3, 126.4, 127.5, 128.0, 136.0, 137.3, 138.8, 142.4, 151.6(s, Ar). IR (Nujol, KBr, ν/cm^{-1}): 1938 (w), 1784 (w), 1654 (w), 1614 (s), 1580 (m), 1459 (s), 1377 (s), 1285 (s), 1253 (m), 1221 (s), 1176 (s), 1159 (s), 1128 (s). Elem. Anal. Calc. for $C_{72}H_{87}CaN_8O_{0.5}$ (1112.57 g/mol): C 77.65; H 7.82; Ca 3.60; N 10.07. Found: C 77.79; H 7.71; Ca 3.67; N 10.02. Complex Ca(N($SiMe_3$)$_2$)(THF)$_2$ was isolated in 33% yield (0,019g, 0,038 mmol). ^{1}H NMR (400 MHz, C_6D_6) 0.40 (s, 36H, $SiMe_3$), 1.26 (m, 8H, β-CH_2 THF), 3.51(m, 8H, α-CH_2 THF). ^{13}C NMR (101 MHz, C_6D_6) δ = 4.1 (CH_3, $SiMe_3$), 25.8 (β-CH_2 THF), 67.5 (α-CH_2 THF). Elem. Anal. Calc. for $C_{20}H_{52}CaN_2O_2Si_4$ (505.07g/mol): C 47.56; H 10.38; Ca 7.94; N 5.55. Found: C 47.77; H 10.41; Ca 8.00; N 5.52.

Typical Hydrophosphinationation Experiments. In a typical reaction with neat substrates the catalyst (*X* μmol) was loaded into NMR tube, and then substrates (olefin (50**X* mmol) and phosphine (50**X* mmol)) were added to the NMR tube using microsyringes in the glovebox. The NMR tube was sealed and shaken vigorously, and the reaction time was started after quickly placing the NMR tube in an oil bath preheated at the desired temperature. After the desired reaction time, the NMR tube was removed from the oil bath, benzene-d_6 (0.5 mL) was added, and the ^{1}H, ^{31}P NMR spectra of the reaction mixture were recorded. Conversion was determined by integrating the remaining styrene and phosphine and the newly formed addition product. Reactions in dry benzene-d_6 were carried out in a similar manner, but with the solvent added at the same time as the substrates to the NMR tube.

X-ray Crystallography. The X-ray data for **1Yb**, **1Ca**, and **2Ca** were collected on Bruker Smart Apex (**1Yb**) and Bruker D8 Quest (**1Ca**, **2Ca**) diffractometers (MoK$_\alpha$-radiation, ω-scans technique, λ = 0.71073 Å, *T* = 100(2) K) using *SMART* and *APEX3*[32] software packages. The structures were solved by direct and dual-space[33] methods and were refined by full-matrix least-squares on F^2 for all data using *SHELX*.[33] *SADABS*[34] was used to perform area-detector scaling and absorption corrections. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. Hydrogen atoms were placed in calculated positions and were refined in the "riding" model with $U(H)_{iso}$ = 1.2U_{eq} of their parent atoms ($U(H)_{iso}$ = 1.5U_{eq} for methyl groups). CCDC−1584253 (**1Yb**), 1584252 (**1Ca**), and 1584254 (**2Ca**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre: ccdc.cam.ac.uk/structures. The crystallographic data and structure refinement details for **1Yb**, **1Ca**, and **2Ca** are given in Table S1 (See Supporting Information).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b00088.

Representative ^{1}H, ^{13}C, and ^{19}F NMR spectra of ytterbium and calcium complexes (PDF)

Accession Codes

CCDC 1584252−1584254 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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