Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 10381–10395

TETRAHEDRON

Synthesis of lanthanide(II)–imine complexes and their use in carbon–carbon and carbon–nitrogen unsaturated bond transformation

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Received 19 April 2003; accepted 23 June 2003

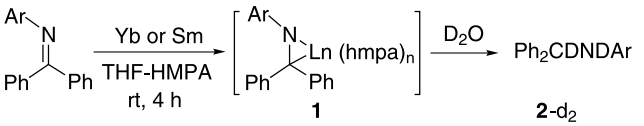
Abstract—Ytterbium and samarium metals reduced aromatic ketimines to give directly divalent azalanthanacyclopropane complexes **1** quantitatively, the structure of which was characterized by X-ray analysis. The imine complexes **1** catalyzed dehydrogenative silylation of terminal alkynes, hydrosilylation of imines and alkenes, and intermolecular hydrophosphination of alkynes. Moreover, dehydrogenative double silylation of conjugated dienes was achieved with **1**.

1. Introduction

Rich chemistry has been explored in organic synthesis by using lanthanides in the last two decades.[1] Of the many lanthanide reagents, we were interested in the reducing ability of low-valent lanthanides, and studied various coupling reactions promoted by ytterbium and samarium metals,[2] and selective C–O bond cleavage of allylic, propargylic, and vinylic ethers with divalent samarocenes leading to the corresponding reactive intermediates.[3] Moreover, we found that aromatic ketones and thioketones were readily reduced to a dianion species that reacted with many electrophiles at the carbonyl-[4] and thiocarbonyl-carbon,[5] respectively. Aromatic ketimines were similarly reduced by two-electron transfer from the metals, but the resulting Ln(II)–imine complexes exhibited very different behavior from the ketone and thioketone complexes. In this article, we would like to disclose the synthesis and chemical properties of the imine complexes and their catalyst activities in some transformations of carbon–carbon and carbon–nitrogen unsaturated bonds.

2. Synthesis, structure and chemical properties of Ln(II)–imine complexes.[6]

When aromatic ketimines were treated with equimolar amounts of ytterbium metal in THF–HMPA solvent at room temperature for 4 h, the metal was mostly consumed, and a reddish-black solution was formed. On quenching the mixture with D_2O, deuterated amine **2**-d_2 was formed quantitatively (Eq. (1)). In contrast, aromatic aldimines were changed to pinacol-type products, 1,2-diaminoethanes, by treatment with Yb.[7] Similar results were obtained by using Sm metal. Deuteration of **2** suggested the formation of dianion species **1** through two-electron reduction. Fortunately, the Yb(II)–imine complex **1a** (Ln=Yb, Ar=Ph, n=3) was isolated as red–black needles in 45% yield, which is not only the first azalanthanacyclopropane, but also the first example of direct synthesis of azametallacycles by the reduction of imines with low-valent metallic reductants.



(1)

Figure 1 shows the structure of **1a** obtained by the X-ray crystallographic study.[8] The complex is five-coordinate and monomeric in contrast to the corresponding dimeric ytterbium(II)–benzophenone complex **3**.[4] The sum of the angles formed by N(10), C(2), and C(8) around C(1) is over 359°, which is larger than that of **3**, suggesting that C(1) is still sp^2-hybridized. The sp^2 character of C(1) is consistent with the Yb–C(1)–N(10) angle (87.8(10)°), which is nearly orthogonal to the C(1)–N(10) bond. The C(1)–N(10) bond distance of the imine moiety in the complex **1a** (1.43(3)Å) can be considered as a C–N single bond. In the ^1H and ^{13}C NMR spectra of **1a**, all signals of the three phenyl groups and the imine carbon are shifted to upfield and appear

Keywords: azalanthanacyclopropane; lanthanide catalyst; hydrosilylation; dehydrogenative silylation; hydrophosphination.
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doi:10.1016/j.tet.2003.06.003

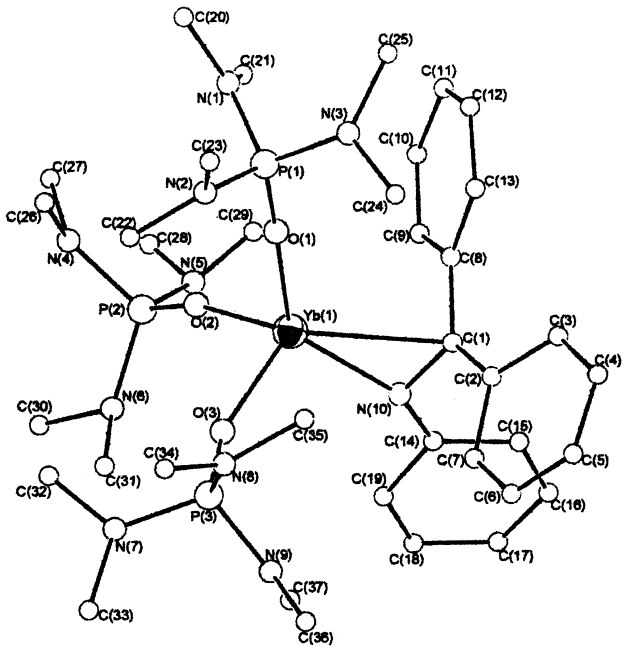
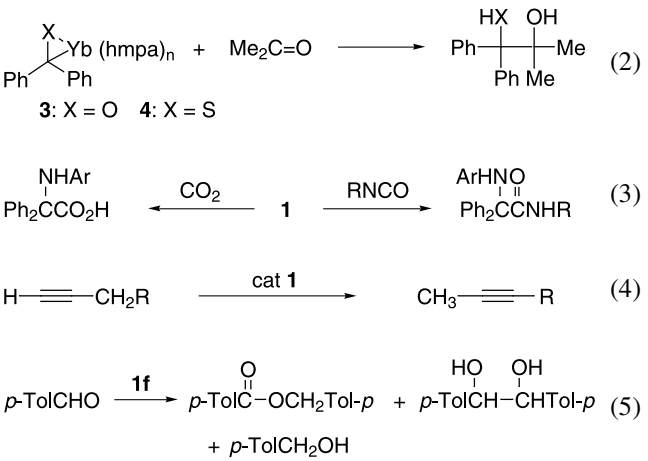


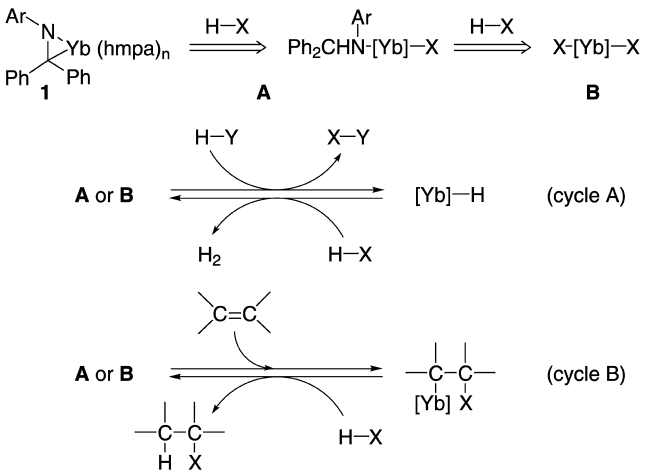
Figure 1. ORTEP drawing of **1a**.

without broadening, as expected for a divalent species.[9] In addition, rotation of the phenyl ring on the nitrogen should be ceased or very slow even in the solution, because their five protons and six carbons are independently observed.

Chemical properties of the Yb–imine complexes **1** were compared with those of the corresponding Yb–benzophenone **3**[4] and Yb–thiobenzophenone complexes **4**.[5] These complexes **1**, **3**, and **4** are extremely air- and moisture-sensitive. Exposure of **1** and **3** to air resulted in the nearly quantitative recovery of the imine and benzophenone, respectively. As mentioned above, the complexes **3** and **4** were umpoled from electrophilic to nucleophilic and, thus, they reacted with many electrophiles: for example, the reaction with acetone gave the addition products in good yields (Eq. (2)). In contrast, the imine complex **1a** abstracted α-D of acetone-d_6 to yield deuterated amine, $Ph_2CDNHPh$, after quenching with H_2O and no addition product was obtained. Exceptionally, the imine complexes **1** reacted with CO_2 and isocyanates to afford α-amino acid[10] and α-aminoacetamide derivatives[11] in high yields, respectively (Eq. (3)). The complexes **1** served as unique base catalysts in the isomerization of 1-alkynes to 2-alkynes, wherein no by-products such as allenes and dienes were contaminated, in contrast to conventional bases (Eq. (4)).[12] The basic feature of the imine complex was also observed on treatment of *p*-tolualdehyde with 10 mol% of **1f** (Ar=2,6-^{i}Pr$_2$C$_6$H$_3$, n=0) in toluene to give the Tishchenko product in 56% yield along with pinacol (6%) and alcohol (10%) (Eq. (5)). The stoichiometric reaction gave selectively the pinacol in 80% yield, indicating the moderate reducing ability of **1f**. Moreover, while the benzophenone and thiobenzophenone complexes **3** and **4** reacted with 2,6-xylyl isocyanide to yield the coupling products through insertion of the isocyanide to the C–Yb bond of **3** and **4**,[13] no reaction occurred in the case of **1**. Thus, it can be concluded that chemical properties of the imine complexes **1** are very different from those of the corresponding benzophenone and thiobenzophenone complexes **3** and **4** in spite of the similar dianion complexes: less nucleophilic and more basic.



Based on these properties of the imine complexes **1**, we intended to use them in catalytic reactions (Scheme 1). The basic character of **1** could abstract acidic protons of the substrate H–X like alkyl ligands of the well-documented trivalent lanthanocene Cp^*_2Ln–R (Cp^*=C_5Me_5) to generate the ring-opened active intermediate **A** having an amide ligand. Further reaction of **A** with the substrate as well as disproportionation of **A** would produce homoleptic intermediate **B**. Once the [Yb]–X species **A** and **B** are generated, various catalytic reactions could be expected. For example, **A** or **B** would react with H–Y to give the coupling product X–Y and [Yb]–H, and the catalyst [Yb]–X could be regenerated with hydrogen evolution (cycle A). If insertion of olefin to **A** or **B** is possible, catalytic addition of H–X to olefin would be realized (cycle B).



Scheme 1.

Recently, lanthanocene complexes have attracted much attention in organic synthesis because of their efficient and powerful catalyst activities in alkyne and alkene transformations such as hydrosilylation, hydroamination, hydrophosphination, and dimerization.[1] Compared with late transition metal catalysts, the synthesis, stocking, and handling of the lanthanocenes are, however, very difficult and, thus, their use seems to be limited actually. The imine complexes **1** can be easily and almost quantitatively

generated in situ from imines and Yb or Sm metal by stirring at room temperature. In addition, non-Cp* complexes **1** may provide different chemistry from that of the lanthanocenes, because the Cp* ligand has been known to control the selectivities of the reaction by the steric and electronic environment around the metal center. On the other hand, catalyst activity of **1** may be decreased, since coordinative unsaturation of the lanthanide metals, the origin of high activities in the case of the lanthanocene, would be diminished by the HMPA ligand and THF solvent that are necessary for solvation and stabilization of **1**. With such consideration in mind, we investigated the catalytic activities of the imine complexes **1**.[14]

3. Dehydrogenative silylation of terminal alkynes.[15]

Although alkynylsilanes are readily obtained from metal alkynides and silyl halides conventionally, the process via catalytic dehydrogenative silylation of terminal alkynes is expected to be advantageous if a methodology can be designed that avoids the stoichiometric use of a base under halogen-free conditions, particularly for the preparation of polyalkynylsilyl compounds.[16] If lanthanocene complexes are used in this process, considerable problems would arise from the side reactions such as oligomerization of hydrosilanes[17] and terminal alkynes,[18] and the coupling reaction of alkynide.[19] The imine complexes **1** were found to serve as good catalysts for the present reaction.

When triphenylsilane and 1-hexyne were successively added to a THF solution of 10 mol% of **1a**, 1-triphenylsilyl-1-hexyne (**5f**) was formed in 82% yield along with hydrogen evolution, and the starting silane and alkyne were recovered in 14 and 12% yields, respectively. But reduced products like hexene and silylhexenes were not produced. Moreover, the isomerization of 1-alkyne to 2-hexyne was suppressed in the presence of the silane.[12] The reactivity of various monohydrosilanes was tested under the same conditions (Table 1). Trialkylsilanes and alkoxysilane gave poor yields of the products, and no alkynylsilane was obtained in the reaction with trichlorosilane, which led to an untractable mixture instead. Diphenylmethylsilane and triphenylsilane gave satisfactory results (runs 5 and 6).

The activity of the imine complexes, [Yb(η^2-Ph_2-CNR)$(hmpa)_4$] (**1**), was greatly influenced by the substituent groups on the imine nitrogen. Generally, electron-withdrawing groups increased the activity, and, in contrast, electron-donating and bulky substituents decreased it. For example, the reaction of 1-hexyne with dimethylphenylsilane showed the following order of decreasing yield of the product **5d**: R=4-FC_6H_4 (**1c**) (51%)>Ph (**1a**) (31%)>4-$MeOC_6H_4$ (**1d**), 2,6-$Me_2C_6H_3$ (**1e**) (23%)>2,6-$^iPr_2C_6H_3$ (**1f**) (17%)>H (**1g**) (7%)>$SiMe_3$ (**1h**) (4%). In addition, the silylation did not take place with the imine complexes **1** prepared in the absence of HMPA.

Silylation of 1-hexyne with di- and trihydrosilanes took place similarly (Table 2). In the reaction with dihydrosilanes, product distribution was mainly determined by the ratio of 1-hexyne to the silanes. Thus, when the ratio was 1/2, monohexynylsilanes **6a** and **6c** were obtained in about five-fold excess of dihexynylsilanes **6b** and **6d**, respectively (runs 1 and 4). On the contrary, use of 2 equiv. of 1-hexyne resulted in the predominant formation of **6b** and **6d** (runs 3 and 6). In the case of phenylsilane, reaction of an equimolar mixture of the two substrates gave the alkynylsilanes **6e–g** in low yields (run 7), which was probably due to

Table 1. Silylation of 1-hexyne with monohydrosilanes

$$C_4H_9C{\equiv}CH + R_3SiH \xrightarrow[\text{THF, rt, 17 h}]{\textbf{1a}\ (10\ \text{mol\%})} C_4H_9C{\equiv}CSiR_3 \quad \textbf{5}$$

Run	Hydrosilane	Product	Yield (%)[a]
1	Et_3SiH	**5a**	7
2	$^tBuMe_2SiH$	**5b**	Trace
3	$(EtO)_3SiH$	**5c**	38
4	$PhMe_2SiH$	**5d**	31 (21)
5	Ph_2MeSiH	**5e**	76
6	Ph_3SiH	**5f**	82 (81)
7	Cl_3SiH		–[b]

[a] GC yield (isolated yield).
[b] No hexynylsilane was obtained.

Table 2. Silylation of 1-hexyne with di- and trihydrosilanes[a]

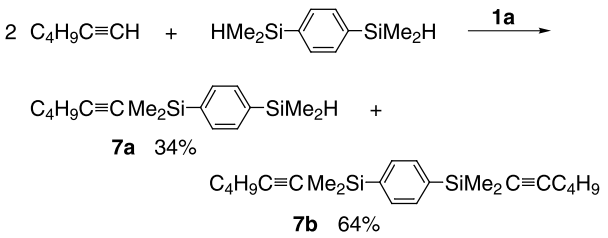
$$m\ C_4H_9C{\equiv}CH + R_xSiH_n \xrightarrow[\text{THF, rt, 17 h}]{\textbf{1a}} (C_4H_9C{\equiv}C)_{m'}SiR_xH_{n'} \quad \textbf{6}$$

Run	Hydrosilane	1-Hexyne/hydrosilane	Product and yield (%)[b]		
	Ph_2SiH_2		$C_6H_9SiHPh_2$ **6a**		$(C_6H_9)_2SiPh_2$ **6b**
1		1/2	54		11
2		1/1	42		25
3[c]		2/1	9		84
	$PhMeSiH_2$		$C_6H_9SiHMePh$ **6c**		$(C_6H_9)_2SiMePh$ **6d**
4		1/2	77		12
5		1/1	46		26
6[c]		2/1	Trace		69
	$PhSiH_3$		$C_6H_9SiH_2Ph$ **6e**	$(C_6H_9)_2SiHPh$ **65**	$(C_6H_9)_3SiPh$ **6g**
7		1/1	5	4	13
8[c]		3/1	0	Trace	60

[a] 10 mol% of **1a**, based on the silane, was used.
[b] GC yield based on the silane, except for runs 1 and 4 (based on 1-hexyne).
[c] 10 mol% of **1a**, based on 1-hexyne, was used.

dehydrogenative oligomerization of the silane.[17] However, trialkynylsilane **6g** was selectively formed in 60% yield with 3 equiv. of 1-hexyne (run 8).

Silylation of 1-hexyne with 1,4-bis(dimethylsilyl)benzene (2/1) gave monohexynyl- and dihexynylsilanes **7a** and **7b** in 34 and 64% yields, respectively (Eq. (6)). However, the reaction with 1,1,2,2-tetraphenyldisilane did not yield any hexynyldisilanes. Instead, hexynylmonosilanes **6a** and **6b** were obtained in 84 and 54% yields, respectively, together with diphenylsilane (Eq. (7)). The catalyst **1a** was proved to cleave the Si–Si bonds of the starting disilane and the expected product, 1,2-di(1-hexynyl)tetraphenyldisilane (**8**). Thus, on treatment with **1a** (10 mol%, rt, 17 h), the disilane gave a mixture of diphenylsilane (43%), tetraphenyldisilane (11%), and oligomers, and **8** prepared separately afforded a mixture of **6a** (11%), **6b** (2%), and **8** (71%).



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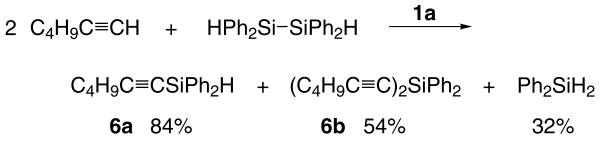
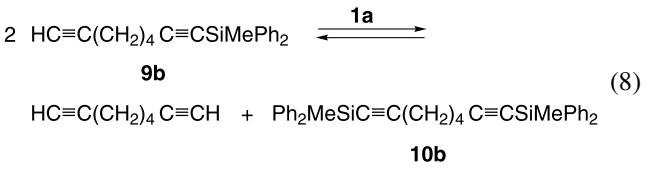


(7)

Next, bissilylation of 1,7-octadiyne with monohydrosilanes was investigated (Table 3). While monosilyl and bissilyl products **9a** and **10a** were obtained in 26 and 59% yields, respectively, by the reaction with 2 equiv. of triphenylsilane in the presence of **1a** (run 1), the reaction with diphenylmethylsilane gave the bissilyl product **10b** in low yield (run 3). Although use of a more active complex **1c′** (n=6) in lieu of **1a** and excess silanes (4 equiv.) improved the yield of **10b** up to 62% (run 4), the low yield would be attributed to slow silylation of the monosilyl compound **9b**. In fact, treatment of **9b** with an equimolar amount of diphenylmethylsilane and **1a** (10 mol%) afforded **10b** only in 14% yield together with 1,7-octadiyne (9%). Interestingly, when **9b** was treated with **1a** in the absence of the silane, a mixture of 1,7-octadiyne, **9b**, and **10b** in a ratio of 1/2/1 was formed (Eq. (8)). A mixture in the same ratio was also obtained from the diyne and **10b**. These results clearly indicate that the equilibrium is attained through a redistribution of the silyl group of alkynylsilanes catalyzed by the imine complexes **1**.



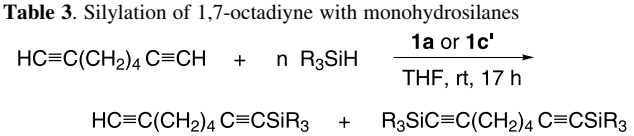
(8)

Co-oligomerization of 1,7-octadiyne and diphenylsilane with **1c** (10 mol%) took place in good conversion yields, from which oligomer **11** (M_W=2907, M_W/M_N=2.1, n≅10) was isolated in 12% yield as the higher molecular weight fraction (Eq. (9)).

(9)

The present reaction would proceed as depicted in cycle A of Scheme 1 (H–X=terminal alkyne, H–Y=hydrosilane). Of the individual steps, silanolysis of the lanthanide–alkynide bond has not been reported, and it seems to be rather difficult compared to that of lanthanide-sp^3 and sp^2 carbon bonds, which has been known as a key process for the hydrosilylation of alkenes and internal alkynes.[20] Nevertheless, the catalytic cycle would be driven by the facile elimination of hydrogen. Thus, the mono-, di-, and trihydrosilanes can be converted to the desired alkynylsilanes selectively by using **1**, including the co-oligomers of α,ω-diynes and dihydrosilanes. Dehydrogenative silylation of 1-octyne with triphenylsilane was not promoted by Cp^*_2-Sm(thf)$_2$ in hexane, which afforded a head-to-tail dimer of the alkyne, 2-hexyldec-1-en-3-yne, instead. Therefore, the success of the present silylation is attributed to the characteristics of the imine complexes **1**.

Table 3. Silylation of 1,7-octadiyne with monohydrosilanes



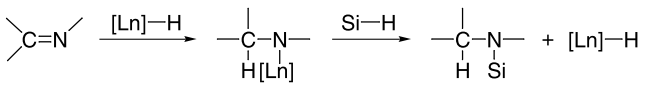
Run	Hydrosilane	Equiv. of silane	Catalyst[a]	Product and yield (%)[b]			
				9		**10**	
1	Ph_3SiH	2	**1a**	**9a**	26	**10a**	59
2		4	**1c′**		31		65
3	Ph_2MeSiH	2	**1a**	**9b**	33	**10b**	14
4[c]		4	**1c′**		26		62

[a] 20 mol% of **1**, based on the diyne, was used. **1c′**=[Yb(η^2-$Ph_2CNC_6H_4F$-4)-(hmpa)$_6$].
[b] Isolated yield.
[c] The reaction was carried out without THF.

4. Dehydrogenative silylation of amines and hydrosilylation of imines.[21]

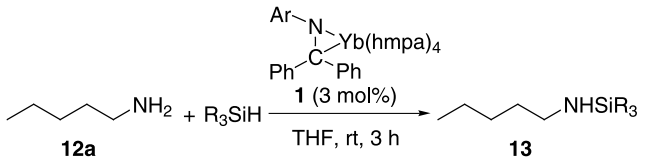
In spite of many useful reactions of alkynes and alkenes catalyzed by organolanthanide complexes, the catalytic reactions of carbonyl and imine functions have been rarely explored, because the catalysts are difficult to regenerate due to strong oxygen– and nitrogen–lanthanide bonds. Marks et al. reported the first example of lanthanide-catalyzed imine hydrogenation, in which acyclic imines were reduced under more severe conditions than olefin hydrogenation.[22] We studied the catalyst activity of the imine complexes **1** for the hydrosilylation of imines, and found that the reaction took place efficiently.

As in olefin hydrosilylation with organolathanides,[20] imine hydrosilylation would involve also two key steps: insertion of imine to the [Ln]–H bond and silanolysis of the resulting



Scheme 2.

Table 4. Dehydrogenative silylation of amylamine



Run	Imine complex (Ar)		Hydrosilane[a]	Product	Yield (%)[b]
1	**1a**	Ph	Ph_3SiH	**13a**	61
2	**1c**	4-FC_6H_4		**13a**	52
3	**1d**	4-$MeOC_6H_4$		**13a**	28
4	**1e**	2,6-$Me_2C_6H_3$		**13a**	93 (92)
5	**1f**	2,6-$^{i}Pr_2C_6H_3$		**13a**	9
6	**1g**	H		**13a**	Trace
7	**1e**		Ph_2MeSiH	**13b**	(90)
8	**1e**		$PhMe_2SiH$	**13c**	(93)
9[c]	**1e**		Et_3SiH	**13d**	(21)
10[c]	**1e**		$(EtO)_3SiH$	**13e**	27

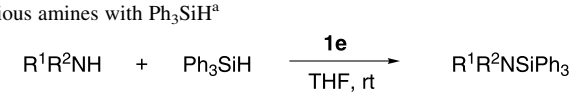
[a] **12a**/R_3SiH=1/1.
[b] GC yield (isolated yield).
[c] Carried out for 15 h.

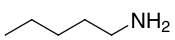
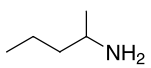
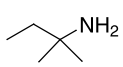
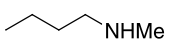
[Ln]–N bond (Scheme 2). The second step is very rare and could be difficult, compared to the reaction of olefin. Thus, we studied at first a catalytic dehydrogenative silylation of amines with **1** to confirm the second step.

As a model reaction, dehydrogenative silylation of amylamine (**12a**) was tested with various hydrosilanes and the imine complexes **1** (Table 4). When triphenylsilane and amylamine (1/1) were successively added to a solution of **1a** (3 mol%) in THF, *N*-triphenylsilylamylamine (**13a**) was produced in 61% yield along with vigorous hydrogen evolution (run 1). The complexes **1** with electron-withdrawing groups generally gave better yields of **13a** than those with electron-donating ones, as observed in the dehydrogenative silylation of terminal alkynes. However, 2,6-xylyl catalyst **1e** showed the highest activity among the imine complexes tested, suggesting that a steric factor can play also an important role in the reaction (run 4). With respect to the reactivity of hydrosilanes, those with a phenyl substituent gave the aminosilanes **13** in over 90% yields (runs 4, 7, and 8), whereas trialkyl and trialkoxysilanes decreased the yield to about 20% (runs 9 and 10).

Dehydrogenative silylation of various primary and secondary amines with Ph_3SiH was studied by using the imine complex **1e** (Table 5). Of the primary amines, *n*- and *sec*-alkylamines **12a** and **12b** were readily converted to **13a** and **13f** in 93 and 97% yields, respectively (runs 1 and 2). Although reaction of *tert*-alkylamine **12c** was very slow (run 3), the product **13g** was formed in 81% yield by

Table 5. Dehydrogenative silylation of various amines with Ph_3SiH[a]

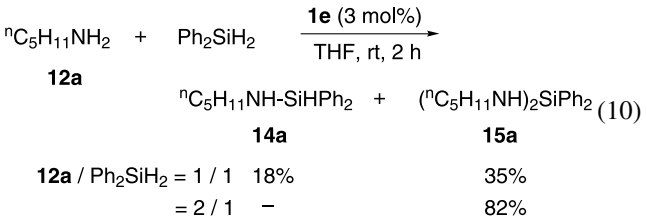


Run		Amine	**1e** (mol%)	Time (h)	Product	Yield (%)[b]
1	**12a**		3	2	**13a**	93
2	**12b**		3	2	**13f**	97
3	**12c**		3	20	**13g**	16
4			10	192	**13g**	81
5	**12d**	$PhNH_2$	10	20	**13h**	56
6	**12e**		10	5	**13i**	95
7	**12f**	BnNHMe	10	2	**13j**	89
8	**12g**		10	2	**13k**	79
9	**12h**	PhNHMe	10	20	No reaction	

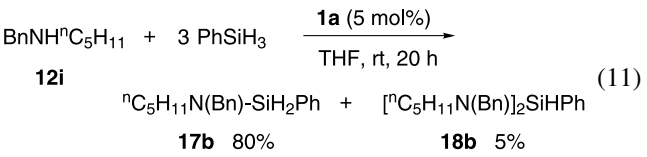
[a] **12**/Ph_3SiH=1/1.
[b] GC yield.

increasing the catalyst amount (10 mol%) and prolonging reaction time (run 4). Secondary amines **12e**–**12g** were silylated similarly in good yields (runs 6–8). In contrast, aniline was converted to the aminosilane **13h** in lower yield (56%) than alkylamines (run 5), and no reaction occurred with *N*-methylaniline (run 9).

Dehydrogenative silylation of amines could be performed with di- and trihydrolsilanes, giving rise to aminosilanes and diaminosilanes (Eqs. (10) and (11)). In the reaction of amylamine (**12a**) with diphenylsilane, when the ratio of **12a**/Ph_2SiH_2 was unity, aminosilane **14a** and diaminosilane **15a** were obtained in 18 and 35% yields, respectively. Use of 2 equiv. of **12a** resulted in the selective formation of **15a**. *N*-Benzylamylamine (**12i**) was silylated with phenylsilane (3 equiv.) in the presence of the imine complex **1a** to afford aminosilane **17b** in 80% yield together with a minor diaminosilane **18b**.

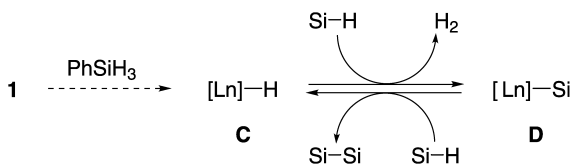


(10)



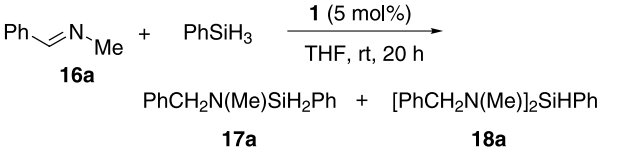
(11)

Since it was confirmed that silanolysis of lanthanide amide, i.e. the second step of imine hydrosilylation (Scheme 2), took place readily, we tried to generate a hydride species from the imine complex **1** for the first step. Fortunately, phenylsilane was found to oligomerize with hydrogen evolution in the presence of **1**.[23] It has been reported that dehydrogenative oligomerization of the silane catalyzed by lanthanocene complexes proceeds through a hydride and silyl species.[17] Therefore, similar intermediates could be generated in the present system as shown in Scheme 3, and if the oligomerization is suppressed, the hydride species **C** can be available for the imine hydrosilylation.



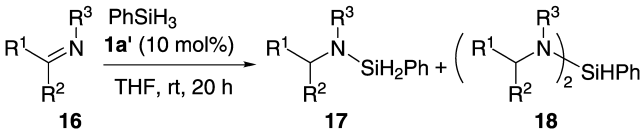
Scheme 3.

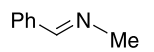
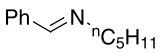
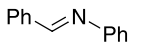
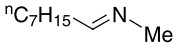
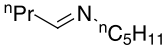
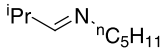
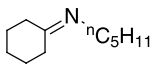
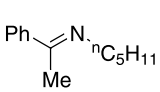
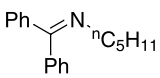
Reaction of benzylidenemethylamine (**16a**) with an equimolar amount of phenylsilane in the presence of **1a** (5 mol%) gave aminosilane **17a** and diaminosilane **18a** in 7 and 65% yields based on **16a** (7 and 32% yields based on the silane), respectively, along with a very small amount of the oligomer (Eq. (12)). Of course, no reaction took place in the absence of **1a**. Substitution of **1a** with **1c** caused an increase of the oligomer, though the products **17a** and **18a** were obtained in similar yields. The imine complex **1e**, the most active catalyst in the dehydrogenative silylation of amines, did not promote any reaction. In addition, triphenylsilane and diphenylsilane could not be used for the present hydrosilylation, probably because a hydride species was not generated effectively in the reaction mixture.



(12)

Table 6. Hydrosilylation of imines with $PhSiH_3$[a]

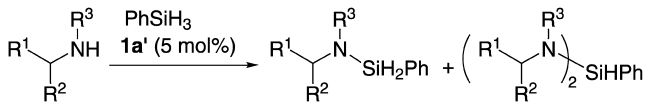


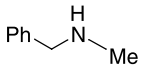
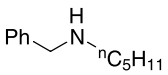
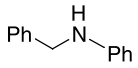
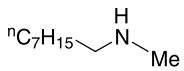
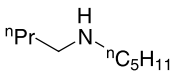
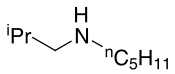
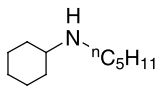
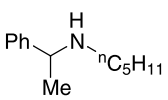
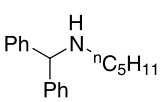
Run		Imine		Product and yield (%)[b]			
				17		**18**	
1	**16a**		**17a**	2	**18a**	95
2	**16b**		**17b**	52	**18b**	35
3	**16c**		**17c**	15	**18c**	47
4	**16d**		**17d**	3	**18d**	89
5	**16e**		**17e**	21	**18e**	64
6	**16f**		**17f**	28	**18f**	43
7	**16g**		**17g**	56	**18g**	0
8	**16h**		**17h**	3	**18h**	17
9	**16i**		No reaction			

[a] **16**/$PhSiH_3$=1/1. **1a'**=[Yb(η²-Ph_2CNPh)(hmpa)$_6$].
[b] GC yield based on **16**.

Hydrosilylation of aldimines and ketimines with phenylsilane was investigated by using the imine complex **1a′** (n=6) (Table 6). Aldimines **16a**–**16f** were converted to aminosilanes **17** and diaminosilanes **18** in good yields (runs 1–6). The diaminosilanes **18** were selectively obtained from *N*-methylimines (runs 1 and 4), whereas the ratio of **17**/**18** was increased in the reaction of *N*-pentylimines (runs 2, 5, and 6). Ketimines **16g**–**16i** were less reactive than aldimines (runs 7–9). While hydrosilylation of ketimine **16g** produced aminosilane **17g** in 56% yield as the sole product, little or no product was obtained in the reaction of **16h** and **16i**.

Table 7. Dehydrogenative silylation of amines with $PhSiH_3$[a]



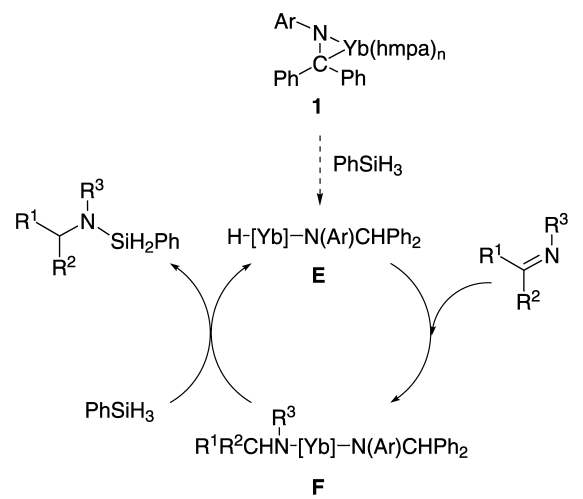
Run		Amine	Product and yield (%)[b]			
			17		**18**	
1	**12f**		**17a**	1	**18a**	93
2	**12i**		**17b**	2	**18b**	86
3	**12j**		**17c**	15	**18c**	47
4	**12k**		**17d**	Trace	**18d**	83
5	**12l**		**17e**	34	**18e**	57
6	**12m**		**17f**	87	**18f**	Trace
7	**12n**		**17g**	38	**18g**	0
8	**12o**		**17h**	7	**18h**	11
9	**12p**		No reaction			

[a] Conditions: **12**/$PhSiH_3$=1/1, THF, 20 h, −35°C (runs 1–5) or rt (runs 6–9).
[b] GC yield based on **12**.

For comparison of hydrosilylation of imines with dehydrogenative silylation of amines, amines corresponding to the imines listed in Table 6 were treated with equimolar amounts of phenylsilane in the presence of the imine complex **1a′** (5 mol%), and these results are summarized in Table 7. As can be seen in Tables 6 and 7, the two reactions are in good agreement as regards product selectivities and yields, except for runs 2 and 6. These results indicate that the two reactions proceed through the same intermediates.

Dehydrogenative silylation of amine can be explained as shown in cycle A of Scheme 1 (H–X=HNR_2, H–Y=hydrosilane), wherein the heteroleptic diamides **A** would be an active species and silanolysis takes place only at one amide moiety derived from the substrate amine. If homoleptic diamide **B** participates in the reaction, all imine complexes **1** bearing a different imine ligand are likely to exhibit similar catalyst activities, contrary to the results in Table 4. Moreover, no aminosilanes derived from the imine ligand were detected in any of the reactions. A possible catalytic cycle for the imine hydrosilylation is outlined in Scheme 4. The cycle is essentially similar to the dehydrogenative silylation of amines in that they both include hydride **E** and diamide **F** as common intermediates. The only difference between the two is the process to form diamide **F**. In the hydrosilylation, insertion of imine to hydride species **E**, which is generated in situ by the reaction of **1** with phenylsilane, affords diamide **F**. Subsequent silanolysis of one Yb–N bond of **F** with phenylsilane yields the product and **E**.

The aminosilanes, particularly those derived from the less crowded imine, would be more reactive than phenylsilane in the second step, probably because metal coordination at their nitrogen atom facilitates this process. Therefore,

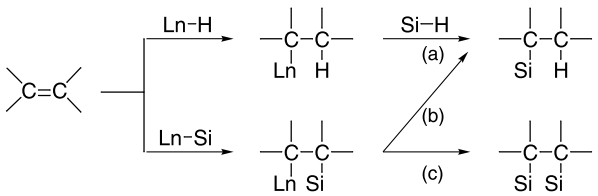


Scheme 4.

diaminosilanes could be obtained as the major product in most of the reactions. Decreased reactivity of ketimines would be attributed to the lower efficiency in the silanolysis step, since substituents on the amide moieties are secondary hydrocarbons. In fact, dehydrogenative silylation of **12n–p** gave lower yields of the products than that of the amines corresponding to aldimines (runs 7–9 versus 1–6, Table 7). Although it has been known that the stoichiometric reaction of imine with lanthanocene hydrides proceeds via C–H activation rather than imine insertion to the Ln–H bond,[22,24] the first lanthanide-catalyzed hydrosilylation of imine is realized with the imine complexes **1**.

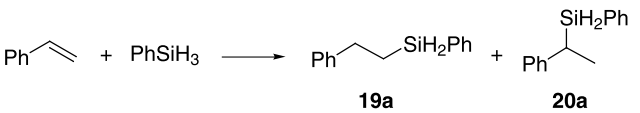
5. Hydrosilylation of olefins and dehydrogenative double silylation of conjugated dienes.[25]

Lanthanocene-catalyzed hydrosilylation has been proved to proceed via insertion of olefins to lanthanide hydride, followed by σ-bond metathesis as depicted in Scheme 5 (path a).[26] In contrast to late transition metal catalysts, there is no precedent for the process initiated by a lanthanide silyl species (path b). However, if the silyl species once added to olefins, this process may lead to double silylation, instead of hydrosilylation, owing to the polarity of hydrosilane in the σ-bond metathesis (path c). For synthetic application of the lanthanide–imine complexes **1**, we studied their catalyst activities in the hydrosilylation of olefins and conjugated dienes.



Scheme 5.

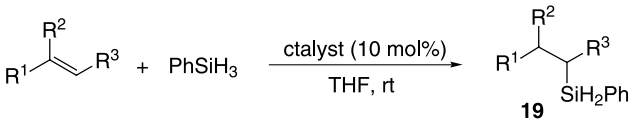
When styrene was treated with an equimolar amount of $PhSiH_3$ in the presence of **1a** in THF at −35°C for 20 h, 2-(phenylsilyl)ethylbenzene (**19a**) was formed in 85% yield together with polyphenylsilane after evolution of hydrogen, but the other regioisomer **20a**, a major product by lanthanocene catalysts,[20] was not detected (Eq. (13)).

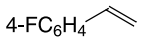
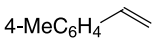
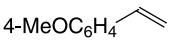
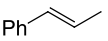
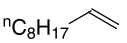


(13)

The reaction at room temperature gave **19a** in lower yield (33%) probably because of the predominant oligomerization of the silane. No noticeable reaction was observed with SmI_2 (10 mol%) and without the catalyst **1a** even under refluxing conditions. Results on the hydrosilylation by using **1a**′ (n=6) are summarized in Table 8 (Method A). Phenylsilane could be substituted by diphenylsilane to afford 2-(diphenylsilyl)ethylbenzene (**19b**) in 76% yield (run 2), but triphenylsilane was inactive. In contrast to the reaction of styrene and 4-fluorostyrene (runs 1–3), this method was not applicable to electron-rich and substituted styrenes nor to α-olefins (runs 4–8).

Table 8. Hydrosilylation of olefins



Run	Olefin	Product and yield (%)[a]		
			Method A[b]	Method B[c]
1		**19a**	85[d]	95
2		**19b**[e]	76	90
3		**19c**	71	94
4		**19d**	10	88
5		**19e**	0	35
6		**19f**	26[f]	95
7		**19g**	0[f]	95
8		**19h**	0[f]	79[g]

[a] GC yield.
[b] Catalyst: **1a**′ (n=6), silane/olefin=1, 20 h.
[c] Catalyst: **21a**, silane/olefin=2, 3 h.
[d] Carried out with **1a** (5 mol%), at −35°C.
[e] Ph_2SiH_2 was used instead of $PhSiH_3$.
[f] 50°C.
[g] Carried out with **21b** at 50°C for 48 h.

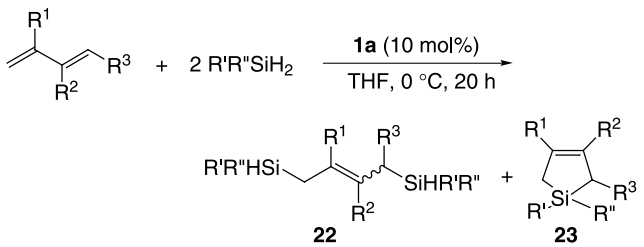
The limitation was significantly improved by addition of equimolar amounts of primary and secondary amines, particularly diphenylamine, to **1a**. Thus, the reaction of styrene with phenylsilane by using **1a** and Ph_2NH (catalyst **21a**) resulted in reduction of the reaction time and increase of the yield of **19a** to 95%. As can be seen in Table 8 (Method B), all styrene derivatives, including α- and β-methylstyrene, were converted to the expected products **19** in good yields, except for 4-methoxystyrene (run 5). In the reaction of 1-decene, the hydrosilylation did not occur with **21a**, but it could be conducted with [Sm(η^2-Ph_2-CNPh)(hmpa)$_0$] (**1b**) and Ph_2NH (1/1, catalyst **21b**) to afford the product **19h** in 79% yield (run 8).

Various features of the reaction were elucidated through the improvement mentioned above. With respect to the catalyst activity of **21**, Yb was superior to Sm for the hydrosilylation of styrene, but the order was reversed for 1-decene. The

HMPA ligand showed the promotive and inhibitory effect in the reaction of styrene and 1-decene, respectively. Moreover, regiochemistry in the reaction of styrene depended on the ligand: linear silane **19a** with HMPA and branched silane **20a** without the ligand were formed exclusively. For example, **20a** was obtained in 72% yield as a single regioisomer with **1a** (n=0) and PhMeNH (1/1).

Next, hydrosilylation of conjugated dienes was investigated (Table 9). The reaction of isoprene with phenylsilane (3 equiv.) in the presence of **1a** at 0°C for 20 h in THF gave 1,4-bis(phenylsilyl)-2-methyl-2-butene (**22a**) and 1-phenyl-3-methyl-3-silacyclopentene (**23a**) in 61 and 13% yields, respectively (run 1). The normally expected 1,4- and 1,2-hydrosilylation products were not detected at all. Use of equimolar or less amounts of the silane only caused a decrease of **22a** (ca. 20%) with similar yields of **23a**. The reaction with diphenylsilane also produced the products **22b** and **23b** in 57 and 16% yields, respectively (run 2). Similarly, the dehydrogenative double silylation took place in the reaction of 2-octyl- and 2,3-dimethylbutadiene (runs 3 and 4), wherein the silacyclopentene **23c** was formed as a major product in the former case. Unfortunately, alkyl substituents on the terminal position seemed to significantly decrease the reaction efficiency as shown by 1,3-pentadiene (run 5). All products **22** were preferentially obtained as (*E*)-isomers. In addition, similar or somewhat better results were obtained with **21a**.

Table 9. Dehydrogenative double silylation of conjugated dienes

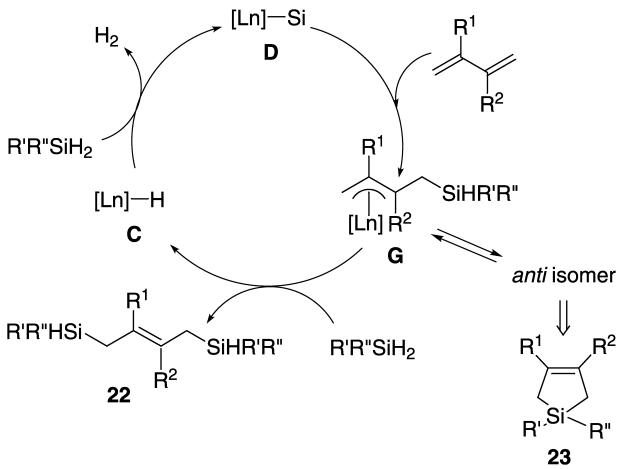


Run	Diene	Hydrosilane[a]	Product, yield (%)[b] and *E*/*Z* ratio			
			22		**23**	
1		$PhSiH_3$	**22a**	61 (93/7)	**23a**	13
2[c]		Ph_2SiH_2	**22b**	57 (93/7)	**23b**	16
3	C_8H_{17}	$PhSiH_3$	**22c**	18 (97/3)	**23c**	41
4		$PhSiH_3$	**22d**	60 (96/4)	**23d**	9
5		$PhSiH_3$	**22e**	19 (71/29)	**23e**	0

[a] Silane/diene=3.
[b] GC yield based on the diene.
[c] Carried out at rt.

These results clearly indicate that the reaction mode is completely different between olefins and conjugated dienes. As mentioned above, lanthanide hydride **C** and silyl species **D** would be generated in the reaction mixture by partial oligomerization of the silanes (Scheme 3). In the case of olefins, it is likely that the reaction was initiated by olefin insertion to the hydride species **C**, and followed by silylation to give the products **19** and **20** (path a in Scheme 5). This mechanism can explain the regiocontrol by the HMPA ligand observed for the reaction of styrene. That is, the [Yb] metal was introduced to the less crowded β-carbon to yield the linear products **19** in the presence of HMPA, and, in contrast, the metal was delivered to the α-carbon for π-coordination of the Ph ring in the absence of the ligand, leading to the blanched products **20**. If styrene inserted to the silyl species **D**, a reverse ligand effect should be observed.

On the other hand, the dehydrogenative double silylation would be initiated by the reaction of diene with the silyl species **D** to yield allylic lanthanide **G** (Scheme 6). Silylation of the *syn* isomer of **G** gave the product **22** and the hydride **C**, and the latter was converted finally to **D** by the reaction with another molecule of the silane with hydrogen evolution. Similarly, intramolecular silylation of the *anti* isomer of **G** would yield the silacyclopentene **23**. The reason for the change in the reaction mode by the two substrates still remains unclear. Alternatively, the two reactions may be explained by the addition of a silyl radical, followed by H abstraction from Si–H for olefin and Si abstraction for diene. However, this process seems less likely, because a radical reaction of dienes with hydrosilane was reported to yield hydrosilylation products,[27] and in fact, **22** and **23** were not formed by the reaction with AIBN.



Scheme 6.

Although some ambiguous points still remain regarding the reaction mechanism, double silylation of conjugated dienes with hydrosilane, not with disilane, has been uniquely catalyzed by the imine complexes **1**, in contrast to the reaction with lanthanocenes that were reported to produce 1,4-hydrosilylation products.[28]

6. Intermolecular hydrophosphination of alkynes and related carbon–carbon multiple bonds.[29]

Hydrophosphorylation and hydrophosphinylation of alkynes via P–H bond activation of pentavalent phosphorous compounds with Pt and Pd catalysts have been extensively investigated in the last decade.[30] However, the reaction of trivalent phosphines has been known to be difficult generally, though a successful example was reported very recently.[31] Besides the group 10 catalysts, trivalent lanthanocenes were reported to exhibit high catalyst activities in the intramolecular hydrophosphination of phosphino-alkynes and alkenes.[32] We have independently found that the intermolecular hydrophosphination of alkynes is effectively catalyzed by the lanthanide–imine complexes **1**.

When diphenylphosphine and equimolar amounts of 1-phenyl-1-propyne (**24c**) were successively added to a THF solution of **1a′** (n=6, 5 mol%) at room temperature, 1-phenyl-2-diphenylphosphino-1-propene (**25c′**) was quantitatively formed within 5 min (E/Z=80/20). The alkenylphosphine **25c′** was isolated in decreased yield (80%) because of a partial oxidation to the corresponding alkenylphosphine oxide **25c** during the usual workup and column chromatography. Thus, it was convenient to isolate the reaction product as the phosphine oxide **25c** after oxidation with H_2O_2. No reaction took place with $Yb(O^iPr)_3$ and SmI_2 (10 mol%, rt, 12 h) nor without the catalyst. Moreover, many products, including polymeric materials, were formed with ^{n}BuLi (10 mol%, rt, 30 min).

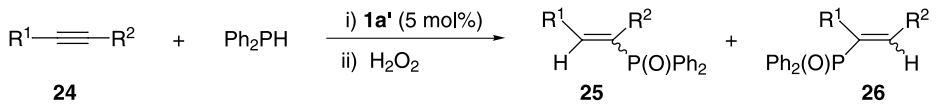
Results on the reaction of various alkynes **24** are summarized in Table 10. The expected products **25** and **26** were obtained in high yields under mild conditions, except for aliphatic internal alkynes **24e–f**, in which the reaction should be heated at 80°C without the solvent (runs 5 and 6). With respect to regiochemistry, a Ph_2P group was introduced into the opposite side to the aryl substituents of the aromatic alkynes exclusively (runs 2–4), and into the less hindered side of the aliphatic alkynes (runs 6–8). Stereochemistry of the products **25** and **26** was dependent on the substrates, i.e. (*E*)- and (*Z*)-isomers were preferentially formed from the aromatic and aliphatic alkynes, respectively. In contrast to these results, direct synthesis of **25** and **26** by the reaction with $Ph_2P(O)H$ was unsuccessful, wherein the catalyst **1** was immediately oxidized with the phosphine oxide to give some trivalent lanthanide species and Ph_2PH.

It has been reported that Ph_2PH reacts with alkynes under radical conditions to yield normally (*E*)-diphenylphosphinoalkenes as the primary products, which isomerize to (*Z*)-isomers finally.[33] Thus, the reaction with AIBN (10 mol%, THF or neat, 80–85°C, without oxidative workup) was performed for comparison with the imine complex **1**. The radical reaction gave the alkenylphosphine **25′** as single regioisomers in lower yields than the latter; particularly, no or minimal products were formed in the reaction of **24b** and **24g**. On monitoring by ^{1}H and ^{31}P NMR, (*Z*)-isomers were preferentially formed irrespective of aromatic and aliphatic alkynes **24**, even at an early stage of the reaction, and this selectivity was not reversed, though decreased, after longer reaction period. These results clearly indicate that the hydrophosphination with **1** is different from the radical reaction in regard to regio- and stereochemistry.

The present hydrophosphination was applied to other carbon–carbon multiple bonds to examine its scope and limitations (Table 11). The reaction of 7,9-hexadecadiyne with Ph_2PH (2 equiv.) gave bis(diphenylphosphinyl)diene **27a** in 51% yield as a single regio- and stereoisomer after the oxidative workup. In contrast, 2,2,7,7-tetramethyl-3,5-octadiyne was converted to a mixture of diene **27b** and allene **28b** in 12 and 71% yields, respectively, under similar conditions. An attempt to get monophosphinylated products with equimolar amounts of the phosphine was unsuccessful because of rapid oligomerization of the diynes even at −78°C. Although the reaction of aliphatic alkenes did not occur, α- and β-methylstyrene afforded **29a** and **29b** in good yields. In the reaction of isoprene, the Ph_2P group was selectively delivered to the less hindered side of the two terminal carbons to give 1,4- and 1,2-addition products **30** and **31** in 64 and 35% yields, respectively. Two olefinic phosphine oxides **32** and **33** were formed in 79 and 13% yields, respectively, by the reaction of cyclohexylallene, but 1-cyclohexyl-3-diphenylphosphinyl-1-propene was not detected in contrast to the radical reaction.[33]

The reaction would proceed as shown in cycle B of Scheme 1 (H–X=HPPh$_2$), in which the active species could

Table 10. Hydrophosphination of alkynes with diphenylphosphine

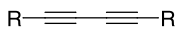
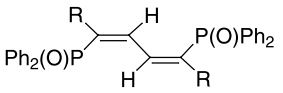
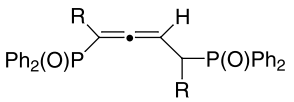
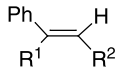
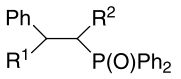
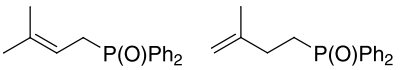
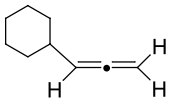
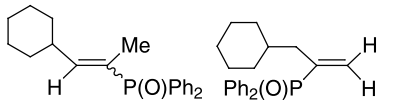


24 **25** **26**

Run	Alkyne	R^1	R^2	Conditions	**25**	Yield[a] (%)	*E*/*Z*	**26**	Yield[a] (%)
1	**24a**	Ph	Ph	THF, rt, 5 min	**25a**	Quant	100/0	–	
2	**24b**	Ph	$SiMe_3$	THF, rt, 4 h	**25b**	Quant	100/0	**26b**	0
3	**24c**	Ph	Me	THF, rt, 5 min	**25c**	Quant	80/20	**26c**	0
4	**24d**	Ph	H	THF, rt, 5 min	**25d**	Quant	76/24	**26d**	0
5	**24e**	^{n}Pr	^{n}Pr	Neat, 80°C, 6 h[b]	**25e**	95	0/100	–	
6	**24f**	^{n}Pen	Me	Neat, 80°C, 6 h[b]	**25f**	61	0/100	**26f**[c]	28
7	**24g**	^{t}Bu	H	THF, rt, 3 h[b]	**25g**	62	0/100	**26g**	10
8	**24h**	^{n}Hex	H	THF, rt, 5 min	**25h**	52	27/73	**26h**	34

[a] GC yield.
[b] 10 mol% of **1a′** was used.
[c] *E*/*Z*=21/79.

Table 11. Hydrophosphination of various C–C multiple bonds with diphenyphosphine[a]

Substrate	Conditions	Product and yield[b] (%)
 a: R = ^{n}Hex b: R = ^{t}Bu	−35°C, 3 h[c]	 **27a** (51), **27b** (12)
		 **28a** (0), **28b** (71)
 a: R^1 = Me, R^2 = H b: R^1 = H, R^2 = Me	rt, 4 h	 **29a** 85, **29b** 95
	0°C, 15 h[d]	 **30** 64 **31** 35
	rt, 30 min	 **32** 79 (E / Z = 71 / 29) **33** 13

[a] All reactions were carried out with 10 mol% of **1a**′ (n=6) in THF and the products were isolated after oxidation with H_2O_2.
[b] GC yield (isolated yield).
[c] 2 equiv. of Ph_2PH were used.
[d] 2 equiv. of isoprene were used.

be diphosphido complex **B**. In fact, $Yb(PPh_2)_2(hmpa)_n$ was isolated by treatment of **1a** with 2 equiv. of Ph_2PH, and the reaction by using this complex gave similar results to **1a**. Stereochemistry of the hydrophosphination would not be determined by isomerization of the products, because their *E*/*Z* ratio was nearly independent of the reaction time. Accordingly, (*Z*)-selectivity for the reaction of aliphatic alkynes seems to be somewhat curious in the light of syn addition, but this point is obscure at present. Thus, a new catalytic intermolecular hydrophosphination of alkynes has been achieved with the Yb–imine complexes **1**, giving rise to alkenylphosphines or phosphine oxides after oxidative workup in high yields under mild conditions. This method is also applicable to a wide range of carbon–carbon multiple bonds such as conjugated diynes and dienes, allenes, and styrene derivatives.

7. Conclusion

Aromatic ketimines were readily reduced with ytterbium and samarium metals to give azalanthanacyclopropanes, $[Ln(\eta^2\text{-}Ph_2CNAr)(hmpa)_n]$ (**1**) in quantitative yields, wherein the metals changed to divalent. Their structures were characterized by X-ray and NMR analyses. These dianion complexes **1** are less nucleophilic and more basic than the corresponding Ln–benzophenone and thiobenzophenone analogs. They can abstract acidic protons of the substrates H–X such as terminal alkynes, amines, and diphenylphosphine through ring-opening to afford reactive species [Ln]–X, which initiate various catalytic reactions. Thus, in the presence of hydrosilane, dehydrogenative silylation of terminal alkynes and amines has been accomplished. Intermolecular hydrophosphination of alkynes also proceeded catalytically via lanthanide diphosphido intermediate. Moreover, with active hydrosilane like $PhSiH_3$, the imine complexes **1** exhibited good catalyst activities for hydrosilylation of olefins and aldimines. In the reaction of conjugated dienes, unusual dehydrogenative double silylation occurred to yield 1,4-bissilyl-2-butene derivatives. These results are very different from those with lanthanocenes, demonstrating the unique reactivities of **1**.

Therefore, combined with simple preparation, the Ln–imine complexes **1** have potential utility in organic synthesis.

8. Experimental

8.1. Synthesis and isolation of the Yb(II)–imine complex (1a)

Ytterbium metal (40 mesh, 346 mg, 2 mmol) and *N*-diphenylmethylideneaniline (515 mg, 2 mmol) were placed in a 20-mL Schlenk tube under argon. THF (8 mL), HMPA (2 mL), and methyl iodide (2 μL, activator of the metal) were successively added into the tube, and the mixture was stirred for 4 h at room temperature to give a red–black suspension. The suspension was moved into another Schlenk tube to remove a small amount of metallic residue. A homogeneous solution was obtained by heating the suspension under reflux, which was allowed to stand at room temperature to precipitate red–black needles. The complex **1a** (860 mg, 45%) was isolated by removing the solvent, followed by drying in vacuo. Crystal data of **1a** have been previously reported,[6] and its selected bond lengths, angles, and NMR data are shown in Refs. 8 and 9, respectively.

8.2. General procedure for the reactions catalyzed by the Yb–imine complexes 1

Generally, the imine complex **1** was generated in situ from Yb metal (0.2 mmol), imine (0.2 mmol), and HMPA (0.8 mmol) in THF (1 mL) as above. Then, hydrosilane (2 mmol) or diphenylphosphine (2 mmol) and the substrate (2 mmol) such as alkyne, alkene, diene, amine, and imine were added successively to the mixture. In the reaction with phenylsilane, a mixture of the silane and the substrate in THF (0.5 mL) was added to the Yb–imine catalyst **1**, because its oligomerization commenced immediately. The reaction was carried out under appropriate conditions indicated in the Tables with monitoring by GC. After completion of the reaction, an internal standard like tridecane was added to the mixture and the reaction was quenched with 2 M HCl and water. The organic layer was extracted with ether, washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The products were purified by column chromatography on silica gel. The unstable products such as aminosilanes were isolated by direct column chromatography without an aqueous workup.

8.2.1. 1,4-Bis(phenylsilyl)-2-methyl-2-butene (22a). Isolated as a mixture of (*E*)- and (*Z*)-isomer (93/7); colorless oil; IR (neat) 1653, 1157, 1117, 876, 841 cm^{-1}; MS *m/z* 282 (M^+), 175 ($M^+-PhSiH_2$), 107 ($PhSiH_2^+$), 105 ($PhSi^+$); ^1H NMR ($CDCl_3$) δ (*E*)-isomer (major) 1.57 (3H, s), 1.79 (2H, dt, *J*=7.8, 3.6 Hz), 1.87 (2H, t, *J*=3.9 Hz), 4.24 (2H, t, *J*=3.6 Hz), 4.31 (2H, t, *J*=3.9 Hz), 5.17 (1H, t, *J*=7.8 Hz), 7.31–7.40 (6H, m), 7.52–7.57 (4H, m); (*Z*)-isomer (minor) (clearly assignable peaks) 1.52 (3H, s), 1.69 (2H, m), 1.82 (2H, t, *J*=4.0 Hz); ^{13}C NMR ($CDCl_3$) δ (*E*)-isomer (major) 12.3, 17.7, 23.1, 118.4, 127.9, 129.6, 130.9, 132.4, 135.2; (*Z*)-isomer (minor) (clearly assignable peaks) 12.6, 16.5, 25.3, 117.3. Anal. calcd for $C_{17}H_{22}Si_2$: C, 72.27; H, 7.85. Found: C, 72.31; H, 7.93.

8.2.2. 1,4-Bis(diphenylsilyl)-2-methyl-2-butene (22b). Isolated as a mixture of (*E*)- and (*Z*)-isomer (93/7); colorless oil; IR (neat) 1157, 1145, 802 cm^{-1}; MS *m/z* 434 (M^+), 252 (M^+-Ph_2Si), 183 (Ph_2SiH^+); ^1H NMR ($CDCl_3$) δ (*E*)-isomer (major) 1.46 (3H, s), 1.98 (2H, dd, *J*=8.2, 3.5 Hz), 2.07 (2H, d, *J*=3.5 Hz), 4.74 (1H, t, *J*=3.5 Hz), 4.84 (1H, t, *J*=3.5 Hz), 5.20 (1H, t, *J*=8.2 Hz), 7.30–7.58 (20H, m); (*Z*)-isomer (minor) (clearly assignable peaks) 1.58 (3H, s), 1.83 (2H, dd, *J*=8.0, 3.6 Hz), 4.77 (1H, t, *J*=3.6 Hz), 4.89 (1H, t, *J*=3.6 Hz), 5.14 (1H, t, *J*=8.0 Hz); ^{13}C NMR ($CDCl_3$) δ (*E*)-isomer (major) 14.4, 18.3, 25.5, 118.4, 127.9, 129.5, 130.7, 134.3, 134.5, 135.1, 135.2; (*Z*)-isomer (minor) (clearly assignable peaks) 13.8, 18.6, 25.7; HRMS calcd for $C_{29}H_{30}Si_2$ (M^+) 434.1887, found 434.1841.

8.2.3. 1-Phenylsilyl-3-phenylsilylmethyl-2-undecene (22c). Isolated as a mixture of (*E*)- and (*Z*)-isomer (97/3); colorless oil; IR (neat) 1115, 876, 841 cm^{-1}; MS *m/z* 380 (M^+), 107 ($PhSiH_2^+$); ^1H NMR ($CDCl_3$) δ (*E*)-isomer (major) 0.87 (3H, t, *J*=7.1 Hz), 1.15–1.44 (12H, m), 1.78 (2H, dt, *J*=8.2, 3.6 Hz), 1.84 (2H, t, *J*=3.6 Hz), 1.94 (2H, t, *J*=7.6 Hz), 4.22 (2H, t, *J*=3.6 Hz), 4.28 (2H, t, *J*=3.6 Hz), 5.14 (1H, br t, *J*=8.2 Hz), 7.31–7.39 (6H, m), 7.51–7.57 (4H, m); (*Z*)-isomer (minor) (clearly assignable peaks) 1.72 (2H, dt, *J*=8.0, 3.7 Hz), 4.24 (2H, t, *J*=3.7 Hz); ^{13}C NMR ($CDCl_3$) δ (*E*)-isomer (major) 12.1, 14.1, 20.2, 22.7, 28.0, 29.3, 29.5, 29.7, 31.4, 31.9, 118.7, 127.9, 129.5, 129.6, 132.4, 132.7, 135.16, 135.22, 135.5.

8.2.4. 1,4-Bis(phenylsilyl)-2,3-dimethyl-2-butene (22d). Isolated as a mixture of (*E*)- and (*Z*)-isomer (96/4); colorless oil; IR (neat) 1169, 1115, 868, 845 cm^{-1}; MS *m/z* 296 (M^+), 107 ($PhSiH_2^+$); ^1H NMR ($CDCl_3$) δ (*E*)-isomer (major) 1.56 (6H, s), 1.87 (4H, t, *J*=3.9 Hz), 4.28 (4H, t, *J*=3.9 Hz), 7.31–7.40 (6H, m), 7.55–7.56 (4H, m); (*Z*)-isomer (minor) (clearly assignable peaks) 1.54 (6H, s), 1.80 (4H, t, *J*=3.9 Hz), 4.24 (4H, *J*=3.9 Hz); ^{13}C NMR ($CDCl_3$) δ (*E*)-isomer (major) 19.4, 20.4, 122.7, 127.9, 129.6, 132.9, 135.2. Anal. calcd for $C_{18}H_{24}Si_2$: C, 72.90; H, 8.16. Found: C, 72.89; H, 8.23.

8.2.5. 1,4-Bis(phenylsilyl)-2-pentene (22e). Isolated as a mixture of (*E*)- and (*Z*)-isomer (71/29); colorless oil; IR (neat) 1119, 934, 837 cm^{-1}; MS *m/z* 282 (M^+), 107 ($PhSiH_2^+$); ^1H NMR ($CDCl_3$) δ (*E*)-isomer (major) 1.13 (3H, d, *J*=7.3 Hz), 1.83 (2H, m), 2.00 (1H, m), 4.17 (2H, d, *J*=2.9 Hz), 4.26 (2H, t, *J*=3.8 Hz), 5.34 (1H, dt, *J*=15.6, 7.7 Hz), 5.45 (1H, dd, *J*=15.6, 7.7 Hz), 7.31–7.40 (6H, m), 7.50–7.57 (4H, m); (*Z*)-isomer (minor) (clearly assignable peaks) 1.06 (3H, d, *J*=7.3 Hz), 1.79 (2H, m), 2.23 (1H, m), 4.19 (2H, d, *J*=2.9 Hz), 4.30 (2H, t, *J*=3.8 Hz); ^{13}C NMR ($CDCl_3$) δ (*E*)-isomer (major) 15.4, 15.9, 22.0, 122.6, 127.9, 129.6, 132.5, 135.3, 135.7; HRMS calcd for $C_{17}H_{22}Si_2$ (M^+) 282.1261, found 282.1304.

8.2.6. 1-Phenyl-3-methyl-3-silacyclopentene (23a). Colorless oil; IR (neat) 1638, 1155, 1117, 866, 804 cm^{-1}; MS *m/z* 174 (M^+), 105 ($PhSi^+$); ^1H NMR ($CDCl_3$) δ 1.51 (1H, dm, *J*=18.8 Hz), 1.59 (1H, dm, *J*=18.8 Hz), 1.70 (1H, dm, *J*=18.8 Hz), 1.76 (1H, dm, *J*=18.8 Hz), 1.82 (3H, s), 4.74

(1H, m), 5.60 (1H, br s), 7.35–7.39 (3H, m), 7.57–7.59 (2H, m); ^{13}C NMR ($CDCl_3$) δ 16.0, 20.2, 22.3, 124.7, 128.0, 129.6, 134.4, 135.7, 140.2; HRMS calcd for $C_{11}H_{14}Si$ (M^+) 174.0865, found 174.0843.

8.2.7. 1,1-Diphenyl-3-methyl-3-silacyclopentene (23b). Colorless oil; IR (neat) 1639, 1157, 941, 845, 806 cm^{-1}; MS *m/z* 250 (M^+), 172 (M^+-PhH), 105 ($PhSi^+$); ^{1}H NMR ($CDCl_3$) δ 1.77 (2H, br s), 1.84 (5H, br s), 5.64 (1H, t, *J*=1.6 Hz), 7.33–7.42 (6H, m), 7.54–7.59 (4H, m); ^{13}C NMR ($CDCl_3$) δ 17.5, 21.7, 22.6, 124.7, 127.9, 129.4, 134.7, 136.2, 140.1; HRMS calcd for $C_{17}H_{18}Si$ (M^+) 250.1178, found 250.1176.

8.2.8. 1-Phenyl-3-octyl-3-silacyclopentene (23c). Colorless oil; IR (neat) 1636, 1153, 1115, 864, 818 cm^{-1}; MS *m/z* 272 (M^+), 105 ($PhSi^+$); ^{1}H NMR ($CDCl_3$) δ 0.87 (3H, t, *J*=7.3 Hz), 1.27–1.54 (13H, m), 1.59 (1H, br d, *J*=18.2 Hz), 1.68 (1H, br d, *J*=18.2 Hz), 1.76 (1H, br d, *J*=18.2 Hz), 2.13 (2H, t, *J*=7.3 Hz), 4.74 (1H, quin, *J*=2.9 Hz), 5.62 (1H, br s), 7.33–7.41 (3H, m), 7.54–7.59 (2H, m); ^{13}C NMR ($CDCl_3$) δ 14.1, 15.6, 17.8, 22.9, 27.6, 29.3, 29.4, 29.5, 31.9, 36.3, 123.8, 127.9, 129.5, 134.4, 135.8, 144.5.

8.2.9. 1-Phenyl-3,4-dimethyl-3-silacyclopentene (23d). Colorless oil; IR (neat) 1173, 1115, 895 cm^{-1}; MS *m/z* 188 (M^+), 105 ($PhSi^+$); ^{1}H NMR ($CDCl_3$) δ 1.60 (2H, br d, *J*=18.7 Hz), 1.76 (6H, s), 1.78 (2H, br d, *J*=18.7 Hz), 4.61 (1H, m), 7.33–7.39 (3H, m), 7.56–7.59 (2H, m); ^{13}C NMR ($CDCl_3$) δ 19.1, 22.6, 127.9, 129.5, 130.8, 134.4, 135.9. Anal. calcd for $C_{12}H_{16}Si$: C, 76.53; H, 8.56. Found: C, 76.39; H, 8.70.

8.2.10. (*E*)-1-Diphenylphosphinyl-1,2-diphenylethylene (25a) [14447-40-6]. White solid; mp 156–157°C; IR (Nujol) 1177 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.92–7.53 (16H, m), 7.58 (1H, d, *J*=21.0 Hz, olefinic), 7.64–7.70 (4H, m); ^{13}C NMR ($CDCl_3$) δ 127.7 (d, *J*=1.5 Hz), 128.16, 128.22 (d, *J*=12.3 Hz), 128.7 (d, *J*=1.6 Hz), 128.9, 129.9 (d, *J*=4.1 Hz), 130.2 (d, *J*=1.6 Hz), 131.0 (d, *J*=103.4 Hz), 131.8 (d, *J*=2.5 Hz), 132.3 (d, *J*=9.0 Hz), 134.9 (d, *J*=2.4 Hz), 135.2 (d, *J*=73.0 Hz), 135.7 (d, *J*=26.3 Hz), 143.0 (d, *J*=9.0 Hz).

8.2.11. (*E*)-2-Diphenylphosphinyl-2-trimethylsilylstyrene (25b). White solid; mp 122–123°C; IR (Nujol) 1177 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.03 (3H, d, *J*=1.0 Hz), 0.0 (6H, s), 7.21–7.82 (16H, m); ^{13}C NMR ($CDCl_3$) δ 1.1 (d, *J*=7.4 Hz), 1.5 (d, *J*=2.5 Hz), 127.2, 127.8, 127.9 (d, *J*=1.4 Hz), 128.0 (d, *J*=1.6 Hz), 128.4 (d, *J*=3.3 Hz), 128.5, 128.8, 131.4 (d, *J*=3.6 Hz), 131.9 (d, *J*=9.9 Hz), 133.4 (d, *J*=99.3 Hz), 134.6 (d, *J*=20.5 Hz), 139.0 (d, *J*=41.1 Hz), 139.4 (d, *J*=77.9 Hz), 141.0 (d, *J*=6.6 Hz). Anal. calcd for $C_{23}H_{25}OPSi$: C, 73.37; H, 6.69. Found: C, 73.04; H, 6.57.

8.2.12. 1-Phenyl-2-diphenylphosphinyl-1-propene (25c) [62556-17-6]. (*E*)-Isomer (major): white solid; mp 129–130°C; IR (Nujol) 1177 cm^{-1}; MS *m/z* 318 (M^+), 303 (M^+-Me), 241 (M^+-Ph), 201 (Ph_2PO^+); ^{1}H NMR ($CDCl_3$) δ 2.03 (3H, d, *J*=14.0 Hz), 7.13 (1H, d, *J*=22.2 Hz), 7.19–7.50 (11H, m), 7.66–7.71 (4H, m); ^{13}C NMR ($CDCl_3$) δ 15.0 (d, *J*=10.7 Hz), 128.3 (d, *J*=4.0 Hz), 128.5, 128.6, 129.4, 129.6 (d, *J*=40.6 Hz), 131.2 (d, *J*=102.5 Hz), 131.9 (d, *J*=2.5 Hz), 132.1 (d, *J*=9.8 Hz), 135.8 (d, *J*=18.9 Hz), 142.7 (d, *J*=11.5 Hz). (*Z*)-Isomer (minor): white solid; mp 120–123°C; IR (Nujol) 1173 cm^{-1}; MS *m/z* 318 (M^+), 303 (M^+-Me), 241 (M^+-Ph), 201 (Ph_2PO^+); ^{1}H NMR ($CDCl_3$) δ 1.90 (3H, dd, *J*=12.3, 1.5 Hz), 6.89–6.96 (3H, m), 7.18–7.31 (8H, m), 7.36 (1H, dm, *J*=37.1, 1.5 Hz), 7.53–7.62 (4H, m); ^{13}C NMR ($CDCl_3$) δ 24.7 (d, *J*=13.1 Hz), 127.5, 127.7, 128.2 (d, *J*=12.3 Hz), 129.3 (d, *J*=1.6 Hz), 129.4 (d, *J*=92.7 Hz), 131.2 (d, *J*=3.3 Hz), 131.3 (d, *J*=9.0 Hz), 132.9 (d, *J*=102.5 Hz), 135.7 (d, *J*=6.6 Hz), 145.7 (d, *J*=7.4 Hz).

8.2.13. 2-Diphenylphosphinylstyrene (25d) [3582-82-9 and 78045-10-0]. Isolated as a mixture of (*E*)- and (*Z*)-isomer (76/24); white solid; mp 87–89°C; IR (Nujol) 1176 cm^{-1}; MS *m/z* 304 (M^+), 227 (M^+-Ph), 201 (Ph_2PO^+), 124 ($PhPO^+$); ^{1}H NMR ($CDCl_3$) δ 6.23 (0.24H, dd, *J*=19.6, 14.0 Hz, *Z*-isomer), 6.76 (0.76H, dd, *J*=22.2, 17.4 Hz, *E*-isomer), 7.07–7.70 (16H, m).

8.2.14. (*Z*)-4-Diphenylphosphinyl-4-octene (25e) [195148-52-8]. Colorless oil; IR (neat) 1188 cm^{-1}; MS *m/z* 312 (M^+), 283 (M^+-Et), 201 (Ph_2PO^+), 185 (Ph_2P^+); ^{1}H NMR ($CDCl_3$) δ 0.65 (3H, t, *J*=7.3 Hz), 0.66 (3H, t, *J*=7.3 Hz), 1.16–1.24 (4H, m), 1.96 (2H, dt, *J*=13.8, 6.9 Hz), 2.16 (2H, dq, *J*=3.0, 7.3 Hz), 6.29 (1H, dt, *J*=37.9, 7.3 Hz), 7.34–7.46 (6H, m), 7.60–7.72 (4H, m); ^{13}C NMR ($CDCl_3$) δ 13.5, 13.6, 22.4 (d, *J*=1.6 Hz), 22.9 (d, *J*=3.3 Hz), 32.6 (d, *J*=7.4 Hz), 37.7 (d, *J*=13.1 Hz), 128.3 (d, *J*=12.3 Hz), 131.5, 131.6 (d, *J*=11.8 Hz), 131.9 (d, *J*=96.8 Hz), 133.8 (d, *J*=100.0 Hz), 148.6 (d, *J*=8.2 Hz).

8.2.15. (*Z*)-2-Diphenylphosphinyl-2-octene (25f) [187471-88-1]. Colorless oil; IR (neat) 1188 cm^{-1}; MS *m/z* 312 (M^+), 269 (M^+-Pr), 201 (Ph_2PO^+), 185 (Ph_2P^+); ^{1}H NMR ($CDCl_3$) δ 0.79 (3H, t, *J*=6.9 Hz), 1.11–1.31 (6H, m), 1.74 (3H, d, *J*=12.3 Hz), 2.29–2.38 (2H, m), 6.41 (1H, dt, *J*=37.5, 6.3 Hz), 7.46–7.54 (6H, m), 7.66–7.72 (4H, m); ^{13}C NMR ($CDCl_3$) δ 13.9, 22.3, 23.8 (d, *J*=14.0 Hz), 28.8, 30.4 (d, *J*=6.6 Hz), 31.3, 126.9 (d, *J*=95.2 Hz), 128.4 (d, *J*=12.3 Hz), 131.48 (d, *J*=4.9 Hz), 131.54 (d, *J*=2.5 Hz), 133.4 (d, *J*=101.7 Hz), 149.8 (d, *J*=8.2 Hz).

8.2.16. (*Z*)-1-Diphenylphosphinyl-3,3-dimethyl-1-butene (25g). White solid; mp 116–117°C; IR (Nujol) 1180 cm^{-1}; MS *m/z* 284 (M^+), 269 (M^+-Me), 201 (Ph_2PO^+), 124 ($PhPO^+$); ^{1}H NMR ($CDCl_3$) δ 1.21 (9H, s), 5.97 (1H, dd, *J*=22.4, 14.6 Hz), 6.68 (1H, dd, *J*=43.5, 14.6 Hz), 7.41–7.50 (6H, m), 7.71–7.77 (4H, m); ^{13}C NMR ($CDCl_3$) δ 30.3 (d *J*=9.8 Hz), 35.4 (d, *J*=5.7 Hz), 119.2 (d, *J*=97.5 Hz), 128.4 (d, *J*=12.3 Hz), 130.8 (d, *J*=9.8 Hz), 131.3, 135.7 (d, *J*=105.0 Hz), 164.5. Anal. calcd for $C_{18}H_{21}OP$: C, 76.04; H, 7.44. Found: C, 76.14; H, 7.32.

8.2.17. 1-Diphenylphosphinyl-1-octene (25h) [195148-53-9 and 178943-30-1]. (*Z*)-Isomer (major): white solid; MS *m/z* 312 (M^+), 255 (M^+-Bu), 241 (M^+-Pen); ^{1}H NMR ($CDCl_3$) δ 0.83 (3H, t, *J*=7.1 Hz), 1.10–1.28 (6H, m), 1.34 (2H, quin, *J*=7.1 Hz), 2.54 (2H, qm, *J*=7.1 Hz), 6.11 (1H, ddt, *J*=25.6, 12.8, 3.0 Hz), 6.69 (1H, ddt, *J*=40.5, 12.8, 7.1 Hz), 7.42–7.51 (6H, m), 7.71–7.77 (4H, m); ^{13}C NMR

($CDCl_3$) δ 14.0, 22.5, 28.76 (d, J=3.3 Hz), 28.78, 30.9 (d, J=8.2 Hz), 31.5, 121.2 (d, J=100.9 Hz), 128.5 (d, J=12.2 Hz), 130.9 (d, J=9.8 Hz), 131.4 (d, J=2.5 Hz), 134.6 (d, J=103.4 Hz), 155.2. (*E*)-Isomer (minor): white solid; ^{1}H NMR ($CDCl_3$) δ 0.87 (3H, t, J=7.0 Hz), 1.17–1.34 (6H, m), 1.48 (2H, quin, J=7.0 Hz), 2.29 (2H, qm, J=7.0 Hz), 6.22 (1H, ddm, J=24.5, 17.0 Hz), 6.73 (1H, ddt, J=19.6, 17.0, 7.0 Hz), 7.27–7.53 (6H, m), 7.67–7.77 (4H, m); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 27.8, 28.8, 31.5, 34.5 (d, J=16.4 Hz), 121.6 (d, J=103.4 Hz), 128.5 (d, J=12.3 Hz), 131.3 (d, J=9.9 Hz), 131.6, 133.2 (d, J=104.2 Hz), 152.9.

8.2.18. 3-Diphenylphosphinyl-2-octene (26f). Isolated as a mixture of (*E*)- and (*Z*)-isomer (21/79); yellow oil; MS *m/z* 312 (M^+), 201 (Ph_2PO^+); ^{1}H NMR ($CDCl_3$) (*Z*)-isomer (major) δ 0.75 (3H, t, J=7.5 Hz), 1.03–1.31 (6H, m), 1.85 (3H, d, J=7.0 Hz), 1.96–2.06 (2H, m), 6.51 (1H, dq, J=37.9, 7.0 Hz), 7.43–7.53 (6H, m), 7.67–7.81 (4H, m); (*E*)-isomer (minor) (clearly assignable peaks) 0.77 (3H, t, J=7.0 Hz), 1.74 (3H, d, J=6.8 Hz), 6.25 (1H, dq, J=21.3, 6.8 Hz).

8.2.19. 2-Diphenylphosphinyl-3,3-dimethyl-1-butene (26g). White solid; mp 133–135°C; IR (Nujol) 1180 cm^{-1}; MS *m/z* 284 (M^+), 227 ($M^+-{}^t$Bu), 201 (Ph_2PO^+), 124 ($PhPO^+$); ^{1}H NMR ($CDCl_3$) δ 1.27 (9H, s), 5.20 (1H, d, J=22.2 Hz), 5.99 (1H, d, J=45.6 Hz), 7.36–7.53 (6H, m), 7.64–7.76 (4H, m); ^{13}C NMR ($CDCl_3$) δ 30.5 (d, J=8.2 Hz), 38.0 (d, J=9.0 Hz), 127.6 (d, J=9.0 Hz), 128.3 (d, J=11.5 Hz), 131.4, 131.6 (d, J=9.8 Hz), 133.6 (d, J=105.0 Hz), 152.7 (d, J=87.8 Hz). Anal. calcd for $C_{18}H_{21}OP$: C, 76.04; H, 7.44. Found: C, 76.09; H, 7.50.

8.2.20. 2-Diphenylphosphinyl-1-octene (26h). White solid; mp 140–142°C; IR (Nujol) 1188 cm^{-1}; MS *m/z* 312 (M^+), 297 (M^+-Me), 269 (M^+-Pr), 241 (M^+-Pen), 201 (Ph_2PO^+); ^{1}H NMR ($CDCl_3$) δ 0.83 (3H, t, J=6.8 Hz), 1.13–1.30 (6H, m), 1.42–1.52 (2H, m), 2.30 (2H, q, J=8.5 Hz), 5.62 (1H, d, J=21.0 Hz), 5.94 (1H, d, J=43.0 Hz), 7.45–7.56 (6H, m), 7.68–7.73 (4H, m); ^{13}C NMR ($CDCl_3$) δ 14.0, 22.5, 28.0 (d, J=5.8 Hz), 28.9, 31.5, 31.6 (d, J=9.0 Hz), 128.5 (d, J=12.3 Hz), 128.6 (d, J=10.7 Hz), 131.5 (d, J=101.7 Hz), 131.8, 131.9 (d, J=9.8 Hz), 144.1 (d, J=91.9 Hz). Anal. calcd for $C_{20}H_{25}OP$: C, 76.90; H, 8.07. Found: C, 76.67; H, 8.13.

Characterization of other products such as alkynylsilanes and aminosilanes is cited in Refs. 15 and 21, respectively.

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8. Selected bond lengths (Å) and angles (deg): Yb–C(1), 2.679 (18), Yb–N(10), 2.318 (15), C(1)–N(10), 1.43 (3), Yb–O(1), 2.320 (14), Yb–O(2), 2.275 (12), Yb–O(3), 2.298 (12), Yb–C(1)–N(10), 87.8 (10), Yb–N(10)–C(1), 59.9 (9), C(1)–Yb–N(10), 32.3 (5), C(2)–C(1)–C(8), 125.6 (15), C(2)–C(1)–N(10), 118.2 (15), C(8)–C(1)–N(10), 115.3 (14), C(1)–N(10)–C(14), 117.5 (15), O(1)–Yb–O(2), 107.1 (5), O(2)–Yb–O(3), 99.7 (5), O(3)–Yb–O(1), 95.6 (5), C(1)–Yb–O(1), 102.7 (6), C(1)–Yb–O(2), 128.2 (6), C(1)–Yb–O(3), 118.6 (5).
9. ^{1}H NMR (THF-d_8/HMPA) (5.52 (1H, t, J=6.8 Hz, *p*-PhN), 5.58 (2H, t, J=7.7 Hz, *p*-PhC), 5.82 (1H, d, J=6.8 Hz, *o*-PhN), 6.30 (1H, t, J=6.8 Hz, *m*-PhN), 6.35 (1H, d, J=6.8 Hz, *o*-PhN), 6.42 (4H, t, J=7.7 Hz, *m*-PhC), 6.56 (1H, t, J=6.8 Hz, *m*-PhN), 6.95 (4H, d, J=7.7 Hz, *o*-PhC). ^{13}C NMR (THF-d_8/HMPA) (94.2 (CN), 105.1 (*p*-PhN), 107.3 (*p*-PhC), 112.8 (*o*-PhN), 116.3 (*o*-PhC), 117.9 (*m*-PhN), 127.4 (*m*-PhN), 128.6 (*m*-PhC), 128.9 (*o*-PhN), 143.4 (ipso-PhC), 162.0 (ipso-PhN).
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14. Because the accurate number of the coordinated HMPA of **1** prepared in situ is unknown, equivalents of this ligand used for generation of **1** are tentatively shown as a coordination number (n) in such a way that [Yb(imine)(hmpa)$_n$]. Activities of **1** increased generally with increasing of the number (n) up to 4, and thus the complex **1** (n=4) was used unless otherwise noted for the catalytic reactions described hereafter.
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23. For example, treatment of $PhSiH_3$ with **1c**^{l} ((10 mol%, rt, 17 h) produced polyphenylsilanes with vigorous hydrogen evolution, from which oligomer (M_W=2966, M_W/M_N=1.1) was isolated in 29% yield by aqueous workup, followed by short-column chromatography on silica gel using hexane–ethyl acetate (1/1).
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