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Half-Sandwich *o*-*N*,*N*-Dimethylaminobenzyl Complexes over the Full Size Range of Group 3 and Lanthanide Metals. Synthesis, Structural Characterization, and Catalysis of Phosphine P–H Bond Addition to Carbodiimides

Wen-Xiong Zhang, Masayoshi Nishiura, Tomohiro Mashiko, and Zhaomin Hou*[a]

Abstract: The acid-base reactions between the rare-earth metal (Ln) tris(*ortho*-*N*,*N*-dimethylaminobenzyl) complexes [Ln($CH_2C_6H_4NMe_2$-*o*)$_3$] with one equivalent of the silylene-linked cyclopentadiene-amine ligand (C_5Me_4H)-$SiMe_2NH(C_6H_2Me_3$-2,4,6) afforded the corresponding half-sandwich aminobenzyl complexes [{$Me_2Si(C_5Me_4)$-($NC_6H_2Me_3$-2,4,6)}Ln($CH_2C_6H_4NMe_2$-*o*)(thf)] (**2-Ln**) (Ln = Y, La, Pr, Nd, Sm, Gd, Lu) in 60–87% isolated yields. The one-pot reaction between $ScCl_3$ and [$Me_2Si(C_5Me_4)(NC_6H_2Me_3$-2,4,6)]$Li_2$ followed by reaction with $LiCH_2C_6H_4NMe_2$-*o* in THF gave the scandium analogue [{$Me_2Si(C_5Me_4)$-($NC_6H_2Me_3$-2,4,6)}Sc($CH_2C_6H_4NMe_2$-*o*)] (**2-Sc**) in 67% isolated yield. **2-Sc** could not be prepared by the acid-base reaction between [Sc($CH_2C_6H_4NMe_2$-*o*)$_3$] and (C_5Me_4H)$SiMe_2NH(C_6H_2Me_3$-2,4,6). These half-sandwich rare-earth metal aminobenzyl complexes can serve as efficient catalyst precursors for the catalytic addition of various phosphine P–H bonds to carbodiimides to form a series of phosphaguanidine derivatives with excellent tolerability to aromatic carbon-halogen bonds. A significant increase in the catalytic activity was observed, as a result of an increase in the metal size with a general trend of La > Pr, Nd > Sm > Gd > Lu > Sc. The reaction of **2-La** with 1 equiv of Ph_2PH yielded the corresponding phosphide complex [{$Me_2Si(C_5Me_4)(NC_6H_2Me_3$-2,4,6)}La($PPh_2$)(thf)$_2$] (**4**), which, on recrystallization from benzene, gave the dimeric analogue [{$Me_2Si(C_5Me_4)$-($NC_6H_2Me_3$-2,4,6)}La(PPh_2)]$_2$ (**5**). Addition of **4** or **5** to *i*PrN=C=N*i*Pr in THF yielded the phosphaguanidinate complex [{$Me_2Si(C_5Me_4)(NC_6H_2Me_3$-2,4,6)}La{*i*PrNC($PPh_2$)N*i*Pr}(thf)] (**6**), which, on recrystallization from ether, afforded the ether-coordinated structurally characterizable analogue [{$Me_2Si(C_5Me_4)(NC_6H_2Me_3$-2,4,6)}La-{*i*PrNC($PPh_2$)N*i*Pr}($OEt_2$)] (**7**). The reaction of **6** or **7** with Ph_2PH in THF yielded **4** and the phosphaguanidine *i*PrN=C(PPh_2)NH*i*Pr (**3a**). These results suggest that the catalytic formation of a phosphaguanidine compound proceeds through the nucleophilic addition of a phosphide species, which is formed by the acid-base reaction between a rare-earth metal *o*-dimethylaminobenzyl bond and a phosphine P–H bond, to a carbodiimide, followed by the protonolysis of the resultant phosphaguanidinate species by a phosphine P–H bond. Almost all of the rare earth complexes reported this paper were structurally characterized by X-ray diffraction studies.

Keywords: carbodiimides · homogeneous catalysis · P–H bond activation · phosphaguanidines · phosphorus · rare-earth metals

Introduction

Rare earth (group 3 and lanthanide) metal alkyl complexes are an important class of organometallic compounds, which can show novel activity in various stoichiometric and catalytic processes.[1,2] Rare-earth metal alkyl complexes bearing the silylene-linked cyclopentadienyl-amido ligand have drawn considerable attention, because they are electronically less saturated and sterically more accessible than the ordinary metallocene analogues that have two cyclopentadienyl ancillary ligands.[2] The first silylene-linked cyclopentadien-

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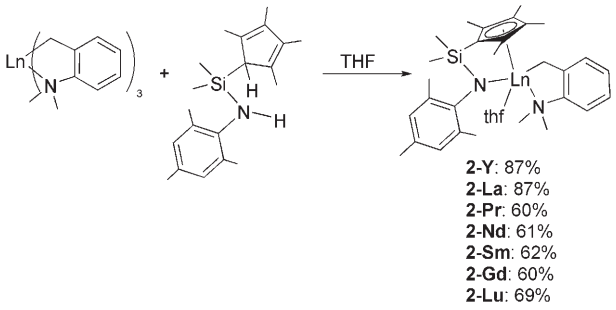
yl-amido rare-earth metal alkyl complex [{$Me_2Si(C_5Me_4)$-(N*t*Bu)}Sc{$CH(SiMe_3)_2$}] was reported in the early 1990s by Bercaw et al., which was obtained by salt metathesis between the scandium chloride complex [{$Me_2Si(C_5Me_4)$-(N*t*Bu)}ScCl] and $LiCH(SiMe_3)_2$.[3] It was later found by Okuda and our group that the acid-base reactions between the rare-earth metal tris(trimethylsilyl)methyl complexes [$Ln(CH_2SiMe_3)_3(thf)_2$] (Ln = Sc, Y, Yb, and Lu) and the silylene-linked cyclopenetadiene-amine ligands (C_5Me_4H)$SiMe_2NHR$ (R = alkyl, aryl) can offer an excellent salt-free route to the corresponding half-sandwich alkyl complexes.[4,5] Marks and coworkers found that the similar acid-base reaction between the bulkier tris{bis(trimethylsilyl)methyl} complexes [$Ln\{CH(SiMe_3)_2\}_3$] (Ln = Yb and Lu) and the neutral ligand (C_5Me_4H)$Me_2SiNHtBu$ could also afford the corresponding analogues, albeit under forcing conditions.[6] Harder and Carpentier reported that the synthesis of yttrium aminobenzyl and alkyl complexes bearing the silylene-linked fluorenyl-amido ligands, such as [{$Me_2Si(\eta^3$-$C_{13}H_8)$(N*t*Bu)}$Y(CH_2C_6H_4NMe_2$-*o*)(thf)][7a] and [{$Me_2Si(\eta^3$-3,6-*t*$Bu_2C_{13}H_6)$(N*t*Bu)}$Y(CH_2SiMe_3)(thf)_2$],[7b] can be achieved by the acid-base reaction of the tris(aminobenzyl) and tris(alkyl) precursors such as [$Y(CH_2C_6H_4NMe_2$-*o*$)_3$] and [$Y(CH_2SiMe_3)_3(thf)_2$] with the corresponding fluorene-amine ligands. We recently found that the reaction of the scandium tris(aminobenzyl) complex [Sc-$(CH_2C_6H_4NMe_2$-*o*$)_3$] with $C_5Me_4(SiMe_3)H$ can afford the corresponding half-sandwich bis(aminobenzyl) complex [$(C_5Me_4SiMe_3)Sc(CH_2C_6H_4NMe_2$-*o*$)_2$], which can serve as a novel catalyst precursor for the polymerization and copolymerization of various olefins.[8] Despite these extensive studies in this area, the rare-earth metal half-sandwich alkyl complexes reported so far in the literature have been limited solely to those of relatively small metals (such as Sc, Y, Yb, and Lu), whereas complexes that contain larger metal ions (ranging from La to Gd) remained unknown. Previous attempts to synthesize a samarium half-sandwich alkyl complex by reaction of [$Sm\{CH(SiMe_3)_2\}_3$] with (C_5Me_4H)-$Me_2SiNHtBu$ at high temperatures were unsuccessful, as a result of the thermal instability of the tris(alkyl) samarium complex.[6] The reactivity of rare-earth metal complexes is usually greatly influenced by the ion size of the central metals. Therefore, synthesis of half-sandwich rare-earth metal alkyl complexes over the full size range of this series of metals is of much interest and importance.

On the other hand, although the nucleophilic addition of main group metal phosphides "R'_2PM" to carbodiimides RN=C=NR is a well-known method for the preparation of the corresponding phosphaguanidinate complexes "[$RNC(PR'_2)NR]M$",[9,10] the reaction of rare-earth metal phosphides with carbodiimides has not been reported previously. Although catalytic addition of phosphine P–H bonds across the C=N bond of carbodiimides could be an efficient method for the synthesis of phosphaguanidines [RN=C-(PR'_2)NHR]—an important class of heteroatom-containing compounds that may be used as building blocks for organic synthesis and as unique ligands for various metal complexes[9]—such a catalytic process remained scarce.[10]

We recently found that half-sandwich rare-earth metal (trimethylsilyl)methyl complexes such as [{$Me_2Si(C_5Me_4)$-(NR)}$Y(CH_2SiMe_3)(thf)_x$] (R = Ph, $C_6H_2Me_3$-2,4,6, *t*Bu) could serve as efficient catalysts for the catalytic addition of terminal alkyne C–H and amine N–H bonds to carbodiimides to give the corresponding propiolamidines[5b] and guanidines,[5c,e] respectively. We wish to report here that such half-sandwich rare-earth metal complexes can also catalyze the addition of phosphine P–H bonds to carbodiimides to afford the corresponding phosphaguanidines. Moreover, by using *ortho*-dimethylaminobenzyl $CH_2C_6H_4NMe_2$-*o* instead of (trimethylsilyl)methyl CH_2SiMe_3 as an alkyl ligand, we have successfully synthesized and structurally characterized the corresponding half-sandwich complexes over the full size range of the rare-earth metal series (Sc, Y, La, Pr, Nd, Sm, Gd, and Lu). Significant effects of the metal ion size on the catalytic activity of these complexes in the catalytic addition of phosphine P–H bonds to carbodiimides were observed. Typical phosphide and phosphaguanidinate reaction intermediates were isolated and their reactivity was also investigated, which offers strong evidence for the understanding of the mechanistic aspects of this catalytic process.

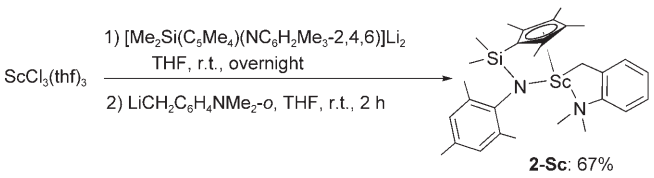
Results and Discussion

Synthesis and structural characterization of rare-earth metal *o*-dimethylaminobenzyl complexes bearing silylene-linked cyclopentadienyl-amido ligands: Similar to the synthesis of the half-sandwich (trimethylsilyl)methyl complex [{Me_2Si-$(C_5Me_4)(NC_6H_2Me_3$-2,4,6))}$Y(CH_2SiMe_3)(thf)$] (**1-Y**),[5b,e] the analogous aminobenzyl complex [{$Me_2Si(C_5Me_4)$-$(NC_6H_2Me_3$-2,4,6)}$Ln(CH_2C_6H_4NMe_2$-*o*)(thf)] (**2-Y**) was easily prepared by the reaction of [$Y(CH_2C_6H_4NMe_2$-*o*$)_3$] with 1 equivalent of (C_5Me_4H)$SiMe_2NH(C_6H_2Me_3$-2,4,6), as shown in Scheme 1. More remarkably, such half-sandwich aminobenzyl complexes **2-Ln** (Ln = La, Pr, Nd, Sm, Gd, and Lu) could be obtained over the whole size range of the lanthanide series in the same manner (Scheme 1). However, an attempt to make the analogous Sc complex by the reaction



Scheme 1. Synthesis of half-sandwich *o*-dimethylaminobenzyl complexes of La, Pr, Nd, Sm, Gd, Lu, and Y.

of $[Sc(CH_2C_6H_4NMe_2\text{-}o)_3]$ with $(C_5Me_4H)SiMe_2NH(C_6H_2Me_3\text{-}2,4,6)$ was unsuccessful, probably because of the much smaller size of the Sc ion, which could render the metal center too crowded to result in a reaction between the aminobenzyl unit and the bulky cyclopentadiene-amine ligand. Alternatively, the metathetical reaction between $ScCl_3$ and $[Me_2Si(C_5Me_4)(NC_6H_2Me_3\text{-}2,4,6)]Li_2$ followed by addition of $LiCH_2C_6H_4\text{-}NMe_2\text{-}o$ in THF, afforded the corresponding half-sandwich scandium aminobenzyl complex $[\{Me_2Si(C_5Me_4)(NC_6H_2Me_3\text{-}2,4,6)\}Sc(CH_2C_6H_4NMe_2\text{-}o)]$ (**2-Sc**) in 67% isolated yield (Scheme 2).



Scheme 2. Synthesis of a half-sandwich scandium *o*-dimethylaminobenzyl complex.

All of these aminobenzyl complexes **2-Ln**, were structurally characterized by X-ray diffraction analyses. Their selected bond lengths and angles are summarized in Table 1, and the ORTEP drawings of **2-La**, **2-Lu**, and **2-Sc** are shown in Figures 1–3, respectively. The complexes of Ln = Y, La, Pr, Nd, Sm, Gd, and Lu contain a THF-coordination ligand, while the smallest Sc complex is THF-free, reflecting the difference in ion size between Sc and other larger metals. All these complexes adopt a similar overall structure. The *o*-dimethylaminobenzyl group is bonded to the metal center in a chelating fashion through both the benzyl unit and the amino group. The cyclopentadienyl group adopts an η^5-coordinate mode in all of these complexes, in contrast with the fluorenyl-ligated yttrium analogue $[\{Me_2Si(\eta^3\text{-}C_{13}H_8)(NtBu)\}Y(CH_2C_6H_4NMe_2\text{-}o)(thf)]$, in which the fluorenyl ligand showed an η^3-coordinate fashion.[7a] Almost all the bond distances around the metal centers decreased as the metal size decreased in the order of La > Pr > Nd > Sm > Gd > Y > Lu > Sc (Table 1). The Lu–N (amino-group) bond (2.714(4) Å), however, is exceptionally longer than the Gd–N(amino-group) bond (2.707(7) Å) and the Y–N(amino-group) bond (2.690(2) Å), this can be explained by the fact that although Lu is smaller than Gd and Y, they all have the same coordination number.[11] These data may suggest that the interaction between the metal center and the dimethylamino group in **2-Lu** is weaker than that in other larger metal complexes, probably because Lu is a little too small to keep the same coordination number as other larger metals do.

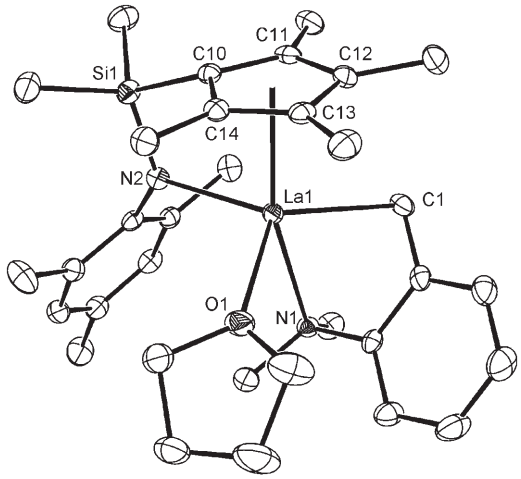


Figure 1. ORTEP drawing of **2-La** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

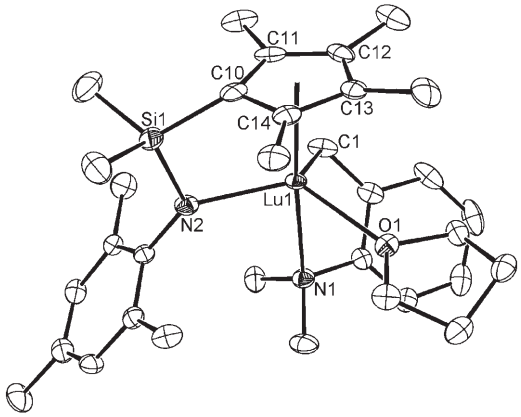


Figure 2. ORTEP drawing of **2-Lu** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for **2-Ln** (Ln = La, Pr, Nd, Sm, Gd, Lu, Y, and Sc).

	2-La	2-Pr	2-Nd	2-Sm	2-Gd	2-Lu	2-Y	2-Sc
Ln–N(Bz)	2.792(2)	2.767(2)	2.748(3)	2.730(4)	2.707(7)	2.714(4)	2.690(2)	2.2908(15)
Ln–N(Ar)	2.416(2)	2.384(2)	2.357(2)	2.343(4)	2.309(6)	2.227(4)	2.288(2)	2.0823(14)
Ln–O	2.564(2)	2.538(2)	2.511(3)	2.483(3)	2.445(5)	2.321(4)	2.4025(19)	–
Ln–C(Bz)	2.609(3)	2.564(3)	2.537(3)	2.503(5)	2.486(7)	2.337(6)	2.445(3)	2.2570(18)
Ln–Cp(centroid)	2.505(3)	2.468(3)	2.447(3)	2.424(5)	2.392(8)	2.356(6)	2.369(3)	2.2570(17)
Ln–Cp(av)	2.782(3)	2.749(3)	2.728(3)	2.707(5)	2.675(8)	2.646(6)	2.659(3)	2.4708(17)
∢N(Ar)–Ln–Cp(centroid)	91.43(8)	92.92(8)	93.20(10)	94.29(15)	95.43(2)	97.76(19)	96.40(9)	104.36(7)
∢N(Ar)–Si–C(Cp)	98.50(11)	98.49(12)	97.81(13)	98.3(2)	97.8(3)	97.9(2)	97.89(11)	95.74(7)
∢Si–N–Ln	105.59(10)	104.95(10)	105.40(12)	104.62(18)	104.2(3)	103.5(2)	103.89(11)	102.77(7)
∢C–Ln–N(Bz)	63.01(8)	64.00(8)	64.14(10)	64.84(14)	65.3(2)	66.97(17)	66.04(8)	77.45(7)

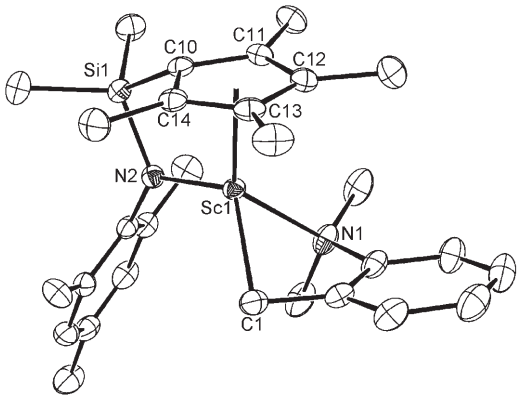
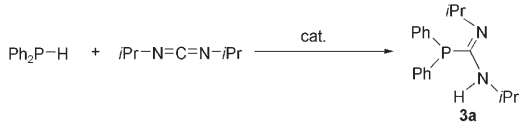


Figure 3. ORTEP drawing of **2-Sc** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

Catalytic addition of phosphines to carbodiimides: The reaction of diphenylphosphine Ph_2PH with *N,N′*-diisopropylcarbodiimide *i*PrN=C=N*i*Pr was first examined under various conditions. As a control experiment, *i*PrN=C=N*i*Pr was heated with Ph_2PH in C_6D_5Cl at 140°C for 12 h, but no reaction was observed (Table 2, entry 1). In contrast, addition of a small amount of the (trimethylsilyl)methyl complex **1-Y** at 80°C, led to rapid addition of Ph_2PH to *i*PrN=C=N*i*Pr to give the corresponding phosphaguanidine **3a** in 86% yield in 1 h (Table 2, entry 2). The aminobenzyl analogue **2-Y** showed the same activity as that of **1-Y** (Table 2, entry 3), which showed that the catalytic activity was not affected by the alkyl group under the present conditions. The scandium complex **2-Sc** showed a significantly lower activity than that of **2-Y** under the same conditions (Table 2, entry 4). Among the lanthanide complexes from Lu to La, the activity increased as the metal size becomes larger (Lu < Gd < Sm < Nd < Pr < La) (Table 2, entries 5–10). The largest lanthanum complex **2-La** showed the highest activity. THF seemed to be a better solvent than benzene or toluene for this reaction (Table 2, entries 10–12). Thus, in the presence of 1 mol% of **2-La**, the reaction of Ph_2PH with *i*PrN=C=N*i*Pr in THF at 80°C yielded the corresponding phosphaguanidine **3a** quantitatively within 1 h (Table 2, entry 13).

Table 3 summarizes some representative results of reactions between various phosphines and carbodiimides catalyzed by the lanthanum complex **2-La**. A wide range of diarylphosphines could be used in this reaction. The reaction was not affected by either electron-withdrawing or -donating substituents, or their positions at the phenyl ring of the phosphines (Table 3, entries 1–10). Aromatic C–Cl (entries 8 and 9) and C–Br (entry 10) bonds survived the catalytic conditions to yield selectively the corresponding halogen-substituted phosphaguanidines **3i–k**, which could serve as useful building blocks for the construction of further larger phosphaguanidine derivatives. The reaction of an alkyl/aryl phosphine such as ethylphenylphosphine (entry 11) with *i*PrN=C=N*i*Pr required a longer time for completion, whereas a dialkyl phosphine could not be utilized in this reaction, probably owing to the weaker acidity of these phosphines compared to that of diarylphosphines. The reaction of $PhPH_2$ with *i*PrN=C=N*i*Pr afforded selectively the mono-addition product *i*PrN=C(PHPh)(NH*i*Pr) (**3m**) (entry 12). In most of the above reactions, the resulting phosphaguanidine products could be isolated in excellent yields, simply by a single recrystallization. The ^1H and ^{13}C NMR spectra of the phosphaguanidine products **3a–n** all showed only one isomer in solution, which could be assigned as the E_{syn} isomer according to literature.[12,9a–c]

Table 2. Catalytic addition of diphenylphosphine to *N,N′*-diisopropylcarbodiimide.[a]

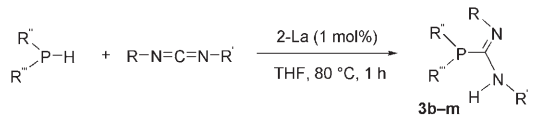


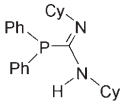
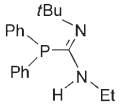
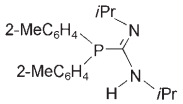
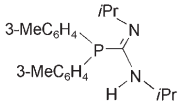
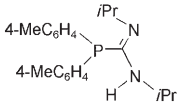
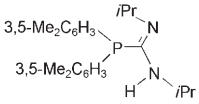
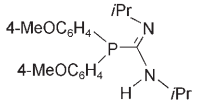
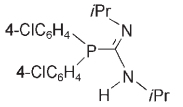
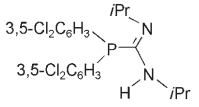
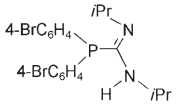
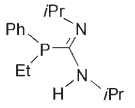
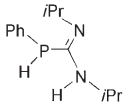
Entry	Catalyst [mol%]	Ionic radius of Ln^{3+} [Å][b]	Solvent	*T* [°C]	*t* [h]	Yield[c] [%]
1	0	–	C_6D_5Cl	140	12	0
2	**1-Y** (3)	0.900	[D_8]THF	80	1	86
3	**2-Y** (3)	0.900	[D_8]THF	80	1	86
4	**2-Sc** (3)	0.745	[D_8]THF	80	1	15
5	**2-Lu** (3)	0.861	[D_8]THF	80	1	50
6	**2-Gd** (3)	0.938	[D_8]THF	80	1	65
7	**2-Sm** (3)	0.958	[D_8]THF	80	1	69
8	**2-Nd** (3)	0.983	[D_8]THF	80	1	93
9	**2-Pr** (3)	0.990	[D_8]THF	80	1	94
10	**2-La** (3)	1.032	[D_8]THF	80	0.5	>99
11	**2-La** (3)	1.032	C_6D_6	110	18	85
12	**2-La** (3)	1.032	[D_8]toluene	110	9	95
13	**2-La** (1)	1.032	[D_8]THF	80	1	>99
14	**2-La** (0.5)	1.032	[D_8]THF	80	2	98

[a] Conditions: diphenylphosphine (0.35 mmol), *N,N(*-diisopropylcarbodiimide (0.34 mmol), Ln catalyst. [b] Ionic radius of six-coordination.[11] [c] Yields were determined by ^{31}P NMR.

Isolation and reactivity of the lanthanum phosphide and phosphaguanidinate intermediates: To gain information on the true catalyst species and the reaction mechanisms, the stoichiometric reaction between **2-La** and diphenylphosphine was first carried out in THF at room temperature for 5 h, which gave the corresponding half-sandwich phosphide complex [{Me_2Si-(C_5Me_4)($NC_6H_2Me_3$-2,4,6)}La-(PPh_2)($thf)_2$] (**4**) in 92% isolated yield (Scheme 3). Complex **4** is highly soluble in THF but sparingly soluble in *n*-hexane. Recrystallization of **4** in THF/ether at room temperature afforded light-yellow single crystals. An X-ray analysis revealed that **4** adopts a monomeric structure in which the metal

Table 3. Catalytic addition of phosphines to carbodiimides.[a]

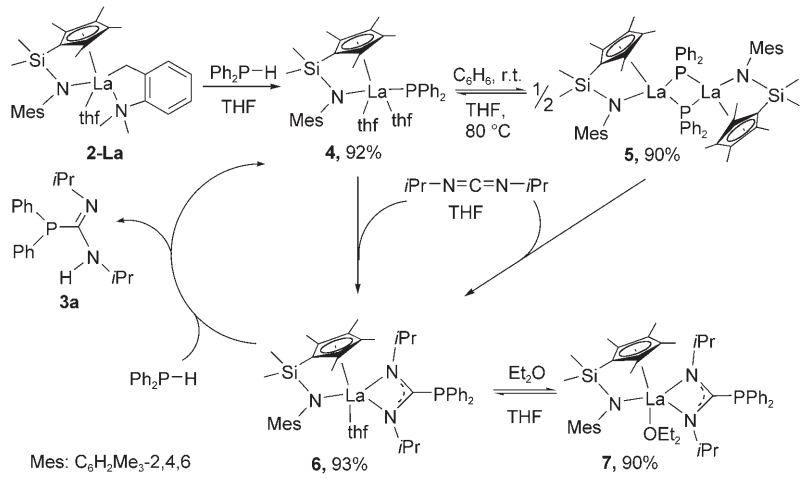


Entry	R″R‴PH	RN=C=NR′	Product	Yield[b] [%]
1	Ph_2PH	CyN=C=NCy		**3b**(99)
2	Ph_2PH	EtN=C=N*t*Bu		**3c**(95)
3	$(2\text{-}MeC_6H_4)_2PH$	*i*PrN=C=N*i*Pr		**3d**(99)
4	$(3\text{-}MeC_6H_4)_2PH$	*i*PrN=C=N*i*Pr		**3e**(99)
5	$(4\text{-}MeC_6H_4)_2PH$	*i*PrN=C=N*i*Pr		**3f**(99)
6	$(3,5\text{-}Me_2C_6H_3)_2PH$	*i*PrN=C=N*i*Pr		**3g**(98)
7	$(4\text{-}MeOC_6H_4)_2PH$	*i*PrN=C=N*i*Pr		**3h**(99)
8	$(4\text{-}ClC_6H_4)_2PH$	*i*PrN=C=N*i*Pr		**3i**(97)
9	$(3,5\text{-}Cl_2C_6H_3)_2PH$	*i*PrN=C=N*i*Pr		**3j**(95)
10	$(4\text{-}BrC_6H_4)_2PH$	*i*PrN=C=N*i*Pr		**3k**(97)
11	PhEtPH	*i*PrN=C=N*i*Pr		**3l**(86)[c]
12	$PhPH_2$	*i*PrN=C=N*i*Pr		**3m**(96)[c]

[a] Conditions: phosphine (2.02 mmol), carbodiimide (2.00 mmol), catalyst (0.02 mmol), solvent (5 mL). [b] Isolated yield. [c] Toluene, 110 °C, 12 h.

center is bonded to one Cp′-amido ligand, one PPh_2 ligand, and two THF ligands (Figure 4). When **4** was recrystallized in benzene, light yellow single crystals of $[\{Me_2Si(C_5Me_4)(NC_6H_2Me_3\text{-}2,4,6)\}La(\mu\text{-}PPh_2)]_2$ (**5**) were obtained (Scheme 3). An X-ray analysis showed that **5** adopts a dimeric structure through the phosphido bridges (Figure 5). There is no THF ligand in **5**. A crystallographic inversion center exists at the center of the molecule. The phosphido bridges are highly unsymmetrical. The length of the bridging La1–P1′ bond (3.0675(13) Å) is significantly shorter than that of the La1–P1 bond (3.1427(12) Å), can be compared even with the terminal La–P bond found in **4** (3.0697(16) Å). The La–Cp(centroid) bond distance in **5** (2.499(3) Å) is significantly shorter than that in **4** (2.541(6) Å), probably because the coordination number of the La ion in **5** (six) is smaller than that in **4** (seven). The La–N bond distances in both **4** (2.372(5) Å) and **5** (2.372(3) Å), however, are almost the same.

At room temperature, the dimeric structure of **5** could remain for about 24 h in THF. It showed a broad ^{31}P NMR peak at 8.53 ppm in $[D_8]$THF, in contrast with that of the monomeric **4**, which gave a sharp singlet at −14.5 ppm. However, on heating in THF at 80 °C for 5 h, **5** was completely converted into **4**. The reaction of **4** or **5** with *i*PrN=C=N*i*Pr in THF at room temperature gave the phosphaguanidinate complex $[\{Me_2Si(C_5Me_4)(NC_6H_2Me_3\text{-}2,4,6)\}La\{i\text{PrNC}(PPh_2)Ni\text{Pr}\}(thf)]$ (**6**) in 93% isolated yield (Scheme 3). Recrystallization of **6** in ether at room temperature yielded the ether-coordinated complex $[\{Me_2Si(C_5Me_4)(NC_6H_2Me_3\text{-}2,4,6)\}La\{i\text{PrNC}(PPh_2)Ni\text{Pr}\}(OEt_2)]$ (**7**) as light-orange crystals suitable for X-ray analysis. A crystallographic study showed that the phosphaguanidinate unit in **7** is bonded to the metal center through the two N atoms, as observed in a normal guanidinate or amidinate complex (Figure 6). The La–N bond distances (2.570(2) and 2.557(2) Å) of the phosphaguanidinate unit in **7** are longer than those in the guanidinate complex [La{CyNC(N-



Scheme 3. Formation of a lanthanum phosphaguanidinate and its reaction with diphenylphosphine.

lanthanide phosphaguanidinate species can be protonated by a phosphine P−H bond.

Reaction mechanism: On the basis of the experimental results described above, a possible reaction mechanism for the catalytic addition of a phosphine P−H bond to a carbodiimide compound by **2-La** could be proposed, as shown in Scheme 4. The acid-base metathesis reaction between a phosphine P−H bond and the La−benzyl bond should yield straightforwardly a phosphide

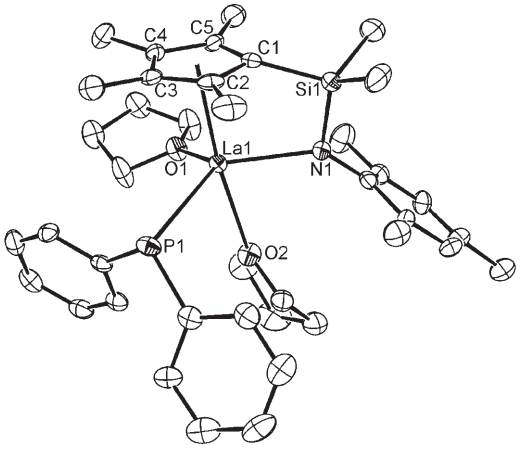


Figure 4. ORTEP drawing of **4** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: La1−P1 3.0697(16), La1−N1 2.372(5), La1−O1 2.560(3), La1−O2 2.583(3), La1−C1 2.670(5), La1−C2 2.772(5), La1−C3 2.9276, La1−C4 2.904(5), La1−C5 2.749(5), La1−Cp(centroid) 2.541(6); N1−La1−Cp(centroid) 92.02(13), P1−La1−Cp(centroid) 98.41(13), N1−La1−P1 119.71(10), O1−La1−O2 77.81(13).

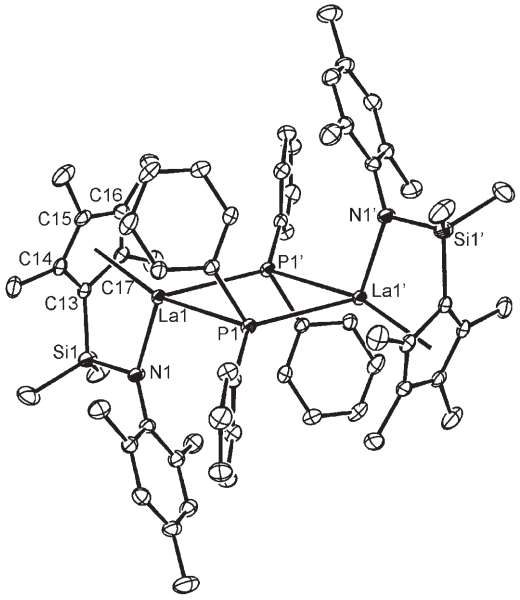


Figure 5. ORTEP drawing of **5** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: La1−P1 3.1427(12), La1−P1′ 3.0675(13), La1−N1 2.372(3), La1−C13 2.677(3), La1−C14 2.752(3), La1−C15 2.866(3), La1−C16 2.852(3), La1−C17 2.734(3), La1−Cp(centroid) 2.499(3); N1−La1−Cp(centroid) 92.15(8), P1−La1−Cp(centroid) 110.80(8), P1′−La1−Cp(centroid) 162.35(8), N1−La1−P1 105.47(7), N1−La1−P(1′) 107.40(8), P1−La1−P1′ 65.37(3), La1−P1−La1′ 114.63(3).

$(SiMe_3)_2)NCy\}(OC_6H_3tBu_2\text{-}2,6)_2]$ (2.448(5) and 2.467(5) Å),[13] but comparable with those found in the cationic amidinate complex $[\{(2,6\text{-}iPr_2C_6H_3N)_2CPh\}La(CH_2SiMe_3)(thf)_4]^+$ (2.534(4) and 2.556(4) Å).[14]

A reaction between **6** and diphenylphosphine was not observed at room temperature in [D_8]THF. However, when a 1:1 mixture of **6** and diphenylphosphine was heated to 80 °C, the phosphaguanidine **3a** and complex **4** were formed almost quantitatively (Scheme 3). The catalytic formation of **3a** was achieved if excess amounts of diphenylphosphine and *i*PrN=C=N*i*Pr (1:1) were added to **6** in [D_8]THF and heated at 80 °C. The analogous reaction between **7** and diphenylphosphine afforded **3a** and complex **4** similarly. These results clearly demonstrate for the first time that a species such as **A**. Nucleophilic addition of the phosphide species to a carbodiimide would afford the phosphaguanidinate species **B**, which on abstraction of a proton from another molecule of phosphine would yield the phosphaguanidine product and regenerate the phosphide **A**. The isolation of **4** and **6** and the transformation of **6** to **3a** and **4** by reaction with diphenylphosphine strongly support this mechanism (see Scheme 3).

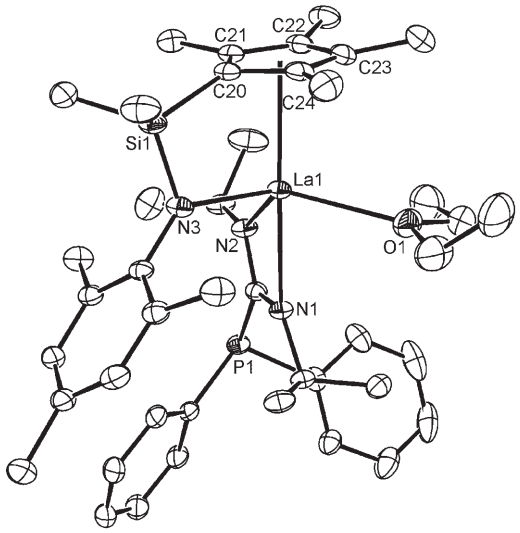
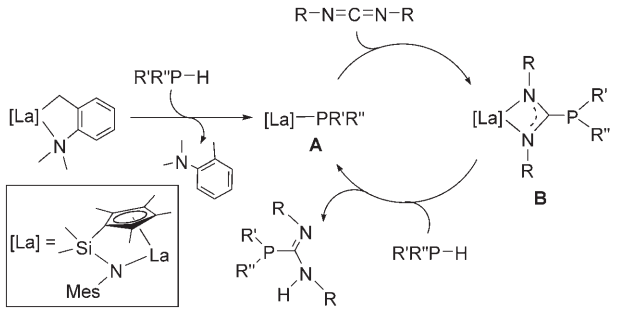


Figure 6. ORTEP drawing of **7** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: La1–N1 2.570(2), La1–N2 2.557(2), La1–N3 2.382(3), La1–O1 2.667(3), N1–C1 1.330(4), N2–C1 1.338(4), P1–C1 1.915(3), La1–C20 2.723(3), La1–C21 2.827(3), La1–C22 2.948(3), La1–C23 2.929(3), La1–C24 2.791(3), La1–Cp(centroid) 2.574(3); N1–La1–Cp(centroid) 171.55(9), N2–La1–Cp(centroid) 119.83(9), N3–La1–Cp(centroid) 90.52(9), O1–La1–Cp(centroid) 99.44(9), N1–La1–N3 95.52(8), N2–La1–N3 106.37(9), N1–La1–N2 52.67(8), C1–N1–La1 94.92(17), C1–N2–La1 95.31(17), N1–C1–N2 117.0(3), N1–C1–P1 126.7(2), N2–C1–P1 116.3(2).



Scheme 4. A possible mechanism of the catalytic addition of a phosphine P–H bond to a carbodiimide compound.

Conclusion

Half-sandwich *o*-dimethylaminobenzyl complexes **2-Ln** (Ln = Sc, Y, La, Pr, Sm, Nd, Gd, Lu) bearing silylene-linked cyclopentadienyl-amido ligands have been synthesized and structurally characterized for the first time over the full size range of the rare-earth metal series. Such complexes serve as efficient catalyst precursors for the catalytic addition of various phosphine P–H bonds to carbodiimides, and have lead to the formation of a series of phosphaguanidine derivatives with excellent tolerability to aromatic carbon-halogen bonds. An increase in the rare-earth metal size, leads to a significant increase in the catalytic activity. The isolation and reactivity investigation of the phosphide (e.g., **4** and **5**) and phosphaguanidinate intermediates (e.g., **6**) suggests that the catalytic formation of a phosphaguanidine compound proceeds through the nucleophilic addition of a phosphide species, which is formed by the acid-base reaction between a rare-earth-metal-alkyl bond and a phosphine P–H bond, to a carbodiimide, followed by the protonolysis of the resultant phosphaguanidinate species by a phosphine P–H bond.

Experimental Section

All reactions were carried out under a dry and inert atmosphere by using either standard Schlenk techniques or under a nitrogen atmosphere in an MBRAUN glovebox. The argon was purified by passage through a Dry-clean column (4 Å molecular sieves, Nikka Seiko) and a Gasclean GC-XR column (Nikka Seiko). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves catalyst unit. The oxygen and moisture concentrations in the glovebox atmosphere were monitored by an O_2/H_2O Combi-Analyzer (MBRAUN) to ensure both were always below 1 ppm. Solvents were distilled from sodium/benzophenone ketyl, and dried over fresh Na. [D_6]Benzene, [D_8]toluene, and [D_8]THF (all 99+atom % D) were obtained from Acros Organics, and were dried over fresh Na chips for NMR reactions. Ph_2PH and $PhPH_2$ were purchased from TCI. $(4\text{-}MeC_6H_4)_2PH$ and $(3,5\text{-}Me_2C_6H_3)_2PH$ were purchased from Strem. Other phosphines were prepared according to literature.[15] $(4\text{-}BrC_6H_4)_2PH$ (new compound) was synthesized analogously.[15a] Phosphaguanidines **3a**[9c] and **3b**[9c] are known compounds. All other phosphaguanidines reported in this paper are new compounds. The amine ligands $(C_5Me_4H)SiMe_2NH(C_6H_2Me_3\text{-}2,4,6)$[5e] and $[Sc(CH_2C_6H_4NMe_2\text{-}o)_3]$[16] were prepared according to their respective published procedures.

IR spectra were obtained by using a Shimadzu IRPrestige-21 spectrophotometer using Nujol mulls between KBr disks. The high-resolution mass spectroscopy (HRMS) data were recorded by using a JEOL JMS-700 instrument operated in EF-FAB$^+$ mode. Samples for NMR spectroscopic measurements were prepared under a dry and oxygen-free argon atmosphere or in the glovebox by use of J. Young valve NMR tubes (Wilmad 528-JY). ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded by means of a JEOL-AL400 spectrometer (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C; 160 MHz for ^{31}P), a JEOL JNM-AL300 spectrometer (FT, 300 MHz for ^{1}H; 75 MHz for ^{13}C) or a JEOL JNM-AL270 spectrometer (FT, 270 MHz for ^{1}H; 68 MHz for ^{13}C) at room temperature, unless otherwise noted. Phosphorus chemical shifts were measured relative to an external 85% aqueous solution of H_3PO_4. Micro elemental analyses were performed by means of a MICRO CORDER JM10 apparatus (J-Science Lab.).

$(4\text{-}BrC_6H_4)_2PH$: This compound was prepared according to literature[15a] via reduction of $(4\text{-}BrC_6H_4)_2POH$ by use of 3 equiv DIBAL-H/THF to yield a colorless solid in 86% yield; ^{1}H NMR (300 MHz, C_6D_6): $\delta = 4.80$ (d, $^1J_{PH} = 216.9$ Hz, 1H; PH), 6.82–6.87 (m, 4H; C_6H_4), 7.11–7.14 ppm (m, 4H; C_6H_4); ^{13}C NMR (75 MHz, C_6D_6): $\delta = 123.6$, 132.0 (d, $^3J_{PC} = 6.2$ Hz), 133.6 (d, $^1J_{PC} = 11.7$ Hz), 135.6 ppm (d, $^2J_{PC} = 17.9$ Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): $\delta = -43.5$ ppm; HRMS: *m/z:* calcd for $C_{12}H_{10}{}^{79}Br_2P$: 342.8887 $[M+H]^+$; found: 342.8895.

$[La(CH_2C_6H_4NMe_2\text{-}o)_3]$: This compound was prepared by a modified literature procedure.[7] $LaBr_3$ instead of $LaCl_3$ was used here. THF (20 mL) was added to $LaBr_3$ (900 mg, 2.377 mmol) at room temperature in a Schlenk tube and sealed with a Teflon stopcock. This tube was taken outside and was heated at 70°C for 5 h to form the thf-coordinated lanthanum complex $LaBr_3(thf)_4$. After cooling down to room temperature, a THF solution (10 mL) of $KCH_2C_6H_4NMe_2\text{-}o$ (1.236 g, 7.131 mmol) was added to a THF suspension of lanthanum bromide at room temperature in the glove box. After stirring for 30 min, the solvent was removed under reduced pressure to give an oily residue, which was then dissolved in toluene (20 mL) and filtered to remove the potassium salt. The filtrate was concentrated and cooled down to −30°C to give yellow cubic crystals (1.125 g, 2.068 mmol, 87% yield). ^{1}H NMR (300 MHz, C_6D_6, 50°C): $\delta =$ 1.63 (s, 6H; CH_2), 1.93 (s, 18H; NMe_2), 6.28 (t, 3H; aryl), 6.61–6.69 ppm

(m, 9H; aryl); ^{1}H NMR (300 MHz, [D$_8$]THF, 25°C): δ=1.58 (s, 6H; CH_2), 2.34 (s, 18H; NMe_2), 6.42 (t, J=7.5 Hz, 3H; aryl), 6.67 (d, J=8.1 Hz, 3H; aryl), 6.82 (t, J=7.5 Hz, 3H; aryl), 7.04 ppm (d, J=8.1 Hz, 3H; aryl).

[Pr(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$]: Starting from $PrBr_3$ (3.806 g, 10 mmol), [Pr(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] was obtained as yellow green cubic crystals (yield, 5.018 g, 9.2 mmol, 92% yield) in a manner analogous to that described for the synthesis of [La(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$]. ^{1}H NMR (300 MHz, [D$_8$]THF, 50°C): δ=−23.37 (brs, 18H; NMe_2), −9.50 (brs, 3H; aryl), −0.85 (brs, 3H aryl), 8.59 (brs, 3H; aryl), 23.38 ppm (brs, 3H; aryl); ^{13}C NMR (75 MHz, [D$_8$]THF, 50°C): δ=−29.4, 78.5, 100.2, 113.1, 135.8, 162.4 ppm; elemental analysis calcd (%) for $C_{27}H_{36}PrN_3$: C 59.67, H 6.68, N 7.73; found: C 59.84, H 6.52, N 7.43. The ^{1}H NMR signals for benzyl protons was not observed.

[Nd(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$]: Starting from anhydrous $NdBr_3$ (1.919 g, 5 mmol), [Nd(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] was obtained as dark green cubic crystals (2.261 g, 4.15 mmol, 83% yield) in a manner analogous to that described for the synthesis of [La(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$]. ^{1}H NMR (300 MHz, [D$_8$]THF, 50°C): δ=−11.94 (brs, 18H; NMe_2), −1.02 (brs, 3H; aryl), 1.12 (brs, 3H aryl), 9.46 (brs, 3H; aryl), 14.69 (brs, 3H; aryl), 17.12 ppm (brs, 6H; CH_2); ^{13}C NMR (68 MHz, [D$_8$]THF, 50°C): δ=85.7, 98.6, 113.5, 139.3, 143.6, 161.2 ppm; elemental analysis calcd (%) for $C_{27}H_{36}NdN_3$: C 59.30, H 6.64, N 7.68; found: C 59.02, H 6.28, N 7.65.

[Y(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$]: This compound was prepared by a modified literature procedure.[7] Li$CH_2C_6H_4NMe_2$-*o* instead of K$CH_2C_6H_4NMe_2$-*o* was used here. Anhydrous yttrium chloride (976 mg, 5 mmol) was suspended in THF(20 mL). A THF solution (20 mL) of Li$CH_2C_6H_4NMe_2$-*o* (2.117 g, 15 mmol) was slowly added at room temperature. After stirring for 30 min, the solvent was removed under reduced pressure. The residue was dissolved in toluene (30 mL) and filtered to remove lithium salt. The filtrate was concentrated and cooled down to −30°C to give [Y(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] as yellow cubic crystals (1.843 g, 75% yield). ^{1}H NMR (400 MHz, C_6D_6): δ=1.63 (s, 6H; CH_2), 2.11 (s, 18H; NMe_2), 6.66 (t, J=6.6 Hz, 3H; aryl), 6.83 (d, J=8.1 Hz, 3H; aryl), 7.00 (t, J=8.1 Hz, 3H; aryl), 7.11 ppm (d, J=6.6 Hz, 3H; aryl).

[Sm(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$]: Starting from anhydrous $SmCl_3$ (1.283 g, 5 mmol), [Sm(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] was obtained as red purple cubic crystals (2.530 g, 4.6 mmol, 92% yield) in a manner analogous to that described for the synthesis of [Y(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$]. ^{1}H NMR (300 MHz, [D$_8$]THF): δ=−1.53 (s, 18H; NMe_2), 4.79 (s, 3H; aryl), 7.05 (s, 3H; aryl), 7.19 (s, 3H aryl), 9.60 (s, 3H; aryl), 13.94 ppm (s, 6H; CH_2); ^{13}C NMR (68 MHz, [D$_8$]THF): δ=40.0, 112.2, 123.6, 124.5, 128.2, 128.9, 131.5, 155.2 ppm; elemental analysis calcd (%) for $C_{27}H_{36}SmN_3$: C 58.65, H 6.56, N 7.60; found: C 59.14, H 6.56, N 7.41.

[Gd(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$]: Starting from anhydrous $GdCl_3$ (2.636 g, 10 mmol), [Gd(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] was obtained as yellow crystals (4.759 g, 8.5 mmol, 85% yield) in a manner analogous to that described for the synthesis of [Y(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$]. The ^{1}H NMR spectrum of [Gd(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] was not informative because of the influence of the paramagnetic Gd(III) ion. Elemental analysis calcd (%) for $C_{27}H_{36}GdN_3$: C 57.92, H 6.48, N 7.51; found: C 57.93, H 6.30, N 7.40.

[Lu(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$]: Starting from anhydrous $LuCl_3$ (2.251 g, 8 mmol), [Lu(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] was obtained as yellow cubic crystals (3.558 g, 6.16 mmol, 77% yield) in a manner analogous to that described for the synthesis of [Y(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$]. ^{1}H NMR (300 MHz, C_6D_6): δ=1.48 (s, 6H; CH_2), 2.17 (s, 18H; NMe_2), 6.70–6.78 (m, 6H; aryl), 7.01 (t, J=7.5 Hz, 3H; aryl), 7.09 ppm (d, J=7.7 Hz, 3H; aryl); ^{13}C NMR (75 MHz, C_6D_6): δ=44.8 (NMe_2), 48.4 (CH_2), 118.8, 119.1, 127.5, 129.6, 139.1, 142.8 ppm (aromatics); elemental analysis calcd (%) for $C_{27}H_{36}LuN_3$: C 56.15, H 6.28, N 7.28; found: C 56.18, H 6.18, N 7.14.

[{Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)}La(CH$_2$C$_6$H$_4$NMe$_2$-*o*)(thf)] (2-La): To a THF solution (10 mL) of [La(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] (1.083 g, 2 mmol) was added a THF solution (2 mL) of (C_5Me_4H)$SiMe_2NH$($C_6H_2Me_3$-2,4,6) (0.627 g, 2 mmol) at room temperature. After stirring for 2 h at room temperature, the solvent was removed under reduced pressure. The residue was washed by ether and dissolved in toluene (50 mL). Slow evaporation of the solvent gave **2-La** as light yellow crystals (1.138 g, 1.74 mmol, 87% yield). ^{1}H NMR (300 MHz, C_6D_6, 50°C): δ=0.70 (s, 6H; $SiMe_2$), 1.10 (brs, 4H; β-CH_2,thf), 1.92 (s, 6H; C_5Me_4), 2.02 (brs, 6H; NMe_2), 2.20 (s, 2H; CH_2), 2.31 (s, 3H; *p*-Me), 2.42, (s, 6H; C_5Me_4 or *o*-Me), 2.49 (s, 6H; C_5Me_4 or *o*-Me), 2.83 (brs, 4H; α-CH_2, thf), 6.25 (t, J=7.8 Hz, 1H; aryl), 6.49 (d, J=7.2 Hz, 1H; aryl), 6.75 (t, J=8.1 Hz, 1H; aryl), 6.86 (d, J=6.3 Hz, 1H; aryl), 6.97 ppm (s, 2H; aryl); ^{1}H NMR (300 MHz, [D$_8$]THF): δ=0.33 (s, 6H; $SiMe_2$), 1.73 (s, 2H; CH_2), 1.97 (brs, 6H; NMe_2), 1.99 (s, 6H; C_5Me_4), 2.17 (s, 3H; *p*-Me), 2.27, (s, 6H; C_5Me_4 or *o*-Me), 2.30 (s, 6H; C_5Me_4 or *o*-Me), 6.36 (t, J=8.7 Hz, 1H; aryl), 6.65 (d, J=6.3 Hz, 1H; aryl), 6.73 (t, J=6.6 Hz, 1H; aryl), 6.76 (s, 2H; aryl), 6.83 ppm (d, J=8.3 Hz, 1H; aryl); ^{13}C NMR (75 MHz, [D$_8$]THF): δ=6.7, 11.4, 14.5, 20.8, 21.3, 26.4, 41.4 (NMe_2), 44.5 (CH_2), 68.2, 107.2, 116.7, 119.1, 121.8, 123.2, 126.89, 126.94 127.2, 127.6, 129.2, 131.6, 136.5, 144.5, 152.0 ppm; elemental analysis calcd (%) for $C_{33}H_{49}N_2OSiLa$: C 60.35, H 7.52, N 4.27; found: C 60.68, H 7.41, N 4.20.

[{Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)}Pr(CH$_2$C$_6$H$_4$NMe$_2$-*o*)(thf)] (2-Pr): To a THF solution (8 mL) of [Pr(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] (0.543 g, 1 mmol) was added a THF solution (2 mL) of (C_5Me_4H)$SiMe_2NH$($C_6H_2Me_3$-2,4,6) (0.314 g, 1 mmol) at room temperature. After stirring for 2 h at 50°C, the solvent was removed under reduced pressure. The residue was washed by hexane and dissolved in THF. Slow evaporation of the solvent gave **2-Pr** as light green crystals (0.396 g, 0.60 mmol, 60% yield). ^{1}H NMR (300 MHz, C_6D_6, 50°C): δ=−8.29 (brs, 4H; thf), 2.39 (brs, 6H; $SiMe_2$), 3.19 (s, 3H; *p*-Me), 6.60 (brs, 2H; aryl), 7.07 (s, 1H; aryl), 14.52 (s, 1H; aryl), 14.59 (s, 1H; aryl), 22.53 ppm (brs, 1H; aryl); ^{1}H NMR (300 MHz, [D$_8$]THF, 50°C): δ=2.25 (brs, 6H; $SiMe_2$), 3.01 (s, 3H; *p*-Me), 6.28 (s, 2H; aryl), 7.36 (s, 1H; aryl), 13.54 (s, 1H; aryl), 16.09 (s, 1H; aryl), 18.63 ppm (s, 1H; aryl), other signals were not observed because of the influence of the paramagnetic Pr(III) ion; ^{13}C NMR (75 MHz, [D$_8$]THF, 50°C): δ=18.0, 26.6, 68.2, 108.4, 117.6, 123.5, 125.1, 134.9, 151.0, 155.7, 166.9 ppm; elemental analysis calcd (%) for $C_{33}H_{49}N_2OSiPr$: C 60.17, H 7.50, N 4.25; found: C 60.26, H 7.60, N 4.34.

[{Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)}Nd(CH$_2$C$_6$H$_4$NMe$_2$-*o*)(thf)] (2-Nd): To a THF solution (5 mL) of [Nd(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] (0.547 g, 1 mmol) was added a THF solution (2 mL) of (C_5Me_4H)$SiMe_2NH$($C_6H_2Me_3$-2,4,6) (0.314 g, 1 mmol) at room temperature. After stirring for 2 h at 50°C, the solvent was removed under reduced pressure. The residue was washed with hexane and dissolved in toluene. Slow evaporation of the solvent gave **2-Nd** as green crystals (0.410 g, 0.61 mmol, 61% yield). ^{1}H NMR (300 MHz, C_6D_6, 50°C): δ=−6.30 (brs, 4H; thf), −2.98 (brs, 4H; thf), 3.66 (s, 3H; *p*-Me), 4.72 (s, 6H; $SiMe_2$), 7.49 (s, 2H; aryl), 10.86 (s, 1H; aryl), 13.35 (s, 1H; aryl), 16.71 ppm (s, 1H; aryl); ^{1}H NMR (300 MHz, [D$_8$]THF, 50°C): δ=3.42 (s, 3H; *p*-Me), 4.35 (s, 6H; $SiMe_2$), 4.86 (s, 1H; aryl), 7.15 (s, 2H; aryl), 11.44 (s, 1H; aryl), 12.89 (s, 1H; aryl), 15.09 (s, 1H; aryl), other signals were not observed because of the influence of the paramagnetic Nd(III) ion; ^{13}C NMR (75 MHz, [D$_8$]THF, 50°C): δ=16.7, 26.6, 68.2, 98.4, 103.4, 117.7, 122.3, 129.1, 138.0, 154.3, 168.0 ppm; elemental analysis calcd (%) for $C_{33}H_{49}N_2OSiNd$: C 59.86, H 7.46, N 4.23; found: C 59.82, H 7.36, N 4.11.

[{Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)}Sm(CH$_2$C$_6$H$_4$NMe$_2$-*o*)(thf)] (2-Sm): To a THF solution (5 mL) of [Sm(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] (0.553 g, 1 mmol) was added a THF solution (2 mL) of (C_5Me_4H)$SiMe_2NH$($C_6H_2Me_3$-2,4,6) (0.314 g, 1 mmol) at room temperature. After stirring for 2 h at 50°C, the solvent was removed under reduced pressure. The residue was washed by hexane and recrystallization from THF gave **2-Sm** as red crystals (0.419 g, 0.62 mmol, 62% yield). ^{1}H NMR (400 MHz, C_6D_6): δ=−0.20 (brs, 4H; thf), 0.59 (brs, 4H; thf), 1.18 (s, 6H; $SiMe_2$), 2.20 (s, 3H; *p*-Me), 6.28 (d, J=7.5 Hz, 1H; aryl), 6.90 (s, 2H; aryl), 7.46 (t, J=7.1 Hz, 1H; aryl), 7.51 (brs, 2H; CH_2), 7.70 (t, J=7.1 Hz, 1H; aryl), 10.15 ppm (d, J=7.9 Hz, 1H; aryl), other signals were not observed because of the influence of the paramagnetic Sm(III) ion; ^{13}C NMR (75 MHz, [D$_8$]THF, 50°C): δ=8.3, 14.8, 21.3, 22.5, 26.5, 43.9, 68.2, 102.9, 114.4, 125.7, 125.8, 127.2, 129.9, 132.0, 139.6, 160.0, 163.7 ppm; elemental analysis calcd (%) for $C_{33}H_{49}N_2OSiSm$: C 59.32, H 7.39, N 4.19; found: C 59.19, H 7.01, N 3.99.

[{Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)}Gd(CH$_2$C$_6$H$_4$NMe$_2$-*o*)(thf)] (2-Gd): To a THF solution (8 mL) of [Gd(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] (0.560 g, 1 mmol) was added a THF solution (2 mL) of (C_5Me_4H)$SiMe_2NH$($C_6H_2Me_3$-2,4,6) (0.314 g, 1 mmol) at room temperature. After stirring for 3 h at 50°C, the

solvent was removed under reduced pressure. The residue was washed by ether and dissolved in toluene (30 mL). Slow evaporation of the solvent gave **2-Gd** as yellow crystals (0.405 g, 0.6 mmol, 60%). The ^{1}H NMR spectrum of **2-Gd** was not informative because of the influence of the paramagnetic Gd(III) ion. Elemental analysis calcd (%) for $C_{33}H_{49}N_2OSiGd$: C 58.71, H 7.32, N 4.15; found: C 58.33, H 7.07, N 4.31.

[{Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)}Lu(CH$_2$C$_6$H$_4$NMe$_2$-*o*)(thf)] (2-Lu): To a THF solution (8 mL) of [Lu(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] (0.578 g, 1 mmol) was added a THF solution (2 mL) of (C$_5$Me$_4$H)SiMe$_2$NH(C$_6$H$_2$Me$_3$-2,4,6) (0.314 g, 1 mmol) at room temperature. After stirring for overnight at 70°C, the solvent was removed under reduced pressure. The residue was washed by hexane and dissolved in toluene (30 mL). Slow evaporation of the solvent gave **2-Lu** as colorless crystals (0.476 g, 0.69 mmol, 69% yield). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.69 (s, 6H; SiMe$_2$), 1.30 (brs, 4H; β-CH$_2$, thf), 1.68 (brs, 8H; NMe$_2$ and CH$_2$), 1.94 (s, 6H; C$_5$Me$_4$), 2.29 (s, 3H; *p*-Me), 2.36 (s, 6H; C$_5$Me$_4$ or *o*-Me), 2.42 (s, 6H; C$_5$Me$_4$ or *o*-Me), 3.37 (brs, 4H; α-CH$_2$, thf), 6.39 (d, J = 8.1 Hz, 1H; aryl), 6.58 (t, J = 6.9 Hz, 1H; aryl), 6.87 (t, J = 6.9 Hz, 1H; aryl), 7.07 ppm (d, J = 7.8 Hz, 1H; aryl); ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 0.33 (s, 6H; SiMe$_2$), 1.50 (brs, 2H; CH$_2$), 2.02 (brs, 6H; NMe$_2$), 2.14 (s, 6H; C$_5$Me$_4$ or *o*-Me), 2.22 (s, 3H; *p*-Me), 2.32 (s, 12H; C$_5$Me$_4$ or *o*-Me), 6.57 (t, J = 7.5 Hz, 1H; aryl), 6.65–6.85 ppm (m, 5H; aryl); ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 5.6, 12.0, 14.8, 20.8, 21.2, 26.4, 44.9 (brs, NMe$_2$), 49.5 (CH$_2$), 68.2, 105.3, 118.0, 119.5, 122.5, 126.6, 127.7, 128.4, 129.2, 132.6, 145.8, 146.2, 152.8 ppm; elemental analysis calcd (%) for $C_{33}H_{49}N_2OSiLu$: C 57.21, H 7.13, N 4.04; found: C 56.58, H 6.78, N 3.89.

[{Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)}Y(CH$_2$C$_6$H$_4$NMe$_2$-*o*)(thf)] (2-Y): To a THF solution (5 mL) of [Y(CH$_2$C$_6$H$_4$NMe$_2$-*o*)$_3$] (0.492 g, 1 mmol) was added a THF solution (2 mL) of (C$_5$Me$_4$H)SiMe$_2$NH(C$_6$H$_2$Me$_3$-2,4,6) (0.314 g, 1 mmol) at room temperature. After stirring for overnight at 50°C, the solvent was removed under reduced pressure. The residue was washed by ether and dissolved in toluene (30 mL). Slow evaporation of the solvent gave **2-Y** as light yellow crystals (0.534 g, 0.87 mmol, 87% yield). ^{1}H NMR (300 MHz, C$_6$D$_6$, 50°C): δ = 0.66 (s, 6H; SiMe$_2$), 1.15 (brs, 4H; β-CH$_2$, thf), 1.92 (brs, 8H; NMe$_2$ and CH$_2$), 2.00 (s, 6H; C$_5$Me$_4$), 2.29 (s, 3H; *p*-Me), 2.39 (s, 6H; C$_5$Me$_4$ or *o*-Me), 2.40 (s, 6H; C$_5$Me$_4$ or *o*-Me), 3.00 (brs, 4H; α-CH$_2$, thf), 6.40–6.47 (m, 2H; aryl), 6.78–6.82 (m, 1H; aryl), 6.95 (s, 2H; aryl), 7.01 ppm (d, J = 7.8 Hz, 1H; aryl); ^{1}H NMR (300 MHz, [D$_8$]THF): δ = 0.30 (s, 6H; SiMe$_2$), 1.60 (brs, 2H; CH$_2$), 2.00 (brs, 6H; NMe$_2$), 2.10 (s, 6H; C$_5$Me$_4$ or *o*-Me), 2.17 (s, 3H; *p*-Me), 2.28 (s, 6H; C$_5$Me$_4$ or *o*-Me), 2.29 (s, 6H; C$_5$Me$_4$ or *o*-Me), 6.48 (t, J = 6.9 Hz, 1H; aryl), 6.75 (s, 2H; aryl), 6.75–6.81 ppm (m, 3H; aryl); ^{13}C NMR (75 MHz, [D$_8$]THF): δ = 5.9, 12.0, 14.8, 20.8, 21.5, 26.4, 43.9 (brs, NMe$_2$), 47.0 (d, $J_{Y,C}$ = 31.1 Hz, CH$_2$), 68.2, 106.1, 118.7, 119.1, 122.6, 123.6, 126.0, 127.0, 127.3, 128.0, 128.9, 129.2, 129.5, 132.0, 142.7, 145.3, 152.8 ppm; elemental analysis calcd (%) for $C_{33}H_{49}N_2OSiY$: C 65.32, H 8.14, N 4.62; found: C 64.64, H 7.81, N 4.35.

[{Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)}Sc(CH$_2$C$_6$H$_4$NMe$_2$-*o*)] (2-Sc): A THF solution of [Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)]Li$_2$, which was prepared by the reaction of (C$_5$Me$_4$H)SiMe$_2$NH(C$_6$H$_2$Me$_3$-2,4,6) (0.879 g, 2.8 mmol) with *n*-butyl lithium (5.6 mmol, 2.67 (M), 2.1 mL), was added to a THF solution (15 mL) of ScCl$_3$ (0.424 g, 2.8 mmol) at room temperature. After stirring for overnight, a THF solution (10 mL) of LiCH$_2$C$_6$H$_4$NMe$_2$-*o* (0.395 g, 2.8 mmol) was slowly added to the solution. After stirring for 2 h, the solvent was removed under reduced pressure. The residue was dissolved in toluene (50 mL) and filtrated to remove Li salt. The solvent was removed under reduced pressure to give orange oil. The product was dissolved in small amount of toluene. Ether was slowly layered to the solution to afford **2-Sc** as yellow crystals (0.992 g, 1.876 mmol, 67% yield). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.64 (s, 3H; SiMe$_2$), 0.71 (s, 3H; SiMe$_2$), 1.15 (s, 3H; Me), 1.28 (d, 1H; J = 10.5 Hz, CH$_2$), 1.78 (s, 3H; Me), 1.87 (s, 3H; Me), 1.97 (d, 1H; J = 10.5 Hz, CH$_2$), 2.13 (s, 3H; Me), 2.16 (s, 3H; Me), 2.24, (s, 3H; Me), 2.30 (s, 3H; Me), 2.40 (s, 3H; Me), 2.41 (s, 3H; Me), 6.45 (d, J = 8.1 Hz, 1H; aryl), 6.68 (t, J = 7.5 Hz, 1H; aryl), 6.91 (s, 2H; *m*-H), 6.92 (t, J = 7.5 Hz, 1H; aryl), 7.02 ppm (d, J = 8.1 Hz, 1H; aryl); ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 4.5, 6.7, 10.2, 11.4, 14.2, 14.7, 20.4, 20.8, 20.9, 42.2, 44.1, 45.8, 46.9, 107.4, 118.4, 121.6, 124.2, 126.2, 127.6, 127.9, 128.2, 129.0, 129.5, 129.8, 131.3, 131.4, 132.2, 138.3, 141.3, 149.0 ppm; elemental analysis calcd (%) for $C_{33}H_{49}N_2OSiSc$: C 70.98, H 8.42, N 5.71; found: C 70.89, H 8.39, N 5.37.

Typical procedures for catalytic addition reactions of phosphines to carbodiimides

NMR tube reaction: In the glovebox, a J. Young valve NMR tube was charged with **2-La** (7 mg, 0.01 mmol), [D$_8$]THF (0.45 mL), diphenylphosphine (63 mg, 0.35 mmol), *N*,*N*′-diisopropylcarbodiimide (43 mg, 0.34 mmol). Release of *o*-dimethylaminotoluene was confirmed by ^{1}H NMR. Formation of **3a** and disappearance of diphenylphosphine were easily monitored by ^{31}P NMR. The conversion of diphenylphosphine was determined by ^{31}P NMR. No other coupling products were observed.

Preparative scale reaction: In the glovebox, a THF solution (3 mL) of diphenylphosphine (376 mg, 2.02 mmol) was added to a THF solution (2 mL) of **2-La** (13 mg, 0.02 mmol) in a Schlenk tube. Then *N*,*N*′-diisopropylcarbodiimide (252 mg, 2.00 mmol) was added to the above reaction mixture. After 1 h of stirring at 80°C, the solvent was removed under reduced pressure. The residue was extracted with hexane and filtered to give a clean solution. After removing the solvent under vacuum, the residue was recrystallized in hexane to provide a colorless solid **3a**.

It should be pointed out that the phosphaguanidine compounds reported in this paper are very sensitive to oxygen, and must be stored under an inert atmosphere.

***i*PrN=C(PPh$_2$)(NH*i*Pr) (3a)**: colorless solid, yield 99%; ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.94 (d, J = 6.6 Hz, 6H; CH(C*H*$_3$)$_2$), 1.23 (d, J = 6.3 Hz, 6H; CH(C*H*$_3$)$_2$), 3.63 (d, ^3J = 6.3 Hz, 1H; NH), 4.28–4.43 (m, 2H; CH), 7.03–7.05 (m, 6H; C$_6$H$_5$), 7.42–7.47 ppm (m, 4H; C$_6$H$_5$); ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 22.5, 25.3, 42.9, 52.2 (d, $^3J_{PC}$ = 35.3 Hz), 129.0 (d, $^3J_{PC}$ = 6.8 Hz), 129.3, 134.3 (d, $^2J_{PC}$ = 19.8 Hz), 135.5 (d, $^1J_{PC}$ = 13.7 Hz), 152.4 ppm (d, $^1J_{PC}$ = 31.6 Hz); ^{31}P{^{1}H} NMR (160 MHz, C$_6$D$_6$): δ = −18.5 ppm; IR (Nujol): $\tilde{\nu}$ = 3431 (N−H), 1599 (C=N), 1462, 1377, 1173, 1026, 743, 696 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{19}H_{26}N_2P$: 313.1834 [*M*+H]$^+$; found: 313.1853.

CyN=C(PPh$_2$)(NHCy) (3b): colorless solid, yield 99%; ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.92–1.93 (m, 20H; Cy), 3.81 (d, ^3J = 6.9 Hz, 1H; NH), 4.05–4.19 (m, 2H; CH), 7.02–7.13 (m, 6H; C$_6$H$_5$), 7.48–7.53 ppm (m, 4H; C$_6$H$_5$); ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 24.6, 25.2, 26.2, 26.3, 32.5, 35.7, 49.1, 60.3 (d, $^3J_{PC}$ = 33.4 Hz), 129.0 (d, $^3J_{PC}$ = 6.8 Hz), 129.3, 134.2 (d, $^2J_{PC}$ = 19.2 Hz), 135.7 (d, $^1J_{PC}$ = 14.9 Hz), 152.4 ppm (d, $^1J_{PC}$ = 31.6 Hz); ^{31}P{^{1}H} NMR (160 MHz, C$_6$D$_6$): δ = −18.1 ppm; IR (Nujol): $\tilde{\nu}$ = 3431 (N−H), 1599 (C=N), 1461, 1377, 1153, 1027, 742, 695 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{25}H_{34}N_2P$: 393.2460 [*M*+H]$^+$; found: 393.2455.

***t*BuN=C(PPh$_2$)(NHEt) (3c)**: colorless solid, yield 95%; ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 1.27 (t, J = 7.2 Hz, 3H; CH$_2$C*H*$_3$), 1.33 (s, 9H; C(CH$_3$)$_3$), 3.72–3.80 (m, 3H; NH and C*H*$_2$CH$_3$), 6.99–7.07 (m, 6H; C$_6$H$_5$), 7.42–7.47 ppm (m, 4H; C$_6$H$_5$); ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 17.7, 28.7, 46.9 (d, $^3J_{PC}$ = 36.5 Hz), 52.1, 129.1 (d, $^3J_{PC}$ = 6.8 Hz), 129.3, 134.3 (d, $^2J_{PC}$ = 19.2 Hz), 135.4 (d, $^1J_{PC}$ = 14.3 Hz), 153.8 ppm (d, $^1J_{PC}$ = 33.4 Hz); ^{31}P{^{1}H} NMR (160 MHz, C$_6$D$_6$): δ = −16.0 ppm; IR (Nujol): $\tilde{\nu}$ = 3433 (N−H), 1609 (C=N), 1462, 1377, 1219, 1028, 743, 696 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{19}H_{26}N_2P$: 313.1834 [*M*+H]$^+$; found: 313.1840.

***i*PrN=C{P(C$_6$H$_4$Me-2)$_2$}(NH*i*Pr) (3d)**: colorless solid, yield 99%; ^{1}H NMR (300 MHz, C$_6$D$_6$): δ = 0.93 (d, J = 6.6 Hz, 6H; CH(C*H*$_3$)$_2$), 1.29 (d, J = 6.0 Hz, 6H; CH(C*H*$_3$)$_2$), 2.41 (s, 6H; Me), 3.70 (d, ^3J = 6.6 Hz, 1H; NH), 4.32–4.43 (m, 2H; CH), 6.94–7.09 ppm (m, 8H; C$_6$H$_4$); ^{13}C NMR (75 MHz, C$_6$D$_6$): δ = 21.1 (d, $^3J_{PC}$ = 21.7 Hz), 22.4, 25.5, 42.7, 52.8 (d, $^3J_{PC}$ = 37.1 Hz), 126.8, 129.6, 130.6 (d, $^3J_{PC}$ = 4.3 Hz), 133.3, 142.9 (d, $^1J_{PC}$ or $^2J_{PC}$ = 26.0 Hz, 2C), 151.9 ppm (d, $^1J_{PC}$ = 30.3 Hz); ^{31}P{^{1}H} NMR (160 MHz, C$_6$D$_6$): δ = −33.5 ppm; IR (Nujol): $\tilde{\nu}$ = 3443 (N−H), 1594 (C=N), 1455, 1377, 1168, 1088, 966, 763 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{21}H_{30}N_2P$: 341.2147 [*M*+H]$^+$; found: 341.2153.

***i*PrN=C{P(C$_6$H$_4$Me-3)$_2$}(NH*i*Pr) (3e)**: colorless solid, yield 99%; ^{1}H NMR (400 MHz, C$_6$D$_6$): δ = 0.85 (d, J = 6.4 Hz, 6H; CH(C*H*$_3$)$_2$), 1.12 (d, J = 6.0 Hz, 6H; CH(C*H*$_3$)$_2$), 1.90 (s, 6H; Me), 3.63 (d, J = 6.4 Hz, 1H; NH), 4.16–4.33 (m, 2H; CH), 6.80 (d, J = 7.6 Hz, 2H; C$_6$H$_4$), 6.93 (dd, J = 7.6 Hz, J = 7.6 Hz, 2H; C$_6$H$_4$), 7.18–7.26 ppm (m, 4H; C$_6$H$_4$); ^{13}C NMR (100 MHz, C$_6$D$_6$): δ = 21.5, 22.8, 25.6, 43.0, 52.3 (d, $^3J_{PC}$ = 35.5 Hz), 129.0 (d, $^3J_{PC}$ = 6.6 Hz), 130.2, 131.3 (d, $^2J_{PC}$ = 17.3 Hz), 135.0 (d, $^2J_{PC}$ = 23.1 Hz),

135.5 (d, $^1J_{PC}$=14.0 Hz), 138.5 (d, $^3J_{PC}$=7.4 Hz), 152.6 ppm (d, $^1J_{PC}$=32.1 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6): δ=−18.3 ppm; IR (Nujol): $\tilde{\nu}$=3429 (N−H), 1599 (C=N), 1462, 1377, 1175, 1119, 777, 696 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{21}H_{30}N_2P$: 341.2147 $[M+H]^+$, found: 341.2150.

***i*PrN=C{P(C$_6$H$_4$Me-4)$_2$}(NH*i*Pr) (3f)**: colorless solid, yield 99%; ^{1}H NMR (300 MHz, C_6D_6): δ=0.89 (d, *J*=6.3 Hz, 6H; CH(CH_3)$_2$), 1.16 (d, *J*=6.0 Hz, 6H; CH(CH_3)$_2$), 1.94 (s, 6H; Me), 3.67 (d, *J*=6.0 Hz, 1H; NH), 4.23–4.35 (m, 2H; CH), 6.85 (d, *J*=7.5 Hz, 4H; C_6H_4), 7.33 ppm (dd, *J*=7.5 Hz, *J*=7.8 Hz, 4H; C_6H_4); ^{13}C NMR (75 MHz, C_6D_6): δ=21.2, 22.6, 25.4, 42.8, 52.0 (d, $^3J_{PC}$=34.6 Hz), 129.9 (d, $^3J_{PC}$=6.8 Hz), 132.3 (d, $^1J_{PC}$=12.4 Hz), 134.4 (d, $^2J_{PC}$=19.2 Hz), 139.3, 153.0 ppm (d, $^1J_{PC}$=31.5 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6): δ=−20.0 ppm; IR (Nujol): $\tilde{\nu}$=3429 (N−H), 1599 (C=N), 1460, 1377, 1175, 1020, 806, 721 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{21}H_{30}N_2P$: 341.2147 $[M+H]^+$; found: 341.2173.

***i*PrN=C{P(C$_6$H$_3$Me$_2$-3,5)$_2$}(NH*i*Pr) (3g)**: colorless solid, yield 98%; ^{1}H NMR (400 MHz, C_6D_6): δ=1.02 (d, *J*=6.8 Hz, 6H; CH(CH_3)$_2$), 1.30 (d, *J*=6.0 Hz, 6H; CH(CH_3)$_2$), 2.04 (s, 12H; Me), 3.89 (d, *J*=6.8 Hz, 1H; NH), 4.34–4.50 (m, 2H; CH), 6.75 (s, 2H; C_6H_3), 7.26 ppm (d, *J*=8.0 Hz, 4H; C_6H_3); ^{13}C NMR (100 MHz, C_6D_6): δ=21.4, 22.8, 25.6, 43.0, 52.2 (d, $^3J_{PC}$=34.6 Hz), 131.2, 132.1 (d, $^2J_{PC}$=19.8 Hz), 135.4 (d, $^1J_{PC}$=14.0 Hz), 138.4 (d, $^3J_{PC}$=7.4 Hz), 153.0 ppm (d, $^1J_{PC}$=33.0 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6): δ=−18.0 ppm; IR (Nujol): $\tilde{\nu}$=3428 (N−H), 1599 (C=N), 1462, 1377, 1175, 1123, 847, 692 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{23}H_{34}N_2P$: 369.2460 $[M+H]^+$; found: 369.2453.

***i*PrN=C{P(C$_6$H$_4$OMe-4)$_2$}(NH*i*Pr) (3h)**: colorless solid, yield 99%; ^{1}H NMR (300 MHz, C_6D_6): δ=1.01 (d, *J*=6.6 Hz, 6H; CH(CH_3)$_2$), 1.24 (d, *J*=6.3 Hz, 6H; CH(CH_3)$_2$), 3.26 (s, 6H; CH_3O), 3.79 (d, *J*=6.6 Hz, 1H; NH), 4.30–4.49 (m, 2H; CH), 6.73 (d, *J*=8.7 Hz, 4H; C_6H_4), 7.43 ppm (dd, *J*=8.1 Hz, *J*=7.5 Hz, 4H; C_6H_4); ^{13}C NMR (75 MHz, C_6D_6): δ=22.6, 25.4, 42.8, 51.8 (d, $^3J_{PC}$=34.1 Hz), 54.7, 114.8 (d, $^3J_{PC}$=8.0 Hz), 126.4 (d, $^1J_{PC}$=11.2 Hz), 135.9 (d, $^2J_{PC}$=21.1 Hz), 153.6 (d, $^1J_{PC}$=33.0 Hz), 161.1 ppm; $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6): δ=−21.2 ppm; IR (Nujol): $\tilde{\nu}$=3427 (N−H), 1597 (C=N), 1498, 1459, 1377, 1285, 1249, 1177, 1092, 1035, 827, 798 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{21}H_{30}N_2O_2P$: 373.2045 $[M+H]^+$; found: 373.2050.

***i*PrN=C{P(C$_6$H$_4$Cl-4)$_2$}(NH*i*Pr) (3i)**: colorless solid, yield 97%; ^{1}H NMR (400 MHz, C_6D_6): δ=0.91 (d, *J*=6.8 Hz, 6H; CH(CH_3)$_2$), 1.23 (d, *J*=6.0 Hz, 6H; CH(CH_3)$_2$), 3.43 (d, *J*=5.6 Hz, 1H; NH), 4.24–4.29 (m, 2H; CH), 7.00 (d, *J*=8.0 Hz, 4H; C_6H_4), 7.09 ppm (dd, *J*=8.0 Hz, *J*=7.6 Hz, 4H; C_6H_4); ^{13}C NMR (75 MHz, C_6D_6): δ=22.3, 25.3, 43.0, 52.3 (d, $^3J_{PC}$=35.3 Hz), 129.4 (d, $^3J_{PC}$=6.8 Hz), 133.5 (d, $^1J_{PC}$=15.5 Hz), 135.4 (d, $^2J_{PC}$=20.4 Hz), 136.1, 151.3 ppm (d, $^1J_{PC}$=31.5 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6): δ=−21.1 ppm; IR (Nujol): $\tilde{\nu}$=3431 (N−H), 1599 (C=N), 1479, 1383, 1173, 1099, 1015, 818, 743 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{19}H_{24}Cl_2N_2P$: 381.1054 $[M+H]^+$; found: 381.1050.

***i*PrN=C{P(C$_6$H$_3$Cl$_2$-3,5)$_2$}(NH*i*Pr) (3j)**: colorless solid, yield 95%; ^{1}H NMR (300 MHz, C_6D_6): δ=0.86 (d, *J*=6.6 Hz, 6H; CH(CH_3)$_2$), 1.16 (d, *J*=6.0 Hz, 6H; CH(CH_3)$_2$), 3.37 (d, *J*=6.3 Hz, 1H; NH), 4.08–4.16 (m, 2H; CH), 7.01 (s, 2H; C_6H_3), 7.21 ppm (d, *J*=7.8 Hz, 4H; C_6H_3); ^{13}C NMR (75 MHz, C_6D_6): δ 22.1, 25.1, 43.3, 52.7 (d, $^3J_{PC}$=37.1 Hz), 130.1, 131.7 (d, $^2J_{PC}$=20.4 Hz), 136.2 (d, $^3J_{PC}$=7.4 Hz), 138.4 (d, $^1J_{PC}$=21.6 Hz), 149.2 ppm (d, $^1J_{PC}$=32.8 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6): δ=−18.1 ppm; IR (Nujol): $\tilde{\nu}$=3436 (N−H), 1604 (C=N), 1555, 1457, 1378, 1135, 860, 799, 676 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{19}H_{22}Cl_4N_2P$: 449.0275 $[M+H]^+$; found: 449.0283.

***i*PrN=C{P(C$_6$H$_4$Br-4)$_2$}(NH*i*Pr) (3k)**: colorless solid, yield 97%; ^{1}H NMR (400 MHz, C_6D_6): δ=0.90 (d, *J*=6.0 Hz, 6H; CH(CH_3)$_2$), 1.22 (d, *J*=6.4 Hz, 6H; CH(CH_3)$_2$), 3.42 (d, *J*=6.8 Hz, 1H; NH), 4.23–4.29 (m, 2H; CH), 7.01 (dd, *J*=8.4 Hz, *J*=6.8 Hz, 4H; C_6H_4), 7.15 ppm (d, *J*=8.4 Hz, 4H; C_6H_4); ^{13}C NMR (100 MHz, C_6D_6): δ=22.5, 25.5, 43.2, 52.5 (d, $^3J_{PC}$=36.3 Hz), 124.4, 132.3 (d, $^3J_{PC}$=6.6 Hz), 134.0 (d, $^1J_{PC}$=15.7 Hz), 135.5 (d, $^2J_{PC}$=20.6 Hz), 151.1 ppm (d, $^1J_{PC}$=32.1 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6): δ −21.2 ppm; IR (Nujol): $\tilde{\nu}$=3421 (N−H), 1601 (C=N), 1462, 1378, 1173, 1068, 1010, 814, 725 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{19}H_{24}{}^{79}Br_2N_2P$: 469.0044 $[M+H]^+$; found: 469.0052.

***i*PrN=C(PEtPh)(NH*i*Pr) (3l)**: colorless liquid, yield, 86%; ^{1}H NMR (400 MHz, C_6D_6): δ=0.94 (d, *J*=6.4 Hz, 3H; CH(CH_3)$_2$), 0.99 (d, *J*=6.8 Hz, 3H; CH(CH_3)$_2$), 1.01–1.17 (m, 3H; CH_2CH_3), 1.27 (d, *J*=6.0 Hz, 3H; CH(CH_3)$_2$), 1.36 (d, *J*=6.0 Hz, 3H; CH(CH_3)$_2$), 1.70–1.79 (m, 2H; CH_2CH_3), 3.54 (d, *J*=6.4 Hz, 1H; NH), 4.25–4.30 (m, 1H; CH), 4.51–4.56 (m, 1H; CH), 7.05–7.15 (m, 3H; C_6H_5), 7.39–7.43 ppm (m, 2H; C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): δ=10.7 (d, $^2J_{PC}$=16.5 Hz), 18.6 (d, $^1J_{PC}$=14.0 Hz), 22.5, 22.8, 25.8, 26.0, 42.6, 52.0 (d, $^3J_{PC}$=36.3 Hz), 128.8 (d, $^3J_{PC}$=8.2 Hz), 128.9, 132.7 (d, $^2J_{PC}$=18.1 Hz), 137.0 (d, $^1J_{PC}$=17.3 Hz), 154.4 ppm (d, $^1J_{PC}$=34.6 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6): δ=−29.0 ppm; IR (Nujol): $\tilde{\nu}$= 3432 (N−H), 1598 (C=N), 1464, 1377, 1174, 1118, 1028, 742, 697 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{15}H_{26}N_2P$: 265.1834 $[M+H]^+$; found: 265.1840.

***i*PrN=C(PHPh)(NH*i*Pr) (3m)**: colorless liquid, yield 96%; ^{1}H NMR (400 MHz, C_6D_6): δ=0.97 (d, *J*=6.4 Hz, 3H; CH(CH_3)$_2$), 1.08 (d, *J*=6.4 Hz, 3H; CH(CH_3)$_2$), 1.24 (d, *J*=6.4 Hz, 3H; CH(CH_3)$_2$), 1.36 (d, *J*=6.4 Hz, 3H; CH(CH_3)$_2$), 4.28–4.39 (m, 4H; PH, NH and CH), 6.99–7.06 (m, 3H; C_6H_5), 7.51–7.55 ppm (m, 2H; C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): δ=22.6, 25.6 (d, $^4J_{PC}$=8.2 Hz), 43.1, 52.9 (d, $^3J_{PC}$=37.1 Hz), 129.3 (d, $^3J_{PC}$=6.6 Hz), 129.6, 133.4 (d, $^1J_{PC}$=18.1 Hz), 134.1 (d, $^2J_{PC}$=19.0 Hz), 151.5 ppm (d, $^1J_{PC}$=36.2 Hz); $^{31}P\{^1H\}$ NMR (160 MHz, C_6D_6): δ=−35.0 ppm; IR (Nujol): $\tilde{\nu}$=3414 (N−H), 1601 (C=N), 1462, 1377, 721 cm^{-1}; HRMS: *m*/*z*: calcd for $C_{13}H_{22}N_2P$: 237.1521 $[M+H]^+$; found: 237.1526.

[{Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)}La(PPh$_2$)(thf)$_2$] (4): In the glovebox, a solution of **2-La** (153 mg, 0.233 mmol) in THF (2 mL) was treated with a solution of diphenylphosphine (43 mg, 0.233 mmol) in THF (3 mL). After stirring at room temperature for 5 h, the solvent was removed under reduced pressure, and the residue was extracted with THF followed by filtering to give a clean solution. The solution volume was reduced under vacuum to precipitate **4** as light yellow crystalline powder (167 mg, 0.214 mmol, 92% yield). Single crystals of **4** suitable for X-ray analysis were grown in THF/ether at room temperature overnight. ^{1}H NMR (400 MHz, [D$_8$]THF): δ=0.20 (s, 6H; $SiMe_2$), 1.72 (br s, 8H; β-CH_2, THF), 1.99 (s, 6H; *o*- $C_6H_2(CH_3)_3$), 2.06 (s, 3H; *p*-$C_6H_2(CH_3)_3$), 2.21 (s, 6H; C_5Me_4), 2.23 (s, 6H; C_5Me_4), 3.57 (br s, 8H; α-CH_2, THF), 6.58 (s, 2H; $C_6H_2(CH_3)_3$), 7.20–7.25 (m, 6H; C_6H_5), 7.31–7.35 ppm (m, 4H; C_6H_5); ^{13}C NMR (100 MHz, [D$_8$]THF): δ=6.2, 10.9, 13.8, 19.9, 20.4, 25.5, 67.3, 107.0, 120.7, 123.8, 125.2, 127.7, 127.9, 128.0 (d, $^3J_{PC}$=5.8 Hz), 130.6, 132.4 (d, $^2J_{PC}$=18.1 Hz), 139.6 (d, $^1J_{PC}$=14.8 Hz), 153.2 ppm; $^{31}P\{^1H\}$ NMR (160 MHz, [D$_8$]THF): δ=−14.5 ppm; IR (Nujol): $\tilde{\nu}$=2956, 2923, 2854, 1572, 1466, 1377, 1229, 1158, 1023, 898, 852, 767, 729 cm^{-1}; elemental analysis calcd (%) for $C_{40}H_{55}LaNO_2PSi$: C 61.61, H 7.11, N 1.80; found: C 61.63, H 8.18, N 1.98.

[{Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)}La(μ-PPh$_2$)]$_2$ (5): In the glovebox, a solution of **2-La** (192 mg, 0.292 mmol) in THF (2 mL) was treated with a solution of diphenylphosphine (55 mg, 0.292 mmol) in THF (3 mL). After stirring at room temperature for 5 h, the solvent was removed under reduced pressure, and the residue was washed with hexane and dried in vacuum at room temperature for 0.5 h to provide light yellow powder. The light yellow powder was dissolved in benzene and reduced under vacuum to precipitate **5** as light yellow crystalline powder (167 mg, 0.131 mmol, 90% yield). Complex **5** could also be obtained by recrystallization of **4** in benzene. Single crystals of **5**·2C_6H_6 suitable for X-ray analysis were grown in benzene at room temperature for one week. ^{1}H NMR (300 MHz, [D$_8$]THF): δ=0.27 (s, 12H; $SiMe_2$), 2.06 (s, 6H; *p*-$C_6H_2(CH_3)_3$), 2.11 (s, 12H; C_5Me_4), 2.14 (s, 12H; C_5Me_4), 2.32 (s, 12H; *o*-$C_6H_2(CH_3)_3$), 6.62 (s, 4H; $C_6H_2(CH_3)_3$), 6.69–6.73 (m, 4H; C_6H_5), 6.91–6.96 (m, 8H; C_6H_5), 7.23–7.28 ppm (m, 8H; C_6H_5); ^{13}C NMR (75 MHz, [D$_8$]THF): δ=5.2, 11.3, 14.2, 19.7, 20.5, 107.0, 122.1, 124.6, 126.4, 127.8 (d, $^3J_{PC}$=5.0 Hz), 128.0, 128.1, 130.0, 130.3 (d, $^2J_{PC}$=17.3 Hz), 149.3 (d, $^1J_{PC}$=41.4 Hz), 151.4 ppm; $^{31}P\{^1H\}$ NMR (160 MHz, [D$_8$]THF): δ=8.53 ppm (br s); IR (Nujol): $\tilde{\nu}$=2951, 2922, 2852, 1572, 1462, 1377, 1298, 1227, 1157, 1024, 899, 831, 764, 706 cm^{-1}; elemental analysis calcd (%) for $C_{64}H_{78}La_2N_2P_2Si_2$: C 60.47, H 6.18, N 2.20; found: C 60.90, H 6.40, N 2.42.

[{Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)}La{*i*PrNC(PPh$_2$)N*i*Pr}(thf)] (6): In the glovebox, a solution of **2-La** (185 mg, 0.282 mmol) in THF (2 mL) was treated with a solution of diphenylphosphine (52 mg, 0.282 mmol) in THF (3 mL). After stirring at room temperature for 5 h, *N*,*N*′-diisopropylcarbodiimide (36 mg, 0.282 mmol) was added to the above reaction

mixture. After 5 h, the solvent was removed under reduced pressure, and the residue was extracted with hexane followed by filtering to give a clean solution. The solution volume was reduced under vacuum to precipitate **6** as light yellow crystalline powder (219 mg, 0.262 mmol, 93% yield). ^{1}H NMR (400 MHz, C_6D_6): $\delta = 0.68$ (d, $J = 6.4$ Hz, 12H; CH-(CH_3)$_2$), 0.71 (s, 6H; $SiMe_2$), 1.25 (brs, 4H; β-CH_2, THF), 2.07 (s, 6H; *o*-$C_6H_2(CH_3)_3$), 2.31 (s, 3H; *p*-$C_6H_2(CH_3)_3$), 2.47 (s, 6H; C_5Me_4), 2.50 (s, 6H; C_5Me_4), 3.37 (brs, 4H; α-CH_2, THF), 4.04–4.11 (m, 2H; C*H*(CH_3)$_2$), 7.02 (s, 2H; $C_6H_2(CH_3)_3$), 7.05–7.08 (m, 2H; C_6H_5), 7.12–7.16 (m, 4H; C_6H_5), 7.49–7.53 ppm (m, 4H; C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 6.4$, 12.4, 14.5, 21.1, 21.7, 25.6, 26.1, 50.4 (d, $^3J_{PC} = 21.5$ Hz), 68.6, 109.1, 124.0, 127.1, 128.0, 128.6 (d, $^3J_{PC} = 5.8$ Hz), 128.7, 129.3, 130.6, 132.2 (d, $^2J_{PC} = 18.9$ Hz), 136.0 (d, $^1J_{PC} = 20.7$ Hz), 151.2, 171.0 ppm (d, $^1J_{PC} = 59.3$ Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): $\delta = -17.3$ ppm; IR (Nujol): $\tilde{\nu} = 2955$, 2924, 2853, 1584, 1459, 1438, 1377, 1357, 1331, 1298, 1233, 1177, 1005, 892, 766, 708 cm^{-1}; elemental analysis calcd (%) for $C_{43}H_{61}LaN_3OPSi$ $C_{46}H_{70}LaN_3OPSi$: C 61.93, H 7.37, N 5.04; found: C 61.60, H 7.58, N 4.81.

[{Me$_2$Si(C$_5$Me$_4$)(NC$_6$H$_2$Me$_3$-2,4,6)}La{*i*PrNC(PPh$_2$)N*i*Pr}(OEt$_2$)] (7): In the glovebox, a solution of **2-La** (185 mg, 0.282 mmol) in THF (2 mL) was treated with a solution of diphenylphosphine (52 mg, 0.282 mmol) in THF (3 mL). After stirring at room temperature for 5 h, *N*,*N*′-diisopropylcarbodiimide (36 mg, 0.282 mmol) was added to the above reaction mixture. After 5 h, the solvent was removed under reduced pressure, and the residue was extracted with hexane/ether followed by filtering to give a clean solution. The solution volume was reduced under vacuum to precipitate **7** as light yellow crystalline powder (212 mg, 0.254 mmol, 90% yield). **7** could also be obtained by recrystallization of **6** in ether. Single crystals of **7**·0.5 hexane suitable for X-ray analysis were grown in hexane/ether at room temperature for 2 days. ^{1}H NMR (400 MHz, C_6D_6): $\delta =$ 0.68 (d, $J = 6.4$ Hz, 12H; CH(CH_3)$_2$), 0.70 (s, 6H; $SiMe_2$), 0.89 (t, $J =$ 7.2 Hz, 3H; CH_3 (hexane)), 0.96 (t, $J = 7.2$ Hz, 6H; CH_3 (ether)), 1.23–1.27 (m, 4H; CH_2 (hexane)), 2.07 (s, 6H; *o*-$C_6H_2(CH_3)_3$), 2.31 (s, 3H; *p*-$C_6H_2(CH_3)_3$), 2.47 (s, 6H; C_5Me_4), 2.50 (s, 6H; C_5Me_4), 3.16 (q, $J =$ 7.2 Hz, 4H; CH_2 (ether)), 4.04–4.11 (m, 2H; C*H*(CH_3)$_2$), 7.02 (s, 2H; $C_6H_2(CH_3)_3$), 7.05–7.08 (m, 2H; C_6H_5), 7.12–7.16 (m, 4H; C_6H_5), 7.49–7.53 ppm (m, 4H; C_6H_5); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 6.5$, 12.4, 14.0, 14.5, 15.3, 21.1, 21.7, 23.2, 26.1, 32.1, 50.4 (d, $^3J_{PC} = 21.5$ Hz), 66.6, 109.1, 124.0, 127.1, 128.0, 128.6 (d, $^3J_{PC} = 5.8$ Hz), 128.7, 129.3, 130.6, 132.2 (d, $^2J_{PC} = 18.9$ Hz), 136.0 (d, $^1J_{PC} = 20.7$ Hz), 151.2, 171.0 ppm (d, $^1J_{PC} =$ 59.3 Hz); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6): $\delta = -17.3$ ppm; IR (Nujol): $\tilde{\nu} =$ 2955, 2924, 2854, 1584, 1459, 1438, 1376, 1357, 1331, 1298, 1233, 1176, 1005, 893, 766, 707 cm^{-1}; elemental analysis calcd (%) for $C_{46}H_{70}LaN_3OPSi$: C 62.85, H 8.03, N 4.78; found: C 63.20, H 7.66, N 4.71.

Table 4. Crystallographic data and structure refinement details for **2-Ln** (Ln: La, Pr, Nd, Sm, Gd, Lu, Y, and Sc).

	2-La	**2-Pr**	**2-Nd**	**2-Sm**
formula	$C_{33}H_{49}LaN_2OSi$	$C_{33}H_{49}N_2OPrSi$	$C_{33}H_{49}N_2NdOSi$	$C_{33}H_{49}N_2OSiSm$
M_w	656.74	658.74	662.07	668.18
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)/*n*	*P*2(1)/*n*
a [Å]	8.7539(6)	8.7244(11)	8.7016(14)	8.6635(19)
b [Å]	18.0371(12)	17.969(2)	17.918(3)	17.891(4)
c [Å]	20.3696(13)	20.404(3)	20.392(3)	20.430(5)
β [°]	92.0520(10)	92.054(2)	91.935(2)	92.027(3)
V [Å^3]	3214.2(4)	3196.7(7)	3177.5(9)	3164.7(12)
Z	4	4	4	4
ρ_{calcd} [g cm^{-3}]	1.357	1.369	1.384	1.402
μ [mm^{-1}]	1.393	1.588	1.698	1.920
F(000)	1360	1368	1372	1380
θ range [°]	1.51–26.01°	1.51–25.07°	1.51–25.03°	1.99–25.12°
no. of reflns collected	18050	13923	15087	12622
no. of indep reflns	6302	5460	5614	5500
no. of variables	354	354	354	354
GOF	1.005	1.035	0.982	0.980
R [$I > 2\sigma(I)$]	0.0285	0.0261	0.0289	0.0384
R_w	0.0414	0.0599	0.0416	0.0877
	2-Gd	**2-Lu**	**2-Y**	**2-Sc**
formula	$C_{33}H_{49}GdN_2OSi$	$C_{33}H_{49}LuN_2OSi$	$C_{33}H_{49}N_2OSiY$	$C_{29}H_{41}N_2ScSi$
M_w	675.08	692.80	606.74	490.69
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
space group	*P*2(1)/*n*	*P*2(1)2(1)2(1)	*P*2(1)/*n*	*P*2(1)/*n*
a [Å]	8.6251(17)	11.0631(13)	8.6019(13)	8.5252(5)
b [Å]	17.800(3)	15.2989(18)	17.748(3)	15.5402(10)
c [Å]	20.426(4)	18.893(2)	20.434(3)	21.2446(13)
β [°]	91.861(3)	90	92.061(2)	90.7630(10)
V [Å^3]	3134.3(11)	3197.8(6)	3117.6(8)	2814.3(3)
Z	4	4	4	4
ρ_{calcd} [g cm^{-3}]	1.431	1.439	1.293	1.158
μ [mm^{-1}]	2.181	3.151	1.936	0.322
F(000)	1388	1416	1288	1056
θ range [°]	1.52–25.08°	1.71–26.51	1.52–26.57°	1.62–25.02°
no. of reflns collected	14832	17331	15264	14436
no. of indep reflns	5536	6546	6423	4945
no. of variables	354	343	354	309
GOF	1.070	1.025	1.008	1.085
R [$I > 2\sigma(I)$]	0.0626	0.0346	0.0377	0.0376
R_w	0.1066	0.0662	0.0751	0.1074

Table 5. Crystallographic data and structure refinement details for **4**, **5**, and **7**.

	4	**5**·2 C_6H_6	**7**·0.5 hexane
formula	$C_{40}H_{55}LaNO_2PSi$	$C_{76}H_{90}La_2N_2P_2Si_2$	$C_{46}H_{70}LaN_3OPSi$
M_w	779.82	1427.44	879.02
crystal system	orthorhombic	triclinic	triclinic
space group	$P2(1)2(1)2(1)$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.5999(8)	12.010(4)	10.9764(8)
b [Å]	19.8229(17)	13.258(5)	11.5061(8)
c [Å]	20.5705(18)	13.476(5)	21.0458(15)
α [°]	90	106.340(4)	96.0770(10)
β [°]	90	102.167(4)	101.0430(10)
γ [°]	90	114.506(4)	115.4280(10)
V [Å^3]	3914.5(6)	1736.9(10)	2302.4(3)
Z	4	1	2
ρ_{calcd} [g cm^{-3}]	1.323	1.365	1.268
μ [mm^{-1}]	1.195	1.336	1.024
$F(000)$	1616	732	922
θ range [°]	1.43–25.01°	1.70–26.53°	2.01–26.53°
no. of reflns collected	20353	8311	13565
no. of indep reflns	6835	6509	9238
no. of variables	424	388	479
GOF	0.640	0.992	0.990
R [$I > 2\sigma(I)$]	0.0387	0.0362	0.0350
R_w	0.0444	0.0549	0.0871

X-ray crystallographic studies: Crystals for X-ray analyses of **2-Ln** (Ln: La, Pr, Nd, Sm, Gd, Lu, Y, and Sc), **4**, **5**, and **7** were obtained as described in the preparations. The crystals were manipulated in the glovebox and were sealed in thin-walled glass capillaries. Data collections were performed at −100 °C on a Bruker CCD APEX diffractometer with a CCD area detector, using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[17] These structures were solved by use of SHELXTL program.[18] Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data, data collection and processing parameters for compounds **2-Ln** (Ln: La, Pr, Nd, Sm, Gd, Lu, Y, and Sc), **4**, **5**, and **7** are summarized in Table 4 and Table 5. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 658060 (**2-La**), 658063 (**2-Pr**), 658062 (**2-Nd**), 658065 (**2-Sm**), 658059 (**2-Gd**), 658061 (**2-Lu**), 658066 (**2-Y**), 658064 (**2-Sc**), 658067 (**4**), 658068 (**5**·2 C_6H_6), and 658069 (**7**·0.5 hexane). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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