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Rare earth alkyl and hydride complexes bearing silylene-linked cyclopentadienyl-phosphido ligands. Synthesis, structures, and catalysis in olefin hydrosilylation and ethylene polymerization

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Abstract—A series of silylene-linked cyclopentadienyl-phosphido rare earth alkyl and hydride complexes of type $Me_2Si(C_5Me_4)(PR')LnR$ (Ln=Y, Yb, Lu; R′=Ph, Cy, $C_6H_2{}^tBu_3$-2,4,6; R=CH_2SiMe_3, H) have been synthesized and structurally characterized, and their activity in ethylene polymerization and olefin hydrosilylation has been studied. These complexes represent the first examples of rare earth alkyl and hydride complexes bearing cyclopentadienyl-phosphido ligands, which are in sharp contrast both structurally and chemically with the analogous cyclopentadienyl-amido and metallocene complexes.

1. Introduction

The organometallic chemistry of rare earth elements has witnessed a spectacular growth in the past two decades. In this development, the rare earth alkyl and hydride complexes bearing two substituted or unsubstituted cyclopentadienyl ancillary ligands (e.g. types **A** and **B**, Chart 1), have occupied a specially important place, because of their high activity in various catalytic processes.[1] More recently, considerable attention has been paid to complexes bearing the silylene-linked cyclopentadienyl-amido ligands (such as type **C**),[2] because of their electronically more unsaturated and sterically more accessible properties than those of the metallocene analogues. In contrast, however, the analogous cyclopentadienyl-phosphido rare earth complexes such as type **D** have received much less attention and remained almost unexplored to date, although such phosphido complexes are of much interest in comparison with the amido analogues.[3,4] We recently reported the synthesis and reactions of the first silylene-linked cyclopentadienyl-phosphido lanthanide complexes of type $Me_2Si(C_5Me_4)(PAr)Ln$ (Ln=Sm, Yb; Ar=$C_6H_2{}^tBu_3$-2,4,6), and showed that such lanthanide(II) complexes could act as a new family of reducing agents and polymerization catalysts.[3] In this paper, we report the synthesis, structures, and ethylene polymerization and olefin hydrosilylation reactions of the yttrium(III), ytterbium(III), and lutetium(III) alkyl and hydride complexes bearing the silylene-linked cyclopentadienyl-phosphido ligands $[Me_2Si(C_5Me_4)PR]^{2-}$ (R=Ph, Cy, $C_6H_2{}^tBu_3$-2,4,6). These complexes are both structurally and chemically in sharp contrast with the previously reported metallocene and amido analogues, and in many cases show a higher activity.

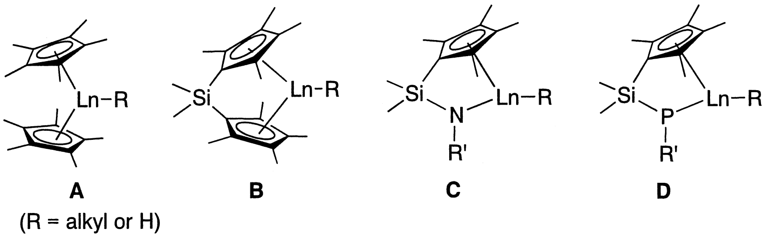

Chart 1.

Keywords: half-metallocene catalysis; linked cyclopentadienyl-phosphido ligand; yttrium; lutetium; ytterbium; polymerization; hydrosilylation; crystal structure.

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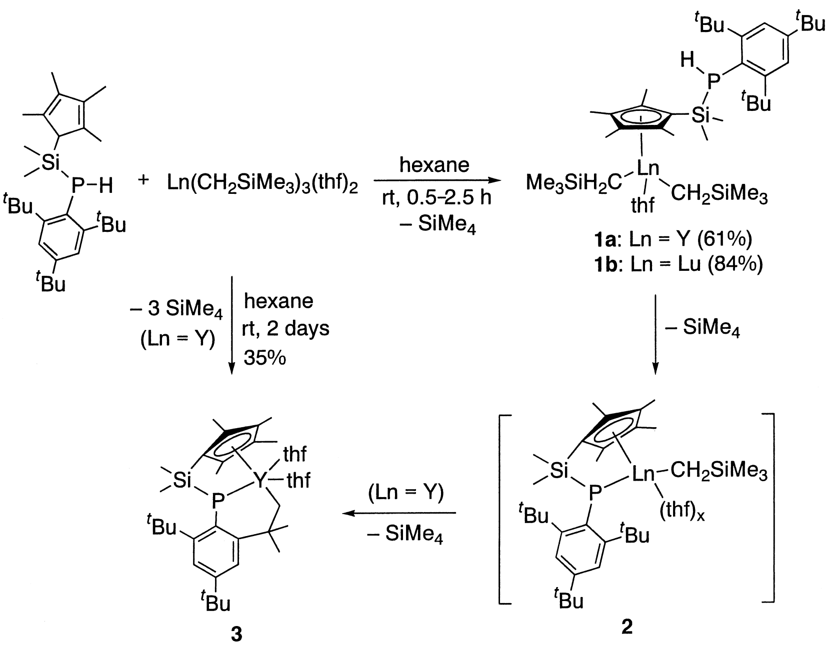


Scheme 1.

2. Results and discussion

2.1. Synthesis and structures of the silylene-linked Cp′-phosphido rare earth alkyl complexes

In attempts to synthesize a cyclopentadienyl-phosphido-supported rare earth alkyl complex, the bulky phosphido ligand $[Me_2Si(C_5Me_4)P(C_6H_2{}^tBu_3\text{-}2,4,6)]^{2-}$, which was previously utilized in our studies on lanthanide(II) complexes,[3] was first examined. The acid–base reaction between $Y(CH_2SiMe_3)_3(thf)_2$ and 1 equiv. of $Me_2Si(C_5Me_4H)P(H)Ar$ ($Ar=C_6H_2{}^tBu_3\text{-}2,4,6$) was carried out in hexane at room temperature,[5] which gave **1a** in 61% isolated yield in less than 30 min (Scheme 1). Similarly, the reaction of $Lu(CH_2SiMe_3)_3(thf)_2$ with $Me_2Si(C_5Me_4H)P(H)Ar$ afforded the Lu analogue **1b** in 84% yield in 2.5 h.

The ^{31}P NMR spectra of **1a**,**b** in C_6D_6 showed a doublet at δ −119.7 with coupling constants of 214 and 213 Hz, respectively, suggesting that a proton remained on the P atom in both complexes. These data together with the ^1H and ^{13}C NMR spectra suggest the formulation of **1a**,**b** as $\{Me_2Si(C_5Me_4)P(H)Ar\}Ln(CH_2SiMe_3)_2(thf)$. The structure of **1b** was confirmed also by a crystallographic study, which revealed that the Lu(III) center is bonded to one cyclopentadienyl unit, two CH_2SiMe_3 ligands, and one THF ligand (Fig. 1 and Table 1). The PHAr unit is directed away from the metal center. The Lu–C σ-bond distances (2.332(5) and 2.328(5) Å) in **1b** are comparable with those found in other lutetium bis(alkyl) complexes such as $(C_5Me_4SiMe_3)Lu(CH_2SiMe_3)_2(thf)$ (2.333(3) and 2.336(6) Å)[6] and $\{C_5Me_4SiMe_2(2\text{-}C_4H_8O)\}Lu(CH_2SiMe_3)_2(thf)$ (2.373(4) and 2.381(4) Å),[7] and so are the Lu–Cp′ bonds.

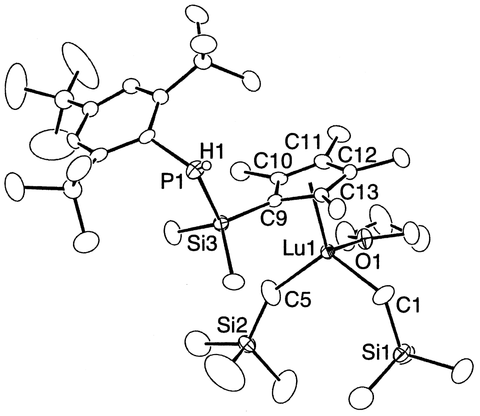


Figure 1. ORTEP drawing of **1b** with 30% thermal ellipsoids.

Table 1. Selected bond distances (Å) and angles (deg.) of **1b**

Lu1–C1	2.332(5)	Lu1–C5	2.328(5)
Lu1–C9	2.566(4)	Lu1–C10	2.580(7)
Lu1–C11	2.625(5)	Lu1–C12	2.634(4)
Lu1–C13	2.628(6)	Lu1–O1	2.258(3)
P1–C20	1.864(5)	P1–Si3	2.302(2)
O1–Lu1–C5	95.2(2)	O1–Lu1–C1	99.4(2)
C5–Lu1–C1	115.7(2)	O1–Lu1–Cp′(ctd)	109.7
C1–Lu1–Cp′(ctd)	113.6	C5–Lu1–Cp′(ctd)	119.1

The PH-functionalized-cyclopentadienyl/bis(alkyl) complexes **1a**,**b** were stable in solid state. When they were left in solution for a longer time, however, dehydrogenation reactions at both the P atom and an *ortho*-^{t}Bu group of the PHAr unit occurred gradually. In the case of **1a**, a structurally characterizable complex **3** was isolated after a few days (Scheme 1). Alternatively, a two-day reaction of $Y(CH_2SiMe_3)_3(thf)_2$ with $Me_2Si(C_5Me_4H)P(H)Ar$ in hexane also afforded **3** in 35% isolated yield. The $^{31}P\{^1H\}$ NMR spectrum of **3** was evident for a Y–P σ-bond, which exhibited a doublet at δ −117.9 with a Y–P coupling constant of 66 Hz. Further decomposition of **3** in solution was also observed, but the identification of the resulting products seemed difficult.

An X-ray analysis of **3** confirmed the metallation at both the

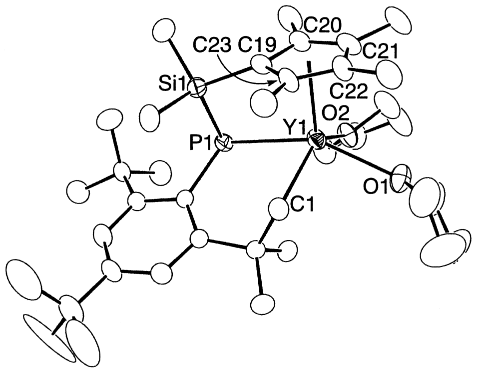


Figure 2. ORTEP drawing of **3** with 30% thermal ellipsoids.

P atom and a methyl atom of an *ortho*-^{t}Bu group in the PHAr unit (Fig. 2 and Table 2). The Y–P bond distance (2.789(2) Å) in **3** is significantly shorter than those in the phosphine complexes such as $Y(OC^tBu_2CH_2PMe_2)_3$ (3.045(2) Å)[8] and $\{Y[(C_5H_4)C_2H_4P(CH_3)_2]_2\}Br$ (2.960(1), 2.933(1) Å),[9] and also shorter than those of the bridging-phosphido bonds in $[(C_5Me_4)_2Y(\mu\text{-}PHPh)]_2$ (3.021(3) Å).[10] The Y1–C1 bond distance in **3** (2.363(5) Å) is comparable with those of the terminal Y–C σ-bonds in $Y\{CH(SiMe_3)_2\}_3$ (av. 2.357(7) Å)[11] and $Y(CH_2SiMe_3)_3(thf)_2$ (av. 2.427(2) Å).[12]

Table 2. Selected bond distances (Å) and angles (deg.) of **3**

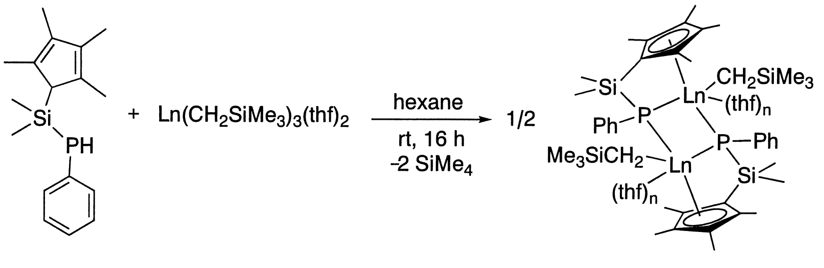
Y1–C1	2.363(5)	Y1–P1	2.789(2)
Y1–C19	2.563(5)	Y1–C20	2.593(6)
Y1–C21	2.678(6)	Y1–C22	2.701(5)
Y1–C23	2.651(5)	Y1–O1	2.432(4)
Y1–O2	2.413(4)	P1–C5	1.873(6)
P1–Si1	2.235(2)		
O1–Y1–C1	89.5(2)	O1–Y1–O2	78.0(2)
O1–Y1–P1	146.7(1)	C1–Y1–P1	81.4(1)
O2–Y1–C1	131.8(2)	O2–Y1–P1	84.3(1)
Cp′(ctd)–Y1–O1	113.10	Cp′(ctd)–Y1–O2	117.3
Cp′(ctd)–Y1–P1	100.1	Cp′(ctd)–Y1–C1	110.5

To avoid the intramolecular C–H bond cleavage observed above, the bulky $C_6H_2{}^tBu_3$-2,4,6 substituent on the P atom was then replaced by a smaller one such as Ph or cyclohexyl (Cy). As shown in Scheme 2, the reactions of $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln=Y, Yb, Lu) with 1 equiv. of $Me_2Si(C_5Me_4H)P(H)Ph$ afforded straightforwardly the corresponding cyclopentadienyl-phosphido rare earth alkyl complexes **4a–c** in 55–69% isolated yields. Similarly, the reactions of $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln=Y, Yb, Lu) with $Me_2Si(C_5Me_4H)P(H)Cy$ gave **5a–c** in 29–61% yields (Scheme 3). The latter reactions were slower than the former, possibly because of the weaker acidity of the cyclohexylphosphine (PHCy) unit than that of the phenylphosphine (PHPh) group. The lower reactivity of the cyclohexylphosphine ligand could be a reason for the lower yields of **5a**,**b**, since the starting yttrium and ytterbium trisalkyl complexes are thermally less stable than the lutetium analogue and could not survive at room temperature for a long time.

Single crystals suitable for X-ray analysis were obtained for **4b**,**c** and **5a–c**. It was shown that these complexes all adopt a similar dimeric structure, in which the two metal centers are bridged by the two phosphido P atoms. A crystallographic inversion center exists at the center of the molecule. The phosphido bridges are asymmetric. The ‘intermolecular’ Ln–P* bonds seem stronger than the corresponding ‘intramolecular’ chelating Ln–P bonds (cf. 2.796(5) vs. 2.836(6) Å in **4b**, 2.786(1) vs. 2.826(1) Å in **4c**, 2.857(2) vs. 2.865(2) Å in **5a**, 2.798(1) vs. 2.826(1) Å in **5b**, 2.789(1) vs. 2.817(1) Å in **5c**). The selected bond distances and angles are summarized in Table 3, and the ORTEP structures of **4c** and **5c** are shown in Figures 3 and 4, respectively, as two representative examples.

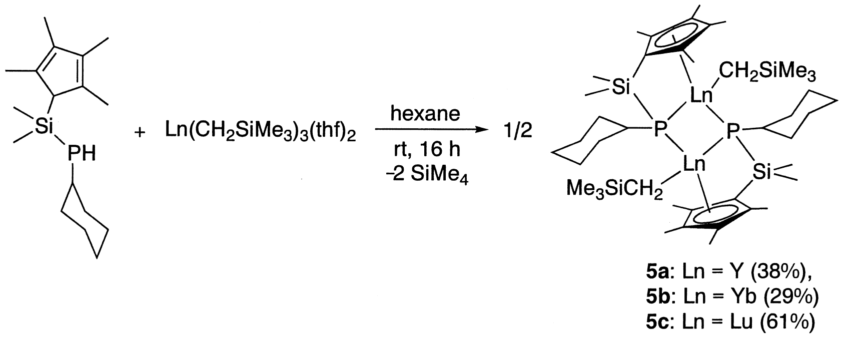
Complexes **4a–c** and **5a–c** represent the first examples of well-defined cyclopentadienyl-phosphido rare earth alkyl complexes. The formation of a P-bridged dimeric structure in these complexes is in sharp contrast with that of a monomeric structure in the analogous cyclopentadienyl-amido complexes.[5] In dimeric rare earth metallocene alkyl complexes, the metal centers are usually bridged by the alkyl ligand.[13]

The ^1H NMR spectra of the diamagnetic complexes **4a**,**c** and **5a**,**c** in C_6D_6 were consistent with their X-ray structures. Four singlets for the $C_5(CH_3)_4$ unit (**4a**: δ 1.58, 2.11, 2.16, 2.23; **4c**: δ 1.50, 2.05, 2.17, 2.28; **5a**: δ 2.00, 2.13, 2.22, 2.45; **5c**: δ 2.01, 2.14, 2.21, 2.51), two singlets for the dimethylsilylene part (**4a**: δ 0.40, 0.94; **4c**: δ 0.20, 0.99; **5a**: δ 0.78, 1.02; **5c**: δ 0.78, 1.01), and two doublets (**4c**: δ −0.39, 0.29, J_{H-H}=11.4 Hz; **5c**: δ −0.66, −0.07, J_{H-H}=11.2 Hz) or two doublets of doublets (**4a**: δ −0.33, 0.09, J_{H-H}=11.1 Hz, J_{Y-H}=1.5 Hz; **5a**: δ −0.46, 0.10, J_{H-H}=11.6 Hz, J_{Y-H}=3.1 Hz) for the methylene group were observed. These data suggest that the dimeric structure remained in the C_6D_6 solution. In THF-d_8, however, the



4a: Ln = Y (67%), n = 1
4b: Ln = Yb(55%), n = 0
4c: Ln = Lu(69%), n = 0

Scheme 2.



Scheme 3.

Table 3. Summary of selected bond distances (Å) and angles (deg.) of the silylene-linked cyclopentadienyl-phosphido rare earth alkyl complexes of type $[Me_2Si(Cp')(\mu\text{-}PR)LnCH_2SiMe_3]_2$

	4b	**4c**	**5a**	**5b**	**5c**
Ln=	Yb	Lu	Y	Yb	Lu
R=	Ph	Ph	Cy	Cy	Cy
Ln–C(Cp′)(av.)	2.586(9)	2.572(4)	2.621(5)	2.595(4)	2.593(4)
Ln–C1	2.318(9)	2.301(4)	2.339(4)	2.298(4)	2.306(5)
Ln–P	2.836(6)	2.826(1)	2.865(2)	2.826(1)	2.817(1)
Ln–P*	2.796(5)	2.786(1)	2.857(2)	2.798(1)	2.789(1)
Ln···Ln	4.188	4.165	4.125	4.035	4.012
∠P–Ln–P*	83.94(10)	84.16(3)	87.76(5)	88.32(3)	88.61(3)
∠Ln–P–Ln*	96.06(10)	95.84(3)	92.24(5)	91.68(3)	91.39(3)
∠P–Ln–C1	112.1(2)	112.1(1)	120.1(1)	109.6(1)	109.7(1)
∠P*–Ln–C1	113.2(3)	113.0(1)	111.4(1)	112.6(1)	112.5(1)
∠Cp′(ctd)–Ln–C1	121.8	121.5	117.9	121.6	121.1
∠Cp′(ctd)–Ln–P	101.6	101.9	100.1	101.1	101.4
∠Cp′(ctd)–Ln–P*	116.6	116.5	115.9	116.8	117.1

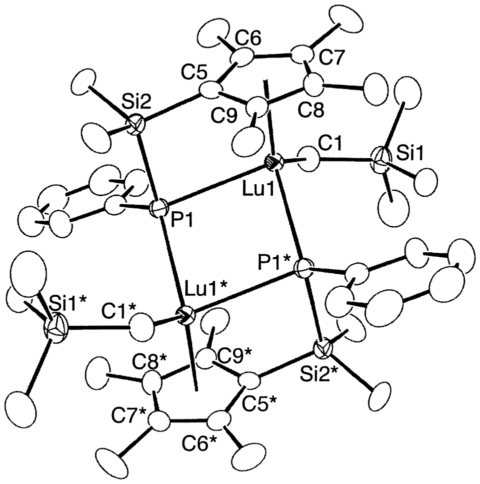


Figure 3. ORTEP drawing of **4c** with 30% thermal ellipsoids.

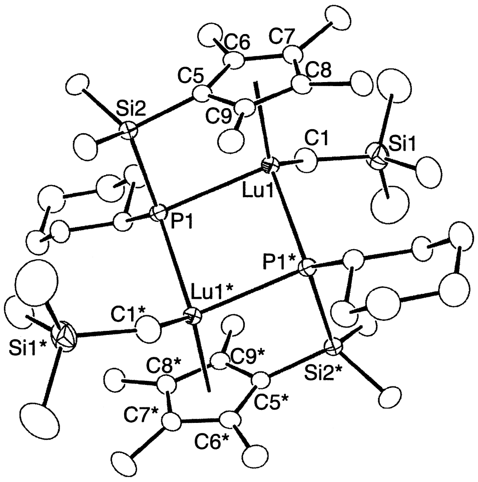


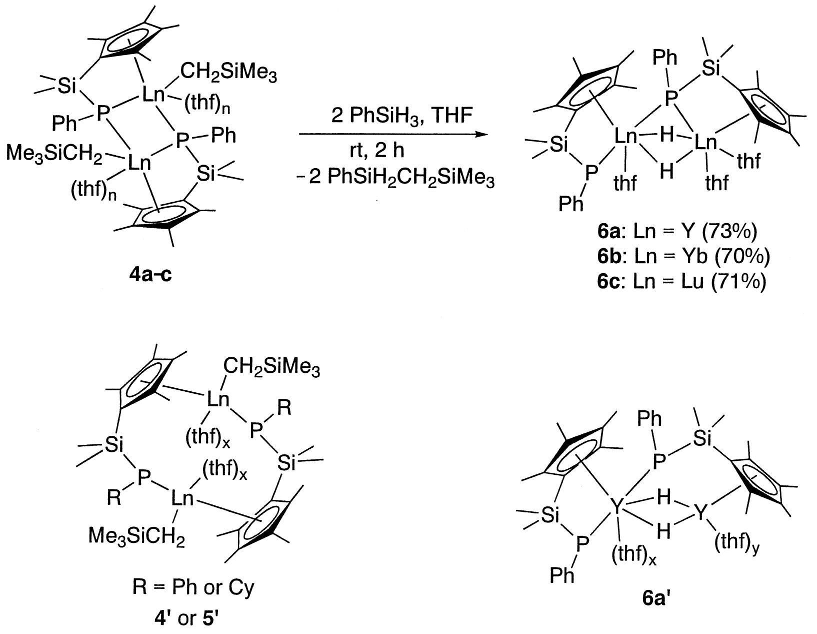
Figure 4. ORTEP drawing of **5c** with 30% thermal ellipsoids.

number of each set of the signals reduced by half, showing that the phosphido-bridge is broken in THF solution.[14] Recrystallization of these complexes from THF, however, did not give a monomeric compound, but instead always yielded the P-bridged dimers,[14] showing that the Ln–P interactions in these complexes are stronger than the Ln–THF bonds in solid state.

2.2. Synthesis and structures of the silylene-linked Cp′-phosphido rare earth hydride complexes

The reactions of the alkyl complexes **4a–c** with 2 equiv. of $PhSiH_3$ in THF easily afforded the corresponding hydrido complexes **6a–c** in 70–73% isolated yields (Scheme 4).[15] Complexes **6a–c** are isostructural and isomorphous with each other. Their selected bond distances and angles are summarized in Table 4. The X-ray structure of **6c** is shown in Figure 5, as a representative example. In contrast with the alkyl precursors **4a–c**, which bear two bridging-phosphido ligands and two terminal alkyl ligands, the hydrido complexes **6a–c** possess one phosphido- and two hydrido-bridges, while the other phosphido ligand is bonded to only one metal center. The metal atom which is bonded to two P atoms bears one THF ligand, while that to one P atom has two THF ligands. Both metal centers in **6a–c** have therefore the same coordination number. Similar to what was observed in the alkyl complexes **4b**,**c** and **5a–c**, the phosphido bridges in **6a–c** are also asymmetric, with the intermolecular $Ln^1–P^2$ bond distance being significantly shorter than that of the corresponding intramolecular chelating $Ln^2–P^2$ bond (cf. 2.890(2) vs. 2.914(2) Å in **6a**, 2.852(3) vs. 2.866(2) Å in **6b**, 2.832(2) vs. 2.861(2) Å in **6c**, Table 4). The 'terminal' $Ln^1–P^1$ bond distances (2.826(2) Å in **6a**, 2.787(3) Å in **6b**, 2.788(2) Å in **6c**) are much shorter than those of the bridging Ln–P bonds. The hydrido ligands in **6a–c** were all found by difference Fourier syntheses. The Ln–H bond distances (1.75(6)–2.33(6) Å) are comparable with those reported for other rare earth hydride complexes.[1f,5e,6]

Complexes **6a–c** are insoluble in hexane and benzene, but



Scheme 4.

Table 4. Summary of selected distances (Å) and angles (deg.) of the silylene-linked cyclopentadienyl-phosphido rare earth hydride complexes of type $Me_2Si(Cp'^1)(P^1Ph)Ln^1(thf)(\mu\text{-}H)_2Ln^2(thf)_2(\mu\text{-}P^2Ph)(Cp'^2)SiMe_2$

	6a	**6b**	**6c**
Ln=	Y	Yb	Lu
Ln^1–C(Cp'^1) (av.)	2.671(5)	2.663(9)	2.642(8)
Ln^2–(Cp'^2) (av.)	2.659(5)	2.628(8)	2.630(8)
Ln^1–P^1	2.826(2)	2.787(3)	2.788(2)
Ln^1–P^2	2.890(2)	2.852(3)	2.832(2)
Ln^2–P^2	2.914(2)	2.866(2)	2.861(2)
Ln^1–H^1	2.13(3)	2.17(5)	2.06(4)
Ln^1–H^2	2.09(3)	2.33(6)	2.21(5)
Ln^2–H^1	2.07(3)	1.95(5)	2.01(4)
Ln^2–H^2	2.13(3)	1.75(6)	1.90(5)
Ln^1–O^1	2.397(3)	2.419(5)	2.371(5)
Ln^2–O^2	2.355(3)	2.395(6)	2.341(5)
Ln^2–O^3	2.426(4)	2.331(6)	2.370(5)
Ln···Ln	3.485(2)	3.407(1)	3.390(1)
$\angle P^1$–Ln^1–P^2	152.04(5)	151.91(7)	152.03(6)
$\angle Ln^1$–P–Ln^2	73.82(4)	73.15(6)	73.08(5)
$\angle Cp'(ctd)^1$–Ln^1–P^1	93.62	94.73	94.83
$\angle Cp'(ctd)^1$–Ln^1–P^2	114.42	113.35	113.13
$\angle Cp'(ctd)^2$–Ln^2–P^2	99.79	100.48	100.83

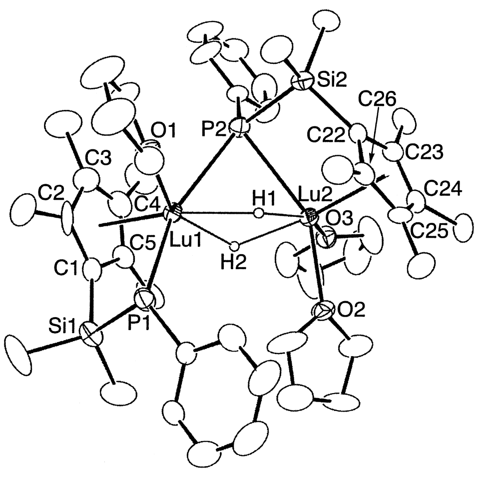
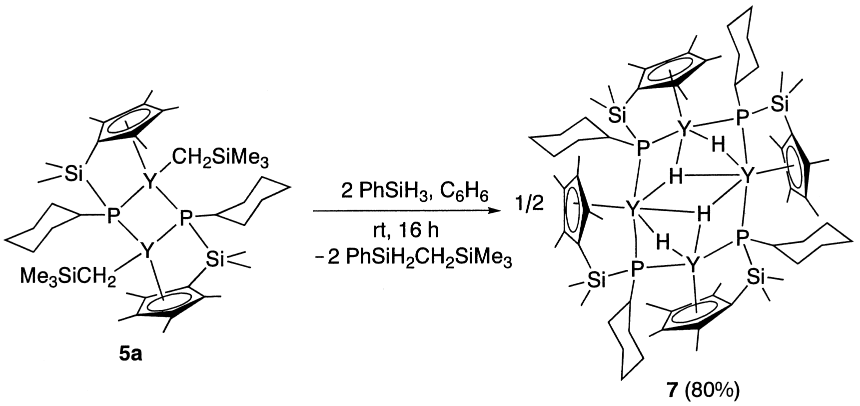


Figure 5. ORTEP drawing of **6c** with 30% thermal ellipsoids.

soluble in THF. The ^1H and ^{31}P NMR spectra of the diamagnetic complexes **6a,c** in THF-d_8 are fluxional and temperature dependent. The ^1H NMR for the hydrides of the yttrium complex **6a** in THF-d_8 gave a broad triplet (δ 5.05, J_{Y-H}=24.4 Hz) at 50°C, a broad singlet (δ 5.03) at 22°C, and two multiplets (δ 4.68–4.89, 5.04–5.24) at −45°C, showing that the hydrido bridges remained in THF solution. However, the ^{31}P NMR spectra of **6a** in THF-d_8 at −45°C gave two doublets (δ −97.9, J_{P-Y}=71.2 Hz; −132.9, J_{P-Y}=53.4 Hz), rather than one doublet and one triplet as expected for its solid structure, suggesting that the weaker “intramolecular” chelating part (Y^2–P^2 bond) of the P-bridge in **6a** might be cleaved by THF to give a species like **6a′**. Further identification of such a species was, however, difficult. In pyridine-d_5, the ^1H NMR signals for the hydrides disappeared gradually, possibly owing to hydride addition to pyridine-d_5. Such addition reactions have been observed previously in other rare earth hydride complexes.[16]

The similar reactions of the cyclohexylphosphido/alkyl complexes **5a–c** with $PhSiH_3$ in THF seemed also to give the corresponding hydrido species, but a structurally characterizable compound was not obtained. In an attempt to obtain a THF-free hydrido complex, a benzene solution of **5c** was treated with $PhSiH_3$ as shown in Scheme 5. After the reaction solution was left standing at room temperature overnight, light-yellow needle-like crystals of **7** were precipitated. Complex **7** was insoluble in almost all common organic solvents such as benzene, THF, pyridine, or HMPA (hexamethylphosphoric triamide), and therefore, its characterization by NMR was difficult. An X-ray analysis showed that **7** is a THF-free, tetranuclear hydrido complex consisting of four $[Me_2Si(C_5Me_4)P(Cy)YH]$ units (Fig. 6 and Table 5). A crystallographic inversion center exists at the center of the molecule. Each P atom bridges two Y atoms. Two of the four hydrido ligands (H1 and H1*) cap three Y atoms, while the other two hydrido ligands (H2 and H2*) bridge two Y atoms. In addition, an intermolecular



Scheme 5.

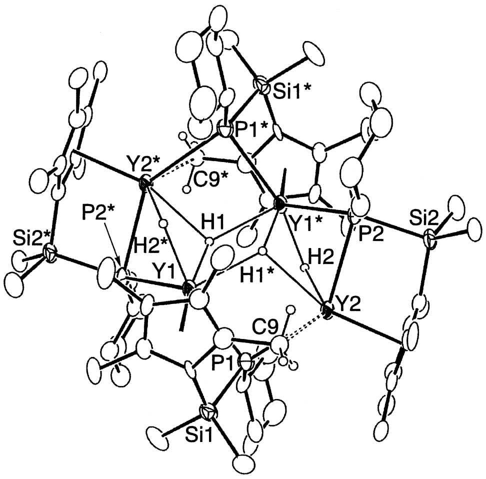


Figure 6. ORTEP drawing of **7** with 30% thermal ellipsoids.

Table 5. Selected bond distances (Å) and angles (deg.) of **7**

Y1–P1	2.905(2)	Y2–P1	2.916(2)
Y1–P2*	2.868(2)	Y2–P2	2.895(2)
Y1–H1	1.85(4)	Y2–H2	2.37(6)
Y1–H1*	2.33(4)	Y2–H1*	2.47(4)
Y1–H2*	2.10(6)	Y2···H9A	2.50(4)
Y1–C(Cp′) (av.)	2.644(6)	Y2–C(Cp′)(av.)	2.655(6)
Y2···C9	2.937(6)		
Cp′(ctd)–Y1–P1	93.23	Cp′(ctd)–Y2–P1	120.52
Cp′(ctd)–Y1–P2*	127.74	Cp′(ctd)–Y2–P2	98.50

agostic interaction between a Cp′ methyl group and a Y atom (cf. Y2–C9=Y2*–C9*: 2.937(6) Å) was also observed. The Y–P bond distances in **7** (2.868(2)–2.916(2) Å) are comparable with those in **6a**–**c** (2.787(3)–2.914(2) Å).

The similar reaction of the PH-functionalized-cyclopentadienyl/bis(alkyl) complexes **1a**,**b** with $PhSiH_3$ in benzene afforded the corresponding phosphido-ligated hydrido complexes **8a**,**b**, instead of a dihydride species such as '$C_5Me_4(SiMe_2PHAr)LnH_2$' (Scheme 6).[5f,6] Further reaction to give an intramolecular C–H bond activation product such as **3** was not observed in this case, demonstrating that the hydride species **8a**,**b** are more stable than their alkyl analogues such as **2**.

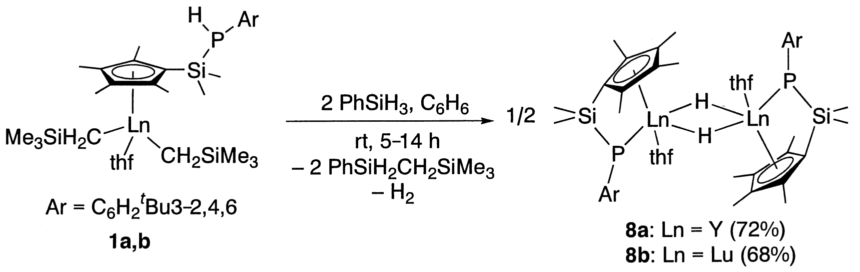
Complexes **8a**,**b** are isostructural and isomorphous. A crystallographic inversion center exists at the center of the molecule, in which the two metal centers are bridged by two hydrido ligands (cf. Fig. 7 and Table 6). In contrast with the phosphido-bridging in the phenylphosphido and cyclohexylphosphido complexes **4**–**7**, the 'Cp′-PAr' ligand in **8a**,**b** is bonded to the same metal center in a chelating fashion and no phosphido bridge is formed probably owing to the bulkiness of the sterically demanding $C_6H_2{}^tBu_3$-2,4,6 (Ar) substituent on the P atom.

Complexes **8a**,**b** are insoluble in hexane and benzene, and soluble to some extent in THF. The ^1H NMR spectrum of the yttrium complex **8a** in THF-d_8 showed a triplet at δ 4.97 with J_{Y-H}=30.1 Hz for the hydride ligands, indicating that the hydrido-bridges remained in THF solution.

2.3. Polymerization of ethylene

The polymerization of ethylene was carried out in toluene (15 or 30 mL) at 25°C under 1 atm of ethylene by use of 0.05 mmol (Ln) of a catalyst. Some representative results are summarized in Table 7.

In the case of **4a**, 1.21 g of polyethylene with M_n=5.85×10^4



Scheme 6.

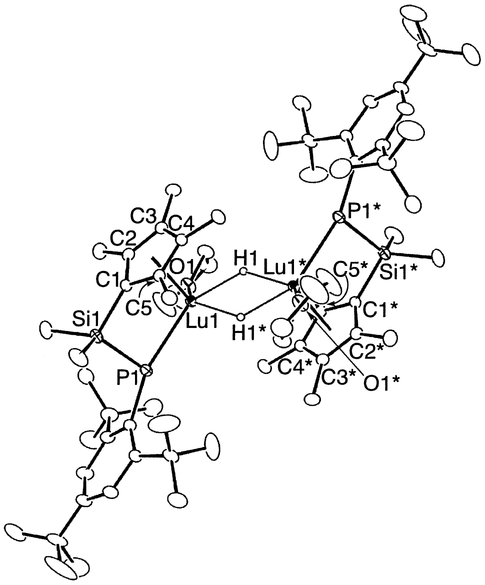


Figure 7. ORTEP drawing of **8b** with 30% thermal ellipsoids.

Table 6. Selected bond distances (Å) and angles (deg.) of **8a** and **8b**

	8a	**8b**
Ln1=	Y	Lu
Ln1–P1	2.724(1)	2.683(1)
Ln1–H1	2.20(2)	1.99(3)
Ln1–H1*	2.12(3)	2.06(3)
Ln1–C(Cp′)(av.)	2.605(3)	2.568(3)
Ln1–O1	2.385(2)	2.322(2)
∠Ln1–H1–Ln1*	110.2	116.4
∠H1–Ln1–H1*	69.8(11)	63.5(13)
∠P1–Ln1–H1	157.9(7)	152.1(8)
∠P1–Ln1–H1*	95.5(7)	99.8(8)
∠P1–Ln1–O1	104.14(6)	102.98(6)
∠O1–Ln1–H1	77.4(6)	76.8(8)
∠O1–Ln1–H1*	134.0(6)	131.1(7)
∠Cp′(ctd)–P1–Ln1	100.4	101.2

Table 7. Polymerization of ethylene by rare earth alkyl and hydride complexes bearing the silylene-linked cyclopentadienyl-phosphido ligands[a]

Entry	Catalyst	Solvent (mL)	Time (min)	Yield (g)	Activity[b]	M_n ($\times10^4$)[c]	M_w/M_n[c]
1	**4a**	15	10	1.21	145.2	5.85	1.46
2	**4a**	15	30	1.31	52.4	6.26	1.47
3	**4a**	30	30	2.55	102.0	12.91	2.21
4	**4a**	60	30	4.58	183.2	12.27	2.14
5	**4b**	15	30	0.29	11.6	2.08	1.26
6	**4c**	15	30	Trace			
7	**5a**	30	30	1.98	79.2	11.17	1.58
8	**5b**	15	30	Trace			
9	**5c**	15	20	Trace			
10	**6a**	15	30	Trace			
11	**8a**	15	30	Trace			

[a] Reaction conditions: catlyst, 0.025 mmol; ethylene, 1 atm; solvent, toluene; 25°C (water bath).

[b] Activity=kg polymer (mol Ln)$^{-1}$ h^{-1}.

[c] Determined at 135°C against polystyrene standard by GPC.

were formed in 10 min in 15 mL of toluene (entry 1). A longer reaction time (e.g. 30 min) did not raise much the polymer yield (1.31 g) (entry 2), but the increase of toluene solvent from 15 mL to 30 mL almost doubled the polyethylene yield (2.55 g) as well as the molecular weight (M_n=12.91×10^4) (cf. entry 2 vs. entry 3). These results suggest that the propagation active species has a rather limited solubility in toluene and creation of a homogeneous active site is critical for the chain propagation reaction. When 60 mL of toluene were used, the yield of polyethylene increased to 4.58 g, while the molecular weight of the polymer (M_n=12.27×10^4, M_w/M_n=2.14) remained almost unchanged (entry 4), indicating that a chain transfer reaction might take place. A clear dependence of activity on the ion size of the central metals was also observed. The largest Y complexes (**4a**, **5a**) showed the highest activity, whereas the smallest lutetium complexes (**4c**, **5c**) were almost inert under the same conditions (cf. entries 2, 5, 6 and entries 7–9).[18] The phenylphosphido complexes (**4a** and **4b**) seemed to have a higher activity than the corresponding cyclohexylphosphido analogues (**5a** and **5b**) (cf. entry 3 vs. entry 7; entry 5 vs. entry 8, Table 7). The hydride complexes (e.g. **6a**, **8a**) were almost inactive for the polymerization of ethylene under the same conditions (25°C, 1 atm), probably owing to the strong hydrido-bridges. Generally, the silylene-linked cyclopentadienyl-phosphido yttrium complexes **4a** and **5a** (52–183 kg polymer (mol Ln)$^{-1}$ h^{-1} atm^{-1}) are much more active than the analogous amido complexes such as $Me_2Si(C_5Me_4)(N^tBu)Y(CH_2SiMe_3)(thf)$ (0.21 kg polymer (mol Y)$^{-1}$ h^{-1} atm^{-1})[5d] or the mixed cyclopentadienyl-aryloxide complex $[(C_5Me_5)Y(OC_6H_3{}^tBu\text{-}2,6)Y(\mu\text{-}H)]_2$ (0.34 kg polymer (mol Y)$^{-1}$ h^{-1} atm^{-1}).[17]

2.4. Hydrosilylation of olefins

To assess the activity of the rare earth complexes bearing cyclopentadienyl-phosphido ligands as catalysts for the hydrosilylation of olefins, 1-decene was first examined as an olefin substrate under standard conditions ($PhSiH_3$, rt, 5 mol% (Ln) of a catalyst).[19] The reaction could be easily monitored by ^{1}H NMR in C_6D_6. Some representative results are shown in Table 8.

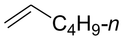
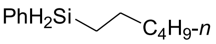
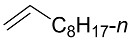
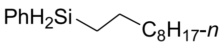
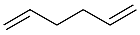
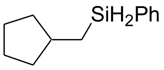
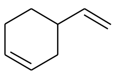
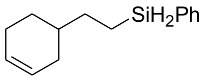
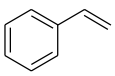
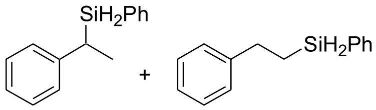
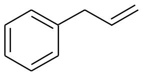
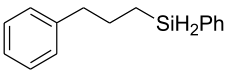
Table 8. Catalytic hydrosilylation of 1-decene by rare earth alkyl and hydride complexes bearing the silylene-linked cyclopentadienyl-phosphido ligands[a]

Entry	Catalyst	Ln	Time	Yield (%)[b]
1	**4a**	Y	1 h	95
2	**4b**	Yb	24 h	30
3	**4c**	Lu	3 h	100
4	**5a**	Y	45 min	100
5	**5b**	Yb	45 min	100
6	**5c**	Lu	10 min	100
7	**1b**	Lu	24 h	100
8	**6a**	Y	3 h	100
9	**6c**	Lu	3 h	100
10	**7**	Y	24 h	0
11	**8b**	Lu	48 h	89

[a] Conditions: 1-hexene (0.4 mmol), H_3SiPh (0.5 mmol), catalyst (0.02 mmol Ln), in C_6D_6 at rt.

[b] Determined by ^{1}H NMR. $CH_3(CH_2)_9SiH_2Ph$ is the only product.

Table 9. Catalytic hydrosilylation of olefins by $[Me_2Si(C_5Me_4)(\mu\text{-}PCy)LuCH_2SiMe_3]_2$ (**5c**)[a]

Entry	Substrate	Time (min)	Product	Yield (%)
1		10		100
2		10		100
3		45		100
4		30		100
5		40	 (54 : 46)	100
6		15		100

[a] Conditions: substrate (0.4 mmol), H_3SiPh (0.5 mmol), **5c** (0.01 mmol), in C_6D_6 at rt.

Almost all of the cyclopentadienyl-phosphido rare earth alkyl or hydride complexes reported in this paper are active for the catalytic hydrosilylation of 1-decene. Among these complexes, the cyclohexylphosphido lutetium alkyl complex **5c** showed the highest activity, which yielded quantitatively the linear silylation product 1-(phenylsilyl)-decane within 10 min (entry 6, Table 8). To our knowledge, this is the most active and regioselective rare earth catalyst ever reported for the hydrosilylation of 1-decene.[1a,5b,15a,19,20] As in the case of rare earth metallocene catalysts, the true catalyst species in the present reactions must be a hydride species.[19] In the case of **5a** (entry 4, Table 8), the structurally characterized hydride complex **7** was isolated after completion of the hydrosilylation reaction. However, in contrast with its active alkyl precursor **5a**, the isolated tetranuclear hydride complex **7** showed no activity under the same conditions, obviously owing to its insolubility (or strong hydride bridges) (entry 10). These results suggest that the hydrosilylation reactions catalyzed by the cyclopentadienyl-phosphido rare earth alkyl complexes might proceed through an in situ generated terminal hydride species, as in the case of some metallocene analogues such as $[(C_5H^t_4Bu)_2Ln(\mu\text{-}Me)]_2$ (Ln=Y, Tb, Yb, Lu).[19a,21]

The lutetium alkyl complex **5c**, which showed the highest activity for 1-decene hydrosilylation, was then chosen as a catalyst for examination of the hydrosilylation of other olefins. As shown in Table 9, various olefins can be quantitatively hydrosilylated in less than 1 h under standard conditions ($PhSiH_3$, rt, 2.5 mol% **5c**). These reactions are much faster than most of the previously reported ones. 1,5-Hexadiene was converted quantitatively into the cyclization/silylation product (phenylsilyl)methylcyclopentane within 45 min (entry 3 Table 9).[19d,g,h] The hydrosilylation of 4-vinyl-1-cyclohexene occurred selectively at the terminal C–C double bond, affording quantitatively the terminal silane product 4-[2-(phenylsilyl)ethyl]cyclohex-1-ene in less than 30 min (entry 4 Table 9).[16a,19i] The reaction of 3-phenylpropylene was completed in 15 min to give cleanly the linear silane product 3-phenyl-1-(phenylsilyl)propane (entry 6, Table 9).[19i] In the case of styrene, a 54:46 (1.2:1) mixture of the two regioisomers $PhCH(CH_3)SiH_2Ph$ and $PhCH_2CH_2SiH_2Ph$ was obtained (entry 6, Table 9). This ratio is similar to that reported for the Me_2SiCH_2-linked cyclopentadienyl-amido complex $Me_2Si(C_5Me_4)(CH_2N^tBu)Y(CH_2SiMe_3)(thf)$ (1.4:1),[5b] but the proportion of the linear silane product $PhCH_2CH_2SiH_2Ph$ (46%) is higher than those reported for rare earth metallocene catalysts.[22]

3. Conclusion

We have demonstrated that the acid–base reaction between $Ln(CH_2SiMe_3)_3(thf)_2$ (Ln=Y, Yb, Lu) and $Me_2Si(C_5Me_4H)(PHR)$ (R=Ph, Cy) offers a convenient route to the corresponding silylene-linked cyclopentadienyl-phosphido rare earth alkyl complexes such as **4a–c** and **5a–c**. In contrast with the analogous cyclopentadienyl-amido or metallocene complexes, the phosphido complexes **4a–c** and **5a–c** adopt a dimeric structure through phosphido-bridging, while the alkyl ligand is placed in a terminal position. The reaction of the alkyl complexes (e.g. **4a–c**) with $PhSiH_3$ in THF easily afforded the corresponding hydride compounds (**6a–c**), which also adopt a dimeric structure but the two metal centers are bridged by two hydrido ligands and one phosphido ligand. The hydrido-bridges are considerably strong and could survive even in a THF solution as shown by the NMR spectra. The intramolecular chelating P-metal bond, which is weaker than the intermolecular bridging one, might be cleaved in THF. In a non-polar solvent such as benzene, however, the phosphido bridges in both the alkyl and hydride complexes apparently remained. This nature could make the metal centers in these complexes more crowded than those in the analogous amido or metallocene complexes during some reactions. When in a THF-free state, a hydride species could form a further highly aggregated, surprisingly stable structure through the hydrido and phosphido bridges, as observed in **7**. If the phosphido unit bears a sterically demanding substituent such as $C_6H_3{}^tBu_3$-2,4,6, the phosphido bridge can be prevented and a simpler, H-bridged dimeric complex (e.g.**8a**,**b**) is formed. Complexes **4a**–**c** and **5a**–**c** represent the first examples of rare earth alkyl complexes bearing cyclopentadienyl-phosphido ligands, and **6a**–**c**, **7**, and **8a**,**b** are the first examples of such type of hydride complexes. Most of these complexes showed high activity for the polymerization of ethylene or hydrosilylation of olefins, although their activity was dependent on the central metals and the phosphido ligands. In the case of olefin hydrosilylation by the alkyl complexes, an extremely active terminal hydride species might be generated in situ and serve as a true catalyst. The unique steric and electronic properties of the cyclopentadienyl-phosphido complexes enabled them in most cases more active and regioselective than the conventional metallocene or amido analogues.

4. Experimental

4.1. General

All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an Mbraun glovebox. The argon was purified by being passed through a Dryclean column (4A molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4A) 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. NMR Samples were prepared in the glovebox by use of J. Young valve NMR tubes (Wilmad 528-JY). ^1H and ^{13}C NMR spectra were recorded on JNM-EX 270 (FT, 270 MHz for ^1H; 67.80 MHz for ^{13}C) spectrometer. ^{31}P NMR spectra were recorded on a JNM-ALPHA 400 (FT, 161.70 MHz) spectrometer. Chemical shifts for the ^{31}P NMR are reported relative to an external 85% H_3PO_4 standard. Elemental analyses were carried out by the Chemical Analysis Team of Advanced D and S Center, RIKEN. The carbon values found for the rare earth phosphido compounds were always lower than the calculated ones and were poorly reproducible probably due to formation of incombustible carbide species, as observed previously in the case of other P-containing rare earth complexes.[3,23] Therefore, not all phosphido complexes were submitted for microanalysis. Solvents were distilled from sodium/benzophenone ketyl, degassed by the freeze-pump-thaw method (three times), and dried over fresh Na chips in the glovebox. $C_6H_5PH_2$, $C_6H_{11}PH_2$ (10 weight% in hexane solution), $LnCl_3$ and $PhSiH_3$ were purchased from STREM. $Me_2Si(C_5Me_4H)PHR$ ($R{=}C_6H_2{}^tBu_3$-2,4,6,[3] C_6H_{11},[4d] C_6H_5[4f]) were prepared according to literature procedures.

4.2. Complex syntheses

4.2.1. $Me_2Si(C_5Me_4)PH(C_6H_2{}^tBu_3\text{-}2,4,6)]Y(CH_2SiMe_3)_2(thf)$ (1a). To a hexane solution (10 mL) of $Y(CH_2SiMe_3)_3(THF)_2$ (0.495 g, 1 mmol) was added $Me_2Si(C_5Me_4H)PH(C_6H_2{}^tBu_3$-2,4,6) (0.457 g, 1 mmol) in hexane (10 mL). The reaction mixture was stirred at room temperature for 30 min. Reduction of the solution volume under vacuum yielded pale yellow crystalline precipitate, which after decantation, was dried under vacuum to **1a** (0.483 g, 0.610 mmol, 61% yield). ^1H NMR (C_6D_6, 22°C): δ −0.68 (s, 4H, J_{Y-H}= 3.1 Hz, CH_2SiMe_3), 0.24 (s, 18H, CH_2SiMe_3), 0.30 (d, 3H, J_{P-H}=3.1 Hz, $C_5Me_4SiMe_2$), 0.43 (d, 3H, J_{P-H}=4.0 Hz, $C_5Me_4SiMe_2$), 1.14 (br m, 4H, THF), 1.35 (s, 9H, *para*-^{t}Bu), 1.56 (s, 18H, *ortho*-^{t}Bu), 1.92 (s, 3H, C_5Me_4), 1.95 (s, 3H, C_5Me_4), 2.18 (s, 3H, C_5Me_4), 2.19 (s, 3H, C_5Me_4), 3.48 (br m, 4H, THF), 4.52 (d, J_{P-H}=213.9 Hz, 1H, PH), 7.45 (d, 2H, J_{P-H}=2.1 Hz, C_6H_2). ^{13}C NMR (C_6D_6, 22°C): δ 2.14 (d, 1C, J_{P-C}=2.8 Hz, $C_5Me_4SiMe_2$), 2.95 (d, 1C, J_{P-C}= 15.6 Hz, $C_5Me_4SiMe_2$), 4.51 (s, 6C, CH_2SiMe_3), 11.51 (s, 2C, C_5Me_4), 14.66, (d, 1C, J_{P-C}=3.7 Hz, C_5Me_4), 14.87 (d, 1C, J_{P-C}=5.5 Hz, C_5Me_4), 24.71 (s, THF), 31.54 (s, 6C, $C(CH_3)_3$), 33.47 (s, 3C, $C(CH_3)_3$), 34.71 (s, 2C, $C(CH_3)_3$), 34.93 (d, 2C, J_{Y-C}=43.9 Hz, CH_2SiMe_3), 38.18 (s, 1C, $C(CH_3)_3$), 70.53 (s, THF), 114.43 (d, 1C, J_{P-C}=10.1 Hz, *ipso*-C_5Me_4), 121.24 (d, 2C, J_{P-C}=3.7 Hz, *meta*-C_6H_2), 123.14, 123.64, 126.08, 126.43 (s, 4C, C_5Me_4), 130.59 (d, 1C, J_{P-C}=34.8 Hz, *ipso*-C_6H_2), 147.19 (s, 2C, *ortho*-C_6H_2), 154.46 (s, 1C, *para*-C_6H_2). ^{31}P NMR (C_6D_6, 22°C): δ −119.7 (d, J_{P-H}=214 Hz). Anal. Calcd for $C_{41}H_{78}POSi_3Y$: C, 62.24; H, 9.94. Found: C, 58.75–60.86; H, 9.77–9.80. The low and poorly reproducible carbon values were probably due to formation of incombustible carbide species, as in the case of other P-containing rare earth complexes.[3,23]

4.2.2. $[Me_2Si(C_5Me_4)PH(C_6H_2{}^tBu_3\text{-}2,4,6)]Lu(CH_2SiMe_3)_2(thf)$ (1b). To a hexane solution (15 mL) of $Lu(CH_2SiMe_3)_3(thf)_2$ (1.162 g, 2.0 mmol) was added $Me_2Si(C_5Me_4H)PH(C_6H_2{}^tBu_3$-2,4,6) (0.914 g, 2.0 mmol) in hexane (15 mL). The reaction mixture was stirred at room temperature for 2.5 h. Reduction of the solution volume under vacuum yielded colorless crystals, which after decantation, was dried under vacuum to give **1b** (1.474 g, 1.68 mmol, 84% yield) as white powder. Single crystals suitable X-ray analysis could be obtained by recrystallization from hexane. ^1H NMR (C_6D_6, 22°C): δ −0.84 (s, 4H, CH_2SiMe_3), 0.27 (s, 18H, CH_2SiMe_3), 0.33 (d, J_{P-H}=1.8 Hz, 3H, $C_5Me_4SiMe_2$), 0.47 (d, J_{P-H}=4.1 Hz, 3H, $C_5Me_4SiMe_2$), 1.10 (m, 4H, THF), 1.37 (s, 9H, ^{t}Bu), 1.59 (s, 18H, ^{t}Bu), 1.93 (s, 3H, C_5Me_4), 1.96 (s, 3H, C_5Me_4), 2.22 (s, 3H, C_5Me_4), 2.23 (s, 3H, C_5Me_4), 3.49 (m, 4H, THF), 4.55 (d, J_{P-H}=214.5 Hz, 1H, PH), 7.46 (d, J_{P-H}=1.8 Hz, 2H, C_6H_2). ^{13}C NMR (C_6D_6, 22°C): δ 2.31 (d, 1C, J_{P-C}=3.7 Hz, $C_5Me_4SiMe_2$), 3.04 (d, 1C, J_{P-C}=15.6 Hz, $C_5Me_4SiMe_2$), 4.70 (s, 6C, CH_2SiMe_3), 11.55 (s, 2C, C_5Me_4), 14.77 (d, 1C, J_{P-C}= 4.4 Hz, C_5Me_4), 14.97 (d, 1C, J_{P-C}=5.0 Hz, C_5Me_4), 24.73 (s, THF), 31.65 (s, 6C, $C(CH_3)_3$), 33.60 (s, 3C, $C(CH_3)_3$), 34.80 (s, 2C, $C(CH_3)_3$), 38.29 (s, 1C, $C(CH_3)_3$), 39.83 (s, 2C, CH_2SiMe_3), 70.73 (s, THF), 114.03 (d, 1C, J_{P-C}= 10.6 Hz, *ipso*-C_5Me_4), 121.39 (d, 2C, J_{P-C}=4.4 Hz, *meta*-C_6H_2), 122.87, 123.29, 126.06, 126.31(s, 4C, C_5Me_4), 130.92 (d, 1C, J_{P-C}=35.5 Hz, *ipso*-C_6H_2), 147.43 (s, 2C, *ortho*-C_6H_2), 154.77 (s, 1C, *para*-C_6H_2). ^{31}P NMR (C_6D_6, 22°C): δ −119.7 (d, J_{P-H}=213 Hz). Anal. Calcd for $C_{41}H_{78}POSi_3Lu$: C, 56.13; H, 8.96. Found: C, 51.77–54.63; H, 8.68–8.77. The low and poorly reproducible carbon values were probably due to formation of incombustible carbide species, as in the case of other P-containing rare earth complexes.[3,23]

4.2.3. Me$_2$Si(C$_5$Me$_4$)(μ-PC$_6$H$_2$(μ-CMe$_2$CH$_2$)-2-^{t}Bu$_2$-4,6)Y(thf)$_2$ (3). To a hexane solution (5 mL) of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.396 g, 0.80 mmol) was added Me$_2$Si(C$_5$Me$_4$H)PH(C$_6$H$_2$^{t}Bu$_3$-2,4,6) (0.365 g, 0.80 mmol) in hexane (5 mL) at room temperature. The reaction mixture was stirred at room temperature for 48 h. Slow reduction of the solution volume under reduced pressure resulted in the precipitation of yellow crystals of **3**·0.5C$_6$H$_{14}$. The crystals were isolated by decantation, washed with hexane, and dried up under vacuum to give **3** as an orange crystalline powder (0.190 g, 0.277 mmol, 35% yield). ^{31}P NMR (C$_6$D$_6$, 22°C): δ −117.9 (d, J_{P-Y}=66 Hz). Satisfactory ^{1}H and ^{13}C NMR spectra of **3** in either C$_6$D$_6$ or THF-d$_8$ were not obtained because of its instability in solution.

4.2.4. [Me$_2$Si(C$_5$Me$_4$)(μ-PC$_6$H$_5$)Y(CH$_2$SiMe$_3$)(thf)]$_2$ (4a). Addition of a hexane solution (5 mL) of Me$_2$Si(C$_5$Me$_4$H)PH(C$_6$H$_5$) (0.577 g, 2 mmol) to Y(CH$_2$SiMe$_3$)(THF)$_3$ (0.990 g, 2 mmol) in hexane (20 mL) at room temperature gradually precipitated pale yellow crystals. The reaction mixture was left standing overnight. The crystals were filtered, washed with hexane, and dried up under vacuum to yield **4a** (0.719 g, 0.672 mmol, 67% yield) as a pale yellow crystalline powders. Single crystals suitable X-ray analysis were obtained directly from the reaction mixture. ^{1}H NMR (C$_6$D$_6$, 22 °C): δ −0.33 (br dd, J_{H-H}=11.1 Hz and J_{Y-H}=1.5 Hz, 2H, C*H*$_2$SiMe$_3$), 0.09 (br dd, J_{H-H}=11.1 Hz and J_{Y-H}=1.5 Hz, 2H, C*H*$_2$SiMe$_3$), 0.40 (s, 6H, C$_5$Me$_4$Si*Me*$_2$), 0.44 (s, 18H, CH$_2$Si*Me*$_3$), 0.94 (s, 6H, C$_5$Me$_4$Si*Me*$_2$), 1.41 (q, J_{H-H}=3.2 Hz, 8H, THF), 1.58 (s, 6H, C$_5$Me$_4$), 2.11 (s, 6H, C$_5$Me$_4$), 2.16 (s, 6H, C$_5$Me$_4$), 2.23 (s, 6H, C$_5$Me$_4$), 3.72 (q, J_{H-H}=3.2 Hz, 8H, THF), 7.00–7.15 (m, 6H, C$_6$H$_5$), 7.63 (m, 4H, C$_6$H$_5$). ^{1}H NMR (THF-d$_8$, 22°C): δ −1.08 (d, J_{Y-H}=2.7 Hz, 2H, C*H*$_2$SiMe$_3$), −0.07 (s, 9H, CH$_2$Si*Me*$_3$), 0.66 (d, J_{P-H}=2.4 Hz, 6H, C$_5$Me$_4$Si*Me*$_2$), 2.02 (s, 6H, C$_5$Me$_4$), 2.14 (s, 6H, C$_5$Me$_4$), 6.66 (t, J_{H-H}=7.2 Hz, 1H, C$_6$H$_5$), 6.85 (t, J_{H-H}=7.1 Hz, 2H, C$_6$H$_5$), 7.23 (t, J_{H-H}=7.1 Hz, 2H, C$_6$H$_5$). ^{13}C NMR (THF-d$_8$, 22 °C): δ 4.63 (d, 3C, J_{Y-C}=4.9 Hz, CH$_2$Si*Me*$_3$), 6.20 (d, 2C, J_{P-C}=8.9 Hz, C$_5$Me$_4$Si*Me*$_2$), 11.98 (s, 2C, C$_5$*Me*$_4$), 14.78 (d, 2C, J_{P-C}=5.6 Hz, C$_5$*Me*$_4$), 28.50 (dd, 1C, J_{Y-C}=40.4 Hz and J_{P-C}=6.1 Hz, *C*H$_2$SiMe$_3$), 112.23 (d, 1C, J_{P-C}=21.2 Hz, *ipso*-*C*$_5$Me$_4$), 121.75 (s, 1C, C$_6$H$_5$), 123.20 (s, 2C, *C*$_5$Me$_4$), 125.16 (s, 2C, *C*$_5$Me$_4$), 127.64 (d, 2C, J_{P-C}=6.2 Hz, C$_6$H$_5$), 133.23 (d, 2C, J_{P-C}=12.5 Hz, C$_6$H$_5$), 149.17 (d, 1C, J_{P-C}=34.9 Hz, *ipso*-C$_6$H$_5$). ^{31}P NMR (THF-d$_8$, 22°C): δ −99.06 (d, J_{P-Y}=73.2 Hz).

4.2.5. [Me$_2$Si(C$_5$Me$_4$)(μ-PC$_6$H$_5$)Yb(CH$_2$SiMe$_3$)]$_2$ (4b). Complex **4b** was isolated as purple crystals (0.605 g, 0.553 mmol, 55% yield) in a manner similar to that for the synthesis of **4a**, by use of Me$_2$Si(C$_5$Me$_4$H)PH(C$_6$H$_5$) (0.577 g, 2 mmol) and Yb(CH$_2$SiMe$_3$)(thf)$_3$ (1.158 g, 2 mmol). Informative NMR spectra were not observed because of the influence of the paramagnetic Yb(III) ion.

4.2.6. [Me$_2$Si(C$_5$Me$_4$)(μ-PC$_6$H$_5$)Lu(CH$_2$SiMe$_3$)]$_2$ (4c). Complex **4c** was isolated colorless crystals (0.755 g, 0.688 mmol, 69% yield) in a manner similar to that for the synthesis of **4a**, by use of Me$_2$Si(C$_5$Me$_4$H)PH(C$_6$H$_5$) (0.577 g, 2 mmol) and Lu(CH$_2$SiMe$_3$)(THF)$_3$ (1.162 g, 2 mmol). ^{1}H NMR (C$_6$D$_6$, 22°C): δ −0.39 (d, J_{H-H}=11.4 Hz, 2H, C*H*$_2$SiMe$_3$), 0.20 (s, 6H, C$_5$Me$_4$Si*Me*$_2$), 0.29 (d, J_{H-H}=11.4 Hz, 2H, C*H*$_2$SiMe$_3$) 0.47 (s, 18H, CH$_2$Si*Me*$_3$), 0.99 (br s, 6H, C$_5$Me$_4$Si*Me*$_2$), 1.50 (s, 6H, C$_5$Me$_4$), 2.05 (s, 6H, C$_5$Me$_4$), 2.17 (s, 6H, C$_5$Me$_4$), 2.28 (s, 6H, C$_5$Me$_4$), 7.01 (m, 6H, C$_6$H$_5$), 7.52 (m, 4H, C$_6$H$_5$). ^{1}H NMR (THF-d$_8$, 22°C): δ −1.13 (s, 2H, C*H*$_2$SiMe$_3$), −0.08 (s, 9H, CH$_2$Si*Me*$_3$), 0.66 (d, J_{P-H}=2.4 Hz, 6H, C$_5$Me$_4$Si*Me*$_2$), 2.02 (s, 6H, C$_5$Me$_4$), 2.16 (s, 6H, C$_5$Me$_4$), 6.66 (t, J_{H-H}=7.1 Hz, 1H, C$_6$H$_5$), 6.87 (t, J_{H-H}=7.5 Hz, 2H, C$_6$H$_5$), 7.21 (t, J_{H-H}=7.5 Hz, 2H, C$_6$H$_5$). ^{13}C NMR (THF-d$_8$, 22°C): δ 4.82 (s, 3C, CH$_2$Si*Me*$_3$), 6.20 (d, 2C, J_{P-C}=9.5 Hz, C$_5$Me$_4$Si*Me*$_2$), 12.02 (s, 2C, C$_5$*Me*$_4$), 14.92 (d, 2C, J_{P-C}=5.5 Hz, C$_5$*Me*$_4$), 33.49 (d, 1C, J_{P-C}=8.9 Hz, *C*H$_2$SiMe$_3$), 111.62 (d, 1C, J_{P-C}=21.0 Hz, *ipso*-C$_5$Me$_4$), 121.74 (s, 1C, C$_6$H$_5$), 122.72 (s, 2C, *C*$_5$Me$_4$), 124.22 (s, 2C, *C*$_5$Me$_4$), 127.54 (d, 2C, J_{P-C}=6.2 Hz, C$_6$H$_5$), 133.25 (d, 2C, J_{P-C}=11.7 Hz, C$_6$H$_5$), 149.59 (d, 1C, J_{P-C}=32.9 Hz, *ipso*-C$_6$H$_5$). ^{31}P NMR (THF-d$_8$, 22°C): δ −94.69 (s).

4.2.7. [Me$_2$Si(C$_5$Me$_4$)(μ-PC$_6$H$_{11}$)Y(CH$_2$SiMe$_3$)]$_2$ (5a). A hexane solution (5 mL) of Me$_2$Si(C$_5$Me$_4$H)PH(C$_6$H$_{11}$) (0.294 g, 1 mmol) was added to Y(CH$_2$SiMe$_3$)(THF)$_3$ (0.494 g, 1 mmol) in hexane (20 mL). After reaction mixture was left standing overnight colorless crystals had precipitated. The crystals were filtered, washed with hexane, and dried up under vacuum to yield **5a** (0.180 g, 0.192 mmol, 38% yield) as colorless crystalline powders. A longer time reaction did not give a better yield of **5a**. Single crystals suitable X-ray analysis were obtained directly from the reaction mixture. ^{1}H NMR (C$_6$D$_6$, 22°C): δ −0.46 (dd, J_{H-H}=11.6 Hz and J_{Y-H}=3.1 Hz, 2H, C*H*$_2$SiMe$_3$), 0.10 (dd, J_{H-H}=11.6 Hz and J_{Y-H}=3.1 Hz, 2H, C*H*$_2$SiMe$_3$), 0.34 (s, 18H, CH$_2$Si*Me*$_3$), 0.78 (s, 6H, C$_5$Me$_4$Si*Me*$_2$), 1.02 (m, 6H, C$_5$Me$_4$Si*Me*$_2$), 1.18–1.30 (m, 6H, C$_6$H$_{11}$), 1.34–1.75 (m, 10H, C$_6$H$_{11}$), 1.85–1.93(m, 2H, C$_6$H$_{11}$), 2.00 (s, 6H, C$_5$Me$_4$), 2.00 (m, 2H, C$_6$H$_{11}$), 2.13 (s, 6H, C$_5$Me$_4$), 2.22 (s, 6H, C$_5$Me$_4$), 2.45 (s, 6H, C$_5$Me$_4$), 2.47 (m, 2H, C$_6$H$_{11}$). ^{1}H NMR (THF-d$_8$, 22 °C): δ −1.17 (d, J_{Y-H}=3.0 Hz, 2H, C*H*$_2$SiMe$_3$), −0.11 (s, 9H, CH$_2$Si*Me*$_3$), 0.53 (d, J_{P-H}=1.9 Hz, 6H, C$_5$Me$_4$Si*Me*$_2$), 1.10–1.36 (m, 6H, C$_6$H$_{11}$), 1.50–1.90 (m, 3H, C$_6$H$_{11}$), 1.96 (s, 6H, C$_5$Me$_4$), 2.11 (s, 6H, C$_5$Me$_4$), 1.91–2.06 (m, 2H, C$_6$H$_{11}$). ^{13}C NMR (THF-d$_8$, 22°C): δ 4.78 (s, 3C, CH$_2$Si*Me*$_3$), 6.78 (d, 2C, J_{P-C}=9.0 Hz, C$_5$Me$_4$Si*Me*$_2$), 11.86 (s, 2C, C$_5$*Me*$_4$), 15.12 (d, 2C, J_{P-C}=5.6 Hz, C$_5$*Me*$_4$), 27.42 (d, 1C, J_{P-C}=1.8 Hz, *para*-C$_6$H$_{11}$), 28.81 (d, 2C, J_{P-C}=9.5 Hz, *meta*-C$_6$H$_{11}$), 29.83 (dd, 1C, J_{Y-C}=38.8 Hz and J_{P-C}=3.6 Hz, *C*H$_2$SiMe$_3$), 33.64 (dd, 1C, J_{P-C}=20.1 Hz and J_{Y-C}=1.0 Hz, *ipso*-C$_6$H$_{11}$), 40.3 (dd, 2C, J_{P-C}=9.5 Hz and J_{Y-C}=1.2 Hz, *ortho*-C$_6$H$_{11}$), 112.67 (d, 1C, J_{P-C}=15.6 Hz, *ipso*-*C*$_5$Me$_4$), 122.34 (s, 2C, *C*$_5$Me$_4$), 125.07 (s, 2C, *C*$_5$Me$_4$). ^{31}P NMR (THF-d$_8$) at −45°C: −108.60 (d, J_{P-Y}=69.7 Hz); at 22°C: δ −105.30 (d, J_{P-Y}=72.9 Hz). Anal. Calcd for C$_{42}$H$_{80}$P$_2$Si$_4$Y$_2$: C, 53.83; H, 8.60. Found: C, 38.52–44.23; H, 7.76–8.09. The low and poorly reproducible carbon values were probably due to formation of incombustible carbide species, as in the case of other P-containing rare earth complexes.[3,23]

4.2.8. [Me$_2$Si(C$_5$Me$_4$)(μ-PC$_6$H$_{11}$)Yb(CH$_2$SiMe$_3$)]$_2$ (5b). Complex **5b** was isolated as purple crystals (0.158 g, 0.143 mmol, 29% yield) in a manner similar to that for the synthesis of **5a**, by use of Me$_2$Si(C$_5$Me$_4$H)PH(C$_6$H$_{11}$) (0.294 g, 1 mmol) and Yb(CH$_2$SiMe$_3$)(THF)$_3$ (0.579 g, 1 mmol). Informative NMR spectra were not observed because of the influence of the paramagnetic Yb(III) ion.

4.2.9. $[Me_2Si(C_5Me_4)(\mu\text{-}PC_6H_{11})Lu(CH_2SiMe_3)]_2$ (5c). Complex **5c** was isolated as colorless crystals (0.338 g, 0.305 mmol, 61% yield) in a manner similar to that for the synthesis of **5a**, by use of $Me_2Si(C_5Me_4H)PH(C_6H_{11})$ (0.294 g, 1 mmol) and $Lu(CH_2SiMe_3)(THF)_3$ (0.581 g, 1 mmol). ^1H NMR (C_6D_6, 22°C): δ −0.66 (d, J_{H-H}=11.2 Hz, 2H, CH_2SiMe_3), −0.07 (d, J_{H-H}=11.2 Hz, 2H, CH_2SiMe_3), 0.34 (s, 18H, CH_2SiMe_3), 0.78 (s, 6H, $C_5Me_4SiMe_2$), 1.01 (m, 6H, $C_5Me_4SiMe_2$), 1.02 (m, 2H, C_6H_{11}), 1.21 (m, 4H, C_6H_{11}), 1.40 (m, 4H, C_6H_{11}), 1.54 (m, 2H, C_6H_{11}), 1.66 (m, 4H, C_6H_{11}), 1.87 (m, 2H, C_6H_{11}), 2.01 (s, 6H, C_5Me_4), 2.03 (m, 2H, C_6H_{11}), 2.14 (s, 6H, C_5Me_4), 2.21 (s, 6H, C_5Me_4), 2.51 (s, 6H, C_5Me_4), 2.56 (m, 2H, C_6H_{11}). ^1H NMR (THF-d_8, 22°C): δ −1.24 (s, 2H, CH_2SiMe_3), −0.10 (s, 9H, CH_2SiMe_3), 0.56 (d, J_{P-H}=2.2 Hz, 6H, $C_5Me_4SiMe_2$), 1.11–1.33 (m, 6H, C_6H_{11}), 1.50–1.85 (m, 5H, C_6H_{11}), 1.91 (s, 6H, C_5Me_4), 2.13 (s, 6H, C_5Me_4). ^{13}C NMR (THF-d_8, 22°C): δ 4.85 (3C, CH_2SiMe_3), 6.41 (d, 2C, J_{P-C}=9.4 Hz, $C_5Me_4SiMe_2$), 11.70 (s, 2C, C_5Me_4), 15.11 (d, 2C, J_{P-C}=6.2 Hz, C_5Me_4), 27.33 (s, 1C, *para*-C_6H_{11}), 28.71 (d, 2C, J_{P-C}=9.9 Hz, *meta*-C_6H_{11}), 33.80 (d, 1C, J_{P-C}=19.3 Hz, *ipso*-C_6H_{11}), 37.22 (d, 1C, J_{P-C}=5.6 Hz, CH_2SiMe_3), 40.49 (d, 2C, J_{P-C}=10.6 Hz, *ortho*-C_6H_{11}), 111.65 (d, 1C, J_{P-C}=13.7 Hz, *ipso*-C_5Me_4), 122.30 (s, 2C, C_5Me_4), 124.70 (s, 2C, C_5Me_4). ^{31}P NMR (THF-d_8, 22°C): δ −102.85 (s). Anal. Calcd for $C_{42}H_{80}P_2Si_4Lu_2$: C, 45.47; H, 7.27. Found: C, 33.99–34.29; H, 7.02–7.04. The low and poorly reproducible carbon values were probably due to formation of incombustible carbide species, as in the case of other P-containing rare earth complexes.[3,23]

4.2.10. $[Me_2Si(C_5Me_4)(PC_6H_5)Y(\mu\text{-}H)]_2(thf)_3$ (6a). $PhSiH_3$ (0.054 g, 0.500 mmol) was added to a THF solution (10 mL) of $[Me_2Si(C_5Me_4)(PC_6H_5)Y(CH_2SiMe_3)(thf)]_2$ (**4a**) (0.260 g, 0.243 mmol). The reaction mixture was stirred at room temperature for 2 h. After filtration, the solution was concentrated under reduced pressure to yield yellow cubic crystals. After decantation, the crystals were washed with hexane and dried under vacuum to give **6a** (0.172 g, 0.177 mmol, 73% yield). ^1H NMR (THF-d_8) at −45°C: δ 0.18 (s, 3H, $C_5Me_4SiMe_2$), 0.53 (s, 3H, $C_5Me_4SiMe_2$), 0.56 (s, 3H, $C_5Me_4SiMe_2$), 0.60 (d, J_{P-H}=4.4 Hz, 3H, $C_5Me_4SiMe_2$), 1.50 (s, 3H, C_5Me_4), 1.70 (s, 3H, C_5Me_4), 1.89 (s, 3H, C_5Me_4), 1.96 (s, 6H, C_5Me_4), 1.98 (s, 3H, C_5Me_4), 2.14 (s, 3H, C_5Me_4), 2.47 (s, 3H, C_5Me_4), 4.68–4.89 (m, 1H, YH), 5.04–5.24 (m, 1H, YH), 6.57 (t, J_{H-H}=7.4 Hz, 1H, C_6H_5), 6.80 (t, J_{H-H}=7.6 Hz, 2H, C_6H_5), 7.04 (s, 2H, C_6H_5), 7.05 (s, 1H, C_6H_5), 7.26 (t, J_{H-H}=6.8 Hz, 2H, C_6H_5), 7.34 (m, 2H, C_6H_5); at 22°C: δ 0.55 (br s, 12H, $C_5Me_4SiMe_2$), 1.91 (br s, 12H, C_5Me_4), 2.08 (br s, 12H, C_5Me_4), 5.03 (br s, 2H, YH), 6.56, 6.79, 7.00 (br s×3, 6H, C_6H_5), 7.31 (br s, 4H, C_6H_5); at 50°C: δ 0.49 (br s, 12H, $C_5Me_4SiMe_2$), 1.77 (br s, 12H, C_5Me_4), 2.15 (br s, 12H, C_5Me_4), 5.05 (br t, J_{Y-H}=24.4 Hz, 2H, YH), 6.89 (br s, 6H, C_6H_5), 7.32 (t, J_{H-H}=6.6 Hz, 4H, C_6H_5). ^1H NMR (C_5D_5N, 22°C): δ 0.94 (s, 6H, $C_5Me_4SiMe_2$), 1.61 (m, 6H, THF), 1.68 (s, 3H, C_5Me_4), 1.70 (s, 3H, C_5Me_4), 2.14 (s, 3H, C_5Me_4), 2.15 (s, 3H, C_5Me_4), 3.65 (m, 6H, THF), 7.00 (t, J_{H-H}=6.9 Hz, 1H, C_6H_5), 7.16 (t, J_{H-H}=7.2 Hz, 2H, C_6H_5), 7.40 (t, J_{H-H}=6.9 Hz, 2H, C_6H_5). ^{31}P NMR (THF-d_8) at −45°C: δ −97.9 (d, J_{P-Y}=71.2 Hz), −132.9 (d, J_{P-Y}=53.4 Hz); at 22°C: δ −93.6 (br), −131.6 (br); at 50°C: δ −92.5 (br), −130.9 (br). The ^{13}C NMR spectrum of **6a** in THF-d_8 gave very broad signals and was not informative, probably owing to its fluxional property. Anal. Calcd for $C_{42}H_{72}O_3P_2Si_2Y_2$: C, 57.02; H, 7.49. Found: C, 50.45–52.51; H, 7.31–7.51. The low and poorly reproducible carbon values were probably due to formation of incombustible carbide species, as in the case of other P-containing rare earth complexes.[3,23]

4.2.11. $[Me_2Si(C_5Me_4)(PC_6H_5)Yb(\mu\text{-}H)]_2(thf)_3$ (6b). $PhSiH_3$ (0.054 g, 0.500 mmol) was added to a THF solution (10 mL) of $[Me_2Si(C_5Me_4)(PC_6H_5)Yb(CH_2SiMe_3)(thf)]_2$ (**4b**) (0.200 g, 0.183 mmol). The reaction mixture was stirred at room temperature for 2 h. After filtration, the solution was concentrated under reduced pressure to yield dark red crystals. After decantation, the crystals were washed with hexane and dried under vacuum to give **6b** (0.146 g, 0.128 mmol, 70% yield). Informative NMR spectra were not observed because of the influence of the paramagnetic Yb(III) ion.

4.2.12. $[Me_2Si(C_5Me_4)(PC_6H_5)Lu(\mu\text{-}H)]_2(thf)_3$ (6c). $PhSiH_3$ (0.030 g, 0.280 mmol) was added to a THF solution (10 mL) of $[Me_2Si(C_5Me_4)(PC_6H_5)Lu(CH_2SiMe_3)(thf)]_2$ (**4c**) (0.100 g, 0.091 mmol). The reaction mixture was stirred at room temperature for 2 h. After filtration, the solution was concentrated under reduced pressure to yield pale yellow cubic crystals of **6c**. After decantation, the crystals were washed with hexane and dried under vacuum to give $[Me_2Si(C_5Me_4)(PC_6H_5)Lu(\mu\text{-}H)]_2(thf)_2$ (**6c′**, 0.069 g, 0.065 mmol, 71% yield) as pale yellow powder. (The loss of one of the three THF ligands in **6c** to give **6c′** under vacuum was confirmed by ^1H NMR in C_5D_5N. Although Ln-H reacted with C_5D_5N, good integrations for the THF signals and the ligand signals could be obtained. ^1H NMR (C_5D_5N, 22°C): δ 0.93 (s, 6H, $C_5Me_4SiMe_2$), 1.61 (m, 4H, THF), 1.68 (s, 3H, C_5Me_4), 1.70 (s, 3H, C_5Me_4), 2.15 (s, 3H, C_5Me_4), 2.16 (s, 3H, C_5Me_4), 3.65 (m, 4H, THF), 7.00 (t, J_{H-H}=6.9 Hz, 1H, C_6H_5), 7.16 (t, J_{H-H}=7.2 Hz, 2H, C_6H_5), 7.40 (t, J_{H-H}=6.9 Hz, 2H, C_6H_5). ^1H NMR (THF-d_8) at −45°C: δ 0.11 (s, 3H, $C_5Me_4SiMe_2$), 0.52 (d, J_{P-H}=1.6 Hz, 3H, $C_5Me_4SiMe_2$), 0.54 (d, J_{P-H}=1.2 Hz, 3H, $C_5Me_4SiMe_2$), 0.57 (d, J_{P-H}=4.4 Hz, 3H, $C_5Me_4SiMe_2$), 1.46 (s, 3H, C_5Me_4), 1.70 (s, 3H, C_5Me_4), 1.90 (s, 3H, C_5Me_4), 1.98 (s, 3H, C_5Me_4), 2.01 (s, 3H, C_5Me_4), 2.02 (s, 3H, C_5Me_4), 2.13 (s, 3H, C_5Me_4), 2.52 (s, 3H, C_5Me_4), 6.57 (t, J_{H-H}=7.0 Hz, 1H, C_6H_5), 6.82 (t, J_{H-H}=7.4 Hz, 2H, C_6H_5), 7.06 (m, 3H, C_6H_5), 7.25 (t, J_{H-H}=6.8 Hz, 2H, C_6H_5), 7.37 (m, 2H, C_6H_5), 7.72 (m, 1H, LuH), 7.92 (m, 1H, LuH); at 22°C: δ 0.54 (br s, 12H, $C_5Me_4SiMe_2$), 1.84 (br s, 12H, C_5Me_4), 2.10 (br s, 12H, C_5Me_4), 6.42–7.15 (m, 6H, C_6H_5), 7.32 (br s, 4H, C_6H_5), 7.62–8.16 (br m, 2H, LuH); at 50°C: δ 0.46 (br s, 12H, $C_5Me_4SiMe_2$), 1.79 (br s, 12H, C_5Me_4), 2.17 (br s, 12H, C_5Me_4), 6.78 (br s, 2H, C_6H_5), 6.92 (br s, 4H, C_6H_5), 7.32 (t, J_{H-H}=6.8 Hz, 4H, C_6H_5), 7.96 (br s, 2H, LuH). ^{31}P NMR (THF-d_8) at −45°C: δ −92.0 (s), −124.5 (s); at 22°C: δ −88.1 (br s), −122.4 (br s); at 50°C: δ −87.7 (br s), −121.1 (br s). The ^{13}C NMR spectrum of **6c** in THF-d_8 gave very broad signals and was not informative, probably owing to its fluxional property. Anal. Calcd for $C_{46}H_{72}O_2P_2Si_2Lu_2$ (**6c**′): C, 48.42; H, 6.36. Found: C, 44.00–44.77; H, 6.30–6.32. The low and poorly reproducible carbon values were probably due to formation of incombustible carbide species, as in the case of other P-containing rare earth complexes.[3,23]

4.2.13. $[Me_2Si(C_5Me_4)(\mu\text{-}PC_6H_{11})Y(\mu\text{-}H)]_4$ (7). Addition of $PhSiH_3$ (0.030 g, 0.278 mmol) to a benzene suspension (5 mL) of $[Me_2Si(C_5Me_4)(PC_6H_{11})Y(CH_2SiMe_3)]_2$ (5a) (0.150 g, 0.159 mmol) yielded immediately a clear light-yellow solution, which after being left standing at room temperature overnight, gave light-yellow needle-like crystals of **7**·$2C_6H_6$. After filtration the crystals were washed with hexane and dried under vacuum to give yellow powders (0.098 g, 0.064 mmol, 80% yield as **7**). This compound was insoluble in benzene, THF, pyridine, or HMPA. Single crystals suitable X-ray analysis were obtained directly from the reaction mixture.

4.2.14. $[Me_2Si(C_5Me_4)(PC_6H_2^tBu_3\text{-}2,4,6)Y(\mu\text{-}H)(thf)]_2$ (8a). Addition of $PhSiH_3$ (0.048 g, 0.444 mmol) to a benzene solution (5 mL) of $Me_2Si(C_5Me_4)PH(C_6H_2^tBu_3\text{-}2,4,6)Y(CH_2SiMe_3)_2(thf)$ (**1a**) (0.160 g, 0.202 mmol) gave an orange solution, from which orange prism type crystals of **8a**·$2C_6H_6$ were grown within a few hours. After removal of the solvent, the crystals were washed with hexane and dried under vacuum to give **8a** (0.090 g, 0.073 mmol, 72% yield). This compound is insoluble in hexane and benzene, and slightly soluble in THF. ^1H NMR (THF-d_8, 22°C): δ 0.16 (s, 12H, $C_5Me_4SiMe_2$), 1.28 (s, 18H, ^{t}Bu), 1.71 (s, 36H, ^{t}Bu), 2.17 (s, 12H, C_5Me_4), 2.22 (s, 12H, C_5Me_4), 4.97 (t, J_{Y-H}=30.1 Hz, 2H, YH), 7.14 (d, 4H, J_{P-H}=2.1 Hz, C_6H_2). ^{31}P NMR (THF-d_8, 50°C): δ −71.66 Hz (br d, J_{P-Y}=84.2 Hz). Anal. Calcd for $C_{66}H_{112}O_2P_2Si_2Y_2$: C, 64.26; H, 9.15. Found: C, 60.01–60.64; H, 8.82–8.97. The low and poorly reproducible carbon values were probably due to formation of incombustible carbide species, as in the case of other P-containing rare earth complexes.[3,23]

4.2.15. $[Me_2Si(C_5Me_4)(PC_6H_2^tBu_3\text{-}2,4,6)Lu(\mu\text{-}H)(thf)]_2$ (8b). $PhSiH_3$ (0.119 g, 1.1 mmol) was added to a benzene solution (10 mL) of $Me_2Si(C_5Me_4)PH(C_6H_2^tBu_3\text{-}2,4,6)Lu(CH_2SiMe_3)_2(thf)$ (**1b**) (0.439 g, 0.50 mmol). The resulting bright yellow solution was stirred at room temperature for 14 h to precipitate fine yellow crystalline powders. After filtration the solid was washed with hexane and vacuum-dried to give **8b** (0.239 g, 0.170 mmol, 68% yield). Leaving the reaction mixture to stand at room temperature for a few days afforded single crystals of **8b**·$2C_6H_6$. This compound is insoluble in hexane and benzene, and slightly soluble in THF. ^1H NMR (THF-d_8, 22°C): δ 0.08 (s, 6H, $C_5Me_4SiMe_2$), 0.22 (s, 6H, $C_5Me_4SiMe_2$), 1.29 (s, 18H, ^{t}Bu), 1.70–1.80 (br m, 36H, ^{t}Bu; overlap with the signals of THF solvent), 2.11 (s, 6H, C_5Me_4), 2.17 (s, 6H, C_5Me_4), 2.25 (s, 6H, C_5Me_4), 2.29 (s, 6H, C_5Me_4), 7.16 (s, 4H, C_6H_2), 8.88 (br m, 2H, LuH). ^1H NMR (C_5D_5N, 22°C): δ 0.56 (s, 6H, $C_5Me_4SiMe_2$), 1.45 (s, 9H, ^{t}Bu), 1.55 (s, 6H, C_5Me_4), 1.60 (m, 4H, THF), 1.73 (s, 6H, C_5Me_4), 2.15 (s, 18H, ^{t}Bu), 3.64 (m, 4H, THF), 7.55 (s, 2H, C_6H_2), 9.94 (s, 1H, LuH). (**8b** reacted slowly with C_5D_5N at room temperature). ^{31}P NMR (THF-d_8, 50°C): δ −60.4(s).

4.3. A typical procedure for the polymerization of ethylene

In the glovebox, **4a** (27 mg, 0.025 mmol), a magnetic stirrer bar, and toluene (30 mL) were placed in a 100 mL three-neck flask. The flask was taken outside, set in a water bath (25°C), and then connected to a Schlenk line, a well-purged ethylene line, and a mercury-sealed one-way stopper. Introduction of ethylene resulted in immediate formation (precipitation) of polyethylene. The mixture was stirred for 30 min, during which a slightly positive ethylene pressure was maintained by the stopper. MeOH (30 mL) was added to stop the reaction. The resultant mixture was poured into 600 mL of MeOH in a 1 L beaker and then stirred to further precipitate the polymer product. After filtration, the polymer product was dried under vacuum in an oven (80°C) overnight, yielding 2.55 g of polyethylene (entry 3, Table 7). The molecular weight (against polystyrene standard) and the molecular weight distribution of the polymer were measured by gel permeation chromatography (GPC) at 135°C using *ortho*-dichlorobenzene as an eluent.

4.4. A typical procedure for the hydrosilylation of olefins

In the glovebox, addition of $PhSiH_3$ (54 mg, 0.5 mmol) to **5c** (11 mg, 0.01 mmol) in C_6D_6 (0.5 mL) in a J. Young-valve NMR tube yielded a homogeneous bright yellow solution, to which 1-decene (56 mg, 0.4 mmol) was then added (entry 6, Table 8). The reaction mixture was monitored by the ^1H NMR. A complete conversion of 1-decene into 1-(phenylsilyl)decane was achieved in 10 min, during which light-yellow precipitates was also observed (in the case of **5a**, the hydride species **7** was isolated). The volatiles were removed under reduced pressure, and the product was extracted with hexane. It was confirmed by GC-MS and ^1H NMR that 1-(phenylsilyl)decane was the only hydrosilylation product. The spectral data for the hydrosilylation products are given below.

4.4.1. 1-(Phenylsilyl)decane.[15a,19h] ^1H NMR (C_6D_6, 22°C): δ 0.75–0.93 (m, 5H), 1.13–1.45 (m, 16H), 4.47 (t, J=3.6 Hz, 2H), 7.13 (m, 3H), 7.47 (m, 2H). GC-MS: *m/z*=248 (M^+).

4.4.2. 1-(Phenylsilyl)hexane.[19f] ^1H NMR (C_6D_6, 22°C): δ 0.74–0.85 (m, 5H), 1.06–1.45 (m, 8H), 4.45 (t, J=3.8 Hz, 2H), 7.11 (m, 3H), 7.46 (m, 2H). GC-MS: *m/z*=192 (M^+).

4.4.3. (Phenylsilyl)methylcyclopentane.[19f,g] ^1H NMR (C_6D_6, 22°C): δ 0.70–1.90 (m, 9H), 4.47 (t, J=3.8 Hz, 2H), 7.14 (m, 3H), 7.48 (m, 2H). GC-MS: *m/z*=190 (M^+).

4.4.4. 4-[2-(Phenylsilyl)ethyl]cyclohex-1-ene.[15a,19h] ^1H NMR (C_6D_6, 22°C): δ 0.73–0.80 (m, 2H), 0.99–1.12 (m, 1H), 1.25–1.58 (m, 5H), 1.87–1.93 (m, 3H), 4.45 (t, J=3.6 Hz, 2H), 5.62 (m, 2H), 7.14 (m, 3H), 7.48 (m, 2H).

4.4.5. 1-Phenyl-1-(phenylsilyl)ethane.[15a,19f] ^1H NMR (C_6D_6, 22°C) δ?1.30 (d, J=7.5 Hz, 3H), 2.31–2.44 (m, 1H), 4.50 (m, 2H), 6.95–7.42 (m, 10H). GC-MS: *m/z*=212 (M^+).

4.4.6. 1-Phenyl-2-(phenylsilyl)ethane.[15a,19h] ^1H NMR

Table 10. Summary of crystallographic data

Compound	**1b**	**3**·0.5C_6H_{14}	**4b**	**4c**	**5a**	**5b**	**5c**	**6a**	**6b**	**6c**	**7**·2C_6H_6	**8a**·2C_6H_6	**8b**·2C_6H_6
Formula	$C_{41}H_{78}POSi_3Lu$	$C_{40}H_{69}PO_2SiY$	$C_{42}H_{68}P_2Si_4Yb_2$	$C_{42}H_{68}P_2Si_4Lu_2$	$C_{42}H_{80}P_2Si_4Y_2$	$C_{42}H_{80}P_2Si_4Yb_2$	$C_{42}H_{80}P_2Si_4Lu_2$	$C_{46}H_{72}P_2O_3Si_2Y_2$	$C_{46}H_{72}P_2O_3Si_2Yb_2$	$C_{46}H_{72}P_2O_3Si_2Lu_2$	$C_{46}H_{72}P_2Si_2Y_2$	$C_{78}H_{124}P_2O_2Si_2Y_2$	$C_{78}H_{124}P_2O_2Si_2Lu_2$
Formula weight	877.24	729.92	1093.34	1097.20	937.18	1105.44	1109.30	968.98	1137.24	1141.10	920.98	1389.72	1561.84
Cryst syst	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	*Cc*(No.9)	$P2_{1/n}$ (No.14)	*P*-1 (No.2)	*P*-1 (No.2)	*C*2/*c* (No.15)	*P*-1 (No.2)	*P*-1 (No.2)	*C*2/*c* (No.15)	*C*2/*c* (No.15)	*C*2/*c* (No.15)	*P*-1 (No.2)	*P*-1 (No.2)	*P*-1 (No.2)
a (Å)	10.3585(13)	14.988(8)	10.27(2)	10.241(2)	23.745(5)	10.356(2)	10.352(1)	39.404(16)	39.488(5)	39.466(6)	11.125(5)	10.885(2)	10.8375(11)
b (Å)	27.917(4)	14.665(8)	11.49(2)	11.506(2)	10.899(2)	12.475(2)	12.470(2)	14.688(6)	14.719(2)	14.709(2)	14.341(7)	11.556(2)	11.5241(12)
c (Å)	16.382(2)	19.617(11)	12.55(3)	12.548(2)	21.690(5)	12.734(2)	12.768(2)	19.859(8)	19.722(3)	19.692(3)	16.213(8)	16.516(3)	16.4205(16)
α (deg.)			92.58(3)	92.606(2)		102.135(3)	102.123(2)				101.755(10)	87.677(3)	87.391(2)
β (deg.)	94.019(2)	103.974(12)	113.80(3)	113.736(2)	117.570(4)	109.624(3)	109.727(2)	119.785(7)	119.888(2)	119.886(3)	103.077(10)	79.742(3)	80.036(2)
γ (deg.)			112.43(3)	112.326(2)		113.744(3)	113.618(2)				103.067(10)	74.444(3)	74.564(2)
V (Å^3)	4725.7(10)	4184(4)	1217(5)	1217.2(3)	4976.1(18)	1299.5(4)	1302.7(3)	9975(7)	9939(2)	9911(3)	2364(2)	1969.5(5)	1947.0(3)
Z	4	4	1	1	4	1	1	8	8	8	2	1	1
D_c (g/cm^3)	1.233	1.159	1.492	1.497	1.251	1.413	1.414	1.290	1.520	1.529	1.294	1.172	1.332
μ (cm$-^1$)	22.26	14.90	40.09	42.22	25.07	37.55	39.45	24.63	38.89	41.10	25.90	15.78	26.34
No. of reflns collcd	17978	31545	8162	9899	18713	10335	10293	37187	30640	30080	17377	12181	14999
No. of reflns with $I_o>2\sigma(I_o)$	9078	11998	5539	5779	6632	7047	7030	13337	9963	9797	12072	7699	9771
No. of variables	480	406	235	235	238	238	238	516	524	516	446	407	407
R_{int}	0.0322	0.1626	0.0360	0.0303	0.1489	0.0247	0.0258	0.1427	0.0578	0.0991	0.1211	0.0335	0.0288
GOF	0.915	0.811	0.969	0.999	0.676	0.948	1.000	0.819	1.127	0.599	0.691	1.090	0.918
R	0.0312	0.0552	0.0402	0.0306	0.0558	0.0390	0.0334	0.0573	0.0363	0.0377	0.0756	0.0460	0.0314
R_w	0.0529	0.0748	0.1137	0.0495	0.0590	0.0488	0.0652	0.0507	0.0736	0.0448	0.1449	0.0781	0.0624
R (all data)	0.0434	0.2703	0.0563	0.0445	0.2020	0.0610	0.0464	0.2557	0.0861	0.1224	0.2900	0.0831	0.0407
R_w (all data)	0.0549	0.0891	0.1186	0.0516	0.0742	0.0514	0.0688	0.0633	0.0785	0.0578	0.1894	0.0819	0.0641

(C_6D_6, 22 °C): δ 1.03–1.11 (m, 2H), 2.55–2.61 (m, 2H), 4.41 (t, J=3.6 Hz, 2H), 6.95–7.42 (m, 10H). GC-MS: m/z=212 (M^+).

4.4.6. 1-Phenyl-3-(phenylsilyl)propane.[24] ^{1}H NMR (C_6D_6, 22°C): δ 0.70–0.79 (m, 2H), 1.55–1.68 (q, J=7.6 Hz, 2H), 2.43 (t, J=7.6 Hz, 2H), 4.42 (t, J=3.8 Hz, 2H), 6.95–7.14 (m, 6H), 7.36–7.43 (m, 4H).

4.5. X-Ray crystallographic studies

Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in the glove box under a microscope mounted on the glovebox window, and were sealed in thin-walled glass capillaries. Data collections were performed at 20°C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo Kα radiation (λ=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. The structures were solved by using SHELXTL program. Refinement was performed on F^2 anisotropically for all the non-hydrogen atoms by the full-matrix least-squares method. All hydrido ligands and the three hydrogen atoms of the C9 methyl group in **7** were located by difference Fourier synthesis and their coordinates and isotropic parameters were refined. Other hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Crystal data and processing parameters are summarized in Table 10. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 210071-210083. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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20. For representative examples, see: Me$_2$Si(C$_5$Me$_4$)(CH$_2$N^{t}Bu)Y(CH$_2$SiMe$_3$)(thf): rt, 1 h, 93% isolated yield;[5b] Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)Y(CH$_2$SiMe$_3$)(thf): rt, 7 h, 80%, a 96:4 mixture of 1-(phenylsilyl)decane and 2-(phenylsilyl)decane;[5b] (C$_5$Me$_5$)$_2$LuMe(thf): rt, 1 h, 98% isolated yield;[19c] (C$_5$Me$_5$)$_2$YCH(SiMe$_3$)$_2$: rt, 14 h, 95% isolated yield;[19i] Me$_2$Si(C$_5$Me$_4$)$_2$YCH(SiMe$_3$)$_2$: 84%, a 31:1 mixture of 1-(phenylsilyl)decane and 2-(phenylsilyl)decane;[19i] (C$_5$Me$_5$)$_2$NdCH(SiMe$_3$)$_2$: 80°C, 2 days, 53% GC yield.[19j].
21. The in situ generated terminal hydride species might probably adopt a dimeric structure through phosphido-bridges, as in their alkyl precursor such as **4a**–**c** and **5a**–**c**.
22. Usually, the branched silane product PhCH(CH$_3$)SiH$_2$Ph is preferred to the linear one PhCH$_2$CH$_2$SiH$_2$Ph in styrene hydrosilylation (cf. Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)Y(CH$_2$SiMe$_3$)(thf) (7.3:1),[5b] (C$_5$Me$_5$)$_2$NdCH(SiMe$_3$)$_2$ (72:16),[19j] [(C$_5$Me$_5$)Sm(μ-H)$_2$]$_6$(μ-H)K(thf)$_2$]$_3$ (93:7),[15b] and Me$_2$Si(C$_5$Me$_4$)$_2$SmCH(SiMe$_3$)$_2$ (>99:1)[19g]), and larger metals or more open ligand systems afford higher proportion of the branched regioisomer, possibly because of easier metal-phenyl π-interactions.[5b,19g] The higher proportion of the linear silane product PhCH$_2$CH$_2$SiH$_2$Ph in the case of **5c** (46%) than those reported for other catalysts might probably be due to the steric hindrance caused by the phosphido bridges.e[21].
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