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Introduction

Since Lappert and co-workers discovered the first heterobimetallic Ln/Al alkyl species,^{1*a*} heterobimetallic Ln/Al alkyl complexes have emerged as an area of intensive research.^{1*b*,*c*} On the one hand, alkylaluminate ligands, acting as disguised alkyl ligands, can supplement more traditional rare-earthmetal alkyl complexes. On the other hand, these heterobimetallic Ln/Al alkyl complexes are highly likely to be potential precursors of rare-earth-metal alkylidene, alkylidyne, or carbide complexes. For instance, it has been confirmed that the methyl group can be transformed into $CH_2^{2^-}$, CH_3^- , and C^{4^-} moieties through C–H bond activation. Efforts in preparing rare-earth-metal methylidene complexes include simple

Phosphaguanidinate yttrium carbene, carbyne and carbide complexes: three distinct C1 functionalities[†]

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The phosphaguanidinate rare-earth-metal bis(aminobenzyl) complexes [(Ph_2P)C(NC₆H₃ⁱPr₂-2,6)₂]Ln(CH₂C₆H₄ NMe_2-o_2 (Ln = Y(1-Y) and Lu(1-Lu)) were synthesized by the protonolysis of (Ph₂P)[C(NHR)(NR)] (R = $2,6-(^{i}Pr)_2C_6H_3)$ with $Ln(CH_2C_6H_4NMe_2-o)_3$ (Ln = Y and Lu). Interestingly, the ring-opening rearrangement product $[o-Me_2NC_6H_4CH_2C(NC_6H_3^{i}Pr_2-2,6)_2]Lu(CH_2C_6H_4NMe_2-o)[O(CH_2)_4PPh_2]$ (2) was obtained when the acid-base reaction was carried out in THF solution at 60 °C for 36 h. Additionally, the trinuclear homometallic yttrium multimethyl/methylidene complex $\{[(Ph_2P)C(NC_6H_3^{iP}Pr_2-2,6)_2]Y(\mu-1)\}$ Me)}₃(μ_3 -Me)(μ_3 -CH₂) (**3**) was synthesized by the treatment of **1-Y** with AlMe₃ (2 equiv.) in toluene at ambient temperature in a good yield. However, the binuclear lutetium methyl complex {[(Ph2P)C $(NC_6H_3^{i}Pr_2-2,6)_2]Lu(\mu-Me)Me\}_2$ (4) can be generated through the same synthetic method. Likewise, the heterobimetallic Ln-Al complexes [(Ph₂P)C(NC₆H₃ⁱPr₂-2,6)₂]Ln(Me)(AlMe₄) (Ln = Y(**6-Y**) and Lu(**6-Lu**)) were afforded from the treatment of complex 1 with $AlMe_3$ (3 equiv.) at ambient temperature for 6 h. Interestingly, upon extending the reaction time of the treatment of 1-Y with three equivalents of AlMe₃, the phosphaguanidinate binuclear yttrium carbyne complex $[(Ph_2P)C(NC_6H_3^iPr_2-2,6)_2]_2Y_2(\mu_4-CH)(\mu-Me)$ (AlMe₃)₂ (7) and the yttrium carbide complex [(Ph₂P)C(NC₆H₃ⁱPr₂-2,6)₂]₂Y₂(μ ₅-C)(AlMe₂)(μ -Me)(AlMe₃)₂ (8) were isolated via multiple C-H bond activation reactions. Furthermore, the heterobimetallic Y-Al complex [(Ph_2P)C($NC_6H_3^iPr_2-2,6$)₂]Y(AlMe₄)₂ (**9**) was also obtained from the treatment of **1-Y** with four equivalents of AlMez.

> methylene bridged species (A and B)^{2,3} and AlMe₃-supported systems (C).4,5 Similarly, rare-earth-metal methylidyne complexes also exist in different bonding modes: simple methine bridged species $(\mathbf{D})^6$ and AlMe₃-supported mononuclear, binuclear, and cluster species (E-G).⁷⁻⁹ Despite these recent achievements, the chemistry of rare-earth-metal carbide complexes is still in its infancy, mainly manifested as multinuclear clusters. This is because the high charge densities of the hard carbon functionalities C⁴⁻ drive the formation of clusters with relatively hard rare-earth-metal cations (M-Q).^{8,9b,10} For example, Anwander and his co-workers found that PMe₃induced alkylaluminate cleavage of $La{Al(CH_3)_4}_3$ yields a cluster containing methylene, methine, and carbide moieties.^{9b} Likewise, Mitzel et al. verified that the action of TMTAC (1,3,5-trimethyl-1,3,5-triazacyclohexane) $Ln{Al(CH_3)_4}_3$ (Ln = Y and Sm) leads to multiple methyl degradations, producing complex aggregates containing methylene, methine, and carbide units.¹⁰ Our laboratory has also isolated guanidinate binuclear yttrium carbide derivatives through C-H activation of the μ_4 -CH₃⁻ moiety.⁸ These results suggest that the use of appropriate ancillary ligands is equally crucial as they provide suitable steric protection and



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electronic support for the metal center, having a significant impact on the characterization of heterobimetallic Ln/Al complexes and their derivatives (Scheme 1).

It is widely known that the development of rare-earth-metal complexes with non-Cp ligands (such as amidinate and guanidinate)¹¹ is due to their unique reactivity compared with analogues having Cp ligands, as well as the characteristics of adjustable steric and electronic effects, which can control the stability and reactivity of the complexes.¹² However, studies on phosphaguanidinate rare-earth-metal complexes are relatively scarce,¹³ although phosphaguanidines were originally reported in the 1980s by Schmidt and his co-workers.¹⁴ In this work, the monoanionic phosphaguanidinate ligand was used in the formation of Ln/Al alkyl complexes to expand our research. This paper provides a comprehensive description of the synthetic and structural chemistry of heterobimetallic Ln/Al complexes with the phosphaguanidinate ligand. The feasible reaction pathways for obtaining rare-earth-metal carbene, carbyne, and carbide complexes that contain highly reactive $\{Ln-(Me)_r-Me\}$ Al} heterobimetallic linkages through C-H bond activation will be described.

Results and discussion

Synthesis and characterization of phosphaguanidinate rareearth-metal bis(aminobenzyl) complexes

The process for preparing phosphaguanidinate rare-earthmetal bis(aminobenzyl) complexes is shown in Scheme 2. A convenient protonolysis method was used to synthesize the complexes $[(Ph_2P)C(NC_6H_3^{i}Pr_2-2,6)_2]Ln(CH_2C_6H_4NMe_2-o)_2$ (Ln = Y(1-Y, 83%) and Lu(1-Lu, 78%)) in solutions of THF or toluene. During this process, CH₃C₆H₄NMe₂-o was produced.

In the ¹H NMR spectra (in C_6D_6) of complexes 1 at room temperature, the methylene protons of $CH_2C_6H_4NMe_2$ -*o* that are bound to the metal ions show up as singlets at δ =



Scheme 1 Classes of rare-earth-metal methylidene, methylidyne and carbide complexes.



Scheme 2 The syntheses of complexes $[(Ph_2P)C(NC_6H_3^{i}Pr_2-2,6)_2]Ln$ $(CH_2C_6H_4NMe_2-o)_2$ (Ln = Y(1-Y) and Lu(1-Lu)) and $[o-Me_2NC_6H_4CH_2C$ $(NC_6H_3^{i}Pr_2-2,6)_2]Lu(o-CH_2C_6H_4NMe_2)[O(CH_2)_4PPh_2]$ (2).

1.80 ppm for complex **1-Y** and at 1.75 ppm for complex **1-Lu**. The resonances of the N*Me*₂ groups appear as broad singlets at $\delta = 2.29$ ppm for **1-Y** and at 2.27 ppm for complex **1-Lu**, respectively. The methine protons display a multiplet signal at $\delta = 3.65$ ppm for complex **1-Y** and at 3.74 ppm for complex **1-Lu**. The methyl protons of the isopropyl groups exhibit two groups of doublets at $\delta = 1.29$ and 1.31 ppm ($J_{\text{H-H}} = 4$ Hz) for **1-Y** and at $\delta = 1.28$ and 1.35 ppm ($J_{\text{H-H}} = 4$ Hz) for complex **1-Lu**. In the ¹³C{¹H}</sup> NMR spectrum of complex **1-Y**, the resonance of the methylene carbon in CH₂C₆H₄NMe₂-*o* results in a doublet at $\delta = 49.4$ ppm ($J_{\text{Y-C}} = 32$ Hz). The signals at $\delta = 6.1$ ppm (**1-Y**) and 7.3 ppm (**1-Lu**) in the ³¹P{¹H} NMR spectra can be attributed to their corresponding phosphorus atoms in the phosphaguanidinate ligand.

Complexes 1 are stable under an inert atmosphere at room temperature and are slightly soluble in hexane. They dissolve easily in THF and aromatic solvents. Pale yellow single crystals of complexes 1 were obtained by growing them from concentrated toluene/n-hexane solutions at -35 °C. The solidstate molecular structures of complexes 1 were further determined through single-crystal X-ray diffraction analysis, confirming the distorted-octahedral geometry of those core structures as shown in Fig. 1. Selected bond distances and angles are presented in Table 1. The average bond lengths of Ln-N_{ligand} (average for Y: 2.439(2) Å; average for Lu: 2.392(4) Å) are longer than those found in amidinate rare-earth-metal complexes $[PhC(NC_6H_3^{\dagger}Pr_2-2,6)_2]Ln(CH_2C_6H_4NMe_2-0)_2$ (average for Y: 2.373(3) Å; average for Lu: 2.349(5) Å), [o-Me₂NC₆H₄CH₂C $(NC_6H_3^{i}Pr_2-2,6)_2$]Ln $(CH_2C_6H_4NMe_2-o)_2$ (average for Y: 2.369(5)) Å; average for Lu: 2.325(4) Å)¹⁵ and guanidinate rareearth-metal complexes [(PhCH₂)₂C(NC₆H₃ⁱPr₂-2,6)₂]Ln $(CH_2C_6H_4NMe_2 - o)_2$ (average for Y: 2.358(3) Å; average for Lu: 2.318(3) Å).¹⁶ In contrast, the average distances of Ln–C bonds for 1-Y (2.438(3) Å) and 1-Lu (2.388(5) Å) are shorter than the corresponding bond lengths in amidinate and guanidinate complexes. Therefore, compared with amidinate and guanidi-



Fig. 1 Molecular structures of complexes **1-Y** (left) and **1-Lu** (right) with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity.

Table 1 Selected bond lengths and angles of complexes 1

	1-Y	1-Lu		
Bond lengths (Å)				
Ln-N1	2.524(2)	2.487(4)		
Ln-N2	2.607(2)	2.559(4)		
Ln-N3	2.403(2)	2.358(4)		
Ln-N4	2.475(2)	2.427(4)		
Ln-C2	2.441(3)	2.381(5)		
Ln-C11	2.436(3)	2.396(5)		
Bond angles (°)				
N1-Ln-C2	68.47(8)	68.39(15)		
N1-Ln-N2	117.76(7)	119.28(14)		
N1-Ln-C11	84.57(9)	81.93(16)		
N2-Ln-C11	67.32(8)	69.21(17)		
N2-Ln-C2	81.04(8)	85.23(17)		
C2-Ln-C11	121.88(10)	124.08(19)		

nate, the interaction force between phosphaguanidinate and rare-earth metals is weaker due to the difference in steric and electronic effects.

Surprisingly, when the reaction of $Lu(o-CH_2C_6H_4NMe_2)_3$ with $(Ph_2P)[C(NR)(NHR)]$ (R = 2,6-(¹Pr)₂C₆H₃) was carried out at 60 °C in THF for 36 hours through a tandem protonolysis-activation reaction, the unexpected ring-opening rearrangement product [o-Me₂NC₆H₄CH₂C(NC₆H₃¹Pr₂-2,6)₂]Lu(CH₂C₆H₄NMe₂o [O(CH₂)₄PPh₂] (2) was obtained in an excellent yield (90%), accompanied by the generation of CH₃C₆H₄NMe₂-o, indicating that the C–P σ -bond of the ligand was cleaved. A few examples of cyclopentadienyl butoxide rare-earth-metal complexes have been obtained by the THF ring-opening insertion into Ln-P bonds,¹⁷ and only three non-Cp analogues have been reported to date.¹⁸ In the ¹H NMR spectrum (in C₆D₆) of complex 2, four multiplet peaks at δ = 4.04, 2.31, 1.98, and 1.78 ppm are presumed to be the CH_2 signals of the terminal $O(CH_2)_4PPh_2$ ligand. The resonance of the Lu-bonded aminobenzyl shows two singlets at δ = 1.47 ppm for CH₂ and 2.88 ppm for NMe₂ (ESI Fig. S7[†]). The ${}^{31}P{}^{1}H$ NMR spectrum of 2 shows a singlet at $\delta = -16.9$ ppm for the phosphaguanidinate ligand.

Complex 2 was also characterized by single-crystal X-ray diffraction analysis. This confirmed that complex 2 has a monometallic structure. The molecular structure profile of

complex 2 is shown in Fig. 2. The bond distances of Lu–C (2.476(5) Å) and Lu–N_{aminobenzyl} (2.535(4) Å) are longer than the corresponding values found in complex **1-Lu** (Ln–C: 2.388(5) Å and Lu–N: 2.523(4) Å). This is because the latter has less steric hindrance and the oxygen atoms have a stronger electron-donating ability. The O(CH₂)₄PPh₂ group coordinates to the lutetium atom in a terminal bonding mode. The bond length of Lu–O(2) (2.044(3) Å) is shorter than those found in $\{[(PhCH_2)_2NC(NC_6H_3^{i}Pr_2-2,6)_2]Lu(Me)[\mu-O(CH_2)_4PPh_2]\}_2$ (2.194(5) and 2.191(5) Å).^{18c} This may be due to the difference in coordination patterns of the O(CH₂)₄PPh₂ group.

Synthesis and structural characterization of the yttrium carbene, carbyne and carbide complexes with a phosphaguanidinate ligand

Based on the previous reaction results of amidinate rare-earthmetal bis-aminobenzyl complexes with AlMe₃ in our group,^{3d} we were able to obtain a series of rare-earth methyl complexes with unique structures and their derivatives by precisely controlling the quantity of methylaluminum. For example, the homometallic trinuclear methyl/methylidene complex {[[Ph₂P] $C(NC_6H_3^{i}Pr_2-2,6)_2$]Y(μ -Me)}₃(μ_3 -Me)(μ_3 -CH₂) (3) was obtained in a good yield when complex **1-Y** was treated with two equivalents of AlMe₃ in toluene at room temperature. Interestingly, when a similar synthetic method was used for the reaction of complex **1-Lu** with AlMe₃ (2 equiv.), the binuclear lutetium methyl complex {[[Ph₂P)C(NC₆H₃ⁱPr₂-2,6)₂]Lu(μ -Me)Me}₂ (4) was isolated instead of the carbene analogues (Scheme 3). This is mainly due to the smaller radius of Lu³⁺ than that of Y^{3+, 19}



Fig. 2 Molecular structure of complex 2 with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Lu(1)–N(1) 2.299(4), Lu(1)–N(2) 2.347(3), Lu (1)–N(4) 2.535(4), Lu(1)–O(2) 2.044(3), Lu(1)–O(1) 2.316(3), and Lu(1)–C (51) 2.476(5); N(1)–Lu(1)–O(2) 107.70(13), N(2)–Lu(1)–O(2) 101.95(13), N(1)–Lu(1)–C(51) 95.68(15), N(2)–Lu(1)–C(51) 95.07(15), N(1)–Lu(1)–O(1) 88.49(12), and N(2)–Lu(1)–O(1) 146.07(12).



which enables the phosphaguanidinate lutetium complex to stabilize in a bimetallic methylated state, whereas the Y analogue tends to transform further into the trinuclear carbene complex. Even when the reaction temperature was increased to 100 °C, the lutetium carbene complex was not detected by ¹³C DEPT-135 NMR spectroscopy. We only obtained the mixed amidinate/phosphaguanidinate lutetium methyl complex $[(Ph_2P)(NC_6H_3^{i}Pr_2-2,6)_2][(Me)C(NC_6H_3^{i}Pr_2-2,6)_2]Lu(Me)$ (5) through the C–P bond cleavage of the phosphaguanidinate ligand. Complexes 3 and 4 are slightly soluble in hexane but readily dissolve in THF and aromatic solvents.

In the ¹H NMR spectrum of complex 3, μ_3 -Me and μ_2 -Me protons appear as two broad singlets at $\delta = 0.90$ ppm and 1.05 ppm, respectively. The quartet signal at $\delta = 2.01$ (J = 4 Hz), which corresponds to two protons according to integration, and a relatively downward doublet signal at $\delta = 109.8$ ($J_{\rm Y-C} = 23$ Hz) can clearly confirm the formation of a methylidene unit based on a comprehensive analysis of the ¹³C{¹H}, ¹³C DEPT-135, and heteronuclear multiple quantum coherence (HMQC) NMR spectra (ESI Fig. S10–13†). The signals at $\delta = 47.5$ ppm and 36.5 ($J_{\rm Y-C} = 22$ Hz) ppm in the ¹³C{¹H} NMR spectra can be attributed to the carbon atoms from the μ_3 -Me and μ_2 -Me moieties respectively, and the signal at $\delta = 1.4$ ppm in the ³¹P{¹H} NMR spectrum can be assigned.

In the ¹H NMR spectrum of complex **4**, we can only observe one singlet for the Lu–Me group at $\delta = 0.82$ ppm due to the rapid exchange between μ_2 -Me and the terminal methyl in solvents at room temperature. Additionally, the singlet at $\delta =$ 43.2 ppm in the ¹³C{¹H} NMR spectrum can be assigned to the carbon atoms of these moieties. The ³¹P{¹H} NMR spectrum of complex **4** shows a singlet at $\delta = -1.3$ ppm. The NMR spectra are consistent with the structure of complex **4**, which is also verified by X-ray structure analysis (Fig. 3). The Lu atom is sur-



Fig. 3 Molecular structure of complex 4 with thermal ellipsoids at 30% probability except for the $2,6-i^{i}Pr)_{2}C_{6}H_{3}$ groups and benzyl groups in the guanidinate ligand. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Lu(1)–Lu(1A) 3.3824(5), Lu (1)–N(1) 2.284(4), Lu(1)–N(2) 2.290(4), Lu(1)–C(1) 2.441(6), Lu(1)–C(1A) 2.428(6), and Lu(1)–C(2) 2.297(6); N(1)–Lu(1)–N(2) 58.58(14), N(1)–Lu(1)–C(1) 141.64(19), N(1)–Lu(1)–C(2) 109.12(19), N(2)–Lu(1)–C(1) 93.35(17), N(2)–Lu(1)–C(2) 111.70(18), C(1)–Lu(1)–C(2) 105.4(2), and C(1A)–Lu(1)–C (2) 110.7(2).

rounded by two nitrogen atoms from the phosphaguanidinate ligand and three carbon atoms from methyl units, and the core of complex 4 adopts a distorted trigonal bipyramidal geometry. The bond length of the terminal Lu–Me (2.297(6) Å) is shorter than the bond lengths in (Tp^{*(Bu,Me)*}LuMe (CH₂SiMe₃) (2.343(2) Å)²⁰ and (Tp^{*(Bu,Me)*}LuMe₂ (2.369(3) Å).²¹ The average distance of the bridged Lu–Me (2.434(6) Å) is close to that of the complex [(η^5 -C₅H₄SiEt₃)₂YMe]₂ (2.523(9) Å) after taking into consideration the difference between metal ionic radii.²²

In the ¹H NMR spectrum (in C₆D₆) of complex 5 at room temperature, the Lu-bonded methyl group shows a singlet at δ = 0.36 ppm, which clearly shifts to a higher field compared with complex 4. The ³¹P{¹H} NMR spectrum of complex 5 shows a singlet at δ = 5.3 ppm. A single crystal of complex 5 could be obtained from concentrated toluene/*n*-hexane solutions, crystallizing in the monoclinic space group *P*2₁/*c* (Fig. 4).



Fig. 4 Molecular structure of complex **5** with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Lu(1)–N(1) 2.305(3), Lu(1)–N(2) 2.316(3), Lu (1)–N(3) 2.244(3), Lu(1)–N(4) 2.308(3), Lu(1)–C(1) 2.308(4), C(39)–C(40) 1.501(5), and C(2)–P(1) 1.878(4); N(1)–Lu(1)–C(1) 93.43(15), N(2)–Lu(1)–C (1) 127.61(16), N(3)–Lu(1)–C(1) 107.38(16), N(4)–Lu(1)–C(1) 102.68(15), N(1)–Lu(1)–N(2) 57.84(11), and N(3)–Lu(1)–N(4) 59.17(11).

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The Lu atom is surrounded by four nitrogen atoms from the phosphaguanidinate and amidinate ligands and one carbon atom from the methyl group, and the core of complex 5 has a distorted square pyramidal geometry. The Lu–Me bond length (2.308(4) Å) is slightly longer than that in complex 4 (2.297(6) Å), but it is significantly shorter than that in the complex [(PhCH₂)₂C(NC₆H₃ⁱPr₂-2,6)₂]Lu(CH₂C₆H₄NMe₂-*o*)(Me) (THF) (2.369(4) Å).^{18c}

As we are aware, the degree of alkylation in the resulting heterobimetallic complexes is highly dependent on the amount of alkylaluminum reagent in the reaction mixture as well as the steric/electronic characteristics of the anionic ligands. As shown in Scheme 4, when three equivalents of AlMe₃ were used to react with phosphaguanidinate rare-earthmetal bis(aminobenzyl) complexes, the heterobimetallic methyl/tetramethylaluminate complexes [(Ph₂P)C(NC₆H₃ⁱPr₂- $2,6)_2$ Ln(Me)(AlMe₄) (Ln = Y(6-Y) and Lu(6-Lu)) were obtained in good yields. The ¹H NMR spectrum of complex 6-Lu is consistent with its structure, in which two signals are observed for the metal-bound methyl protons, one broad singlet at δ = 0.16 ppm corresponding to twelve protons, and one singlet at δ = 0.29 ppm with an integral intensity of three protons. Only one signal is observed and is assigned to AlMe₄, likely due to the rapid exchange between the bridged and terminal methyl groups in C_6D_6 at room temperature.^{4a} In the ³¹P{¹H} NMR spectrum of complex 6-Lu, a singlet appears at $\delta = -0.6$ ppm.



Unexpectedly, when the same reaction was carried out at room temperature for 24 h, the binuclear phosphaguanidinate yttrium carbyne complex $[(Ph_2P)C(NC_6H_3^{~i}Pr_2-2,6)_2]_2Y_2(\mu_4\text{-}CH)$ ($\mu\text{-}Me)(AlMe_3)_2$ (7) and the rare carbide complex $[(Ph_2P)C(NC_6H_3^{~i}Pr_2-2,6)_2]_2Y_2(\mu_5\text{-}C)(AlMe_2)(\mu\text{-}Me)(AlMe_3)_2$ (8) (31% yield) were obtained. Indeed, complex 6-Y could transform into complexes 7 and 8 in toluene solution for 24 h. However, such a reaction was not feasible for the smaller-sized lutetium center.⁸

Single crystal X-ray diffraction analysis of complex **6-Lu** was performed using a toluene/hexane mixture, which is a fivecoordinate complex (Fig. 5). The bond length of the terminal Lu–Me (2.307(3) Å) is similar to that in complex 5 (2.308(4) Å).



Fig. 5 Molecular structure of complex **6-Lu** with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Lu(1)–C(1) 2.307(3), Lu(1)–C(2) 2.472 (4), Lu(1)–C(3) 2.431(4), Al(1)–C(4) 1.959(3), Lu(1)–N(1) 2.276(2), and Lu (1)–N(2) 2.273(2); C(1)–Lu(1)–N(1) 112.43(11), C(1)–Lu(1)–N(2) 111.55(11), C(1)–Lu(1)–C(2) 102.93(13), and C(1)–Lu(1)–C(3) 105.83(14).



Fig. 6 Molecular structure of complex **7** with thermal ellipsoids at 30% probability except for the $2,6-i^{|}Pr)_2C_6H_3$ groups and benzyl groups in the guanidinate ligand. All of the hydrogen atoms (except for H2) are omitted for clarity. Selected bond distances (Å) and angles (°): Y(1)–C(1) 2.538(3), Y(1)–C(2) 2.390(2), Y(2)–C(1) 2.508(3), Y(2)–C(2) 2.414(2), C(2)–Al(1) 1.992(3), C(2)–Al(2) 1.983(3), Y(1)–C(3) 2.593(3), Y(1)–C(6) 2.646(3), Y(2)–C(5) 2.601(3), and Y(2)–C(8) 2.609(3); C(1)–Y(1)–C(2) 85.28(9), C(1)–Y(2)–C(2) 85.42(9), Y(1)–C(1)–Y(2) 91.50(11), and Y(1)–C(2)–Y(2) 97.58(8).

The single crystal X-ray diffraction analysis of complex 7 shows that two distorted octahedral yttrium centers are linked by μ_4 -CH and μ_2 -Me units to form a distorted square, and two AlMe₃ groups act as bulky ligands to stabilize this binuclear carbyne complex (Fig. 6). It is notable that the Y–C1(μ_4 -CH) bond lengths of 2.390(2) Å and 2.414(2) Å are similar to those in [(PhCH₂)₂NC(NC₆H₃ⁱPr₂-2,6)₂]₂Y₂(μ_2 -Me)(AlMe₃)₂ (μ_4 -CH) (2.398 (5) Å and 2.418(5) Å), but they are shorter than those in [{(C₅Me₅)Y(μ_2 -Me)₂AlMe}₂(μ_2 -Me)(μ_4 -CH)]₂ (2.444(3)–2.464(3) Å)^{9a} due to the steric effect. The average Y–C2(μ_2 -Me) bond length (2.523(3) Å) is shorter than that in [(PhCH₂)₂NC (NC₆H₃ⁱPr₂-2,6)₂]₂Y₂(μ_2 -Me)(AlMe₃)₂(μ_4 -CH) (2.535(5) Å) due to the lower electron-donating ability of the phosphaguanidinate



Fig. 7 Molecular structure of complex **8** with thermal ellipsoids at 30% probability except for the $2,6-({}^{i}Pr)_{2}C_{6}H_{3}$ groups and benzyl groups in the guanidinate ligand. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Y(1)-Y(2) 3.6371(5), Y(1)-C(1) 2.429(3), Y(1)-C(2) 2.597(3), Y(1)-C(5) 2.574(3), Y(1)-C(8) 2.562(3), Y(2)-C(3) 2.620(3), Y(2)-C(6) 2.583(3), Y(2)-C(1) 2.421(3), Y(2)-C(2) 2.566(2), C(1)-Al(1) 1.939(3), C(1)-Al(2) 1.973(3), and C(1)-Al(3) 1.972(3); C(1)-Y(1)-C(2) 86.18(9), C(1)-Y(2)-C(2) 87.05(9), Y(1)-C(1)-Y(2) 97.17(9), Y(1)-C(2)-Y(2) 89.57(8), Al(1)-C(1)-Al(2) 93.82(12), Al(1)-C(1)-Al(3) 96.52(12), and Al(2)-C(1)-Al(3) 169.63(15).

The single crystal X-ray diffraction analysis of complex 8 shows that the stabilization of the carbide unit (C^{4-}) is achieved by alkylaluminate ligands. The carbide carbon atom has a unique distorted trigonal bipyramidal geometry, where three Al atoms are located in the equatorial plane and two Y atoms occupy the axial positions (Fig. 7). The average Y–C2(μ_2 -Me) bond length (2.581(2) Å) is longer than that in $[(PhCH_2)_2NC(NC_6H_3)^{i}Pr_2 - 2, 6)_2]_2Y_2(\mu_2 - Me)(AlMe_3)_2(\mu_4 - CH)$ (2.535) (5) Å).⁸ It is notable that the average Y–C1(μ_5 -C) bond length of 2.425(3) Å is similar to that in $[(PhCH_2)_2NC (NC_6H_3)^iPr_2$ - $(2,6)_2]_2Y_2(\mu_2-SMe)(AlMe_3)_2(\mu_5-C)(AlMe_2)$ (average 2.434(3) Å), but it is shorter than the Y–C(μ_6 -C) bond in [(TMTAC)Y][Y_2(μ_2 -Me)][{(μ_6 -C)[Al(μ_2 -Me)₂(Me)]₃}{(μ_3 -CH₂)(μ_2 -Me)AlMe₂}₂] (average 2.696(6) Å),¹⁰ possibly due to the higher coordination numbers of the carbide atoms in the latter. A similar trend is observed for the Al-C(μ -Me) bond lengths (2.562(3)-2.620(3) Å) compared to 2.588(4)-2.687(5) Å for Al-C(µ-Me),8 probably due to the difference in the electron-donating ability of the surrounding ligand. The results suggest a bimolecular reaction in which the $[CH]^{3-}$ group is deprotonated by the methyl in the AlMe₃ ligand to form a more stable carbide complex with the release of CH₄. The ¹H NMR spectrum of the coordinated AlMe₃ in complex 8 shows that the terminal methyl and μ_2 -Me (Y-Me-Y) overlap with a singlet at $\delta = -0.12$ ppm, and an integral value of 12 at $\delta = 0.77$ ppm is attributed to μ_2 -Me (Y–Me–Al), which is mainly referenced to the methyl in the coordinated AlMe₃ that does not undergo rapid exchange in C₆D₆ at room temperature. μ_4 -CAlMe₂ has a singlet at $\delta = -0.73$ ppm with an integral value of 6. In the ${}^{13}\mathrm{C}\{{}^{1}\mathrm{H}\}$ NMR spectrum, the peaks at δ = -0.3 ppm and 8.1 ppm are attributed to μ_4 -CAlMe₂ and AlMe₃, respectively. The carbon signal of μ_2 -Me exists in the form of a triple peak at δ = 32.0 (J_{Y-C} = 20 Hz) ppm due to the coupling

Table 2 Structural and spectroscopic data for selected yttrium methylidene, methylidyne and carbide complexes

Formula	Y–C distances (Å)	CN	¹ H (ppm)	¹³ C (ppm)	Solv.	Ref.
${Y(C_5Me_5)(THF)}_3(\mu_3-CH_2)(\mu-Cl)_3(\mu_3-CI)$	2.424(2)-2.450(2)	3	-0.39, -0.85	_	THF-D ₈	3 <i>a</i>
$\{Y(C_5Me_5)(THF)\}_3(\mu_3-CH_2)(\mu-Br)_3(\mu_3-Br)$	2.431(3) - 2.532(3)	3	-0.33	_	THF-D ₈	3g
${Y(C_5Me_4SiMe_3)(THF)}_{3}(\mu_3-CH_2)(\mu-Cl)_{3}(\mu_3-CI)$	_ ``	3	-0.42	—	THF-D ₈	3g
${Y(C_5Me_4SiMe_3)(THF)}_{3}(\mu_3-CH_2)(\mu-Br)_{3}(\mu_3-Br)$	_	3	-0.42	—	THF-D ₈	3 <i>g</i>
$\{Y(C_5Me_5)(THF)\}_3(\mu_2-Me)_3(\mu_3-Me)(\mu_3-CH_2)$	2.283(4) - 2.477(3)	3	-0.31	—	C_6D_6	3 <i>g</i>
$\{Y\{N(Dipp)(SiMe_3)\}_3(THF)\}_3(\mu_3-Me)_3(\mu_3-Me)(\mu_3-CH_2)$	2.345(5) - 2.424(4)	3	2.32	100.2	C_6D_6	3 <i>b</i>
${Y[PhC(NC_6H_3^{i}Pr_2-2,6)_2]}_{3}(\mu-Me)_{3}(\mu_3-Me)(\mu_3-CH_2)$	2.388(5) - 2.408(5)	3	2.27	108.5	C_6D_6	23
$[Al(Tp^{tBu,Me})Me]Y(AlMe_4)[(\mu_3-CH_2)(\mu-Me)AlMe_2]_2(AlMe_2)$	2.344(8) - 2.411(9)	3	0.35, 0.25	31.3, 31.0	C_6D_6	5a
$[(TMTAC)Y][Y_2(\mu_2-Me)]{(\mu_6-C)[Al(\mu_2-Me)_2Me]_3}[(\mu_3-CH_2)(\mu_2-Me)AlMe_2]_2$	2.367(5) - 2.452(5)	3		—	—	10
${[Y(Ph_2P)C(NC_6H_3^{1}Pr_2-2,6)_2](\mu-Me)}_{3}(\mu_3-Me)(\mu_3-CH_2)$		3	2.01	109.9	C_6D_6	This work
${Y[PhC(NC_{6}H_{3}^{i}Pr_{2}-2,6)_{2}]}_{3}(\mu_{2}-Me)_{3}(\mu_{3}-CCSiMe_{3})(\mu_{3}-CH_{2})$	2.382(7) - 2.418(8)	3	2.33	113.8	C_6D_6	23
${Y[PhC(NC_6H_3^{i}Pr_2-2,6)_2]}_{3}(\mu_2-Me)_2(\mu_3-CH_2)(\mu_3-\eta^1:\eta^2:\eta^2-S_2C = CH_2)$		3	2.13	116.7	C_6D_6	23
$[{Y(C_5Me_5)(\mu-Me)_2AIMe}_2(\mu-Me)(\mu_4-CH)]_2$	2.444(3) - 2.464(3)	4	_	_	_	9a
$\{Y(PhCH_2)_2NC(NC_6H_3^{-1}Pr_2-2,6)_2\}_2(\mu-Me)(AIMe_3)_2(\mu_4-CH)$	2.398(5) - 2.418(5)	4	2.36	90.2	C_6D_6	8
$\{Y(Ph_2P)C(NC_6H_3^{-1}Pr_2-2,6)_2\}_2(\mu-Me)(AIMe_3)_2(\mu_4-CH)$	2.390(2) - 2.414(2)	4	_	_	_	This work
${Y(TMTAC)}{Y_{2}[(\mu-Me)_{2}AIMe)]}(\mu 6-C)(\mu_{3}-CH_{2}){(\mu-Me)_{2}AIMe}{(\mu-Me)}$	2.436(5) - 2.696(6)	6	_	_	_	10
$AlMe_2$						
$\{(PhCH_2)_2NC(NC_6H_3^{i}Pr_2-2,6)_2\}_2Y_2(\mu_2-SMe)(AlMe_3)_2(\mu_5-C)(AlMe_2)$	2.434(3)	5	_	_	_	8
${Y(Ph_2P)C(NC_6H_3^{1}Pr_2-2,6)_2}_{2}(\mu-Me)(AIMe_3)_{2}(\mu_5-C)(AIMe_2)$	2.429(3) - 2.566(2)	5	_	—	_	This work



Fig. 8 Molecular structure of complex **9** with thermal ellipsoids at 30% probability. All hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Y(1)-N(1) 2.326(4), Y(1)-N(2) 2.351(4), Y(1)-C(1) 2.528(4), Y(1)-C(2) 2.558(4), Y(1)-C(5) 2.541(4), and Y(1)-C(6) 2.570 (4); C(1)-Y(1)-N(1) 103.90(11), C(1)-Y(1)-N(2) 97.65(11), C(2)-Y(1)-N(1) 94.93(12), C(2)-Y(1)-N(2) 150.89(13), C(5)-Y(1)-N(1) 96.19(11), C(5)-Y(1)-N(2) 99.99(12), C(6)-Y(1)-N(1) 151.81(13), C(6)-Y(1)-N(2) 95.77(12), C(1)-Y(1)-C(2) 79.89(13), and C(5)-Y(1)-C(6) 79.65(13).

cleavage of the bridged methyl carbon by Y^{3+} . The ${}^{31}P{}^{1}H$ NMR spectrum of complex 8 shows a singlet at δ = 5.7 ppm (Table 2).

As depicted in Scheme 4, when four equivalents of AlMe₃ were employed to react with complex **1-Y**, the heterobimetallic bis(tetramethylaluminate) complex $[(Ph_2P)C(NC_6H_3^iPr_2-2,6)_2]Y$ (AlMe₄)₂ (**9**) was isolated in a good yield. However, attempts to prepare the lutetium analogue through a similar synthetic process were unsuccessful. Due to the smaller-sized lutetium center, we only separated out complex **6-Lu** as the major product. The ¹H NMR spectrum of complex **9** is identical to its structure. Only one signal at $\delta = 0.07$ ppm is assigned to [AlMe₄]⁻, likely because of the rapid exchange between the bridged methyl and terminal methyl groups in C₆D₆ at ambient temperature.^{4a} X-ray single crystals of complex **9-Y** were obtained from a toluene/hexane mixture (Fig. 8), and the Y–Me bond length (2.552(6) Å) is close to that in [(PhCH₂)₂NC (NC₆H₃ⁱPr₂-2,6)₂]Y(AlMe₄)₂ (2.556(7)–2.573(7) Å).⁸

Conclusions

In conclusion, phosphaguanidinate rare-earth-metal bis(aminobenzyl) complexes were synthesized through protonolysis reactions, and the THF ring-opening rearrangement product was isolated with an excellent yield as well. Moreover, a series of heterobimetallic Ln/Al complexes containing a phosphaguanidinate ligand were obtained in good yields. The degree of alkylation in the resulting heterobimetallic complexes is highly dependent on the amount of alkylaluminum reagent and the steric/electronic characteristics of the anionic ligands. We have successfully developed a synthesis method starting from heterobimetallic Y/Al complexes, which leads to the formation of yttrium carbene, carbyne, and carbide complexes *via* multiple C-H activation reactions. Additionally, studies on the reactivity of these complexes towards organic substrates are currently underway in our laboratory.

Experimental section

General procedures and materials

All manipulations were performed under the rigorous exclusion of air and moisture using standard Schlenk techniques and an MBRAUN glovebox (Unilab; <1 ppm O₂, <1 ppm H₂O). Solvents (toluene, hexane, and THF) were purified using Grubbs-type columns (MBRAUN SPS-800, solvent purification system) and dried over fresh Na chips in the glove box. Bis(2,6diisopropylphenyl) carbodiimide was obtained from Tokyo Chemical Industry Co., Ltd and used without purification. CH₃C₆H₄NMe₂-o was purchased from Sigma-Aldrich and used without purification. Ph₂PH, ⁿBuLi (2.5 mol L⁻¹ in hexane), diphenylphosphine and $AlMe_3$ (1 mol L^{-1} in hexane) were purchased from J&K and used without purification. C6D6 was obtained from J&K and dried using sodium chips. The complexes Ln(CH₂C₆H₄NMe₂-o)₃ were prepared according to the literature procedures.²⁴ The ¹H NMR, ¹³C{¹H} NMR and ³¹P {¹H} NMR spectra were recorded using a JEOL ECA-400 NMR spectrometer (FT, 400 MHz for ¹H; 100 MHz for ¹³C{¹H}; and 161.88 MHz for ${}^{31}P{}^{1}H$ in C₆D₆ at room temperature. X-ray crystallographic data were obtained using a Bruker SMART APEX or Bruker SMART APEX II (at 173 K or 296 K) diffractometer with a CCD area detector using graphite-monochromated Mo/Ga K α radiation ($\lambda = 0.71073 \text{ Å}/\lambda = 1.34138 \text{ Å}$). The structure was solved using the SHELXTL program. Refinement was performed using F^2 anisotropically with the full-matrix least-squares method for all the non-hydrogen atoms. Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre. 2389279 (for 1-Y), 2389282 (for 1-Lu), 2389309 (for 2), 2389276 (for 4), 2389280 (for 5), 2389278 (for 6-Lu), 2389281 (for 7), 2389283 (for 8) and 2389277 (for 9)† contain the supplementary crystallographic data for this paper. The combustion method was used for the analysis of carbon, hydrogen and nitrogen using an Elementar Vario EL III analyzer at Fudan University (China).

Synthesis of $[(Ph_2P)C(NC_6H_3^iPr_2-2,6)_2]Y(CH_2C_6H_4NMe_2-o)_2$ (1-Y). A THF solution (10 mL) of Y(o-CH₂C₆H₄NMe₂)₃ (0.25 g, 0.5 mmol) was added into a stirred solution (20 mL) of (Ph_2P) [C(NR)(NHR)] (R = 2,6-ⁱPr₂C₆H₃) (0.27 g, 0.5 mmol) in THF or toluene. The reaction solution was allowed to stir for 24 h at room temperature and all volatiles were removed under vacuum. The oily residue was washed with cold hexane and a yellow powder was obtained by filtration. The yellow powder was recrystallized in toluene at -35 °C for one day to give a pale yellow powder of 1-Y (0.38 g, 83%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) = 1.29 (d, 12H, ³J_{H-H} = 4 Hz, CHMe₂), 1.31 (d, ³J_{H-H} = 4 Hz, 12H, CHMe₂), 1.80 (s, 4H, CH₂C₆H₄NMe₂), 2.29 (s, 12H, CH₂C₆H₄NMe₂), 3.65 (m, 4H, CHMe₂), 6.59–6.60 (m, 4H, Ar), 6.77–6.78 (m, 6H, Ar), 6.85–6.95 (m, 8H, Ar), 7.00–7.02 (m, 2H, Ar), 7.12–7.14 (m, 4H, Ar). $^{13}C{^{1}H}$ NMR (100 MHz, C_6D_6 , 25 °C): δ (ppm) = 24.7 (d, J = 5 Hz, CHMe₂), 25.7 (s, CHMe₂), 29.4 (d, J = 1 Hz, CHMe₂), 46.5 (s, CH₂C₆H₄NMe₂), 49.4 (d, J_{YC} = 32 Hz, CH₂C₆H₄NMe₂), 118.4 (s, Ar), 120.7 (s, Ar), 124.1 (s, Ar), 125.3 (s, Ar), 126.7 (s, Ar), 127.6 (d, J = 5 Hz, Ar), 129.2 (s, Ar), 134.4 (d, J = 15 Hz, Ar), 135.8 (d, J = 23 Hz, Ar), 142.8 (s, Ar), 144.2 (d, J = 3 Hz, Ar), 145.1 (s, Ar), 145.9 (s, Ar), 178.1 (d, J = 78 Hz, NCN). $^{31}P{^{1}H}$ NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) = 6.1 (q, J = 8.1 Hz, CPPh₂). Anal. calcd for C₅₅H₆₈N₄PY(%): C, 72.99; H, 7.57; N, 6.19. Found: C, 73.06; H, 7.21; N, 6.23.

Synthesis of $[(Ph_2P)C(NC_6H_3^{\dagger}Pr_2-2,6)_2]Lu(CH_2C_6H_4NMe_2-o)_2$ (1-Lu). A toluene solution (10 mL) of $Lu(o-CH_2C_6H_4NMe_2)_3$ (0.29 g, 0.5 mmol) was added into a stirred solution (20 mL) of $(Ph_2P)[C(NR) (NHR)]$ (R = 2,6⁻ⁱPr₂C₆H₃) (0.27 g, 0.5 mmol) in toluene. The reaction solution was allowed to stir for 24 h at 60 °C and all volatiles were removed under vacuum. The oily residue was washed with cold hexane and a yellow powder was obtained by filtration. The yellow powder was recrystallized in toluene at -35 °C for three days to give a yellow powder of 1-Lu (0.38 g 78%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) = 1.28 (d, ${}^{3}J_{H-H} = 4$ Hz, 12H, CHMe₂), 1.35 (d, ${}^{3}J_{H-H} = 4$ Hz, 12H, CHMe₂), 1.75 (s, 4H, CH₂C₆H₄NMe₂), 2.27 (s, 12H, CH₂C₆H₄NMe₂), 3.74 (m, 4H, CHMe₂), 6.50-6.58 (m, 4H, Ar), 6.75 (m, 6H, Ar), 6.84 (m, 5H, Ar), 6.88-6.92 (m, 2H, Ar), 7.01–7.05(m, 2H, Ar), 7.10–7.13(m, 5H, Ar). ${}^{13}C{}^{1}H$ NMR (100 MHz, C_6D_6 , 25 °C): δ (ppm) = 24.9 (d, J = 5 Hz, CHMe₂), 25.8 (s, CHM e_2), 29.2 (d, J = 5 Hz, CHM e_2), 47.0 (s, CH₂C₆H₄NMe₂), 54.0 (s, CH₂C₆H₄NMe₂), 117.9 (s, Ar), 121.1 (s, Ar), 124.2 (s, Ar), 125.7 (s, Ar), 126.4 (s, Ar), 127.6 (d, J = 9 Hz, Ar), 129.8 (s, Ar), 134.2 (d, J = 15 Hz, Ar), 136.0 (d, J = 23 Hz, Ar), 143.2 (s, Ar), 144.2 (d, J = 4 Hz, Ar), 146.2 (d, J = 21 Hz, Ar), 178.5 (d, J = 79 Hz, NCN). ³¹P{¹H} NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) = 7.3 (s, CPPh₂). Anal. calcd for C₅₅H₆₈N₄PLu (%): C, 66.65; H, 6.92; N, 5.65. Found: C, 66.81; H, 6.88; N, 5.73.

Synthesis of $[o-Me_2NC_6H_4CH_2C(NC_6H_3^{i}Pr_2-2,6)_2]Lu$ $(CH_2C_6H_4NMe_2-o)[O(CH_2)_4PPh_2]$ (2). A THF solution (10 mL) of Lu(o-CH₂C₆H₄ NMe₂)₃ (0.29 g, 0.5 mmol) was added into a stirred solution (20 mL) of $(Ph_2P)[C(NR)(NHR)]$ (R = $2,6^{-1}Pr_2C_6H_3$ (0.27 g, 0.5 mmol) in THF. The reaction solution was allowed to stir for 36 h at 60 °C and all volatiles were removed under vacuum. The oily residue was washed with cold hexane and a yellow powder was obtained by filtration. The yellow powder was recrystallized in toluene at -35 °C for one day to give a pale yellow powder of 2 (0.51 g, 90%). ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) = 1.09 (br s, 4H, β -THF), 1.39 $(d, 24H, {}^{3}J_{H-H} = 4 Hz, CHMe_{2}), 1.78 (m,$ 2H, $O(CH_2)_2CH_2CH_2PPh_2$, 1.88 (s, 8H, $CH_2C_6H_4NMe_2-o$ and CH₂C₆H₄NMe₂), 1.98 (m, 2H, OCH₂CH₂(CH₂)₂ PPh₂), 2.31 (m, 2H, O(CH₂)₃CH₂PPh₂), 2.47 (s, 6H, CH₂C₆H₄NMe₂), 3.30 (br s, 4H, α-THF), 3.84 (br, 6H, CHMe₂ and CH₂C₆H₄NMe₂), 4.04 (m, 2H, OCH₂(CH₂)₃PPh₂), 6.59–6.63 (m, 2H, Ar), 6.76 (d, 1H, ³J_{H-H} = 4 Hz, Ar), 6.87 (t, 1H, ${}^{3}J_{H-H}$ = 8 Hz, Ar), 6.92 (t, 2H, ${}^{3}J_{H-H}$ = 8 Hz, Ar), 7.00–7.15 (m, 13H, Ar), 7.57 (m. 4H, Ar), 7.65 (d. ³J_{H-H} = 4 Hz, 1H, Ar). ${}^{13}C{}^{1}H$ NMR (100 MHz, C₆D₆, 25 °C): δ (ppm)

= 23.4 (d, J = 16 Hz, O(CH₂)₂CH₂CH₂PPh₂), 24.7 (s, β -THF), 25.6 (s, CHMe₂), 26.8 (s, CHMe₂), 28.1 (br, CHMe₂), 29.6 (d, J = 13 Hz, $O(CH_2)_3 CH_2 PPh_2$, 29.9 (s, $CH_2C_6H_4NMe_2$), 38.6 (d, J =11 Hz, OCH₂CH₂(CH₂)₂PPh₂), 44.5 (s, CH₂C₆H₄NMe₂), 44.7 (s, 46.4 $CH_2C_6H_4NMe_2$), $CH_2C_6H_4NMe_2$), (s, 69.3 (s, OCH₂(CH₂)₃PPh₂), 69.9 (s, α-THF), 116.8 (s, Ar), 118.6 (s, Ar), 120.2 (s, Ar), 123.9 (s, Ar), 124.6 (s, Ar), 124.7 (s, Ar), 127.0 (s, Ar), 128.7 (s, Ar), 128.8 (s, Ar), 129.3 (s, Ar), 132.1 (s, Ar), 133.1 (s, Ar), 133.3 (d, J = 18 Hz, Ar), 140.1 (d, J = 15 Hz, Ar), 140.7 (s, Ar), 143.1 (s, Ar), 143.9 (br, Ar), 147.6 (s, Ar), 152.7 (s, Ar), 176.6 (s, NCN). ${}^{31}P{}^{1}H{}$ NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) = -16.9 (s, O(CH₂)₄*P*Ph₂). Anal. calcd for C₆₃H₈₄N₄PO₂Lu(%): C, 64.82; H, 7.25; N, 4.80. Found: C, 64.52; H, 7.20; N, 4.57.

Synthesis of $\{[(Ph_2P)C(NC_6H_3^{i}Pr_2-2,6)_2]Y(\mu-Me)\}_3(\mu_3-Me)(\mu_$ CH₂) (3). A solution of AlMe₃ (1.0 mL, 1 M in hexane, 1 mmol) in toluene (2 mL) was added slowly to a stirred solution of complex 1-Y (0.45 g, 0.5 mmol) in toluene (10 mL) at ambient temperature. The reaction mixture was allowed to stir for 3 h. The toluene was removed under vacuum, and the oily yellow residue turned into a white powder after washing twice with hexane (2 mL), which was collected by filtration and dried. The white powder was crystallized in toluene and stored at -35 °C to yield complex 3 (0.30 g, 92%) as colorless crystals. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) = 0.90 (s, 3H, μ_3 -Me), 1.05 (s, 9H, μ_2 -Me), 1.26 (d, ${}^{3}J_{H-H}$ = 4 Hz, 36H, CHMe₂), 1.30 (d, ${}^{3}J_{H-H}$ = 8 Hz, 36H, CHMe2), 2.01 (s, 2H, µ3-CH2), 3.71 (br s, 12H, $CHMe_2$, 6.83 (br s, 36H, Ar), 7.25 (br s, 12H, Ar). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) = 23.7 (s, CHMe₂), 27.8 (s, CHMe₂), 29.0 (s, CHMe₂), 36.5 (t, J = 24 Hz, μ_2 -Me), 47.6 (s, μ_3 -*Me*), 109.9 (d, J_{Y-C} = 23 Hz, μ_3 -*C*H₂), 123.8 (s, Ar), 125.4 (s, Ar), 128.1 (s, Ar), 128.4 (s, Ar), 129.0 (s, Ar), 135.0 (d, J = 22 Hz, Ar), 136.3 (d, J = 16 Hz, Ar), 142.4 (s, Ar), 142.9 (s, Ar), 179.1 (d, J = 67 Hz, NCN). ³¹P{¹H} NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) = 1.4 (s, CPPh₂). Anal. calcd for C₁₁₆H₁₄₆N₆P₃Y₃(%): C, 70.22; H, 7.42; N, 4.24. Found: C, 70.01; H, 7.20; N, 4.04.

Synthesis of $\{[(Ph_2P)C(NC_6H_3^{i}Pr_2-2,6)_2]Lu(\mu-Me)Me\}_2$ (4). A solution of AlMe₃ (1.0 mL, 1 M in hexane, 1 mmol) in toluene (2 mL) was added slowly to a stirred solution of complex 1-Lu (0.49 g, 0.5 mmol) in toluene (10 mL) at ambient temperature. The reaction mixture was allowed to stir for 3 h. The toluene was removed under vacuum, and the oily yellow residue turned into a white powder after washing twice with hexane (2 mL), which was collected by filtration and dried. The white powder was crystallized in toluene and stored at -35 °C to yield complex 4 (0.29 g, 78%) as colorless crystals. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) = 0.82 (br, 12H, Lu–*Me*), 1.18 (d, ${}^{3}J_{H-H} = 4$ Hz, 24H, CHMe₂), 1.33 (d, ${}^{3}J_{H-H} = 8$ Hz, 24H, CHMe₂), 3.69 (m, 8H, CHMe₂), 6.71-6.73 (m, 8H, Ar), 6.79-6.84 (m, 8H, Ar), 7.01-7.07 (m, 6H, Ar), 7.12-7.13 (m, 4H, Ar) 7.29–7.32 (m, 6H, Ar). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) = 21.4 (s, CHMe₂), 22.8 (s, CHMe₂), 26.8 (s, CHMe₂), 29.0 (s, CHMe₂), 30.2 (s, CHMe₂), 43.2 (s, Lu-Me), 123.5 (s, Ar), 125.7 (s, Ar), 128.2 (s, Ar), 128.6 (s, Ar), 129.1 (s, Ar), 129.3 (s, Ar), 134.5 (d, J = 13 Hz, Ar), 135.3 (d, J = 23 Hz, Ar), 137.9 (s, Ar), 141.5 (s, Ar), 142.3 (s, Ar). ³¹P{¹H} NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) = -1.3 (s, CPPh₂). Anal. calcd for

 $C_{78}H_{100}N_4P_2Lu_2$ (%): C, 62.23; H, 6.70; N, 3.72. Found: C, 62.02; H, 6.91; N, 4.02.

Synthesis of $[(Ph_2P)C(NC_6H_3^iPr_2-2,6)_2]](Me)C(NC_6H_3^iPr_2-2,6)_2]](Me)C(NC_6H_3^iPr_2-2,6)_2][(Me)C(NC_6H_3^iPr_2-2,6)_2]](Me)C(NC_6H_3^iPr_2-2,6)_2]](Me)C(NC_6H_3^iPr_2-2,6)_2][(Me)C(NC_6H_3^iPr_2-2,6)_2]](Me)C(NC_6H_3^iPr_2-2,6)_2][(Me)C(NC_6H_3^iPr_2-2,6)_2]](Me)C(NC_6H_3^iPr_2-2,6)_2][(Me)C(NC_6H_3^iPr_2-2,6)_2]](Me)C(NC_6H_3^iPr_2-2,6)_2][(Me)C(NC_6H_3^iPr_2-2,6)_2][(Me)C(NC_6H_3^iPr_2-2,6)_2]](Me)C(NC_6H_3^iPr_2-2,6)_2][(Me)C(NC_6H_3^iPr_2-2,6)_2][(Me)C(NC_6H_3^iPr_2-2,6)_2]](Me)C(NC_6H_3^iPr_2-2,6)_2][(Me)C(NC_6H$ 2,6)₂]Lu (Me) (5). 10 mL of a toluene solution of complex 4 (0.75 g, 0.5 mmol) was allowed to stir at 100 °C for 36 h. Then the toluene was removed under vacuum, and the oily yellow residue turned into a white powder after washing twice with hexane (2 mL), which was collected by filtration and dried. The white powder was crystallized in toluene and stored at -35 °C to yield complex 5 (0.21 g, 37%) as colorless crystals. ¹H NMR (400 MHz, C_6D_6 , 25 °C): δ (ppm) = 0.36 (s, 3H, Lu–*Me*), 1.01 (d, ${}^{3}J_{H-H} = 8$ Hz, 12H, CHMe₂), 1.06 (br, 12H, CHMe₂), 1.13 (d, ${}^{3}J_{H-H} = 8$ Hz, 12H, CHMe₂), 1.22 (d, ${}^{3}J_{H-H} = 2$ Hz, 6H, CHMe₂), 1.39 (s, 3H, NC(Me)N), 1.43 (d, ${}^{3}J_{H-H} = 8$ Hz, 6H, CHMe₂), 3.30 (br, 4H, CHMe₂), 3.56 (m, 2H, CHMe₂), 3.84 (m, 2H, CHMe₂), 6.72-6.80 (m, 10H, Ar), 7.04 (br s, 6H, Ar), 7.15-7.19 (m, 6H, Ar). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) = 17.6 (s, NC(Me)N), 22.8 (s, CHMe₂), 23.1 (d, J = 4 Hz, CHMe₂), 24.6 (d, J = 5 Hz, CHMe₂), 25.0 (s, CHMe₂), 28.6 (d, J = 18 Hz, CHMe₂), 28.9 (s, $CHMe_2$), 29.3 (d, J = 4 Hz, $CHMe_2$), 35.7 (s, Lu-Me), 123.2 (d, J = 22 Hz, Ar), 124.0 (s, Ar), 125.2 (d, J = 47 Hz, Ar), 127.9 (s, Ar), 128.2 (s, Ar), 128.4 (s, Ar), 134.5 (d, J = 13 Hz, Ar), 135.0 (d, J = 23 Hz, Ar), 141.7 (d, J = 5 Hz, Ar), 142.7 (s, Ar), 142.9 (s, Ar), 143.2 (s, Ar), 143.8 (s, Ar), 177.0 (s, NC(Me)N), 178.5 (d, J = 69 Hz, NC(P)N). ³¹P{¹H} NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) = 5.3 (s, CPPh₂). Anal. calcd for C₆₄H₈₅N₄PLu (%): C, 68.86; H, 7.68; N, 5.02. Found: C, 68.90; H, 7.39; N, 5.05.

Synthesis of $[(Ph_2P)C(NC_6H_3^{i}Pr_2-2,6)_2]Y(AlMe_4)(Me)$ (6-Y). A solution of AlMe₃ (1.5 mL, 1 M in hexane, 1.5 mmol) in toluene (2 mL) was added slowly to a stirred solution of 1-Y (0.45 g, 0.5 mmol) in toluene (10 mL) at ambient temperature. The reaction mixture was allowed to stir for 2 h. Complex 6-Y is unstable in solution, and we could only detect the formation of 6-Y by ¹H NMR of the reaction solution (about 95% NMR yield).^{8 1}H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) = -0.13 (s, 12H, AlMe₄), 0.30 (s, 3H, Y-Me), 1.25 (br s, 24H, CHMe₂), 3.58 (br s, 4H, CHMe₂), 6.54–7.28 (m, Ar). ³¹P{¹H} NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) = -0.9 (s, CPPh₂).

Synthesis of $[(Ph_2P)C(NC_6H_3)^{i}Pr_2-2,6)_2]Lu(AlMe_4)(Me)$ (6-Lu). A solution of AlMe₃ (1.5 mL, 1 M in hexane, 1.5 mmol) in toluene (2 mL) was added slowly to a stirred solution of 1-Lu (0.49 g, 0.5 mmol) in toluene (10 mL) at ambient temperature. The reaction mixture was allowed to stir for 3 h. The toluene was removed under vacuum, and the oily yellow residue turned into a white powder after washing twice with hexane (2 mL), which was collected by filtration and dried. The white powder was crystallized in toluene and stored at -35 °C to yield complex 6-Lu (0.30 g, 74%) as colorless crystals. $^1\mathrm{H}$ NMR (400 MHz, C_6D_6 , 25 °C): δ (ppm) = 0.16 (s, 12H, AlMe₄), 0.29 (s, 3H, Lu-Me), 0.97-1.26 (br s, 24H, CHMe2), 3.61 (br s, 4H, CHMe₂), 6.73–6.85 (m, 12H, Ar), 7.25–7.29 (m, 4H, Ar). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) = 6.4 (s, AlMe₄), 22.6 (br s, CHMe₂), 26.2 (br s, CHMe₂), 27.7 (br s, CHMe₂), 29.1 (s, CHMe₂), 35.7 (s, CHMe₂), 123.6 (s, Ar), 126.2 (s, Ar), 128.2 (s, Ar), 129.3 (s, Ar), 134.0 (d, J = 13 Hz, Ar), 135.0 (d, J = 23 Hz,

Ar), 140.7 (d, J = 5 Hz, Ar), 142.4 (br s, Ar), 181.4 (d, J = 62 Hz, NCN). ³¹P{¹H} NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) = -0.6 (s, CPPh₂). Anal. calcd for C₄₂H₅₉N₂PLuAl (%): C, 61.16; H, 7.21; N, 3.40. Found: C, 60.92; H, 7.20; N, 3.18.

Synthesis of $[(Ph_2P)C(NC_6H_3^{i}Pr_2-2,6)_2]_2Y_2(\mu_4-CH)(AlMe_3)_2(\mu-Me)$ (7). A solution of AlMe₃ (1.5 mL, 1 M in hexane, 1.5 mmol) in toluene (2 mL) was added slowly to a stirred solution of 1-Y (0.45 g, 0.5 mmol) in toluene (10 mL) at ambient temperature. The reaction mixture was allowed to stir for 24 h. Due to the extremely low yield, sufficient quantities of complex 7 which can be used to data collections such as NMR (except for X-ray single crystal structures) were not obtained.

Synthesis of $[(Ph_2P)C(NC_6H_3^{i}Pr_2-2,6)_2]_2Y_2(\mu_5-C)(AlMe_2)$ $(AlMe_3)_2(\mu-Me)$ (8). A solution of AlMe₃ (1.5 mL, 1 M in hexane, 1.5 mmol) in toluene (2 mL) was added slowly to a stirred solution of 1-Y (0.45 g, 0.5 mmol) in toluene (10 mL) at ambient temperature. The reaction mixture was allowed to stir for 24 h. The toluene was removed under vacuum, and the oily vellow residue turned into a white powder after washing twice with hexane (2 mL), which was collected by filtration and dried. The white powder was crystallized in toluene and stored at -35 °C to yield complex 8 (0.12 g, 31%) as colorless crystals. ¹H NMR (400 MHz, C₆D₆, 25 °C): δ (ppm) = -0.73 (br s, 6H, μ_4 -CAlMe₂), -0.13 (br s, 9H, $(\mu_2$ -Me)₂AlMe and μ_2 -Me), 0.77 (br s, 12H, $(\mu_2 - Me)_2$ AlMe), 1.25 (s, 24H, CHMe₂), 1.30 (s, 24H, CHMe₂), 3.62 (br s, 8H, CHMe₂), 6.72 (br s, 24H, Ar), 7.12 (m, 8H, Ar). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) = -0.2 $(s, \mu_4$ -CAlMe₂), 8.24 $(s, AlMe_3)$, 23.4 $(s, CHMe_2)$, 28.9 (s, e_3) CHMe₂), 29.1 (s, CHMe₂), 32.0 (t, J_{Y-C} = 20 Hz, μ_2 -Me), 115.4 (s, Ar), 123.6 (s, Ar), 126.2 (s, Ar), 127.9 (s, Ar), 128.0 (s, Ar), 135.2 (d, J = 15 Hz, Ar), 135.9 (d, J = 24 Hz, Ar), 141.7 (d, J = 5 Hz, Ar), 143.1 (s, Ar), 180.8 (d, J = 69 Hz, NCN). ³¹P{¹H} NMR (162 MHz, C_6D_6 , 25 °C): δ (ppm) = 5.7 (s, CPPh₂). Anal. calcd for C₈₄H₁₁₅N₄P₂Al₃Y₂(%): C, 67.20; H, 7.72; N, 3.73. Found: C, 67.01; H, 7.40; N, 4.11.

Synthesis of $[(Ph_2P)C(NC_6H_3^{i}Pr_2-2,6)_2]Y(AlMe_4)_2$ (9). A solution of AlMe₃ (2.0 mL, 1 M in hexane, 2 mmol) in toluene (2 mL) was added slowly to a stirred solution of 1-Y (0.452 g, 0.5 mmol) in toluene (10 mL) at ambient temperature. The reaction mixture was allowed to stir for 3 h. The toluene was removed under vacuum, and the oily yellow residue turned into a white powder after washing twice with hexane (2 mL), which was collected by filtration and dried. The white powder was crystallized in toluene and stored at -35 °C to yield complex 9 (0.34 g, 85%) as colorless crystals. ¹H NMR (400 MHz, C_6D_6 , 25 °C): δ (ppm) = 0.07 (s, 24H, AlMe₄), 1.16 (d, ${}^{3}J_{H-H} = 4$ Hz, 12H, CHMe₂), 1.21 (d, ${}^{3}J_{H-H} = 8$ Hz, 12H, CHMe₂), 3.54 (m, 4H, CHMe₂), 6.67-6.74 (m, 6H, Ar), 6.77-6.79 (m, 4H, Ar), 6.82–6.84 (m, 2H, Ar), 7.08–7.12 (m, 4H, Ar). ¹³C {¹H} NMR (100 MHz, C₆D₆, 25 °C): δ (ppm) = 3.5 (s, AlMe₄), 23.5 (d, J = 7 Hz, CHMe₂), 28.2 (s, CHMe₂), 29.1 (d, J = 2 Hz, CHMe₂), 124.2 (s, Ar), 126.8 (s, Ar), 128.2 (s, Ar), 128.3 (s, Ar), 128.9 (s, Ar), 134.9 (s, Ar), 135.1 (d, J = 24 Hz, Ar), 140.8 (d, J = 5 Hz, Ar), 143.3 (s, Ar). ${}^{31}P{}^{1}H$ NMR (162 MHz, C₆D₆, 25 °C): δ (ppm) = 4.2 (s, CPPh₂). Anal. calcd for C₄₅H₆₈N₂PAl₂Y (%): C, 66.65; H, 8.45; N, 3.46. Found: C, 67.01; H, 8.29; N, 3.35.

Data availability

The data that support the findings of this study are available in the ESI† of this article.

Conflicts of interest

The authors declare no conflict of interest.

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