Reactivity of Rare-Earth Metal Complexes Stabilized by an Anilido-Phosphinimine Ligand

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Treatment of anilido-phosphinimine-ligated yttrium mono(alkyl) complex **1a**, LY($CH_2Si(CH_3)_3$)(THF) (L = *o*-(2,6-$C_6H_3{}^iPr_2$)$NC_6H_4P(C_6H_4)(C_6H_5)N$(2,4,6-$C_6H_2Me_3$)), with 2 equiv of phenylsilane in DME afforded methoxy-bridged complex **2**, $[LY(\mu\text{-}OCH_3)]_2$, via the corresponding hydrido intermediate. When excess isoprene was added to the mixture of **1a** and phenylsilane, a η^3-isopentene product, **3**, $LY(CH_2C(CH_3){=}CHCH_3)$(THF), was isolated. A lutetium chloride, LLuCl(DME) (**4**), was generated through the reaction of lutetium mono(alkyl) complex **1b**, $LLu(CH_2Si(CH_3)_3)$(THF), with $[Ph_3C][B(C_6F_5)_4]\cdot LiCl$ accompanied by the formation of $[Li(DME)_3]^+[B(C_6F_5)_4]^-$. Metathesis reaction of **1b** with excess $AlMe_3$ at room temperature gave a methyl-terminated counterpart, **5**, $LLu(CH_3)(THF)_2$. In all these reactions, the $Ln-C_{phenyl}$ bonds of complexes **1** remained untouched. However, protonolysis of complex **1b** with 2 equiv of phenylacetylene in DME provided a lutetium bis(acetylide), $LHLu(C{\equiv}CPh)_2$(DME) (**6**), and the linkage of the $Ln-C_{phenyl}$ bond was cleaved, indicating that the activated C−H bond was recovered.

Introduction

Ligand design is becoming an increasingly important part of organometallic chemistry due to the subtle control that ligands exert on the metal center. To date, many cyclopentadienyl[1] and non-cyclopentadienyl ligands[2] have been applied to stabilize group 3 metal complexes. The recent surge of activity in the use of phosphinimine donors in organotransition metal chemistry directed a new path for rare-earth organometallic chemistry.[3] By introducing "large" and "soft" phosporus donor, phosphorus chelating complexes were expected to possess the potential for catalytic activity toward nonpolar monomers[4] and new stoichiometric chemistry. Our group has successfully isolated a series of rare-earth metal complexes bearing the anilido-phosphinimine and amino-phosphine ligands, which have shown unique C−H activation and unprecedented catalysis on the regioselective cycloaddition of organic azides and aromatic alkynes.[5] These results intrigued us to apply these phosphide ligands to stabilize the rare-earth metal hydrido and cationic species that have been single-component catalysts or precursors for the polymerizations of olefins and dienes.[6] Owing to the hard Lewis acidity and large ionic radii of Ln^{3+} ions, rare-earth metal cations and hydrides have been dominated by cyclopentadienyl,[7] heterocy-

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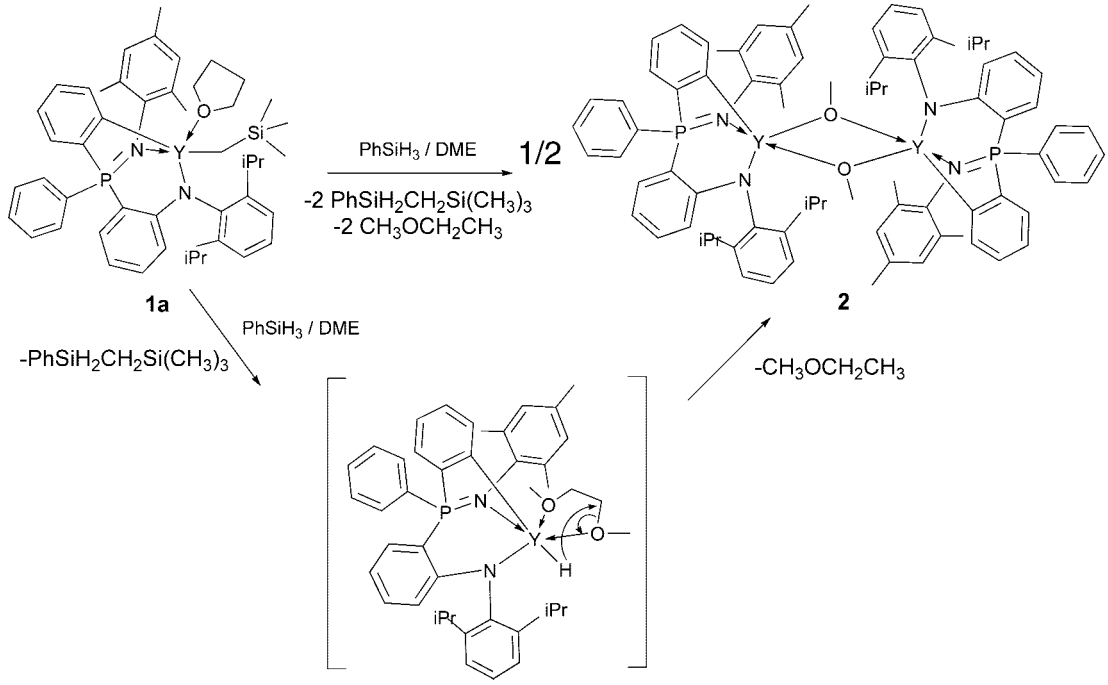
Scheme 1. Preparation of Complex 2



clopentadienyl,[8] and few bulky non-cyclopentadienyl ligands such as β-diketimine,[9] amidinate,[6a,b,10] anilido-imine,[11] aza crown ethers,[12] and tri(pyrazoly).[13] Herein, we report the synthesis of rare-earth metal hydrido and cationic intermediates stabilized by anilido-phosphinimine auxiliary ligands and their derivatives. Moreover, the reactions of the lutetium complex with trimethylaluminum and phenylacetylene are also presented.

Results and Discussion

Synthesis of a Yttrium Hydride Intermediate and Its Reactivity. Addition of phenylsilane to the hexane suspension of yttrium mono(alkyl) complex **1a**, $LY(CH_2Si(CH_3)_3)(THF)$ ($L = o$-(2,6-$C_6H_3{}^iPr_2$)$NC_6H_4P(C_6H_4)(C_6H_5)N$(2,4,6-$C_6H_2Me_3$)),[5a] at room temperature formed a clear solution within 1 h, which was concentrated to 1 mL under reduced pressure and then kept at −30 °C for several days. However, the hydrido complex could not be obtained due to its good solubility. Using DME solvent instead of hexane, anticipated to stabilize the metal-hydride species, afforded a methoxy group bridged complex, **2**, $[LY(\mu\text{-}OCH_3)]_2$ (δ 2.66 ppm for OCH_3) (Scheme 1). This suggested that the hydride complex was indeed formed, albeit as an intermediate. Activated by the Lewis-acidic yttrium center, the hydrido ligand nucleophilically attacked the methylene carbon of DME with cleavage of the C−O bond. Meanwhile the $Y-C_{Phenyl}$ bond remained untouched, which gave a doublet at 197.06 ppm, typical for the metal phenyl carbon $Y-C_{Phenyl}$. This result is different from the reaction between the linked amido-cyclopentadienyl-ligated yttrium hydrido complex and DME, in which the hydrido ligand neclueophilically attacks the methyl carbon of DME to give a 2-methoxyethoxy-bridging complex, $[Y(L)(\mu\text{-}OCH_2CH_2OMe\text{-}\kappa O)]_2$.[7k] X-ray diffraction analysis shows that each yttrium atom is coordinated by a CNN tridentate ligand to form the dimeric complex **2** of C_i symmetry with two bridging methoxy groups. The molecule adopts a pseudopyramidal geometry with the N(2) atom apical and atoms N(1), C(12), O, and O(0A) equatorial (Figure 1, Table 1, and STable 1). The bridging Y−O bond distances are nearly equivalent (Y−O = 2.2276(16) Å, Y−O(0A) = 2.2622(16) Å), close to those in the dimeric enolate complex $[Y(\eta^5\text{-}MeC_5H_4)_2(\mu\text{-}OCH{=}CH_2)]_2$.[14]

Table 1. Selected Bond Lengths and Bond Angles of Complex 2

Bond Lengths (Å)			
Y−O	2.2276(16)	Y−O(0A)	2.2622(16)
Y−N(1)	2.3042(18)	Y−N(2)	2.3311(19)
Y−C(12)	2.435(2)	O−C(40)	1.425(3)
P−C(7)	1.811(2)	C(7)−C(12)	1.404(3)
Bond Angles (deg)			
O−Y−O(0A)	72.24(6)	Y−O−Y(0A)	107.76(6)
C(40)−O−Y	136.92(15)	C(40)−O−Y(0A)	115.27(14)
N(1)−Y−C(12)	87.97(7)	O−Y−C(12)	132.48(7)
O(0A)−Y−N(1)	122.29(6)	O−Y−N(2)	92.00(6)
O(0A)−Y−N(2)	156.70(6)	N(1)−Y−N(2)	80.96(6)
N(2)−Y−C(12)	77.73(7)	C(7)−C(12)−Y	107.23(16)

Due to the difficulty in the isolation of the yttrium hydrido complex, we investigated its properties *in situ*. Excess isoprene

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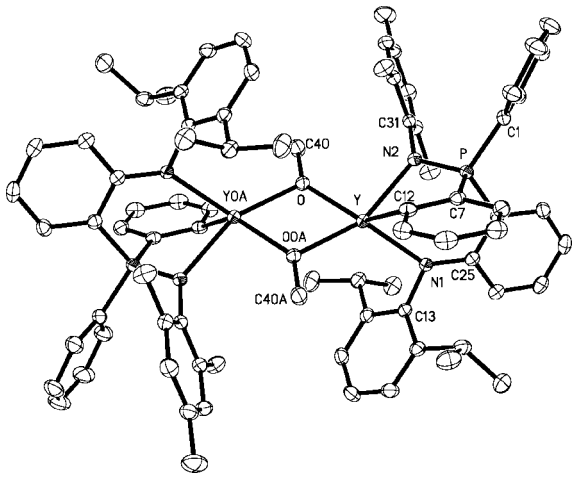


Figure 1. Molecular structure of **2** (hydrogen atoms omitted for clarity; thermal ellipsoids with 50% probability).

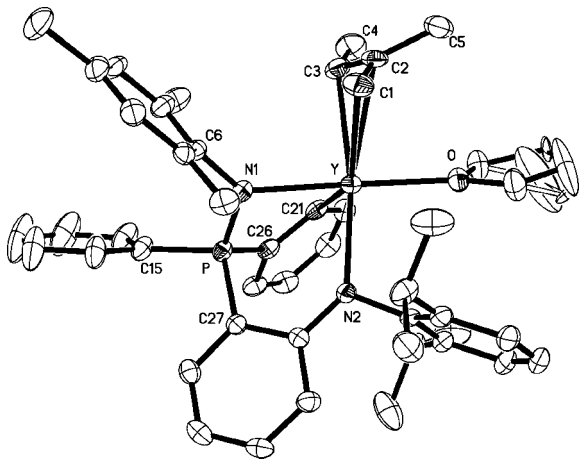


Figure 2. Molecular structure of **3** (hydrogen atoms omitted for clarity; thermal ellipsoids with 50% probability).

was added to the mixture of **1a** and phenylsilane to explore the coordination behavior of an isoprene molecule. Concentration of the reaction solution under reduced pressure followed by cooling to −30 °C gave white solids of complex **3**. The solid-state structure of **3** determined by X-ray analysis (Stable 1) has proved that one isoprene molecule inserts into a Y−H bond. The resultant pentenyl unit adopts a *syn*-form coordinating to the Lu ion in a η^3-mode via atoms C(1) and C(3) (Figure 2). The bond angle of C(1)−Y−C(3) (55.53(13)°) is in agreement with a η^3-coordination mode. The C(2)−C(3) bond length of 1.362(5) Å, which is close to that of a C═C double bond (1.34 Å), indicates that the Y−H species reacts via 1,4-addition with the isoprene molecule. According to Evans' group's result that in the ^{1}H NMR spectrum of Cp*Sm(η^3-$CH_2CHCHCH_3$) the separate signals of the allyl moiety are assigned to the *syn* and *anti* protons,[7i] the newly formed pentenyl moiety of complex **3** gave two sets of signals that could also be attributed to the *syn*-π-allylic and *anti*-π-allylic isomers (Scheme 2). The methylene protons of *syn*- and *anti*-$CH_2C(CH_3)CHCH_3$ showed two different doublets at 0.75 and 0.62 ppm (^2J(Y,H) = 6.4 Hz), respectively, with an intensity ratio of 3:1. This indicates that the *anti*-isomer is less stable than the *syn*-isomer due to steric repulsion, which is consistent with the DFT calculation on the

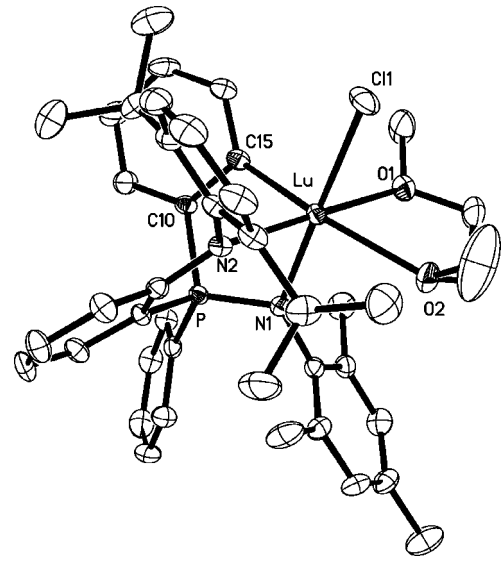
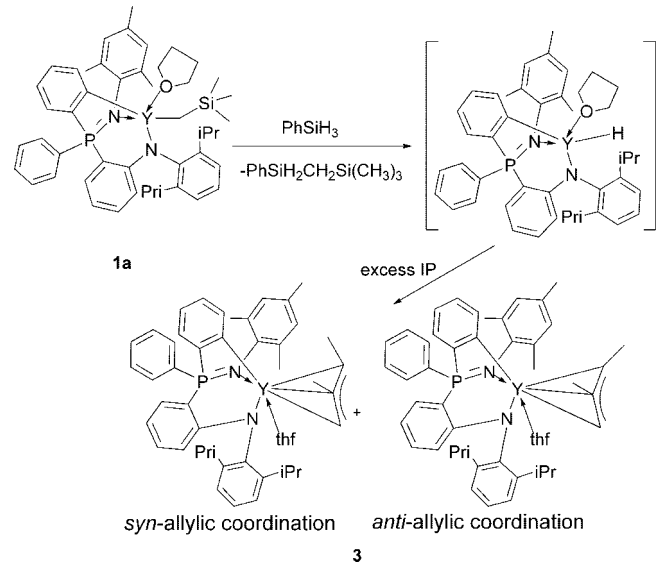


Figure 3. Molecular structure of **4** (hydrogen atoms omitted for clarity; thermal ellipsoids with 50% probability).

Scheme 2. Preparation of Complex 3



anti- and *syn*-π-allylic isomers of Cp*Sm(η^3-$CH_2CHCHCH_3$).[15] The CNN tridentate ligand, the *syn*-pentenyl moiety, and a THF molecule form a twisted trigonal-bipyramidal geometry around the central metal with atoms C(21), N(1), and O in equatorial and the pentenyl moiety and N(2) in axial positions. The bond length of Y−C(1) (2.496(4) Å) is slightly shorter than those of Y−C(2) (2.715(3) Å) and Y−C(3) (2.702(4) Å), which are close to the values in the literature.[16] The bond angle of C(1)−C(2)−C(3) (121.1(4)°) is smaller than that in [Y(η^3-C_3H_5)$_3$(μ-$C_4H_8O_2$)]$_\infty$ (126.4(7)°).[16a] The pentenyl group is nearly coplanar with C(4) and C(5), lying 0.05 and 0.17 Å above the C(1)C(2)C(3) plane, respectively (Table 2).

Synthesis and Reactivity of the Lutetium Cationic Complex. Addition of equimolar [Ph_3C][$B(C_6F_5)_4$]·LiCl[17] to a toluene solution of **1b** gradually afforded a white precipitate.

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Table 2. Selected Bond Lengths and Bond Angles of Complex 3

Bond Lengths (Å)			
Y−N(1)	2.322(3)	Y−N(2)	2.361(3)
Y−O	2.364(2)	Y−C(21)	2.443(3)
Y−C(1)	2.496(4)	Y−C(2)	2.715(3)
Y−C(3)	2.702(4)	C(1)−C(2)	1.426(5)
C(2)−C(3)	1.362(5)	C(3)−C(4)	1.519(5)
C(21)−C(26)	1.409(5)		
Bond Angles (deg)			
N(1)−Y−C(21)	76.60(10)	O−Y−C(21)	97.42(10)
N(1)−Y−O	174.01(8)	C(1)−Y−C(3)	55.53(13)
C(3)−C(2)−C(1)	121.1(4)	C(26)−C(21)−Y	108.1(2)
N(1)−Y−N(2)	82.71(9)	N(2)−Y−O	97.68(8)
N(2)−Y−C(21)	89.87(10)	C(2)−C(3)−C(4)	125.9(4)
N(2)−Y−C(2)	159.09(10)		

Filtration and removal of the volatiles left a yellow oil, which was dissolved in DME/hexane to afford colorless crystals of **4**, which were characterized by X-ray analysis as the lutetium chloride LLuCl(DME). The proposed reaction pathway was that, first, complex **1b** reacted with $[Ph_3C][B(C_6F_5)_4]$ to afford the cationic intermediate **A**, $[LLu(DME)]^+[B(C_6F_5)_4]^-$, which transformed into **4** via metathesis reaction with LiCl (Scheme 3). This was proved further by the fact that the white precipitates were $[Li(DME)_3]^+[B(C_6F_5)_4]^-$, confirmed by X-ray analysis (SFigure 1). To the best of our knowledge, this represents the first reaction between rare-earth metal cationic species and inorganic salts, although Evans' group had reported the reaction of $[Sm(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}Ph)_2BPh_2]$ with alkyl lithium or potassium to afford bis(pentamethylcyclopentadienyl) rare-earth metal alkyl complexes.[18] The ^{13}C NMR spectrum analysis indicated that the $Ln-C_{phenyl}$ bond remained untouched by giving a typical downfield shift at 202.56 ppm. The auxiliary ligands adopt bipyramidal geometry around the metal center (Figure 3 and STable 1). Atoms N(2), C(15), O(1), and O(2) are equatorial, with Lu lying 0.2491 Å below the plane, while atoms Cl(1) and N(1) are located at the axial positions. The bond length Lu−Cl(1) (2.5339(10) Å) (Table 3) is slightly shorter than 2.619 Å (av) for $Ln-Cl_{terminal}$ given in the literature due to the lesser steric environment around the Cl(1) atom.[19]

Reaction of Lutetium Monoalkyl Complex with Trimethyl Aluminum. Our group has found that in some cases rare-earth metal alkyl complexes activated by a perfluorinated tetraphenylborate counterion, such as $[Ph_3C][B(C_6F_5)_4]$, were inert to the polymerization of dienes. Upon addition of AlR_3, the ternary system showed versatile activities depending on the molar ratio of [Al]/[Ln].[20] Moreover, the sterics of the R group influenced the regioselectivity.[4c,6d,g] These results prompted us to probe the reaction between rare-earth metal alkyl complexes and aluminum trialkyls. Treatment of a THF solution of **1b** by excess $AlMe_3$ (ca. 10 equiv) gave a methyl-terminated counterpart, **5**. The procedure might be depicted as shown in Schemes 4 and 5. Trimethyl aluminum coordinates to the metal center by extruding a THF molecule to afford complex **B**.[21] The methylene protons of $LuCH_2Si(CH_3)_3$ in **B** give one signal at −0.35 ppm, which is different from the AB spin system with signals at −0.78 and −0.87 ppm found in the precursor **1b**.[13] The formation of **B** from **1b** is reversible. Complex **B** is cleaved by the electron donor THF to give complex **5** as the major product. This behavior was similar to that of $[Me_2Si(2\text{-}Me\text{-}C_9H_5)_2]Y[(\mu\text{-}Me)(\mu\text{-}^i Bu)Al^i Bu_2]$ decomposing to $[Me_2Si(2\text{-}Me\text{-}C_9H_5)_2]YMe(THF)$ and $[Me_2Si(2\text{-}Me\text{-}C_9H_5)_2]Y^i Bu(THF)$ in THF (ca. 6:1 molar ratio).[22] $LuCH_3$ shows a singlet at a relatively upfield position (−0.65 ppm) in contrast to that of the bridging methyl in $(NCN^{dipp})Y[(\mu\text{-}Me)_2AlMe_2]_2$ (0.02 ppm)[6e] and $\{[\kappa^3\text{-}1\text{-}(NDipp)\text{-}2\text{-}(PPh(C_6H_4)=NDipp)C_6H_4]ScMe\}_2$ (0.50 ppm).[23] This result is consistent with the X-ray diffraction analysis, where the methyl group of complex **5** coordinates to the metal center in a terminal mode (STable 1 and Table 4). The auxiliary ligand adopts a distorted octahedral geometry around the metal center. Atoms C(1), O(1), C(35), and N(1) are equatorial, while atoms O(2) and N(2) are located at the axial positions. The bond length of Lu−C(1) (2.444(6) Å) is longer than that in the analogous scandium dimethyl complex (av 2.343 Å), owing to the large radius of the Lu ion.[24]

Reaction of Lutetium Monoalkyl Complex with Phenylacetylene. Rare-earth metal aryl complexes have been covered in the recent literature;[25] however, their reactivities have been less explored. According to the structures of **2**, **3**, and **5**, we concluded that the weak Lewis acid, such as $PhSiH_3$ and $AlMe_3$, did not react with the metal phenyl group in complexes **1**. Thus, complex **1b** was treated with a relatively strong Lewis acid, phenylacetylene, to give complex **6**. Obviously, the $Lu-C_{phenyl}$ bond was cleaved by phenylacetylene due to the absence of the resonance for a metal phenyl carbon at ca. 200 ppm. X-ray analysis confirmed that complex **6** is a monomeric lutetium bis(alkynyl) complex, which, to the best of our knowledge, represents the first non-Cp-ligated monomeric bis(alkynyl) lanthanide. Complex **6** crystallizes in a triclinic unit cell (STable 1) with the ligands adopting a distorted octahedral geometry around the Lu atom (Figures 4 and 5). The acetylide groups are located at apexes forming a larger C−Lu−C angle (155.1(2)°) in contrast to that (106.8(2)°) in the Cp-ligated monomeric lutetium bis(acetylide), where the acetylide groups construct the equator of a square-bipyramid. The acetylide bond lengths Lu(1)−C(1) and Lu(1)−C(9) (2.395(6) and 2.424(6) Å) are close to those (av 2.39 Å) in $[Cp^*Lu(CCPh)_2(bipy)(py)]$.[26] The triple-bond distances C(1)−C(2) of 1.199(9) and C(9)−C(10) of 1.204(9) Å are comparable to the literature values (av 1.209 Å) (Table 5).[26,27]

Conclusion

A yttrium mono(alkyl) complex stabilized by an anilido-phosphinimine ligand reacted with $PhSiH_3$ to afford the hydrido intermediate. The hydrido group shows strong nucleophilicity and attacks the methylene carbon of DME accompanied by the

(17) The synthesis procedure of $[Ph_3C][B(C_6F_5)_4]\cdot LiCl$ was included in the Supporting Information.

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Scheme 3. Preparation of Complex 4

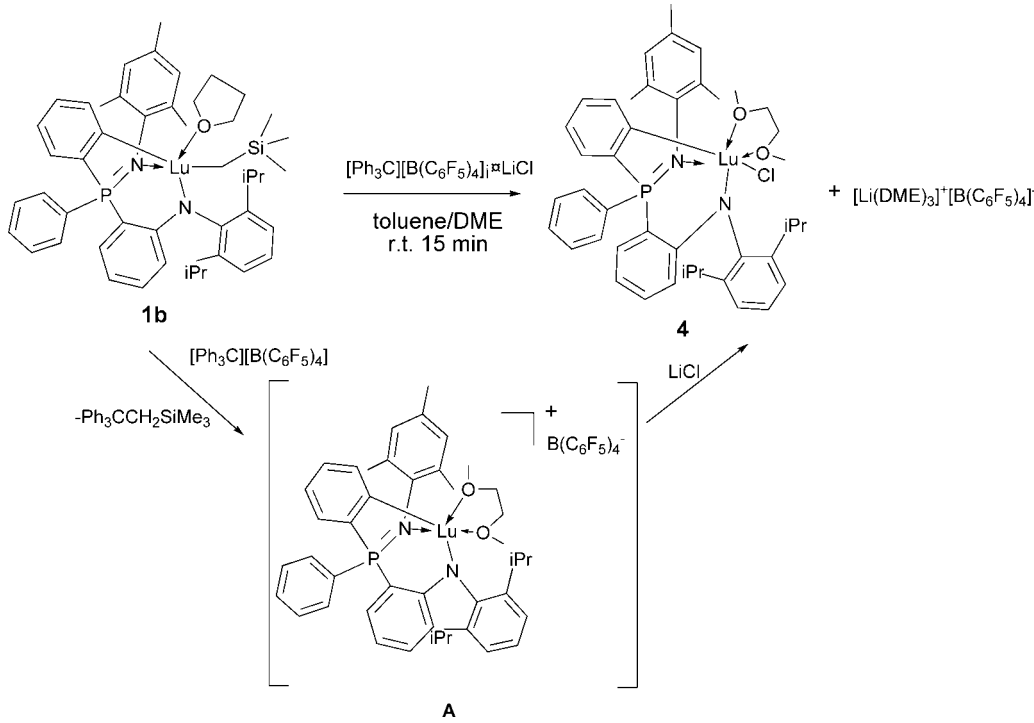


Table 3. Selected Bond Lengths and Bond Angles of Complex 4.

	Bond Lengths (Å)		
Lu−N(1)	2.276(3)	Lu−N(2)	2.285(3)
Lu−O(1)	2.417(3)	Lu−O(2)	2.378(3)
Lu−Cl(1)	2.5339(10)	Lu−C(15)	2.359(4)
C(10)−C(15)	1.417(5)	P−C(10)	1.807(3)
	Bond Angles (deg)		
O(2)−Lu−O(1)	67.73(10)	C(15)−Lu−O(1)	85.29(11)
N(2)−Lu−C(15)	90.54(11)	N(2)−Lu−O(2)	115.16(10)
N(2)−Lu−Cl(1)	98.62(7)	N(1)−Lu−N(2)	84.85(10)
C(15)−Lu−Cl(1)	99.80(9)	N(1)−Lu−C(15)	78.57(11)
C(10)−C(15)−Lu	112.6(2)	O(1)−Lu−Cl(1)	86.76(7)
O(2)−Lu−Cl(1)	91.26(8)	O(1)−Lu−N(1)	89.68(10)
O(2)−Lu−N(1)	88.61(10)	N(1)−Lu−Cl(1)	176.21(7)
O(1)−Lu−N(2)	173.70(10)	C(15)−Lu−O(2)	150.25(11)

cleavage of a C−O bond, leading to the formation of a methoxy-bridged complex, while isoprene insertion into the metal hydride group gives a η^3-pentenyl complex via 1,4-addition. The lutetium mono(alkyl) analogue reacted with $[Ph_3C][B(C_6F_5)_4]\cdot$ LiCl and $AlMe_3$ to afford the corresponding rare-earth metal chloride and methyl complexes, respectively. In these processes the metal−C_{phenyl} bonds have survived. However, treatment of lutetium mono(alkyl) complex with PhC≡CH generated a relatively strong Lewis acid, the first non-Cp-ligated monomeric lanthanide bis(alkynyl), via metathesis reaction between phenylacetylene and metal-alkyl and the cleavage of the metal−C_{phenyl} bond.

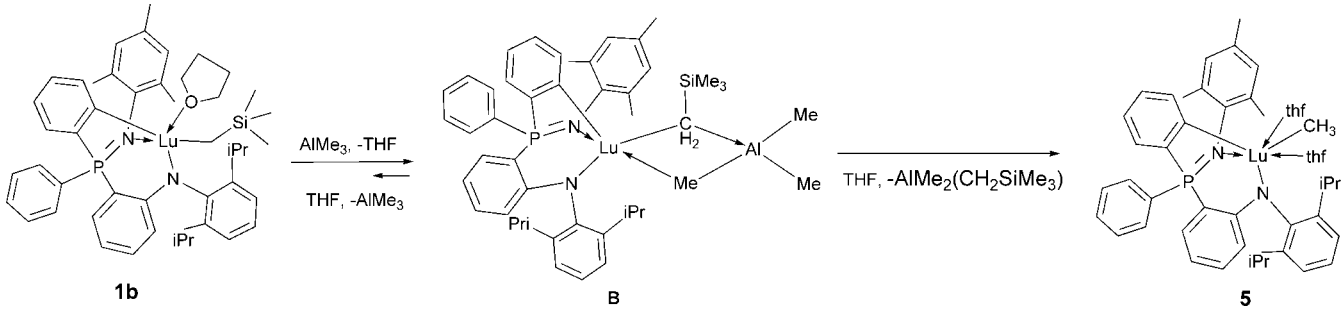
Experimental Section

General Methods. All reactions were carried out under a dry and oxygen-free argon atmosphere using Schlenk techniques or in a glovebox. Solvents were purified by a MBraun SPS system. All starting materials were purchased from Aldrich or Fluka and distilled before use. Syntheses of rare earth metal alkyl complexes, LLn($CH_2Si(CH_3)_3$)(THF) (L = *o*-(2,6-$C_6H_3{}^iPr_2$)$NC_6H_4P(C_6H_5)(C_6H_4)$-N(2,4,6-$C_6H_2Me_3$), **1a**, Ln = Y; **1b**, Ln = Lu),[5a] were carried out according to the literature.

Instruments and Measurements. Organometallic samples for NMR spectroscopic measurements were prepared in a glovebox. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^1H; 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by $^1H-^1H$ (COSY) and $^1H-^{13}C$ (HMQC) experiments when necessary. Crystals for X-ray analysis were obtained as described in the Experimental Section. The crystals were manipulated in a glovebox. Data collections were performed at −86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation (λ = 0.71073 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 the SHELXTL program. CCDC-678678 (**2**), 6678679 (**3**), 678677 (**4**), 678676 (**5**), and 678675 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry.

Yttrium Methoxy Complex 2. To a DME solution of complex **1a** (0.15 g, 0.18 mmol), LY($CH_2Si(CH_3)_3$)(THF), was added phenylsilane (0.04 g, 0.37 mmol) in DME (1 mL). After 1 h, the reaction mixture was concentrated to 0.5 mL under reduced pressure, then diluted with hexane (1 mL). The solution was cooled to −30 °C for several days to give white solids of complex **2**, $[LY(\mu\text{-}OCH_3)]_2$ (0.09 g, 73%). Crystals for X-ray analysis were obtained through recrystallization from benzene/hexane at room temperature. ^1H NMR(400 MHz, [D6]benzene, 25 °C): δ 0.62(d, ^2J(H, H) = 6.8 Hz, 3H, NC_6H_3-($CH(CH_3)_2$)$_2$), 0.73(d, ^2J(H, H) = 6.8 Hz, 3H, NC_6H_3(CH-(CH_3)$_2$)$_2$), 1.45(d, ^2J(H, H) = 6.8 Hz, 3H, $NC_6H_3(CH(CH_3)_2)_2$), 1.92(d, ^2J(H, H) = 6.4 Hz, 3H, $NC_6H_3(CH(CH_3)_2)_2$), 1.95(m, 1H, $NC_6H_3(CH(CH_3)_2)_2$), 2.03(s, 3H, $NC_6H_2(CH_3)_3$), 2.14(s, 3H, $NC_6H_2(CH_3)_3$), 2.57(s, 3H, $NC_6H_2(CH_3)_3$), 2.66(s, 3H, $YOCH_3$), 3.70(m, 1H, $NC_6H_3(CH(CH_3)_2)_2$), 6.33(dd, ^3J(H,H) = 8.0 Hz, ^4J(H,P) = 6.0 Hz, 1H, *o*-YC_6H_4P), 6.55(td, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 2.8 Hz, 1H, *m*-PC_6H_4Y), 6.60(s, 1H, *m*-$NC_6H_2Me_3$), 6.87(s, 1H, *m*-$NC_6H_2Me_3$), 6.95(td, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.8 Hz, 2H, *m*-PC_6H_5), 7.00(dd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.6 Hz, 1H, *m*-$NC_6H_3{}^iPr_2$),7.06(m, 1H, *p*-PC_6H_5, 1H, *p*-PC_6H_4Y), 7.20(m, 1H, *p*-$NC_6H_3{}^iPr_2$, 1H, *m*-PC_6H_4N), 7.34(t, ^3J(H,H) = 7.2 Hz, 1H,

Scheme 4. Metathetic Reaction between Complex 1b and $AlMe_3$



Scheme 5. Preparation of Complex 6

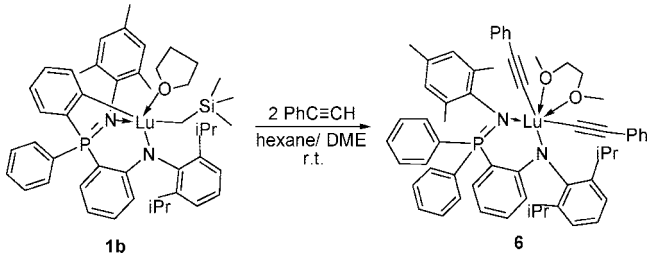


Table 4. Selected Bond Lengths and Bond Angles of Complex 5

	Bond Lengths (Å)		
Lu−N(1)	2.325(5)	Lu−N(2)	2.270(5)
Lu−O(1)	2.432(5)	Lu−O(2)	2.350(4)
C(1)−Lu	2.444(6)	C(35)−Lu	2.477(7)
C(35)−C(40)	1.396(9)	C(40)−P	1.812(6)
	Bond Angles (deg)		
N(2)−Lu−C(35)	77.04(19)	N(2)−Lu−N(1)	84.27(17)
N(1)−Lu−C(35)	88.1(2)	O(1)−Lu−C(1)	83.2(2)
O(2)−Lu−O(1)	81.09(19)	O(2)−Lu−C(1)	92.0(2)
N(2)−Lu−C(1)	93.5(2)	N(1)−Lu−O(2)	96.79(17)
C(40)−C(35)−Lu	108.1(4)	O(1)−Lu−C(35)	82.1(2)
O(2)−Lu−C(35)	96.95(19)	N(2)−Lu−O(1)	96.8(2)
N(1)−Lu−C(1)	107.09(19)	N(1)−Lu−O(1)	169.59(18)
N(2)−Lu−O(2)	173.89(16)	C(35)−Lu−C(1)	161.4(2)

p-PC_6H_4N), 7.41(dd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.6 Hz, 1H, *m*-$NC_6H_3{}^i Pr_2$), 7.53(dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 1.6 Hz, 1H, *o*-PC_6H_4Y), 7.63(d, ^3J(H,H) = 7.2, 1H, *o*-PC_6H_4N), 7.73(d, ^3J(H,H) = 7.2 Hz, 1H, *o*-PC_6H_5), 7.76(d, ^3J(H,H) = 7.2 Hz, 1H, *o*-PC_6H_5), 8.05 ppm (d, ^3J(H,H) = 7.1 Hz, 1H, *o*-NC_6H_4P). ^{13}C NMR (400 MHz, [D6]benzene, 25 °C): δ 20.19(s, 1C, *p*-$NC_6H_2(CH_3)_3$), 21.24(s, 1C, *o*-$NC_6H_2(CH_3)_3$),22.14(s, 1C, *o*-$NC_6H_2(CH_3)_3$), 24.70(s, 1C, $NC_6H_3(CH(CH_3)_2)_2$), 25.54(s, 1C, $NC_6H_3(CH(CH_3)_2)_2$), 25.76(s, 1C, $NC_6H_3(CH(CH_3)_2)_2$), 27.25(s, 1C, $NC_6H_3(CH(CH_3)_2)_2$), 27.83(s, 1C, $NC_6H_3(CH(CH_3)_2)_2$), 30.86(s, 1C, $NC_6H_3(CH(CH_3)_2)_2$), 50.46(s, 1C, $YOCH_3$), 113.48(d, ^3J(C,P) = 12 Hz, 1C, *m*-PC_6H_4Y), 114.07(s, 1C, *o*-$NC_6H_3{}^i Pr_2$), 115.02(s, 1C, *o*-$NC_6H_3{}^i Pr_2$), 117.32 (d, ^3J(C,P) = 8 Hz, 1C, *o*-YC_6H_2P), 124.28(s, 1C, *p*-$NC_6H_3{}^i Pr_2$), 125.08, 125.26(s, 1C, *o*-PC_6H_4Y, 1C, *p*-PC_6H_4N), 126.65, 126.93(s, 2C, *m*-$NC_6H_3{}^i Pr_2$), 128.00(overlap, 1C, *m*-PC_6H_4N), 129.00, 129.26, 129.57(s, 1C, *m*-$NC_6H_2Me_3$, 1C, *p*-PC_6H_5, 1C, *p*-PC_6H_4Y), 131.65, 132.04, 132.15, 132.30(s, 2C, *m*-PC_6H_5, 1C, *m*-$NC_6H_2Me_3$, 1C, *o*-PC_6H_4N), 132.87(s, 1C, *p*-$NC_6H_2Me_3$), 134.74(s, 1C, *o*-PC_6H_5), 134.81(s, 1C, *o*-PC_6H_5), 135.41(d, ^3J(C,P) = 5 Hz, 1C, *o*-$NC_6H_2Me_3$), 136.46(d, ^3J(C,P)=6 Hz, 1C, *o*-$NC_6H_2Me_3$), 137.25(s, 1C, *o*-NC_6H_4P), 137.48(s, 1C, *ipso*-PC_6H_4N), 141.46(s, 1C, *ipso*-NC_6H_4P), 144.69(d, ^1J(C,P) = 9 Hz, 1C, *ipso*-PC_6H_4Y), 145.41(s, 1C, *ipso*-$NC_6H_3{}^i Pr_2$), 150.25(s, 1C, *ipso*-$NC_6H_2Me_3$), 159.88(d, ^1J(C,P) = 5 Hz, 1C, *ipso*-PC_6H_5), 197.06 ppm

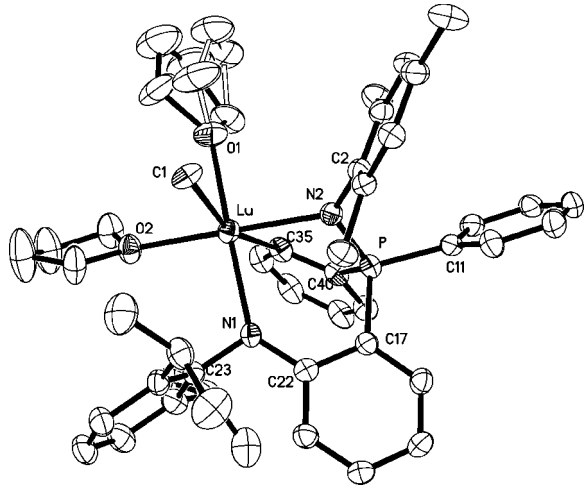


Figure 4. Molecular structure of **5** (hydrogen atoms omitted for clarity; thermal ellipsoids with 50% probability).

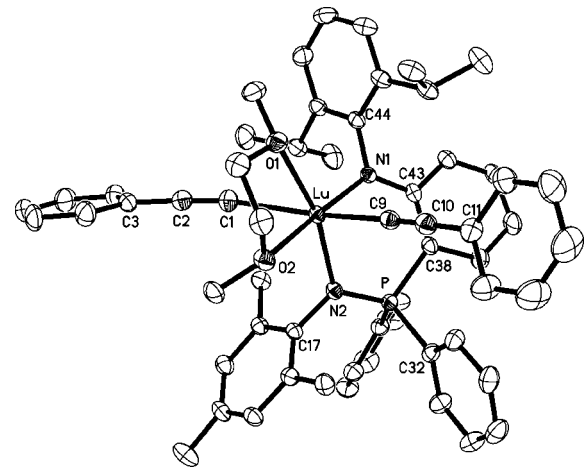


Figure 5. Molecular structure of **6** (hydrogen atoms omitted for clarity; thermal ellipsoids with 50% probability).

Table 5. Selected Bond Lengths and Bond Angles of Complex 6

	Bond Lengths (Å)		
Lu−N(1)	2.253(4)	Lu−N(2)	2.259(5)
Lu−C(1)	2.395(6)	Lu−C(9)	2.424(6)
Lu−O(1)	2.469(4)	Lu−O(2)	2.421(4)
C(1)−C(2)	1.199(9)	C(2)−C(3)	1.442(9)
C(9)−C(10)	1.204(9)	C(10)−C(11)	1.443(9)
	Bond Angles (deg)		
N(1)−Lu−O(1)	109.31(15)	O(2)−Lu−O(1)	69.92(14)
N(2)−Lu−O(2)	95.17(15)	N(1)−Lu−N(2)	85.97(16)
C(1)−Lu−C(9)	155.1(2)	C(2)−C(1)−Lu	166.9(5)
C(10)−C(9)−Lu	175.9(5)	C(1)−C(2)−C(3)	176.4(7)
C(9)−C(10)−C(11)	179.0(7)	C(9)−Lu−O(1)	83.13(17)
C(9)−Lu−O(2)	79.87(17)	C(9)−Lu−N(1)	95.15(17)
C(9)−Lu−N(2)	99.42(18)	C(1)−Lu−O(1)	75.63(18)
C(1)−Lu−O(2)	80.71(18)	C(1)−Lu−N(1)	103.98(18)
C(1)−Lu−N(2)	97.71(19)	N(2)−Lu−O(1)	164.32(15)
N(1)−Lu−O(2)	175.01(15)		

(d, ^1J(C,Y) = 36 Hz, 1C, *ipso*-YC_6H_4P). Anal. Calcd for $C_{80}H_{98}N_4O_2P_2Y_2$: C, 69.26; H, 7.12; N, 4.04. Found: C, 69.25; H, 7.10; N, 4.03.

Yttrium Pentenyl Complex 3. Phenylsilane (0.03 g, 0.27 mmol) in toluene (1 mL) was dropwise added into a toluene solution of **1a** (0.12 g, 0.15 mmol), LY($CH_2Si(CH_3)_3$)$_2$(THF). After 1 h, isoprene (0.68 g, 10 mmol) was added to the above solution. AFter stirring for 6 h at room temperature, the reaction mixture was concentrated to 0.5 mL under reduced pressure, then diluted with hexane (1 mL). The solution was cooled at −30 °C for several days to give white solids of complex **3** (0.08 g, 71%), LLn($CH_2C(CH_3)$═$CHCH_3$)(THF). Recrystallization from benzene/hexane at room temperature afforded crystals that were good enough for X-ray analysis. ^{1}H NMR (400 MHz, [D6]benzene, 25 °C): δ 0.62(d, ^2J(Y,H) = 6.4 Hz, 2H, *anti*-C*H*$_2$C(CH_3)═$CHCH_3$), 0.75(d, ^2J(Y,H) = 6.4 Hz, 2H, *syn*-C*H*$_2$C(CH_3)═$CHCH_3$), 1.34(br, 4H, THF), 1.44(d, ^3J(H,H) = 6.8 Hz, 3H, NC_6H_3(CH(C*H*$_3$)$_2$)$_2$), 1.46(d, ^3J(H,H) = 7.2 Hz, 3H, NC_6H_3-(CH(C*H*$_3$)$_2$)$_2$), 1.54(d, ^3J(H,H) = 7.2 Hz, 3H, NC_6H_3-(CH(C*H*$_3$)$_2$)$_2$), 1.62(d, ^3J(H,H) = 7.2 Hz, 3H, NC_6H_3(CH(C*H*$_3$)$_2$)$_2$), 1.95(s, 3H, *syn*-$CH_2C(CH_3)$═$CHCH_3$), 2.05(s, 3H, *anti*-$CH_2C(CH_3)$═$CHCH_3$) 2.11(d, ^3J(H,H) = 2.4 Hz, 3H, *anti*-$CH_2C(CH_3)$═$CHCH_3$), 2.14(d, ^3J(H,H) = 2.0 Hz, 3H, *syn*-$CH_2C(CH_3)$═$CHCH_3$), 2.23(multi, 1H, *syn*-$CH_2C(CH_3)$═$CHCH_3$), 2.33(multi, 1H, *anti*-$CH_2C(CH_3)$═$CHCH_3$), 2.66(s, 3H, *p*-$C_6H_2(CH_3)_3$), 2.79(s, 6H, *o*-$C_6H_2(CH_3)_3$), 3.44(br, 4H, THF), 3.78(multi, 1H, NC_6H_3(C*H*(CH_3)$_2$)$_2$), 4.42(multi, 1H, NC_6H_3(C*H*(CH_3)$_2$)$_2$), 6.26(dd, ^3J(H,H) = 8.0 Hz, ^3J(H,Y) = 6.0 Hz, 1H, *syn-o*-YC_6H_4P), 6.33(dd, ^3J(H,H) = 8.0 Hz, ^3J(H,Y) = 6.0 Hz, 1H, *anti-o*-YC_6H_4P), 6.48(td, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 2.8 Hz, 1H, *m*-PC_6H_4Y), 6.57(s, 1H, *m*-$NC_6H_2Me_3$), 6.87(s, 1H, *m*-$NC_6H_2Me_3$), 6.93(td, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.8 Hz, 2H, *m*-PC_6H_5), 7.01(dd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.6 Hz, 1H, *m*-$NC_6H_3{}^i$Pr$_2$), 7.05(m, 1H, *p*-PC_6H_5, 1H, *p*-PC_6H_4Y), 7.22(m, 1H, *p*-$NC_6H_3{}^i$Pr$_2$, 1H, *m*-PC_6H_4N), 7.31(t, ^3J(H,H) = 7.2 Hz, 1H, *p*-PC_6H_4N), 7.42(dd, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.6 Hz, 1H, *m*-$NC_6H_3{}^i$Pr$_2$), 7.54−7.73(m, 1H, *o*-PC_6H_4Y, 1H, *o*-PC_6H_4N, 1H, *o*-PC_6H_5), 7.80(d, ^3J(H,H) = 7.2 Hz, 1H, *o*-PC_6H_5), 8.27(d, ^3J(H,H) = 7.2 Hz, 1H, *syn-o*-NC_6H_4P), 8.43 ppm (d, ^3J(H,H) = 6.8 Hz, 1H, *anti-o*-NC_6H_4P). Anal. Calcd for $C_{48}H_{58}N_2OPLu$ C, 65.15; H, 6.61; N, 3.17. Found: C, 65.13; H, 6.60; N, 3.16.

Lutetium Chloro Complex 4. $[Ph_3C][B(C_6F_5)_4]$·LiCl (0.13 g, 0.13 mmol) in 2 mL of DME was added to a toluene solution of complex **1b** (0.12 g, 0.13 mmol). After 30 min, filtration afforded a white solid, which was $[Li(DME)_3]^+[B(C_6F_5)_4]^-$, confirmed by X-ray analysis. Removal of the volatiles of the filtrate left a yellow oil, which was diluted by hexane/DME. The mixture was kept at −30 °C for several days to afford complex **4**, LLuCl(DME) (0.10 g, 90%), as colorless crystals. ^{1}H NMR(400 MHz, [D6]benzene, 25 °C): δ 0.74(d, ^2J(H, H) = 6.8 Hz, 3H, NC_6H_3(CH(C*H*$_3$)$_2$)$_2$), 1.49(d, ^2J(H, H) = 6.8 Hz, 3H, NC_6H_3(CH(C*H*$_3$)$_2$)$_2$), 1.50(d, ^2J(H, H) = 6.8 Hz, 3H, NC_6H_3(CH(C*H*$_3$)$_2$)$_2$), 1.67(d, ^2J(H, H) = 6.8 Hz, 3H, NC_6H_3(CH(C*H*$_3$)$_2$)$_2$), 1.90(s, 3H, $NC_6H_2(CH_3)_3$), 2.16(s, 3H, $NC_6H_2(CH_3)_3$), 2.61(multi, 1H, NC_6H_3(C*H*(CH_3)$_2$)$_2$), 2.71(s, 3H, $NC_6H_2(CH_3)_3$), 3.06(br, 4H, (CH_3OCH_2)$_2$), 3.19(s, 6H, (CH_3OCH_2)$_2$), 4.01(multi, 1H, NC_6H_3(C*H*(CH_3)$_2$)$_2$), 6.35(dd, ^3J(H,H) = 8.4 Hz, ^3J(H,Lu) = 6.4 Hz, 1H, *o*-YC_6H_4P), 6.44(td, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 2.8 Hz, 1H, *m*-PC_6H_4Y), 6.52(s, 1H, *m*-$NC_6H_2Me_3$), 6.86(s, 1H, *m*-$NC_6H_2Me_3$), 6.95−7.05(mutil, 1H, *m*-$NC_6H_3{}^i$Pr, 2H, *m*-PC_6H_5, 1H, *p*-PC_6H_5,), 7.24(t, ^3J(H,H) = 7.6 Hz, 1H, *p*-PC_6H_4Y), 7.36−7.54(m, 1H, *p*-$NC_6H_3{}^i$Pr$_2$, 1H, *m*-PC_6H_4N, 1H, *p*-PC_6H_4N, 1H, *m*-$NC_6H_3{}^i$Pr$_2$, 1H, *o*-PC_6H_4Y), 7.68(dd, ^3J(H,H) = 8.4 Hz, ^3J(H,P) = 8.4 Hz,1H, *o*-PC_6H_4N), 7.88(d, ^3J(H,H) = 7.2 Hz, 1H, *o*-PC_6H_5), 7.90(d, ^3J(H,H) = 7.2 Hz, 1H, *o*-PC_6H_5), 8.51 ppm (d, ^3J(H,H) = 6.8 Hz, 1H, *o*-NC_6H_4P). ^{13}C NMR (400 MHz, [D6]benzene, 25 °C): δ 20.46(s, 1C, $NC_6H_2(CH_3)_3$), 21.14(s, 1C, $NC_6H_2(CH_3)_3$), 21.25(s, 1C, $NC_6H_2(CH_3)_3$), 24.93(s, 1C, NC_6H_3(CH(*C*H$_3$)$_2$)$_2$), 25.12(s, 1C, NC_6H_3(CH(*C*H$_3$)$_2$)$_2$), 26.33(s, 1C, NC_6H_3(CH(*C*H$_3$)$_2$)$_2$), 27.32(s, 1C, NC_6H_3(CH(*C*H$_3$)$_2$)$_2$), 28.69(s, 1C, NC_6H_3(*C*H(CH$_3$)$_2$)$_2$), 29.40(s, 1C, NC_6H_3(*C*H(CH$_3$)$_2$)$_2$), 59.23(s, 1C, (CH_3OCH_2)$_2$), 62.53(s, 1C, (CH_3OCH_2)$_2$), 71.38(s, 1C, (CH_3OCH_2)$_2$), 72.40(s, 1C, (CH_3OCH_2)$_2$), 113.48(d, ^3J(C,P) = 12 Hz, 1C, *m*-PC_6H_4Y), 115.40(s, 1C, *o*-$NC_6H_3{}^i$Pr$_2$), 115.62(s, 1C, *o*-$NC_6H_3{}^i$Pr$_2$), 119.41 (d, ^3J(C,P) = 9 Hz, 1C, *o*-YC_6H_2P), 122.44(s, 1C, *p*-$NC_6H_3{}^i$Pr$_2$), 124.68, 125.84(s, 1C, *o*-PC_6H_4Y, 1C, *p*-PC_6H_4N), 126.34, 126.43(s, 2C, *m*-$NC_6H_3{}^i$Pr$_2$), 126.82(s, 1C, *m*-PC_6H_4N), 129.94, 130.25, 130.47(s, 1C, *m*-$NC_6H_2Me_3$, 1C, *p*-PC_6H_5, 1C, *p*-PC_6H_4Y), 131.20, 131.31, 132.22, 132.43(s, 2C, *m*-PC_6H_5, 1C, *m*-$NC_6H_2Me_3$, 1C, *o*-PC_6H_4N), 133.07(s, 1C, *p*-$NC_6H_2Me_3$), 133.17(s, 1C, *o*-PC_6H_5), 133.83(s, 1C, *o*-PC_6H_5), 134.83(d, ^3J(C,P) = 8 Hz, 1C, *o*-$NC_6H_2Me_3$), 136.84(d, ^3J(C,P) = 6 Hz, 1C, *o*-$NC_6H_2Me_3$), 137.76(s, 1C, *o*-NC_6H_4P), 139.63(s, 1C, *ipso*-PC_6H_4N), 139.86(s, 1C, *ipso*-NC_6H_4P), 145.33(s, 1C, *ipso*-PC_6H_4Y), 147.67(s, 1C, *ipso*-$NC_6H_3{}^i$Pr$_2$), 149.07(s, 1C, *ipso*-$NC_6H_2Me_3$), 161.24(d, ^1J(C,P) = 5 Hz, 1C, *ipso*-PC_6H_5), 202.56 ppm (d, ^1J(C,P) = 35 Hz, 1C, *ipso*-YC_6H_4P). Anal. Calcd for $C_{43}H_{51}N_2O_2PclLu$: C, 59.41; H, 5.91; N, 3.22. Found: C, 59.41; H, 5.92; N, 3.21.

Lutetium Methyl Complex 5. To a THF solution of complex **1b** (0.15 g, 0.17 mmol), LLu($CH_2Si(CH_3)_3$)(THF), was added $AlMe_3$ (0.12 g, 1.70 mmol) in THF (1 mL). After 2 h, the reaction mixture was concentrated to 0.5 mL under reduced pressure, then diluted with hexane (1 mL) followed by cooling to −30 °C, and kept for several days, giving white solids of complex **5**, LLu(CH_3)(THF)$_2$ (0.09 g, 60%). ^{1}H NMR (400 MHz, [D6]benzene, 25 °C): δ −0.65(s, 3H, LuC*H*$_3$), 0.80(d, ^3J(H,H) = 7.2 Hz, 6H, NC_6H_3(CH(C*H*$_3$)$_2$)$_2$), 1.49(br, 8H, THF), 1.34(d, ^3J(H,H) = 7.2 Hz, 6H, NC_6H_3(CH(C*H*$_3$)$_2$)$_2$), 2.32(s, 3H, $NC_6H_2(CH_3)_3$), 2.49(s, 3H, $NC_6H_2(CH_3)_3$), 2.58(s, 3H, $NC_6H_2(CH_3)_3$), 3.67(br, 8H, THF), 3.81(multi, 2H, NC_6H_3(C*H*(CH_3)$_2$)$_2$), 6.31(d, ^3J(H,H) = 8.0 Hz, 1H, *o*-LuC$_6$*H*$_4$P), 6.49(t, ^3J(H,H) = 7.2 Hz, 1H, *m*-PC_6H_4Lu), 6.72(s, 1H, *m*-$NC_6H_2Me_3$), 6.78(s, 1H, *m*-$NC_6H_2Me_3$), 6.93−6.99(multi, 2H, *m*-$NC_6H_3{}^i$Pr$_2$), 7.09(m, 1H, *p*-PC_6H_5, 1H, *p*-PC_6H_4Y), 7.20(m, 1H, *p*-$NC_6H_3{}^i$Pr$_2$, 1H, *m*-PC_6H_4N), 7.37(t, ^3J(H,H) = 7.2 Hz, 1H, *p*-PC_6H_4N), 7.43−7.53(multi, 1H, *o*-PC_6H_4Y, 2H, *m*-PC_6H_5), 7.56(d, ^3J(H,H) = 7.2, 1H, *o*-PC_6H_4N), 7.79(multi, 2H, *o*-PC_6H_5), 8.07 ppm (d, ^3J(H,H) = 7.1 Hz, 1H, *o*-NC_6H_4P). ^{13}C NMR (400 MHz, [D6]benzene, 25 °C): δ 20.13(s, 1C, $NC_6H_2(CH_3)_3$), 21.33(s, 1C, $NC_6H_2(CH_3)_3$), 21.92(s, 1C, $NC_6H_2(CH_3)_3$), 23.49(s, 2C, NC_6H_3(CH(*C*H$_3$)$_2$)$_2$), 24.63(s, 2C, NC_6H_3(CH(*C*H$_3$)$_2$)$_2$), 26.19(s, 4C, THF), 27.39(s, 1C, NC_6H_3(*C*H(CH$_3$)$_2$)$_2$), 29.78(s, 1C, NC_6H_3(*C*H(CH$_3$)$_2$)$_2$), 68.54(s, 4C, THF), 113.41(s, 1C, *m*-PC_6H_4Lu), 113.53(s, 1C, *o*-$NC_6H_3{}^i$Pr$_2$), 114.13(s, 1C, *o*-$NC_6H_3{}^i$Pr$_2$), 117.86(s, 1C, *o*-LuC_6H_2P), 123.71(s, 1C, *p*-$NC_6H_3{}^i$Pr$_2$), 124.90(s, 1C, *o*-PC_6H_4Lu), 125.40(, 1C, *p*-PC_6H_4N), 126.23(s, 2C, *m*-$NC_6H_3{}^i$Pr$_2$), 126.91(s, 1C, *m*-PC_6H_4N), 131.10, 131.67, 132.07(s, 1C, *m*-$NC_6H_2Me_3$, 1C, *p*-PC_6H_5, 1C, *p*-PC_6H_4Y), 132.39, 132.65, 132.80(s, 2C, *m*-PC_6H_5, 1C, *m*-$NC_6H_2Me_3$, 1C, *o*-PC_6H_4N), 134.10(s, 1C, *p*-$NC_6H_2Me_3$), 134.58(s, 2C, *o*-PC_6H_5), 134.86(s, 1C, *o*-$NC_6H_2Me_3$), 135.97(s, 1C, *o*-$NC_6H_2Me_3$), 137.83(s, 1C, *o*-NC_6H_4P), 139.74(s, 1C, *ipso*-PC_6H_4N), 139.92(s, 1C, *ipso*-NC_6H_4P), 143.43(s, 1C, *ipso*-PC_6H_4Lu), 147.50(s, 1C, *ipso*-$NC_6H_3{}^i$Pr$_2$), 148.34(s, 1C, *ipso*-$NC_6H_2Me_3$), 150.08(d, ^1J(C,P) = 5 Hz, 1C, *ipso*-PC_6H_5), 201.56 ppm (s, 1C, *ipso*-LuC_6H_4P). Anal. Calcd for $C_{48}H_{60}N_2O_2Plu$: C, 63.85; H, 6.70; N, 3.10. Found: C, 63.84; H, 6.68; N, 3.09.

Lutetium Bis(alkynyl) Complex 6. Phenylacetylene (0.03 g, 0.29 mmol) in DME (1 mL) was dropwise added into a DME solution of **1a** (0.13 g, 0.14 mmol), LLu($CH_2Si(CH_3)_3$)(THF). After stirring for 2 h at room temperature, the reaction mixture was concentrated to 0.5 mL under reduced pressure, then diluted with hexane (1 mL) followed by cooling at −30 °C for several days, to give red crystals of complex **6** (0.10 g, 66%), LLu(C≡CPh)$_2$(DME). ^{1}H NMR (400 MHz, [D6]benzene, 25 °C): δ 1.48(d, ^2J(H, H) = 6.8 Hz, 6H, NC_6H_3(CH(C*H*$_3$)$_2$)$_2$), 1.78(d, ^2J(H, H) = 6.8 Hz, 6H, NC_6H_3(CH(C*H*$_3$)$_2$)$_2$), 2.23(s, 3H, *p*-$NC_6H_2(CH_3)_3$), 2.35(s, 6H, *o*-$NC_6H_2(CH_3)_3$), 2.98(s, 6H, (CH_3OCH_2)$_2$), 3.42(br, 4H, (CH_3OCH_2)$_2$), 4.49(br, 2H, NC_6H_3(C*H*(CH_3)$_2$)$_2$), 6.25(dd, ^3J(H,H) = 8.0 Hz, ^3J(H,P) = 8.0 Hz, 1H, *o*-PC_6H_4N), 6.53(t, ^3J(H,H) = 6.8 Hz, *m*-NC_6H_4P), 6.87(s, 2H, *m*-$NC_6H_2Me_3$), 6.92(d, ^3J(H,H) = 7.2 Hz, *o*-NC_6H_4P),

7.03−7.11(m, 2H, *p*-C≡CC$_6H_5$, 2H, *p*-P(C$_6H_5$)$_2$, 4H, *m*-P(C$_6H_5$)$_2$, 1H, *p*-NC$_6H_4$P), 7.20(t, ^3J(H,H) = 7.6 Hz, 4H, *m*-C≡CC$_6H_5$), 7.43(t, ^3J(H,H) = 7.2 Hz, 1H, *p*-NC$_6H_3$^{i}Pr$_2$), 7.52−7.58(m, 4H, *o*-C≡CC$_6H_5$, 2H, *m*-NC$_6H_3$^{i}Pr$_2$), 8.03(d, ^3J(H,H) = 7.6 Hz, 2H, *o*-PC$_6H_5$), 8.06 ppm (d, ^3J(H,H) = 7.6 Hz, 2H, *o*-PC$_6H_5$). ^{13}C NMR (400 MHz, [D6]benzene, 25 °C): δ 21.33(s, 1C, *p*-NC$_6$H$_2$(*C*H$_3$)$_3$), 21.40(s, 2C, *o*-NC$_6$H$_2$(*C*H$_3$)$_3$), 25.22(s, 2C, NC$_6$H$_3$(CH(*C*H$_3$)$_2$)$_2$), 27.08(s, 2C, NC$_6$H$_3$(CH(*C*H$_3$)$_2$)$_2$), 29.21(s, 2C, NC$_6$H$_3$(*C*H(CH$_3$)$_2$)$_2$), 60.47(s, 2C, (*C*H$_3$OCH$_2$)$_2$), 72.29(s, 2C, (CH$_3$O*C*H$_2$)$_2$), 106.83(s, 2C, C≡*C*C$_6$H$_5$), 112.83(d, ^2J(P,C) = 15 Hz, 1C, *o*-PC$_6$H$_4$N), 119.65(d, ^3J(P,C) = 9 Hz, 1C, *m*-N*C*$_6$H$_4$P), 124.74(s, 1C, *p*-N*C*$_6$H$_2$Me$_3$), 125.72(s, 2C, *o*-C≡C*C*$_6$H$_5$), 125.90(s, 2C, *o*-C≡C*C*$_6$H$_5$), 126.61(s, 1C, *p*-N*C*$_6$H$_3$^{i}Pr$_2$), 128.50(overlap, 4C, *m*-C≡CC$_6H_5$), 129.25(s, 2C, *p*-P(C$_6H_5$)$_2$), 130.42(s, 2C, *m*-N*C*$_6$H$_2$Me$_3$), 131.38(s, 2C, *o*-N*C*$_6$H$_2$Me$_3$), 132.04(s, 2C, *m*-N*C*$_6$H$_3$^{i}Pr$_2$), 132.16(s, 4C, *m*-P(*C*$_6$H$_5$)$_2$), 133.08(s, 1C, *m*-C≡C*C*$_6$H$_5$), 133.17(s, 1C, *m*-C≡C*C*$_6$H$_5$), 133.75(s, 2C, *p*-C≡CC$_6H_5$), 134.03(s, 1C, *p*-N*C*$_6$H$_4$P), 135.69(d, ^2J(P,C) = 9 Hz, 4C, *o*-P(*C*$_6$H$_5$)$_2$), 137.51(s, 1C, *o*-N*C*$_6$H$_4$P), 137.65(s, 2C, *o*-N*C*$_6$H$_3$^{i}Pr$_2$), 139.19(s, 1C, *ipso*-P*C*$_6$H$_4$N), 139.68(s, 2C, *ipso*-P(*C*$_6$H$_5$)$_2$), 143.29(s, 1C, *o*-N*C*$_6$H$_4$P), 149.64(s, 1C, *ipso*-N*C*$_6$H$_2$Me$_3$), 157.76(s, 1C, *ipso*-N*C*$_6$H$_3$^{i}Pr$_2$), 162.63 ppm (s, 2C, C≡*C*C$_6$H$_5$). Anal. Calcd for $C_{59}H_{62}N_2O_2PLu$: C, 68.33; H, 6.03; N, 2.70. Found: C, 68.31; H, 6.03; N, 2.69.

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