Rare-earth metal complexes stabilized by amino-phosphine ligand. Reaction with mesityl azide and catalysis of the cycloaddition of organic azides and aromatic alkynes†

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Stoichiometric reactions between mesityl azide ($MesN_3$, Mes = 2,4,6-$C_6H_2Me_3$) and amino-phosphine ligated rare-earth metal alkyl, LLn(CH_2SiMe_3)$_2$(THF) (L = (2,6-$C_6H_3Me_2$)$NCH_2C_6H_4P(C_6H_5)_2$; Ln = Lu (**1a**), Sc (**1b**)), amide, LLu(NH(2,6-$C_6H_3{}^iPr_2$))$_2$(THF) (**2**) and acetylide at room temperature gave the amino-phosphazide ligated rare-earth metal bis(triazenyl) complexes, [L($MesN_3$)]Ln[($MesN_3$)(CH_2SiMe_3)]$_2$ (Ln = Lu (**3a**); Sc (**3b**)), bis(amido) complex [L($MesN_3$)]Lu[NH(2,6-$C_6H_3{}^iPr_2$)]$_2$ (**4**), and bis(alkynyl) complex (**5**) (L($MesN_3$)Lu (C≡CPh)$_2$)$_2$, respectively. The triazenyl group in **3** coordinates to the metal ion in a rare η^2-mode *via* N^β and N^γ atoms, generating a triangular metallocycle. The amino-phosphazide ligand, L($MesN_3$), in **3**, **4** and **5** chelates to the metal ion in a η^3-mode *via* N^α and N^γ atoms. In the presence of excess phenylacetylene, complex **3a** isomerized to **3′**, where the triazenyl group coordinates to the metal ion in a η^3 mode *via* N^α and N^γ atoms. Complexes **1**, **2**, **3** and **4** have shown an unprecedented catalytic activity towards the cycloaddition of organic azides and *aromatic* alkynes to afford 1,5-disubstituted 1,2,3-triazoles selectively.

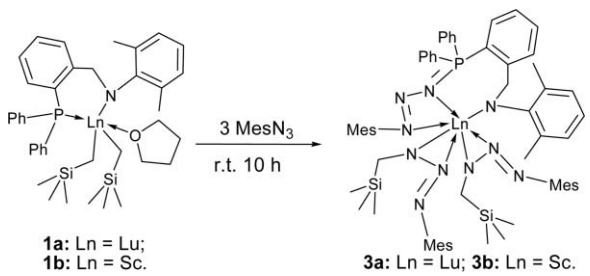
Introduction

Rare-earth metal complexes have shown rich and unique reactivities[1] and distinguished catalytic capabilities toward organic synthesis.[2] For instance rare-earth metal complexes can catalyze hydrogenation, hydrosilylation, hydroamination and hydrophosphination,[3] trimerization of benzonitrile,[4] and dimerization of terminal alkynes[1h,i] as well as the addition of terminal alkynes to carbodiimines.[5] Such properties, to some extent, are affected by the steric and electronic environment of the metal center. Therefore, the novel reactivity and catalytic activity of rare-earth metal complexes can be achieved through careful ligand-design. Our group has successfully synthesized rare-earth metal bis(alkyl) complexes bearing amino-phosphine ligands with "large" and "soft" phosphorus donors, which have shown unique C–H activation motivated by the insertion of carbodiimide into the lutetium-alkyl species.[6] This result interested us in exploiting other reactivities of this series of rare-earth metal complexes. Herein, we wish to report the reactions between these complexes and mesityl azide to afford amino-phosphazide ligated rare-earth metal complexes with unique coordination geometry. In addition the unprecedented catalytic activity of these complexes for the 1,5-selective cycloaddition of organic azides and *aromatic* alkynes at ambient temperature will also be presented.

Result and discussion

Reaction of the alkyl complexes with mesityl azide ($MesN_3$)

Treatment of the lutetium bis(alkyl) complex **1a** LLu(CH_2SiMe_3)$_2$(THF) (L = (2,6-$C_6H_3Me_2$)$NCH_2C_6H_4P(C_6H_5)_2$),[1e] with $MesN_3$ (Mes = 2,4,6-$C_6H_2Me_3$) at a molar ratio of 1:3 gave an amino-phosphazide supported triazenyl complex **3a**, [L($MesN_3$)]Lu[($MesN_3$)(CH_2SiMe_3)]$_2$. In this process, one $MesN_3$ inserted into the Lu–P bond, whilst another two molecules of $MesN_3$ inserted into Lu–CH_2SiMe_3 bonds, which was evidenced by the downfield shifting of the methylene resonances of CH_2SiMe$_3$ to 3.48 and 3.53 ppm as compared with –0.33 ppm in **1a** (Scheme 1).



Scheme 1 Stoichiometric reaction of **1** with mesityl azide.

Complex **3a** adopts butterfly geometry with the phosphazide ligand forming the body and the two triazenyl moieties generating

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† Electronic supplementary information (ESI) available: Molecular structure of **3b**, ^{1}H NMR and ^{13}C NMR spectra of the isolated triazoles. CCDC reference numbers 670207–670210 and 673960. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b811363g

the wings (Fig. 1).‡ It is noteworthy that the triazenyl moiety coordinates to the Lu ion in a η^2-mode *via* N^β and N^γ atoms, generating a rare triangular metallocycle. Azide compounds usually exist as **A** and **B** resonances, and the latter is favored when they are attacked by a nucleophilic agent.[7] Therefore, nucleophilic addition of the metal alkyl species $Lu–CH_2Si(CH_3)_3$ in **1a** to the terminal nitrogen (N^γ) of mesityl azide gave **3a** *via* intermediate **D**[8] (Scheme 2). It is known that an azide ligand coordinates to a transition metal center in three modes: η^1-mode *via* a N^α[9] or N^γ[10] atom and η^3-mode *via* N^α and N^γ atoms.[11] Thus the η^2-mode *via* N^β and N^γ atoms as seen in **3a** is unprecedented, as far as we are aware.

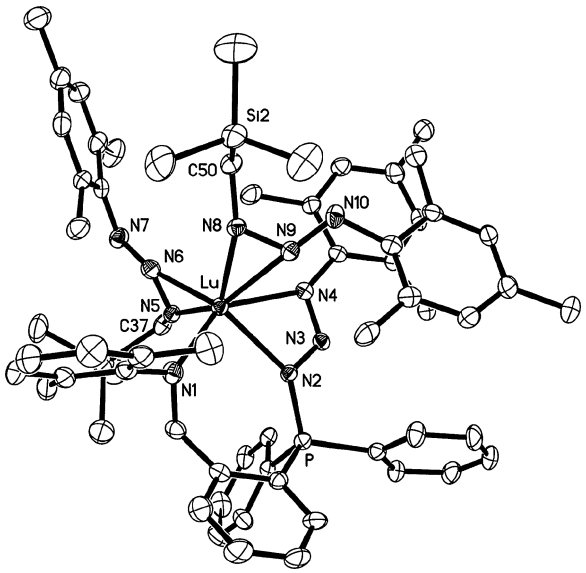
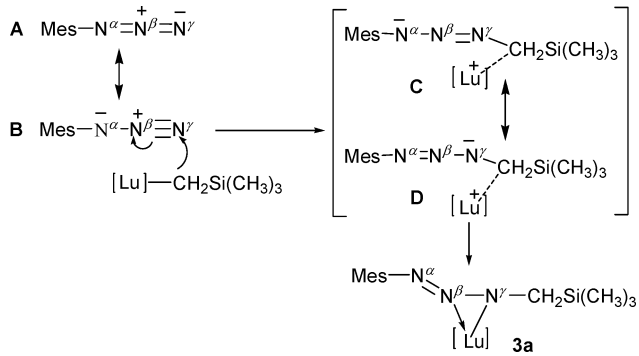


Fig. 1 Molecular structure of **3a** (hydrogen atoms omitted for clarity, thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (deg.): Lu–N(1) 2.151(7), Lu–N(2) 2.367(7), Lu–N(4) 2.565(6), N(2)–N(3) 1.377(8), N(3)–N(4) 1.289(8), Lu–N(5) 2.264(6), Lu–N(6) 2.332(7), Lu–N(8) 2.228(6), Lu–N(9) 2.388(6), N(5)–N(6) 1.313(8), N(6)–N(7) 1.304(9), N(8)–N(9) 1.323(9), N(9)–N(10) 1.298(8); N(2)–Lu–N(4) 52.1(2), N(5)–Lu–N(6) 33.14(19), N(8)–Lu–N(9) 33.1(2).



Scheme 2 The probable reaction pathway for the formation of complex **3a**.

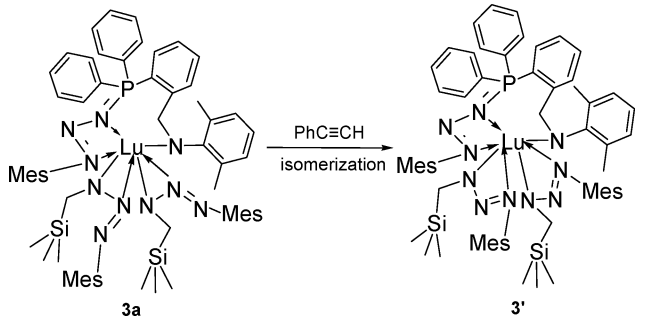
The bond lengths formed by the Lu atom and the amido nitrogen atoms, Lu–N(1) (2.151(7) Å), Lu–N(5) (2.264(6) Å) Lu–N(8) (2.228(6) Å) are comparable to the values in the literature.[12] The bond distances between the Lu atom and the imido nitrogen atoms, Lu–N(2) (2.367(7) Å), Lu–N(4) (2.565(6) Å), Lu–N(6) (2.332(7) Å) Lu–N(9) (2.388(6) Å) are within the reasonable range for a $Lu–N_{imido}$ interaction.[13] The bond length of P–N(2), 1.638(7) Å, is shorter than that of a P–N single bond[11] but longer than that of a P=N double bond.[14] The average N–N bond length (1.310 Å) in the triazenyl moieties falls in between those for the single bond and double bond, indicating delocalized π-electrons over the N–N–N linkage. The bond angles of N(5)–Lu–N(6) and N(8)–Lu–N(9) (av. 33.12°) are much smaller than that of N(2)–Lu–N(4) (52.1(2)°), in agreement with η^2- and η^3-coordination modes, respectively.

Following a similar procedure, the reaction of the scandium bis(alkyl) complex **1b**, $LSc(CH_2SiMe_3)_2(THF)$, with 3 equiv. $MesN_3$ gave **3b**, $[L(MesN_3)]Sc[(MesN_3)(CH_2SiMe_3)]_2$ (Scheme 1). X-Ray analysis confirmed that **3b**†‡ is an analogue of **3a**. The average bond angle of N(5)–Sc–N(6) and N(8)–Sc–N(9) (av. 34.47(8)°) is larger than that in complex **3a** and the corresponding bond lengths of $Sc–N_{amido}$ and $Sc–N_{imino}$ in **3b** are slightly shorter than those in **3a**, which is due to the smaller radius of the scandium ion.[15]

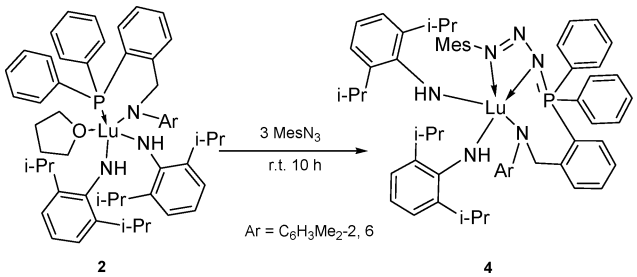
In the presence of excess phenylacetylene, **3a** isomerized to **3′**, but the replacement of the triazenyl ligand by the excess phenylacetylene as in the case of cobalt azide complex did not happen (Scheme 3).[16]

The ^1H NMR spectrum of **3′** was far from that of **3a**: two singlets at 0.18 ppm and 0.21 ppm were assignable to the silylmethyl that showed as a singlet at 0.26 ppm in **3a**; the resonances of the benzyl protons, $CH_2C_6H_4P$, shifted obviously downfield (4.33 ppm, 5.62 ppm) as compared with those in **3a** (2.23 and 2.26 ppm). Complex **3′** is an isomer of **3a** with the triazenyl moities coordinating to the Lu ion in η^3-mode *via* N^α and N^γ atoms (Fig. 2).‡ The bond angles of N(5)–Lu–N(7) and N(8)–Lu–N(10)

‡ **Crystal data of 3a**: $C_{62}H_{80}N_{10}Si_2PLu$, Mr = 1227.48, Monoclinic, space group P2(1), a = 12.1586(10), b = 21.8677(17), c = 12.8260(10) Å, α = 90, β = 112.5040(10), γ = 90°, V = 3150.5(4) Å^3, Z = 2, ρ_{calcd} = 1.294 gcm^{-3}, μ(MoKa) = 1.675 mm^{-1}, 17814 reflections measured, and 8638 reflections with $I>2\sigma(I)$. R(int) = 0.0672, Final $R1$ = 0.0499 (observed data), $wR2$ = 0.0981 (all data).**Crystal data of 3b**: $C_{62}H_{80}N_{10}Si_2PSc$, Mr = 1097.47, Monoclinic, space group P2(1), a = 12.0822(10), b = 21.7373(18), c = 12.8265(10) Å, α = 90, β = 112.7380(10), γ = 90°, V = 3106.9(4) Å^3, Z = 2, ρ_{calcd} = 1.173 gcm^{-3}, μ(MoKa) = 0.228 mm^{-1}, 17592 reflections measured, and 9196 reflections with $I>2\sigma(I)$. R(int) = 0.0424, Final $R1$ = 0.0456 (observed data), $wR2$ = 0.0772 (all data).**Crystal data of 3′**: The unit cell of **3′** was found to contain one and a half molecules of benzene. $C_{71}H_{89}N_{10}Si_2PLu$, Mr = 1344.64, Monoclinic, space group P2(1)/n, a = 14.5568(9), b = 21.7750(13), c = 22.0756(13) Å, α = 90, β = 91.3220(10), γ = 90°, V = 6995.5(7) Å^3, Z = 4, ρ_{calcd} = 1.277 gcm^{-3}, μ(MoKa) = 1.515 mm^{-1}, 38977 reflections measured, and 10545 reflections with $I>2\sigma(I)$. R(int) = 0.0532, Final $R1$ = 0.0424 (observed data), $wR2$ = 0.0885 (all data).**Crystal data of 4**: $C_{60}H_{72}N_6$ PLu, Mr = 1083.18, Triclinic, space group P-1, a = 13.2430(19), b = 13.321(2), c = 19.106(3) Å, α = 71.435(3), β = 84.227(3), γ = 83.052(3)°, V = 3164.6(8) Å^3, Z = 2, ρ_{calcd} = 1.137 gcm^{-3}, μ(MoKa) = 1.622 mm^{-1}, 17730 reflections measured, and 6317 reflections with $I>2\sigma(I)$. R(int) = 0.0914, Final $R1$ = 0.0906 (observed data), $wR2$ = 0.2072 (all data). There is a large void in the structure, forming a channel along the c-axis. This contains highly disordered solvent molecules which could not be successfully modelled.**Crystal data of 5**: The unit cell of **5** was found to contain two molecules of benzene, these molecules exhibit disorder which could not be modeled successfully. $C_{116}H_{104}N_8P_2Lu_2$, Mr = 2021.95, Triclinic, space group P-1, a = 13.6136(10), b = 14.4341(11), c = 27.0624(19) Å, α = 79.4710(10), β = 76.8340(10), γ = 73.9160(10)°, V = 4934.5(6) Å^3, Z = 2, ρ_{calcd} = 1.361 gcm^{-3}, μ(MoKa) = 2.074 mm^{-1}, 27957 reflections measured, and 13680 reflections with $I>2\sigma(I)$. R(int) = 0.0369, Final $R1$ = 0.0486 (observed data), $wR2$ = 0.1005 (all data).



Scheme 3 Isomerization of complex **3a** in the presence of excess phenylacetylene.



Scheme 4 Stoichiometric reaction of **2** with mesityl azide.

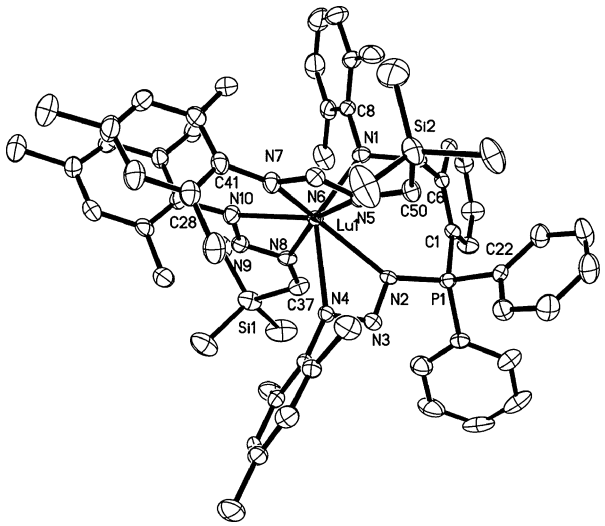


Fig. 2 Molecular structure of **3′** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (deg.): Lu(1)–N(1) 2.173(3), Lu(1)–N(2) 2.424(3), Lu(1)–N(4) 2.544(3), N(2)–N(3) 1.371(4), N(3)–N(4) 1.266(4), Lu(1)–N(5) 2.439(3), Lu(1)–N(7) 2.359(3), Lu(1)–N(8) 2.411(3), Lu(1)–N(10) 2.357(3), N(5)–N(6) 1.294(4), N(6)–N(7) 1.327(4), N(8)–N(9) 1.302(4), N(9)–N(10) 1.322(4), N(8)–C(37) 1.461(5), N(5)–C(50) 1.463(5); N(2)–Lu(1)–N(4) 51.39(10), N(7)–Lu(1)–N(5) 53.12(11), N(10)–Lu(1)–N(8) 53.24(11).

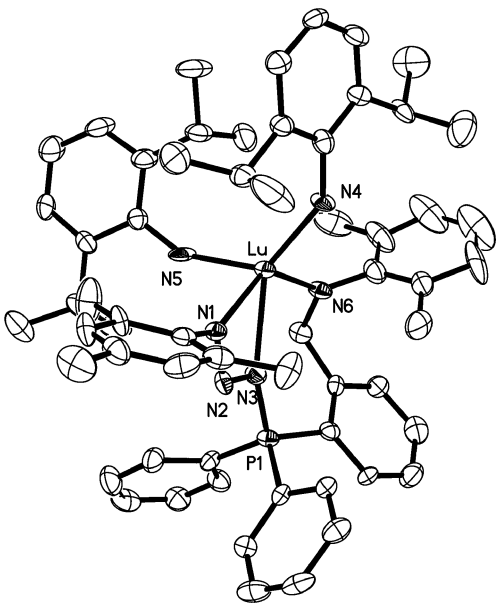


Fig. 3 Molecular structure of **4** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (deg.): Lu–N(1) 2.532(9), Lu–N(3) 2.407(9), Lu–N(4) 2.175(9), Lu–N(5) 2.142(10), Lu–N(6) 2.165(9), N(1)–N(2) 1.261(11), N(2)–N(3) 1.377(11), N(3)–P(1) 1.669(9); N(1)–Lu–N(3) 51.4(3), N(4)–Lu–N(5) 125.7(3), N(2)–N(1)–Lu 98.6(6), N(2)–N(3)–Lu 101.0(6), N(1)–N(2)–N(3) 108.8(8), N(2)–N(1)–C(52) 111.0(9), N(2)–N(3)–P(1) 110.9(7), P(1)–N(3)–Lu 148.1(5).

(av. 53.18(11)°) are similar to that of N(2)–Lu–N(4) (51.39(10)°), in agreement with η^3- coordination mode.

Reaction of the amido complex with $MesN_3$

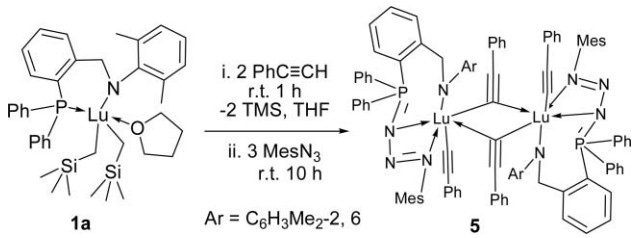
Stoichiometric reaction between lutetium bis(amido) complex **2**, LLu(NH(2,6-$C_6H_3{}^iPr_2$))$_2$(THF), and $MesN_3$ afforded an amino-phosphazide supported amido complex **4**, [L($MesN_3$)]Lu[NH(2,6-$C_6H_3{}^iPr_2$)]$_2$, indicating insertion of one $MesN_3$ molecule into the Lu–P bond whilst the two amido groups remained untouched (Scheme 4).

The resonances at 3.24 and 3.45 ppm and the singlet at 6.70 ppm were assigned to the methyl and aryl protons of $MesN_3$, respectively. The molecular structure of **4** was figured out to be a heteroleptic monomer (Fig. 3).‡ The monoanionic phosphazide ligand and two amino moieties coordinate to the Lu ion, forming a distorted trigonal-bipyramidal geometry. Atoms N(1), N(3), N(4) are equatorial, with Lu lying out the plane (0.875 Å). While atoms N(5) and N(6) are located at the axial positions. The bond lengths and angles of the amino-phosphazide moiety within complex **4** are similar to those in complexes **3**. The N(4)–Lu–N(5) bond angle, 125.7(3)°, is larger than the corresponding N(3)–Lu–N(2) (119.7(3)°) in **2**.

Reaction of the alkynyl complex with $MesN_3$

Protonolysis of the lutetium complex **1a** with phenylacetylene led to the formation of an acetylide intermediate by release of TMS. Upon addition of $MesN_3$ to this acetylide intermediate, an amino-phosphazide ligated complex **5**, (L($MesN_3$)Lu(C≡CPh)$_2$)$_2$, was obtained *via* $MesN_3$ insertion into the Lu–P bond similar to that in **3** and **4** (Scheme 5).

X-Ray analysis confirmed that complex **5** is a dimer (Fig. 4).‡ The acetylide groups coordinate to the Lu ions in bridging and terminal modes, respectively. The two *trans*-located amino phosphazide moieties bond to the Lu ions in η^3- mode *via* N^α and N^γ atoms. Each metal center adopts a distorted tetragonal bipyramidal geometry. Atoms C(1), C(9), N(2) and C(17) are equatorial, while atoms N(1) and N(4) are located at the axial



Scheme 5 Synthesis of complex **5**.

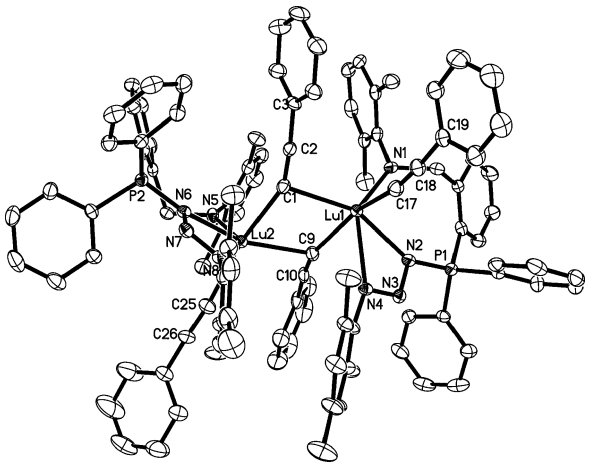


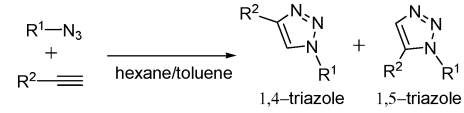
Fig. 4 Molecular structure of **5** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (deg.): Lu(1)–C(1) 2.465(5), Lu(2)–C(9) 2.474(5), Lu(1)–C(17) 2.372(6), Lu(2)–C(25) 2.344(6), Lu(1)–C(9) 2.474(6), Lu(2)–C(1) 2.482(6), C(1)–C(2) 1.212(7), C(9)–C(10) 1.219(7), C(17)–C(18) 1.211(7), C(25)–C(26) 1.224(7); C(1)–Lu(1)–C(9) 79.22(18), C(9)–Lu(2)–C(1) 78.89(18), Lu(1)–C(1)–Lu(2) 99.78(19), Lu(2)–C(9)–Lu(1) 99.8(2), C(2)–C(1)–Lu(1) 102.2(4), C(2)–C(1)–Lu(2) 151.9(4).

positions. The Lu(1)(μ–CCPh)$_2$Lu(2) core is a twisted plane as seen from the dihedral angle Lu(1)–C(1)–Lu(2)–C(9) of –11.70°. This angle is smaller than that found in lanthanum bis(alkynyl) complex (–20.07(6)°).[1g] The μ-acetylide bridges are asymmetric, leading to a much larger Lu(2)–C(1)–C(2) bond angle (151.9(4)°) as compared with Lu(1)–C(1)–C(2) (102.2(4)°). The bond length of Lu–μ–C (av. 2.474 Å) is reasonably longer than that of Lu–σ–C (av. 2.358 Å), comparable to that found in the lutetium terminal alkynyl complex bearing a Cp ligand.[1d]

Catalysis of the cycloaddition of organic azides and alkynes

1,2,3-Triazoles have received increasing attention[17] owing to their important applications in organic, organometallic and material chemistries as well as in the pharmaceutical and agricultural industries.[18] Huisgen's dipolar cycloaddition of organic azides and alkynes is the most convenient route to afford 1,2,3-triazoles, however, it generates mixtures of regioisomers.[19] For instance, when a mixture of mesityl azide ($MesN_3$) and phenylacetylene was stirred at 60 °C for 3 days, approximately equivalent 1,4- and 1,5-disubstituted 1,2,3-triazole isomers were obtained (Table 1, entry 1). The well known synthetic method for 1,4-disubstituted 1,2,3-triazoles is the "click" reaction of alkynes and azides catalyzed by a Cu(I) system at room temperature.[20] Meanwhile,

Table 1 Cycloaddition of alkynes and organic azides catalyzed by rare-earth metal complexes[a]



Entry	Cat.	R^1	R^2	Yield (%)[c]	Microstructure 1,4-[c]	Microstructure 1,5-[c]
1[b]	–	Mes	C_6H_5	99	55	45
2	**1a**	Mes	C_6H_5	93	0	100
3	**1b**	Mes	C_6H_5	93	0	100
4	**2**	Mes	C_6H_5	94	0	100
5	**1a**	C_6H_5	C_6H_5	92	0	100
6	**1a**	$C_6H_5CH_2$	C_6H_5	93	0	100
7	**1a**	$(CH_2)_4CH$	C_6H_5	91	0	100
8	**1a**	$CH_3(CH_2)_3$	C_6H_5	92	0	100
9	**1a**	Mes	*p*-C_6H_4Me	92	0	100
10	**1a**	Mes	*m*-C_6H_4F	93	0	100
11	**3a**	Mes	C_6H_5	99	0	100
12	**3b**	Mes	C_6H_5	98	0	100
13	**4**	Mes	C_6H_5	99	0	100

[a] Temperature: r.t.; Time: 72 h; R^1N_3:R^2CCH:Cat. = 100:100:2; [R^1N_3] = 0.5 M. [b] Temperature: 60 °C. [c] The products were isolated through silica gel with hexane/EtOAc (3:1) as the eluent.

[Cp*RuCl] derivatives are also efficient catalysts for the cycloaddition of alkynes and azides to give 1,5-disubstituted 1,2,3-triazoles at high temperature, which represents the only catalytic system providing 1,5-selectivity to date.[21] Strikingly, at room temperature, complexes **1a**, **1b** and **2** could catalyze the cycloaddition of azides and alkynes to afford 1,5-disubstituted triazoles exclusively within 72 h.[22]

The changes of central metal type from lutetium (**1a**) to scandium (**1b**) and the σ-bonded group from alkyl (**1a**) to amido (**2**) had no influence on the catalytic activity and the selectivity (Table 1, entries 2–4). Similarly, varying from *aromatic* azides to *aliphatic* azides, the corresponding 1,5-disubstituted 1,2,3-triazoles were also isolated quantitatively and selectively (Table 1, entries 5–8),[23] indicating that variation in the sterics and electronics of the substituents of the organic azides did not induce changes in the conversion and regio-regularity of the products, at least to the extent represented by the cases herein. In contrast, the catalytic performances of these complexes were strongly dependent on the nature of the alkynes. Although treatment of mesityl azide with different *aromatic* alkynes generated 1,5-selective 1,2,3-triazoles in high yields (Table 1, entries 9,10), only traces of cycloaddition products were obtained when switching to the *aliphatic* alkynes. Moreover no cycloaddition between internal alkynes and azides was observed with this present system. This result is in striking contrast to the [Cp*RuCl] based system, where the regio-selectivity and conversion are obviously influenced by the nature of azides not alkynes.[21a]

Complex **3** provided the same catalytic performances as its congener **1** (Table 1, entry 11,12), however, complexes **3′** and **5** couldn't catalyze the cycloaddition. These results suggested that in the cycloaddition process, $MesN_3$ reacted with **1** prior to the phenylacetylene to form intermediate **3**. This was further proved by monitoring the reaction using NMR technique. No TMS resonance was detected, indicating that the protonolysis reaction

between **1** and phenylacetylene did not occur. Therefore complex **3** was the true catalyst, when the cycloaddition was catalyzed by the alkyl complex. This is in contrast to the Cu(I) catalyzed "click" reaction, where copper(I) firstly deprotonates the alkyne to afford the corresponding acetylide intermediate.[20] Complex **4** also provided the same catalytic performances as its congener **2** (Table 1, entry 13), acting as the true active species. The similarity among the intermediates **3** and **4** is that both of them contain a bulky amino phosphazide ligand. Thus, the selectivity might be governed by the bulky environment of the metal center.[24]†

Conclusions

Reactions of mesityl azide with amino-phosphine ligated rare-earth metal alkyl, amide and acetylide, respectively, afforded the corresponding rare-earth metal triazenyl, amido and alkynyl complexes based on amino-phosphazide ligands. The triazenyl moiety coordinated to the metal ion with N^{β} and N^{γ} atoms, forming a rare η^2- mode, which transformed into η^3- mode in the presence of excess phenylacetylene. These complexes exhibited an unprecedented catalytic activity for the cycloaddition of organic azides and *aromatic* alkynes to afford 1,5-disubstituted 1,2,3-triazoles, of which the selective formation might be governed by the bulkiness of the metal center. We are in the process of investigating the details of the mechanism.

Experimental section

General conditions

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. Solvents were purified by MBRAUN SPS system. Starting materials for the synthesis of compounds were purchased from Aldrich or Fluka, and distilled before use.

Instruments and measurements

Organometallic samples for NMR spectroscopic measurements were prepared in a glovebox by the use of NMR tubes sealed by paraffin film. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV300 (FT, 300 MHz for ^{1}H; 75 MHz for ^{13}C) and AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometers. NMR assignments were confirmed by ^{1}H-^{1}H (COSY) and ^{1}H-^{13}C (HMQC) experiments when necessary. Crystals for X-ray analysis were obtained as described in the experimental section. The crystals were manipulated in the 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 ($\lambda = 0.71073$ 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 using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry.

Complex 3a

To a hexane suspension of complex **1a** (0.15 g, 0.18 mmol), mesityl azide (0.06 g, 0.37 mmol, 1 mL hexane) was added. The precipitate disappeared gradually with the addition. After 30 min, an orange precipitate appeared, and the stirring of the reaction mixture was continued for 10 h at room. Complex **3a** was obtained by filtration (0.14 g, 58%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.26(s, 18H, Si(CH_3)$_3$), 1.90(s, 6H, $C_6H_3(CH_3)_2$), 2.10(s, 3H, $C_6H_2(CH_3)_3$), 2.23(d, ^2J(H, H) = 6.4 Hz, 1H, $CH_2C_6H_4P$), 2.26(d, ^2J(H, H) = 6.4 Hz, 1H, $CH_2C_6H_4P$), 2.33(s, 6H, $C_6H_2(CH_3)_3$, 6H, $C_6H_2(CH_3)_3$), 2.37(s, 12H, $C_6H_2(CH_3)_3$), 3.48(d, ^2J(H, H) = 12.4 Hz, 2H, CH_2Si), 3.53(broad, 2H, CH_2Si), 6.64(s, 2H, $C_6H_2(CH_3)_3$), 6.66(d, ^3J(H, H) = 4.8 Hz, 1H, C_6H_4), 6.77(td, ^3J(H, H) = 6.8 Hz, ^4J(H, H) = 2.8 Hz, 1H, C_6H_4), 6.83(s, 4H, $C_6H_2(CH_3)_3$), 6.91(t, ^3J(H, H) = 7.6 Hz, 1H, C_6H_4), 7.00(dd, ^3J(P, H) = 15.2 Hz, ^3J(H, H) = 7.6 Hz, 1H, C_6H_4), 7.09(t, ^3J(H, H) = 7.6 Hz, 1H, $C_6H_3(CH_3)_2$), 7.13(broad, 4H, $P(C_6H_5)_2$), 7.20(t, ^3J(H, H) = 7.2 Hz, 2H, $P(C_6H_5)_2$), 7.30(d, ^3J(H, H) = 7.2 Hz, 2H, $C_6H_3(CH_3)_2$), 7.45(d, ^3J(H, H) = 7.2 Hz, 2H, $P(C_6H_5)_2$), 7.48 ppm(d, ^3J(H, H) = 7.2 Hz, 2H, $P(C_6H_5)_2$). ^{13}C NMR (400 MHz, C_6D_6, 25 °C): δ = 0.71(s, 6C, Si(CH_3)$_3$), 20.34(s, 4C, $C_6H_2(CH_3)_3$), 21.22(s, 2C, $C_6H_2(CH_3)_3$), 21.51(s, 1C, $C_6H_2(CH_3)_3$), 21.91(s, 2C, $C_6H_2(CH_3)_3$), 45.33(s, 1C, CH_2Si), 56.53(s, 1C, CH_2Si), 118.95(s, 1C, $C_6H_2(CH_3)_3$), 120.06(s, 2C, $C_6H_2(CH_3)_3$), 122.19(s, 1C, $C_6H_3(CH_3)_2$), 126.14(d, ^3J(C, P) = 14 Hz, 1C, C_6H_4), 129.42(s, 2C, $C_6H_3(CH_3)_2$), 129.81(s, 4C, $P(C_6H_5)_2$), 129.88(s, 4C, $C_6H_2(CH_3)_3$), 130.01(s, 2C, $P(C_6H_5)_2$), 130.64 (s, 4C, $C_6H_2(CH_3)_3$), 131.0(s, 2C, $C_6H_2(CH_3)_3$), 131.60(s, 1C, $P(C_6H_5)_2$), 132.17(d, ^4J(C, P) = 11 Hz, 1C, C_6H_4), 132.73(s, 1C, $P(C_6H_5)_2$), 133.84(s, 2C, $P(C_6H_5)_2$), 134.19(s, 2C, $P(C_6H_5)_2$, 2C, C_6H_4), 134.76(d, ^2J(C, P) = 20 Hz, 1C, C_6H_4), 135.15(d, J(C, P) = 15 Hz, 4C, $P(C_6H_5)_2$), 136.32(s, 4C, $C_6H_2(CH_3)_3$), 137.58(s, 2C, $C_6H_2(CH_3)_3$), 143.74(s, 2C, $C_6H_2(CH_3)_3$), 149.43(d, ^2J(C,P) = 17.5 Hz, 1C, C_6H_4), 151.74(s, 1C, $C_6H_2(CH_3)_3$), 151.82(s, 1C, $C_6H_3(CH_3)_2$), 154.39 ppm(s, 2C, $C_6H_3(CH_3)_2$). Anal. Calc. for $C_{62}H_{80}N_{10}Si_2PLu$: C, 60.67; H, 6.57; N, 11.41. Found: C, 60.65; H, 6.56; N, 11.38.

Complex 3b

Following the same procedure, treatment of complex **1b** $LSc(CH_2SiMe_3)_2(THF)$ (0.11 g, mmol), with mesityl azide (0.08 g, mmol) gave complex **3b** (0.09 g, 55%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.26(s, 18H, Si(CH_3)$_3$), 2.01(s, 6H, $C_6H_3(CH_3)_2$), 2.09(s, 3H, $C_6H_2(CH_3)_3$), 2.24(multi, 2H, $CH_2C_6H_4P$), 2.35(s, 6H, $C_6H_2(CH_3)_3$, 6H, $C_6H_2(CH_3)_3$), 2.42(s, 12H, $C_6H_2(CH_3)_3$), 3.50(multi, 4H, CH_2Si), 6.48(multi, 1H, C_6H_4), 6.70(s, 2H, $C_6H_2(CH_3)_3$), 6.82(t, ^3J(H, H) = 7.2 Hz, 1H, C_6H_4), 6.87(s, 4H, $C_6H_2(CH_3)_3$), 6.97(dd, ^3J(P, H) = 15.2 Hz, ^3J(H, H) = 7.6 Hz, 1H, C_6H_4), 6.91(t, ^3J(H, H) = 7.6 Hz, 1H, C_6H_4), 7.05(t, ^3J(H, H) = 7.6 Hz, 1H, $C_6H_3(CH_3)_2$), 7.13(broad, 4H, $P(C_6H_5)_2$), 7.22(broad, 2H, $P(C_6H_5)_2$, 2H, $C_6H_3(CH_3)_2$), 7.52(d, ^3J(H, H) = 7.6 Hz, 2H, $P(C_6H_5)_2$), 7.55 ppm(d, ^3J(H, H) = 8.0 Hz, 2H, $P(C_6H_5)_2$). ^{13}C NMR (400 MHz, C_6D_6, 25 °C): δ = 1.02(s, 6C, Si(CH_3)$_3$), 20.44(s, 4C, $C_6H_2(CH_3)_3$), 20.97(s, 2C, $C_6H_2(CH_3)_3$),

21.51(s, 1C, $C_6H_2(CH_3)_3$), 22.40(s, 2C, $C_6H_2(CH_3)_3$), 46.04(s, 1C, CH_2Si), 56.77(s, 1C, CH_2Si), 119.58(s, 1C, $C_6H_2(CH_3)_3$), 120.68(s, 2C, $C_6H_2(CH_3)_3$), 122.87(s, 1C, $C_6H_3(CH_3)_2$), 126.28(d, ^3J(C, P) = 15 Hz, 1C, C_6H_4), 128.26(s, 2C, $C_6H_3(CH_3)_2$), 129.02(s, 4C, $P(C_6H_5)_2$), 129.84(s, 4C, $C_6H_2(CH_3)_3$), 129.99(s, 2C, $P(C_6H_5)_2$), 130.83(s, 4C, $C_6H_2(CH_3)_3$), 131.10(s, 2C, $C_6H_2(CH_3)_3$), 131.80(s, 1C, $P(C_6H_5)_2$), 132.38(d, ^4J(C, P) = 11 Hz, 1C, C_6H_4), 132.93(s, 1C, $P(C_6H_5)_2$), 133.77(s, 2C, $P(C_6H_5)_2$), 133.86(s, 2C, $P(C_6H_5)_2$, 1C, C_6H_4, 1C, C_6H_4), 134.32(s, 1C, C_6H_4), 135.42(d, J(C, P) = 15 Hz, 4C, $P(C_6H_5)_2$), 136.11(s, 4C, $C_6H_2(CH_3)_3$), 137.54(s, 2C, $C_6H_2(CH_3)_3$), 143.86(s, 2C, $C_6H_2(CH_3)_3$), 148.92(s, 1C, C_6H_4), 151.04(s, 1C, $C_6H_2(CH_3)_3$), 151.13(s, 1C, $C_6H_3Me_2$), 153.11 ppm(s, 2C, $C_6H_3Me_2$). Anal. Calc. for $C_{62}H_{80}N_{10}Si_2PSc$: C, 67.85; H, 7.35; N, 12.76. Found: C, 67.84; H, 7.33; N, 12.74.

Complex 3′

A toluene solution of phenylacetylene (0.06 g, 0.58 mmol) was dropped into a solution of **3a** (0.15 g, 0.12 mmol). The stirring of the reaction mixture was continued for 1.5 h at room temperature. Removal of the volatiles afforded an oily residue which was dissolved with hexane (1 mL) and then cooled to −30 °C to give complex **3′**. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 0.18(s, 9H, Si(CH_3)$_3$), 0.21(s, 9H, Si(CH_3)$_3$), 2.06(s, 6H, $C_6H_3(CH_3)_2$), 2.13(s, 3H, $C_6H_2(CH_3)_3$), 2.16(s, 3H, $C_6H_2(CH_3)_3$), 2.17(s, 3H, $C_6H_2(CH_3)_3$), 2.18(s, 3H, $C_6H_2(CH_3)_3$), 2.21(s, 3H, $C_6H_2(CH_3)_3$), 2.23(s, 3H, $C_6H_2(CH_3)_3$), 2.27(s, 2H, CH_2Si), 2.35(s, 6H, $C_6H_2(CH_3)_3$), 2.71(s, 3H, $C_6H_2(CH_3)_3$), 2.98(s, 1H, CH_2Si), 3.02(s, 1H, CH_2Si), 4.33(d, ^2J(H, H) = 17 Hz, 1H, $CH_2C_6H_4P$), 5.62(d, ^2J(H, H) = 17 Hz, 1H, $CH_2NC_6H_3(CH_3)_2$), 6.60(s, 2H, $C_6H_2(CH_3)_3$), 6.63(s, 2H, $C_6H_2(CH_3)_3$), 6.78(td, ^3J(H, H) = 6.8 Hz, ^4J(H, H) = 2.8 Hz, 1H, C_6H_4), 6.83(s, 2H, $C_6H_2(CH_3)_3$), 6.90(d, ^3J(H, H) = 8.0 Hz, 1H, C_6H_4), 6.95(t, ^3J(H, H) = 8.0 Hz, 1H, $C_6H_3(CH_3)_2$), 6.98(dd, ^3J(P, H) = 7.6 Hz, ^4J(H, H) = 3.2 Hz, 1H, C_6H_4), 7.30(dd, ^3J(H, H) = 7.6 Hz, ^4J(H, H) = 1.6 Hz, 2H, $C_6H_3(CH_3)_2$), 7.14(multi, 4H, $P(C_6H_5)_2$, 2H, $P(C_6H_5)_2$), 7.29(d, 1H, C_6H_4), 7.42(d, ^3J(H, H) = 7.2 Hz, 2H, $P(C_6H_5)_2$), 7.52 ppm(d, ^3J(H, H) = 7.2 Hz, 2H, $P(C_6H_5)_2$). ^{13}C NMR (100 MHz, C_6D_6, 25 °C): δ = 0.02(s, 3C, Si(CH_3)$_3$), 0.29(s, 3C, Si(CH_3)$_3$), 20.12(s, 2C, $C_6H_2(CH_3)_3$), 20.55(s, 2C, $C_6H_2(CH_3)_3$), 21.08(s, 1C, $C_6H_2(CH_3)_3$), 21.29(s, 1C, $C_6H_2(CH_3)_3$), 21.34(s, 1C, $C_6H_2(CH_3)_3$), 21.42(s, 1C, $C_6H_2(CH_3)_3$), 21.74(s, 1C, $C_6H_2(CH_3)_3$), 48.15(s, 1C, CH_2Si), 57.62(s, 1C, CH_2Si), 122.26(s, 1C, $C_6H_2(CH_3)_3$), 126.46(s, 2C, $C_6H_2(CH_3)_3$), 127.94(s, 1C, $C_6H_3(CH_3)_2$), 129.56(d, ^3J(C, P) = 13 Hz, 1C, C_6H_4), 129.83(s, 2C, $C_6H_3(CH_3)_2$), 129.94(s, 4C, $P(C_6H_5)_2$), 131.81(s, 4C, $C_6H_2(CH_3)_3$), 131.92(s, 2C, $P(C_6H_5)_2$), 132.67(s, 4C, $C_6H_2(CH_3)_3$), 133.00(s, 2C, $C_6H_2(CH_3)_3$), 133.16(s, 1C, $P(C_6H_5)_2$), 133.50(d, ^4J(C, P) = 10 Hz, 1C, C_6H_4), 133.79(s, 1C, $P(C_6H_5)_2$), 133.96(s, 2C, $P(C_6H_5)_2$), 134.26(s, 2C, $P(C_6H_5)_2$), 134.67(s, 1C, C_6H_4), 134.90(d, ^2J(C, P) = 9 Hz, 1C, C_6H_4), 135.27(s, 1C, C_6H_4), 135.75(d, J(C, P) = 11 Hz, 4C, $P(C_6H_5)_2$), 136.77(s, 4C, $C_6H_2(CH_3)_3$), 137.04(s, 2C, $C_6H_2(CH_3)_3$), 146.49(s, 2C, $C_6H_2(CH_3)_3$), 146.81(s, 1C, C_6H_4), 152.52(s, 1C, $C_6H_2(CH_3)_3$), 152.61(s, 1C, $C_6H_3Me_2$), 155.71 ppm(s, 2C, $C_6H_3Me_2$). Anal. Calc. for $C_{62}H_{80}N_{10}Si_2PLu$: C, 60.67; H, 6.57; N, 11.41. Found: C, 60.66; H, 6.55; N, 11.40.

Complex 4

The addition of 3 equiv. mesityl azide (0.07 g, 0.45 mmol) to a hexane suspension of **2** (0.15 g, 0.15 mmol) started the reaction immediately. After 10 h, the reaction solution was concentrated under reduced pressure to gave an orange precipitate of complex **4** (0.10 g, 60%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ = 1.25(d, ^3J(H, H) = 6.8 Hz, 12H, $C_6H_3(CH(CH_3)_2)_2$), 1.32(d, ^3J(H, H) = 6.8 Hz, 12H, $C_6H_3(CH(CH_3)_2)_2$), 2.23(multi, 4H, $C_6H_3(CH(CH_3)_2)_2$), 2.32(s, 6H, $C_6H_3(CH_3)_2$), 3.20(broad, 2H, NHC_6H_3), 3.24(s, 6H, $C_6H_2(CH_3)_3$), 3.45(s, 3H, $C_6H_2(CH_3)_3$), 4.76(s, 2H, $CH_2C_6H_4P$), 6.58(multi, 1H, C_6H_4), 6.70(s, 2H, $C_6H_2(CH_3)_3$), 6.75(td, ^3J(H, H) = 7.2 Hz, ^4J(H, H) = 2.4 Hz, 1H, C_6H_4), 6.90(t, ^3J(H, H) = 7.2 Hz, 1H, $C_6H_3(CH_3)_2$), 6.92–7.08(multi, 2H, $C_6H_3(CH_3)_2$, 4H, $P(C_6H_5)_2$, 2H, $P(C_6H_5)_2$, 1H, C_6H_4, 1H, C_6H_4), 7.10–7.20(multi, 2H, $C_6H_3(CH(CH_3)_2)_2$, 4H, $C_6H_3(CH(CH_3)_2)_2$), 7.49(d, ^3J(H, H) = 7.2 Hz, 2H, $P(C_6H_5)_2$), 7.52 ppm(d, ^3J(H, H) = 7.2 Hz, 2H, $P(C_6H_5)_2$). ^{13}C NMR(100 MHz, C_6D_6, 25 °C): δ = 20.12(s, 1C, $C_6H_2(CH_3)_3$), 20.23(s, 2C, $C_6H_2(CH_3)_3$), 23.04(s, 2C, $C_6H_3(CH_3)_2$), 24.20(s, 4C, $C_6H_3(CH(CH_3)_2)_2$), 24.31(s, 4C, $C_6H_3(CH(CH_3)_2)_2$), 30.15(s, 4C, $C_6H_3(CH(CH_3)_2)_2$), 56.62(s, 1C, $CH_2C_6H_4P$), 115.82(s, 2C, $C_6H_3(CH(CH_3)_2)_2$), 122.83(s, 1C, $C_6H_2(CH_3)_3$), 123.17(s, 1C, $C_6H_3(CH_3)_2$), 123.59(s, 4C, $C_6H_3(CH(CH_3)_2)_2$), 127.94(s, 1C, C_6H_4), 129.32(s, 2C, $P(C_6H_5)_2$), 129.43(s, 4C, $P(C_6H_5)_2$), 129.94(s, 1C, C_6H_4), 130.06(s, 2C, $C_6H_3(CH_3)_2$), 130.65(s, 1C, C_6H_4), 132.28(s, 2C, $_3C_6H_2(CH_3)_3$), 132.66(s, 4C, $P(C_6H_5)_2$), 134.20(s, 1C, C_6H_4), 134.29(s, 1C, C_6H_4), 134.61(d, ^1J(C,N) = 9 Hz, 2C, $C_6H_3(CH(CH_3)_2)_2$), 134.86(s, 2C, $P(C_6H_5)_2$), 136.80(s, 2C, $C_6H_2(CH_3)_3$), 137.90(s, 4C, $C_6H_3(CH(CH_3)_2)_2$), 149.93(d, ^2J(C,P) = 17.5 Hz, 1C, C_6H_4), 151.70(s, 1C, $C_6H_2(CH_3)_3$), 153.75(s, 1C, $C_6H_3(CH_3)_2$), 154.79 ppm(s, 2C, $C_6H_3(CH_3)_2$). Anal. Calc. for $C_{60}H_{72}N_6PLu$: C, 66.53; H, 6.70; N, 7.76. Found: C, 66.51; H, 6.69; N, 7.73.

Complex 5

Phenylacetylene (0.03 g, 0.29 mmol) in toluene (1 mL) was dropped into a toluene solution of **1a** (0.12 g, 0.15 mmol). After 1 h, mesityl azide (0.07 g, 0.45 mmol) was added to the above solution. The reaction mixture was stirred for 10 h at room temperature and then was concentrated to 0.5 mL under reduced pressure. Addition of 1 mL hexane and cooling at −30 °C for several days gave light yellow crystals of complex **5** (0.06 g, 41%). The ^{1}H NMR and ^{13}C NMR spectra were not informative due to lots of aryl protons. Anal. Calc. for $C_{104}H_{92}N_8P_2Lu_2$: C, 66.95; H, 4.97; N, 6.01. Found: C, 66.94; H, 4.85; N, 5.76.

A typical procedure for the cycloaddition reaction

To a toluene (7 mL) solution of mesityl azide (0.59 g, 3.66 mmol) and phenylacetylene (0.37 g, 3.66 mmol), complex **1a** (0.06 g, 0.07 mmol) was added. After 3 days, the volatiles were removed and then the residue chromatographed through silica gel with hexane/EtOAc (3:1) as the eluent to isolate the 1,5-triazole (0.89 g, yield: 93%).

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24 Treatment of $MesN_3$ with phenylacetylene in the presence of lutetium mono(alkyl) complex stabilized by anilido-phosphinimine ligand afforded approximately equivalent 1,4- and 1,5-disubstituted 1,2,3-triazole. See the ESI†.

