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Synthesis and molecular structures of divalent bridged bis(guanidinate) europium complexes and their application in intermolecular hydrophosphination of alkenes and alkynes

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Reaction of anhydrous EuCl₃ with one equiv. of lithium salt of a three-carbon bridged bis(guanidinate) Li_2L^1 ($L^1 = [^iPr(Me_3 Si)NC(N^iPr)N(CH_2)_3NC(N^iPr)N(SiMe_3)^iPr]$) in THF afforded the chloride $Eu^{III}L^1Cl(THF)_2$ (1). Reduction reaction of compl-ex 1 with Na/K alloy in a molar ratio of 1:1.2 in THF gave a novel Eu^{II} complex supported by an unexpected new bridged b -is(guanidinate) ligand L^3 , $[Eu^{II}L^3]_2$ ($L^3 = [^iPr(Me_3Si)NC(N^iPr)N(CH_2)_3N(SiMe_3)C(N^iPr)_2]$) (2), through the redistribution of one guanidinate in L^1 during the reduction. Complex 2 was structurally characterized to be a binuclear complex in which tw -o Eu metals are connected together by two L^3 ligands adopted a μ - η^1 : η^2 : η^2 coordination mode for one L^3 ligand and a μ - η^2 : η^2 : η^2 mode for the other. Treatment of the *in situ* formed $Eu^{III}L^2Cl(THF)_2$ ($L^2 = 1.8-C_{10}H_6$ {NC(NⁱPr)(NHⁱPr)}_2) by the reacti -on of EuCl₃ with 0.5 equiv. of [Li_2L^2_2Li_2] in THF with Na/K alloy yielded a novel Eu^{II} complex $[Eu^{II}L^2(THF)]_2$ (3) in good yield. Complex 3 was characterized by an X-ray crystal structure analysis. Complex 3 features an unusual μ - $\eta^1:\eta^2:\eta^2$ coordin -ation mode of the bridged bis(guanidinate) ligand onto Eu^{II} . Complexes 2 and 3 are efficient pre-catalysts for the intermolec -ular hydrophosphination of alkenes and alkynes to give exclusively anti-Markovnikov products and mainly anti-addition pr -oducts for the alkyne reactions. For these transformations, the best performances were observed with complex 2.

Introduction

Divalent lanthanide (Ln^{II}) complexes, due to their pronounced reductive properties¹ and larger ion radii,² have received increasing interest as catalysts or pre-catalysts in various transformations of unsaturated and saturated substrates such as polymerization and organic reactions, and much progress has been made.³⁻⁴ Hydrophosphination, the addition of the P-H bond of a primary or secondary phosphine to an unsaturated C-C bond, provides a potentially powerful and atom-economic process to organic phosphine derivatives, which are an important class of compound widely employed as synthetic reagents in organic synthesis⁵ and as ligands for transitionmetal complexes in organometallic catalysis.⁶ Metal-catalyzed hydrophosphination was revealed to be an attractive method that generally offers better control over regio- and stereoselectivity. Therefore, development of efficient metal catalysts for hydrophosphination becomes one of the most interesting themes in organometallic and organic chemistry. Much

progress has been made in the field of alkaline earth metal⁷ and transition metal complexes.⁸ However, the application of Ln^{II} complexes in this transformation has still attracted much less attention till 1998,9 even the intramolecular hydrophosphination by Ln^{III} has been well documented.¹⁰ Very recently, the intermolecular hydrophosphination has made success by use of Ln^{II} amide complexes,¹¹ such as Yb^{II} amide species supported by tridentate imino-amidinate,7a amide complexes of Yb^{II} and $\mathrm{Eu}^{\mathrm{II}}$ bearing an iminoanilide ligand, 7b $\mathrm{Yb}^{\mathrm{II}}$ amide complexes stabilized by amidinate and 1,3,6,8-tetra-tert-butylcarbazol-9-yl ligands^{11a,11b} and heteroleptic amido Yb^{II} and Sm^{II} complexes bearing aminoether-phenolate ligands^{11c} as well as Yb^{II} amide complexes stabilized by N-heterocyclic carbene ligands.^{11d} All these amide complexes were found to catalyze the intermolecular hydrophosphination of alkenes and alkynes with high activity and selectivity to afford anti-Markovnikov regiospecific product under mild conditions.

Eu^{II} complexes, in comparison with the Yb^{II} and Sm^{II} analogues, have received much less attention as active species in homogeneous catalysis. Therefore, development of novel Eu^{II} complexes as efficient catalysts in homogeneous catalysis is required. Our recent work indicated that the Eu^{II} complexes bearing two β -diketiminate ligands are highly active precatalysts (even more active than the Yb^{II} analogue) for catalytic addition of amines to carbodiimides to substituted guanidines. Moreover, they show different reaction mode from that with Sm^{II} and Yb^{II} complexes, no oxidation step was included in the

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 $[\]dagger$ Electronic supplementary information (ESI) available: crystallographic data and spectral data (1H NMR, ^{31}P NMR and ^{13}C NMR). CCDC reference numbers 1494633 (for 1·THF), 1485799 (for 2) and 1487480 (for 3·2THF). For crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

catalytic cycle.¹² The results stimulated us to further synthesize novel Eu^{II} complexes and examine their performance in catalytic intermolecular hydrophosphination of alkenes.

Bridged guanidinate ligands not only have the tunable steric and electronic effects by variation of the substituents on the nitrogen atoms, but also can provide the metal center with rigid framework and more open coordination sphere, which are useful in homogeneous catalysis. The Yb^{II} complex supported by a naphthalene-bridged bis(guanidinate) ligand was recently reported by us to exhibit unique reactivity toward various nitriles.¹³ Based on these results the two bridged bis(guanidinate) ligands, a three carbon- and a naphthalene- L^2 L^1 $(L^1$ briged guanidinates and $[^{i}Pr(Me_{3}Si)NC(N^{i}Pr)N(CH_{2})_{3}NC(N^{i}Pr)N(SiMe_{3})^{i}Pr]; L^{2} = 1.8 C_{10}H_6{NC(N^iPr)(NH^iPr)}_2$ were chosen as the ancillary ligands, and the syntheses of Eu^{II} complexes bearing these ligands by the reduction of the corresponding Eu^{III} chlorides were tried. It was found that the reduction of Eu^{III}L¹Cl(THF)₂ by Na/K alloy afforded an unexpected bimetallic Eu^{II} complex bearing a newly formed bridged bis(guanidinate) ligand L^3 , (L³ $[Eu^{II}L^3]_2$ $[^{i}Pr(Me_{3}Si)NC(N^{i}Pr)N(CH_{2})_{3}N(SiMe_{3})C(N^{i}Pr)_{2}])$ (2), by the redistribution of one guanidinate group of the original ligand L^1 while the reduction of Eu^{III}L²Cl(THF)₂ yielded a new binuclear Eu^{II} complex $[Eu^{II}L^2(THF)]_2$ (3). The two Eu^{II} complexes were found to act as highly active pre-catalysts in intermolecular hydrophosphination of alkenes and alkynes to Ph₂PH affording selectively anti-Markovnikov products. Here we report the results.

Results and discussion

Syntheses and characterizations of Eu^{III} chloride $Eu^{III}L^1CI(THF)_2$ (1) and Eu^{II} complex $[Eu^{II}L^3]_2$ (2)

Reduction reaction of the corresponding Eu^{III} chlorides with Na/K alloy were conducted here for the syntheses of the title Eu^{II} complexes. Therefore, the Eu^{III} chloride supported by the three-carbon bridged bis(guanidinate) ligand L^1 was first synthesized as it has not been reported yet. Reaction of anhydrous $EuCl_3$ with one equiv. of freshly prepared lithium salt of the ligand Li_2L^1 , which was formed by the published procedure, ¹⁴ in THF at room temperature for 24 h afforded the chloride $Eu^{III}L^1CI(THF)_2$ (1) in 75% yield as red crystals upon crystallization from a mixture of THF/hexane (Scheme 1).

Elemental analysis of complex 1 is consistent with its formula. The IR spectra of complex 1 showed the strong absorption of C=N stretch at approximate 1620 cm^{-1} , indicative of the delocalized double bond of N-C-N linkage.

Complex 1 was further confirmed by an X-ray single-crys-



Scheme 1 Synthesis of 1

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 $\begin{array}{l} \label{eq:Fig. 1} \mbox{Molecular structure of complex 1. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Eu(1)–N(1) 2.485(6), Eu(1)–N(2) 2.367(6), Eu(1)–N(3) 2.3 84(7), Eu(1)–N(4) 2.456(6), Eu(1)–O(1) 2.473(6), Eu(1)–O(2) 2.425(5), Eu(1)–C(2) 2.876(8), Eu(1)–C(1) 2.875(8), Eu(1)–C(1) 2.709(2), N(1)–C(1) 1.309(11), N (2)–C(1) 1.325(10), N(5)–C(1) 1.431(11), N(3)–C(2) 1.318(11), N(4)–C(2) 1.327 (10), N(6)–C(2) 1.424(10), N(1)–Eu(1)–N(2) 54.1(2), N(3)–Eu(1)–N(4) 54.3(2), O(1)–Eu(1)–C(1) 86.97(15), O(1)–Eu(1)–O(2) 176.38(19), N(3)–Eu(1)–N(1) 127 2(2), N(1)–C(1)–N(2) 114.2(7), N(3)–C(2)–N(4) 113.4(7). \end{array}$

crystal structure analysis. As shown in Fig. 1, the complex adopts monomeric structure in the solid state. The center metal Eu^{III} ion is ligated by two guanidinate moieties of one ligand L¹, one chlorine atom, and two oxygen atoms in a distorted trigonal bipyramid, if the guanidinate ligands are considered to be point donors located at the central carbon atoms. The molecular structure of complex 1 is quite similar to those of Nd, Yb and Y analogues reported.¹⁴ The two C–N bond distances in each Eu–N–C–N unit are almost equal, indicating the electron delocalization within the NCN units. The bond parameters are well comparable to those for the Nd, Yb and Y complexes¹⁴ (see the supporting materials).



Scheme 2 Synthesis of 2.

The reduction reaction of complex 1 by Na/K alloy was then carried out at a molar ratio of 1:1.2 in THF at room temperature. Evaporation of volatiles, filtration to remove the LiCl from toluene solution and subsequent crystallization of the residual solids from n-hexane at -5 °C afforded red crystals in 53% yield.

The red crystals were further characterized by elemental analysis, IR spectrum and X-ray crystal structure analysis, as the strong paramagnetic shown by Eu^{II}, which prevents to get a resolved nuclear magnetic spectrum. The IR spectrum of the crystals shows a strong absorption at near 1630 cm⁻¹ assigned to the N-C-C stretching mode of the guanidinate groups. The X-ray crystal structure analysis indicated the red crystals to be the novel Eu^{II} complex [Eu^{II}L³]₂ (**2**) with a newly formed ligand L³ not the original ligand L¹ (Scheme 2). The elemental analysis is consistent with its formula.

The molecular structure of complex **2** is shown in Fig. 2. Complex **2** crystallizes in the triclinic space group $P\bar{1}$ without f-



Fig. 2 Molecular structure of complex **2**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances and angles are listed in Table 1.

Table 1 Selected bond lengths (Å) and angles (°) for complex 2							
		2					
Bond lengths		Bond angles					
Eu(1) - N(1)	2.564(8)	N(9) - Eu(1) - N(1)	113.0(3)				
Eu(1)-N(2)	2.692(8)	N(9)-Eu(1)-N(10)	52.5(3)				
Eu(1) - N(7)	2.659(8)	N(1)-Eu(1)-N(10)	134.3(3)				
Eu(1)–N(11)	2.820(9)	N(9)-Eu(1)-N(7)	118.9(3)				
Eu(1)-N(9)	2.521(8)	N(1)-Eu(1)-N(7)	125.3(3)				
Eu(1)–N(10)	2.571(9)	N(10)-Eu(1)-N(7)	92.6(3)				
N(1)-C(1)	1.291(13)	N(9)-Eu(1)-N(2)	125.3(3)				
N(2)-C(1)	1.361(12)	N(1)-Eu(1)-N(2)	50.9(3)				
N(5)-C(1)	1.450(13)	N(1)-Eu(1)-N(11)	94.3(3)				
N(4)-C(2)	1.353(14)	N(10)-Eu(1)-N(11)	93.9(3)				
N(3)-C(2)	1.331(13)	N(2)–Eu(1)–N(11)	87.5(2)				
N(6)–C(2)	1.450(11)	N(1)-C(1)-N(2)	116.9(9)				
N(7)-C(24)	1.308(13)	N(10)-Eu(1)-N(2)	174.4(3)				
N(11)-C(24)	1.358(13)	N(4)-Eu(2)-N(7)	176.6(3)				
N(9)–C(25)	1.306(14)						
N(10)-C(25)	1.340(14)						

ree solvent molecule in its unit cell. It's unexpected that complex 2 is a binuclear complex bearing a newly formed bridged bis(guanidinate) ligand L^3 not the original ligand L^1 . The formation of L³ should be resulted from the redistribution of one guanidinate group of the original ligand L¹ by the change of the nitrogen atoms coordinated to Eu metal center from the original N(5) and N(2) to the present N(2) and N(1) for Eu(1) and N(8), N(11) to N(11) and N(7) for Eu(2) as confirmed by the distances of these Eu-N bonds, followed by the shift of the $-SiMe_3$ group on the N(5) (N(11)) to the present bridgehead N(2) (N(8)). The change of the original ligand skeleton during the formation of complex 2 might be because of the need of steric effect. The coordination environment of the two metals is different. Eu(1) is six-coordinate bounded by four nitrogen atoms of one bridged guanidinate group and two nitrogen atoms of the other one. The coordination geometry around Eu(1) can be described as a distorted octahedron. The two nitrogen atoms (N(2) and N(10)) are located at axial positions with an N(2)-Eu(1)-N(10) angle of 174.4(3)°, while four nitrogen atoms N(1), N(7), N(11) and N(9) occupy equatorial positions. The center metal Eu(2) is five-coordinate around by five nitrogen atoms in a distorted trigonal bipyramid. The two nitrogen atoms of N(4) and N(7) are located at axial positions with an N(4)-Eu(2)-N(7) angle of 176.6(3)°, while

N(2), N(3) and N(11) occupy equatorial positions. Interestingly, the distance of Eu(2) to C(10) is 3.0915 Å, indicating that there is a weak interaction¹⁵ between Eu(2) and C(10). Moreover, an agostic interaction between two hydrogen atoms (H(10A) and H(10C)) on C(10) and Eu(2) was also observed as the distances of Eu(2) to the two H atoms are 2.835 and 2.734 Å, respectively.¹⁶ The distances of the two C–N bonds in each Eu–N–C–N unit are almost equal (Table 1), indicating π electrons are delocalized in N–C–N unit. The average Eu–N bond distance is comparable with those for the Yb^{II} guanidinate complexes, if the differences in ionic radii between the two metals were considered.¹³

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Complex 2 can also be synthesized by the reduction of the *in situ* formed complex 1 by the reaction of $EuCl_3$ with one equiv. of Li_2L^1 in THF with Na/K alloy under the same conditions in 62% yield (Scheme 2).

Syntheses and characterizations of Eu^{\parallel} complex $(Eu^{\parallel}L^2)_2$ (3)

The reduction reaction of the chloride $Eu^{III}L^2Cl(THF)_2$ formed *in situ* by the reaction of anhydrous $EuCl_3$ with $[Li_2L^2_2Li_2]^{13}$ with Na/K alloy at a molar ratio of 1:1.5 in THF at room temperature afforded complex **3** as red crystals in 60% yield upon crystallization from a mixture of THF-hexane (Scheme 3). The crystals are very sensitive to air and moisture. It is soluble in THF and toluene, but poorly soluble in hexane.





The elemental analysis of the crystals is consistent with the formula. The IR spectrum shows a strong absorption at near 1630 cm⁻¹ assigned to the N-C-C stretching mode of the guanidinate groups. The identity of complex **3** was unequivocally established by an X-ray crystal structure determination.



Fig. 3 Molecular structure of complex 3. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms (except those on the nitrogen atoms) and THF molecule are omitted for clarity. Selected bond distances and angles are listed in Table 2.

		3	
Bond lengths		Bond angles	
Eu(1) - N(1)	2.534(5)	N(1)-Eu(1)-N(2)	47.30(15)
Eu(1)-N(2)	2.933(6)	N(4A)-Eu(1)-N(5A)	48.76(15)
Eu(1)–N(4)	2.491(5)	N(4A)-Eu(1)-N(4)	142.12(16)
Eu(1)-N(4A)	2.711(5)	Eu(1)-N(4)-Eu(1A)	109.23(11)
Eu(1)-N(5A)	2.675(5)	N(1)-C(1)-N(2)	113.7(5)
Eu(1)-O(1)	2.662(5)	N(2)-C(1)-N(3)	123.6(6)
N(1)-C(1)	1.341(8)	N(3)-C(1)-N(1)	122.8(5)
N(2)-C(1)	1.316(8)	N(5)-C(2)-N(4)	116.4(6)
N(3)-C(1)	1.369(7)	N(5)-C(2)-N(6)	123.6(6)
N(4) - C(2)	1.375(8)	N(4)-C(2)-N(6)	119.9(6)
N(5)-C(2)	1.302(8)		
N(6)-C(2)	1.406(9)		

The molecular diagram of complex 3 is shown in Fig. 3 and the selected bond distances and angles are listed in Table 2. Complex 3 crystallizes in the monoclinic space group $P2_1/c$ with a crystallographic inversion center located at the center of the Eu(1)-N(4)-Eu(1A)-N(4A) plane. The two metals are connected together by the two bridging guanidinate species from the two ligands. Thus, both L^2 ligands here adopt a μ - η^1 : η^2 : η^2 coordination mode. Each Eu metal is six-coordinate and bound to five nitrogen atoms of the three guanidinate groups and an oxygen atom from a THF molecule. The coordination geometry around each metal can be described as a pseudo-trigonal pyramid, if each guanidinate group in the complex is considered to occupy a single coordination site at the central C atom of the N-C-N fragment. The solid state structure of complex 3 is quite similar to that of its Yb^{II} analogue.¹³ The bond parameters within Eu(1)-N(1)-C(1)-N(2) unit match those of the related Eu(II) complexes supported by non-bridging guanidinate. 17 The average Eu-N $_{\mu\text{-guanidinate}}$ bond distance (2.623(0) Å) is about 0.181 Å shorter than that for the Eu-N_{guanidinate} bonds (2.804(5) Å), which was likely that the naphthalene bridge in complex 3 shortens the bond distance between the bridge head N and the center metal. The three C-N bond distances of each guanidine group (N(1)-C(1) = 1.341(8)), N(2)-C(1) = 1.316(8) and N(3)-C(1) = 1.369(7) Å) indicate that the π electron of the C=N double bond is not delocalized within the CN₃ unit. The same bonding type is also found in the complexes with the sterically bulky amidinate or guanidinate ligands.¹⁸ The bond parameters are well compared to those of the Yb^{II} complex reported, if the differences in the ion radius between Yb^{II} and Eu^{II} were considered.¹³

Intermolecular hydrophosphination reaction of alkenes and alkynes with Ph_2PH catalyzed by complexes 2 and 3

With these novel complexes in hand the intermolecular hydrophosphination reaction of styrene with Ph_2PH was first examined as a model reaction at 60 °C under solvent free. We were pleased to see that the reaction of styrene with Ph_2PH proceeded smoothly by use of 1 mol% of complex 2 to give the anti-Markovnikov addition product 4a exclusively in excellent yield after 12 h (Table 3, entry 1). Complex 2 is highly active in this transformation. Even the loading of complex 2 decreased to 0.8 mol%, the reaction still gave product 4a in a 91% yield after 12 h (Table 3, entry 2). Complex 3 is also an efficient pre-

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catalyst in this reaction to give the same anti-Markovnikov addition product **4a** selectively. However, complex **3** is somew-

Table 3	Hydrophosphination of diphenylphosphane to styrene by complexes 2 and 3^a	
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+ Ph ₂ PH	Cat.
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Entry	Cat. (mol)	Solvent	Temp. (°C)	Time (h)	Yield ^b (%)	
1	2 (1%)	-	60	12	98	
2	2 (0.8%)	-	60	12	91	
3	3 (1%)	-	60	12	85	
4	2 (1%)	HMPA	60	12	99	
5	2 (1%)	CHCl ₃	60	12	91	
6	2 (1%)	PhCl	60	12	96	
7	2 (1%)	toluene	60	12	95	
8	2 (1%)	n-hexane	60	12	90	
9	2 (1%)	THF	60	12	94	
10	2 (1%)	-	60	6	98	
11	2 (1%)	-	40	12	91	
12	2 (1%)	-	r.t.	12	77	

^a Conditions: neat substrates in a 1:1 ratio, 60 °C. ^b Yield determined by ¹H NMR and ³¹P NMR spectroscopy in CDCl₃.

hat less active in comparison with complex **2** (Table 3, entry 3). Several reaction conditions were then examined using complex **2** and the results are shown in Table 3. The reactions with a loading of 1 mol% of complex **2** at 60 °C could also take place smoothly in HMPA (hexamethylphosphoramide), CHCl₃ or in the non-polar and polar solvents, such as toluene, chlorobenzene, hexane and THF affording the product **4a** in excellent to good yields (Table 3, entries 4–9). Shortening the reaction time to 6 h did not result in the decreasing of the yield (Table 3, entry 10). The reaction temperature shows an effect on the activity: decreasing the reaction temperature led to the decreasing of the yield (Table 3, entries 11 and 12).

Thus complex 2 was chosen as the pre-catalyst, and the hydrophosphination reactions with various alkene substrates were evaluated using 1 mol% of catalyst loading at 60 °C. Representative results are summarized in Table 4. It can be seen that all the reactions with the halogen atom substituted styrene afforded the corresponding products in excellent yields (Table 4, entries 2-6). The substituted styrenes with electrondonating groups, such as OMe, Me or Ph, could also proceed well to give the addition products in excellent yields, except for the substrate with ^tBu group on the phenyl ring (Table 4, entries 7-10). Compared with those of alkaline earth metal, 7a-7d,7f transition metal,^{8b,8c,8e,8g,8n,8q} and Ln^{II} complexes^{7c,9,11a,11c}, the performance of this system is well-matched. Steric factor of the substrate has a great influence on the reactivity. For example, more hindered styrene derivatives are less active (Table 4, entry 11). The similar situation was also documented in the published work.^{8b,8c,11c} Interestingly, the reactions with 2-vinylpyridine and 4-vinylpyridine also proceeded in the presence of CH₃CN affording the anti-Markovnikov addition product in 84% and

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68% yields, respectively (Table 4, entries 12 and 13), which can be well compared with transition metal complexes^{8b,8g,8n,8q} and Ln^{II} complexes.^{11c} However, these reactions under solvent free afforded the product in much lower yields, because of the polymerization side reaction. The reaction with α -methyl styrene did not afford the addition product, but the oligomer of α -methyl styrene instead (Table 4, entry 14). The phenomenon was also found in the catalytic systems reported.7b,8c,8e,11c The application of hydrophosphination in the simple synthesis of phosphinoester product is highlighted, as the phosphinoester core is a dominant sector in the composition of diazo compounds applied in biochemistry. Thus, the reaction with methyl acrylate was examined and found that it could also proceed affording the product 40 in 70% yield (Table 4, entry

the catalyst loading decreased to 0.5 mol%, the addition could still be realized smoothly to afford the conversion of 98% after 2.5 h (Table 5, entry 7). The reaction with a loading of 1 mol% of complex 2 could also carry out smoothly in polar solvent THF (Table 5, entry 3) with 83% translation, whereas, the usage of toluene and chlorobenzene as solvent led to obviously decrease the conversion of phenylacetylene (Table 5, entries 4, 5). In comparison with complex 2, complex 3 showed rather low activity (Table 5, entry 9), which indicated that the framework of the ligand around the Eu metal had great effect on the reactivity. The present hydrophosphination of diphenylphosphine to alkyne is stereoselective, which mainly l-

Table 5 Hydrophosphination of alkynes by complex 2 and 3^a

15).							R-==	∃ + Ph₂PH	Cat.	R	Pho + _	PPh ₂
Table 4	Intermolecular hy R ₂	drophospl	nination of alke	nes to Ph ₂ PH by co	mplex 2^a					z	· ··2 R	E
R	1 + Ph2PH	1 mol%	Cat 2	PPh ₂		Entry	R	Solvent	T (°C)	Time (h)	Conv. (%) ^b	Selectivity ^b
D .	P		D	+	NC 110 (0/)	_ 1	Ph	-	60	2	100	Z:E = 78:22
Entry	R ₁	R_2	Product	Conv.º (%)	Yield ^e (%)	_ 2	Ph	-	60	1.5	98	Z:E = 79:21
1	Ph	Н	4 a	98	91	3	Ph	THF	r.t.	2.5	83	Z:E = 86:14
2	3-BrPh	Н	4b	94	86	4	Ph	toluene	r.t.	2.5	13	Z:E = 100:0
3	4-BrPh	Н	4c	91	85	5	Ph	PhCl	r.t.	2.5	34	Z:E = 85:15
4	2-ClPh	Н	4d	92	86	6	Ph	-	r.t.	2.5	100	Z:E = 77:23
5	3-ClPh	Н	4e	96	89	7^c	Ph	-	r.t.	2.5	98	Z:E = 76:24
6	4-ClPh	Н	4 f	95	88	8	Ph	-	r.t.	1.5	91	Z:E = 74:26
7^d	4-OMePh	Н	4g	96	89	9^d	Ph	-	r.t.	2.5	22	Z:E = 84:16
8^d	4-MePh	Н	4h	96	85	10	4-MePh	-	r.t.	2.5	80	Z:E = 91:9
9^e	4-PhPh	Н	4i	91	82	11	4-OMePh	-	r.t.	2.5	96	Z:E = 97:3
10^d	4- ^t BuPh	Н	4j	86	80	12	2-pyridinyl	-	rt	2.5	100	$Z \cdot E = 70.30$
11^f	Ph	Ph	4k	68	61	13	4-ClPh	-	rt	2.5	100	Z = 75.25
12 ^g	2-Py	Н	41	84	75					2.0	100	
13^h	4-Py	Н	4m	68	60	^a Condi Based (itions: alkyne (1	.0 mmol), Pl	h_2 PH (1.0	0 mmol, 1	l eq), 2 (12.	.5 mg, 1 mol%). ^b 2 ^d Complex 3
14	Ph	CH ₃	4n	-	-	Daseu		sinc specifies	copy m c	JJC13. 0.	.5 1101/0 01	2. Complex 3.
15 ⁱ	COOMe	Н	40	70	63	eads	to anti-addi	tion prod	lucts a	nd Z is	omers a	re preferable

^a Conditions: alkene (1.00 mmol), Ph₂PH (1.00 mmol, 1 eq.), 2 (12.5 mg, 1 mol%), neat, 60 °C, 6 h. ^b Based on ¹H and ³¹P NMR spectroscopy. Isolated yield. ^d 24 h. ^e 24 h, when the loading of 2 up to 2 mol%, 76% conv. ^f24 h. PhCl as solvent (0.200 mL/1 mmol), ^g CH₃CN as solvent (0.200 mL/1 mmol). ^h CH₃CN as solvent (0.600 mL/1 mmol). ⁱ 12 h.

The activity of complexes 2 and 3 for the catalytic intermolecular hydrophosphination of alkyne to Ph2PH was then examined taking the model reactions between phenylacetylene and Ph₂PH. The preliminary results are listed in Table 5. Complex 2 is a highly active pre-catalyst in this transformation, and the activity is higher than that of alkene reaction mentioned above.

The reaction could be conducted at room temperature using 1 mol% of catalyst amount after 2.5 h to give the products in a conversion as high as those obtained at 60°C (Table 5, entries 1, 2 and 6). The reaction still gave the conversion as high as 91% after 1.5 h (Table 5, entry 8). Even

re preferable (Table 5, entries 1-8). The stereoselectivity shown by complex 2 is different from that of the tridentate imino-amidinate Yb^{II} complex reported previously. With the latter one, a syn-addition of diphenylphosphine to alkynes is favorable in most cases.^{7b} differences in stereoselectivity These for the hydrophosphination of alkynes has also been reported with different calcium complexes¹⁹ along with iron^{8f} and zirconium complexes.²⁰ For example, regioselective single hydrophosphination of terminal arylalkynes with secondary phosphines was achieved with an iron complex,^{8f} however, more time and higher temperature were required in that catalytic system compared with our system. The differences shown by various metal complexes in stereoselectivity reveal the impact of the ligand geometry on catalytic performance.

The reactions of the substrate with electron-donating groups of -Me and -OMe lowered the activity, but increase the anti-addition selectivity (Table 5, entries 10 and 11). For example the -OMe group substituted substrate could afford the

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product with a much higher anti-addition selectivity (Z : E = 97: 3) in 96% yield (Table 5, entry 11). The reaction with the electron-withdrawing Cl group substituted substrate yielded the product with the same high level as that for phenylacetylene in the anti-addition selectivity in almost quantitative yield (Table 5, entry 13). The reaction with 2-enthylnylpyridine proceeded well under the present conditions to yield the product in a quantitative conversion. Steric factor of the substrate has a great influence on this transformation. More hindered diphenylacetylene did not afford the addition product under the conditions used.

Conclusions

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Two novel Eu^{II} complexes 2 and 3 supported by bridged bis(guanidinate) ligands were synthesized and structurally characterized. Complex 2 is a bimetallic complex bearing two newly formed three carbon-briged guanidinates through the change of the N atoms coordinated to Eu metal in a μ - η^{1} : η^{2} : η^{2} coordination mode for one ligand and a μ - η^2 : η^2 : η^2 mode for the other interestingly. Complex **3** features an unusual μ - η^1 : η^2 : η^2 coordination mode of the naphthalene-bridged guanidinates onto Eu^{II}. Both complexes can serve as highly active preintermolecular hydrophosphination catalysts for of diphenylphosphine to styrene derivatives and alkynes affording anti-Markovnikov addition products exclusively and mainly anti-addition products in the reactions with alkynes. Further development of new high active Eu^{II} complexes with high selectivity and the investigation of the mechanism of the intermolecular hydrophosphination by Eu^{II} complexes are ongoing in our laboratory.

Experimental

General procedures

All manipulations of air-sensitive materials were carried out under an atmosphere of dry argon by using modified Schlenk line and glovebox techniques. The solvents of THF, toluene, and n-hexane were dried and freed of oxygen by distilling from sodium benzophenone ketyl under argon before use. Diphenylphosphine was purchased from Aldrich and used as received. All the liquid alkenes and alkynes were dried over CaH₂, freshly distilled, and freeze-thaw degassed prior to use. NMR spectra were recorded on a Bruker AVANCE III HD-400 spectrometer (CDCl₃ as solvent). Chemical shifts for ¹H and ¹³C and ³¹P NMR spectra were referenced internally using the residual solvent resonances and reported relative to TMS. Lanthanide metal analysis was carried out by EDTA titration with a xylenol orange indicator and a hexamine buffer. Elemental analysis was performed by directly using a Carlo-Erba EA1110 instrument. The IR spectra were recorded on a Magna-IR 550 spectrometer as KBr pellets. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges.

 $Eu^{III}L^1Cl(THF)_2(1)$. A newly formed Li_2L^1 (1.61 g, 2.90 mmol) was added slowly to an activated solution of EuCl₃ (0.75

g, 2.90 mmol) in THF (15 mL). The mixture was stirred for 24 h at room temperature. The solvent was evaporated under vacuu m to dryness and extracted with toluene to remove the LiCl. Th e black red toluene solution was evaporated under vacuum to dr yness. The solids was washed with hexane three times. Comple x **1** was obtained as red crystals in the solution of THF-hexane (1.90 g, 75%). Anal. Calcd for $C_{31}H_{68}ClN_6O_2Si_2Eu$ (800.49): C, 46.51; H, 8.56; N, 10.50, Eu, 18.98. Found: C, 46.92; H, 8.98; N, 10.94, Eu, 19.42. IR (KBr, cm⁻¹): 2973 (CH₃, s), 2872 (m), 1 628 (C=N, s), 1524 (m), 1470 (m), 1242(m), 1164 (m), 890 (w), 842 (m), 636 (w).

 $[Eu^{II}L^3]_2(2)$

Method1. Into a solution of Na/K alloy (0.11 g, 4.08 mmol) in toluene (4 mL) was added a solution of Eu^{III}L¹Cl(THF)₂(2.97 g, 3.40 mmol) in THF (20 mL). The reaction mixture was stirred for 48 h at room temperature. The precipitate was removed by centrifugation. The volatiles was evaporated under vacuum to dryness and extracted with toluene to remove the NaCl. The clear solution was dried in vacuo, the residual solids crystallized under n-hexane at -5 °C afforded complex **2** as red crystals (1.12 g, 53%). Anal. Calcd for C₄₆H₁₀₄N₁₂Si₄Eu₂ (1241.69): C, 44.50; H, 8.44; N, 13.54; Eu, 24.48. Found: C, 44.88; H, 8.25; N, 13.79; Eu, 24.73.IR (KBr, cm⁻¹): 2971 (s), 1628 (s), 1527 (m), 1456 (m), 1238(m), 1189 (m), 890 (w), 842 (m), 639 (w).

Method2. A newly formed Li_2L^1 (2.92 g, 5.26 mmol) was added slowly to a white suspention solution of EuCl₃ (1.36 g, 5.26 mmol) in THF (30 mL). The color of the solution turned clearly red immediately. The mixture was stirred for 24 h at room temperature. The solvent was evaporated under vacuum to dryness and extracted twice with toluene followed by centrifugation to remove the LiCl. Into a solution of Na/K alloy (0.24 g, 9.47 mmol) in toluene (10 mL) was added the abovementioned clear solution. The reaction mixture was stirred for 48 h at room temperature. The precipitate was removed by centrifugation. The solvent was evaporated under vacuum to dryness, washed with hexane three times and dried in vacuo and extracted with toluene followed by centrifugation to remove the NaCl. The volume of the extract was reduced to 5 mL. Complex **2** was obtained as red crystals (2.02 g, 62%).

 $[Eu^{II}L^2(THF)]_2$ (3). A newly formed Li₂L²₂Li₂ (2.49 g, 2.71 mmol) in THF (16 mL) was added slowly to a white suspention solution of EuCl₃ (1.40 g, 5.43 mmol) in THF (30 mL). The color of the solution turned clearly tan immediately, The mixture was stirred for 24 h at room temperature. The solvent was evaporated under vacuum to dryness and extracted twice with toluene followed by centrifugation to remove the LiCl. Into a solution of Na/K alloy (0.21 g, 8.14 mmol) in toluene (10 mL) was added the above-mentioned clear solution. The color of the solution changed from tan to claret, The reaction mixture was stirred for 48 h at room temperature. The undissolved portion was removed by centrifugation, the volatiles were removed under reduced pressure and washed with hexane three times and dried in vacuo, then extracted with toluene followed by centrifugation to remove the NaCl and dried in vacuo. The extract was crystallized from a mixture of THF-hexane at 0 °C for 2 days gave complex 3 as red crystals

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 $\begin{array}{l} (2.30 \ g, \ 60\%). \ Anal. \ Calcd \ for \ C_{56}H_{88}N_{12}O_2Eu_2 \ (1265.30): \ C, \\ 53.16; \ H, \ 7.01; \ N, \ 13.28; \ Eu, \ 24.02. \ Found: \ C, \ 53.58; \ H, \ 7.45; \\ N, \ 13.70; \ Eu, \ 24.45. \ IR \ (KBr, \ cm^{-1}): \ 3342 \ (m), \ 2971 \ (m), \ 2865 \\ (w), \ 1616 \ (s), \ 1554 \ (s), \ 1546 \ (s), \ 1370 \ (w), \ 1368 \ (w), \ 1195 \ (s), \\ 1153 \ (s), \ 821 \ (w), \ 764 \ (m), \ 620 \ (m), \ 555 \ (m). \end{array}$

NMR-scale catalytic reactions

The catalyst (0.01 mmol, 1 mol%) was loaded in a 10 mL Sample bottle (with a stirring bar) in the nitrogen glovebox. To the bottle were added the Ph₂PH (5.747 M, 1.00 mmol) and the alkene/alkyne (1.00 mmol). The reaction time started at 60 °C or room temperature in a prepared apparatus. After the desired reaction time, CDCl₃ was added to the selected reaction mixture, and the ¹H NMR and ³¹P NMR spectrum was recorded shortly after at regular time intervals. Conversion was determined by integrating the remaining alkene/alkyne and the newly formed addition product.

Preparative-scale catalytic reactions

The complex 2 (12.5 mg, 0.01 mmol) was loaded in a 10 mL Sample bottle (with a stirring bar) in the nitrogen glovebox. To the bottle were added the Ph_2PH (0.175 mL, 5.747 M, 1.00 mmol) and the alkene (1.00 mmol). The reaction time started at 60 °C in a preheated apparatus. After the reaction was complete, the product was purified by chromatography on silica gel (ethyl acetate/petroleum ether). The identity of the product was confirmed by NMR spectroscopy and TLC.

X-ray Crystallography

Crystals of complexes 1-3 fit for X-ray diffraction were sealed in thin-walled glass capillary filled with argon. Diffraction data were collected on a Agilent Xcalibur CCD area detector in the ω scan mode using Mo Kα radiation (λ = 0.71073 Å) for complex 1 and on a Rigaku Saturn CCD area detector in the ω scan mode using Mo K α radiation ($\lambda = 0.71075$ Å) for complexes 2, 3. The diffracted intensities were corrected for Lorentz-polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in the supporting materials. The structures were solved by direct methods and refined by full-matrix leastsquares procedures based on $|F|^2$. All of the non-hydrogen atoms were refined with anisotropic displacement coefficients. The hydrogen atoms in these complexes were all generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. The structures were solved and refined using SHELXL-2014/7 programs.

These data can be obtained free of charge from the Cambri dge Crystallographic Data Centre via www. ccdc. cam. ac. uk/d ata_request/cif.

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Synthesis and molecular structures of divalent bridged bis(guanidinate) europium complexes and their application in intermolecular hydrophosphination of alkenes and alkynes

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The bimetallic Eu^{II} complexes supported by bridged bis(guanidinate) ligands are efficient precatalysts for the intermolecular hydrophosphination of alkenes and alkynes.