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Synthesis of Bis(NHC)-Based CNC-Pincer Rare-Earth-Metal Amido Complexes and Their Application for the Hydrophosphination of Heterocumulenes

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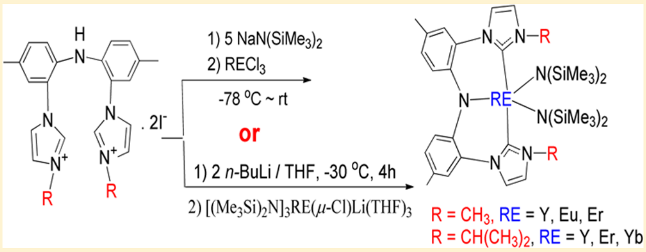
Ⓢ *Supporting Information*

ABSTRACT: The bis(NHC) (NHC = N-heterocyclic carbene)-based CNC-pincer rare-earth-metal amido complexes $LRE[N(SiMe_3)_2]_2$ ($\mathbf{L}$ = 4-CH_3-2-{R-[$N(CH)_2CN$]}$C_6H_3]_2N$; $\mathbf{L^2}$, R = CH_3; $\mathbf{L^3}$, R = $CH(CH_3)_2$) were synthesized and characterized, and their catalytic activities toward hydrophosphination of heterocumulenes were developed. Reactions of bis[2-(3-methylimidazolium)-4-methylphenyl]amine diiodide ($H_3\mathbf{L^2}I_2$) or bis[2-(3-isopropylimidazolium)-4-methylphenyl]amine diiodide ($H_3\mathbf{L^3}I_2$) with 5 equiv of $NaN(SiMe_3)_2$ followed by treatment with 1 equiv of $RECl_3$ in THF at −78 °C afforded the bis(NHC)-based CNC-pincer rare-earth-metal amido complexes $\mathbf{L}RE[N(SiMe_3)_2]_2$ ($\mathbf{L^2}$ = [4-CH_3-2-{CH_3-[$N(CH)_2CN$]}$C_6H_3]_2N$, RE = Y (**1**), Eu (**2**), Er (**3**); $\mathbf{L^3}$ = [4-CH_3-2-{$(CH_3)_2CH$-[$N(CH)_2CN$]}$C_6H_3]_2N$, RE = Y (**4**), Er (**5**), Yb (**6**)). Complexes **4**−**6** can also be prepared by stepwise reactions of $H_3\mathbf{L^3}I_2$ with *n*-BuLi in THF followed by reactions with $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$. Stepwise reactions of $H_3\mathbf{L^2}I_2$ with *n*-BuLi in THF followed by treatment with $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ generated the bis(NHC)-based CNC-pincer rare-earth-metal amido complexes $\mathbf{L^2}RE[N(SiMe_3)_2]_2$ (RE = Y (**1**), Er (**3**)) together with the fused-heterocyclic compound 3,8,9-trimethyl-8a,9-dihydro-8*H*-benzo[4,5]imidazo[2′,1′:2,3]imidazo[1,2-*a*]imidazo[2,1-*c*]quinoxaline (**7**), which formed through carbene C−C and C−N coupling. Attempts to prepare complexes of the type $\mathbf{L}RE[N(SiMe_3)_2]_2$ by reaction of $H_3\mathbf{L^3}I_2$ with $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ in THF, however, afforded mixed complexes of the bis(NHC)-based CNC-pincer ytterbium complex $\mathbf{L^3}Yb[N(SiMe_3)_2]_2$ (**6**) and the unexpected bis(NHC)-based CNC-pincer monoamido ytterbium iodide $\mathbf{L^3}YbI[N(SiMe_3)_2]$ (**8**). Investigation of the catalytic activity of complexes **1**−**6** and **8** indicated that all complexes displayed high activity toward the addition of the phosphine P−H bond to heterocumulenes, producing the corresponding phosphaguanidines, phosphaureas, and phosphathioureas, which represents the first example of bis(NHC)-based CNC-pincer type rare-earth-metal amido complexes as catalysts for the catalytic addition of the phosphine P−H bond to heterocumulenes with high efficiency in the presence of a low catalyst loading at room temperature.



■ INTRODUCTION

Rare-earth-metal complexes have been successfully used as catalysts or precatalysts in a range of chemical transformations, including various types of polymerization and copolymerization,[1] hydroamination,[2] hydrosilylation,[3] hydroboration,[4] hydroalkoxylation,[5] hydrothiolation,[5e,6] and hydrophosphination.[2a,7] Organolanthanide-catalyzed hydrophosphination was focused on the area of intramolecular hydrophosphination/cyclization of alkenes and alkynes and intermolecular hydrophosphination of alkenes and alkynes.[2a,7] Rare-earth-metal amido complex promoted intermolecular hydrophosphination of heterocumulenes has still been poorly investigated.[8]

Functionalized N-heterocyclic carbene (NHC) ligands have undergone an upsurge in research interest since their first discovery.[9] Different types of NHC lanthanide complexes have been developed in the past decade.[10] Advantages of the bis(NHC)-incorporated tridentate pincer ligand with strongly electron donating ylidene carbons and the precise tailoring of the metal coordination sphere could provide viable complexes and enable the complexes to be used as homogeneous catalysts.[11] However, bis(NHC)-incorporated tridentate pincer rare-earth-metal complexes have been less developed.[10b,d,f] Recently, we reported the synthesis of a series of the CNC-pincer diarylamido bis(NHC)-ligated rare-earth-metal complexes under different reaction conditions which exhibited a

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high catalytic activity toward the addition of the terminal alkyne C−H bond to carbodiimides.[10b] In order to offer more useful information on the preparation of different types of bis(NHC)-incorporated rare-earth-metal complexes, reactions of different substituted imidazolium salts H_3LI_2 (**L** = [4-CH_3-2-{(R-[N(CH)$_2$CN]}-C_6H_3]$_2$N; **L**^{2}, R = CH_3; **L**^{3}, R = $CH(CH_3)_2$) with different bases followed by treatment with $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ or $RECl_3$ under different reaction conditions were examined.

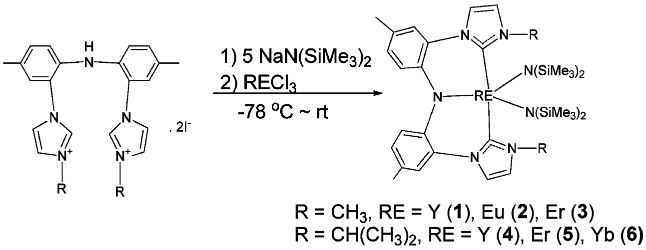
On the other hand, catalytic addition of the phosphine P−H bond to the heterocumulenes could provide a straightforward and atom-economical route to valuable phosphorus analogues of phosphaguanidines, phosphaureas, and phosphathioureas which could be used as ligands for the metal complexes,[12] in medicine,[13] in materials chemistry,[14] and as synthons in organic chemistry.[15] Early investigations demonstrated that alkali-metal and alkaline-earth-metal amides could serve as catalysts for the hydrophosphination of carbodiimides.[16] Recently, Hou et al. reported that the half-sandwich rare-earth-metal (trimethylsilyl)methyl alkyl complexes could catalyze the addition of the phosphines P−H bond to carbodiimides,[8a] but these reactions required an elevated temperature (80 °C). Schmidt and co-workers showed that homoleptic α-metalated dimethylbenzylamine lanthanide complexes could efficiently catalyze the hydrophosphination of heterocumulenes; however, these catalysts required a high loading (5 mol %), and 1.15 equiv of Ph_2PH to offset the amount of consumed phosphine in the process of activation of the precatalyst.[8b] Thus, catalysts operating at room temperature exhibiting a high activity with low catalyst loading and solvent compatibility for the catalytic addition of the phosphine P−H bond to heterocumulenes are highly required. Here, we wish to report the synthesis of bis(NHC)-based CNC-pincer rare-earth-metal amido complexes which displayed a high catalytic activity toward the hydrophosphination of heterocumulenes in different solvents at room temperature. To the best of our knowledge, this represents the first example of bis(NHC)-based CNC-pincer rare-earth-metal amido complexes used as catalysts for catalytic addition of the phosphine P−H bonds to heterocumulenes, producing phosphaguanidines, phosphaureas, and phosphathioureas with high efficiency.

■ RESULTS AND DISCUSSION

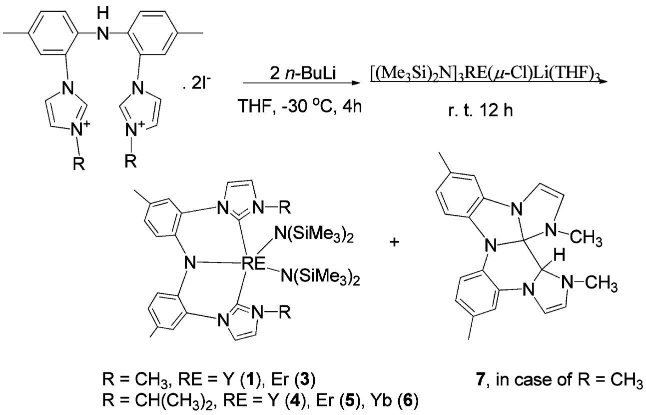
Synthesis and Characterization of Bis(NHC)-Based CNC-Pincer Rare-Earth-Metal Amido Complexes. The bis(NHC)-based CNC-pincer rare-earth-metal amido complexes $\mathbf{L}^2RE[N(SiMe_3)_2]_2$ ($\mathbf{L}^2$ = [4-CH_3-2-{CH_3[N-(CH)$_2$CN]}C_6H_3]$_2$N; RE = Y (**1**), Eu (**2**), Er (**3**)) were prepared in moderate yields by treatment of bis[2-(3-methylimidazolium)-4-methylphenyl]amine diiodide ($H_3\mathbf{L}^2I_2$) with 5 equiv of $NaN(SiMe_3)_2$ followed by reaction with 1 equiv of $RECl_3$ in THF at −78 °C (Scheme 1). The bis(NHC)-based CNC-pincer rare-earth-metal amido complexes $\mathbf{L}^3RE[N(SiMe_3)_2]_2$ ($\mathbf{L}^3$ = [4-CH_3-2-{$(CH_3)_2CH$[N(CH)$_2$CN]}-C_6H_3]$_2$N; RE = Y (**4**), Er (**5**), Yb (**6**)) could be obtained under similar conditions.

In our previous work, we found that the stepwise treatment of bis[2-(3-benzylimidazolium)-4-methylphenyl]amine dichloride ($H_3\mathbf{L}^1Cl_2$) with *n*-BuLi in THF at −30 °C followed by reactions with $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ generated the zwitterionic complexes $[\{\mathbf{L}^1{}_2RE\}\{RECl[N(SiMe_3)_2]_3\}]$ ($\mathbf{L}^1$ = [4-CH_3-2-{($C_6H_4CH_2$-[N(CH)$_2$CN]}C_6H_3]$_2$N) and a fused-heterocyclic compound.[10b] However, following this method, the complexes $\mathbf{L}^2RE[N(SiMe_3)_2]_2$ (RE = Y (**1**), Er (**3**)), not the zwitterionic analogues, were isolated in moderate yields, but the fused-heterocyclic compound 3,8,9-trimethyl-8a,9-dihydro-8*H*-benzo[4,5]imidazo[2′,1′:2,3]imidazo[1,2-*a*]imidazo[2,1-*c*]-quinoxaline (**7**) was also isolated as a byproduct (Scheme 2 and Figure 1). The fused-heterocyclic compound **7** was formed through carbene C−C and C−N coupling. This result was similar to that in our previous work in part.[10b] When the bis[2-(3-methylimidazolium)-4-methylphenyl]amine diiodide

Scheme 1. Synthetic Pathway for Preparation of Diarylamido-Linked Bis(NHC) Rare-Earth-Metal Amides



Scheme 2. Stepwise Reactions of $H_3L^2I_2$ or $H_3L^3I_2$ with Base Followed by Reaction with $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$



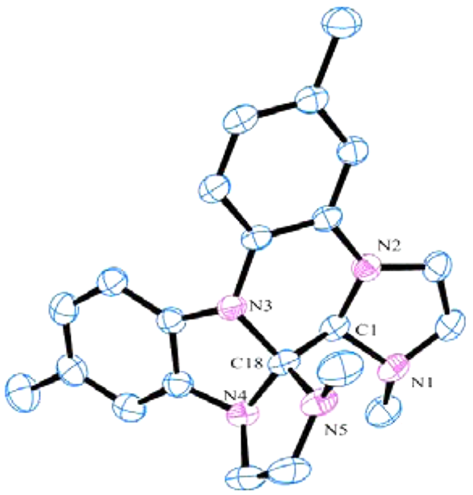
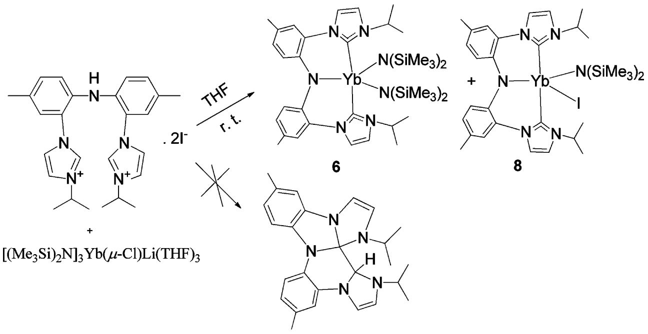


Figure 1. Structure of fused-heterocyclic compound **7**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C(1)−C(18), 1.528(3); N(3)−C(18), 1.491(3); N(4)−C(18), 1.473(3); N(5)−C(18), 1.456(3).

($H_3L^2I_2$) was changed to bis[2-(3-isopropylimidazolium)-4-methylphenyl]amine diiodide ($H_3L^3I_2$), only the bis(NHC)-based CNC-pincer rare-earth-metal amido complexes $L^3RE[N(SiMe_3)_2]_2$ (RE = Y (**4**), Er (**5**), Yb (**6**)) were isolated under the same conditions; neither the analogues of the fused-heterocyclic compound **7** nor the zwitterionic complexes were isolated. These results suggested that the substituents on the imidazolium ring have a significant influence on the final products.

Another method for the preparation of the bis(NHC)-based CNC-pincer rare-earth-metal complexes was also tested by reaction of $[(Me_3Si)_2N]_3Yb(\mu\text{-Cl})Li(THF)_3$ with 1 equiv of bis[2-(3-isopropylimidazolium)-4-methylphenyl]amine diiodide ($H_3L^3I_2$) in THF at room temperature, after workup, producing the bis(NHC)-based CNC-pincer ytterbium amido complex $L^3Yb[N(SiMe_3)_2]_2$ (**6**) and the unexpected bis(NHC)-based CNC-pincer monoamido ytterbium iodide $L^3YbI[N(SiMe_3)_2]$ (16% yield) (**8**) (Scheme 3 and Figure 2). The result is also different from that of the reaction of $[(Me_3Si)_2N]_3Yb(\mu\text{-Cl})Li(THF)_3$ with $H_3L^1Cl_2$, which only afforded a fused-heterocyclic compound.[10b]

Scheme 3. Reactions of $H_3L^3I_2$ with $[(Me_3Si)_2N]_3Yb(\mu\text{-Cl})Li(THF)_3$



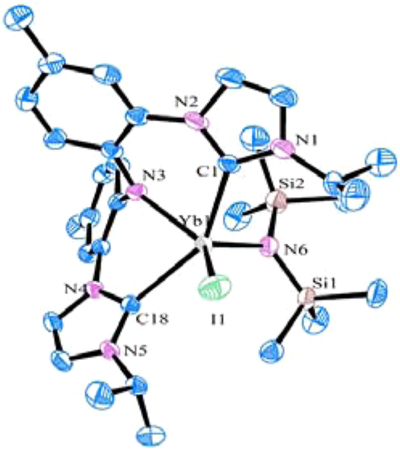


Figure 2. Structure of complex **8**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Yb(1)−C(1), 2.420(8); Yb(1)−C(18), 2.485(8); Yb−C_{av}, 2.453(8); Yb(1)−N(3), 2.228(6); Yb(1)−N(6), 2.187(7); Yb(1)−I, 2.9506(9).

The molecular structures of complexes **1**−**6** and **8** were determined by single-crystal X-ray analyses. The representative structural diagrams of complexes **1** and **4** are shown in Figures 3 and 4, respectively. The important bond distances and angles are summarized in Table 1.

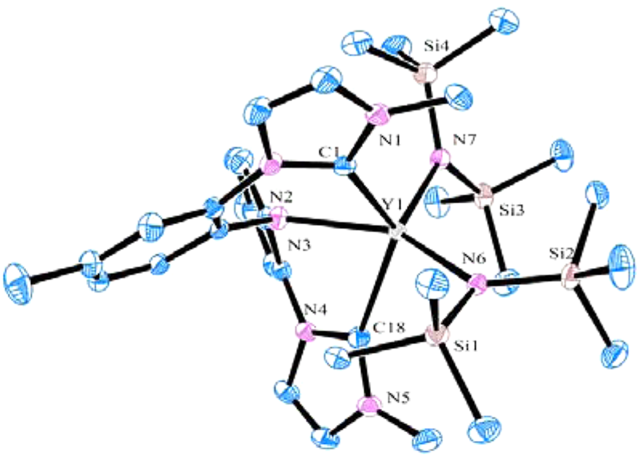


Figure 3. Molecular structure of complex **1**. Hydrogen atoms are omitted for clarity.

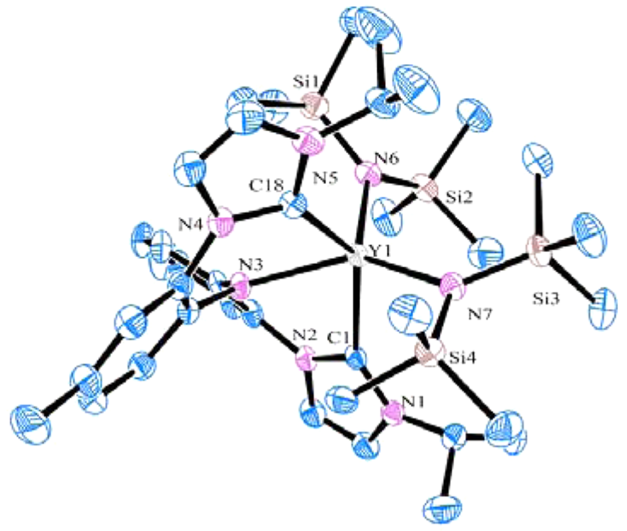


Figure 4. Molecular structure of complex **4**. Hydrogen atoms are omitted for clarity.

X-ray analyses revealed that complexes **1**−**6** adopt a similar structure. The diarylamido-linked bis(NHC) ligand coordinates to the central metal ion in a tridentate mode by the amido nitrogen and the two carbene carbon atoms, forming a distorted-trigonal-bipyramidal geometry with the two silylamido N″ groups and the amido group occupying the equatorial positions having sums of the angles of N(3)−RE−N(6), N(6)−RE−N(7), and N(7)−RE−N(3) of 359.34(9)° for **1**, 359.30(11)° for **2**, 359.5(2)° for **3**, 359.91(14)° for **4**, 359.91(11)° for **5**, and 359.9(3)° for **6** and the two carbene carbon atoms at the axial sites. The average RE−$C_{carbene}$ bond lengths, 2.532(3) Å in **1**, 2.579(4) Å in **2**, 2.548(9) Å in **3**, 2.547(4) Å in **4**, 2.517(4) Å in **5**, and 2.494(9) Å in **6**, fall in the range of the linkage of a lanthanide metal ion and an ylidene carbon[10f,17] and are quite consistent with the trend of ionic radii of the corresponding lanthanide elements. These average RE−$C_{carbene}$ bond lengths are comparable to the corresponding RE−$C_{carbene}$ bond lengths found in previous reports.[10b,f,h] The ^1H (or ^{13}C) NMR spectra for **1** and **4** were also indicative of the formation of the bis(NHC)-based CNC-pincer complexes. The ^1H NMR spectrum of the complex **1** showed the disappearance of the proton resonances of N*H*, and NC(*H*)

Table 1. Selected Bond Distances (Å) and Angles (deg) for Complexes 1−6

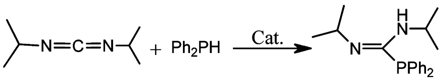
	RE					
	Y (**1**)	Eu (**2**)	Er (**3**)	Y (**4**)	Er (**5**)	Yb (**6**)
RE(1)−N(3)	2.322(2)	2.364(3)	2.329(6)	2.321(3)	2.305(3)	2.279(8)
RE(1)−N(6)	2.300(2)	2.342(3)	2.293(6)	2.313(4)	2.299(3)	2.265(8)
RE(1)−N(7)	2.260(3)	2.303(3)	2.244(7)	2.272(4)	2.262(3)	2.267(8)
RE(1)−C(1)	2.505(3)	2.606(4)	2.489(7)	2.553(4)	2.513(4)	2.493(9)
RE(1)−C(18)	2.559(3)	2.552(4)	2.608(9)	2.542(4)	2.521(4)	2.495(9)
RE−C_{av}	2.532(3)	2.579(4)	2.548(9)	2.547(4)	2.517(4)	2.494(9)
N(3)−RE(1)−N(6)	139.53(9)	137.65(11)	139.6(2)	135.96(13)	136.46(11)	137.4(3)
N(3)−RE(1)−N(7)	101.88(9)	102.64(11)	102.5(2)	101.85(13)	101.82(11)	101.5(3)
N(6)−RE(1)−N(7)	117.93(9)	119.01(11)	117.4(2)	122.10(14)	121.63(11)	121.0(3)
C(1)−RE(1)−C(18)	131.25(11)	128.17(13)	130.8(2)	140.56(15)	141.47(12)	142.8(3)

N at 5.30 and 9.55 ppm assigned to the free ligand $H_3L^2I_2$. The ^{13}C NMR spectrum of complex **1** showed a doublet carbene carbon resonances at about 192.0 ppm ($^1J_{Y-C}$ = 38 Hz), suggesting that the carbene carbons were bound to the metal center. Similarly, the formation of complex **4** can also be proved by the NMR results.

The above results indicated that the substituents on the bis(imidazolium) salts had a significant influence on controlling the reaction pathway and the final complexes. The fact that a low-temperature reaction could prevent the in situ formed bis(NHC) from coupling is noted. The results provided useful information for the preparation of different types of NHC-ligated rare-earth-metal complexes.

Catalytic Activity toward Addition of the Phosphine P−H Bond to Heterocumulenes. Catalytic hydrophosphination of heterocumulenes could be a straightforward and atom-economical route to the phosphorus analogues of guanidines, ureas, thioureas, and amidines. Previously developed rare-earth-metal complexes as catalysts for the catalytic addition of the phosphine P−H bond to the carbodiimides and heterocumulenes required harsh conditions such as elevated reaction temperatures of 80 °C,[8a] were only active in polar solvents, and required a high catalyst loading (5 mol %).[8b] The fact that the carbene ligands have a strongly electron donating property which affects the catalytic activity of the complexes has been established;[10b] with the above bis(NHC)-based CNC-pincer rare-earth-metal amido complexes in hand, the catalytic activities of these complexes toward the hydrophosphination of heterocumulenes were examined. The catalytic reaction of diphenylphosphine (Ph_2PH) with *N*,*N*′-diiospropylcarbodiimide ($^iPrN{=}C{=}N^iPr$) was examined under various conditions (Table 2).

Table 2. Optimization of the Conditions for the Catalytic Addition of the Diphenylphosphine P−H Bond to Diisopropylcarbodiimide[a]



9a

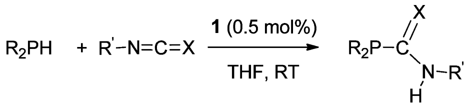
entry	cat. (amt (mol %))[c]	solvent	yield (%)[b]
1	**1** (1)	THF	100
2	**1** (0.5)	THF	99
3	**1** (0.25)	THF	47
4	**1** (0.5)	toluene	98
5	**1** (0.5)	hexane	96
6	**2** (0.5)	THF	99
7	**3** (0.5)	THF	98
8	**4** (0.5)	THF	99
9	**5** (0.5)	THF	98
10	**6** (0.5)	THF	96
11	**8** (0.5)	THF	94

[a] Reaction conditions: diisopropylcarbodiimide (2.0 mmol), diphenylphosphine (2.0 mmol), solvent (5 mL), room temperature, 0.5 h. [b] Isolated yields. [c] cat.: $L^2RE[N(SiMe_3)_2]_2$ (RE = Y (**1**), Eu (**2**), Er (**3**)); $L^3RE[N(SiMe_3)_2]_2$ (RE = Y (**4**), Er (**5**), Yb (**6**)); $L^3YbI[N(SiMe_3)_2]$ (**8**).

The catalytic reaction of diphenylphosphine (Ph_2PH) with *N*,*N*′-diisopropylcarbodiimide ($^iPrN{=}C{=}N^iPr$) was first examined in the presence of a 1 mol % loading of complex **1** in THF; the reaction was completed in 0.5 h with a quantitative conversion of the substrate to the final product. Decreasing the catalyst loading to 0.5 mol % also afforded the product in almost quantitative yield. Different solvents such as toluene and *n*-hexane only slightly affected the yields of the reaction, indicating the solvent compatibility of the catalysts. Different catalysts **2**−**6** and **8** also exhibited an excellent catalytic activity for the reaction. These results indicated that the bis(NHC)-based CNC-pincer type rare-earth-metal amido complexes have the advantages of high activity, solvent compatibility, and high efficiency.

Next, different substrates of phosphines and heterocumulenes were tested under the above optimized conditions (0.5 mol % loading of catalyst **1**, room-temperature reaction in THF). It is found that both Ph_2PH and $(4\text{-}MeC_6H_4)_2PH$ worked well with *N*,*N*′-diisopropylcarbodiimide and *N*,*N*′-dicyclohexylcarbodiimide, producing the corresponding final products in almost quantitative yields. However, the sterically bulky *N*,*N*′-di-*tert*-butylcarbodiimide is inactive in the reaction, probably due to steric effects. This result is parallel to that previously reported (Table 3, entry 3).[16b] The hydrophosphination reaction also worked well with the isothiocyanates; the reaction was tolerant of both electron-donating groups such as CH_3O- and CH_3- and electron-withdrawing groups such as F− and Br−, producing the corresponding phosphathioureas in very good to quantitative yields. However, isothiocyanates with electron-withdrawing substituted groups such as F− and Br− afforded better results than isothiocyanates with electron-donationg groups such as CH_3O- and CH_3- on the phenyl ring (Table 3, entries 7−10); these results can be attributed to the electron-withdrawing groups making the carbons more electron deficient favorable following addition of the diphenylphosphinyl group (RE−PPh_2) to the carbon. Again, it is found that the $(4\text{-}MeC_6H_4)_2PH$ worked well with the isothiocyanates, producing the corresponding products in good to quantitative yields. Electronic effects for the substrates

Table 3. Catalytic Addition of Various Phosphines to Heterocumulenes by Catalyst 1[a]



entry	R_2PH	R′/X	product R/R′/X	yield (%)[b]
1	Ph_2PH	$^iPr/N^iPr$	$Ph/^iPr/N^iPr$	**9a** (99)
2	Ph_2PH	Cy/NCy	Ph/Cy/NCy	**9b** (99)
3	Ph_2PH	$^tBu/N^tBu$	no product	
4	$(4\text{-}MeC_6H_4)_2PH$	$^iPr/N^iPr$	$4\text{-}MeC_6H_4/^iPr/N^iPr$	**9c** (99)
5	$(4\text{-}MeC_6H_4)_2PH$	Cy/NCy	$4\text{-}MeC_6H_4$/Cy/NCy	**9d** (98)
6	Ph_2PH	Ph/S	Ph/Ph/S	**9e** (100)
7	Ph_2PH	$4\text{-}FC_6H_4/S$	$Ph/4\text{-}FC_6H_4/S$	**9f** (100)
8	Ph_2PH	$4\text{-}BrC_6H_4/S$	$Ph/4\text{-}BrC_6H_4/S$	**9g** (100)
9	Ph_2PH	$4\text{-}MeC_6H_4/S$	$Ph/4\text{-}MeC_6H_4/S$	**9h** (94)
10	Ph_2PH	$4\text{-}MeOC_6H_4/S$	$Ph/4\text{-}MeOC_6H_4/S$	**9i** (86)
11	$(4\text{-}MeC_6H_4)_2PH$	Ph/S	$4\text{-}MeC_6H_4/Ph/S$	**9j** (99)
12	$(4\text{-}MeC_6H_4)_2PH$	$4\text{-}FC_6H_4/S$	$4\text{-}MeC_6H_4/4\text{-}FC_6H_4/S$	**9k** (99)
13	$(4\text{-}MeC_6H_4)_2PH$	$4\text{-}BrC_6H_4/S$	$4\text{-}MeC_6H_4/4\text{-}BrC_6H_4/S$	**9l** (96)
14	$(4\text{-}MeC_6H_4)_2PH$	$4\text{-}MeC_6H_4/S$	$4\text{-}MeC_6H_4/4\text{-}MeC_6H_4/S$	**9m** (90)
15	$(4\text{-}MeC_6H_4)_2PH$	$4\text{-}MeOC_6H_4/S$	$4\text{-}MeC_6H_4/4\text{-}MeOC_6H_4/S$	**9n** (81)
16	Ph_2PH	Cy/O	Ph/Cy/O	**9o** (97)
17	Ph_2PH	$4\text{-}FC_6H_4/O$	-	**10a**[c]

[a]Reaction conditions: heterocumulenes (2.0 mmol), phosphine (2.0 mmol), catalyst (0.01 mmol), THF (5 mL). [b]Isolated yields. [c]The trimerized isocyanate product **10a**.

of the isothiocyanates similar to those of the reactions of Ph_2PH with isothiocyanates were found (Table 3, entries 12−15). However, when the isocyanates were used for the reaction, only an aliphatic substrate such as CyN═C═O worked well, producing the phosphaurea in very high yield (Table 3, entry 16). The aromatic isocyanates all produced the cyclotrimerization products; no phosphaureas could be isolated (Table 3, entry 17). These results were different from previous observations.[8b]

■ CONCLUSION

In summary, we have demonstrated that a variety of bis(NHC)-based CNC-pincer rare-earth-metal amido complexes can be synthesized and characterized. The results indicated that the reaction conditions and substituents of imidazolium salts both play important roles in the formation of final products. This work offers useful information for the preparation of different types of bis(NHC)-based rare-earth-metal complexes. The bis(NHC)-based CNC-pincer rare-earth-metal amides displayed a high catalytic activity toward the addition of the phosphine P−H bond to heterocumulenes, producing the corresponding phosphaguanidines, phosphaureas, and phosphathioureas with low catalyst loading at room temperature. Further studies on the reactivity and catalytic activities of these kinds of complexes are in progress.

■ EXPERIMENTAL SECTION

General Procedure. All manipulations were carried out under a dry oxygen-free argon atmosphere using standard Schlenk techniques or in a glovebox unless otherwise stated. All solvents (hexane, THF, diethyl ether) were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. $RECl_3$,[18] $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Y, Eu, Er, Yb),[19] bis[2-(3-methylimidazolium)-4-methylphenyl]amine diiodide ($H_3\mathbf{L}^2I_2$),[20] and bis[2-(3-isopropylimidazolium)-4-methylphenyl]amine diiodide ($H_3\mathbf{L}^3I_2$)[20] were prepared according to the literature methods. Elemental analysis data were obtained on a PerkinElmer Model 2400 Series II macro-elemental analyzer. ^1H NMR, ^{13}C NMR, and ^{31}P NMR spectra for analyses of compounds were recorded on a Bruker 300 or 500 NMR spectrometer (300 MHz for ^1H; 75 MHz for ^{13}C; 500 MHz for ^1H; 125 MHz for ^{13}C; 121 MHz for ^{31}P), and all chemical shift values refer to TMS (δ 0.00 ppm), $CDCl_3$ ($\delta(^1H)$, 7.26 ppm; $\delta(^{13}C)$, 77.16 ppm), C_6D_6 ($\delta(^1H)$, 7.15 ppm; $\delta(^{13}C)$, 128.06 ppm), or C_4D_8O ($\delta(^1H)$, 1.72, 3.58 ppm; $\delta(^{13}C)$, 25.31, 67.21 ppm). J values are reported in Hz. Phosphorus chemical shifts were measured relative to an external 85% aqueous solution of H_3PO_4. IR spectra were recorded on a Shimadzu Model FTIR-8400s spectrometer (KBr pellet). Mass spectra were performed on an Agilent Model 6220 Micromass GCT-MS spectrometer. Crystallographic X-ray data were collected on a SMART 1000 CCD area detector diffractometer.

Preparation of $[L^2Y\{[N(SiMe_3)_2]_2\}]$ (1). To a suspension of bis[2-(3-methylimidazolium)-4-methylphenyl]amine diiodide $H_3\mathbf{L}^2I_2$ (920 mg, 1.50 mmol) in THF (20 mL) was added a solution of 2 M $NaN(SiMe_3)_2$ in THF (3.75 mL, 7.50 mmol)) dropwise with stirring for 8 h at −78 °C, and then a THF suspension of YCl_3 (293 mg, 1.50 mmol) was added to the mixture. The mixture was slowly warmed to room temperature overnight. The solvent was removed under reduced pressure to afford a yellow solid, which was recrystallized from hexane to give yellow crystals of **1** in 38% yield (437 mg) for X-ray analysis. ^1H NMR (500 MHz, C_6D_6/d_8-THF 3/1 v/v): δ 6.92−6.91 (d, J = 5.0 Hz, 2H, imi-H), 6.87−6.86 (d, J = 5.0 Hz, 2H, imi-H), 6.69−6.68 (d, J = 5.0 Hz, 1H, Ar-H), 6.67−6.66 (d, J = 5.0 Hz, 1H, Ar-H), 6.61 (s, 1H, Ar-H), 6.59 (s, 1H, Ar-H), 6.26−6.26 (d, J = 1.7 Hz, 2H, Ar-H), 3.70 (s, 6H, Ar-CH_3), 2.07 (s, 6H, N-CH_3), 0.25 (s, 18H, $Si(CH_3)_3$), −0.20 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (125 MHz, C_6D_6/d_8-THF 3/1 v/v): δ 192.0 (NCN, d, $^1J_{Y-C(\text{carbene})}$ = 38 Hz), 146.9, 132.4, 129.0, 127.0, 123.3 (Ar-C), 121.2, 120.1 (imi-C), 38.2 (NCH_3), 20.4 ($ArCH_3$), 6.7 ($Si(CH_3)_3$), 4.5 ($Si(CH_3)_3$). Anal. Calcd for $C_{34}H_{58}N_7Si_4Y$: C, 53.30; H, 7.63; N, 12.80. Found: C, 53.03; H, 7.67; N, 12.44. Mp: 162−164 °C. IR (KBr pellets, cm^{-1}): ν 2951 (s), 1663 (w), 1605 (w), 1585 (m), 1516 (s), 1485 (m), 1381 (m), 1310 (m), 1076 (m), 934 (s), 837 (m), 746 (s), 667 (m).

Preparation of $[L^2Eu\{[N(SiMe_3)_2]_2\}]$ (2). This complex was prepared as purple crystals in 35% yield (435 mg) following the procedures similar to those described for the preparation of **1** by treatment of a THF suspension of $H_3\mathbf{L}^2I_2$ (920 mg, 1.50 mmol) with a solution of 2 M $NaN(SiMe_3)_2$ in THF (3.75 mL, 7.50 mmol), followed by reaction with a THF suspension of $EuCl_3$ (387 mg, 1.50 mmol). Anal. Calcd for $C_{34}H_{58}N_7Si_4Eu \cdot C_6H_{14}$ (**2**·C_6H_{14}): C, 52.49; H, 7.93; N, 10.71. Found: C, 52.74; H, 7.62; N, 10.77. Mp: 167−169 °C. IR (KBr pellets, cm^{-1}): ν 2963 (s), 1670 (m), 1577 (w), 1516 (m), 1400 (m), 1312 (w), 1251 (s), 1096 (m), 1031 (m), 939 (s), 918 (s), 843 (m), 802 (s), 700 (m).

Preparation of [$L^2Er\{[N(SiMe_3)_2]_2\}$] (3). This complex was prepared as yellow crystals in 30% yield (380 mg) following procedures similar to those described for the preparation of **1** by treatment of a THF suspension of $H_3\mathbf{L}^2I_2$ (920 mg, 1.50 mmol) with a solution of 2 M $NaN(SiMe_3)_2$ in THF (3.75 mL, 7.50 mmol), followed by reaction with a THF suspension of $ErCl_3$ (410 mg, 1.50 mmol). Anal. Calcd for $C_{34}H_{58}N_7Si_4Er \cdot 1.5C_6H_{14}$ (**3**·$1.5C_6H_{14}$): C, 53.04; H, 8.18; N, 10.07. Found: C, 53.04,; H, 7.84; N, 10.38. Mp: 161−163 °C. IR (KBr pellets, cm^{-1}): ν 2951 (m), 1681 (w), 1572 (m), 1512 (s), 1491 (s), 1302 (m), 1240 (m), 1177 (m), 1138 (m), 1064 (m), 1016 (w), 945 (s), 837 (m), 793 (s), 669 (m).

Preparation of [$L^3Y\{[N(SiMe_3)_2]_2\}$] (4). This complex was prepared as yellow crystals in 36% yield (453 mg) following the procedures similar to those described for the preparation of **1** by treatment of a THF suspension of $H_3\mathbf{L}^3I_2$ (1.004 g, 1.50 mmol) with a solution of 2 M $NaN(SiMe_3)_2$ in THF (3.75 mL, 7.50 mmol), followed by reaction with a THF suspension of YCl_3 (293 mg, 1.50 mmol). ^1H NMR (500 MHz, C_6D_6/d_8-THF, 1/5 v/v): δ 7.64 (d, J = 1.8 Hz, 2H, imi-H), 7.51 (d, J = 1.4 Hz, 2H, imi-H), 7.15 (s, 2H, Ar-H), 6.73 (dd, J = 8.3, 1.7 Hz, 2H, Ar-H), 6.43 (d, J = 8.3 Hz, 2H, Ar-H), 5.23 (dt, J = 13.2, 6.6 Hz, 2H, $CH(CH_3)_2$), 2.24 (s, 6H, CH_3), 1.60 (d, J = 6.5 Hz, 6H, $CH(CH_3)_2$), 1.53 (d, J = 6.6 Hz, 6H, $CH(CH_3)_2$), 0.09 (s, 18H, $Si(CH_3)_3$), −0.38 (s, 18H, $Si(CH_3)_3$). ^{13}C NMR (125 MHz, C_6D_6/d_8-THF, 1/5 v/v): δ 190.3 (NCN, d, $^1J_{Y-C(carbene)}$ = 38 Hz), 147.1, 132.8, 128.5, 128.4, 128.3, 125.9, 123.6 (Ar-C), 121.6, 116.8 (imi-C), 51.6 ($CH(CH_3)_3$), 20.0 ($ArCH_3$), 6.7 ($CH(CH_3)_3$), 4.6 ($Si(CH_3)_3$), 2.1 ($Si(CH_3)_3$). Anal. Calcd for $C_{38}H_{66}N_7Si_4Y \cdot C_6H_{14}$ (**4**·C_6H_{14}): C, 58.18; H, 8.88; N, 10.79. Found: C, 58.44; H, 8.65; N, 10.83. Mp: 145−147 °C. IR (KBr pellets, cm^{-1}): ν 2955 (s), 1663 (s), 1603 (m), 1512 (s), 1368 (m), 1250 (m), 1180 (m), 1138 (m), 1074 (w), 1005 (w), 934 (s), 883 (m), 839 (s), 750 (m), 683 (m), 660 (m).

Preparation of [$L^3Er\{[N(SiMe_3)_2]_2\}$] (5). This complex was prepared as yellow crystals in 32% yield (432 mg) following procedures similar to those described for the preparation of **1** by treatment of a THF suspension of $H_3\mathbf{L}^3I_2$ (1.004 g, 1.50 mmol) with a solution of 2 M $NaN(SiMe_3)_2$ in THF (3.75 mL, 7.50 mmol), followed by reaction with a THF suspension of $ErCl_3$ (410 mg, 1.50 mmol). Anal. Calcd for $C_{38}H_{66}N_7Si_4Er$: C, 50.68; H, 7.39; N, 10.89. Found: C, 50.33; H, 7.47; N, 10.74. Mp: 139−141 °C. IR (KBr pellets, cm^{-1}): ν 2955 (s), 1655 (s), 1605 (w), 1560 (w), 1545 (m), 1510 (s), 1481 (m), 1369 (m), 1314 (w), 1250 (m), 1180 (m), 1136 (m), 1074 (w), 1007 (w), 934 (m), 883 (m), 837 (s), 748 (m), 683 (m), 660 (w).

Preparation of [$L^3Yb\{[N(SiMe_3)_2]_2\}$] (6). This complex was prepared as yellow crystals in 31% yield (421 mg) following procedures similar to those described for the preparation of **1** by treatment of a THF suspension of $H_3\mathbf{L}^3I_2$ (1.004 g, 1.50 mmol) with a solution of 2 M $NaN(SiMe_3)_2$ in THF (3.75 mL, 7.50 mmol), followed by reaction with a THF suspension of $YbCl_3$ (419 mg, 1.50 mmol). Anal. Calcd for $C_{38}H_{66}N_7Si_4Yb \cdot 0.6C_6H_{14}$ (**6**·$0.6C_6H_{14}$): C, 52.15; H, 7.83; N, 10.23. Found: C, 52.51; H, 7.57; N, 10.63. Mp: 150−152 °C. IR (KBr pellets, cm^{-1}): ν 2949 (s), 1662 (s), 1605 (w),1553 (w), 1514 (s), 1499 (m), 1427 (w), 1381 (m), 1238 (s), 1194 (s), 1140 (m), 1074 (w), 983 (m), 883 (m), 804 (s), 689 (m), 663 (w), 615 (w).

Complexes **1** and **3**−**6** can also be prepared in 32%, 38%, 46%, 40%, and 33% yields, respectively, by the stepwise treatment of $H_3\mathbf{L}^2I_2$ ($H_3\mathbf{L}^3I_2$) with n-BuLi (2 equiv) in THF at −30 °C for 4 h followed by reaction with $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$.

The fused-heterocyclic compound 3,8,9-trimethyl-8a,9-dihydro-8H-benzo[4,5]imidazo[2′,1′:2,3]imidazo[1,2-a]imidazo[2,1-c]quinoxaline ($C_{22}H_{23}N_5$, **7**) was isolated in 22% and 25% yields, respectively, in the preparation of **1** and **3** following this method. ^1H NMR (300 MHz, C_6D_6, ppm): δ 7.30 (d, J = 7.3 Hz, 1H, Ar-H), 7.12 (d, J = 8.0 Hz, 1H, Ar-H), 6.71−6.62 (m, 3H, Ar-H), 6.45 (s, 1H, Ar-H), 5.87 (d, J = 2.6 Hz, 1H, NCHCHN), 5.58 (d, J = 2.4 Hz, 1H, NCHCHN), 5.37 (d, J = 2.6 Hz, 1H, NCHCHN), 5.31 (d, J = 2.4 Hz, 1H, NCHCHN), 4.30 (s, 1H, NCHN), 2.56 (s, 3H, N-CH_3), 2.44 (s, 3H, N−CH_3), 2.24 (s, 3H, Ar-CH_3), 2.19 (s, 3H, Ar-CH_3). ^{13}C NMR (125 MHz, C_6D_6): δ 138.3, 135.8, 129.9, 128.2, 127.1, 123.2, 121.1, 120.5, 118.2, 116.0, 112.9 (Ar-C), 108.8, 108.7, 105.0, 104.9 (NCHCHN), 94.9 (NCN), 80.3 (NCHN), 37.7, 31.6 (N-CH_3), 18.8, 18.5 (Ar-CH_3). HRMS (ESI): calcd for $C_{22}H_{24}N_5$ ($[M + 1]^+$) m/z 358.2026 ($[M + 1]^+$), found 358.2025. Anal. Calcd for $C_{22}H_{23}N_5$: C, 73.92; H, 6.49; N, 19.59. Found: C, 73.65; H, 6.40; N, 19.55. Mp: 97−99 °C. IR (KBr pellets, cm^{-1}): ν 2940 (w), 2886 (w), 1618 (m), 1605 (m), 1570 (m), 1520 (m), 1489 (s), 1464 (m), 1445 (m), 1333 (m), 1300 (s), 1242 (w), 1184 (w), 1173 (m), 1053 (w), 1016 (m), 999 (m), 943 (w), 843 (m), 791 (m), 764 (m), 735 (m), 656 (m).

Preparation of [$L^3YbI\{N(SiMe_3)_2\}$] (8). To a THF solution of $[(Me_3Si)_2N]_3Yb(\mu\text{-}Cl)Li(THF)_3$ (1.369 g, 1.50 mmol) was added $H_3\mathbf{L}^3Cl_2$ (1.004 g, 1.50 mmol) suspended in THF (30 mL), the mixture was stirred for 12 h at room temperature. The solvent was removed under reduced pressure to afford a yellow solid which was recrystallized from hexane, giving red crystals of **8** (209 mg, 16% yield), and yellow crystals of **6** (258 mg, 19% yield). Anal. Calcd for $C_{32}H_{48}N_6ISi_2Yb$: C, 44.03; H, 5.54; N, 9.63. Found: C, 44.02; H, 5.70; N, 9.31. Mp: 149−150 °C. IR (KBr pellets, cm^{-1}): ν 2955 (s), 1663 (m), 1605 (m),1547 (m), 1508 (s), 1483 (m), 1466 (w), 1375 (m), 1312 (m), 1259 (s), 1180 (s), 1136 (m), 1065 (w), 982 (w), 883 (m), 839 (s), 748 (m), 683 (m), 658 (m).

General Procedures for the Hydrophosphination of Heterocumulenes.[8b] *Method A.* In the glovebox, a Schlenk tube was charged with complex **1** (8 mg, 0.01 mmol), diphenylphosphine (252 mg, 2.0 mmol), and THF (5 mL). Then the carbodiimide (2.0 mmol) was added to the mixture. The mixture was stirred at room temperature for 0.5 h. After the solvent was removed under reduced pressure, the residue was triturated with hexane (2 mL), extracted with hexane, filtered, concentrated, and recrystallized from hexane at −20 °C to afford the related phosphaguanidines **9a**−**d**.

Method B. In the glovebox, the Schlenk tube was charged with complex **1** (8 mg, 0.01 mmol), diphenylphosphine (252 mg, 2.0 mmol), and THF (5 mL). Then the heterocumulene (2.0 mmol) was added to the mixture. The mixture was stirred at room temperature for 0.5 h. After the solvent was removed under reduced pressure, the residue was triturated with hexane (2 mL), washed with hexane, filtered, and dried under vacuum, yielding the corresponding phosphathioureas **9e**−**n** or phosphaurea **9o**.

Crystal Structure Determination. Suitable crystals of complexes **1**−**6** and **8**, fused-heterocyclic compound **7**, and the trimerized isocyanate **10a** were each mounted on a sealed capillary. Diffraction was performed on a SMART CCD area detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program.[21] All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using SHELXTL-97.[22] All hydrogen atoms were refined using a riding model. Crystal and refinement data can be found in the Supporting Information.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00628.

Characterization data and spectra for compounds and crystallographic data and structure refinement details for **1**−**8** and **10a** (PDF)

X-ray crystallographic files for structure determinations of complexes **1−6** and **8** and fused-heterocyclic compound **7** and **10a** (CIF)

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Notes

The authors declare no competing financial interest.

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