ORGANOMETALLICS

CNC-Pincer Rare-Earth Metal Amido Complexes with a Diarylamido Linked Biscarbene Ligand: Synthesis, Characterization, and Catalytic Activity

Xiaoxia Gu,[†] Xiancui Zhu,^{*,†} Yun Wei,[†] Shaowu Wang,^{*,†,‡} Shuangliu Zhou,[†] Guangchao Zhang,[†] and Xiaolong Mu^{\dagger}

[†]Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, Institute of Organic Chemistry, School of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, People's Republic of China

[‡]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

Supporting Information

ABSTRACT: In preparation of CNC-pincer rare-earth metal amido complexes with a diarylamido linked biscarbene ligand, it is found that conditions have a key influence on final products. Reaction of a THF suspension of bis[2-(3-benzylimidazolium)-4-methylphenyl]amine dichlorides (H₃LCl₂) with [(Me₃Si)₂N]₃RE(μ -Cl)Li(THF)₃ (RE = Yb, Eu, Sm) in THF at room temperature afforded the only unexpected fused-heterocyclic compound 8,9-dibenzyl-3,14-dimethyl-8*a*,9-dihydro-8*H*-benzo[4,5]imidazo-[2',1':2,3]imidazo[1,2-*a*]imidazo[2,1-*c*]quinoxaline (1) containing an imidazolyl ring and a piperidyl ring, which formed through carbene C–C and C–N coupling. However, the reaction of H₃LCl₂ with [(Me₃Si)₂N]₃Er(μ -Cl)Li(THF)₃ in toluene afforded the CNC-pincer erbium amido complex incorporating a diarylamido linked biscarbene ligand LEr[N(SiMe₃)₂]₂ (2) in low yield and the above fused-heterocyclic compound 1. The stepwise reaction of H₃LCl₂ with strong bases (*n*-BuLi or LiCH₂SiMe₃) in THF for 4



h, followed by treatment with $[(Me_3Si)_2N]_3RE(\mu$ -Cl)Li(THF)₃, generated zwitterion complexes $[L_2RE][RECl{N(SiMe_3)_2}_3]$ (L = $[4-CH_3-2-\{(C_6H_4CH_2-[N(CH)_2CN]\}C_6H_3]_2N$; RE = Y (3), Er (4), Yb (5)) in less than 20% yields together with fusedheterocyclic compound 1. Additionally, the reaction of H_3LCl_2 with 6 equiv of NaN(SiMe_3)₂ in THF for 4 h, followed by treatment with YbCl₃, generated a novel discrete complex $[L_2Yb][{Na(\mu-N(SiMe_3)_2)}_5(\mu_5-Cl)]$ (6). The one-pot reaction of H_3LCl_2 with *n*-BuLi, followed by reaction with $[(Me_3Si)_2N]_3RE(\mu-Cl)Li(THF)_3$ in THF at -78 °C, generated the CNC-pincer lanthanide bisamido complexes LRE[N(SiMe_3)_2] (RE = Er (2), Y (7), Sm (8), Eu (9)) in moderate yields. These kinds of biscarbene supported pincer bisamido complexes could also be prepared by a one-pot reaction of bis(imidazolium) salt (H_3LCl_2) with 5 equiv of NaN(SiMe_3)₂, followed by treatment with RECl₃, in good yields at -78 °C. Investigation of the catalytic activity of complexes 2 and 7–9 indicated that all complexes showed a high activity toward the addition of terminal alkynes to carbodiimides producing propiolimidines, which represents the first example of rare-earth metal CNC-pincer-type catalysts applied for catalytic C–H bond addition of terminal alkynes to carbodiimides at room temperature.

INTRODUCTION

Functionalized N-heterocyclic carbene (NHC) ligands have attracted an increasing attention in organometallic chemistry for their strong electron-donating property, easy modification, and stablility since their first discovery. Thus, different types of carbene ligands have been developed and applied in organometallic chemistry.^{1,2} Recently, several examples of rare-earth metal complexes bearing alkoxo-,³ aryloxo-,⁴ salicylamido-,⁵ amido-,⁶ indenyl-,⁷ and fluorenyl-⁸functionalized NHC ligands and their catalytic activities in lactide polymerization,^{3a} olefin copolymerization,^{8a,b} and isoprene polymerization⁹ were documented. Bis(NHC)-incorporated tridentate CNC-pincer ligand¹⁰ having strong electron-donating ylidene carbons and

the precise tailoring of the metal coordination sphere could provide liable complexes and enable the complexes to be used as homogeneous catalysis. Transition-metal complexes with bis(NHC) ligands have been found to be efficient catalysts in different catalytic reactions.¹¹ However, bis(NHC)-incorporated tridenate pincer rare-earth metal complexes are quite rare: Cui et al. reported CCC-pincer 2,6-xylentyl bis(NHC) rareearth metal dibromides,¹² which exhibited a high activity and *cis*-1,4 selectivity for isoprene polymerization in the presence of cocatalysts;^{9b} Arnold et al. reported the synthesis and reactivity

Received: April 3, 2014 **Published:** April 29, 2014 of a yttrium complex with a tridentate amino bis(NHC) ligand.¹³ The chemistry of rare-earth metal complexes with bis(NHC) ligands requires to be developed.

Propiolamidines $(RN=C(C\equiv CR)(NHR))$ are important amidine derivatives not only being applicable in biological and pharmaceutical systems¹⁴ but also being used as heteroallylic ligands in coordination chemistry and catalysis.¹⁵ It is wellestablished that the amidines $\{RNC(R)NHR\}$ can be easily prepared by the nucleophilic addition of organometallic reagents RM to carbodiimides, followed by hydrolysis.¹⁶ However, the corresponding propiolamidines RN=C(C=CR)(NHR), which contain a conjugated $C \equiv C$ triple bond, could hardly be obtained by hydrolysis of the propiolamidinate precursors because of their high sensitivity to hydrolysis.^{16h} The addition of C-H bonds of terminal alkynes to carbodiimides could provide a straightforward and atom-efficient route to propiolamidines. Hou and co-workers for the first time developed the half-sandwich yttrium alkyl complex {Me2Si- $(C_5Me_4)(NPh)$ } $(CH_2SiMe_3)(THF)^{17}$ as a catalyst to accomplish the catalytic addition of C-H bonds of terminal alkynes to carbodiimides; we found that the sandwich-type lanthanocene amido complexes (EBI)LnN(SiMe₃)₂ (EBI = ethylenebis- $(\eta^{5}-\text{indenyl}))^{18a}$ and cyclopentadienyl-free complexes {(CH₂-SiMe₂)[(2,6-iPr₂C₆H₃)N]₂}LnN(SiMe₃)₂(THF)^{18b} could catalyze the addition of the terminal alkyne C-H bond to carbodiimides to produce the corresponding propiolamidines $RN = C(C \equiv CR)(NHR)$. However, elevated reaction temperatures (for example, 80 or 60 °C) are required to accomplish the reaction to produce the desired products, so catalysts operated at room temperature for catalytic addition of terminal alkynes C-H bonds to carbodiimides are highly required. Here, we will report the synthesis of CNC-pincer rare-earth metal complexes bearing a diarylamido linked bis(NHC) ligand, and their room temperature catalytic application for the addition of terminal alkynes to carbodiimides. To the best our knowledge, it represents the first example of CNC-pincer rare-earth metal amido complexes incorporating a diarylamido linked bis(NHC) ligand as catalysts for catalytic addition of terminal C-H bonds of alkynes to carbodiimides for preparation of propiolamidines at room temperature.

RESULTS AND DISCUSSION

Attempts for Synthesis of CNC-Pincer Diarylamido Linked Bis(NHC) Rare-Earth Metal Amido Complexes. To synthesize the CNC-pincer diarylamido linked bis(NHC) rareearth metal amido complexes, the reaction of $[(Me_3Si)_2N]_3$ -RE(μ -Cl)Li(THF)₃ (RE = Sm, Eu, Yb) with 1 equiv of bis[2-(3-benzylimidazolium)-4-methylphenyl]amine dichlorides (H₃LCl₂) was first run in THF at room temperature; after work-up, the unexpected novel fused-heterocylclic compound 8,9-dibenzyl-3,14-dimethyl-8*a*,9-dihydro-8*H*-benzo[4,5]imidazo[2',1':2,3]imidazo[1,2-*a*]imidazo[2,1-*c*]quinoxaline (1), instead of the desired CNC-pincer complex (Scheme 1, Figure 1), was isolated (as high as 42% yield). This compound is believed to form through carbene C–C coupling, followed by C–N coupling.

When the solvent was changed from THF to toluene, an equimolar reaction between $[(Me_3Si)_2N]_3Er(\mu-Cl)Li(THF)_3$ and H_3LCl_2 run at room temperature, after work-up, generated the CNC-pincer erbium bisamido complex $LEr[N(SiMe_3)_2]_2$ (2) (as low as 13% yield) together with the fused-heterocyclic compound 1 (Scheme 2). However, for other rare-earth metals,

Scheme 1. Formation of Fused-Heterocyclic Compound 1





Figure 1. Structure of fused-heterocyclic compound 1. Hydrogen atoms were omitted for clarity. Selected bond lengths: N(3)-C(10), 1.489(2) Å; N(2)-C(10), 1.474(2) Å; N(1)-C(10), 1.457(2) Å; N(27)-C(10), 1.533(2) Å.

the corresponding complexes similar to complex 2 could not be obtained under the same conditions.

Next, we tried to prepare the CNC-pincer diarylamido linked bis(NHC) rare-earth metal amido complexes using the Arnold's conditions.¹³ However, the stepwise treatment of H_3LCl_2 with *n*-BuLi in THF at -30 °C, followed by reaction with $[(Me_3Si)_2N]_3RE(\mu$ -Cl)Li(THF)_3, generated the novel zwitterionic complexes $[L_2RE][RECl{N(SiMe_3)_2}_3]$ (L = [4-CH₃-2-{(C₆H₄CH₂-[N(CH)₂CN]}-C₆H₃]_2N; RE = Y (3), Er (4), Yb (5)) (less than 20% yields), together with isolation of the fused-heterocyclic compound 1. Complexes 3-5 could also be prepared by treatment of H_3LCl_2 with LiCH₂SiMe₃, followed by reaction with [(Me₃Si)₂N]₃RE(μ -Cl)Li(THF)₃ (Scheme 3).

Another stepwise reaction that in situ deprotonation of H_3LCl_2 with NaN(SiMe₃)₂ in THF at -78 °C, followed by treatment with YbCl₃, only generated a novel discrete complex 6 that contains cationic $[L_2Yb]^+$ with an inverse crown counter pentagonal anion $[{Na(\mu-N(SiMe_3)_2)}_5(\mu_5-Cl)]^-$ (Scheme 4). No fused-heterocyclic compound 1 was observed, probably for the reason that low-temperature reaction might prevent the carbene carbon from coupling.



Scheme 3. Stepwise Reactions of H_3LCl_2 with Bases, Followed by Addition to $[(Me_3Si)_2N]_3RE(\mu-Cl)Li(THF)_3$



Scheme 4. Synthesis of the Discrete Complex 6



The molecular structures of complexes 3-6 were determined by single-crystal X-ray analyses. The representative structure diagrams of 4 and 6 are shown in Figures 2 and 3. The important bond distances and angles are shown in Table 1.

X-ray analyses revealed that complexes 3–6 formulated as discrete complexes. The central metal ions in complexes 3–6 have the same coordination numbers; the central metal ions of the cation adopt a distorted octahedral geometry surrounded by two diarylamido linked bis(NHC) ligands. Complex 6 is a novel discrete complex containing cationic $[L_2Yb]^+$ incorporating two diarylamido linked bis(NHC) ligands and an inverse crown counter pentagonal anion $[{Na(\mu-N(SiMe_3)_2)}_5(\mu_5-Cl)]^{-.19}$ The average RE–C_{carbene} bond lengths, 2.518(3) Å in 3, 2.477(5) Å in 4, 2.461(6) Å in 5, and 2.456(4) Å in 6, are well-consistent with the trend of ionic radii of the corresponding lanthanide elements and are distinctly shorter than those of the previously reported corresponding 6-coordinated cationic complexes.^{4d}

The above results indicated that the CNC-pincer diarylamido linked bis(NHC)-ligated bisamido complexes (type of complex 2) could not be satisfactorily synthesized by changing solvents from THF to toluene, or by lowering preparation reaction temperatures from room temperature to -30 °C. We were delighted to find that the CNC-pincer rare-earth amido complexes LRE[N(SiMe₃)₂], (RE = Er (2), Y (7), Sm (8), Eu (9) could be prepared in moderate yields by one-pot reaction of H₃LCl₂ with 2 equiv of n-BuLi, followed by treatment with $[(Me_3Si)_2N]_3RE(\mu-Cl)Li(THF)_3$ in THF at -78 °C (Scheme 5, upper path). These kinds of complexes can also be prepared in moderate yields by treatment of H₃LCl₂ with 5 equiv of $NaN(SiMe_3)_{2}$, followed by reaction with 1 equiv of RECl₃ in THF at -78 °C (Scheme 5, lower path). The fused-heterocyclic compound 1 has not been found in both pathways; the results further indicated that low temperature could prevent the in situ formed bis(NHC) from coupling.

The ¹H NMR spectra of 3, 7, and 8 revealed the absence of the NH, and NC(H)N proton resonances of the bis-(imidazolium) salt (H₃LCl₂) at 8.51 and 10.46 ppm. The ¹³C NMR spectra of complex 3 showed carbene carbon resonances at 194.2 and 194.5 ppm. Similarly, complex 7 showed carbene carbon resonances at 192.0 and 192.5 ppm, and those of carbene carbons in complex 8 resonate at 152.5 ppm, probably due to the paramagnetic property of the complex. The molecular structures of complexes 2 and 7–9 were determined by single-crystal X-ray analyses. A representative structure diagram is shown in Figure 4. The selected bond distances and angles are compiled in Table 2.

As expected, the diarylamido linked bis(NHC) ligand coordinates to the central metal ion in a tridenate 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 the sum of the angles of (N(3)-RE-N(6), N(6)-RE-N(7), and N(7)-RE-N(3)) of 359.83(9)° for 2, 359.81(11)° for 7, 359.87(9)° for 8, and $359.80(2)^{\circ}$ for 9, and the two carbene atoms at the axial sites. The average $RE-C_{carbene}$ bond lengths, 2.525(4) Å in 7, 2.589(3) Å in 8, 2.564(9) Å in 9, and 2.510(3) Å in 2, fall in the range of the linkage of a lanthanide metal ion and an ylidene carbon,⁹ and are well-consistent with the trend of ionic radii of the corresponding lanthanide elements. The average $\rm Y-C_{carbene}$ bond length of 2.525(4) Å in 7 is both shorter than 2.541(3) Å in the CCC-pincer bis(NHC)-ligated rare-earth metal dibromides (PBNHC)YBr₂(THF)((PBNHC) = 2,6-(2,4,6-Me₃C₆H₂NCHCHNCCH₂)₂C₆H₃)^{9b} and 2.569(3) Å in the



Figure 2. Molecular structure of complex 4. Hydrogen atoms were omitted for clarity.



Figure 3. Molecular structure of complex 6. Hydrogen atoms were omitted for clarity.

Table	1. Selected	Bond Distan	ces (Å) and	Angles (de	eg) for Co	mplexes 3-6

	Y (3)	Er (4)	Yb (5)	Yb (6)
RE(1)-N(3)	2.308(2)	2.309(4)	2.284(4)	2.278(3)
RE(1)-N(8)	2.330(2)	2.305(4)	2.290(4)	2.266(3)
RE-N _{av}	2.319(2)	2.307(4)	2.287(4)	2.272(3)
RE(1)-C(10)	2.522(3)	2.481(5)	2.457(5)	2.457(4)
RE(1)-C(27)	2.523(3)	2.470(5)	2.461(6)	2.447(4)
RE(1)-C(44)	2.511(3)	2.482(5)	2.462(6)	2.463(4)
RE(1) - C(61)	2.517(3)	2.474(5)	2.463(6)	2.455(4)
RE-C _{av}	2.518(3)	2.477(5)	2.461(6)	2.456(4)
N(3)-RE(1)-C(10)	76.13(9)	76.45(17)	77.41(16)	78.80(12)
C(10)-RE(1)-N(8)	102.91(10)	102.89(17)	102.14(16) 1	01.95(12)
N(8)-RE(1)-C(27)	104.14(10)	103.46(16)	103.25(17)	00.67(13)
C(27)-RE(1)-N(3)	76.84(9)	77.20(16)	77.20(17)	78.58(13)
C(44)-RE(1)-C(61)	151.46(11)	154.45(17)	155.11(19) 1	56.68(14)

Scheme 5. Synthetic Pathways for Preparation of Diarylamido Linked Bis(NHC) Rare-Earth Metal Amides





Figure 4. Representative molecular structure of complexes 2 and 7–9. Hydrogen atoms were omitted for clarity.

CNC-pincer bis(NHC)-ligated rare-earth metal monoamido complex $\{CH_2CH_2(1-C[NCHCHNMes])\}_2NY(Cl)N-(SiMe_3)_2$.¹³ In contrast, the C(10)–Er–C(27) bond angle of 141.39(10)° in **2** is larger than 141.07(13)° of C(10)–Y–

C(27) in 7, 138.3(3)° of C(10)-Eu-C(27) in 9, and 138.01(10)° of C(10)-Sm-C(27) in 8.

Catalytic Activity on Addition of Terminal Alkyne C– H Bonds to Carbodiimides. The addition of C–H bonds of terminal alkynes to carbodiimides could provide a straightforward, atom-efficient route to propiolamidines. Previously developed rare-earth metal complexes as catalysts for catalytic addition of terminal C–H bonds of alkynes to carbodiimides required elevated reaction temperatures at 80 or 60 °C.^{17,18} The fact that the carbene ligands have a strong electrondonating property is established, with the CNC-pincer diarylamido linked bis(NHC) supported rare-earth metal amido complexes in hand, the catalytic activities of these complexes on terminal C–H bond addition to carbodiimides were examined (Table 3).

Table 3. Optimization of the Conditions in the Catalytic Reaction of Terminal Alkynes to Carbodiimides^a

	CyN=C=NCy +	Ph-=-	-H <u>Cat.</u> ► Ph N - N- H	-Су -Су
entries	cat. (mol %) ^c	solvent	temp (°C)/time (h)	yield $(\%)^b$
1	9 (2%)	THF	r.t./12	64
2	9 (3%)	THF	r.t./12	81
3	9 (5%)	THF	r.t./12	88
4	9 (5%)	toluene	r.t./12	82
5	9 (5%)	THF	60/12	88
6	2 (5%)	THF	r.t./12	87
7	7 (5%)	THF	r.t./12	87
8	8 (5%)	THF	r.t./12	85

^{*a*}Reaction conditions: dicyclohexylcarbodiimide (2.0 mmol), phenylacetylide (2.1 mmol), solvent (5 mL). ^{*b*}Isolated yields. ^{*c*}Cat.: [LREN(SiMe₃)₂] (RE = Er (2), Y (7), Sm (8), Eu (9)).

Results showed that the yields of the catalytic addition reaction were raised along with an increase of catalyst loading (Table 3, entries 1-3) and THF seemed to be a better solvent than toluene for the reaction (Table 3, entries 3 and 4). The propiolamidine **10** was obtained in 87, 87, 85, and 88% yields using the catalysts **2** and 7-9 in 12 h (Table 3, entries 5-8), respectively, indicating that the central metal ions of the complexes had little influence on the catalytic activities of the addition of terminal alkynes to carbodiimides. It was worth noting that the addition reaction of phenylacetylide to dicyclohexylcarbodiimide was conducted at room temperature immediately. The reaction yield of the product was unchanged

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 2 and 7-9

	Er (2)	Y (7)	Sm (8)	Eu (9)
RE(1)-N(3)	2.321(2)	2.340(3)	2.395(2)	2.389(6)
RE(1)-N(6)	2.246(3)	2.261(3)	2.318(3)	2.317(7)
RE(1)-N(7)	2.288(2)	2.296(3)	2.338(3)	2.312(7)
RE-N _{av}	2.267(3)	2.279(3)	2.328(3)	2.315(7)
RE(1)-C(10)	2.511(3)	2.529(4)	2.593(3)	2.552(9)
RE(1)-C(27)	2.509(3)	2.521(4)	2.584(3)	2.575(8)
RE-C _{av}	2.510(3)	2.525(4)	2.589(3)	2.564(9)
N(3)-RE(1)-N(6)	103.32(9)	103.53(11)	104.18(9)	104.0(2)
N(3)-RE(1)-N(7)	137.88(9)	137.56(11)	135.09(9)	136.5(2)
N(6)-RE(1)-N(7)	118.63(9)	118.72(12)	120.60(9)	119.3(2)
C(10)-RE(1)-C(27)	141.39(10)	141.07(13)	138.01(10)	138.3(3)

by elevating the reaction temperature to 60 $^{\circ}$ C (Table 3, entry 5).

Under the optimized reaction conditions, we next examined the substrate scope of the catalytic addition of the terminal alkynes to carbodiimides in the presence of the complex 9 (Table 4). It is found that the catalyst displayed a high catalytic

Table 4. Addition of Various Terminal Alkyne	s to
Carbodiimides Catalyzed by Catalyst 9 ^a	

F	RN=C=NR +	Ar— <u>—</u> H_ <u>9</u>	→ Ar-=	N—R N—R
entries	R	Ar	product	yield $(\%)^b$
1	Су	Ph	10	88
2	ⁱ Pr	Ph	11	90
3	Су	4-MeOC ₆ H ₄	12	73
4	ⁱ Pr	4-MeOC ₆ H ₄	13	79
5	Су	4-MeC ₆ H ₄	14	70
6	ⁱ Pr	$4-MeC_6H_4$	15	81
7	Су	$4-FC_6H_4$	16	92
8	ⁱ Pr	$4-FC_6H_4$	17	95
9	Су	4-ClC ₆ H ₄	18	90
10	ⁱ Pr	4-ClC ₆ H ₄	19	93
11	Су	4-BrC ₆ H ₄	20	89
12	ⁱ Pr	4-BrC ₆ H ₄	21	91
13	Су	<i>n</i> -C ₅ H ₁₁	22	68
14	ⁱ Pr	$n-C_5H_{11}$	23	72

^{*a*}Reaction conditions: carbodiimides (2.0 mmol), terminal alkynes (2.1 mmol), catalyst loading (5 mol %), THF (5 mL), room temperature, reaction time (12 h). ^{*b*}Isolated yields.

activity on addition of terminal alkyne C-H bonds to carbodiimides with substrates of aromatic alkynes or aliphatic alkynes at room temperature. The substituents on the phenyl ring of the aromatic alkynes can be electron-donating groups, such as CH₃O- and CH₃-, or electron-withdrawing groups, such as F-, Cl-, and Br-. However, reactions of alkynes with electron-withdrawing substituted groups (Table 4, entries 7-12) afforded much more better results than those of alkynes with electron-donating groups on the phenyl ring with carbodiimides (Table 4, entries 3-6), probably owing to the stronger acidity of the former, which may favor the alkyneamido exchange process in the catalytic initation step; this result is parallel to the previous results.¹⁸ In the case of alkyl alkynes (Table 4, entries 13 and 14), the reaction can go smoothly, but gives results a bit poorer than those of aromatic alkynes performed, probably owing to their weaker acidity.

CONCLUSION

In summary, we have demonstrated that a variety of the CNCpincer diarylamido bis(NHC)-ligated rare-earth metal complexes can be synthesized and characterized. Results indicated that conditions play a key role in the formation of final products. The diarylamido linked bis(NHC) rare-earth metal amides can be used as catalysts to accomplish the catalytic addition of terminal C–H bonds of alkynes to carbodiimides at room temperature with a high catalytic activity, which represents the first example of organo rare-earth metal complexes as catalysts applied for catalytic addition of C–H bonds of alkynes to carbodiimides at room temperature. Further studies on the reactivity and catalytic reactivities 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 (toluene, hexane, THF, diethyl ether) were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. RECl_3^{20} [(Me_3Si)_2N]_3RE(μ -Cl)Li(THF)_3 (RE = Y, Sm, Eu, Er, Yb),²¹ and bis[2-(3-benzylimidazolium)-4-methylphenyl]amine dichlorides (H₃LCl₂)¹¹c were prepared according to literature methods. Elemental analyses data were obtained on a macro-elemental analyzer. ¹H NMR and ¹³C NMR spectra for analyses of compounds were recorded on a 300/500 NMR spectrometer (300 MHz for ¹H; 75 MHz for ¹³C; 500 MHz for ¹H; 126 MHz for ¹³C), and all chemical shift values refer to δ TMS 0.00 ppm, CDCl₃ (δ (¹H), 7.26 ppm; δ (¹³C), 77.16 ppm), C_6D_6 (δ (¹H), 7.15 ppm; δ (¹³C), 128.06 ppm), and $C_4 D_8 O$ (δ (¹H), 1.72, 3.58 ppm; δ (¹³C), 25.31, 67.21 ppm). J values are reported in Hz. IR spectra were recorded on an FT-IR spectrometer (KBr pellet). Mass spectra were performed on a Micromass GCT-MS spectrometer. Crystallographic X-ray data were collected on a SMART 1000 CCD area detector diffractometer.

Preparation of 8,9-Dibenzyl-3,14-dimethyl-8a,9-dihydro-8H-benzo[4,5]imidazo[2',1':2,3]imidazo[1,2-a]imidazo[2,1-c]quinoxaline (1). [(Me₃Si)₂N]₃Yb(µ-Cl)Li(THF)₃ (1.616 g, 1.77 mmol) was added to H₃LCl₂ (1.031 g, 1.77 mmol) in THF (30 mL), and 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 to yield colorless crystals of 1 (379 mg, 42% yield): C₃₄H₃₁N₅. ¹H NMR (300 MHz, C₆D₆, ppm): δ 7.45-7.42 (d, 2H, J = 7.3 Hz, Ar-H), 7.32–7.30 (d, 1H, J = 8.0 Hz, Ar-H), 7.26– 7.05 (m, 9H, Ar-H), 7.08-7.05 (d, 1H, J = 9.0 Hz, Ar-H), 6.70-6.68 (d, 1H, J = 6.0 Hz, Ar-H), 6.61–6.59 (d, 1H, J = 6.0 Hz, Ar-H), 6.29 (s, 1H, Ar-H), 5.76–5.76 (d, 1H, J = 2.4 Hz, NCH₂), 5.59–5.58 (d, J = 2.4 Hz, NCH₂), 5.53–5.52 (d, J = 2.1 Hz, NCH₂), 5.47–5.46 (d, 1H, J = 2.4 Hz, NCH₂), 4.63 (s, 1H, NCHN), 4.44-4.34 (d, 1H, J = 13.2 Hz, NCHCHN), 4.22–4.18 (d, 1H, J = 13.7 Hz, NCHCHN), 3.86– 3.82 (d, 1H, J = 13.9 Hz, NCHCHN), 3.72-3.68 (d, 1H, J = 13.2 Hz, NCHCHN), 2.18–2.16 (d, 6H, J = 5.0 Hz, Ar–CH₃). ¹³C NMR (75 MHz, C₆D₆, ppm): δ 19.9 (Ar-CH₃), 20.2 (Ar-CH₃), 50.1 (NCH₂), 56.1 (NCH₂), 79.4 (NCHN), 96.2 (NCN), 106.6 (NCHCHN), 107.7 (NCHCHN), 110.6 (NCHCHN), 111.2 (NCHCHN), 114.2, 117.6, 118.7, 119.8, 121.8, 122.6, 125.8, 126.3, 126.5, 126.8, 127.1, 127.4, 127.6, 128.2, 128.7, 129.2, 131.3, 137.2, 137.5, 138.2, 139.27 (Ar-C). HRMS (ESI): calcd for $C_{34}H_{32}N_5$: m/z 510.2652 ([M + 1]⁺), Found: 510.2651. Anal. Calcd for $C_{34}H_{31}N_5$: C, 80.13; H, 6.13; N, 13.74. Found: C, 80.66; H, 6.70; N, 13.12. mp: 92 °C. IR (KBr pellets, cm⁻¹): v 3064 (w), 2953 (w), 2918 (w), 2862 (w), 1666 (m), 1606 (m), 1514 (m), 1454 (m), 1307 (m), 1249 (w), 1180 (w), 1029 (w), 1012 (w), 933 (w), 881 (s), 840 (s), 731 (s), 700 (s).

When $[(Me_3Si)_2N]_3RE(\mu-Cl)Li(THF)_3$ (RE = Eu, Sm) were used instead of $[(Me_3Si)_2N]_3Yb(\mu-Cl)Li(THF)_3$, the fused-heterocyclic compound 1 could also be isolated in 34% and 36% yield, respectively.

Preparation of [LEr{[N(SiMe₃)₂]₂]] (2). Reaction between-[(Me₃Si)₂N]₃Er(μ -Cl)Li(THF)₃ (1.098 g, 1.21 mmol) and H₃LCl₂ (705 mg, 1.21 mmol) in toluene was stirred for 12 h at room temperature and, after work-up, generated pink crystals of the CNC-pincer bis(NHC)-ligated erbium complex LEr[N(SiMe₃)₂]₂ (2) (157 mg, 13% yield) and fused-heterocyclic compound 1 (217 mg, 35% yield). Complex LEr[N(SiMe₃)₂]₂ (2) can also be prepared in 22% yield (317 mg) by treatment of H₃LCl₂ (848 mg, 1.46 mmol) with a solution of 2 M NaN(SiMe₃)₂ in THF (3.6 mL, 7.28 mmol), followed by treatment with a suspension of ErCl₃ (398 mg, 1.46 mmol). Anal. Calcd for C₄₆H₆₆N₇Si₄Er(C₆H₁₄)_{0.5}: C, 56.60; H, 7.08; N, 9.43. Found: C, 56.78; H, 6.74; N, 10.01. mp: 134 °C. IR (KBr pellets, cm⁻¹): ν 3061 (w), 2862 (w), 1604 (m), 1546 (m), 1508 (m), 1483 (w), 1365 (w), 1307 (w), 1251 (w), 1180 (w), 1138 (w), 933 (w), 883 (s), 837 (s), 682 (s), 657 (s).

Preparation of $[L_2Y][YCl{[N(SiMe_3)_2]_3]}$ (3). A solution of H_3LCl_2 (926 mg, 1.59 mmol) in THF (30 mL) was cooled to -30 °C, and a solution of *n*-BuLi (2.50 mL, 3.18 mmol) in hexane was added dropwise with stirring for 4 h at -30 °C. $[(Me_3Si)_2N]_3Y(\mu$ -

Cl)Li(THF)₃ (1.318 g, 1.59 mmol) was then added to the mixture, and the mixture was allowed to warm slowly to room temperature overnight. The solvent was removed under reduced pressure to afford a yellow solid, which was washed with hexane to yield colorless crystals of 1 (324 mg, 40% yield), and recrystallization of the remaining solid from diethyl ether afforded yellow crystals of 3 (466 mg, 19% yield). ¹H NMR (500 MHz, C_4D_8O): δ 7.69 (s, 4H, imi-H), 7.22–7.16 (m, 12H, imi-H and Ar-H), 7.05-6.99 (d, J = 7.0 Hz, 8H, Ar-H), 6.70-6.68 (d, J = 6.6 Hz, 8H, Ar-H), 6.49–6.48 (d, J = 7.8 Hz, 4H, Ar-H), 6.37-6.35 (d, J = 8.0 Hz, 4H, Ar-H), 4.91-4.88 (d, J = 14.7 Hz, 4H, NCH₂), 4.06–4.03 (d, J = 14.8 Hz, 4H, NCH₂), 2.10 (s, 12H, ArCH₃), 0.17 (s, 36H, Si(CH₃)₃), 0.04 (s, 18H, Si(CH₃)₃). ¹³C NMR (126 MHz, C₄D₈O): δ 2.1(Si(CH₃)₃), 6.2 (Si(CH₃)₃), 20.0 (ArCH₃), 52.7 (NCH₂), 120.7, 121.8, 124.8 (imi-C), 127.9, 128.2, 128.6, 129.2, 132.6, 136.7, 147.0 (Ar-C), 194.2 (carbene-C), 194.5 (carbene-C). Anal. Calcd for C86H114ClN13Si6Y2: C, 60.35; H, 6.71; N, 10.64. Found: C, 60.67; H, 6.20; N, 10.28. mp: 150 °C. IR (KBr pellets, cm⁻¹): v 2963 (w), 2351 (m), 2318 (m), 1672 (s), 1632 (s), 1580 (s), 1454 (m), 1373 (m), 1261 (m), 1105 (m), 1018 (m), 966 (m), 935 (s), 881 (s), 802 (s), 691 (vs).

Preparation of [L₂Er][ErCl{[N(SiMe₃)₂]₃] (4). Following the procedure similar to that described for the preparation of 3, 1 (268 mg, 35% yield) and 4 (420 mg, 15% yield) were isolated from a reaction of a solution of H₃LCl₂ (874 mg, 1.50 mmol) and *n*-BuLi (3.4 mL, 3.0 mmol) at -30 °C for 4 h, followed by reaction with $[(Me_3Si)_2N]_3Er(\mu$ -Cl)Li(THF)₃ (1.361 g, 1.50 mmol) at -30 °C. Anal. Calcd for C₈₆H₁₁₄ClN₁₃Si₆Er₂: C, 55.28; H, 6.15; N, 9.75. Found: C, 55.16; H, 6.15; N, 9.88. mp: 153 °C. IR (KBr pellets, cm⁻¹): ν 2954 (w), 2358 (w), 2342 (w), 1657 (m), 1647 (m), 1549 (m), 1510 (m), 1452 (s), 1400 (s), 1311 (m), 1250 (m), 1173 (m), 1138 (m), 1113 (m), 1011 (m), 934 (m), 839 (m), 714 (m), 669 (m).

Preparation of [L₂Yb][YbCl{[N(SiMe₃)₂]₂}] (5). Following the procedure similar to that described for the preparation of **3**, **1** (209 mg, 37% yield) and **5** (385 mg, 16% yield) were isolated from a reaction of a solution of H₃LCl₂ (747 mg, 1.28 mmol) and *n*-BuLi (1.4 mL, 2.56 mmol) at -30 °C for 4 h, followed by reaction with [(Me₃Si)₂N]₃Yb(μ -Cl)Li(THF)₃ (1.170 g, 1.28 mmol) at -30 °C. Anal. Calcd for C₈₆H₁₁₄ClN₁₃Si₆Yb₂(C₆H₁₄): C, 56.20; H, 6.56; N, 9.26. Found: C, 56.31; H, 6.37; N, 9.64. mp: 156 °C. IR (KBr pellets, cm⁻¹): ν 2959 (w), 2378 (m), 2320 (m), 1647 (w), 1632 (w), 1549 (m), 1508 (m), 1400 (m), 1339 (m), 1312 (m), 1254 (m), 1180 (m), 1138 (s), 1115 (s), 1013 (m), 935 (s), 885 (s), 839 (m), 750 (m), 669 (m).

Preparation of [L₂Yb][{Na(\mu-N(SiMe₃)₂)₅(\mu₅-Cl)] (6). To a solution of H₃LCl₂ (1.403 g, 1.79 mmol) in THF (30 mL) at -78 °C was dropwise added a solution of 2 M NaN(SiMe₃)₂ in THF (5.4 mL, 10.74 mmol) with stirring for 4 h; a THF suspension of YbCl₃ (250 mg, 0.895 mmol) was then added to the mixture. The reaction mixture was allowed to slowly warm to room temperature overnight. The solvent was removed under reduced pressure to yield a yellow solid that was recrystallized from hexane/toluene to afford yellow crystals of 6 (959 mg, 25% yield) for X-ray analysis. Anal. Calcd for C₉₈H₁₅₀N₁₅Si₁₀ClNa₃Yb(C₇H₈)_{0.5}: C, 55.70; H, 7.09; N, 9.60. Found: C, 55.56; H, 6.58; N, 9.28. mp: 200 °C. IR (KBr pellets, cm⁻¹): \nu 3061 (w), 3030 (w), 2954 (w), 1664 (m), 1618 (m), 1514 (m), 1454 (m), 1398 (w), 1309 (w), 1242 (w), 1182 (w), 983 (w), 933 (w), 839 (s), 813 (s),744 (s), 711 (s).

Preparation of [LY{[N(SiMe₃)₂]₂] (7). To a suspension of H₃LCl₂ (1.132 g, 1.94 mmol) in THF (30 mL) was added a solution of 2 M NaN(SiMe₃)₂ in THF (4.9 mL, 9.72 mmol)) dropwise with stirring for 8 h at -78 °C; then a THF suspension of YCl₃ (379 mg, 1.94 mmol) was added to the mixture. The mixture was allowed to slowly warm to room temperature overnight. The solvent was removed under reduced pressure to afford a yellow solid, which was recrystallized from hexane to yield yellow crystals of 7 in 20% yield (389 mg) for X-ray analysis. ¹H NMR (300 M Hz, C₆D₆, ppm): δ 7.31–7.29 (d, *J* = 6.0 Hz, 4H, imi-H), 7.18–7.05 (m, 8H, Ar-H), 6.94–6.84 (dd, *J* = 19.6, 11.0 Hz, 6H, Ar-H₃), 6.30 (s, 2H, Ar-H), 6.13–6.08 (d, *J* = 14.9 Hz, 2H, NCH₂), 5.59–5.54 (d, *J* = 14.9 Hz, 2H, NCH₂), 2.21 (s, 6H, ArCH₃), 0.41 (s, 18H, Si(CH₃)₃), 0.09 (s, 18H, Si(CH₃)₃). ¹³C NMR (75 MHz,

 $\begin{array}{l} C_6D_6, \ ppm): \ \delta \ 4.7 \ (SiC(CH_3)_3), \ 6.7 \ (SiC(CH_3)_3), \ 20.3 \ (ArCH_3)), \\ 55.3 \ (NCH_2), \ 119.2, \ 120.0, \ 123.4 \ (imi-C), \ 127.0, \ 127.5, \ 127.8, \ 128.1, \\ 128.3, \ 128.3, \ 128.8, \ 129.0, \ 129.1, \ 132.2, \ 135.0, \ 147.0 \ (Ar-C), \ 192.0 \ (carbene-C), \ 192.5 \ (carbene-C). \ Anal. \ Calcd \ for \ C_{46}H_{66}N_7Si_4Y: \ C, \\ 60.16; \ H, \ 7.24; \ N, \ 10.68. \ Found: \ C, \ 60.32; \ H, \ 7.30; \ N, \ 10.39. \ mp: \ 146 \ ^{\circ}C. \ IR \ (KBr \ pellets, \ cm^{-1}): \ \nu \ 3030 \ (w), \ 2962 \ (w), \ 2926 \ (w), \ 2858 \ (w), \ 1662 \ (w), \ 1608 \ (w), \ 1548 \ (w), \ 1512 \ (w), \ 1452 \ (w), \ 1400 \ (w), \\ 1261 \ (s), \ 1095 \ (s), \ 1022 \ (s), \ 925 \ (w), \ 802 \ (s), \ 700 \ (w), \ 669 \ (w). \end{array}$

Preparation of [LSm{[N(SiMe₃)₂]₂]] (8). This complex was prepared as yellow crystals in 27% yield (331 mg) following the procedure similar to that described for the preparation of 7 by treatment of a THF suspension of H₃LCl₂ (664 mg, 1.14 mmol) with a solution of 2 M NaN(SiMe₃)₂ in THF (2.8 mL, 5.69 mmol), followed by reaction with a THF suspension of SmCl₃ (293 mg, 1.14 mmol). ¹H NMR (300 MHz, C_6D_{61} ppm): δ 8.81–8.79 (d, J = 8.2 Hz, 2H, imi-H), 7.71–7.70 (d, J = 7.0 Hz, 2H, imi-H), 7.59–7.56 (dd, J = 8.3, 1.7 Hz, 2H, Ar-H), 6.92–6.90 (m, 8H, Ar-H), 6.64 (d, J = 1.7 Hz, 2H, Ar-H), 6.65–6.47 (dd, J = 7.5, 1.9 Hz, 4H, Ar-H), 5.29–5.29 (d, J = 1.7 Hz, 2H, NCH₂), 4.75-4.70 (d, J = 14.9 Hz, 2H, NCH₂), 2.60 (s, 6H, ArCH₃), 1.04 (s, 18H, Si(CH₃)₃), 1.03 (s, 18H, Si(CH₃)₃). ¹³C NMR (75 MHz, $C_6 D_{67}$ ppm): δ 1.9 (SiC(CH₃)₃), 6.0 (SiC(CH₃)₃), 19.9 (ArCH₃), 51.7 (NCH₂), 115.2, 115.3, 117.0, 117.1 (imi-C), 124.2, 126.5, 126.8, 127.0, 127.2, 127.6, 127.8, 128.0, 129.4, 133.0, 133.1, 133.2 (Ar-C), 152.5 (carbene-C). Anal. Calcd for C46H66N7Si4Sm: C, 56.39; H, 6.79; N, 10.01. Found: C, 56.24; H, 6.78; N, 9.81. mp: 140 °C. IR (KBr pellets, cm⁻¹): ν 3084 (w) 3024 (w), 2945 (w), 2910 (w), 2837 (w), 1666 (m), 1610 (m), 1566 (m), 1517 (s), 1492 (w), 1454 (w), 1404 (w), 1373 (w), 1350 (s), 1325 (s), 1296 (w), 1180 (w), 1130 (w), 1026 (w), 939 (w), 860 (s), 842 (s), 758 (s), 696 (s), 669 (s).

Preparation of [LEu{[N(SiMe₃)₂]₂] (9). This complex was prepared as yellow crystals in 30% yield (981 mg) following a procedure similar to that described for the preparation of 7 by treatment of a THF suspension of H₃LCl₂ (1.078 g, 1.85 mmol) with a solution of 2 M NaN(SiMe₃)₂ in THF (4.6 mL, 9.24 mmol), followed by reaction with EuCl₃ (478 mg, 1.85 mmol). Anal. Calcd for C₄₆H₆₆N₇Si₄Eu: C, 56.30; H, 6.78; N, 9.99. Found: C, 56.02; H, 6.56; N, 9.72. mp: 168 °C. IR (KBr pellets, cm⁻¹): ν 3061 (w), 3028 (w), 2954 (w), 2918 (w), 2862 (w), 1604 (m), 1585 (m), 1514 (m), 1398 (w), 1309 (w), 1247 (w), 1180 (w), 1138 (w), 1028 (w), 983 (w), 933 (w), 840 (s), 817 (s), 702 (s), 650(s).

Complexes 2 and 7–9 can also be prepared in 25, 28, 31, and 36% yield, respectively, by a one-pot reaction of H_3LCl_2 (1 equiv) with *n*-BuLi (2 equiv), followed by reaction with 1 equiv of $[(Me_3Si)_2N]_3$ -RE(μ -Cl)Li(THF)₃ (RE = Er, Y, Sm, Eu) in THF at -78 °C for 4 h.

General Experimental Procedure for the Catalytic Addition of Terminal Alkynes to Carbodiimides (10 as an example). In the glovebox, a Schlenk tube was charged with complex 9 (98 mg, 0.10 mmol), phenylacetylide (214 mg, 2.10 mmol), and THF (5 mL). Then, dicyclohexylcarbodiimide (413 mg, 2.00 mmol) was added to the mixture. The mixture was stirred at room temperature for 12 h. After the solvent was removed under reduced pressure, the residue was extracted with hexane and filtered to give a clean solution. The solvent was evaporated under vacuum, and the residue was recrystallized from hexane to afford the N,N'-dicyclohexyl-3-phenylpropiolamidine 10 (543 mg, 88% yield).

Crystal Structure Determination. Suitable crystals of fusedheterocyclic compound 1 and complexes 2–9 were each mounted in a sealed capillary. Diffraction was performed on a SMART CCD area detector diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using the SADABS program.²² 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-97.²³ All hydrogen atoms were refined using a riding model. Crystal and refinement data can be read in the Supporting Information.

Organometallics

ASSOCIATED CONTENT

S Supporting Information

Characterization data and spectra for compounds, tables of crystallographic data and structure refinement for 1-9, and X-ray crystallographic files, in CIF format, for structure determination of fused-heterocyclic 1 and complexes 2-9. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: swwang@mail.ahnu.edu.cn (S. Wang); zxc5872271@ 126.com (X. Zhu).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was cosupported by the National Natural Science Foundation of China (Grants 21372010, 21172003) and the National Basic Research Program of China (2012CB821600).

REFERENCES

 Arduengo, A. J.; Tamm, M.; McLain, S. J.; Calabrese, J. C.; Davidson, F.; Marshall, W. J. J. Am. Chem. Soc. 1994, 116, 7927–7928.
 (a) Arnold, P. L.; Liddle, S. T. Chem. Commun. 2006, 3959– 3971.
 (b) Liddle, S. T.; Edworthy, I. S.; Arnold, P. L. Chem. Soc. Rev. 2007, 36, 1732–1744.
 (c) Arnold, P. L.; Casely, I. J. Chem. Rev. 2009, 109, 3599–3611.

(3) (a) Patel, D.; Liddle, S. T.; Mungur, S. A.; Rodden, M.; Blake, A. J.; Arnold, P. L. *Chem. Commun.* **2006**, 1124–1126. (b) Arnold, P. L.; Casely, I. J.; Turner, Z. R.; Carmichael, C. D. *Chem.—Eur. J.* **2008**, *14*, 10415–10422. (c) Turner, Z. R.; Bellabarba, R.; Tooze, R. P.; Arnold, P. L. J. Am. Chem. Soc. **2010**, *132*, 4050–4051. (d) Arnold, P. L.; Turner, Z. R.; Bellabarba, R.; Tooze, R. P. J. Am. Chem. Soc. **2011**, *133*, 11744–11756.

(4) (a) Yao, H. S.; Zhang, Y.; Sun, H. M.; Shen, Q. Eur. J. Inorg. Chem. 2006, 1124–1126. (b) Wang, Z. G.; Sun, H. M.; Yao, H. S.; Yao, Y. M.; Shen, Q.; Zhang, Y. J. Organomet. Chem. 2006, 691, 3383– 3390. (c) Wang, Z. G.; Sun, H. M.; Yao, H. S.; Yao, Y. M.; Shen, Q.; Zhang, Y. Organometallics 2006, 25, 4436–4438. (d) Yao, H. S.; Zhang, J. G.; Zhang, Y.; Sun, H. M.; Shen, Q. Organometallics 2010, 29, 5841–5846.

(5) Zhang, J. G.; Yao, H. S.; Zhang, Y.; Sun, H. M.; Shen, Q. Organometallics 2008, 27, 2672–2675.

(6) (a) Arnold, P. L.; McMaster, J.; Liddle, S. T. Chem. Commun.
2009, 818–820. (b) Liddle, S. T.; Arnold, P. L. Organometallics 2005, 24, 2597–2605. (c) Arnold, P. L.; Mungur, S. A.; Blake, A. J.; Wilson, C. Angew. Chem., Int. Ed. 2003, 42, 5981–5984.

(7) Wang, B. L.; Wang, D.; Cui, D. M.; Gao, W.; Tang, T.; Chen, X. S.; Jing, X. B. Organometallics **2007**, *26*, 3167–3172.

(8) (a) Wang, B. L.; Tang, T.; Li, Y.; Cui, D. M. Dalton Trans. 2009, 38, 8963–8969. (b) Yao, C. G.; Wu, C. J.; Wang, B. L.; Cui, D. M. Organometallics 2013, 32, 2204–2209.

(9) (a) Wang, B. L.; Cui, D. M.; Lv, K. Macromolecules 2008, 41, 1983–1988. (b) Lv, K.; Cui, D. M. Organometallics 2010, 29, 2987–2993.

(10) (a) Moulton, C. J.; Shaw, B. L. J. Chem. Soc., Dalton Trans. 1976, 1020–1024. (b) Pugh, D.; Danopoulos, A. Coord. Chem. Rev. 2007, 251, 610–641. (c) Mata, J.; Poyatos, M.; Peris, E. Coord. Chem. Rev. 2007, 251, 841–859. (d) Mas-Marza, E.; Poyatos, M.; Sanau, M.; Peris, E. Organometallics 2004, 23, 323–325. (e) Han, V. H.; Dan, Y.; Yuan, H. Dalton Trans. 2009, 7262–7268.

(11) (a) Huckaba, A. J.; Hollis, T. K.; Howell, T. O.; Valle, H. U.; Wu, Y. S. Organometallics **2013**, 32, 63–69. (b) Zuo, W. W.; Braunstein, P. Organometallics **2012**, 31, 2606–2615. (c) Wei, W.; Qin, Y. C.; Luo, M. M.; Xia, P. F.; Shing, M.; Wong, M. Organometallics 2008, 27, 2268–2272. (d) Bauer, E. B.; Senthil Andavan, G. T.; Hollis, T. K.; Rubio, R. J.; Cho, J.; Kuchenbeiser, G. R.; Helgert; Christopher, T. R.; Letko, S.; Tham, F. S. Org. Lett. 2008, 10, 1175–1178. (e) Edworthy, I.; Blake, A.; Wilson, C.; Arnold, P. L. Organometallics 2007, 26, 3684–3689. (f) Tulloch, A.; Danopoulos, A.; Tizzard, G. J.; Coles, S.; Hursthouse, M.; Hay-Motherwell, R.; Motherwell, W. Chem. Commun. 2001, 1270–1271.

(12) Lv, K.; Cui, D. M. Organometallics 2008, 27, 5438-5440.

(13) Edworthy, I.; Blake, A.; Wilson, C.; Arnold, P. L. Organometallics 2007, 26, 3684–3689.

(14) (a) Sienkiewich, P.; Bielawski, K.; Bielawska, A.; Palka, J. Environ. Toxicol. Pharmacol. 2005, 20, 118–124. (b) Sielecki, T. M.; Liu, J.; Mousa, S. A.; Racanelli, A. L.; Hausner, E. A.; Wexler, R. R.; Olson, R. E. Bioorg. Med. Chem. Lett. 2001, 11, 2201–2204. (c) Stephens, C. E.; Tanious, E.; Kim, S.; Wilson, D. W.; Schell, W. A.; Perfect, J. R.; Franzblau, S. G.; Boykin, D. W. J. Med. Chem. 2001, 44, 1741–1748. (d) Rowley, C. N.; DiLabio, G. A.; Barry, S. T. Inorg. Chem. 2005, 44, 1983–1991.

(15) (a) Cole, M. L.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Cerón, D. P.; Wang, J. Dalton Trans. 2010, 39, 6732–6738.
(b) Edelmann, F. T. Chem. Soc. Rev. 2012, 41, 7657–7672.

(16) (a) Ong, T. G.; O'Brien, J. S.; Korobkov, I.; Richeson, D. S. Organometallics 2006, 25, 4728-4730. (b) Brown, D. J.; Chisholm, M. H.; Gallucci, J. C. Dalton Trans. 2008, 1615-1624. (c) Dröse, P.; Hrib, C. G.; Edelmann, F. T. J. Organomet. Chem. 2010, 695, 1953-2051. (d) Casely, I. J.; Ziller, J. W.; Evans, W. J. Organometallics 2011, 30, 4873-4881. (e) Yi, W.; Zhang, J.; Li, M.; Chen, Z.; Zhou, X. G. Inorg. Chem. 2011, 50, 11813-11824. (f) Zhang, W. X.; Hou, Z. M. Org. Biomol. Chem. 2008, 6, 1720. (g) Ryan, J. S.; Martyn, P. C. Organometallics 2013, 32, 5277-5280. (h) Fujita, H.; Endo, R.; Aoyama, A.; Ichii, T. Bull. Chem. Soc. Jpn. 1972, 45, 1846-1852.

(17) Zhang, W. X.; Nishiura, M.; Hou, Z. M. J. Am. Chem. Soc. 2005, 127, 16788–16789.

(18) (a) Zhou, S. L.; Wang, S. W.; Yang, G. S.; Li, Q. H.; Zhang, L. J.;
Yao, Z.; Zhou, H.; Song, H. Organometallics 2007, 26, 3755–3761.
(b) Wu, Y. J.; Wang, S. W.; Zhang, Z.; Yang, G.; Zhu, X.; Zhou, Z.;
Zhu, H.; Wu, S. Eur. J. Org. Chem. 2010, 326–332.

(19) Daniel, W.; Michael, B.; Daniel, O. S.; Richard, E. P. W.; Richard, A. L. Dalton Trans. 2011, 40, 10918-10923.

(20) (a) Taylor, M. D.; Carter, C. P. J. Inorg. Nucl. Chem. **1962**, 24, 387–391. (b) Edleman, N. L.; Marks, T. J.; et al. Inorg. Chem. **2002**, 41, 5005–5023. (c) Huang, W.; Upton, B. M.; Khan, S. I.; Diaconescu, P. L. Organometallics **2013**, 32, 1379–1386.

(21) Zhou, S. L.; Wang, S. W.; Yang, G. S.; Liu, X.; Sheng, E.; Zhang, K.; Cheng, L.; Huang, Z. *Polyhedron* **2003**, *22*, 1019–1024.

(22) Sheldrick, G. M. SADABS: Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Göttingen, Germany, 1996.

(23) SHELXTL Program, version 5.1; Siemens Industrial Automation, Inc.: Madison, WI, 1997.