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Cite this: DOI: 10.1039/c0xx00000x

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ARTICLE TYPE

Carboxylation of Terminal Alkynes with Carbon Dioxide Catalyzed by Bridged Bis(amidate) Rare-Earth Metal Amides Hao Cheng,[†] Bei Zhao,^{*, †} Yingming Yao^{*, †}, Chengrong Lu[†]

Received (in XXX, XXX) Xth XXXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX 5 DOI: 10.1039/b000000x

Three novel bis(amidate) rare-earth metal amides $\{LRE[N(SiMe_3)_2]\cdot THF\}_2$ (H₂L= N,N'-(cyclohexane-1,2-diyl)bis(4-*tert*-butylbenzamide); RE = La(1), Nd(2), Y(3)), which were prepared by the treatment of the bridged amide proligand H₂L with RE[N(SiMe_3)_2]_3 in tetrahydrofuran, had been characterized by single-crystal X-ray diffraction, elemental analyses, and NMR for complexes 1 and 3. All the complexes were found as efficient catalysts for the direct carboxylation of terminal alkynes with CO₂ at ambient pressure for the first time. And the Nd-based catalyst 2 showed the highest reactivity. Various propiolic acids with good functional group tolerance were successfully synthesized in high to excellent yields under mild condition.

Introduction

- Carbon dioxide (CO₂), as the primary part of greenhouse gas, 15 is a growing problem in climatic change. How to realize emission reduction and comprehensive utilization are two great challenges to our mankind. Chemical fixation of carbon dioxide has become an effective strategy and attracted much attention because of its intriguing features, such as abundant, inexpensive, non-toxic and 20 renewable.¹ Many chemists have applied CO₂, which is an important C1 carbon feedstock, in synthetic chemistry successfully.^{1a, 2} Since 2010, preparation of alkynyl carboxylic acids and esters, which are important synthons in synthetic and medicinal chemistry,³ became much more easier than ever
- ²⁵ before.⁴ Atom economic reactions of the direct carboxylation of terminal alkynes with CO₂ in the presence of copper-based catalysts were independently developed by Gooßen ⁵ and Zhang ⁶ almost at the same time. Soon after, silver(I)-catalyzed systems were successively raised by Lu⁷ and Gooßen, ⁸ respectively, and
- ³⁰ many functionalized propiolic acids could be obtained in good to excellent yields. Subsequently, Zhang and his coworkers successfully grafted silver nanoparticle to an N-heterocyclic carbene (NHC) polymer to obtain a high activity, excellent stability and reusability catalyst in the carboxylation of terminal ³⁵ alkynes with carbon dioxide at ambient conditions.⁹ Moreover,
- mild base cesium carbonate, itself, proved to be efficient singlecomponent catalyst in the transformation.¹⁰ Though all these methodologies gave us good outcome, harsh terms of relative high temperature (120 °C) ¹⁰ and relative high pressure (2-5 atm)
- ⁴⁰ ^{5,7,10} were required in some catalytic systems. The types of catalysts were still restricted to transition metals of copper and silver and their complexes. Hence, to improve these deficiencies, developing new series of catalysts was desirable.
- During the past two decades, rare-earth metal amides revealed ⁴⁵ excellent catalytic activities in organic synthesis because of their unique nature and rich sources.¹¹ Among these catalyst systems, the noncyclopentadienyl ancillary ligands, such as amidinate, ^{11a-b} guanidinate, ^{11a-b} imino- or amido-functionalized pyrrolyl ligands, ^{11c-e} and indolyl ^{11f-g} were well designed and widely used.
- ⁵⁰ Amidates are another simple N,O-chelating ligands and had attracted some chemists attention in lanthanide chemistry.¹² Recently, Schafer and Zi independently investigated the synthesis and applications of amidate rare-earth metal complexes, which showed good to high activities in the ring-opening polymerization

⁵⁵ of lactones and lactides,^{12a-b} amidation,^{12c} and hydroamination.^{12d} Our group also has interested in the preparation of various amidate rare-earth metal amides for some time and employed them to several significant catalytic reactions successfully, such as the ring-opening polymerization of *rac*-lactide,^{12e} direct ⁶⁰ addition of terminal alkynes to aromatic nitriles,^{12f} and hydrophosphonylation of aldehydes and unactivated ketones.^{12g}

Consideration of the advantages of the bridged ligand, that is, it can afford a relative rigid and stable framework for the central metal, easily modify the ligand of its steric and electronic 65 properties, and restrain the ligand redistribution,¹³ we turned to an unmet challenge item to develop bridged bis(amidate) rare-earth metal complexes. Fortunately, we obtained three novel bridged bis(amidate) rare-earth metal amides $\{LRE[N(SiMe_3)_2] \cdot THF\}_2$ $(H_2L = N,N'-(cyclohexane-1,2-diyl)$ bis(4-tert-butylbenzamide); $_{70}$ RE = La(1), Nd(2), Y(3)) via the treatment of the bridged amide proligand H₂L with RE[N(SiMe₃)₂]₃. The complexes 1-3 were found to be high efficient catalysts for the direct carboxylation by insertion CO2 into terminal alkynes at ambient pressure. And the Nd-based catalyst 2 showed the highest reactivity. Various 75 propiolic acids with good functional group tolerance were successfully synthesized in high to excellent yields under mild condition.

Results and Discussion

- The bridged bis(amidate) rare-earth metal amides 1-3 were prepared by silylamine elimination reactions of proligand H₂L, N,N'-(cyclohexane-1,2-diyl) bis(4-*tert*-butylbenzamide), with appropriate rare-earth metal precursors RE[N(SiMe₃)₂]₃ in THF at 25 °C for 24 h. After workup, bridged bis(amidate) rare-earth approximate of the second seco
- ss metal amides {LRE[N(SiMe₃)₂]·THF}₂·3THF (RE = La (1), Nd (2), Y (3)) were obtained in good to high yields (Scheme 1). All the complexes are air and moisture sensitive, and slightly soluble in THF.



RE = La (1, 85%), Nd (2, 88%), Y (3, 67%)

Scheme 1. Synthesis of bridged bis(amidate) rare-earth metal amides 1-3.

The solid state structures of unknown complexes 1-3 were determined by X-ray diffraction analysis of single crystals obtained from THF solution. They all crystallized in the triclinic crystal system, P-1 space group, and have binuclear 5 centrosymmetric structures. Since complexes 1-3 are isomorphous, only the molecular structure of complex 2 is depicted in Figure 1 as a representation. It shows that complex 2 is composed of two equivalent subunits, bearing a Nd(III) center for each moiety. The bridged bis(amidate) group coordinated to 10 each central metal adopts two bonding modes, including κ^2 -(N,O): µ-O bonding mode and monodentate O-bound. This unique coordination mode is firstly observed in bridged bis(amidate) rare-earth metal amides, which is not quite the same as the bonding mode in binaphthyl-based amido ytterium complex.14 15 Each cyclohexane-1,2-diyl group takes a most stable chair conformation and the two C-N bonds are located approximately along the equator of the six-membered ring. It is the bridged oxygen atom in the κ^2 -(N,O): μ -O bonding amido group coordinates to a neodymium atom from the other moiety to 20 connect two parts of the complex. Thus, the coordination number of each neodymium is six, that is, three oxygens from two different bis(amidate) groups, one nitrogen from a bis(amidate) group, one nitrogen from a silyamido group and one oxygen from a solvated THF. The geometry around Nd(III) can be described as 25 a distorted octahedron, with N(3) and O(2) at the two apical positions (O(2)-Nd(1)-N(3) 132.68(17)°), and O(1), O(3), O(2A), and N(2) approximately coplanar with the neodymium atom (the sum of the central angles is 350.8°).

The bond parameters in complexes 1 and 3 are similar to the 30 corresponding values in complex 2, thinking about the differences in ionic radii.



Figure 1. Structure of bridged bis(amidate) neodymium amide 2.3THF. Hydrogen atoms and the molecule of THF in the unit 35 cell are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): Nd(1)-N(3) 2.346(5), Nd(1)-O(1) 2.223(4), Nd(1)-N(2) 2.526(5), Nd(1)-O(2) 2.593(4), Nd(1)-O(2A) 2.395(4), O(1)-C(1) 1.323(8), N(1)-C(1) 1.289(8), O(2)-C(18) 1.322(7), N(2)-C(18) 1.295(7); O(1)-Nd(1)-O(3) 79.46(17), O(3)-Nd(1)-40 O(2A) 77.63(17), O(2A)-Nd(1)-N(2) 116.76(15), N(2)-Nd(1)-O(1) 76.92(17), N(3)-Nd(1)-O(2) 132.68(17).

Carboxylation of Terminal Alkynes with Carbon Dioxide Catalyzed by Bridged Bis(Amidate) Rare-45 Earth Metal Amides.

Based on the mechanism raised by Zhang,⁶ Lu,⁷ and Gooßen,⁸ metal acetylide is one of the key intermediates in the carboxylation of terminal alkyne with carbon dioxide catalyzed by metal-based catalyst. Since we predicted that treatment of rare 50 earth metal amide with alkyne produce rare-earth metal acetylide,

^{12f} we believe that the novel bis(amidate) rare-earth metal amides 1-3 can catalyze the carboxylation of terminal alkyne with CO_2

3 equiv. base $-H + CO_2$ sol., 24h (balloon) 4a Entry Cat Base Solvent 2 Cs₂CO₃ 1 2 6 Cs₂CO₃ 3 2 Cs₂CO₃ 4 _ 5 2 Cs₂CO₃ 6 2 Cs₂CO₃ 7 2 Cs₂CO₃ DMSO 8 1 Cs₂CO₃ DMSO 9 3 Cs₂CO₃ DMSO 10 2 K₂CO₃ DMSO 2 11 Na₂CO₃ DMSO 12 2 NaOH DMSO 2 13 **EtONa** DMSO 14 2 DEA DMSO

15

16

17

18

19

2

2

2

2

2

70 Na₂CO₃, NaOH, EtONa, diethylamine (DEA), and CsOH were screened and no desired product was detected, while addition of triethylamine (TEA) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) led to very low yields of phenylpropiolic acid (Table 1, entries 10-17). It shows Cs₂CO₃ is the ideal additive in the 75 carboxylation reaction, which is consistent with the result in published work. ¹⁰ Presumably the relative high temperature could led to the unexpected decarboxylation process, ⁶ 40 °C is proved to be the optimal temperature (Table 1, entries 18-20). The dosage of catalyst, additive cesium carbonate and solvent DMSO, 80 and reaction time play important roles in the carboxylation reaction of phenylacetylene with CO₂ as well. After carefully investigation, this transformation produced the desired phenylpropiolic acid up to 94% yield using 4 mol% catalyst 2 in

smoothly via the same process. Complex 2 was first employed in

the template carboxylation reaction of phenylacetylene (4a) with

transformation was successfully accomplished using complex 2 in the presence of Cs₂CO₃ (Table 1, entry 1). The yields of target

phenylpropiolic acid (5a) were unsatisfactory while using either

the catalyst precursor 6 $Nd[N(TMS)_2]_3$ (Table 1, entry 2) or just

addition of base without rare-earth metal catalyst (Table 1, entry

4). When the reaction temperature was raised to 60 °C, the

increasing yield of phenylpropiolic acid was observed, varying from 58% to 72% (Table 1, entries 1 and 5). It was found

65 dimethyl sulfoxide (DMSO) was the optimal solvent in this

transformation (Table 1, entries 5-7). To our delight, La-based

complex 1 and Y-based complex 3 also behaved as active

catalysts in the template reaction under the same condition as for

complex 2 (Table 1, entries 7-9). Various bases, such as K_2CO_3 ,

60 complex 2 itself as the catalyst (Table 1, entry 3), or just the

55 CO₂ under the atmospheric pressure. As we expected, the

the presence of 2 equiv. Cs₂CO₃ in 5 mL DMSO for 24 hours 85 under constant pressure (See SI, Table 3).

Table 1 Screening of the optimal conditions of the carboxylation of phenylacetylene with CO₂^a 4 mol % cat.

HCL

DMF

DMF

DMF

DMF

DMF

Tol

DMSO

DMSO

DMSO

DMSO

DMSO

- 61
Str
Str
Str
istr
listr
nistr
mistr
mistr
mistr
emistr
emistr
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Ъ

Yield/%¹

58

13

trace

8

72

20

89

80

80

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15

40

90

86

5a

T/°C

25

25

60

60

60

60

60

60

60

60

60

60

60

60

60

60

60

40

50

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	20	2	Cs_2CO_3	DM	SO	80	87	
90	^a Reaction	condition:	phenyla	cetylene	(1.0	mmol),	base	(3.0
	mmol), ca	talyst (0.04	mmol),	CO ₂ (ball	loon),	solvent	(10 m	L). ^b
	Isolated yi	elds.						

TEA

DBU

CsOH

Cs₂CO₃

Cs₂CO₃

With respect to terminal alkynes, the tolerance of substituent groups was explored under the optimized reaction conditions. Various substituted terminal alkynes were examined, and the results are listed in Table 2. The electronic effect of substituent 5 groups on the phenyl ring affects the reactions greatly. Excellent yields, varied from 90-99%, are achieved when the substrates are bearing electron withdrawing groups (EWG), both weak EWG halides (Table 2, 5b-f) and very strong EWG nitro group and trifluoromethyl group (Table 2, 5g-i). The high yields of 80-86% ¹⁰ are obtained when the substrates bearing electron donating groups, such as methyl group, tert-butyl group, and phenyl group (Table 2, 5j-m). However, the yield dramatically drops to 70% when the substituent is a methoxy group, which may be attributes to the poison of the catalyst by the methoxy group (Table 2, 5n). The 15 high efficient catalyst system also performed excellent in the case of hetero aromatic rings and fused aromatic ring (Table 2, entries **50-q**). Dialkynes, for example 1,3- and 1,4-diethynylbenzene also give us the corresponding dicarboxylic acids in satisfactory yields

- with the loading of the starting materials are reduced by half ²⁰ (Table 2, **5r-s**). Unfortunately, the bridged bis(amidate) rare-earth metal amides are found to be unreactive towards aliphatic alkynes, e.g. ethynyltrimethylsilane and 1-hexyne, and could not afford the desired products under the current reaction conditions.
- Table 2. Substrate scope for the catalytic carboxylation of terminal alkynes with CO₂. ^{a, b}



^aReaction condition: alkyne (1.0 mmol), Cs₂CO₃ (2.0 mmol), catalyst **2** (0.04 mmol), CO₂ (balloon), DMSO (5 mL). ^b Isolated ³⁰ yields. ^c alkyne (0.5 mmol).

A Possible Mechanism of the Carboxylation

Catalyzed by Bridged Bis(amidate) Rare-Earth Metal Amides.

³⁵ To gain some insights into the mechanism of the carboxylation reaction, a stoichiometric reaction of Y-based catalyst 3 with phenylacetylene was carried out in d_8 -THF in a NMR tube. The change of chemical shifts of (SiMe₃)₂N⁻ groups during reaction is illustrated in Figure 2. Signals assignable to coordinating $_{40}$ (SiMe₃)₂N⁻ groups in catalyst **3** are observed at 0.20 and 0.04 ppm, respectively (a). 30 min after the addition of phenylacetylene, the integration of the downfield signal significantly decreased, while a new resonance appeared at 0.05 ppm which overlaps with the original signal at 0.04 ppm (b). ⁴⁵ After 6 h reaction, the signal at 0.20 ppm completely disappeared. Only the new signal at 0.05 ppm remained with the integration of 36H, which can be assigned to the methyl groups of $HN(SiMe_3)_2$ that results from the aminolysis of amide with phenylacetylene (c). The identity of HN(SiMe₃)₂ was further confirmed by adding 50 additional HN(SiMe₃)₂ into the NMR tube.



Figure 2. ¹H NMR monitoring of the stoichiometric reaction between Y-based catalyst **3** and phenylacetylene. (a) the spectrum ⁵⁵ of catalyst **3**; (b) 30 min after the addition of phenylacetylene; (c) 6 h after the addition of phenylacetylene.

Based on this finding and some literature reports,⁶⁻⁸ we proposed a possible mechanism for our catalytic system in Scheme 2. The ⁶⁰ metal acetylide intermediate **A** was speculated to form after the aminolysis of the bridged bis(amidate) rare-earth metal amides. Subsequently, carbon dioxide coordinated and inserted into the Ln-C bond of intermediate **A** to generate the rare-earth metal carboxylate **B**. In the presence of a large amount of cesium ⁶⁵ carbonate and alkyne substrates, the transmetallation occurred rapidly, and the formation of cesium carboxylate **C** and regeneration of **A** was instantly completed. After the mixture was quenched by acidic aqueous, the desired product **D** was achieved.



Scheme 2. A possible mechanism for the carboxylation catalyzed

by bridged bis(amidate) rare-earth metal amides.

uncorrected.

Experimental All manipulations and reactions were conducted under purified argon or CO₂ atmosphere by using standard Schlenk techniques. ⁵ Rare-earth metal amides $RE[N(SiMe_3)_2]_3$ (RE = La, Nd, Y), and (N,N'-(cyclohexane-1,2-diyl)-bis(4-tertproligand H_2L butylbenzamide) were prepared according to literature methods.¹⁵ Solvents were distilled from sodium benzophenone ketyl under argon prior to use unless otherwise noted. Solid alkynes were 10 degassed before use, and liquid alkynes were distilled from molecular sieve prior to use. The single crystal X-ray diffraction data were recorded on a Rigaku Mercury CCD X-ray diffractometer. ¹H, ¹³C and ¹⁹F NMR spectra were obtained on a Unity Inova-400 spectrometer in DMSO-d₆ or CDCl₃. Carbon, 15 hydrogen, and nitrogen analyses were performed by direct combustion on a Carlo-Erba EA-1110 instrument. Metal analyses were carried out by complexometric titration. Melting points were determined in sealed Ar-filled capillary tubes and are

General procedure for the synthesis of {LRE[N(SiMe₃)₂]·THF}₂

To a stirred THF solution of RE[N(SiMe₃)₂]₃ (1.49 mmol, 10 of THF), N,N'-(cyclohexane-1,2-diyl)-bis(4-tertmL 25 butylbenzamide) (0.65 g, 1.49 mmol) in 10 mL THF was slowly added. After the mixture was stirred at 25 °C for 24 h, the solvent was pumped off, and the residue was recrystallized from THF at room temperature to give pure crystals. Characterized data for complexes 1-3 were collected as follows.

{LLa[N(SiMe₃)₂]·THF}₂ (1): colorless crystals. Yield: 1.02 g (85%). Mp. 294.5-296.4 °C. Anal. Calcd for C₇₆H₁₂₆N₆O₆La₂Si₄ (1606.69): C 56.70, H 7.89, N 5.22, La 17.26; Found: C 56.98, H 8.02, N 5.23, La 17.30. ¹H NMR (THF-*d*₈, 400 MHz): δ 7.94 (d, *J* 35 = 8.5 Hz, 1H, ArH); 7.77 (d, J = 8.3 Hz, 1H, ArH); 7.62 (d, J = 8.4 Hz, 3H, ArH); 7.55-7.52 (m, 4H, ArH); 7.38 (d, J = 8.5 Hz, 1H, ArH); 7.30 - 7.22 (m, 6H, ArH); 3.68 - 3.63 (m, 8H); 1.84 -1.79 (m, 8H); 1.53 - 1.18 (m, 56H); 0.27 (s, 6H); 0.08-0.05 (m, 30H) ppm.

{LNd[N(SiMe₃)₂]·THF}₂ (2): blue crystals. Yield: 1.06 g (88%). Mp. 293.8-295.3 °C. Anal. Calcd for C₇₆H₁₂₆N₆O₆Nd₂Si₄ (1614.69): C 56.32, H 7.84, N 5.19, Nd 17.80; Found: C 56.40, H 7.98, N 5.23, Nd 17.85.

{LY[N(SiMe₃)₂]·THF}₂ (3): colorless crystals. Yield: 0.75g (67%). Mp. 294.2-296.1 °C. Anal. Calcd for C₇₆H₁₂₆N₆O₆Y₂Si₄ (1506.69): C 60.45, H 8.41, N 5.57, Y 11.78; Found: C 60.52, H 8.48, N 5.61, Y 11.90. ¹H NMR (THF-*d*₈, 400 MHz): δ 7.84 (d, *J* ⁵⁰ = 8.4 Hz, 3H, ArH); 7.55 – 7.49 (m, 3H, ArH); 7.39 (s, 6H, ArH); 7.30 - 7.23 (m, 4H, ArH); 3.63 - 3.58 (m, 8H); 1.82 - 1.75 (m, 8H); 1.37-1.31 (m, 56H); 0.20 (s, 18H); 0.04 (s, 18H) ppm.

X-ray structure determination of complexes 1-3

Owing to their air and moisture sensitivity, suitable single crystals of complexes 1-3 were each sealed in thin-walled glass capillaries. Intensity data were collected on a Rigaku Mercury CCD equipped with graphite-monochromatized Mo K α (λ = 0.71075 Å) radiation for complexes 1-3. Details of the intensity 60 data collection and crystal data are given in Tables 1 and 2 in SI. The crystal structures of these complexes were solved by direct methods, expanded by Fourier techniques and refined by using

the SHELXL-97 program.¹⁶ Atomic coordinates and thermal

parameters were refined by full matrix least-squares analysis on

 $_{65}$ F^2 . All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically with assigned appropriate isotropic thermal parameters.

General procedure for the synthesis of propiolic acids from 70 reactions of terminal alkynes with CO₂ by complex 2

- A 15 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with the complex 2 (61.8 mg, 0.04 mmol) and Cs₂CO₃ (621 mg, 1.91 mmol). Alkyne (1.0 mmol) and anhydrous DMSO (5 mL) were added with syringe in turn, shortly after 75 purging the Schlenk flask with CO₂ three times. Whereafter, carbon dioxide was introduced with a balloon at ambient pressure. The reaction mixture was stirred at 40 °C for 24 h, then cooled down to room temperature. The reaction mixture was filtrated
- followed by quenched with water (15 mL), then acidified with so aqueous HCl (6 N, 20 mL), and extracted with diethyl ether (4 \times 10 mL). The combined organic layers were washed with brine, dried over anhydrous Na2SO4 and filtered. The solvent was removed under vacuum to afford the target acid product. Data for $^1\mathrm{H}$ and $^{13}\mathrm{C}$ NMR of acids were all conducted in CDCl3 or
- 85 DMSO- d_6 , and consistent with the data in reported literatures.

Phenylpropiolic acid (5a). ¹H NMR (400 MHz, CDCl₃): δ 7.62 (m, J = 8.4 Hz, 2H, ArH); 7.49 (m, J = 7.5 Hz, 1H, ArH); 7.40 (m, J = 7.5 Hz, 100 Hz); 7.40 (m, J = 7.5 Hz); 7.40J = 7.5 Hz, 2H, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 158.1, 90 133.4, 131.2, 128.8, 119.3, 88.8, 80.3 ppm. HRMS (ESI, m/z)

calcd. for $C_9H_6O_2H^+$: 147.0440, found: 147.0452.

2-Fluorophenylpropiolic acid (5b). ¹H NMR (400 MHz, DMSO d_6): δ 7.71 (td, J_1 = 7.5, J_2 = 1.7 Hz, 1H, ArH); 7.64-7.56 (m, 1H, 95 ArH); 7.40 (t, J = 9.1 Hz, 1H, ArH); 7.32 (t, J = 7.6 Hz, 1H, ArH) ppm. ¹³C NMR (100 MHz, DMSO- d_6): δ 162.9 (¹ J_{C-F} = 251.0 Hz), 154.1, 134.6, 133.5 (${}^{3}J_{C-F} = 8.0 \text{ Hz}$), 125.2 (${}^{4}J_{C-F} = 3.0 \text{ Hz}$), 116.1 $({}^{2}J_{C-F} = 13.0 \text{ Hz}), 107.6 ({}^{2}J_{C-F} = 15.0 \text{ Hz}), 86.3 ({}^{3}J_{C-F} = 3.0 \text{ Hz})$ Hz) ,77.7 ppm. ¹⁹F NMR (376.5 MHz, DMSO-*d*₆): δ -109.0 ppm. 100 HRMS (ESI, m/z) calcd. For C₉H₅O₂F Na⁺: 187.0165, found:

187.0167.

4-Fluorophenylpropiolic acid (5c). ¹H NMR (400 MHz, CDCl₃): δ 7.65-7.60 (m, 2H, ArH); 7.13-7.07 (m, 2H, ArH) ppm. ¹³C ¹⁰⁵ NMR (100 MHz, CDCl₃): δ 164.4 (¹J_{C-F} = 253.0 Hz), 158.2, 135.8 (${}^{3}J_{C-F} = 9.0 \text{ Hz}$), 116.5 (${}^{2}J_{C-F} = 13.0 \text{ Hz}$), 115.3 (${}^{4}J_{C-F} = 3.0 \text{ Hz}$) Hz), 88.1, 80.1 ppm. ¹⁹F NMR (376.5 MHz, CDCl₃): δ -105.4 ppm. HRMS (ESI, m/z) calcd. For C₉H₅O₂F H⁺: 165.0346, found: 165.0347. 110

4-Chlorophenylpropiolic acid (5d). ¹H NMR (400 MHz, DMSO d_{6}): δ 7.66 (d, J = 8.2 Hz, 2H, ArH); 7.55 (d, J = 8.4 Hz, 2H, ArH) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ 154.1, 135.8, 134.4, 129.3, 117.8, 83.1, 82.5 ppm. HRMS (ESI, m/z) calcd. For ¹¹⁵ C₉H₅O₂Cl Na⁺: 202.9870, found: 202.9876.

4-Bromophenylpropiolic acid (5e). ¹H NMR (400 MHz, DMSO d_6): δ 7.69 (d, J = 8.2 Hz, 2H, ArH); 7.58 (d, J = 7.8 Hz, 2H, ArH) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ 154.1, 134.4, 120 132.1, 124.7, 118.2, 83.2, 82.6 ppm. HRMS (ESI, m/z) calcd. For C₉H₅O₂Br Na⁺: 246.9365, found: 246.9365.

3-Bromophenylpropiolic acid (5f). ¹H NMR (400 MHz, DMSO d_6): δ 7.85 (t, J = 1.6 Hz, 1H, ArH); 7.75 (d, J = 8.1 Hz, 1H, ArH); $_{125}$ 7.64 (d, J = 7.8 Hz, 1H, ArH); 7.42 (t, J = 7.9 Hz, 1H, ArH) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ 154.0, 134.6, 133.9, 131.6, 131.1, 121.9, 121.2, 82.6, 82.4 ppm. HRMS (ESI, m/z) calcd. For $C_9H_5O_2Br Na^+$: 246.9365, found: 246.9370.

4-Nitrophenylpropiolic acid (5g). ¹H NMR (400 MHz, DMSO d_6): δ 8.29 (d, J = 8.8 Hz, 2H, ArH); 7.91 (d, J = 8.8 Hz, 2H, ArH) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ 153.8, 148.2, 133.8, 125.6, 124.0, 85.0, 81.7 ppm. HRMS (ESI, m/z) calcd. For 5 C₉H₅O₄N Na⁺: 214.0110, found: 214.0115.

4-Trifluoromethylphenylpropiolic acid (5h). ¹H NMR (400 MHz, DMSO- d_6): δ 7.92 – 7.76 (m, 4H, ArH) ppm. ¹³C NMR (100 MHz, DMSO- d_6): δ 154.4, 133.8, 130.8 (${}^2J_{C-F}$ = 30.0 Hz), 126.3 10 (${}^{3}J_{C-F} = 4.0$ Hz), 125.5, 124.1(${}^{1}J_{C-F} = 271.0$ Hz), 83.9, 82.7 ppm.

calcd. For C₁₀H₅O₂F₃ H⁺: 215.0314, found: 215.03116.

3-(3,5-bis(trifluoromethyl)phenyl)propiolic acid(5i). ¹H NMR 15 (400 MHz, DMSO-d₆): δ 8.38 (s, 2H, ArH); 8.28 (s, 1H, ArH) ppm. ¹³C NMR (100 MHz, DMSO-d₆): δ 154.2, 133.6 (³J_{C-F} = 4.0 Hz), 131.5 (${}^{2}J_{C-F}$ = 33.4 Hz), 124.5, 123.2 (${}^{1}J_{C-F}$ = 272.0 Hz), 122.4, 84.4, 81.0 ppm. ¹⁹F NMR (376.5 MHz, DMSO-*d*₆): δ -61.6 ppm. HRMS (ESI, m/z) calcd. For C₁₁H₄O₂F₆ H⁺: 283.0188, 20 found: 283.0191.

4-Methylphenylpropiolic acid (5j). ¹H NMR (400 MHz, CDCl₃): δ 7.51 (d, J = 8.1 Hz, 2H, ArH); 7.20 (d, J = 8.0 Hz, 2H, ArH); 2.39(s, 3H, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 25 158.4, 142.0, 133.4, 129.6, 116.1, 89.7, 79.9, 21.9 ppm. HRMS (ESI, m/z) calcd. For C₁₀H₈O₂ H⁺: 161.0597, found: 161.0596.

3-Methylphenylpropiolic acid (5k). ¹H NMR (400 MHz, CDCl₃): δ 7.46 – 7.39 (m, 2H, ArH); 7.29 (m, J = 5.7, 0.8 Hz, ³⁰ 2H, ArH); 2.36 (s, 3H, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 158.4, 138.6, 133.9, 132.2, 128.7, 119.0, 89.5, 21.3 ppm. HRMS (ESI, m/z) calcd. For C₁₀H₈O₂ Na⁺: 183.0416, found: 183.0422.

35 4-tert-Butylphenylpropiolic acid (51). ¹H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.5 Hz, 2H, ArH); 7.42 (d, J = 8.5 Hz, 2H, ArH); 1.32(s, 9H, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 158.5, 155.0, 133.3, 125.9, 116.1, 89.7, 79.9, 35.2, 31.1 ppm. HRMS (ESI, m/z) calcd. For C₁₃H₁₄O₂ Na⁺: 225.0886, found: 40 225.0887.

3-(biphenyl-4-yl)propiolic acid (5m). ¹H NMR (400 MHz, DMSO- d_6): δ 7.90 – 7.62 (m, 6H, ArH); 7.50 (t, J = 7.5 Hz, 2H, ArH); 7.42 (t, J = 7.3 Hz, 1H, ArH) ppm. ¹³C NMR (100 MHz, 45 DMSO-d₆): δ 154.3, 142.3, 138.7, 133.3, 129.1, 128.3, 127.2, 126.8, 117.8, 84.4, 82.4 ppm. HRMS (ESI, m/z) calcd. For C₁₅H₁₀O₂ Na⁺: 245.0573, found: 245.0569.

4-Methoxylphenylpropiolic acid (5n). ¹H NMR (400 MHz, ⁵⁰ CDCl₃): δ 7.57 (d, J = 8.9 Hz, 2H, ArH); 6.90 (d, J = 8.9 Hz, 2H, ArH); δ 3.85 (s, 3H, CH₃) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 162.0, 158.3, 135.4, 114.5, 111.0, 90.0, 79.8, 55.6 ppm. HRMS (ESI, m/z) calcd. For $C_{10}H_8O_3$ H⁺: 177.0546, found: 177.0559.

55 3-(thiophen-2-yl)propiolic acid (50). ¹H NMR (400 MHz, CDCl₃): δ 7.55 (dd, J_1 = 3.7 Hz, J_2 = 1.1 Hz, 1H, ArH); 7.52 (dd, $J_1 = 5.1$ Hz, $J_2 = 1.1$ Hz, 1H, ArH); 7.08 (dd, $J_1 = 5.1$ Hz, $J_2 = 3.8$ Hz, 1H, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 158.2, 137.5, 132.2, 127.8, 119.0, 84.6, 83.3 ppm. HRMS (ESI, m/z) calcd. For 60 C₇H₄O₂S H⁺: 153.0005, found: 153.0010.

3-(thiophen-3-yl)propiolic acid (5p). ¹H NMR (400 MHz, DMSO-d₆): δ 8.19 (s, 1H, ArH); 7.70 (s, 1H, ArH); 7.33 (s, 1H, ArH) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ 154.4, 134.9, 65 129.9, 127.8, 117.9, 81.5, 80.3 ppm. HRMS (ESI, m/z) calcd. For C₇H₄O₂S H⁺: 153.0005, found: 153.0010.

3-(pyren-1-yl)propiolic acid (5q). ¹H NMR (400 MHz, DMSO d_6): $\delta 8.53 - 8.37$ (m, 4H, ArH); 8.37 - 8.28 (m, 3H, ArH); 8.24⁷⁰ (d, J = 8.9 Hz, 1H, ArH); 8.16 (t, J = 7.7 Hz, 1H) ppm. ¹³C NMR (100 MHz, DMSO-*d*₆): δ 154.9, 131.3, 131.0, 130.7, 130.2, 130.0, 127.6, 127.4, 127.1, 125.4, 123.4, 113.2, 87.6, 83.9 ppm. HRMS (ESI, m/z) calcd. For C₁₉H₁₀O₂H⁺: 271.0753, found: 271.0768.

¹⁹F NMR (376.5 MHz, DMSO-*d*₆): δ -61.6 ppm. HRMS (ESI, *m/z*) ₇₅ 3,3'-(1,3-phenylene)dipropiolic acid (**5r**). ¹H NMR (400 MHz, DMSO- d_6): δ 7.86 (s, 1H, ArH); 7.78 (dd, J = 7.8, 1.5 Hz, 2H, ArH); 7.57 (t, J = 7.8 Hz, 1H) ppm. ¹³C NMR (100 MHz, DMSO-d₆): δ 154.5, 136.3, 135.1, 130.3, 120.4, 83.0, 82.9 ppm. HRMS (ESI, m/z) calcd. For C₁₂H₆O₄ Na⁺: 237.0158, found: 80 237.0150.

> 3,3'-(1,4-phenylene)dipropiolic acid (5s). ¹H NMR (400 MHz, DMSO-d₆): δ 7.71 (s, 4H, ArH) ppm. ¹³C NMR (100 MHz, DMSO-d₆): δ 154.1, 133.0, 121.2, 83.8, 83.0 ppm. HRMS (ESI, m/z) calcd. For C₁₂H₆O₄ Na⁺: 237.0158, found: 237.0151.

Conclusion

In summary, three novel bridged bisamidate rare earth metal amides $\{LRE[N(SiMe_3)_2] \cdot THF\}_2$ (RE = La (1), Nd (2), Y(3); H₂L

90 = N,N'-(cyclohexane-1,2-diyl)bis(4-tert-butylbenzamide)) had been prepared through the reactions of the bridged amide proligand H₂L with RE[N(SiMe₃)₂]₃ in good yields. X-ray structural analysis shows that compounds 1-3 are binuclear centrosymmetric structures. It is the first time that the bridged 95 bisamidate rare earth metal amides were successfully employed in the valuable carboxylation of terminal alkynes with CO_2 in the presence of cesium carbonate under constant pressure. Especially, complex 2 with central metal Nd performed the highest activity among those amides and gave us high to excellent yields for 100 aromatic substrates with good tolerance of substituents. It is a convenient access to important propiolic acid and its derivatives. Many efforts to make clear of the catalytic mechanism and to explore of new efficient catalysts were still in process in our lab.

Notes

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- 110 † Electronic Supplementary Information (ESI) available: General procedures for preparations of complexes and substrates and catalysis, characterization data, 1 H and 13 C NMR spectra, crystallographic data for complexes 1-3 [CCDC: 1017174 (1), 1017173 (2), 1017176 (3)] and figures depicting solid state 115 structures. See DOI: 10.1039/b000000x/

Acknowledgment

We gratefully acknowledge financial supports from the National Natural Science Foundation of China (Grant Nos. 21172165, 21132002 and 21372172), PAPD, the Major Research Project of 120 the Natural Science Foundation of the Jiangsu Higher Education Institutions (Project 14KJA150007), and the Qing Lan Project.

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Published on 16 December 2014. Downloaded by University of Prince Edward Island on 17/12/2014 17:52:52

Graphic Abstract

Carboxylation of Terminal Alkynes with Carbon Dioxide Catalyzed

by Bridged Bis(amidate) Rare-Earth Metal Amides

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Three bis(amidate) rare-earth metal amides {LRE[N(SiMe₃)₂]·THF}₂ (RE = La(1), Nd(2), Y(3)), which were prepared by the treatment of the bridged amide proligand H₂L (N,N'-(cyclohexane-1,2-diyl)bis(4-*tert*-butylbenzamide) with RE[N(SiMe₃)₂]₃ in THF, had been characterized by single-crystal X-ray diffraction, elemental analyses, and NMR for complexes **1** and **3**. All the complexes were found as efficient catalysts for the direct carboxylation of terminal alkynes with CO₂ at ambient pressure for the first time. A series of terminal alkynes with good functional group tolerance were converted to the corresponding propiolic acids in high to excellent yields using the highest reactive Nd-based catalyst **2** at 40 °C.