RSC Advances



View Article Online

View Journal | View Issue

PAPER

Check for updates

Cite this: RSC Adv., 2017, 7, 42792

Received 10th July 2017 Accepted 28th August 2017

DOI: 10.1039/c7ra07565k

rsc.li/rsc-advances

Introduction

In the past decade, the β -diketiminato supported metal complexes, as some of the typical nonmetallocene complexes, have seen great development, because the monodeprotonated β-diketiminato ligand is isoelectronic with the cyclopentadienyl anion. Compared with the cyclopentadienyl ligand, the β -diketiminato ligand displayed different coordination modes,¹ and tunable steric and electronic properties.1-3 The reactivities of rare-earth metal complexes incorporating different β-diketiminato ligands have also been widely investigated.4-6 Some of them displayed high catalytic activities in polymerization, such as olefins polymerization,15,4a methyl methacrylate polymerization,1g,5b copolymerization of epoxide and CO2,1d,5d and ringopening polymerization of ε-caprolactone or lactides.^{5f-5j} Recently, we reported rare-earth metal complexes bearing cyclohexyl bridged β-diketiminato ligands.⁶ As a continuation of our own interest in cyclohexyl bridged β -diketiminato ligands,

Synthesis, characterization and catalytic activity of rare-earth metal amides incorporating cyclohexyl bridged bis(β -diketiminato) ligands \dagger

Hui Miao,^{ab} Shaowu Wang, ^(b)*^{ac} Xiancui Zhu, ^{*a} Shuangliu Zhou,^a Yun Wei,^a Qingbing Yuan^a and Xiaolong Mu^a

A series of organo rare-earth metal amides incorporating chiral cyclohexyl bridged bis(B-diketiminato) ligands with general formula LREN(SiMe₃)₂ ($L^1 = (1S,2S)-1,2-Cy[NC(Me)CHC(Me)NAr]_2$, Ar = 2, 6-Et₂C₆H₃, RE = Nd (1a), Dy (1b), Yb (1c), Y (1d); $L^2 = (1R,2R)-1,2-Cy[NC(Me)CHC(Me)NAr]_2$, Ar = 2, $6-i-Pr_2C_6H_3$, RE = Nd (2a), Gd (2b), Dy (2c), Er (2d), Y (2e)) were synthesized in good yields via reactions of $[(Me_3Si)_2N]_3RE^{III}(\mu-CI)Li(THF)_3$ with H_2L^1 and H_2L^2 . All compounds were fully characterized by spectroscopic methods and elemental analyses. The complexes 1d and 2e were also characterized by ${}^{1}H$ NMR and ¹³C NMR spectral analyses. The structures of complexes **1a-d** were determined by singlecrystal X-ray analyses. Investigation of the catalytic properties of the complexes indicated that all complexes exhibited a high catalytic activity towards the addition of diphenylphosphine oxide to β -nitroalkene and α , β -unsaturated carbonyl derivatives with an excellent regioselectivity.

> we further explored the chiral cyclohexyl bridged β-diketiminato supported rare-earth metal complexes to expand their catalytic applications. We report herein the synthesis and characterization of a series of the rare-earth metal amides incorporating chiral cyclohexyl bridged bis(β-diketiminato) ligands and their catalytic activity towards the hydrophosphination of β -nitroalkene and α , β -unsaturated carbonyl derivatives.

Results and discussion

Synthesis and characterization of complexes

Treatment of H_2L^1 or H_2L^2 with 1 equiv. of the rare-earth metal amides [(Me₃Si)₂N]₃RE^{III}(µ-Cl)Li(THF)₃ in toluene at 60–80 °C afforded the rare-earth metal complexes with general formula LREN(SiMe₃)₂ ($L^1 = (1S, 2S)$ -1,2-Cy[NC(Me)CHC(Me)NAr]₂, Ar = 2, 6-Et₂C₆H₃, RE = Nd (1a), Dy (1b), Yb (1c), Y (1d); $L^2 = (1R, 2R)$ - $1,2-Cy[NC(Me)CHC(Me)NAr]_2, Ar = 2, 6-i-Pr_2C_6H_3, RE = Nd(2a),$ Gd (2b), Dy (2c), Er (2d), Y (2e)) (Scheme 1). The complexes are



Scheme 1 Preparation of the rare-earth metal complexes.

^aLaboratory of Functional Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241000, P. R. China. E-mail: swwang@ahnu.edu. cn; zxc0805@ahnu.edu.cn; Fax: +86 553 3883517; Tel: +86 553 5910015

^bSchool of Chemistry and Materials Engineering, Fuyang Normal College, Fuyang, Anhui 236037, P. R. China

^{&#}x27;State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, P. R. China

[†] Electronic supplementary information (ESI) available: Characterization spectra (¹H NMR and ¹³C NMR) for complexes 1d, 2e and compounds 4a-n. CCDC 1553833-1553836 for 1a-d. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c7ra07565k

Paper

sensitive to air and moisture; and they have a good solubility in either polar solvents or nonpolar solvents. All complexes were fully characterized by IR and elemental analyses. The complexes **1d** and **2e** were also characterized by ¹H NMR and ¹³C NMR spectra analyses. The structures of complexes **1a–d** were determined by single-crystal X-ray analyses.

Molecular structures of the complexes

X-ray structure analyses revealed that complexes 1a-d are mononuclear structures crystallized in the orthorhombic system with chiral space group $P2_12_12_1$, they are isostructural

Fig. 1 Representative structure of rare-earth metal amides incorporating chiral bridged bis(β -diketiminato) ligand. Hydrogen atoms were omitted for clarity.

and isomorphous. Representative structural diagram of complex **1d** is shown in Fig. 1. The rare-earth metal adopts a distorted square pyramid, in which the N(SiMe₃)₂ ligand occupies the apical position and the four N atoms of the chiral bridged β -diketiminato moieties form the basis. The substituted aryl groups take the transoid fashion in all complexes with one aryl substituent pointing away from the amido group and the other aryl group pointing towards the amido group. The selected bond lengths and angles are listed in Table 1.

From Table 1, we can see that the usual consequence of the ionic radius of the RE³⁺ ion when moving from Nd³⁺ to Yb³⁺ is clearly reflected by the average RE-N distances of 2.407(3) Å found in 1a, 2.324(2) Å found in 1b, 2.267(5) Å found in 1c, 2.316(3) Å found in 1d. The average RE-N distances of complexes 1a [2.407(3) Å], 1b [2.324(2) Å] and 1d [2.316(3) Å] were compared with the corresponding RE-N distances in the similar rare-earth complexes containing the cyclohexyl-linked bis(β -diketiminato) Cy[NC(Me)CHC(Me)NAr]₂REN(SiMe₃)₂ (Ar $= 2, 6 \cdot {}^{i}Pr_{2}C_{6}H_{3}, RE = Nd [2.433(2) Å], Dy [2.350(2) Å], Y [2.340(2) Å]$ Å]).6 The lanthanide contraction is contrary reflected by the average RE-C (C8–C10 and C23–C25) contacts of 3.062(3) Å in 1a, 3.104(3) Å in 1b, 3.117(5) Å in 1c, 3.108(3) Å in 1d, which is consistent with rare-earth complexes containing cyclohexyllinked bis(β-diketiminato) Cy[NC(Me)CHC(Me)NAr]2-REN(SiMe₃)₂ (Ar = 2, 6^{i} Pr₂C₆H₃), probably due to steric effects of ligands on the Ln-C interaction.6

Catalytic activities of the complexes

Development of new catalysts for hydrophosphination is of interest and importance due to 100% atom economy pathway

Table 1	Selected bond	length (Å)	and bond	angle (°) fe	or complexes	1a-c
---------	---------------	------------	----------	--------------	--------------	------

	$\mathbf{1a} (RE = Nd)$	$\mathbf{1b} (RE = Dy)$	$\mathbf{1c} (RE = Yb)$	$\mathbf{1d} (RE = Y)$
RE(1)-N(1)	2.421(3)	2.332(3)	2.294(6)	2.324(3)
RE(1)-N(2)	2.400(3)	2.323(3)	2.278(5)	2.321(3)
RE(1)-N(3)	2.385(3)	2.323(2)	2.227(5)	2.320(3)
RE(1)-N(4)	2.467(3)	2.360(3)	2.297(6)	2.346(3)
RE(1)-N(5)	2.364(2)	2.284(3)	2.240(5)	2.273(3)
RE(1)-Nav.	2.407(3)	2.324(3)	2.267(5)	2.316(3)
RE(1)-C(8)	2.950(3)	2.997(3)	3.015(5)	2.998(3)
RE(1)-C(9)	3.037(3)	3.114(3)	3.212(5)	3.149(3)
RE(1)-C(10)	3.054(3)	3.042(3)	3.049(5)	3.059(3)
RE(1)-C(23)	3.049(3)	3.100(3)	3.088(5)	3.093(3)
RE(1)-C(24)	3.169(3)	3.259(3)	3.254(5)	3.245(3)
RE(1)-C(25)	3.111(3)	3.112(3)	3.084(5)	3.105(3)
RE(1)-Cav.	3.062(3)	3.104(3)	3.117(5)	3.108(3)
N(1)-RE(1)-N(2)	73.38(11)	76.15(10)	78.0(2)	77.14(11)
N(1)-RE(1)-N(3)	65.96(12)	68.20(10)	69.4(2)	68.28(11)
N(1)-RE(1)-N(4)	138.60(12)	144.13(10)	146.9(2)	144.33(12)
N(1)-RE(1)-N(5)	95.50(11)	93.70(10)	93.8(2)	94.03(11)
N(2)-RE(1)-N(3)	96.34(9)	95.43(10)	94.9(2)	95.71(12)
N(2)-RE(1)-N(4)	125.32(10)	121.41(10)	117.2(2)	120.36(12)
N(2)-RE(1)-N(5)	126.89(8)	122.73(10)	121.4(2)	122.31(12)
N(3)-RE(1)-N(4)	75.61(10)	78.54(10)	79.8(2)	78.63(11)
N(3)-RE(1)-N(5)	130.04(10)	133.15(10)	136.4(2)	133.98(12)
N(4)-RE(1)-N(5)	96.74(11)	99.64(10)	100.8(2)	99.76(12)

through the additions of dialkyl phosphites, secondary phosphines and diarylphosphine oxides to the unsaturated substrates.⁷ In the addition of diarylphosphine oxide to the α , β unsaturated derivatives, rare-earth metal complexes have advantages of lower catalysts loadings (3-5 mol%), available materials, solvents compatibility and easy preparation, compared with the reported chiral bicyclic guanidinate catalyst (10 mol% loading, Et₂O as solvent) and chiral multifunctional amine-thiourea catalyst (10 mol% loading, CH2Cl2 as solvent).8 In our previous study, we have reported the rare-earth metal amido complexes as catalysts for various C-P bond formation.9a,b,f,g In order to further explore the chiral rare-earth metal amido complexes for the catalytic C-P bond formation, we examined the chiral rare-earth complexes as catalysts for the catalytic hydrophosphination of β -nitroalkene and α , β -unsaturated carbonyl derivatives.

Addition of diphenyphosphine oxide to the β -nitrostyrene was tested as a template by employing complex **1d** as a catalyst, and results were summarized in Table 2. Results showed that 3 mol% of the catalyst **1d** could catalyze the hydrophosphination of β -nitrostyrene in solvents such as toluene, THF, diethyl ether and *n*-hexane at room temperature. The catalytic reaction was run in *n*-hexane to afford the product **4a** in a 49% yield, probably due to solubility of catalyst. It is a pity that

Table 2	Influence of the conditions on the reaction of β -nitrostyrene
with dip	henyphosphine oxide ^a



Entry	Cat. (mol%)	Solvent	Temp. (°C)	Time (h)	Yield (%)
1	1d (1%)	Toluene	r.t.	24	58
2	1d (3%)	Toluene	r.t.	24	96
3	1d (5%)	Toluene	r.t.	24	96
4	1d (3%)	Toluene	r.t.	6	95
5	1d (3%)	Toluene	r.t.	1	57
6	1d (3%)	Toluene	r.t.	3	78
7	1d (3%)	Toluene	45	6	93
8	1d (3%)	Toluene	0	6	67
9	1d (3%)	Toluene	-10	6	45
10	1d (3%)	THF	r.t.	6	93
11	1d (3%)	Et_2O	r.t.	6	92
12	1d (3%)	n-Hexane	r.t.	6	49
13	1a (3%)	Toluene	r.t.	6	95
14	1b (3%)	Toluene	r.t.	6	94
15	1c (3%)	Toluene	r.t.	6	95
16	2a (3%)	Toluene	r.t.	6	93
17	2b (3%)	Toluene	r.t.	6	92
18	2c (3%)	Toluene	r.t.	6	94
19	2d (3%)	Toluene	r.t.	6	95
20	2e (3%)	Toluene	r.t.	6	94

^{*a*} Reactions were performed with 0.5 mmol of diphenyphosphine oxide and 0.5 mmol of β-nitrostyrene in 5 mL of solvent.

the addition products catalyzed by the above chiral rare-earth complexes was racemic under the conditions screened, probably due to the ligands' chiral backbone far from the metal centre which cannot control the stereochemistry of the product, but the reactions afforded the products with a high regioselectivity. The catalytic activities of the above different rare-earth metal amides on hydrophosphination of β -nitrostyrene were investigated with 3 mol% of catalyst loading using toluene as a solvent (Table 2, entries 4, 13–20). It is found that all complexes **1a–d**, **2a–e** exhibited high catalytic activities on the hydrophosphination of β -nitrostyrene, indicating that the ionic radii of the rare-earth metals and the substituent groups on phenyl ring have little influence on the catalytic activities of the catalysts.

Under the optimized reaction conditions, we next examined the substrate scope of the catalytic addition of diphenyphosphine oxide to different β -nitroalkene employing 1d as a catalyst (Table 3). From Table 3, we can see that the complex 1d exhibited a high catalytic activity towards different β-nitroalkene despite of the electronic nature and the steric effect of the substituents on the aryl groups of the substrates (entries 1-8, Table 3). Furthermore, the additions of diphenyphosphine oxide to various α,β -unsaturated carbonyl derivatives have also examined. The catalytic system could suit well for the α,β unsaturated amides, esters and chalcones producing the corresponding 1,4-regioselective addition products in high yields (entries 9-14, Table 3). In contrast to the imino-hydroxyquinolyl functionalized rare-earth metal catalysts,^{8c} the catalytic loadings of new synthesized rare-earth metal complexes supported by chiral cyclohexyl bridged bis(β-diketiminato) ligand were reduced to 3 mol%, and the substrates could be different α , β unsaturated amides, esters and chalcones, indicating ligands effects on the catalytic activity of the catalysts.

The catalytic addition mechanism of diphenylphosphine oxide to the β -nitrostyrene and α , β -unsaturated carbonyl derivatives is proposed (Scheme 2). Interaction of the catalyst with diphenyphosphine oxide produced the intermediate **A** *via* silylamine elimination, coordination of the substrate with **A** produced **B**, which subsequently underwent 1,4-conjugate addition to form **C**, **C** then interacted with diphenyphosphine oxide to regenerate intermediate **A** finishing a catalytic cycle. The stereocenters of the ligands are far from the reactive site in the intermediate **B** which controls the stereochemistry to produce racemic products. The metal center will have little influence on the catalytic activity.

Experimental section

Materials and methods

All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and oxygen-free atmosphere using standard Schlenk techniques or in a glove box. All solvents were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. $[(Me_3Si)_2N]_3RE^{III}(\mu-CI)Li(THF)_3$ (RE = Nd, Gd, Dy, Er, Yb and Y) were prepared according to literature methods.⁹⁹ (1*S*,2*S*)-(+)-1,2-diaminocyclohexane, 2,6-diethylaniline, (1*R*,2*R*)-(-)-1,2-

This article is licensed under a Creative Commons Attribution 3.0 Unported Licence.

8

Open Access Article. Published on 05 September 2017. Downloaded on 8/11/2025 9:01:35 PM.

Table 3Addition of diphenyphosphine oxide to β -nitroalkene and α , β -unsaturated carbonyl derivatives catalyzed by 1d





^a Isolated yields. ^b Reaction conditions: catalyst loading 1 mol%, time: 1 hour.

diaminocyclohexane, 2,6-diisopropylaniline, acetylacetone were purchased and used without purification. 2-((2,6-Diisopropylphenyl)imido)-2-penten-4-one and 2-((2,6-diethylphenyl)imido)-2-penten-4-one were synthesized by following the literature procedures.¹⁰ Elemental analyses data were obtained on a Perkin-Elmer 2400 Series II elemental analyzer. ¹H NMR and ¹³C NMR spectra for analyses of compounds were recorded on a Bruker AV-300 NMR spectrometer (300 MHz for ¹H; 75.0 MHz for ¹³C) in C₆D₆ for

lanthanide complexes and in $CDCl_3$ for organic compounds. Chemical shifts (δ) were reported in ppm. *J* values are reported in Hz. IR spectra were recorded on a Perkin-Elmer 983(G) spectrometer (KBr pellet).

Preparation of H_2L^1. (1*S*,2*S*)-(+)-1,2-Diaminocyclohexane (1.142 g, 10.0 mmol), 2-((2,6-diethylphenyl)imido)-2-penten-4one (5.090 g, 22.0 mmol), and a catalytic amount of *p*-toluenesulfonic acid in toluene (30 mL) were combined and refluxed overnight. The water produced during the reaction was removed



Scheme 2 The proposed mechanism of the catalytic reaction.

as a toluene azeotrope using a water separator. The toluene was removed *in vacuo* after the reaction was completed. The product was extracted with hexane and crystallized at -20 °C affording the product H₂L¹ (2.590 g, 48% yield). ¹H NMR (300 MHz, CDCl₃, 25 °C, ppm): $\delta = 10.94$ (br s, 2H, NH), 7.09 (m, 4H, C₆H₃), 6.96 (m, 2H, C₆H₃), 4.58 (s, 2H, β -CH), 3.15 (br s, 2H, ring-CH), 2.43 (m, 8H, CH₂CH₃), 1.95 (s, 6H, CH₃), 1.70 (m, 2H, ring-CH₂), 1.66 (m, 2H, ring-CH₂), 1.60 (s, 6H, CH₃), 1.24–1.10 (m, 4H, ring-CH₂), 1.15 (m, 6H, CH₃CH₂), 1.12 (d, 6H, CH₃CH₂). ¹³C NMR (75 MHz, CDCl₃, 25 °C, ppm): $\delta = 165.31$, 154.16, 147.65, 132.87, 132.68, 124.78, 124.55, 121.22, 91.90, 56.92, 32.52, 24.02, 23.66, 23.32, 20.62, 18.58, 13.39. IR (KBr pellet, cm⁻¹): $\nu = 2928$ (w), 2859 (w), 1906 (w), 1842 (w), 1626 (s), 1553 (m), 1450 (s), 1371 (w), 1308 (w), 1242 (s), 1184 (s), 1130 (m), 1024 (s), 959 (m), 870 (s), 797 (s), 731 (vs.), 610 (s), 525 (m).

Preparation of H_2L^2 . (1R,2R)-(-)-1,2-Diaminocyclohexane (1.142 g, 10.0 mmol), 2-((2,6-diisopropylphenyl)imido)-2penten-4-one (5.700 g, 22.0 mmol), and a catalytic amount of p-toluenesulfonic acid in toluene (30 mL) were combined and refluxed overnight. The water produced during the reaction was removed as a toluene azeotrope using a water separator. The toluene was removed in vacuo after the reaction was completed. The product was extracted with hexanes and crystallized at -20 °C affording the product H₂L² (3.040 g, 51% yield). ¹H NMR (300 MHz, CDCl₃, 25 °C, ppm): δ = 11.02 (br s, 2H, NH), 7.08 (m, 4H, C_6H_3), 7.01 (m, 2H, C_6H_3), 4.60 (s, 2H, β -CH), 3.17 (br s, 2H, ring-CH), 2.88 (m, 4H, CHCH₃), 1.97 (s, 6H, CH₃), 1.92 (m, 2H, ring-CH₂), 1.61 (m, 2H, ring-CH₂), 1.54 (s, 6H, CH₃), 1.26-1.09 (m, 4H, ring-CH₂), 1.15 (d, 12H, J = 6.5 Hz, CH₃CH), 1.11 (d, 12H, J = 4.7 Hz, CH₃CH). ¹³C NMR (75 MHz, CDCl₃, 25 °C, ppm): $\delta = 166.60, 154.99, 146.86, 138.29, 138.21, 122.77, 122.67,$ 122.53, 92.96, 57.24, 32.42, 27.98, 27.79, 24.30, 23.98, 23.11, 22.82, 21.73, 19.43. IR (KBr pellet, cm^{-1}): $\nu = 3059$ (w), 2959 (m), 2932 (w), 2864 (m), 1624 (s), 1555 (s), 1435 (m), 1362 (m), 1308 (s), 1180 (s), 1130 (m), 1099 (m), 1024 (m), 935 (m), 787 (s), 760 (vs.), 733 (vs.), 698 (m), 610 (m).

Preparation of L¹NdN(SiMe₃)₂ (1a). To a toluene (10.0 mL) solution of H_2L^1 (1) (0.626 g, 1.16 mmol) was added a toluene (20.0 mL) solution of [(Me₃Si)₂N]₃Nd^{III}(µ-Cl)Li(THF)₃ (1.078 g, 1.22 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was then heated at 80 °C for 12 h, the color of the solution was gradually changed from blue to red. The solvent was evaporated under reduced pressure. The residue was extracted with n-hexane (15.0 mL). The extractions were combined and concentrated to about 10.0 mL. The yellow green crystals were obtained by cooling the concentrated solution at 0 °C for several days (0.763 g, 78% yield). IR (KBr pellet, cm⁻¹): $\nu = 3063$ (w), 2928 (w), 2866 (w), 2361 (m), 2332 (m), 1626 (s), 1553 (m), 1450 (w), 1373 (w), 1310 (m), 1242 (s), 1186 (vs.), 1130 (m), 1103 (s), 1024 (s), 932 (m), 885 (w), 762 (m), 731 (m), 610 (w); Anal. calc. for C₄₂H₆₈N₅NdSi₂ (843.4358): C, 59.81; H, 8.13; N, 8.30. Found: C, 59.62; H, 8.08; N, 8.34%.

Preparation of L¹DyN(SiMe₃)₂ (1b). This compound was prepared as yellow crystals in 80% (0.850 g) yield following the procedures described for the preparation of complex **1a** from the reaction of H₂L¹ (0.670 g, 1.24 mmol) with [(Me₃Si)₂N]₃-Dy^{III}(μ-Cl)Li(THF)₃ (1.178 g, 1.30 mmol). IR (KBr pellet, cm⁻¹): ν = 3061 (w), 2927 (w), 2866 (w), 2331 (m), 1626 (s), 1552 (m), 1451 (w), 1309 (m), 1242 (m), 1186 (s), 1130 (m), 1024 (s), 931 (m), 885 (w), 761 (m), 731 (m), 609 (w); Anal. calc. for C₄₂H₆₈DyN₅Si₂ (861.6938): C, 58.54; H, 7.95; N, 8.13. Found: C, 58.39; H, 8.01; N, 8.10%.

Preparation of L¹YbN(SiMe₃)₂ (1c). This compound was prepared as yellow crystals in 79% (1.160 g) yield following the procedures described for the preparation of complex **1a** from the reaction of H₂L¹ (0.913 g, 1.69 mmol) with [(Me₃Si)₂N]₃-Yb^{III}(μ-Cl)Li(THF)₃ (1.623 g, 1.78 mmol). IR (KBr pellet, cm⁻¹): ν = 3062 (w), 2961 (w), 2867 (w), 2361 (m), 1626 (s), 1552 (m), 1450 (w), 1373 (w), 1309 (m), 1243 (s), 1185 (*vs.*), 1103 (m), 1024 (s), 933 (m), 886 (w), 761 (m), 732 (m), 610 (w); Anal. calc. for C₄₂-H₆₈N₅Si₂Yb (872.2478): C, 57.83; H, 7.86; N, 8.03. Found: C, 57.97; H, 7.87; N, 7.98%.

Preparation of L¹YN(SiMe₃)₂ (1d). This compound was prepared as yellow crystals in 80% (0.625 g) yield following the procedures described for the preparation of complex 1a from the reaction of H_2L^1 (0.536 g, 0.99 mmol) with $[(Me_3Si)_2N]_3Y^{III}(\mu$ -Cl)Li(THF)₃ (0.868 g, 1.05 mmol). ¹H NMR (300 MHz, C₆D₆, 25 °C, ppm): $\delta = 7.22-6.98$ (m, 6H, C₆H₃), 5.07 (s, 1H, β -CH), 4.42 (m, 1H, ring-CH), 4.03 (s, 1H, β-CH), 3.29 (m, 1H, ring-CH), 3.30-2.32 (m, 8H, CH₂CH₃), 2.59 (m, 2H, ring-CH₂), 2.07 (s, 3H, CH₃CN), 1.65 (s, 3H, CH₃CN), 1.50 (s, 3H, CH₃CN), 1.89-1.07 (m, 6H, ring-CH₂), 1.42 (s, 3H, CH₃CN), 1.46 (m, 3H, CH₃CH₂), 1.31 (m, 3H, CH₃CH₂), 1.23 (m, 3H, CH₃CH₂), 1.10 (m, 3H, CH₃CH₂), 0.24 (s, 18H, SiCH₃); ¹³C NMR (75 MHz, C₆D₆, 25 °C, ppm): $\delta = 162.5, 162.4, 161.7, 161.0$ (CNCH₃), 147.7, 146.5, 136.6, 136.2, 136.1, 135.8, 124.4, 123.9, 123.7, 123.6, 123.2, 122.7 (aryl), 100.4, 93.4 (β-CH), 69.4, 64.3 (ring-CH), 32.0, 31.7, 26.0, 25.0 (ring-CH₂), 24.4, 24.1, 23.8, 23.3 (CH₂CH₃), 22.6, 21.9, 24.0, 21.5, 19.4, 13.8, 13.7, 12.0 (CH₃), 4.5 (SiCH₃, 6C); IR (KBr pellet, cm⁻¹): $\nu = 3062$ (w), 2962 (w), 2866 (w), 2361 (m), 1624 (s), 1552 (m), 1450 (w), 1309 (m), 1243 (s), 1186 (vs.), 1130 (m), 1024

Paper

(s), 933 (m), 886 (w), 761 (m), 732 (m), 609 (w); Anal. calc. for C₄₂H₆₈N₅Si₂Y (788.0997): C, 64.01; H, 8.70; N, 8.89. Found: C, 64.25; H, 8.89; N, 8.53%.

Preparation of L²NdN(SiMe₃)₂ (2a). To a toluene (10.0 mL) solution of H_2L^2 (0.682 g, 1.14 mmol) was added a toluene (20.0 mL) solution of $[(Me_3Si)_2N]_3Nd^{III}(\mu$ -Cl)Li(THF)₃ (1.012 g, 1.14 mmol) at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was then heated at 80 °C for 12 h, the color of the solution was gradually changed from blue to dark red. The solvent was evaporated under reduced pressure. The residue was extracted with nhexane (15.0 mL). The solvent was evaporated under reduced pressure. The yellow green solid was obtained (0.892 g, 87% yield). IR (KBr pellet, cm⁻¹): $\nu = 2958$ (w), 2864 (w), 1624 (s), 1555 (s), 1437 (w), 1379 (w), 1362 (w), 1310 (w), 1250 (s), 1244 (w), 1180 (m), 1024 (w), 934 (m), 883 (w), 841 (w), 758 (w), 689 (w); Anal. calc. for C46 H76 N5Nd Si2 (899.5421): C, 61.42; H, 8.52; N, 7.79. Found: C, 61.50; H, 8.57; N, 7.60%.

Preparation of L^2GdN(SiMe₃)₂ (2b). This compound was prepared as yellow crystals in 85% (0.866 g) yield by treatment of H_2L^2 (0.665 g, 1.12 mmol) with $[(Me_3Si)_2N]_3Gd^{III}(\mu-Cl)Li(THF)_3$ (1.001 g, 1.12 mmol) using the procedures similar to those described above for the preparation of **2a**. IR (KBr pellet, cm^{-1}): $\nu = 2959$ (m), 2864 (s), 1624 (m), 1555 (m), 1503 (w), 1435 (w), 1362 (w), 1310 (s), 1250 (s), 1180 (vs.), 1148 (w), 1101 (m), 1024 (m), 934 (vs.), 841 (m), 758 (s), 733 (w), 685 (w); Anal. Calc. for C₄₆H₇₆GdN₅Si₂ (912.5501): C, 60.54; H, 8.39; N, 7.67. Found: C, 60.26; H, 8.65; N, 7.60%.

Preparation of L^2 DyN(SiMe₃)₂ (2c). This compound was prepared as yellow crystals in 86% (1.026 g) yield following the procedures described for the preparation of complex 2a from the reaction of H_2L^2 (0.778 g, 1.30 mmol) with $[(Me_3Si)_2N]_3$ - $Dy^{III}(\mu-Cl)Li(THF)_3$ (1.177 g, 1.30 mmol). IR (KBr pellet, cm⁻¹): ν = 3059 (w), 2958 (w), 2865 (w), 1624 (m), 1554 (s), 1435 (w), 1310 (m), 1257 (m), 1180 (s), 1100 (s), 1024 (m), 934 (s), 843 (m), 698 (w), 609 (w); Anal. calc. for C₄₆H₇₆DyN₅Si₂ (917.8001): C, 60.20; H, 8.35; N, 7.63. Found: C, 60.66; H, 8.54; N, 7.57%.

Preparation of L^2ErN(SiMe₃)₂ (2d). This compound was prepared as yellow crystals in 83% (0.888 g) yield following the procedures described for the preparation of complex 2a from the reaction of H_2L^2 (0.693 g, 1.16 mmol) with $[(Me_3Si)_2N]_3$ - $Er^{III}(\mu$ -Cl)Li(THF)₃ (1.054 g, 1.16 mmol). IR (KBr pellet, cm⁻¹): ν = 3059 (w), 2959 (w), 2864 (w), 1624 (s), 1554 (s), 1504 (m), 1435 (w), 1379 (w), 1310 (m), 1223 (m), 1180 (vs.), 1150 (w), 1099 (s), 934 (s), 883 (m), 787 (m), 733 (m), 698 (w), 610 (w); Anal. calc. for C46 H76 ErN5Si2 (922.5591): C, 59.89; H, 8.30; N, 7.59. Found: C, 59.57; H, 8.66; N, 7.56%.

Preparation of L^2YN(SiMe₃)₂ (2e). This compound was prepared as yellow crystals in 85% (0.875 g) yield following the procedures described for the preparation of complex 2a from the reaction of H_2L^2 (0.729 g, 1.22 mmol) with [(Me_3Si)_2N]_3Y^{III}(\mu-Cl)Li(THF)₃ (1.010 g, 1.22 mmol). ¹H NMR (300 MHz, C₆D₆, 25 °C, ppm): δ = 7.23–7.06 (m, 6H), 5.22 (s, 1H, β –CH), 4.39 (m, 1H, ring-CH), 4.12 (s, 1H, β-CH), 3.49 (m, 1H, ring-CH), 3.34 (m, 1H, CHCH₃), 3.27-3.14 (m, 2H, CHCH₃), 3.07 (m, 1H, CHCH₃), 2.40 (m, 2H, ring-CH₂), 2.00 (s, 3H, CH₃CN), 1.77 (s, 3H, CH₃CN), 1.65 (s, 3H, CH₃CN), 1.68–1.09 (m, 6H, ring-CH₂), 1.44

(s, 3H, CH₃CN), 1.68-1.09 (m, 15H, CH₃CH), 1.17 (d, 3H, $CH_3CH, J = 6.75 Hz$), 1.10 (d, 3H, $CH_3CH, J = 6.72 Hz$), 0.99 (d, $3H, CH_3CH, J = 6.63 Hz$, $0.38 (s, 9H, CH_3Si), 0.10 (s, 9H, CH_3Si)$; ¹³C NMR (75 MHz, C₆D₆, 25 °C, ppm): δ = 165.1, 161.8, 161.5, 161.4 (CNCH₃), 153.9, 147.4, 146.4, 141.6, 141.4, 141.1, 141.0, 137.2, 124.0, 123.2, 123.0, 121.9 (aryl), 101.9, 90.3 (β-CH), 69.0, 65.2 (ring-CH), 32.4, 31.7, 29.9, 27.6 (ring-CH₂), 26.8, 25.8, 25.7, 24.8 (CHCH₃), 24.6, 24.4, 24.2, 24.0, 23.3, 23.1, 23.0, 22.1, 21.8, 20.6, 20.0, 18.2 (CH₃), 5.6 (SiCH₃, 3C), 4.9 (SiCH₃, 3C); IR (KBr pellet, cm⁻¹): $\nu = 3061$ (w), 2959 (w), 2936 (w), 2864 (w), 1910 (w), 1624 (s), 1557 (m), 1504 (m), 1435 (w), 1362 (w), 1310 (m), 1250 (s), 1180 (s), 1024 (s), 758 (m), 698 (w), 685 (w); Anal. calc. for C₄₆ H₇₆N₅Si₂Y (844.2060): C, 65.45; H, 9.07; N, 8.30. Found: C, 65.54; H, 9.02; N, 8.36%.

X-ray structure determination. A suitable crystal of the complex 1a, 1b, 1c and 1d was mounted in a sealed capillary. Diffraction was performed on a Siemens SMART CCD-area detector diffractometer using the graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å); temperature 293(2) K; ψ and ω scan technique; SADABS effects and empirical absorption were applied in the data corrections.11 All structures were solved by direct methods (SHELXL-97), completed by subsequent difference Fourier syntheses, and refined by full-matrix leastsquare calculations based on F² (SHELXL-97).¹² Crystal data and details of data collection are given in ESI.[†]

General procedures for hydrophosphination of β -nitroalkene and α , β -unsaturated carbonyl derivatives (4a as an example)

A 30.0 mL Schlenk tube under dried argon was charged with complex 1d (11.8 mg, 0.015 mmol), diphenyphosphine oxide (0.101 g, 0.5 mmol), and 5.0 mL of toluene, and then β nitrostyrene (0.075 g, 0.5 mmol) was added to the mixture. The mixture was stirred at room temperature for 6 hours. After the reaction was completed, the reaction mixture was hydrolyzed by water, extracted with ethyl ether, dried over anhydrous sodium sulfate, and then filtered. After the solvent was removed under reduced pressure, the final products were further purified by recrystallization from ethyl acetate or column chromatography. Compound 4a was isolated as a white solid (0.167 g, 95%).

Conclusion

A series of novel rare-earth metal amides bearing chiral cyclohexyl bridged bis(β-diketiminato) ligands were synthesized via the reactions of [(Me₃Si)₂N]₃RE^{III}(µ-Cl)Li(THF)₃ with the corresponding chiral cyclohexyl bridged bis(β-diketimines) in good yields. These complexes exhibited an excellent catalytic activity on the hydrophosphination of β-nitroalkene and α,β -unsaturated carbonyl derivatives with a high regioselectivity. The catalysts have the advantages of a high efficiency, a low catalysts loading, a wide of solvents and substrates compatibility, and mild conditions. The method provides a highly atomic efficient way for the preparation functionalized phosphine oxides, which can be easy transferred to useful phosphines.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was co-supported by the National Natural Science Foundation of China (Grant No. 21432001, 21372010, 21402029, 21372009) and Foundation for Young Talents in College of Anhui Province (2013SQRL058ZD). We are also grateful for the assistance of Fuyang Teachers College.

Notes and references

- (a) L. Bourget-Merle, M. F. Lappert and J. R. Severn, Chem. Rev., 2002, 102, 3031; (b) V. C. Gibson and K. Spitzmesser, Chem. Rev., 2003, 103, 283; (c) P. M. Zeimentz, S. Arndt, B. R. Elvidge and J. Okuda, Chem. Rev., 2006, 106, 2404; (d) M. R. Kember, A. Buchard and C. K. Williams, Chem. Commun., 2011, 47, 141; (e) M. Zimmermann and R. Anwander, Chem. Rev., 2010, 110, 6194; (f) M. Nishiura and Z. Hou, Nat. Chem., 2010, 2, 257; (g) E. Y.-X. Chen, Chem. Rev., 2009, 109, 5157; (h) F. T. Edelmann, Coord. Chem. Rev., 2017, 338, 27; (i) F. T. Edelmann, Coord. Chem. Rev., 2016, 318, 29.
- 2 (a) L. R. Rieth, D. R. Moore, E. B. Lobkovsky and G. W. Coates, J. Am. Chem. Soc., 2002, 124, 15239; (b) F. Basuli, J. C. Huffman and D. J. Mindiola, Inorg. Chem., 2003, 42, 8003; (c) X. Dai, P. Kapoor and T. H. Warren, J. Am. Chem. Soc., 2004, 126, 4798; (d) E. Kogut, A. Zeller, T. H. Warren and T. Strassner, J. Am. Chem. Soc., 2004, 126, 11984; (e) H. Y. Gao, W. J. Guo, F. Bao, G. Q. Gui, J. K. Zhang, F. M. Zhu and Q. Wu, Organometallics, 2004, 23, 6273; (f) C. M. Byrne, S. D. Allen, E. B. Lobkovsky and G. W. Coates, J. Am. Chem. Soc., 2004, 126, 11404; (g) E. A. Gregory, R. J. Lachicotte and P. L. Holland, Organometallics, 2005, 24, 1803; (h) A. M. Reynolds, E. A. Lewis, N. W. Aboelella and W. B. Tolman, Chem. Commun., 2005, 2014; (i) C. Shimokawa and S. Itoh, Inorg. Chem., 2005, 44, 3010; (j) G. C. Bai, P. R. Wei, A. K. Das and D. W. Stephan, Dalton Trans., 2006, 1141; (k) Y. Yu, J. M. Smith, C. J. Flaschenriem and P. L. Holland, Inorg. Chem., 2006, 45, 5742; (l) Y. M. Yao, Z. Q. Zhang, H. M. Peng, Y. Zhang, Q. Shen and J. Lin, Inorg. Chem., 2006, 45, 2175; (m) E. C. Brown, B. N. Itsik, J. T. York, N. W. Aboelella and W. B. Tolman, Inorg. Chem., 2007, 46, 486; (n) Y. C. Tsai, P. Y. Wang, K. M. Lin, S. A. Chen and J. M. Chen, Chem. Commun., 2008, 205; (o) Y. Yu, A. R. Sadique, J. M. Smith, T. R. Dugan, R. E. Cowley, W. W. Brennessel, C. J. Flaschenriem, E. Bill, T. R. Cundari and P. L. Holland, J. Am. Chem. Soc., 2008, 130, 6624; (p) S. Pfirrmann, C. Limberg and B. Ziemer, Dalton Trans., 6689; (q) M. S. Hill, P. B. Hitchcock and 2008. Pongtavornpinyo, Dalton Trans., 2008, 2854; (r) R. K. C. MacLeod, J. L. Conway, L. Tang, J. J. Smith, L. D. Corcoran, K. H. D. Ballem, B. O. Patrick and K. M. Smith, Organometallics, 2009, 28, 6798; (s) K. Ding,

T. R. Dugan, W. W. Brennessel, E. Bill and P. L. Holland, Organometallics, 2009, 28, 6650; (t) R. E. Cowley, N. J. DeYonker, N. A. Eckert, T. R. Cundari, S. DeBeer, E. Bill, X. Ottenwaelder, C. Flaschenriem and P. L. Holland, Inorg. Chem., 2010, 49, 6172; (u) K. M. Lin, P. Y. Wang, Y. J. Shieh, H. Z. Chen, T. S. Kuo and Y. C. Tsai, New J. Chem., 2010, 34, 1737; (v) Z. J. Tonzetich, F. Heroguel, L. H. Do and S. J. Lippard, Inorg. Chem., 2011, 50, 1570; (w) S. Schulz, J. Spielmann, D. Bläser and Wölper, Chem. Commun., 2011, 47, 2676; (x) С. R. E. Cowley, N. A. Eckert, S. Vaddadi, T. M. Figg, T. R. Cundari and P. L. Holland, J. Am. Chem. Soc., 2011, 133, 9796; (y) N. C. Tomson, J. Arnold and R. G. Bergman, Dalton Trans., 2011, 40, 7718; (z) K. C. Chang, C. F. Lu, P. Y. Wang, D. Y. Lu, H. Z. Chen, T. S. Kuo and Y. C. Tsai, Dalton Trans., 2011, 40, 2324.

- 3 (a) M. H. Chisholm, J. Gallucci and K. Phomphrai, Chem. Commun., 2003, 48; (b) H. M. El-Kaderi, M. J. Heeg and C. H. Winter, Organometallics, 2004, 23, 4995; (c) M. R. Crimmin, I. J. Casely and M. S. Hill, J. Am. Chem. Soc., 2005, 127, 2042; (d) G. W. Coates and D. R. Moore, Angew. Chem., Int. Ed., 2004, 43, 6618; (e) Y. Peng, H. Fan, H. Zhu, H. W. Roesky, J. Magull and C. E. Hughes, Angew. Chem., Int. Ed., 2004, 43, 3443; (f) J. Chai, V. Jancik, S. Singh, H. Zhu, C. He, H. W. Roesky, H. G. Schmidt, M. Noltemeyer and N. S. Hosmane, J. Am. Chem. Soc., 2005, 127, 7521; (g) Y. X. Cheng, P. B. Hitchcock, M. F. Lappert and M. Zhou, Chem. Commun., 2005, 752; (h) M. S. Hill, R. Pongtavornpinyo and P. B. Hitchcock, Chem. Commun., 2006, 3720; (i) A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock and P. A. Procopiou, Organometallics, 2007, 26, 4076; (j) A. Jana, H. W. Roesky and C. Schulzke, Inorg. Chem., 2009, 48, 9543; (k) S. P. Sarish, H. W. Roesky, M. John, A. Ringe and J. Magull, Chem. Commun., 2009, 2390; (1) M. R. Crimmin, A. G. M. Barrett, M. S. Hill, D. J. MacDougall, M. F. Mahon and P. A. Procopiou, Dalton Trans., 2009, 9715; (m) W. Y. Wang, S. Inoue, S. L. Yao and M. Driess, Chem. Commun., 2009, 2661; (n) M. R. Crimmin, M. Arrowsmith, A. G. M. Barrett, I. J. Casely, M. S. Hill and P. A. Procopiou, J. Am. Chem. Soc., 2009, 131, 9670; (o) M. R. Crimmin, M. S. Hill, P. B. Hitchcock and M. F. Mahon, New J. Chem., 2010, 34, 1572; (p) G. G. Sandra, J. Vojtech, A. D. R. Alma and M. C. Monica, Chem., 2011, 50, 4226; (q) S. I. Diego, Inorg. J. V. H. Miriam, H. L. Raul and J. Vojtech, Inorg. Chem., 2011, 50, 8907; (r) M. Arrowsmith, M. R. Crimmin, A. G. M. Barrett, M. S. Hill, K. K. Gabriele and P. A. Procopiou, Organometallics, 2011, 30, 1493; (s) F. Drouin, T. J. J. Whitehorne and F. Schaper, Dalton Trans., 2011, 40, 1396; (t) A. Stasch and C. Jones, Dalton Trans., 2011, 40, 5659.
- 4 (a) P. G. Hayes, W. E. Piers and R. McDonald, J. Am. Chem. Soc., 2002, 124, 2132; (b) P. G. Hayes, W. E. Piers and M. Parvez, J. Am. Chem. Soc., 2003, 125, 5622; (c)
 O. Eisenstein, P. B. Hitchcock, A. V. Khvostov, M. F. Lappert, L. Maron, L. Perrin and A. V. Protchenko, J. Am. Chem. Soc., 2003, 125, 10790; (d) A. G. Avent,

C. F. Caro, P. B. Hitchcock, M. F. Lappert, Z. Li and X. H. Wei, Dalton Trans., 2004, 1567; (e) L. K. Knight, W. E. Piers, P. Fleurat-Lessard, M. Parvez and R. McDonald, Organometallics, 2004, 23, 2087; (f) P. B. Hitchcock, M. F. Lappert and A. V. Protchenko, Chem. Commun., 2005, 951; (g) P. G. Hayes, W. E. Piers and M. Parvez, Organometallics, 2005, 24, 1173; (h) S. Bambirra, H. Tsurugi, D. Leusen and B. Hessen, Dalton Trans., 2006, 1157; (i) S. K. Ibrahim, A. V. Khvostov, M. F. Lappert, L. Maron, L. Perrin, C. J. Pickett and A. V. Protchenko, Dalton Trans., 2006, 2591; (j) R. Jiao, X. D. Shen, M. Q. Xue, Y. Zhang, Y. M. Yao and Q. Shen, Chem. Commun., 2010, 46, 4118; (k) M. P. Coles, P. B. Hitchcock, A. V. Khvostov, M. F. Lappert and A. V. Protchenko, Dalton Trans., 2010, 39, 6426; (1) E. L. Lu, J. X. Chu, Y. F. Chen, M. V. Borzov and G. Y. Li, Chem. Commun., 2011, 47, 743; (m) W. Q. Mao, L. Xiang, C. A. Lamsfus, L. Maron, X. B. Leng and Y. F. Chen, J. Am. Chem. Soc., 2017, 139, 1081; (n) M. Q. Xue, Y. Zheng, Y. B. Hong, Y. M. Yao, F. Xu, Y. Zhang and Q. Shen, Dalton Trans., 2015, 44, 20075.

- 5 (a) Y. M. Yao, Y. Zhang, Q. Shen and K. B. Yu, Organometallics, 2002, 21, 819; (b) Y. M. Yao, Y. Zhang, Z. Q. Zhang, Q. Shen and K. B. Yu, Organometallics, 2003, 22, 2876; (c) F. Basuli, J. Tomaszewski, J. C. Huffman and D. J. Mindiola, Organometallics, 2003, 22, 4705; (d) D. V. Vitanova, F. Hampel and K. C. Hultzsch, J. Organomet. Chem., 2005, 690, 5182; (e) D. V. Vitanova, F. Hampel and K. C. Hultzsch, Dalton Trans., 2005, 1565; (f) M. Q. Xue, Y. M. Yao, Q. Shen and Y. Zhang, J. Organomet. Chem., 2005, 690, 4685; (g) Y. L. Duan, J. X. He, W. Wang, J. J. Zhou, Y. Huang and Y. Yang, Dalton Trans., 2016, 26, 10807; (h) Y. M. Yao, Z. Q. Zhang, H. M. Peng, Y. Zhang, Q. Shen and J. Lin, Inorg. Chem., 2006, 45, 2175; (i) X. Xu, X. Y. Xu, Y. F. Chen and J. Sun, Organometallics, 2008, 27, 758; (j) M. Schmid, S. M. Guillaume and P. W. Roesky, Organometallics, 2014, 33, 5392; (k) P. B. Hitchcock, A. V. Khvostov, M. F. Lappert and A. V. Protchenko, Dalton Trans., 2009, 2383; (l) E. L. Lu, Y. X. Li and Y. F. Chen, Chem. Commun., 2010, 46, 4469; (m) E. L. Lu, W. Gan and Y. F. Chen, Dalton Trans., 2011, 40, 2366; (n) C. Wang, J. L. Zhou, X. F. Zhao, L. Maron, X. B. Leng and Y. F. Chen, Chem.-Eur. J., 2016, 22, 1258; (o) S. V. Klementyeva, M. Y. Afonin, A. S. Bogomyakov, P. W. Roesky and S. N. Konchenko, Eur. J. Inorg. Chem., 2016, 3666.
- 6 H. Miao, S. L. Zhou, S. W. Wang, L. J. Zhang, Y. Wei, S. Yang,
 F. H. Wang, Z. Chen, Y. Chen and Q. B. Yuan, *Sci. China: Chem.*, 2013, 56, 329.
- 7 (a) D. Enders, A. Saint-Dizier, M. I. Lannou and A. Lenzen, *Eur. J. Org. Chem.*, 2006, 29; (b) A. D. Sadow and A. Togni, *J. Am. Chem. Soc.*, 2005, 127, 17012; (c) Y. Zhu, J. P. Malerich and V. H. Rawal, *Angew. Chem., Int. Ed.*, 2010, 49, 153; (d) D. Zhao, Y. Yuan, A. S. C. Chan and R. Wang, *Chem.-Eur. J.*, 2009, 15, 2738.

- 8 (a) X. Fu, Z. Jiang and C.-H. Tan, *Chem. Commun.*, 2007, 47, 5058; (b) S. G. Wen, P. F. Li, H. B. Wu, F. Yu, X. M. Liang and J. X. Ye, *Chem. Commun.*, 2010, 46, 4806; (c) Q. B. Yuan, S. L. Zhou, X. C. Zhu, Y. Wei, S. W. Wang, X. L. Mu, F. S. Yao, G. C. Zhang and Z. Chen, *New J. Chem.*, 2015, 39, 7626; (d) K. Yamakoshi, S. J. Harwood, M. Kanai and M. Shibasaki, *Tetrahedron Lett.*, 1999, 40, 2565.
- 9 (a) S. Yang, X. C. Zhu, S. L. Zhou, S. W. Wang, Z. J. Feng, Y. Wei, H. Miao, L. P. Guo, F. H. Wang, G. C. Zhang, X. X. Gu and X. L. Mu, Dalton Trans., 2014, 43, 2521; (b) Q. B. Yuan, S. L. Zhou, X. C. Zhu, Y. Wei, S. W. Wang, X. L. Mu, F. S. Yao, G. C. Zhang and Z. Chen, New J. Chem., 2015, 39, 7626; (c) X. X. Gu, L. J. Zhang, X. C. Zhu, S. W. Wang, S. L. Zhou, Y. Wei, G. C. Zhang, X. L. Mu, Z. M. Huang, D. J. Hong and F. Zhang, Organometallics, 2015, 34, 4553; (d) X. X. Gu, X. C. Zhu, Y. Wei, S. W. Wang, S. L. Zhou, G. C. Zhang and X. L. Mu, Organometallics, 2014, 33, 2372; (e) F. H. Wang, S. W. Wang, X. C. Zhu, S. L. Zhou, H. Miao, X. X. Gu, Y. Wei and Q. B. Yuan, Organometallics, 2013, 32, 3920; (f) S. L. Zhou, Z. S. Wu, J. W. Rong, S. W. Wang, G. S. Yang, X. C. Zhu and L. J. Zhang, Chem.-Eur. J., 2012, 18, 2653; (g) Y. J. Wu, S. W. Wang, L. J. Zhang, G. S. Yang, X. C. Zhu, Z. H. Zhou, H. Zhu and S. H. Wu, Eur. J. Org. Chem., 2010, 326; (h) X. C. Zhu, J. X. Fan, Y. J. Wu, S. W. Wang, L. J. Zhang, G. S. Yang, Y. Wei, C. W. Yin, H. Zhu, S. H. Wu and H. T. Zhang, Organometallics, 2009, 28, 3882; (i) L. J. Zhang, H. P. Wu, S. P. Su and S. W. Wang, Chin. J. Chem., 2009, 27, 2061; (j) Y. J. Wu, S. W. Wang, L. J. Zhang, G. S. Yang, X. C. Zhu, C. Liu, C. W. Yin and J. W. Rong, Inorg. Chim. Acta, 2009, 362, 2814; (k) Y. J. Wu, S. W. Wang, X. C. Zhu, G. S. Yang, Y. Wei, L. J. Zhang and H. B. Song, Inorg. Chem., 2008, 47, 5503; (1) Q. H. Li, S. W. Wang, S. L. Zhou, G. S. Yang, X. C. Zhu and Y. Y. Liu, J. Org. Chem., 2007, 72, 6763; (m) S. L. Zhou, S. W. Wang, G. S. Yang, Q. H. Li, L. J. Zhang, Z. J. Yao, Z. K. Zhou and H. B. Song, Organometallics, 2007, 26, 3755; (n) L. J. Zhang, S. W. Wang, S. L. Zhou, G. S. Yang and E. H. Sheng, J. Org. Chem., 2006, 71, 3149; (o) L. J. Zhang, S. W. Wang, E. H. Sheng and S. L. Zhou, Green Chem., 2005, 7, 683; (p) S. L. Zhou, S. W. Wang, G. S. Yang, X. Y. Liu, E. H. Sheng, K. H. Zhang, L. Cheng and Z. X. Huang, Polyhedron, 2003, 22, 1019; (q) M. Nishiura, F. Guo and Z. M. Hou, Acc. Chem. Res., 2015, 48, 2209; (r) Y. D. Lv, J. L. Zhou, X. B. Leng and Y. F. Chen, New J. Chem., 2015, 39, 7582.
- 10 X. H. He, Y. Z. Yao, X. Luo, J. Zhang, Y. Liu, L. Zhang and Q. Wu, *Organometallics*, 2003, **22**, 4952.
- 11 G. M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1996.
- 12 G. M. Sheldrick, *SHELXTL 5.10 for Windows NT: Structure Determination Software Programs*, Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.