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

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A series of organo rare-earth metal amides incorporating chiral cyclohexyl bridged bis(β-diketiminato) ligands with general formula LREN(SiMe$_3$)$_2$ (L^1 = (1*S*,2*S*)-1,2-Cy[NC(Me)CHC(Me)NAr]$_2$, Ar = 2, 6-Et$_2$C$_6$H$_3$, RE = Nd (**1a**), Dy (**1b**), Yb (**1c**), Y (**1d**); L^2 = (1*R*,2*R*)-1,2-Cy[NC(Me)CHC(Me)NAr]$_2$, Ar = 2, 6-*i*-Pr$_2$C$_6$H$_3$, RE = Nd (**2a**), Gd (**2b**), Dy (**2c**), Er (**2d**), Y (**2e**)) were synthesized in good yields *via* reactions of [(Me$_3$Si)$_2$N]$_3$RE^{III}(μ-Cl)Li(THF)$_3$ with H$_2$L^1 and H$_2$L^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 ^{13}C NMR spectral analyses. The structures of complexes **1a–d** were determined by single-crystal 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.

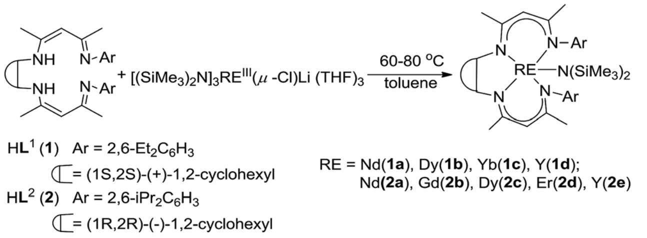
Introduction

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,[1f,4a] methyl methacrylate polymerization,[1g,5b] copolymerization of epoxide and CO$_2$,[1d,5d] and ring-opening 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, 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$_2$**L**^{1} or H$_2$**L**^{2} with 1 equiv. of the rare-earth metal amides [(Me$_3$Si)$_2$N]$_3$RE^{III}(μ-Cl)Li(THF)$_3$ in toluene at 60–80 °C afforded the rare-earth metal complexes with general formula **L**REN(SiMe$_3$)$_2$ (**L**^{1} = (1*S*,2*S*)-1,2-Cy[NC(Me)CHC(Me)NAr]$_2$, Ar = 2, 6-Et$_2$C$_6$H$_3$, RE = Nd (**1a**), Dy (**1b**), Yb (**1c**), Y (**1d**); **L**^{2} = (1*R*,2*R*)-1,2-Cy[NC(Me)CHC(Me)NAr]$_2$, Ar = 2, 6-*i*-Pr$_2$C$_6$H$_3$, 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.

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† Electronic supplementary information (ESI) available: Characterization spectra (^{1}H NMR and ^{13}C 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

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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 ^{1}H NMR and ^{13}C 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 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 $N(SiMe_3)_2$ 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.

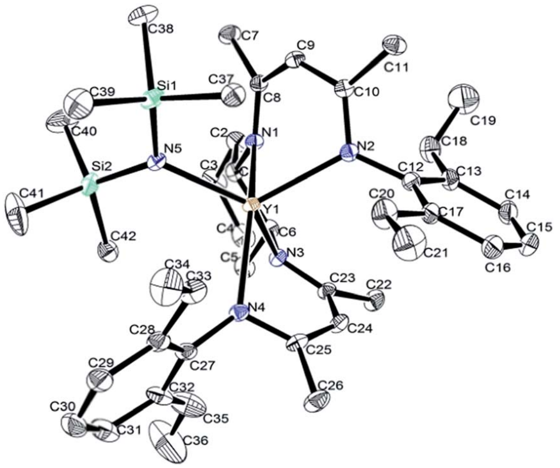

Fig. 1 Representative structure of rare-earth metal amides incorporating chiral bridged bis(β-diketiminato) ligand. Hydrogen atoms were omitted for clarity.

From Table 1, we can see that the usual consequence of the ionic radius of the RE^{3+} ion when moving from Nd^{3+} to Yb^{3+} 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) $Cy[NC(Me)CHC(Me)NAr]_2REN(SiMe_3)_2$ (Ar = 2, 6-$^i Pr_2C_6H_3$, RE = Nd [2.433(2) Å], Dy [2.350(2) Å], Y [2.340(2) 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 cyclohexyl-linked bis(β-diketiminato) $Cy[NC(Me)CHC(Me)NAr]_2REN(SiMe_3)_2$ (Ar = 2, 6-$^i Pr_2C_6H_3$), 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 (°) for complexes **1a–d**

	1a (RE = Nd)	**1b** (RE = Dy)	**1c** (RE = Yb)	**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)-$N_{av.}$	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)-$C_{av.}$	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)

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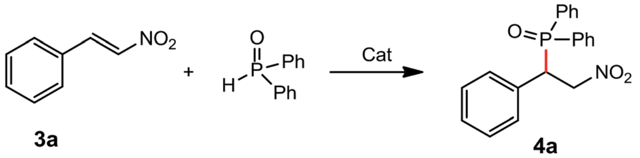
through the additions of dialkyl phosphites, secondary phosphines and diarylphosphine oxides to the unsaturated substrates.[7] In the addition of diarylphosphine oxide to the α,β-unsaturated derivatives, rare-earth metal complexes have advantages of lower catalysts loadings (3–5 mol%), available materials, solvents compatibility and easy preparation, compared with the reported chiral bicyclic guanidinate catalyst (10 mol% loading, Et_2O as solvent) and chiral multifunctional amine-thiourea catalyst (10 mol% loading, CH_2Cl_2 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 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.

Table 2 Influence of the conditions on the reaction of β-nitrostyrene with diphenyphosphine 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.

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. $[(Me_3Si)_2N]_3RE^{III}(\mu\text{-Cl})Li(THF)_3$ (RE = Nd, Gd, Dy, Er, Yb and Y) were prepared according to literature methods.[9p] (1*S*,2*S*)-(+)-1,2-diaminocyclohexane, 2,6-diethylaniline, (1*R*,2*R*)-(−)-1,2-

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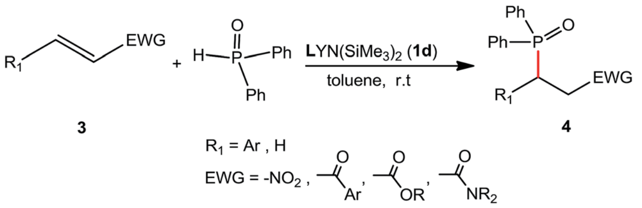
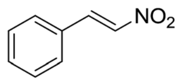
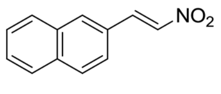
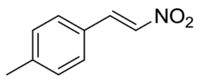
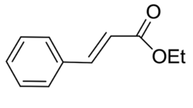
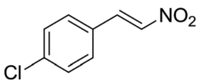
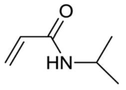
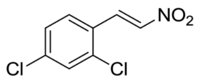
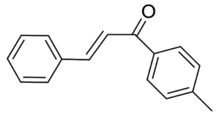
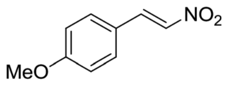
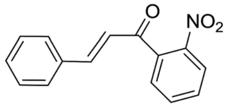
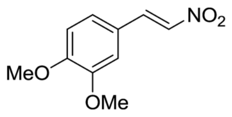
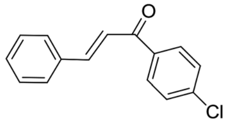
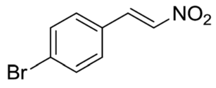
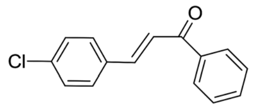
Table 3 Addition of diphenyphosphine oxide to β-nitroalkene and α,β-unsaturated carbonyl derivatives catalyzed by **1d**



Entry	Substrate	Product	Yield[a] (%)	Entry	Substrate	Product	Yield[a] (%)
1	 **3a**	**4a**	95	8	 **3h**	**4h**	89
2	 **3b**	**4b**	92	9	 **3i**	**4i**	95[b]
3	 **3c**	**4c**	90	10	 **3j**	**4j**	99[b]
4	 **3d**	**4d**	93	11	 **3k**	**4k**	94[b]
5	 **3e**	**4e**	96	12	 **3l**	**4l**	88[b]
6	 **3f**	**4f**	98	13	 **3m**	**4m**	93[b]
7	 **3g**	**4g**	90	14	 **3n**	**4n**	91[b]

[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. ^{1}H NMR and ^{13}C NMR spectra for analyses of compounds were recorded on a Bruker AV-300 NMR spectrometer (300 MHz for ^{1}H; 75.0 MHz for ^{13}C) in C_6D_6 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-4-one (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

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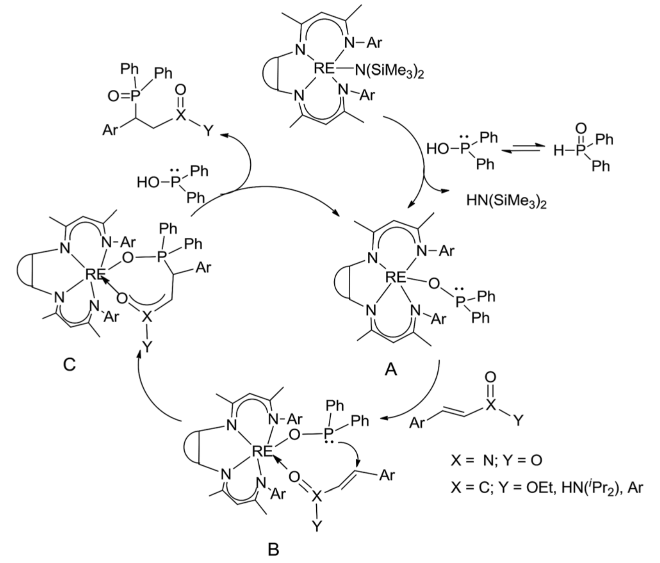

Scheme 2 The proposed mechanism of the catalytic reaction.

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 H_2L^1 (2.590 g, 48% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): $\delta = 10.94$ (br s, 2H, NH), 7.09 (m, 4H, C_6H_3), 6.96 (m, 2H, C_6H_3), 4.58 (s, 2H, β–CH), 3.15 (br s, 2H, ring-CH), 2.43 (m, 8H, CH_2CH_3), 1.95 (s, 6H, CH_3), 1.70 (m, 2H, ring-CH_2), 1.66 (m, 2H, ring-CH_2), 1.60 (s, 6H, CH_3), 1.24–1.10 (m, 4H, ring-CH_2), 1.15 (m, 6H, CH_3CH_2), 1.12 (d, 6H, CH_3CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 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. (1*R*,2*R*)-(−)-1,2-Diaminocyclohexane (1.142 g, 10.0 mmol), 2-((2,6-diisopropylphenyl)imido)-2-penten-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 H_2L^2 (3.040 g, 51% yield). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm): $\delta = 11.02$ (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, $CHCH_3$), 1.97 (s, 6H, CH_3), 1.92 (m, 2H, ring-CH_2), 1.61 (m, 2H, ring-CH_2), 1.54 (s, 6H, CH_3), 1.26–1.09 (m, 4H, ring-CH_2), 1.15 (d, 12H, $J = 6.5$ Hz, CH_3CH), 1.11 (d, 12H, $J = 4.7$ Hz, CH_3CH). ^{13}C NMR (75 MHz, $CDCl_3$, 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 $L^1NdN(SiMe_3)_2$ (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 $[(Me_3Si)_2N]_3Nd^{III}(\mu\text{-Cl})Li(THF)_3$ (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 $C_{42}H_{68}N_5NdSi_2$ (843.4358): C, 59.81; H, 8.13; N, 8.30. Found: C, 59.62; H, 8.08; N, 8.34%.

Preparation of $L^1DyN(SiMe_3)_2$ (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 H_2L^1 (0.670 g, 1.24 mmol) with $[(Me_3Si)_2N]_3Dy^{III}(\mu\text{-Cl})Li(THF)_3$ (1.178 g, 1.30 mmol). IR (KBr pellet, cm^{-1}): $\nu = 3061$ (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 $C_{42}H_{68}DyN_5Si_2$ (861.6938): C, 58.54; H, 7.95; N, 8.13. Found: C, 58.39; H, 8.01; N, 8.10%.

Preparation of $L^1YbN(SiMe_3)_2$ (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 H_2L^1 (0.913 g, 1.69 mmol) with $[(Me_3Si)_2N]_3Yb^{III}(\mu\text{-Cl})Li(THF)_3$ (1.623 g, 1.78 mmol). IR (KBr pellet, cm^{-1}): $\nu = 3062$ (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 $C_{42}H_{68}N_5Si_2Yb$ (872.2478): C, 57.83; H, 7.86; N, 8.03. Found: C, 57.97; H, 7.87; N, 7.98%.

Preparation of $L^1YN(SiMe_3)_2$ (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 $[(Me_3Si)_2N]_3Y^{III}(\mu\text{-Cl})Li(THF)_3$ (0.868 g, 1.05 mmol). ^{1}H NMR (300 MHz, C_6D_6, 25 °C, ppm): $\delta = 7.22$–6.98 (m, 6H, C_6H_3), 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, CH_2CH_3), 2.59 (m, 2H, ring-CH_2), 2.07 (s, 3H, CH_3CN), 1.65 (s, 3H, CH_3CN), 1.50 (s, 3H, CH_3CN), 1.89–1.07 (m, 6H, ring-CH_2), 1.42 (s, 3H, CH_3CN), 1.46 (m, 3H, CH_3CH_2), 1.31 (m, 3H, CH_3CH_2), 1.23 (m, 3H, CH_3CH_2), 1.10 (m, 3H, CH_3CH_2), 0.24 (s, 18H, $SiCH_3$); ^{13}C NMR (75 MHz, C_6D_6, 25 °C, ppm): $\delta = 162.5$, 162.4, 161.7, 161.0 ($CNCH_3$), 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-CH_2), 24.4, 24.1, 23.8, 23.3 (CH_2CH_3), 22.6, 21.9, 24.0, 21.5, 19.4, 13.8, 13.7, 12.0 (CH_3), 4.5 ($SiCH_3$, 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

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(s), 933 (m), 886 (w), 761 (m), 732 (m), 609 (w); Anal. calc. for $C_{42}H_{68}N_5Si_2Y$ (788.0997): C, 64.01; H, 8.70; N, 8.89. Found: C, 64.25; H, 8.89; N, 8.53%.

Preparation of $L^2NdN(SiMe_3)_2$ (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 $[(Me_3Si)_2N]_3Nd^{III}(\mu\text{-Cl})Li(THF)_3$ (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 *n*-hexane (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}): ν = 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 C_{46} H_{76} N_5Nd Si_2 (899.5421): C, 61.42; H, 8.52; N, 7.79. Found: C, 61.50; H, 8.57; N, 7.60%.

Preparation of $L^2GdN(SiMe_3)_2$ (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 $[(Me_3Si)_2N]_3Gd^{III}(\mu\text{-Cl})Li(THF)_3$ (1.001 g, 1.12 mmol) using the procedures similar to those described above for the preparation of **2a**. IR (KBr pellet, cm^{-1}): ν = 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 $C_{46}H_{76}GdN_5Si_2$ (912.5501): C, 60.54; H, 8.39; N, 7.67. Found: C, 60.26; H, 8.65; N, 7.60%.

Preparation of $L^2DyN(SiMe_3)_2$ (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 $[(Me_3Si)_2N]_3$-$Dy^{III}(\mu\text{-Cl})Li(THF)_3$ (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 $C_{46}H_{76}DyN_5Si_2$ (917.8001): C, 60.20; H, 8.35; N, 7.63. Found: C, 60.66; H, 8.54; N, 7.57%.

Preparation of $L^2ErN(SiMe_3)_2$ (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 $[(Me_3Si)_2N]_3$-$Er^{III}(\mu\text{-Cl})Li(THF)_3$ (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 C_{46} H_{76} ErN_5Si_2 (922.5591): C, 59.89; H, 8.30; N, 7.59. Found: C, 59.57; H, 8.66; N, 7.56%.

Preparation of $L^2YN(SiMe_3)_2$ (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 $[(Me_3Si)_2N]_3Y^{III}(\mu\text{-Cl})Li(THF)_3$ (1.010 g, 1.22 mmol). ^1H NMR (300 MHz, C_6D_6, 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, $CHCH_3$), 3.27–3.14 (m, 2H, $CHCH_3$), 3.07 (m, 1H, $CHCH_3$), 2.40 (m, 2H, ring-CH_2), 2.00 (s, 3H, CH_3CN), 1.77 (s, 3H, CH_3CN), 1.65 (s, 3H, CH_3CN), 1.68–1.09 (m, 6H, ring-CH_2), 1.44 (s, 3H, CH_3CN), 1.68–1.09 (m, 15H, CH_3CH), 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); ^{13}C NMR (75 MHz, C_6D_6, 25 °C, ppm): δ = 165.1, 161.8, 161.5, 161.4 ($CNCH_3$), 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-CH_2), 26.8, 25.8, 25.7, 24.8 ($CHCH_3$), 24.6, 24.4, 24.2, 24.0, 23.3, 23.1, 23.0, 22.1, 21.8, 20.6, 20.0, 18.2 (CH_3), 5.6 ($SiCH_3$, 3C), 4.9 ($SiCH_3$, 3C); IR (KBr pellet, cm^{-1}): ν = 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 C_{46} $H_{76}N_5Si_2Y$ (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-Kα radiation (λ = 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 least-square calculations based on F^2 (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 $[(Me_3Si)_2N]_3RE^{III}(\mu\text{-Cl})Li(THF)_3$ 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.

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Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 (*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.*, 2008, 6689; (*q*) M. S. Hill, P. B. Hitchcock and R. Pongtavornpinyo, *Dalton Trans.*, 2008, 2854; (*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 C. Wölper, *Chem. Commun.*, 2011, **47**, 2676; (*x*) 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; (*l*) 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, *Inorg. Chem.*, 2011, **50**, 4226; (*q*) S. I. Diego, 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,

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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; (*l*) 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; (*l*) 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.