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ARTICLE TYPE

Heterometallic rare-earth metal complexes with imino-functionalized 8-hydroxyquinolyl ligand: Synthesis, characterization and catalytic activity towards hydrophosphinylation of trans-*β*-nitroalkene

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Reactions of rare-earth metal amides $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ with different equiv. of 2-(2,6-diisopropylphenylimino)-8-hydroxyquinoline (**1**) afforded the different heterometallic rare-earth metal complexes, and catalytic activity of the resulting complexes was investigated. Reactions of rare-earth metal amides $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Y, Er, Dy) with 1 equiv. of compound **1** afforded the heterobimetallic rare-earth metal and lithium complexes **2-4** bridged by the oxygen atom of 2-(2,6-diisopropylphenylimino)-8-hydroxyquinoline and the nitrogen atom of $N(SiMe_3)_2$. However, treatment of rare-earth metal amides $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Sm, Er, Yb) with 2 equiv. of compound **1** gave the different heterobimetallic rare-earth metal and lithium complexes **5-7** bridged by the oxygen atoms of 2-(2,6-diisopropylphenylimino)-8-hydroxyquinoline. Complex **6** can also be prepared by treatment of **3** with 1 equiv. of **1**. Complexes **2**-7 were fully characterized by spectroscopic methods, elemental analyses and single crystal X-ray diffraction. Investigation of the catalytic properties of the complexes indicated that all complexes exhibited a high catalytic activity towards the addition of diphenylphosphine oxide to the trans-*β*-nitroalkenes to afford *β*-nitrophosphonates under mild conditions.

Introduction

Non-Cp ligands based on N and O atoms have been extensively applied to stabilize rare-earth metal complexes, due to their strong coordinative abilities and finely tuning the sizes and electronic properties of the substituents.[1] Rare-earth metal complexes stabilized by β-diketiminates,[2] amidinates,[3] guanidinates,[4] bridged bisphenolate,[5] diamido ligands,[6] and modified pyrrolyl or indolyl ligands[7] have been synthesized and applied in various organic transformations. Recently, 8-hydroxy or 8-aminoquinoline derivates have been used as ligands for rare-earth metal[8] and group 4 metal complexes[9] because of its excellent coordination properties and near infrared luminescence.

The Michael addition of phosphorus compounds to nitroalkenes provides a practical route to the β-nitrophosphonates, which can be transformed to the corresponding 1,4-addition products, β-amino phosphonates, through simple reduction of the nitro group.[10] Previous studies mainly focus on catalytic addition of nucleophiles such as dialkyl phosphites $[(RO)_2P(O)H]$[11] and secondary phosphines (R_2PH)[12] to β-nitroalkenes. However, the diarylphosphine oxides $[Ar_2P(O)H]$[13] have been much neglected even though the adducts possess synthetic potential and may be used as useful analogues of phosphonates. In our previous study, we have reported that the lanthanide amides displayed high catalytic activities towards hydrophosphonylation of aldehydes, unactivated ketones and imines.[14] Recently, we have also developed a series of rare-earth metal amides as catalysts for high regioselective addition of phosphites to α,β-unsaturated carbonyl compounds.[15] As our continuous interests in development of organo rare-earth metal amido complexes as catalysts for the C-P formation reaction, we herein report the synthesis, characterization and catalytic activity of rare-earth metal complexes with tridentate imino-functionalized 8-hydroxyquinolyl ligand towards the addition of diphenylphosphine oxide to the trans-*β*-nitroalkenes.

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 glovebox. All solvents were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. $[(Me_3Si)_2N]_3RE(\mu\text{-}Cl)Li(THF)_3$ (RE = Y, Sm, Dy, Er, Yb)[16] and 2-(2,6-diisopropylphenylimino)-8-hydroxyquinoline (**1**)[9] were prepared according to literature methods. Elemental analyses data were obtained on a Perkin-Elmer 2400 Series II elemental analyzer. ^1H NMR and ^{13}C NMR spectra for analyses of compounds were recorded on a Bruker AV-300 NMR spectrometer (300 MHz for ^1H; 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. IR spectra were

recorded on a Shimadzu FTIR-8400S spectrometer (KBr pellet).

Synthesis of {η^I:η^I-[2-(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH]-8-OC$_9$H$_6$N]Li[μ-N(SiMe$_3$)$_2$]}RE[N(SiMe$_3$)$_2$]$_2$ (RE = Y(2), Er(3), Dy(4)).

To a toluene (10.0 mL) solution of compound **1** (0.300 g, 0.90 mmol) was added a toluene (20.0 mL) solution of [(Me$_3$Si)$_2$N]$_3$Y(μ-Cl)Li(THF)$_3$ (0.746 g, 0.90 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 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 colorless crystals **2** were obtained by cooling the concentrated solution at 0 °C for several days (0.345 g, 38% yield). IR (KBr pellet, cm^{-1}): ν = 2961, 2868, 2361, 2342, 2170, 1638, 1618, 1560, 1458, 1369, 1341, 1261, 1182, 1098, 932, 841, 745. ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 7.62 (s, 1H), 7.31-7.24 (m, 3H), 7.12-7.08 (m, 3H), 6.87-6.84 (m, 2H), 2.97 (s, 2H), 1.41 (s, 12H), 0.35 (s, 36H), 0.18 (s, 9H), 0.05 (s, 9H). ^{13}C NMR (125 MHz, C$_6$D$_6$): δ 162.3, 160.7, 148.1, 142.7, 138.9, 137.3, 131.9, 131.2, 125.5, 123.2, 120.1, 117.3, 115.4, 28.3, 23.5, 5.2, 4.5, 2.6. Anal. Calc. for C$_{40}$H$_{77}$LiN$_5$OSi$_6$Y: C, 52.89; H, 8.54; N, 7.71. found: C, 53.37; H,8.40; N, 7.16.

Complex **3** was prepared as pink crystals in 42 % (0.414 g) yield by treatment of compound **1** (0.300 g, 0.90 mmol) with [(Me$_3$Si)$_2$N]$_3$Er(μ-Cl)Li(THF)$_3$ (0.816 g, 0.90 mmol) using the procedures similar to those described above for preparation of **2**. IR (KBr pellet, cm^{-1}): ν = 3063, 2959, 2868, 2361, 2342, 2185, 1630, 1591, 1553, 1458, 1371, 1341, 1252, 1180, 1099, 1057, 841, 750. Anal. Calc. for C$_{40}$H$_{77}$LiN$_5$OSi$_6$Er·C$_4$H$_8$O: C, 49.91; H, 8.09; N, 6.61. found: C, 50.08; H, 7.92; N, 6.35.

Complex **4** was prepared as colorless crystals in 39 % (0.383 g) yield by treatment of compound **1** (0.300 g, 0.90 mmol) with [(Me$_3$Si)$_2$N]$_3$Dy(μ-Cl)Li(THF)$_3$ (0.812 g, 0.90 mmol) using the procedures similar to those described above for preparation of **2**. IR (KBr pellet, cm^{-1}): ν = 3061, 2959, 2868, 2361, 2342, 1630, 1589, 1553, 1460, 1553, 1460, 1369, 1341, 1182, 1099, 932, 839, 745. Anal. Calc. for C$_{40}$H$_{77}$LiN$_5$OSi$_6$Dy·C$_7$H$_8$: C, 52.55; H, 7.98; N, 6.52. found: C, 52.29; H, 7.87; N, 6.46.

Synthesis of {η^I:η^I-[η^I:η^I-2-(2,6-^{i}Pr$_2$C$_6$H$_3$)N=CH-8-OC$_9$H$_6$N]$_2$Li}RE[N(SiMe$_3$)$_2$]$_2$ (RE = Sm(5), Er(6), Yb(7)).

To a toluene (10.0 mL) solution of compound **1** (0.465 g, 1.40 mmol) was added a toluene (20.0 mL) solution of [(Me$_3$Si)$_2$N]$_3$Sm(μ-Cl)Li(THF)$_3$ (0.623 g, 0.70 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 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 crystals **5** were obtained by cooling the concentrated solution at 0 °C for several days (0.456 g, 40%). IR (KBr pellet, cm^{-1}): ν = 3059, 2961, 2868, 2361, 2342, 1630, 1589, 1551, 1458, 1369, 1341, 1252, 1098, 841, 748. Anal. Calc. for C$_{56}$H$_{81}$LiN$_6$O$_2$Si$_4$Sm: C, 59.00; H, 7.16; N, 7.37. found: C, 58.92; H, 7.20; N, 7.25

Complex **6** was prepared as pink crystals in 41 % (0.50 g) yield by treatment of compound **1** (0.465g, 1.40 mmol) with [(Me$_3$Si)$_2$N]$_3$Er(μ-Cl)Li(THF)$_3$ (0.635 g, 0.70 mmol) using the procedures similar to those described above for preparation of **5**. IR (KBr pellet, cm^{-1}): ν = 3059, 2959, 2868, 2361, 1630, 1589, 1553, 1458, 1369, 1341, 1182, 1099, 932, 840, 745. Anal. Calc. for C$_{56}$H$_{81}$LiN$_6$O$_2$Si$_4$Er: C, 58.14; H, 7.06; N, 7.26. found: C, 57.59; H, 7.09; N, 6.99.

Complex **6** can also be prepared by treatment of **3** with 1 equiv. of **1** by employed the procedures similar to those used for preparation of complex **5**.

Complex **7** was prepared as yellow crystals in 43 % yield by treatment of compound **1** (0.465 g, 1.40 mmol) with [(Me$_3$Si)$_2$N]$_3$Yb(μ-Cl)Li(THF)$_3$ (0.639 g, 0.70 mmol) using the procedures similar to those described above for preparation of **5**. IR (KBr pellet, cm^{-1}): ν = 3059, 2959, 2868, 1630, 1589, 1553, 1458, 1371, 1340, 1182, 1099, 932, 849, 745. Anal. Calc. for C$_{56}$H$_{81}$LiN$_6$O$_2$Si$_4$Yb: C, 57.85; H, 7.02; N, 7.23. found: C, 57.62; H, 7.09; N, 6.99.

Crystal Structure Determinations.

Suitable crystal of complexes **2-7** was each mounted in a sealed capillary. Diffraction was performed on a Bruker SMART CCD area detector diffractometer using graphite-monochromated *Mo-K$_\alpha$* radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the *SADABS* program. All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, refined anisotropically for all nonhydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package. All hydrogen atoms were refined using a riding model. See the table 4 for crystallographic data. *CCDC 1048534-1048539 for complexes 2-7 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.*

Table 4. Crystallographic data for of the complexes **2-7**.

	2	**3**	**4**	**5**	**6**	**7**
formula	$C_{40}H_{77}YLiN_5OSi_6$	$C_{40}H_{77}ErLiN_5OSi_6$	$C_{40}H_{77}DyLiN_5OSi_6$	$C_{56}H_{81}LiN_6O_2Si_4Sm$	$C_{56}H_{81}LiN_6O_2Si_4Er$	$C_{56}H_{81}LiN_6O_2Si_4Yb$
formula weight	908.46	986.81	982.05	1140.93	1156.83	1162.61
cryst system	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
space group	P-1	$Pbca$	$Pbca$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	15.529(1)	15.531(1)	15.561(1)	16.567(1)	16.457(2)	16.489(1)
b (Å)	23.551(1)	23.556(2)	23.561(2)	17.468(1)	17.610(2)	17.569(1)
c (Å)	33.002(2)	32.975(2)	33.081(3)	22.508(2)	22.508(2)	22.319(1)
β(deg)	90	90	90	104.071(1)	104.279(1)	104.437(1)
V (Å^3)	12069.7(11)	12063.7(13)	12128.4(19)	6318.1(8)	6265.4(10)	6261.4(6)
T (K)	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Z	8	8	8	4	8	4
D_{calcd} (g cm^{-3})	1.000	1.087	1.076	1.199	1.227	1.234
μ (mm^{-1})	1.114	1.539	1.379	1.046	1.457	1.611
F (000)	3888	4120	4104	2388	2412	2416
θ range (deg)	1.69 to 27.50	1.69 to 27.45	1.68 to 27.69	1.49 to 27.80	1.39 to 25.00	1.49 to 27.59
reflns collected	101453	99412	99998	54457	44071	53755
unique reflns	13849	13766	14131	14810	11042	14452
	(R_{int} = 0.1617)	(R_{int} = 0.0673)	(R_{int} = 0.1144)	(R_{int} = 0.0405)	(R_{int} = 0.0386)	(R_{int} = 0.0432)
parameters	509	509	509	651	651	651
R_1 (I > 2σ(I))	0.0564	0.0420	0.0689	0.0442	0.0363	0.0394
wR_2 (I > 2σ(I))	0.1075	0.1063	0.2024	0.0982	0.1034	0.0661
Goodness of fit	1.069	1.059	0.998	1.022	1.071	1.009
largest diff peak/hole (e Å^{-3})	0.335 and -0.409	1.033 and -0.616	1.601 and -1.061	1.523 and -0.714	1.337 and -0.988	1.187 and -1.124

General procedure for hydrophosphination of β-nitroalkene derivatives (8 as an example).

A 30.0 mL Schlenk tube under dried argon was charged with complex **7** (11.8 mg, 0.05 mmol), diphenylphosphine oxide (0.202 g, 1.0 mmol), and 5.0 mL of toluene, and then β-nitrostyrene (0.150 g, 1.0 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 **8** was isolated as a white solid (0.332 g, 95%). The full characterization data for the resulting products can be found in the Electronic Supplementary Information.

Results and discussion

Synthesis of rare-earth metal complexes with imino-functionalized 8-hydroxyquinolyl ligand.

Treatment of rare-earth metal amides [(Me$_3$Si)$_2$N]$_3$RE(μ-Cl)Li(THF)$_3$ (RE = Y, Er, Dy) with 1 equiv. of 2-(2,6-diisopropylphenylimino)-8-hydroxyquinoline (**1**) in toluene at 40 °C produced the heterometallic rare-earth metal complexes **2-4** (Scheme 1). While reactions of rare-earth metal amides [(Me$_3$Si)$_2$N]$_3$RE(μ-Cl)Li(THF)$_3$ (RE = Sm, Er, Yb) with 2 equiv. of compound **1** in toluene at 40 °C gave the heterometallic rare-earth metal complexes **5-7**. Complex **3** further reacted with 1 equiv. of compound **1** to also afford complex **6** (Scheme 1). Complexes **2-7** are sensitive to air and moisture, they have a good solubility in either polar solvents or nonpolar solvents. The complexes were fully characterized by spectroscopic methods, elemental analyses, and single crystal X-ray diffraction.
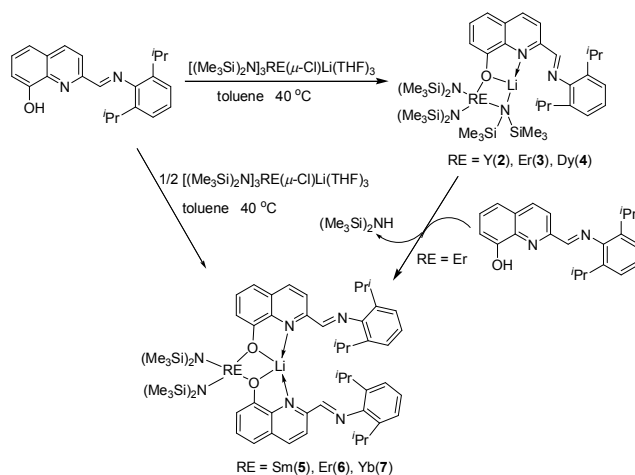
Scheme 1 Synthesis of heterometallic rare-earth metal complexes **2-7**.

X-ray diffraction analyses revealed that complexes **2-4** were isostructural heterometallic rare-earth metal and lithium complexes bridged by the oxygen atom of the 2-(2,6-diisopropylphenylimino)-8-hydroxyquinolyl and the nitrogen atom of the N(SiMe$_3$)$_2$. Rare-earth metal adopted a four-coordinated distorted tetrahedral configuration, and lithium adopted a three-coordinated distorted trigonal configuration. A representative structure diagram of complex **3** is shown in Figure 1. Complexes **5-7** were another type of heterometallic rare-earth metal and lithium bridged by the oxygen atoms of the 2-(2,6-diisopropylphenylimino)-8-hydroxyquinolyl ligand, and a representative structure diagram of complex **6** is shown in Figure 2. In complexes **5-7**, rare-earth metal and lithium all adopted a four-coordinated distorted tetrahedral configuration. The selected bond lengths and angles were listed in Table 1.
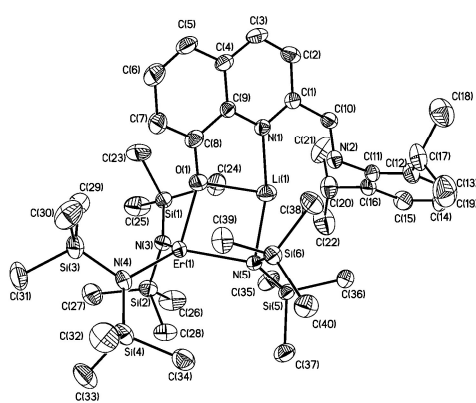
Fig. 1 Representative molecular structure of complex **3**. Hydrogen atoms were omitted for clarity.
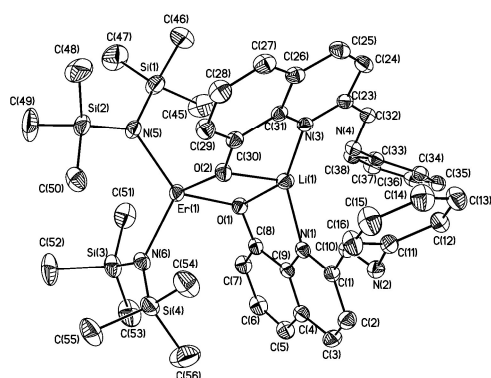
Fig. 2 Representative molecular structure of complex **6**. Hydrogen atoms and isopropyl groups were omitted for clarity.

Cl)Li(THF)$_3$[16a] and 2.211(5) Å in [(Me$_3$Si)$_2$N]$_3$Yb(μ-Cl)Li(THF)$_3$.[16b] The average Yb-O bond length of 2.143(2) Å in **7** is compared with 2.179(8) Å in L$_2$YbN(TMS)$_2$ (L = 3,5-^{t}Bu$_2$-2-(O)-C$_6$H$_2$CH=N-8-C$_9$H$_6$N).[8b]

Table 1. Selected bond lengths (Å) and bond angles (°).

|	**2** (Y)	**3** (Er)	**4** (Dy)
RE(1)-O(1)	2.149(2)	2.142(3)	2.172(5)
RE(1)-N(3)	2.259(3)	2.229(3)	2.260(6)
RE(1)-N(4)	2.242(3)	2.241(3)	2.251(6)
RE(1)-N(5)	2.338(3)	2.327(3)	2.357(6)
Li(1)-N(1)	2.029(6)	2.030(9)	2.049(17)
Li(1)-N(2)	2.649(7)	2.656(10)	2.672(18)
Li(1)-N(5)	2.232(7)	2.236(9)	2.222(17)
Li(1)-O(1)	2.221(7)	2.213(9)	2.208(18)
O(1)-RE(1)-N(3)	82.53(9)	82.57(11)	82.5(2)
O(1)-RE(1)-N(4)	117.11(9)	117.22(13)	117.6(2)
O(1)-RE(1)-N(5)	100.89(9)	100.88(13)	99.8(2)
N(3)-RE(1)-N(4)	113.23(10)	113.19(12)	113.8(2)
N(3)-RE(1)-N(5)	123.36(10)	123.00(12)	123.9(2)
N(4)-RE(1)-N(5)	113.23(10)	114.12(12)	112.9(2)
O(1)-Li(1)-N(1)	78.5(2)	78.0(3)	77.8(6)
O(1)-Li(1)-N(5)	83.4(2)	83.2(3)	84.9(6)
N(1)-Li(1)-N(5)	158.8(4)	157.3(5)	158.7(9)
Li(1)-N(5)-RE(1)	88.78(19)	88.5(3)	88.2(5)
RE(1)-O(1)-Li(1)	94.05(17)	93.9(2)	93.4(4)
	5 (Sm)	**6** (Er)	**7** (Yb)
RE(1)-O(1)	2.287(2)	2.201(2)	2.178(2)
RE(1)-O(2)	2.208(2)	2.129(2)	2.107(2)
RE(1)-N(5)	2.288(3)	2.215(3)	2.193(3)
RE(1)-N(6)	2.285(3)	2.212(3)	2.182(3)
Li(1)-O(1)	1.989(6)	1.978(7)	1.978(6)
Li(1)-O(2)	2.281(7)	2.276(8)	2.243(7)
Li(1)-N(1)	2.043(7)	2.041(7)	2.037(7)
Li(1)-N(3)	2.009(6)	2.004(7)	2.008(6)
O(1)-RE(1)-O(2)	82.29(8)	84.64(9)	84.35(8)
N(5)-RE(1)-N(6)	118.72(11)	118.31(13)	117.91(11)
O(1)-RE(1)-N(5)	128.65(10)	128.42(11)	129.58(10)
O(1)-RE(1)-N(6)	102.46(9)	103.23(10)	102.09(9)
O(2)-RE(1)-N(5)	96.44(10)	97.75(11)	97.58(10)
O(2)-RE(1)-N(6)	124.87(11)	120.82(12)	122.30(11)
O(1)-Li(1)-O(2)	87.4(3)	86.2(3)	85.7(2)
N(1)-Li(1)-N(3)	128.8(3)	127.1(3)	126.7(3)
O(1)-Li(1)-N(1)	84.0(2)	84.8(3)	85.0(2)
O(1)-Li(1)-N(3)	145.7(4)	145.8(4)	146.3(3)
O(2)-Li(1)-N(1)	102.3(3)	100.7(3)	102.1(3)
O(2)-Li(1)-N(3)	76.8(2)	76.7(2)	77.3(2)
RE(1)-O(1)-Li(1)	97.7(2)	97.4(2)	97.4(2)
RE(1)-O(2)-Li(1)	91.91(18)	91.00(18)	91.81(18)

In Table 1, the bond length of the corresponding RE(1)-N(5) is slightly longer than RE(1)-N(3) and RE(1)-N(4) in complexes **2-4**, due to the different coordination environment. The bond lengths of Li(1)-N(2) in complexes **2** (2.649(7) Å), **3** (2.656(10) Å), **4** (2.672(18) Å) are dramatically longer than the corresponding bond lengths of Li(1)-N(1) and Li(1)-N(5) ranging from 2.029(6) Å to 2.236(9) Å. Therefore, lithium metals were thought to adopt a three-coordinated distorted trigonal configuration. The average RE−N bond lengths of 2.280(3) Å in **2**, 2.266(3) Å in **3**, and 2.289(6) Å in **4** are well consistent with their ionic radii sequence. The average Y−N bond length of 2.280(3) Å in **2** is shorter than that of 2.456 (4) Å found in [2-(2,6-^{i}Pr$_2$C$_6$H$_3$NC(H)C$_6$H$_4$-C$_9$H$_6$N)Y(CH$_2$SiMe$_3$)$_2$(THF),[8a] probably due to the bulkiness of the ligand and different coordinated number of rare-earth metal. In complexes **5-7**, RE(1), Li(1), O(1), and O(2) are nearly coplanar to form a square plane with a sum of the bond angles of 359.29° for **5**, 359.24° for **6** and 359.26° for **7**. The average RE−N bond lengths of 2.287(3) Å in **5**, 2.214(3) Å in **6**, and 2.188(6) Å in **7** are well consistent with their ionic radii sequence due to the lanthanide contraction. The average RE−N bond lengths of 2.287(3) Å in **5**, and 2.188(6) Å in **7** are compared with the corresponding of RE−N bond lengths of 2.319(6) Å in [(Me$_3$Si)$_2$N]$_3$Sm(μ-

Catalytic addition of diphenylphosphine oxide to *trans*-β-nitroalkenes.

With above complexes in hand, the catalytic addition of diphenylphosphine oxide to the *trans-β*-nitrostyrene was examined, and results were summarized in Table 2. Complex **2** was first employed as a catalyst for the hydrophosphination of β-nitrostyrene. Results showed that 5 mol% of the catalyst **2** could efficiently catalyze the hydrophosphination of β-nitrostyrene to afford the product **8** as the only regioselective product. It was found that running the reactions in solvents such as toluene, THF, and diethyl ether afforded the product **8** in high yields (Table 2,

entries 1-7), while running the reaction in *n*-hexane afforded the product **8** in a low yield (Table 2, entry 8). When the reaction was conducted in the absence of catalyst, no addition product **8** was isolated under the same conditions. The catalytic activities of
5 the above different rare-earth metal complexes towards hydrophosphination of *β*-nitrostyrene were investigated with 5 mol% of catalyst loading using THF as a solvent. It is found that all complexes **2-7** exhibited a high catalytic activity on the hydrophosphination of β-nitrostyrene (Table 2, entry 9-13),
10 indicating that the ionic radii of the lanthanide metals and coordination modes of the central metal have little influence on the catalytic activities of the catalysts.

Table 2. Optimizations for the addition of diphenyphosphine oxide to *β*-nitrostyrene.[a]
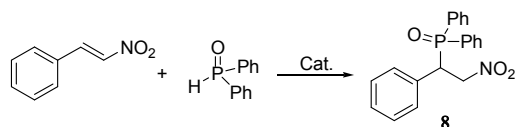
Entry	Cat. (mol%)	Solvent	Time (h)	Yield (%)[b]
1	**2** (1)	THF	24	51
2	**2** (3)	THF	24	78
3	**2** (5)	THF	24	95
4	**2** (5)	THF	6	95
5	**2** (5)	THF	1	42
6	**2** (5)	toluene	6	90
7	**2** (5)	Et$_2$O	6	92
8	**2** (5)	*n*-hexane	6	25
9	**3** (5)	THF	6	94
10	**4** (5)	THF	6	93
11	**5** (5)	THF	6	90
12	**6** (5)	THF	6	91
13	**7** (5)	THF	6	93

[a] Reactions were performed with 1.0 mmol of diphenyphosphine oxide and 1.0 mmol of *β*-nitrostyrene, solvent (5 mL), room temperature. [b] Isolated yield.

20 Evidences that different lanthanide metal complexes exhibited a similar catalytic activity. Next, we examined the substrate scope of the catalytic addition of diphenylphosphine oxide to different *β*-nitroalkene employing complex **7** as a catalyst, and the results were listed in Table 3. From Table 3, we can see that complex **7**
25 exhibited a high catalytic activity on the catalytic addition for different β-nitroalkene despite of the electronic nature and the steric effect of the substituents on the aryl groups (Table 3, entries 1-9). When the substituents on the phenyl ring are the electron-donating groups such as CH$_3$O-, CH$_3$-, the products **9–11**
30 can be isolated in high yields (Table 3, entries 2–4). When the substituents on the phenyl ring are the electron-withdrawing ones such as Cl-, Br-, the products **12–15** can also be isolated in satisfactory yields (Table 3, entries 5–8). For (*E*)-2-(2-nitrovinyl)naphthalene, the product **16** was also obtained in a
35 good yield of 89% (Table 3, entry 9).

Table 3. Addition of diphenyphosphine oxide to *β*-aryl nitroalkene catalyzed by complex **7**.[a]
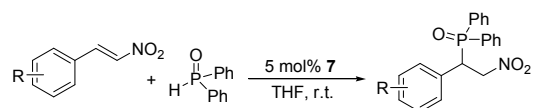
Entry	Substrate	Product	Yield (%)[b]
1		**8**	95
2		**9**	85
3		**10**	93
4		**11**	96
5		**12**	89
6		**13**	87
7		**14**	90
8		**15**	90
9		**16**	89

[a] Reaction conditions: substrate (1.0 mmol), Ph$_2$P(O)H (1.0 mmol),
40 reaction time: 6 hour. [b] Isolated yield.

Based on the previous mechanism on hydrophosphination of phosphinoalkenes catalyzed by lanthanide amides,[17] the catalytic addition pathway of diphenylphosphine oxide to the trans-*β*-
45 nitroalkene is proposed involving the initial Ln-N(SiMe$_3$)$_2$ protonolysis to generate a Ln-OPPh$_2$, followed by intramolecular addition of the phosphorous to the coordinated C-C double bond of the nitroalkene and finally protonolysis of the intermediate by diphenylphosphine oxide to release the addition product with a
50 completion of the catalytic cycle (Scheme 2).

Scheme 2 Proposed mechanism of addition of diphenylphosphine oxide to trans-β-nitroalkenes catalyzed by rare-earth metal complexes

Conclusions

Two series of novel heterometallic rare-earth metal complexes bearing imino-functionalized 8-hydroxyquinolyl ligand were synthesized *via* reactions of [(Me$_3$Si)$_2$N]$_3$RE(μ-Cl)Li(THF)$_3$ with the different equiv. of 2-(2,6-diisopropylphenylimino)-8-hydroxyquinoline. X-ray diffraction analyses revealed that complexes **2-4** were isostructural heterometallic rare-earth metal and lithium complexes bridged by the oxygen atom of the 2-(2,6-diisopropylphenylimino)-8-hydroxyquinoline and the nitrogen atom of N(SiMe$_3$)$_2$. However, complexes **5-7** were another type of heterometallic rare-earth metal and lithium bridged by the oxygen atoms of the 2-(2,6-diisopropylphenylimino)-8-hydroxyquinoline. All complexes exhibited an excellent catalytic activity on the hydrophosphinylation of *β*-nitroalkene derivatives.

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Notes and references

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