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Introduction

Heterometallic rare-earth metal complexes with imino-functionalized 8-hydroxyquinolyl ligands: synthesis, characterization and catalytic activity towards hydrophosphinylation of *trans*-βnitroalkene[†]

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Reactions of rare-earth metal amides $[(Me_3Si)_2N]_3RE(\mu-Cl)Li(THF)_3$ with different equiv. of 2-(2,6-diisopropylphenylimino)-8-hydroxyquinoline (**1**) afforded different heterometallic rare-earth metal complexes, and catalytic activity of the resulting complexes was investigated. Reactions of rare-earth metal amides $[(Me_3Si)_2N]_3RE(\mu-Cl)Li(THF)_3$ (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, the treatment of rare-earth metal amides $[(Me_3Si)_2N]_3RE(\mu-Cl)Li(THF)_3$ (RE = Sm, Er, Yb) with 2 equiv. of compound **1** gave 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 the treatment of **3** with 1 equiv. of **1**. Complexes **2–7** were fully characterized using 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 *trans*- β -nitroalkenes to afford β -nitrophosphonates under mild conditions.

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 tuned sizes and electronic properties of the substituents.¹ Rare-earth metal complexes stabilized by β -diketiminates,² amidinates,³ guanidinates,⁴ bridged bisphenolates,⁵ diamido ligands,⁶ and modified pyrrolyl or indolyl ligands⁷ have been synthesized and applied in various organic transformations. Recently, 8-hydroxy or 8-aminoquinoline derivatives have been used as ligands for rare-earth metal⁸ and group 4 metal complexes⁹ because of their excellent coordination properties and near infrared luminescence.

The Michael addition of phosphorus compounds to nitroalkenes provides a practical route to β -nitrophosphonates, which can be transformed into the corresponding 1,4-addition products, β-amino phosphonates, through a simple reduction of the nitro group.¹⁰ Previous studies mainly focus on the catalytic addition of nucleophiles such as dialkyl phosphites $[(RO)_2 P(O)H]^{11}$ and secondary phosphines $(R_2 PH)^{12}$ to β -nitroalkenes. However, the diarylphosphine oxides [Ar₂P(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 the high regioselective addition of phosphites to α,β -unsaturated carbonyl compounds.¹⁵ As our continuous interest in the 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 ligands towards the addition of diphenylphosphine oxide to *trans*-β-nitroalkenes.

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Experimental section

Materials and methods

All syntheses and manipulations of air- and moisture-sensitive materials were performed under a dry argon and an oxygenfree 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. [(Me₃Si)₂N]₃RE(μ -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. Data of elemental analyses 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 CDCl₃ for organic compounds. Chemical shifts (δ) were reported in ppm. IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer (KBr pellets).

Synthesis of $\eta^1: \eta^1 - [2 - (2, 6^{-i} Pr_2 C_6 H_3)N = CH] - 8 - OC_9 H_6 N]Li- [\mu - N(SiMe_3)_2]RE[N(SiMe_3)_2]_2$ (RE = Y (2), Er (3), Dy (4))

To a toluene (10.0 mL) solution of compound 1 (0.300 g, 0.90 mmol) a toluene (20.0 mL) solution of [(Me₃Si)₂N]₃Y(µ-Cl)-Li(THF)₃ (0.746 g, 0.90 mmol) was added at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was then heated at 40 °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 pellets, cm^{-1}): $\nu = 2961, 2868, 2361, 2342, 2170, 1638, 1618, 1560, 1458,$ 1369, 1341, 1261, 1182, 1098, 932, 841, 745. ¹H NMR (300 MHz, C₆D₆): 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). ¹³C NMR (125 MHz, C₆D₆): 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 C40H77LiN5OSi6Y: 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 the treatment of compound 1 (0.300 g, 0.90 mmol) with $[(Me_3Si)_2N]_3Er(\mu-Cl)Li(THF)_3$ (0.816 g, 0.90 mmol) using the procedures similar to those described above for the preparation of 2. IR (KBr pellets, cm⁻¹): ν = 3063, 2959, 2868, 2361, 2342, 2185, 1630, 1591, 1553, 1458, 1371, 1341, 1252, 1180, 1099, 1057, 841, 750. Anal. calc. for C₄₀H₇₇LiN₅OSi₆Er·C₄H₈O: 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 the treatment of compound 1 (0.300 g, 0.90 mmol) with $[(Me_3Si)_2N]_3Dy(\mu-Cl)Li(THF)_3$ (0.812 g, 0.90 mmol) using the procedures similar to those described above for the preparation of 2. IR (KBr pellets, cm⁻¹): ν = 3061, 2959, 2868, 2361, 2342, 1630, 1589, 1553, 1460, 1553, 1460, 1369, 1341, 1182, 1099, 932, 839, 745. Anal. calc. for C₄₀H₇₇LiN₅OSi₆Dy·C₇H₈: C, 52.55; H, 7.98; N, 6.52. Found: C, 52.29; H, 7.87; N, 6.46.

Synthesis of $\eta^1:\eta^1:(\eta^1:\eta^1-2-(2,6-iPr_2C_6H_3)N=CH-8-OC_9H_6N]_2$ -LiRE[N(SiMe₃)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) a toluene (20.0 mL) solution of $[(Me_3Si)_2N]_3Sm(\mu-Cl)-Li(THF)_3$ (0.623 g, 0.70 mmol) was added at room temperature. After the reaction mixture was stirred at room temperature for 6 h, the mixture was then heated at 40 °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 pellets, cm⁻¹): $\nu = 3059$, 2961, 2868, 2361, 2342, 1630, 1589, 1551, 1458, 1369, 1341, 1252, 1098, 841, 748. Anal. calc. for $C_{56}H_{81}LiN_6O_2Si_4Sm: C$, 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 the treatment of compound **1** (0.465 g, 1.40 mmol) with $[(Me_3Si)_2N]_3Er(\mu-Cl)Li(THF)_3$ (0.635 g, 0.70 mmol) using the procedures similar to those described above for the preparation of **5**. IR (KBr pellets, cm⁻¹): ν = 3059, 2959, 2868, 2361, 1630, 1589, 1553, 1458, 1369, 1341, 1182, 1099, 932, 840, 745. Anal. calc. for C₅₆H₈₁LiN₆O₂Si₄Er: 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 the treatment of 3 with 1 equiv. of 1 by employing the procedures similar to those used for the preparation of complex 5.

Complex 7 was prepared as yellow crystals in 43% yield by the treatment of compound 1 (0.465 g, 1.40 mmol) with $[(Me_3Si)_2N]_3Yb(\mu-Cl)Li(THF)_3$ (0.639 g, 0.70 mmol) using the procedures similar to those described above for the preparation of 5. IR (KBr pellets, cm⁻¹): ν = 3059, 2959, 2868, 1630, 1589, 1553, 1458, 1371, 1340, 1182, 1099, 932, 849, 745. Anal. calc. for C₅₆H₈₁LiN₆O₂Si₄Yb: C, 57.85; H, 7.02; N, 7.23. Found: C, 57.62; H, 7.09; N, 6.99.

Crystal structure determination

Suitable crystals of complexes 2–7 were each mounted in a sealed capillary. Diffraction was performed on a Bruker SMART CCD area detector diffractometer using graphite-monochromated Mo-K_{α} radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using the SADABS program. 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 Table 4 for crystallographic data.

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 THF, 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 ESI.†

Results and discussion

Synthesis of rare-earth metal complexes with iminofunctionalized 8-hydroxyquinolyl ligands

Treatment of rare-earth metal amides $[(Me_3Si)_2N]_3RE(\mu-Cl)Li-(THF)_3$ (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 $[(Me_3Si)_2N]_3RE(\mu-Cl)Li(THF)_3$ (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.

X-ray diffraction analyses revealed that complexes 2–4 were isostructural heterometallic rare-earth metal and lithium complexes bridged by the oxygen atom of 2-(2,6-diisopropylphenylimino)-8-hydroxyquinolyl and the nitrogen atom of $N(SiMe_3)_2$. 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 Fig. 1. Complexes 5–7 were another type of heterometallic rare-earth metal and lithium bridged by the oxygen atoms of the 2-(2,6-diisopropylphenyl-imino)-8-hydroxyquinolyl ligand, and a representative structure diagram of complex 6 is shown in Fig. 2. In complexes 5–7, rare-earth metal and lithium all adopted a four-coordinated



Scheme 1 Synthesis of heterometallic rare-earth metal complexes 2–7.



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.

distorted tetrahedral configuration. The selected bond lengths and angles were listed in Table 1.

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-ⁱPr₂C₆H₃NC(H)-C₆H₄-C₉H₆N)Y(CH₂SiMe₃)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

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)

corresponding RE–N bond lengths of 2.319(6) Å in [(Me₃Si)₂N]₃Sm-(μ -Cl)Li(THF)₃^{16*a*} and 2.211(5) Å in [(Me₃Si)₂N]₃Yb(μ -Cl)Li(THF)₃.^{16*b*} The average Yb–O bond length of 2.143(2) Å in 7 is compared with 2.179(8) Å in L₂YbN(TMS)₂ (L = 3,5^{-*t*}Bu₂-2-(O)-C₆H₂CH=N-8-C₉H₆N).^{8*b*}

Catalytic addition of diphenylphosphine oxide to *trans*-βnitroalkenes

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 Optimizations for the addition of diphenylphosphine oxide to β -nitrostyrene^a

	NO2 +	O H_Ph <u>Cat</u> H_Ph	Ph O=p-F	Ph ∕NO₂
Entry	Cat. (mol%)	Solvent	Time (h)	$\operatorname{Yield}^{b}(\%)$
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_2O	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 diphenylphosphine oxide and 1.0 mmol of β-nitrostyrene, solvent (5 mL), room temperature. ^{*b*} Isolated yield.

Table 3 Addition of diphenylphosphine oxide to $\beta\text{-aryl}$ nitroalkene catalyzed by complex $\textbf{7}^a$



 a Reaction conditions: substrate (1.0 mmol), $\rm Ph_2P(O)H$ (1.0 mmol), reaction time: 6 hour. b Isolated yield.

	2	3	4	5	6	7
Formula	C40H77YLiN5OSi6	C40H77ErLiN5OSi6	C40H77DyLiN5OSi6	C ₅₆ H ₈₁ LiN ₆ O ₂ Si ₄ Sm	C ₅₆ H ₈₁ LiN ₆ O ₂ Si ₄ Er	C ₅₆ H ₈₁ LiN ₆ O ₂ Si ₄ Yb
Formula weight	908.46	986.81	982.05	1140.93	1156.83	1162.61
Cryst system	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	Pbca	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)
$V(\dot{A}^3)$	12069.7(11)	12063.7(13)	12128.4(19)	6318.1(8)	6265.4(10)	6261.4(6)
$T(\mathbf{K})$	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Z	8	8	8	4	8	4
$D_{\text{calcd}} (\text{g cm}^{-3})$	1.000	1.087	1.076	1.199	1.227	1.234
$\mu (\mathrm{mm}^{-1})$	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	101 453	99 412	99 998	54 457	44 071	53 755
Unique reflns	13 849	13 766	14 131	14810	11042	14 452
-	$(R_{\rm int} = 0.1617)$	$(R_{\rm int} = 0.0673)$	$(R_{\rm int} = 0.1144)$	$(R_{\rm int} = 0.0405)$	$(R_{\rm int} = 0.0386)$	$(R_{\rm int} = 0.0432)$
Parameters	509	509	509	651	651	651
$R_1 (I > 2\sigma(I))$	0.0564	0.0420	0.0689	0.0442	0.0363	0.0394
$wR_2 (I > 2\sigma(I))$	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

 Table 4
 Crystallographic data for complexes 2–7

(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 a catalyst, no addition product **8** was isolated under the same conditions. The catalytic activities of 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, entries 9–13), 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.

Evidence 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 exhibited a high catalytic activity on the catalytic addition for different β -nitroalkene despite 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 CH₃O-, CH₃-, products 9-11 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-, products 12-15 can also be isolated in satisfactory yields (Table 3, entries 5-8). For (E)-2-(2-nitrovinyl)naphthalene, product 16 was also obtained in a good yield of 89% (Table 3, entry 9).

Based on the previous mechanism on hydrophosphination of phosphinoalkenes catalyzed by lanthanide amides,¹⁷ the catalytic addition pathway of diphenylphosphine oxide to *trans*- β -nitroalkene is proposed involving the initial Ln-N(SiMe₃)₂ protonolysis to generate Ln-OPPh₂, followed by the intramolecular



Scheme 2 Proposed mechanism of the addition of diphenylphosphine oxide to $trans-\beta$ -nitroalkenes catalyzed by rare-earth metal complexes.

addition of phosphorous to the coordinated C–C double bond of nitroalkene and finally protonolysis of the intermediate by diphenylphosphine oxide to release the addition product with a completion of the catalytic cycle (Scheme 2).

Conclusions

Two series of novel heterometallic rare-earth metal complexes bearing imino-functionalized 8-hydroxyquinolyl ligands were synthesized *via* reactions of $[(Me_3Si)_2N]_3RE(\mu-Cl)Li(THF)_3$ with 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

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complexes bridged by the oxygen atom of 2-(2,6-diisopropylphenylimino)-8-hydroxyquinoline and the nitrogen atom of N(SiMe₃)₂. However, complexes 5–7 were another type of heterometallic rare-earth metal and lithium bridged by the oxygen atoms of 2-(2,6-diisopropylphenylimino)-8-hydroxyquinoline. All complexes exhibited an excellent catalytic activity on the hydrophosphinylation of β -nitroalkene derivatives.

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