

Rare-earth Metal Dialkyl Complexes Supported by 1,3-Disubstituted Indolyl Ligand: Synthesis, Characterization and Catalytic Activity for Isoprene Polymerization^①

GUO Li-Ping^{a, b} SONG Ren-Yuan^{a②}

^a (Anhui Provincial Engineering Laboratory of Silicon-based Materials, Bengbu University, Bengbu 233030, China)

^b (The Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Normal University, Wuhu 241000, China)

ABSTRACT Rare-earth metal dialkyl complexes [1-Bn-3-(DippN=CH)C₈H₄N]RE(CH₂SiMe₃)₂(thf)₂ (Dipp = 2,6-*i*-Pr₂C₆H₃, RE = Y (**1**) and Er (**2**)) were prepared through the cyclometalation reactions of the N-Bn-3-imino-functionalized indolyl ligand 1-Bn-3-(DippN=CH)C₈H₅N with one equivalent of rare-earth metal trialkyl precursors. The structures of compounds **1** and **2** were confirmed by X-ray crystal analyses and characterized by elemental analysis, IR, NMR spectroscopy wherein applicable. In the presence of cocatalysts, these rare-earth metal dialkyl complexes initiated isoprene polymerization with a high activity (95% conversion of 2000 equivalent of isoprene in 360 min), producing polymers with high regioselectivity (1,4-polymers up to 91%).

Keywords: indolyl ligand, rare-earth metal dialkyl complex, isoprene, polymerization;

DOI: 10.14102/j.cnki.0254-5861.2011-3172

1 INTRODUCTION

In the past decades rare-earth metal dialkyl complexes have attracted much attention for their high reactivity in organic synthesis and excellent catalytic activity and selectivity for olefin polymerization^[1, 2]. Ligands have played a very important role in stabilizing these rare-earth metal dialkyl complexes for their easy decomposition to the corresponding monoalkyl complexes *via* ligands redistribution. To date, Cp (Cp = cyclopentadienyl)^[3], β -diketiminato^[4], Tp (Tp = tris(pyrazolyl)borate)^[5] and amidante^[6] with the advantage of easy modulation of the steric and electronic properties have been successfully used in the development of rare-earth metal dialkyl complexes. Indole and its derivatives have been widely used as ligand platform in coordination chemistry to facilitate the discovery of new multihapto-binding modes^[7]. Previously, we have reported the reaction of 1-alkyl-3-imino functionalized indolyl ligands with lithium reagents or rare-earth trialkyl precursors^[8]. The rare-earth metal monoalkyl complexes obtained by the reactions of corresponding ligands with rare-earth metal

trialkyl precursors in the molar ratio of 2:1 have shown high activity and selectivity in isoprene polymerization. In this paper, we describe the synthesis of two rare-earth metal dialkyl complexes [1-Bn-3-(DippN=CH)C₈H₄N]RE(CH₂SiMe₃)₂(thf)₂ (RE = Y (**1**) and Er (**2**)), focusing on their crystal structures and catalytic activity toward isoprene polymerization.

2 EXPERIMENTAL

2.1 Instruments and reagents

All syntheses and manipulations of air- and moisture-sensitive materials were carried out under an atmosphere of argon using standard Schlenk techniques or in an argon-filled glovebox. THF, toluene and hexane were refluxed and distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. Dichloromethane and chlorobenzene were distilled over CaH₂ under argon before use. Benzyl chloride was dried by stirring with P₂O₅ for 48 hours and distilled under reduced pressure prior to use. B(C₆F₅)₃, [Ph₃C][B(C₆F₅)₄] and [PhNM₂H][B(C₆F₅)₄] were purchased from STREM. AlMe₃, AlEt₃ and Al^{*i*}Bu₃ were

Received 10 March 2021; accepted 16 April 2021 (CCDC 2069053 for **1** and 2069054 for **2**)

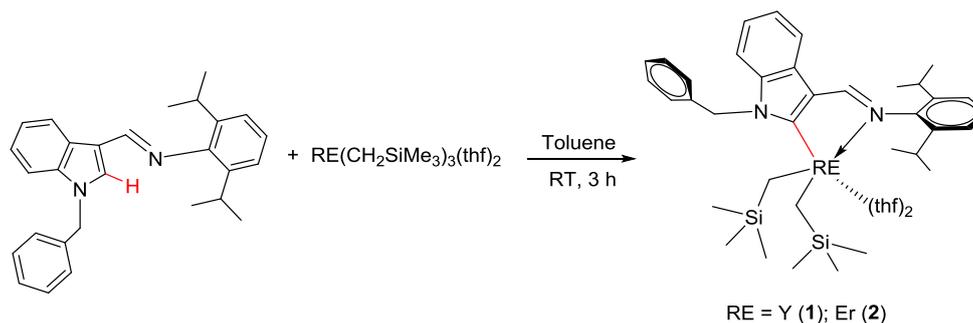
① This project was supported by the Natural Science Foundation of Anhui Province (No. 2008085ME174) and financial support from Anhui Normal University (FMS201915)

② Corresponding author. E-mail: guoliping251@126.com (Guo Li-Ping)

commercial from Sigma-Aldrich and used as received. Isoprene was available from TCI, dried with CaH_2 , and distilled before use. 1-Benzyl-3-indolealdehyde and the ligand were prepared following the literature procedures^{18, 91}. Elemental analyses data were obtained on a Perkin-Elmer Model 2400 Series II elemental analyzer. ^1H NMR and ^{13}C NMR spectra of the compounds were recorded on a Bruker AV-500 NMR spectrometer (500 MHz for ^1H ; 125 MHz for ^{13}C) in C_6D_6 for compound **1** and in CDCl_3 for polyisoprene. Chemical shifts (δ) were reported in ppm, and J values in Hz. IR spectra were recorded on a Shimadzu Model FTIR-8400s spectrometer (KBr pellet). Gel permeation chromatography (GPC) analyses of the polymer samples were carried out at 30 °C using THF as an eluent on a Waters-2414 instrument and calibrated using monodispersed polystyrene standards at a flow rate of 1.0 mL·min⁻¹.

2.2 Syntheses of compounds 1 and 2

The general procedure for the synthesis of compounds **1** and **2** is shown in Scheme 1. To a toluene (15 mL) solution of **HL** (0.394 g, 1.0 mmol) was added a toluene (5 mL) solution



Scheme 1. Preparation of the rare-earth metal dialkyl compounds **1** and **2**

Compound **2** was obtained as yellow crystals in 72% yield by the treatment of $\text{Er}(\text{CH}_2\text{SiMe}_3)(\text{thf})_2$ (0.57 g, 1.0 mmol) with **HL** (0.394 g, 1.0 mmol) following procedure similar to the preparation of **1**. The color of the solution changed from pink to yellow during the reaction. Calcd. (%) for $\text{C}_{44}\text{H}_{67}\text{N}_2\text{O}_2\text{Si}_2\text{Er}$: C, 60.09; H, 7.68; N, 3.19. Found (%): C, 59.74; H, 7.66; N, 2.95. IR (KBr pellets, cm^{-1}): ν 2958 (w), 2864 (s), 1627 (w), 1543 (s), 1465 (s), 1388 (s), 1361 (s), 1253 (s), 1161 (s), 1033 (s), 854 (s), 746 (s).

2.3 Crystal data collection and structure determination

A suitable crystal of compound **1** or **2** was each mounted in a sealed capillary. Diffraction data collection was performed on a Bruker SMART APEX II CCD area detector diffractometer equipped with graphite-monochromatic $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) with an ω - ϕ scan mode at 293(2) K. For compound **1**, a total of 39346 reflections with 10637

of $\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{thf})_2$ (0.49 g, 1.0 mmol). The mixture was stirred for 3 h at room temperature, and the color of the solution changed from pistachio to yellow in the process. The solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (15 mL). Yellow crystals were obtained at 0 °C for several days (0.6 g, 75% yield). ^1H NMR (500 MHz, C_6D_6): δ -0.35 (s, 4H, CH_2SiMe_3), 0.22 (s, 18H, CH_2SiMe_3), 1.10 (d, $J = 5.0$ Hz, 6H, CHMe_2), 1.16 (m, 8H, β - CH_2 THF), 1.22 (d, $J = 5.0$ Hz, 6H, CHMe_2), 3.25 (m, $J = 5.0$ Hz, 2H, CHMe_2), 3.58 (m, 8H, α - CH_2 THF), 5.71 (s, 2H, $\text{CH}_2\text{C}_6\text{H}_5$), 6.95~7.01 (m, 4H), 7.07~7.13 (m, 7H), 7.51 (d, $J = 10.0$ Hz, 1H), 8.53 (s, 1H, $\text{CH}=\text{N}$). ^{13}C NMR (125 MHz, C_6D_6): δ 4.5, 23.0, 25.2, 26.0, 28.6, 31.9, 54.9, 70.4, 111.8, 116.5, 121.5, 121.7, 123.8, 125.9, 127.0, 127.2, 128.7, 130.7, 138.8, 141.5, 141.9, 149.3, 168.5, 206.5 (d, $J_{\text{Y-C}} = 37.5$ Hz, 2-indolyl). Calcd. (%) for $\text{C}_{44}\text{H}_{67}\text{N}_2\text{O}_2\text{Si}_2\text{Y}$: C, 65.97; H, 8.43; N, 3.50. Found (%): C, 65.67; H, 8.23; N, 3.43. IR (KBr pellets, cm^{-1}): ν 2956 (s), 2866 (s), 1620 (w), 1535 (w), 1460 (s), 1423 (s), 1381 (s), 1361 (s), 1247 (s), 1161 (s), 1045 (s), 860 (w), 744 (w), 694 (s).

unique ones ($R_{\text{int}} = 0.0581$) were collected in the ranges of $1.88 \leq \theta \leq 27.58^\circ$; $-25 \leq h \leq 27$, $-13 \leq k \leq 12$ and $-28 \leq l \leq 28$, of which 6380 were observed with $I > 2\sigma(I)$. For **2**, in the ranges of $1.88 \leq \theta \leq 27.74^\circ$; $-27 \leq h \leq 27$, $-13 \leq k \leq 13$ and $-28 \leq l \leq 26$, 38870 total reflections were collected with 10733 unique ones ($R_{\text{int}} = 0.0319$), of which 9036 were observed with $I > 2\sigma(I)$. An empirical absorption correction was applied using the SADABS program^[10]. Both structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package^[11]. The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities were of no chemical significance.

2.4 Isoprene polymerization

The procedures for the isoprene polymerization catalyzed by compounds **1** and **2** were similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask equipped with a magnetic stirring bar was charged a desired amount of solvent, the rare-earth metal complex, borate, alkyl aluminium and isoprene. Then the mixture was stirred vigorously for the desired time, during which an increase of viscosity was observed. The reaction mixture was quenched by the addition of 30 mL of acidified methanol. The polymer was coagulated, washed with methanol twice and finally dried under vacuum to a constant weight.

3 RESULTS AND DISCUSSION

Reactions of the ligand 1-Bn-3-(DIPP=CH)C₈H₅N with one equivalent of rare-earth metal trialkyl precursor in toluene afforded the carbon σ -bonded indolyl supported rare-earth metal dialkyl compounds **1** and **2** through sp^2 C–H activation in good yields. Compounds **1** and **2** were fully characterized by spectroscopic methods and elemental analyses. The structures were determined by single-crystal X-ray diffraction. These complexes are soluble in hexane, toluene and THF. The disappearance of proton at the 2-indolyl position (at δ 6.89 in C₆D₆ for free ligand) in ¹H NMR spectra of the diamagnetic yttrium compound **1** proved sp^2 C–H activation. In addition, the signals centered at 206.5 ppm in the ¹³C NMR spectra are assigned to the resonance of carbon atom at the 2 position of the indolyl ligand coupled to the yttrium nucleus with $J_{Y-C} = 37.5$ Hz, which is smaller than that found in the corresponding monoalkyl compound supported by the same ligand ($J_{Y-C} = 50.0$ Hz)^[8a]. In the spectrum of compound **1**, the signal at high field –0.35 ppm is assigned to the methylene protons of the Y-CH₂SiMe₃

groups. The protons of the Me₂CH groups show two doublets at 1.10 and 1.22 ppm, respectively, with the J value to be 5.0 Hz.

Single crystals of compounds **1** and **2** suitable for X-ray diffraction study were obtained by cooling the concentrated hexane solution at 0 °C. The crystal structures of compounds **1** and **2** with atom numbering are shown in Figs. 1 and 2, respectively, and the selected bond lengths and bond angles are listed in Table 1. X-ray diffraction revealed that **1** and **2** are isomorphous and crystallize in the monoclinic $P2_1/c$ space group and adopt monomeric structures. The rare-earth ions of compounds **1** and **2** are in a distorted octahedral coordination environment, with one THF oxygen atom and carbon atom of CH₂SiMe₃ group occupying the axial positions, while the other oxygen atom of THF molecule and carbon atom of CH₂SiMe₃ group as well as carbon atom of indolyl moiety and the nitrogen atom of imino group lie in the equatorial positions. The RE–C(sp^2) (2.491(3) Å for **1** and 2.477(3) Å for **2**) are much longer than RE–C(sp^3) (av. 2.399(3) Å for **1** and av. 2.383(3) Å for **2**) and comparable to the values observed in six-coordination yttrium complexes [C₄H₂S-2-CH₂N-(2,6-ⁱPr₂C₆H₃)]YCH₂SiMe₃(thf)₃ (2.423(3) Å)^[12] and [N₂^{EtTh}YCH₂SiMe₃(thf)₂] [N₂^{EtTh}H = C₃H₃N-2-CMe₂NH(2,6-ⁱPr₂C₆H₃)-6-(2-EtC₄H₂S)] (2.482(2) Å)^[13] if the difference of Ln³⁺ ionic radii is counted (for six-coordinate ionic radii: Y³⁺: 0.900 Å; Er³⁺: 0.890 Å)^[14]. The atoms C(1), C(2), C(16), N(2) and RE formed a five-membered ring through cyclometalation reaction and are almost coplanar with the mean deviations of 0.0635 and 0.0636 Å for compounds **1** and **2**, respectively. The bite angles of C(1)–RE–N(2) (70.53(8)° for **1** and 70.79(9)° for **2**) and the angles of the axial C(29)–RE–O(2) (173.84(8)° for **1** and 173.68(9)° for **2**) both indicate the geometry of the rare-earth centers deviation from ideal octahedral configuration.

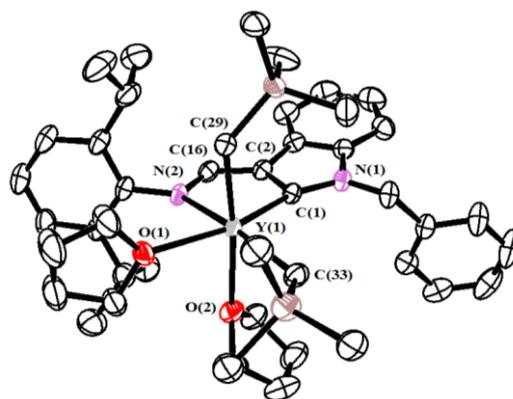


Fig. 1. ORTEP diagram of compound **1** with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity

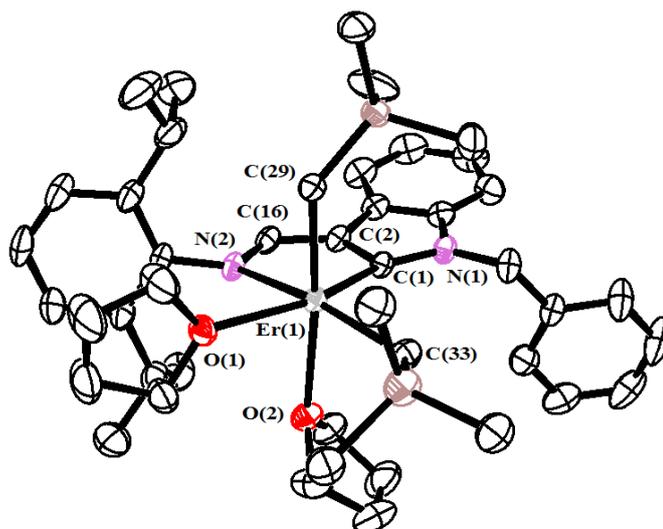


Fig. 2. ORTEP diagram of compound 2 with thermal ellipsoids at 30% probability level. Hydrogen atoms are omitted for clarity

Table 1. Selected Bond Lengths (Å) and Bond Angles (°)

Compound 1					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Y(1)–C(1)	2.491(3)	Y(1)–C(29)	2.382(3)	Y(1)–C(33)	2.415(3)
Y(1)–N(2)	2.588(2)	Y(1)–O(1)	2.3940(19)	Y(1)–O(2)	2.495(2)
C(1)–C(2)	1.405(4)	C(2)–C(16)	1.429(4)	C(16)–N(2)	1.285(3)
Angle	(°)	Angle	(°)	Angle	(°)
C(1)–Y(1)–N(2)	70.53(8)	C(1)–Y(1)–C(29)	98.05(9)	C(1)–Y(1)–O(1)	152.22(8)
C(1)–Y(1)–O(2)	87.76(8)	C(1)–Y(1)–C(33)	103.27(10)	C(29)–Y(1)–N(2)	96.07(9)
C(29)–Y(1)–O(1)	88.22(8)	C(29)–Y(1)–O(2)	173.84(8)	C(29)–Y(1)–C(33)	95.93(11)
N(2)–Y(1)–O(1)	81.94(8)	N(2)–Y(1)–O(2)	83.92(7)	N(2)–Y(1)–C(33)	167.17(9)
O(1)–Y(1)–O(2)	85.67(7)	O(1)–Y(1)–C(33)	102.95(10)	O(2)–Y(1)–C(33)	84.63(9)
Compound 2					
Bond	Dist.	Bond	Dist.	Bond	Dist.
Er(1)–C(1)	2.477(3)	Er(1)–C(29)	2.371(3)	Er(1)–C(33)	2.394(3)
Er(1)–N(2)	2.587(2)	Er(1)–O(1)	2.391(2)	Er(1)–O(2)	2.504(2)
C(1)–C(2)	1.405(4)	C(2)–C(16)	1.427(4)	C(16)–N(2)	1.284(4)
Angle	(°)	Angle	(°)	Angle	(°)
C(1)–Er(1)–N(2)	70.79(9)	C(1)–Er(1)–C(29)	98.09(10)	C(1)–Er(1)–O(1)	152.14(9)
C(1)–Er(1)–O(2)	87.86(9)	C(1)–Er(1)–C(33)	103.18(11)	C(29)–Er(1)–N(2)	96.23(9)
C(29)–Er(1)–O(1)	88.37(9)	C(29)–Er(1)–O(2)	173.68(9)	C(29)–Er(1)–C(33)	95.84(12)
N(2)–Er(1)–O(1)	81.61(8)	N(2)–Er(1)–O(2)	83.68(8)	N(2)–Er(1)–C(33)	167.17(11)
O(1)–Er(1)–O(2)	85.37(8)	O(1)–Er(1)–C(33)	103.07(11)	O(2)–Er(1)–C(33)	84.79(11)

Rare-earth metal monolalkyl complexes supported by N-protected-3-imino indolyl ligands exhibited high activity and excellent regio- and stereoselectivity for isoprene polymerization^[8a]. The catalytic activities of compounds **1** and **2** toward isoprene polymerization were investigated. None of the above rare-earth dialkyl complexes could initiate the polymerization of isoprene. After the abstraction of one CH_2SiMe_3 group by adding one equivalent of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, the forming cationic rare-earth metal monoalkyl complex also could not initiate the polymerization of isoprene. It might be the reason of two residual THF

molecules around the metal center blocking the coordination of olefin. The ternary system of **1**/ $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{AlR}_3$ could initiate the polymerization. The catalytic activity and selectivity were affected by the aluminum alkyls. When the more steric bulky Al^iBu_3 was used, quantitative polyisoprene was obtained in 120 min with 91% 1,4-content and high molecular weight (Entry 4). A previous report showed that the solvent has a significant impact on the group 3 metal cationic species, which in turn influences the activity and selectivity of the olefin polymerization^[15]. In this account, compound **1** for isoprene polymerization was tested in different solvents.

When the polymerization was carried out in $C_6H_5CH_3$ or C_6H_5Cl , the 1,4-selectivity decreases to 67%, although the catalytic activity was enhanced (Entries 6 and 7). The results are different from that found in N-alkyl-3-imino indolyl supported rare-earth monoalkyl system, in which solvents CH_2Cl_2 and C_6H_5Cl exhibited high activity and selectivity than $C_6H_5CH_3$. The organic borate also affected the activity and selectivity of the system. When $[PhNMe_2H][B(C_6F_5)_4]$ was used, the activity of the system declined although the selectivity was preserved (Entry 5). In case of $B(C_6F_5)_3$, the

ternary system showed no catalytic activity for isoprene polymerization (Entry 1). The Er analogue **2** showed a similar activity to that of yttrium complex **1** with 90% 1,4-selectivity (Entry 8). Furthermore, the catalyst system $1/[Ph_3C][B(C_6F_5)_4]/Al^iBu_3$ could initiate isoprene polymerization with different monomers to initiate ratios. On increasing the monomer to complex ratio from 1000 to 2000, the molecular weight of the resulting polymers increases from 11.7×10^4 to 23.0×10^4 with almost unchanged regioselectivity (Entry 9).

Table 2. Isoprene Polymerization by the Title Compounds^a

Entry	Precatalyst (solvent)	Borate	Cocatalyst	Time (mins)	Conv. (%)	Structure ^b		Mn ^c ($\times 10^4$)	PDI ^c
						1,4-	3,4-		
1	1 (CH_2Cl_2)	A	$AlMe_3$	720	–	–	–	–	–
2	1 (CH_2Cl_2)	B	$AlMe_3$	720	84	80	20	16.5	3.0
3	1 (CH_2Cl_2)	B	$AlEt_3$	300	97	81	19	14.2	3.0
4	1 (CH_2Cl_2)	B	Al^iBu_3	120	100	91	9	11.7	3.2
5	1 (CH_2Cl_2)	C	Al^iBu_3	240	95	90	10	9.6	2.5
6	1 ($C_6H_5CH_3$)	B	Al^iBu_3	40	100	67	33	20.7	3.2
7	1 (C_6H_5Cl)	B	Al^iBu_3	40	90	67	33	23.5	3.0
8	2 (CH_2Cl_2)	B	Al^iBu_3	120	100	90	10	11.6	3.9
9 ^d	1 (CH_2Cl_2)	B	Al^iBu_3	360	95	89	11	23.0	3.9

^a General conditions: $[RE] = 10 \mu mol$, $[RE]:[Ph_3C][B(C_6F_5)_4]:[IP] = 1:1:1000$, Temperature = 30 °C, $Vol(IP)/Vol(solvent) = 1:10$.

A = $B(C_6F_5)_3$; B = $[Ph_3C][B(C_6F_5)_4]$; C = $[PhNMe_2H][B(C_6F_5)_4]$; ^b Determined by ¹H NMR;

^c Determined by means of GPC against polystyrene standards in THF at 30 °C;

^d $[RE]:[Ph_3C][B(C_6F_5)_4]:[IP] = 1:1:2000$

REFERENCES

- (1) Nishiura, M.; Hou, Z. M. Novel polymerization catalysts and hydride clusters from rare-earth dialkyls. *Nat. Chem.* **2010**, *2*, 257–268.
- (2) Cheng, J. H.; Hou, Z. M. Rare-earth dialkyl and dihydride complexes bearing monoanionic ancillary ligands. *Sci. China Chem.* **2011**, *54*, 2032–2037.
- (3) Arndt, S.; Okuda, J. Mono(cyclopentadienyl) complexes of the rare-earths. *Chem. Rev.* **2002**, *102*, 1953–1976.
- (4) Mao, W. Q.; Chen, Y. F. Rare-earth metal complexes of β -diketiminato ligands bearing pendant nitrogen or oxygen donors. *Coord. Chem. Rev.* **2017**, *346*, 77–90.
- (5) (a) Cheng, J. H.; Saliu, K.; Kiel, G. Y.; Ferguson, M. J.; McDonald, R.; Takats, J. Scorpionate-supported dialkyl and dihydride lanthanide complexes: ligand- and solvent-dependent cluster hydride formation. *Angew. Chem. Int. Ed.* **2008**, *49*, 4910–4913.
(b) Yi, W. Y.; Zhang, J.; Zhang, F. J.; Zhang, Y.; Chen, Z. X.; Zhou, X. G. Versatile reactivity of scorpionate-anchored yttrium-dialkyl complexes towards unsaturated substrates. *Eur. J. Chem.* **2013**, *19*, 11975–11983.
- (6) (a) Yu, X. Y.; Li, M.; Hong, J. Q.; Zhou, X. G.; Zhang, L. X. Living 3,4-(co)polymerization of isoprene/myrcene and one-pot synthesis of a polyisoprene blend catalyzed by binuclear rare-earth metal amidinate complexes. *Chem. Eur. J.* **2019**, *25*, 2569–2576.
(b) Rad'kova, N. Y.; Tolpygin, A. O.; Rad'kov, V. Y.; Khamaletdinova, N. M.; Cherkasov, A. V.; Fukin, G. K.; Trifonov, A. A. Bis(alkyl) rare-earth complexes coordinated by bulky tridentate amidinate ligands bearing pendant $Ph_2P=O$ and $Ph_2P=NR$ groups. Synthesis, structures and catalytic activity in stereospecific isoprene polymerization. *Dalton Trans.* **2016**, *45*, 18572–18584.
- (7) (a) Zhu, X.; Zhou, S.; Wang, S.; Wei, Y.; Zhang, L.; Wang, F.; Wang, S. Y.; Feng, Z. Rare-earth metal complexes having an unusual indolyl-1,2-dianion through C–H activation with a novel $\eta^1:(\mu_2-\eta^1:\eta^1)$ bonding with metals. *Chem. Commun.* **2012**, *48*, 12020–12022.
(b) Feng, Z.; Zhu, X.; Wang, S.; Wang, S. Y.; Zhou, S.; Wei, Y.; Zhang, G.; Deng, B.; Mu, X. Synthesis, structure and reactivity of lanthanide complexes incorporating indolyl ligands in novel hapticities. *Inorg. Chem.* **2013**, *52*, 9549–9556.
(c) Zhu, X.; Wang, S.; Zhou, S.; Wei, Y.; Zhang, L.; Wang, F.; Feng, Z.; Guo, L.; Mu, X. Lanthanide amido complexes incorporating

- amino-coordinate lithium bridged bis(indolyl) ligands: synthesis, characterization, and catalysis for hydrophosphonylation of aldehydes and aldimines. *Inorg. Chem.* **2012**, 51, 7134–7143.
- (d) Zhang, G.; Wei, Y.; Guo, L.; Zhu, X.; Wang, S.; Zhou, S.; Mu, X. Dinuclear rare-earth metal alkyl complexes supported by indolyl ligands in $\mu\text{-}\eta^2\text{:}\eta^1\text{:}\eta^1$ hapticities and their high catalytic activity for isoprene 1,4-*cis*-polymerization. *Chem. Eur. J.* **2015**, 21, 2519–2526.
- (e) Yu, L.; Wang, F. H.; Wang, H.; Wang, S. Y.; Wu, Y. J.; Gu, X. X. Synthesis, structure and catalytic activity of rare-earth metal amino complexes incorporating imino-functionalized indolyl ligand. *J. Organo. Chem.* **2021**, 934, 121661.
- (f) Hong, D. J.; Zhu, X. C.; Wang, S. W.; Wei, Y.; Zhou, S. L.; Huang, Z. M.; Zhu, S.; Wang, R. R.; Yue, W. R.; Mu, X. L. Synthesis, characterization, and reactivity of dinuclear organo-rare-earth metal alkyl complexes supported by 2-amidate functionalized indolyl ligands: substituent effects on coordination and reactivity. *Dalton Trans.* **2019**, 48, 5230–5242.
- (g) Wei, Y.; Song, L. L.; Jiang, L.; Huang, Z. M.; Wang, S. W.; Yuan, Q. B.; Mu, X. L.; Zhu, X. C.; Zhou, S. L. Aluminum complexes with Schiff base bridged bis(indolyl) ligands: synthesis, structure, and catalytic activity for polymerization of *rac*-lactide. *Dalton Trans.* **2019**, 48, 15290–15299.
- (h) Feng, Z. J.; Huang, Z. M.; Wang, S. W.; Wei, Y.; Zhou, S. L.; Zhu, X. C. Synthesis and characterization of 2-*t*-butylimino-functionalized indolyl rare-earth metal amido complexes for the catalytic addition of terminal alkynes to carbodiimides: the dimeric complexes with the alkynide species in the $\mu\text{-}\eta^1\text{:}\eta^2$ bonding modes. *Dalton Trans.* **2019**, 48, 11094–11102.
- (8) (a) Guo, L. P.; Zhu, X. C.; Zhang, G. C.; Wei, Y.; Ning, L. X.; Zhou, S. L.; Feng, Z. J.; Wang, S. W.; Mu, X. L.; Chen, J.; Jiang, Y. Z. Synthesis and characterization of organo-rare-earth metal monoalkyl complexes supported by carbon σ -bonded indolyl ligands: high specific isoprene 1,4-*cis* polymerization catalysts. *Inorg. Chem.* **2015**, 54, 5725–5731.
- (b) Guo, L. P.; Wang, S. W.; Wei, Y.; Zhou, S. L.; Zhu, X. C.; Mu, X. L. Reactivity of 1,3-disubstituted indoles with lithium compounds: substituents and solvents effects on coordination and reactivity of resulting 1,3-disubstituted-2-indolyl lithium complexes. *Inorg. Chem.* **2017**, 56, 6197–6207.
- (9) (a) Wenkert, E.; Udelhofen, J. H.; Bhattacharyya, N. K. 3-Hydroxymethyleneoxindole and its derivatives. *J. Am. Chem. Soc.* **1959**, 81, 3763–3768.
- (b) Zheng, C.; Lu, Y.; Zhang, J.; Chen, X.; Chai, Z.; Ma, W.; Zhao, G. The enantioselective, organocatalyzed Diels-Alder reaction of 2-vinylindoles with α , β -unsaturated aldehydes: an efficient route to functionalized tetrahydrocarbazoles. *Chem. Eur. J.* **2010**, 16, 5853–5857.
- (c) Kalir, A.; Szara, S. Synthesis of 1-benzyltryptamine. *J. Med. Chem.* **1966**, 9, 793–794.
- (10) Sheldrick, G. M. *SADABS: Program for Empirical Absorption Correction of Area Detector Data*. University of Göttingen, Germany **1996**.
- (11) Sheldrick, G. M. *SHELXTL 5.10 for Windows NT: Structure Determination Software Programs*, Bruker Analytical X-ray Systems, Inc., Madison, WI **1997**.
- (12) Wang, D.; Cui, D. M.; Miao, W.; Li, S. H.; Huang, B. T. Rare earth metal complexes bearing thiophene amido ligand: synthesis and structural characterization. *Dalton Trans.* **2007**, 4576–4581.
- (13) Luconi, L.; Lyubov, D. M.; Bianchini, C.; Rossin, A.; Faggi, C.; Fukin, G. K.; Cherkasov, A. V.; Shavyrin, A. S.; Trifonov, A. A.; Giambastiani, G. Yttrium-amidopyridinate complexes: synthesis and characterization of yttrium-alkyl and yttrium-hydrido derivatives. *Eur. J. Inorg. Chem.* **2010**, 608–620.
- (14) Shannon, R. D. Revised effective ionic radii and systematic studied of interatomic distances in halides and chalcogenides. *Acta Cryst.* **1976**, A32, 751–767.
- (15) Hayes, P.; Piers, W.; Parvez, M. Cationic organoscandium β -dikediminato chemistry: arene exchange kinetics in solvent separated ion pairs. *J. Am. Chem. Soc.* **2003**, 125, 5622–5623.