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## Synthesis, characterization and reactivity of dinuclear organorare-earth metal alkyl complexes supported by 2-amidatefunctionalized indolyl ligands: substituent effects on coordination and reactivity

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Two series of new dinuclear organo-rare-earth metal alkyl complexes supported by 2-amidate functionalized indolyl ligands in different hapticities were synthesized and characterized. Treatment of  $[RE(CH_2SiMe_3)_3(THF)_2]$  with 1 equiv of 2- $(2,6^{-i}Pr_2C_6H_3NHC=O)C_8H_5NH(H_2L^1)$  and 2- $(2^{-i}BuC_6H_4NHC=O)C_8H_5NH(H_2L^2)$  in toluene gave the dinuclear organo-rare-earth metal alkyl complexes { $[\eta^1:(\mu_2-\eta^1:\eta^1)-L^1]RE(CH_2SiMe_3)(THF)_2$ } [RE = Gd(1a), Dy(1b), Y(1c), Er(1d), Yb(1e)] and { $[\eta^1:(\mu_2-\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:\eta^1:q^1-L^2]RE(CH_2SiMe_3)(THF)_2$ } [RE = Gd(2a), Dy(2b), Y(2c), Er(2d), Yb(2e)] in good yields. When [RE(CH\_2SiMe\_3)\_3(THF)\_2] were treated with 2 equiv of  $H_2L^1$  or  $H_2L^2$  in THF, the dinuclear organo-rare-earth metal complexes { $(\eta^1:\eta^1:\eta^1-HL)[\eta^1:(\mu_2-\eta^1:\eta^1):\eta^1-L]RE(THF)_2$  (1ca: RE = Y, L = L<sup>1</sup>; 2ea: RE = Yb, L = L<sup>2</sup>) were obtained. The complexes could react with small organic molecules such as N, N'-diisopropylcarbodiimide (DIC), phenylisocyanate, N-methylallylamine, phenylacetylene, pyridine, N-phenylimidazole or 4-dimethylaminopyridine (DMAP) to give a series of new complexes with findings of different reactivity patterns with reported rare-earth metal alkyl complexes. In the presence of co-catalysts, the dinuclear organo-rare-earth metal alkyl complexes could initiate the isoprene polymerization with a high activity (100% conversion of 2000 equiv of isoprene in 12 h) producing polymers with high regioselectivity (1,4- polymers up to 96.1%).

## Introduction

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Indole and its derivatives, as an alternative indenyl ligand, have been proverbially used in transition organometallic chemistry with findings of various hapticity modes such as  $\eta^1$ ,  $\eta^2$ ,  $\eta^3$ ,  $\eta^5$ ,  $\eta^6$ , etc, and high active catalysts for small molecules transformations.<sup>1-5</sup> Recently, we developed several kinds of rare-earth metal mononuclear and dinuclear complexes bearing different functionalized indolyl ligands with findings of new bonding modes of the ligands with rare-earth metal

centers and different kind of high efficient and high regio- and stereoselectively isoprene polymerization catalysts.<sup>4-6</sup> In addition, there were other very valid amidate ligands derived from amides, which were found plenty of coordination chemistry including monodentate: *O*-bond or *N*-bond with metal center,<sup>7</sup> bridging modes,<sup>8</sup> and chelating forms,<sup>9-10</sup> resulting in different kinds of complexes. These complexes supported by the amidate ligands were found to display good catalytic activity for norbornene polymerization,<sup>11</sup> three-component Strecker reaction<sup>12</sup> and symmetric intermolecular Heck Reaction,<sup>13</sup> hydroboration of unactivated imines and nitriles,<sup>14</sup> etc.

The synthesis of complexes supported by amidate ligands has been developed through isocyanate insertion reaction,<sup>9d,15</sup> single electron reductive coupling reaction<sup>16</sup> and direct reaction of amidate ligands with metal complexes.<sup>17</sup> Although the chemistry of transition metal complexes with amidate ligands was well developed, apart from those of derived from insertion reaction of corresponding compounds with isocyanates, the chemistry of rare-earth metal complexes with target amidate ligands is far less be documented.<sup>15a-b,18</sup> To integrate the multiple hapticitic capabilities of both indolyl and amidate ligands, and as our continuous interest in designing multinuclear catalysts,<sup>4-6</sup> the 2-amido functionalized indolyl compounds were designed and synthesized as pro-ligands,

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Electronic Supplementary Information (ESI) available: CCDC Nos 1574045-1574047 for 1a-1c; 1574048-1574050 for 1ca-1cc; 1574051-1574052 for 1d-1e; 1574053-1574058 for 1ea-1ef; 1574059-1574063 for 2a-2e; 1574064-1574065 for 2ea-2eb; 1574066 for 3a contain the supplementary crystallographic data for this paper. be obtained free These data can of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033. NMR spectra for characterization of the new ligands of  $H_2L^1$ ,  $H_2L^2$ , complexes 1c, 1cb and 1cc (PDF). See DOI: 10.1039/x0xx00000x

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which interacted with rare-earth metal alkyls  $RE(CH_2SiMe_3)_3(THF)_x$ , producing different ligated rare-earth metal complexes depending on substituents on the amides. The catalytic activity of these complexes in the presence of co-catalysts, and their reactivity toward small organic molecules were investigated with findings of different activities from those reported in the literatures.<sup>19</sup> In this paper, we will report the results.

#### **Results and discussion**

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Synthesis and characterization of organo-rare-earth metal alkyl complexes supported by 2-amidate indolyl ligands. The proligands  $H_2L^1$  and  $H_2L^2$  can be obtained by the reactions of the appropriate carbonyl chlorides with corresponding amines in 90% yields. The pro-ligands were fully characterized by spectroscopic methods and HR-MS analyses. Treatment of  $[RE(CH_2SiMe_3)_3(THF)_2]$  with 1 equiv of  $H_2L^1$  and  $H_2L^2$  in toluene gave the dinuclear organo-rare-earth metal alkyl complexes 1a-1e and 2a-2e in good yields (Scheme 1). All the dinuclear organo-rare-earth metal alkyl complexes 1a-1e and 2a-2e were fully characterized by spectroscopic methods, elemental analyses, and the structures of these complexes were determined by single-crystal X-ray diffraction. <sup>1</sup>H NMR spectra showed the signals centered at -0.34 ppm which can be assigned to the resonances of the protons of the -CH<sub>2</sub>- group of the trimethyl<br/>silylmethyl group for complex  $\mathbf{1c}$  in  $C_6 D_6$  at 25 °C. The signals centered at 165.6 ppm in <sup>13</sup>C NMR spectra were assigned to the resonances of the carbon atoms of the amidate group, the signals centered at 25.1 ppm were assigned to the resonances of the carbon atoms of the trimethylsilylmethyl group coupled to the yttrium nucleus with  $J_{\rm Y-C} = 50 \, {\rm Hz}.$ 

X-ray analyses revealed that the indole units and the amides groups of  $H_2L^1$  or  $H_2L^2$  were deprotonated by the metal alkyl CH<sub>2</sub>SiMe<sub>3</sub> moiety, affording a dianionic species that bridges two rare-earth metal alkyl units in  $\eta^1:(\mu_2-\eta^1:\eta^1)$  or  $\eta^1:(\mu_2-\eta^1:\eta^1):\eta^1$  bonding modes forming the dinuclear organo-rareearth metal alkyl complexes with central symmetry (Figure 1 and Figure 2), in which the oxygen atoms of the ligands adopted  $\mu_2$  bonding modes coordinated with two metal centers. The central metals of the complexes 1a-1e



Scheme 1. Synthesis of the dinuclear complexes 1a-1e and 2a-2e.



**Figure 1.** Representative ortep diagram of complexes **1a-1e**. Thermal ellipsoids are set at 30% probability level. All hydrogen atoms and Dipp (2,6-diisopropylphenyl) groups on N2 and N2(i) are omitted for clarity.



**Figure 2.** Representative ortep diagram of complexes **2a-2e**. Thermal ellipsoids are set at 30% probability level. All hydrogen atoms and  $o^{-t}BuC_6H_4$  groups on N2 and N2(i) are omitted for clarity.

coordinated by the carbon atom of the trimethylsilylmethyl group CH<sub>2</sub>SiMe<sub>3</sub> and the nitrogen atom of indolyl moiety and the oxygen atom of amidate group and the oxygen atoms of THF adopting a six-coordinate distorted octahedral geometry. While in the complexes **2a-2e**, the amidate fragments of the ligands adopted the chelate motifs with the oxygen atoms taking bridged coordination modes, while the nitrogen atoms of the amidate group coordinated to one of rare-earth metal ions. This coordination mode is different from those found in complexes **1a-1e**, and those found in the literatures with comparison the distances of the nitrogen atom of the amidate to central metal ion.<sup>20</sup> These results suggest that substituents on the nitrogen atom of the amidate group can make a significant influence on the coordination modes of the amidate motifs with the central rare-earth metal.

From Table 1, it was found that the bond lengths of RE-C<sub>CH2SiMe3</sub>, RE-N1 and RE-O1 in complexes **1a-1e** and **2a-2e** are decreased as ionic radii decrease from  $Gd^{3+}$  to  $Yb^{3+}$ , these results are in good agreement with the lanthanide contraction. The distances of RE1-N2(i) [3.004(3) Å for **1a**, 3.051(4) Å for **1b**, 3.069(6) Å for **1c**, 3.089(4) Å for **1d**, 3.176(4) Å for **1e**], found in complexes **1a-1e** are significantly longer than the Published on 08 March 2019. Downloaded on 3/12/2019 3:46:56 AM.

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Table 1. Selected bond lengths (Å) and angles (°) of complexes1a-1e and 2a-2e.

	1a	1b	1c	1d	1e
RE1-01	2.298(3)	2.284(3)	2.269(4)	2.259(3)	2.237(2)
RE1-N1	2.410(4)	2.371(4)	2.367(6)	2.331(5)	2.315(3)
RE1-N2(i) <sub>dist.</sub>	3.004(3)	3.051(4)	3.069(6)	3.089(4)	3.176(4)
RE1-C22	2.416(7)	2.388(8)	2.376(6)	2.367(7)	2.326(5)
C9-O1	1.338(5)	1.333(6)	1.336(7)	1.330(6)	1.347(4)
C9-N2	1.283(6)	1.276(7)	1.298(8)	1.283(6)	1.262(5)
N1-RE1-O1	66.59(12)	67.23(13)	67.97(17)	68.61(15)	70.02(10)
N2-C9-O1	116.1(4)	116.1(5)	115.0(6)	116.9(5)	117.6(3)
	<b>a</b> .	-	-	~ .	-
	Za	26	2c	2d	2e
RE1-01	<b>za</b> 2.324(2)	2 <b>b</b> 2.297(2)	2c 2.279(2)	2d 2.271(2)	2e 2.254(4)
RE1-O1 RE1-N1	2a 2.324(2) 2.398(3)	2b 2.297(2) 2.364(2)	2c 2.279(2) 2.367(2)	2d 2.271(2) 2.341(3)	2e 2.254(4) 2.304(6)
RE1-O1 RE1-N1 RE1-N2(i)	2a 2.324(2) 2.398(3) 2.770(3)	2b 2.297(2) 2.364(2) 2.783(2)	2c 2.279(2) 2.367(2) 2.790(2)	2d 2.271(2) 2.341(3) 2.811(3)	2e 2.254(4) 2.304(6) 2.888(6)
RE1-O1 RE1-N1 RE1-N2(i) RE1-C20	2.324(2) 2.398(3) 2.770(3) 2.424(4)	2b 2.297(2) 2.364(2) 2.783(2) 2.413(3)	2c 2.279(2) 2.367(2) 2.790(2) 2.412(3)	2d 2.271(2) 2.341(3) 2.811(3) 2.395(4)	2e 2.254(4) 2.304(6) 2.888(6) 2.346(9)
RE1-O1 RE1-N1 RE1-N2(i) RE1-C20 C9-O1	2a 2.324(2) 2.398(3) 2.770(3) 2.424(4) 1.320(4)	2b 2.297(2) 2.364(2) 2.783(2) 2.413(3) 1.333(4)	2c 2.279(2) 2.367(2) 2.790(2) 2.412(3) 1.324(3)	2d 2.271(2) 2.341(3) 2.811(3) 2.395(4) 1.329(4)	2e 2.254(4) 2.304(6) 2.888(6) 2.346(9) 1.320(9)
RE1-O1 RE1-N1 RE1-N2(i) RE1-C20 C9-O1 C9-N2	2a 2.324(2) 2.398(3) 2.770(3) 2.424(4) 1.320(4) 1.292(4)	2b 2.297(2) 2.364(2) 2.783(2) 2.413(3) 1.333(4) 1.288(3)	2c 2.279(2) 2.367(2) 2.790(2) 2.412(3) 1.324(3) 1.288(3)	2d 2.271(2) 2.341(3) 2.811(3) 2.395(4) 1.329(4) 1.287(4)	2e 2.254(4) 2.304(6) 2.888(6) 2.346(9) 1.320(9) 1.298(9)
RE1-O1 RE1-N1 RE1-N2(i) RE1-C20 C9-O1 C9-N2 N1-RE1-O1	2a 2.324(2) 2.398(3) 2.770(3) 2.424(4) 1.320(4) 1.292(4) 66.39(9)	2b 2.297(2) 2.364(2) 2.783(2) 2.413(3) 1.333(4) 1.288(3) 67.07(7)	2c 2.279(2) 2.367(2) 2.790(2) 2.412(3) 1.324(3) 1.288(3) 67.43(7)	2d 2.271(2) 2.341(3) 2.811(3) 2.395(4) 1.329(4) 1.287(4) 67.75(8)	2e 2.254(4) 2.304(6) 2.888(6) 2.346(9) 1.320(9) 1.298(9) 68.3(2)
RE1-O1 RE1-N1 RE1-N2(i) RE1-C20 C9-O1 C9-N2 N1-RE1-O1 N2-C9-O1	23 2.324(2) 2.398(3) 2.770(3) 2.424(4) 1.320(4) 1.292(4) 66.39(9) 114.4(3)	2b 2.297(2) 2.364(2) 2.783(2) 2.413(3) 1.333(4) 1.288(3) 67.07(7) 114.5(3)	2c 2.279(2) 2.367(2) 2.790(2) 2.412(3) 1.324(3) 1.288(3) 67.43(7) 114.5(3)	2d 2.271(2) 2.341(3) 2.811(3) 2.395(4) 1.329(4) 1.287(4) 67.75(8) 114.6(3)	2e 2.254(4) 2.304(6) 2.888(6) 2.346(9) 1.320(9) 1.298(9) 68.3(2) 114.6(7)

corresponding bond lengths of RE1-N2(i) [2.770(3) Å for 2a, 2.783(2) Å for 2b, 2.790(2) Å for 2c, 2.811(3) Å for 2d, 2.888(6) Å for 2e], which are also significantly longer than those found in  $\{LY[N(SiMe_3)_2] \cdot THF\}_2$  ( $H_2L = N, N'$ -(cyclohexane-1,2-diyl)bis(4tert-butylbenzamide), 2.443(6) Å)<sup>20a</sup>, {LYb[N(SiMe<sub>3</sub>)<sub>2</sub>]·THF}<sub>2</sub>  $(H_2L = N, N' - (cyclohexane - 1, 2 - diyl)bis(4 - tert - butylbenzamide),$ 2.405(5) Å)<sup>20b</sup>,  $[Yb_3L_6] \cdot 2C_7H_8$  (L = 2,6-<sup>*i*</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NC(O)Ph, 2.443(4) Å, 2.445(5) Å, 2.493(4) Å)  $^{20c}$  indicating substituents on the amidate motifs have a great effect on bond length. It is also found that the distances and bond lengths of RE1-N2(i) in complexes 1 and 2 increased as the ionic radii decreased from Gd<sup>3+</sup> to Yb<sup>3+</sup>, indicating that the steric effects increase will result in the weak interactions between N2 and the rare-earth metal as the ionic radii decrease. The steric effects not only have influence on the bond lengths of the RE-X [X = O1, N2], but also have an impact on the C-O, C-N bond lengths and the O-C-N angles of the amidate motifs. For example, the C-O bond lengths in 1 are generally longer than those found in 2, while the C-N bond distances in 1 are generally shorter than those found in 2. These results indicated that the O-C-N moieties in 2 are more delocalized than those in 1. It is found that the O-C-N angles of 115.0(6)° to 117.6(3)° found in 1 from gadolinium to ytterbium complexes are larger than the angles of 114.4(3)° to 114.6(7)° found in 2. The O-C-N angles found in 2 are very close to the chelate form found in the tantalum amidate complexes (average  $113.5(2)^{\circ}$ ),<sup>21</sup> they are also close to the angles found in the bridged bis(amidate) rare-earth metal amides (average  $115.5(4)^{\circ}$ ).<sup>20</sup> The results of C-O, C-N bond lengths and RE1-N2(i) distances and the O-C-N angles suggested that the amidate moieties in complexes 2 take the chelate coordination sphere having oxygen atom adopted bridge form with the rare-earth metals. The O-C-N angles found in 1 fall between that 127.34(18)° found in the monodentate amidate ligated tantalum complex<sup>21</sup> and those found in 2.

In order to investigate the effect of the coordination environment on the bonding modes of the amidate with the central metals, different ratio reactions of  $H_2L^1$  or  $H_2L^2$  with  $[RE(CH_2SiMe_3)_3(THF)_2]$  were carried out. Treatment of  $[RE(CH_2SiMe_3)_3(THF)_2]$  with 2 equiv of  $H_2L^1$  or  $H_2L^2$  in THF produced the dinuclear organo-rare-earth metal complexes **1ca** and **2ea** in good yields (Scheme 2). They were fully

characterized by spectroscopic methods, elemental analyses, and X-ray crystallographic analyses. X-rage and X-ray crystallographic analyses. The rage and the X-ray crystallographic analyses. X-rage and X-ray crystallographic analyses. X-rage and X-ray crystallographic analyses. The rage and the X-Ray crystallographic analyses and the X-ray crystallographic analyses. X-rage and X-ray crystallographic analyses and the X-ray crystallographic analyses. X-rage and X-ray crystallographic analyses and the X-ray crystallographic analyses and the X-ray crystallographic analyses. X-rage and X-ray crystallographic analyses and the X-ray crystallographic analyses analyses and the X-ray crystallographic analyses and







**Figure 3**. ORTEP diagram of complex **1ca**. Thermal ellipsoids are set at 30% probability level. All hydrogen atoms and Dipp groups on N2 and N2(i) are omitted for clarity.



**Figure 4**. ORTEP diagram of complex **2ea**. Thermal ellipsoids are set at 30% probability level. All hydrogen atoms and  $o^{-t}BuC_6H_4$  groups on N2 and N2(i) are omitted for clarity.

**Reactivity study**. With above new alkyl complexes in hand, their reactivity properties towards small molecules were explored firstly. Fortunately, several definite results were obtained (Scheme 3). The reaction of complex **1c** with 2 equiv

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Table 2. Selected bond lengths (Å) and angles (°) of complexes 1ca and 2ea.

	1ca		2ea
Y1-N1	2.345(3)	Yb1-N1	2.319(6)
Y1-N2(i)	2.650(3)	Yb1-N2(i)	2.534(6)
Y1-N3	2.340(3)	Yb1-N3	2.307(6)
Y1-01	2.307(2)	Yb1-O1	2.268(4)
Y1-O1(i)	2.316(2)	Yb1-O1(i)	2.328(4)
Y1-02	2.332(3)	Yb1-O2	2.247(4)
C9-O1	1.321(4)	C9-O1	1.328(8)
C9-N2	1.290(5)	C9-N2	1.286(8)
C30-O2	1.274(5)	C28-O2	1.275(10)
C30-N4	1.331(5)	C28-N4	1.329(9)
N2-C9-O1	114.8(3)	N2-C9-O1	113.6(6)
N4-C30-O2	120.8(4)	N4-C28-O2	121.5(7)

(diisopropylcarbodiimide) of DIC in toluene at room temperature took place rapidly. Bis(amidinate)-ligated complex 1cb (Scheme 3), formed through carbodiimide insertion into the  $Y\text{-}C_{\text{CH2SiMe3}}$  bonds in  $\textbf{1c,}^{22}$  was isolated as a white crystalline solid in 33% yield from a mixture of THF/nhexane solution at -30 °C. The reaction of complex 2e with 2 equiv of phenylisocyanate in toluene at room temperature afforded the bis(amidate) ligated complex 2eb (Scheme 3) as a red crystalline solid in 48% yield through isocyanate insertion into the Yb- $C_{CH2SiMe3}$  bonds in **2e**.<sup>10</sup> The molecular structures of 1cb and 2eb are given in Figure S39 and Figure S53 in the ESI. From the structural data of 1cb and 2eb, it can be concluded that the amidate motifs connected to the indolyl rings adopted the same coordination forms as those found in 1c and 2e, respectively. While the amidate moiety in 2eb formed through insertion reaction took the chelate form bonded with the central metals. Then, the reactivities of the above alkyl complexes with secondary amine bearing C=C double bond and the terminal alkyne with sp C-H bond were examined. The reaction of complex 1c with 2 equiv of N-methylallylamine in toluene at ambient temperature was found to form the allyl amido complex via N-H activation (Scheme 3, Figure S40 in ESI). This observation is different from those of the reactions of group IV metal complexes with N-methylallylamine, which produced the azabutadiene complex via activation of the N-H bond and C-H bond neighbour to the nitrogen atom.<sup>23</sup> This difference could be attributed to the steric bulky in 1c which prevents the C=C double bond from the central metal. The

reaction of phenylacetylene with 1e, Which 1976 Rec 5075 terminal bonding alkynyl ytterbium complex 1ea (Scheme 3, Figure S41 in ESI). This terminal bonding mode is different from the mostly reported alkynyl rare-earth metal complexes in which alkynyl adopted bridged bonding mode,<sup>24</sup> indicating steric effects of the ligands. It has been reported that rareearth metal alkyl complexes can react with pyridine or imidazole derivatives to produce the C-H activation products,<sup>19,25</sup> however, when complex **1e** was treated with 2 equiv of pyridine or N-phenylimidazole afforded the ligands

exchange products 1eb and 1ec (Scheme 3), no C-H bond

activation was observed as reported in literatures.<sup>25</sup> These

results can be attributed to ligands steric effects which prevent

the C-H bond of the pyridine or N-phenylimidazole from

interaction with the alkyl groups of the complexes, and the

activity of the alkyl groups may also be responsible for the

results. The molecular structures of 1eb and 1ec are given in

Figure S42 and Figure S43 in the ESI. From the structural data

of all the above reactions produced complexes 1cb, 1cc, 1ea,

1eb, 1ec, and 2eb, it was found that the amidate motifs

adopted O bridged ligation when the Ar is 2,6-

diisopropylphenyl, and the amidate moiety took the chelate

When 1e was treated with 4 equiv of DMAP in THF at room

temperature for 3 h to give the only ligands exchange product

1ed (Scheme 4, Path A). Complex 1ed could also be

synthesized by treatment of 3a (X-ray identified) with 1 equiv

of  $H_2L^1$  in toluene at room temperature (Scheme 4, Path B), no

C-H bond activation was found from the two synthetic paths,

which is different from the reported reactivities of the earth

metal alkyl complexes with pyridine.<sup>25</sup> It is worth mentioning

that the -CH<sub>2</sub>SiMe<sub>3</sub> group lied in an equatorial position of the

distorted octahedral geometry in complex 1e, but it was

changed to the axial position in complex 1ed. This result

suggested that the strong donor ligand DMAP could change

the coordination geometry of the rare-earth metal complex.

The molecular structures of 3a and 1ed are given in Figure S54

form with O bridge ligation when the Ar is 2-tert-butylphenyl.

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#### Scheme 4. Synthesis of complexes 1ed-1ef.

N-methylimidazole or N-benzylimidazole instead of DMAP was used to treat with Yb(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> firstly followed by treatment with  $H_2L^1$ , the non-centrosymmetrical complexes 1ee and 1ef were isolated (Figure 5 for 1ee). Again, no C-H bond activation was found from the two synthetic reaction processes. From the structural data, it was found that the two metal centers have different coordination sphere, one of Yb<sup>3+</sup> ion was coordinated by two N atoms of the indolyl moiety, two O atoms of the bridged amidate groups, three N atoms of the imidazole ligands. Another Yb<sup>3+</sup> ion was coordinated by two amidate groups in chelated form, one O atom of the amidate group, one N atom of the indolyl ring, one N atom of the imidazole ring. It is also found that the amidate groups also adopted different coordination modes with the central metals, two amidate groups took chelate form with O bridged two metal centers, the other amidate group only has the O atom bonded with metal center. The molecular structure of  ${\bf 1ef}$  is given in Figure S46 in the ESI. All complexes mentioned above can be stored as solids for months without any indication of decomposition under inert conditions, but they decompose immediately in the presence of oxygen or atmospheric moisture.



**Figure 5**. ORTEP diagram of complex **1ee**. Thermal ellipsoids are set at 30% probability level. All hydrogen atoms and Dipp group on N2 and N4 are omitted for clarity.

**Catalytic activities of the dinuclear organ-rare-earth alkyl complexes towards isoprene polymerization.** As reported, the mono- and dinuclear organo-rare-earth alkyl complexes exhibited an excellent catalytic activity for isoprene polymerization in the presence of cocatalyst.<sup>4-6</sup> With the above new dinuclear organ-rare-earth alkyl complexes in hand, their catalytic activities for the isoprene polymerization were investigated. Representative data are summarized in Table 3 and Table 4.

None of the above dinuclear organ-rare-earth alkyl complexes alone could initiate the polymerization of isoprene, and the binary systems of complexes/AlR<sub>3</sub> or complexes/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] also could not catalyze the isoprene polymerization. Fortunately, the ternary systems of complexes/[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]/AlR<sub>3</sub> could initiate the isoprene polymerization.

The data in Table 3 are the representative results of polymerization of isoprene based on complexes 1a-1e as pre-The catalysts. ternary systems of complex/ $[Ph_3C][B(C_6F_5)_4]/AIR_3$  could not initiate the isoprene polymerization when the AIR<sub>3</sub> is AIMe<sub>3</sub> or AIEt<sub>3</sub> (Table 3, entries 1 and 2). The ternary system complex/[Ph<sub>3</sub>C][B( $C_6F_5$ )<sub>4</sub>]/Al'Bu<sub>3</sub> could polymerize the isoprene in chlorobenzene, but the polymerization did not happen in other solvents such as toluene or dichloromethane (Table 3, entries 5 and 6). With lengthening the polymerization time, the 1,4-content and the molecular weight were increased (Table 3, Entries 3 and 4). The 1,4-content and the molecular weight of polymers decreased when the [PhMe<sub>2</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was used as co-catalyst instead of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (Table 3, comparison the data of entries 4 and 7). It is found that the metal centers have a great influence on the activity and regioselectivity of the ternary catalyst systems (Table 3, entries 4, 10, 11, 13 and 14). With decrease of the ionic radii of the central metal ions, the catalytic activity, 1,4- content and the molecular weight were decreased, but the Gd analogue was abnormal, which made the variation trend look like a parabola. Unfortunately, ytterbium analogue 1e showed no catalytic

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activity for the isoprene polymerization under the same reported, which is probably due to the  $Yb^{3+}/Yb^{2+}$  redox activity for the isoprene polymerization under the same conditions. This result is consistent with previously literature in the presence of aluminum alkyls.<sup>4-6,26</sup> DOI: 10.1039/C9DT00507B

Та	<b>ble 3</b> . Re	presentative da	ta of polyme	rization of i	soprene b	ased on compl	exes <b>1a-1e</b> a	is pre-catalys	ts <sup>a</sup>	
	Entry	Cat.(Sol.)	[IP]/[Cat. ]	AIR <sub>3</sub>	t(h)	Conv.(%) <sup>b</sup>	Str 1,4	ucture <sup>c</sup> 3,4	— Mn <sup>d</sup> (×10 <sup>-4</sup> )	$PDI^d$
	1	<b>1b</b> (C <sub>6</sub> H <sub>5</sub> Cl)	500:1	AlMe₃	12	0	/	/	/	/
	2	<b>1b</b> (C <sub>6</sub> H₅Cl)	500:1	AlEt <sub>3</sub>	12	0	/	/	/	/
	3	<b>1b</b> (C <sub>6</sub> H <sub>5</sub> Cl)	500:1	Al <sup>′</sup> Bu₃	6	100	77.4	22.6	25.3	1.68
	4	$1b(C_6H_5CI)$	500:1	Al <sup>′</sup> Bu₃	12	100	88.6	11.4	36.8	1.67
	5	<b>1b</b> (toluene)	500:1	Al <sup>′</sup> Bu₃	12	0	/	/	/	/
	6	<b>1b</b> (DCM)	500:1	Al <sup>′</sup> Bu₃	12	0	/	/	/	/
	7 <sup>e</sup>	<b>1b</b> (C <sub>6</sub> H <sub>5</sub> Cl)	500:1	Al <sup>′</sup> Bu₃	12	100	76.9	23.1	33.9	1.68
	8	<b>1b</b> (C <sub>6</sub> H₅Cl)	1000:1	Al <sup>′</sup> Bu₃	12	100	74.3	25.7	26.0	1.82
	9	<b>1b</b> (C <sub>6</sub> H₅Cl)	2000:1	Al <sup>′</sup> Bu₃	12	100	68.8	31.2	48.3	1.90
	10	1a(C <sub>6</sub> H₅Cl)	500:1	Al <sup>′</sup> Bu₃	12	100	75.3	24.7	25.2	1.91
	11	1c(C <sub>6</sub> H₅Cl)	500:1	Al <sup>′</sup> Bu₃	12	100	78.1	21.9	31.2	1.47
	12	1c(C <sub>6</sub> H₅Cl)	1000:1	Al <sup>′</sup> Bu₃	12	66	77.8	22.2	35.5	1.95
	13	$1d(C_6H_5CI)$	500:1	Al <sup>i</sup> Bu₃	12	45	77.2	22.8	16.7	1.32
	1/	10(C-H-CI)	500.1		12	Ο	/	/	1	1

<sup>*a*</sup>General conditions: [Cat.] = 10  $\mu$ mol, [Cat.]:[Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]:[AlR<sub>3</sub>] = 1:1:2, room temperature, Vol(IP):Vol(Sol.) = 1:10, charging sequence: [Cat.], [B], [AI], [IP]. <sup>*b*</sup>Determined by the weight of polymer materials in comparison with that of monomer. <sup>*c*</sup>Determined by <sup>1</sup>H and <sup>13</sup>C NMR spectrosocopy in CDCl<sub>3</sub>. <sup>*d*</sup>Determined by means of GPC against polystyrene standards in THF at 35 °C, PDI = polydispersity index. <sup>*e*</sup>[B] = [PhMe<sub>2</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].

Table 4. Representative data of polymerization of isoprene based on complexes 2a-2e as pre-catalysts<sup>a</sup>

Entry	Cat (Sol.)			t(h)	$Conv (\%)^b$	Structure <sup>c</sup>		$Mn^{d}(x10^{-4})$	
Littiy	Cat.(501.)		Anglequiv	(II)	CONV.(70)	1,4	3,4	Will (×10 )	
1	2b(C <sub>6</sub> H₅Cl)	500:1	AlMe₃(5)	12	79	84.6	15.4	13.5	2.82
2	2b(C <sub>6</sub> H₅Cl)	500:1	AIMe <sub>3</sub> (20)	12	100	94.6	5.4	13.5	1.58
3	<b>2b</b> (toluene)	500:1	AIMe <sub>3</sub> (20)	12	100	96.1	3.9	8.5	1.57
4 <sup>e</sup>	2b(toluene)	500:1	AIMe <sub>3</sub> (20)	12	100	95.2	4.8	8.1	1.55
5	2b(toluene)	1000:1	AIMe <sub>3</sub> (20)	12	100	95.6	4.4	9.4	2.84
6	2b(toluene)	1500:1	AIMe <sub>3</sub> (20)	12	100	94.8	5.2	12.9	1.99
7	2a(toluene)	500:1	AIMe <sub>3</sub> (20)	12	79	94.8	5.2	8.4	2.26
8	2b(C <sub>6</sub> H₅Cl)	500:1	AlEt <sub>3</sub> (5)	12	99	85.3	14.7	18.5	1.77
9	2b(toluene)	500:1	AlEt <sub>3</sub> (5)	12	99	86.7	13.3	6.2	1.73
$10^{e}$	2b(toluene)	500:1	AlEt <sub>3</sub> (5)	12	100	89.4	10.6	8.1	2.50
$11^e$	2b(toluene)	1000:1	AlEt <sub>3</sub> (5)	12	97	91.4	8.3	19.6	2.38
$12^e$	2b(toluene)	1500:1	AlEt <sub>3</sub> (5)	12	91	86.6	13.4	27.1	2.53
13 <sup>e</sup>	2c(toluene)	500:1	AlEt <sub>3</sub> (5)	12	99	87.5	12.5	4.2	2.28
$14^e$	2c(toluene)	1000:1	AlEt <sub>3</sub> (5)	12	93	82.0	18.0	13.9	3.16
$15^{e}$	2c(toluene)	1500:1	AlEt <sub>3</sub> (5)	12	95	84.9	15.1	19.5	2.51
16	2b(C <sub>6</sub> H₅Cl)	500:1	Al <sup>′</sup> Bu₃(5)	12	74	83.9	16.1	10.2	2.86
17	2b(toluene)	500:1	Al <sup>′</sup> Bu₃(5)	12	100	81.8	18.2	8.4	5.93
$18^e$	2b(C <sub>6</sub> H₅Cl)	500:1	Al <sup>′</sup> Bu₃(5)	12	31	78.2	21.8	12.9	2.08
19	2a(C <sub>6</sub> H₅Cl)	500:1	Al <sup>′</sup> Bu₃(5)	12	62	80.4	19.6	17.1	2.13
20	<b>2c</b> (C <sub>6</sub> H <sub>5</sub> Cl)	500:1	Al <sup>′</sup> Bu₃(5)	12	95	75.9	24.1	6.9	3.45

<sup>*a*</sup>General conditions: [Cat.] = 10  $\mu$ mol, [Cat.]: [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] = 1:1, room temperature, Vol(IP): Vol(Sol.) = 1:10, charging sequence: [Cat.], [B], [AI], [IP]. <sup>*b*</sup>Determined by the weight of polymer materials in comparison with that of monomer. <sup>*c*</sup>Determined by <sup>1</sup>H and <sup>13</sup>C NMR spectrosocopy in CDCl<sub>3</sub>. <sup>*d*</sup>Determined by means of GPC against polystyrene standards in THF at 35 °C, PDI = polydispersity index. <sup>*e*</sup>[B] = [PhMe<sub>2</sub>NH][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>].

Table 4 gave the representative results of polymerization of isoprene based on complexes **2a-2e** as pre-catalysts. It is found that they displayed prominent differences on catalytic activities on the isoprene polymerization from the complexes **1a-1e** did: (1) Different aluminum alkyls as co-catalysts could display activities for the isoprene polymerization for the series of complexes **2a-2e** (Table 4), while only Al<sup>i</sup>Bu<sub>3</sub> as co-catalyst displayed activity for the isoprene polymerization for the

complexes **1a-1e**. In case of different AlR<sub>3</sub> used in catalytic systems of **2a-2e**, 20 equiv of AlMe<sub>3</sub> were required for high conversion of monomer, only 5 equiv of AlEt<sub>3</sub> or Al<sup>i</sup>Bu<sub>3</sub> could reach the high conversion, but producing relatively low 1,4-regioselectivity polymers than those with AlMe<sub>3</sub> as the co-catalyst (Table 4); (2) Toluene and chlorobenzene are good solvents for the polymerization for the complexes **2a-2e** (Table 4), while only chlorobenzene can be solvent for the

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polymerization for the complexes 1a-1e; (3) The AlMe<sub>3</sub> is the best co-catalyst for the 1,4-regioselectively polymerization producing polymers having 1,4-regioselectivity as high as 96.1%. For complex **2b**, when the AlR<sub>3</sub> is AlMe<sub>3</sub>, decrease the ratio of [Cat.]/[AIMe<sub>3</sub>] resulted in the increase of 1,4-content of the polymers from 84.6% to 94.6%, and resulted in a narrow molecular weight distribution (Table 4, entries 1 and 2). The 1,4-regioselectivity is only slightly different when the polymerization was carried out in toluene or in chlorobenzene (Table 4, entries 2 and 3). The <sup>13</sup>C-int NMR spectra showed that the selectivity of the 1,4-cis-selectivity were significant enhanced from 37.8% in toluene to 58.6% in chlorobenzene (see ESI). This result is consistent with previously literature reported that the 1,4-cis-component is propitious to the coordination ability of solvents (the less coordinated solvent chlorobenzene vs toluene).<sup>27</sup> The borate  $[PhMe_2NH][B(C_6F_5)_4]$ and  $[Ph_3C][B(C_6F_5)_4]$  exhibited a similar activity for the polymerization producing polymers having very close 1,4regioselectivity and molecular weight (Table 4, entries 3 and 4). With increase of the ratio of [IP]/[Cat.], the 1,4-regioselectivity decreased and the molecular weight increased (Table 4, entries 3, 5 and 6 for complex 2b; and entries 13-15 for complex 2c). In comparison, the molecular weights of the polymers catalyzed by the series of complexes 1a-1e are significantly larger than those catalyzed by the series of complexes 2a-2e. Make a comprehensive survey of the data showed in Table 3 and Table 4, the different substituent groups on ligands make a different bonding mode between complexes 1a-1e and 2a-2e, and thus result in differences on their catalytic activities for isoprene polymerization.

#### Conclusions

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In summary, 2-amidate functionalized indolyl ligands were developed for the rare-earth metal chemistry. Reactions of these functionalized indolyl ligands with RE(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> produced the new dinuclear organo-rare-earth metal alkyl complexes with different coordination modes depending on the substituents. Study of the reactivities of the dinuclear organo-rare-earth metal alkyl complexes with small organic as *N*,*N*'-diisopropylcarbodiimide molecules such (DIC), N-methylallylamine, phenylacetylene, phenylisocyanate, pyridine, N-phenylimidazole or 4-dimethylaminopyridine (DMAP) resulted in findings of the reactivity differences from those of reported rare-earth metal alkyl complexes, indicating that ligands steric effects on the reactivities of the complexes. Study of the catalytic activity of these complexes indicated that these dinuclear organo-rare-earth metal alkyl complexes are good pre-catalysts for the isoprene polymerization upon activation with aluminum alkyls and borate producing polymers with an excellent regioselectivity (1,4-selectivity up to 96.1%) at room temperature. It is also found that substituents on the amidate group of the ligands in the complexes not only have influence on the coordination of ligands and reactivity of the complexes, but also have influence on their catalytic activity towards polymerization of isoprene in the presence of co-catalysts. This work implies that amidate functionalized electron-rich indolyl ligands might have universality as supporting ligands for 1000 struction 500f multinuclear organometallic complexes as catalysts for the regioselectively polymerization of olefins. Further work in this field is now in progress.

#### **Experiment Section**

General Procedures. All syntheses and manipulations of air- and moisture-sensitive materials were performed under a dry and oxygen free argon atmosphere using standard Schlenk techniques or in an argon-filled glovebox. All solvents such as THF, toluene and n-hexane were distilled over sodium benzophenone ketyl under argon prior to use unless otherwise noted. Dichloromethane and chlorobenzene were distilled over  $CaH_2$  under argon prior to use.  $B(C_6F_5)_3$ ,  $[Ph_3C][B(C_6F_5)_4]$ and  $[PhNMe_2H][B(C_6F_5)_4]$  were purchased from STREM and used as received. AIMe<sub>3</sub>, AIEt<sub>3</sub>, and Al'Bu<sub>3</sub> were purchased from Sigma-Aldrich, and used as received. Isoprene was purchased from TCI, dried with CaH<sub>2</sub>, and distilled over CaH<sub>2</sub> before use. Elemental analyses data were obtained on an Model Vario EL Series III elemental analyzer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for analyses of compounds were recorded on a Bruker Model AV-300 or AV-500 NMR spectrometer (300 or 500 MHz for <sup>1</sup>H; 75 or 125 MHz for <sup>13</sup>C) in  $C_6D_6$  or THF- $d_8$  for rare-earth metal complexes, in DMSO- $d_6$  for the ligands and in  $CDCI_3$  for polyisoprene. Chemical shifts ( $\delta$ ) were reported in ppm. J values were reported in Hertz. IR spectra were recorded on a Shimadzu Model FTIR-8400s spectrometer (KBr plate). HR-MS measurements were conducted with an Agilent model 6220-TOF mass spectrometer. Gel permeation chromatography (GPC) analyses of the polymer samples were carried out at 35 °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<sup>-1</sup>.

Preparation of 2-(2,6-<sup>*i*</sup> $Pr_2C_6H_3NHC=O$ )C<sub>8</sub>H<sub>5</sub>NH (H<sub>2</sub>L<sup>1</sup>). 1Hindole-2-carboxylic acid (8.06 g, 50.0 mmol) was dissolved in thionyl chloride (20.0 mL), and reacted for 4 h at 40 °C, then the excess thionyl chloride was evaported under reduced pressure to give the yellow powder product 1H-indole-2carbonyl chloride. Then 50.0 mL dry THF was added to flask to dissolve the yellow powder, and dry K<sub>2</sub>CO<sub>3</sub> (8.29 g, 60.0 mmol) as acid binding agent was added to give a yellow turbid mixture. The mixture was cooled with an ice-water bath with stirring. To the mixture was added a THF (20.0 mL) solution of 2,6-diisopropylaniline (9.75 g, 55.0 mmol) slowly. The mixture was stirred at 0 °C for 2 h. The solvent was evaported under reduced pressure, the residue was washed with ethyl acetate to give the product as a yellow solid (14.42 g, 90% yield based on 1*H*-indole-2-carboxylic acid). M. p.: 342 °C. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>, 25 °C): δ 11.73 (s, 1H, -NH-), 9.78 (s, 1H, -CONH-), 7.66 (d, J = 7.64 Hz, 1H, indole-Ar-H), 7.44 (d, J = 8.00 Hz, 1H, indole-Ar-H), 7.38 (s, 1H, indole-Ar-H), 7.32 (t, J = 7.50 Hz, 1H, indole-Ar-H), 7.22 (d, J = 7.50 Hz, 2H, Ar-H), 7.20 (s, 1H, indole-Ar-H), 7.07 (t, J = 7.50 Hz, 1H, Ar-H), 3.14 (m, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.15 (m, 12H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>,

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25 °C): δ 161.0 (-CONH-), 146.4 (indole-Ar-2-C), 136.7 (indole-Ar-3-C), 132.2, 131.4, 127.8, 127.2, 123.6, 123.0, 121.6, 120.0, 112.4, 103.2, 28.2 (CH(Me)<sub>2</sub>), 23.5 (CH<sub>3</sub>). HRMS (APCI) m/z calcd. for  $C_{21}H_{25}N_2O$  (M + H<sup>+</sup>): 321.1961. Found: 321.1960. IR (KBr plate, cm<sup>-1</sup>): v 3568 (w), 2964 (s), 2870 (m), 1643 (s), 1541 (s), 1498 (s), 1413 (s), 1384 (m), 1336 (m), 1307 (s),1240 (s), 1182 (m), 821 (m), 806 (m), 767 (m), 746 (s), 648 (m).

**Preparation of 2-(2-**<sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>NHC=O)C<sub>8</sub>H<sub>5</sub>NH (H<sub>2</sub>L<sup>2</sup>). A method similar to that for the preparation of compound  $H_2L^1$  was used, with 2-tert-Butylaniline (8.21 g, 55.0 mmol) to replace 2,6diisopropylaniline to give the product as a yellow solid (13.16 g, 90% yield based on 1*H*-indole-2-carboxylic acid). M. p.: 251 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, 25 °C): δ 11.70 (s, 1H, -N*H*-), 9.77 (s, 1H, -CONH-), 7.67 (d, J = 8.00 Hz, 1H, indole-Ar-H), 7.48-7.44 (m, 2H, Ar-H), 7.33 (s, 1H, indole-Ar-H), 7.31-7.28 (m, 2H, Ar-H), 7.22-7.17 (m, 2H, Ar-H), 7.06 (t, J = 7.50 Hz, 1H, Ar-H), 1.36 (s, 9H, -C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>, 25 °C): δ 160.9 (-CONH-), 147.3 (indole-Ar-2-C), 136.6 (indole-Ar-3-C), 135.6, 132.0, 131.8, 127.3, 127.2, 126.9, 126.5, 123.5, 121.6, 119.9, 112.4, 103.4, 35.0 (-CMe<sub>3</sub>), 30.9 (-C(CH<sub>3</sub>)<sub>3</sub>). HRMS (APCI) m/z calcd. for  $C_{19}H_{21}N_2O$  (M + H<sup>+</sup>): 293.1648. Found: 293.1642. IR (KBr plate, cm<sup>-1</sup>): v 3569 (w), 3049 (m), 3005 (m), 2907 (m), 2866 (m), 1647 (w), 1624 (w), 1541 (w), 1498 (w), 1443 (m), 1412 (w), 1362 (w), 1339 (w), 1308 (w), 1250 (w), 1086 (s), 1051 (s), 986 (s), 907 (s), 820 (m), 764 (w), 746 (w), 739 (w), 700 (s), 650 (s), 573 (s), 534 (s), 478 (m), 430 (s).

Preparation  $\{[\eta^1:(\mu_2-\eta^1:\eta^1)-2-(2,6$ of <sup>1</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCO)Ind]Gd(CH<sub>2</sub>SiMe<sub>3</sub>)(THF)<sub>2</sub>}<sub>2</sub> (1a). A toluene (15.0 mL) solution of [Gd(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub>] (0.56 g, 1.0 mmol) and  $H_2L^1$  (0.32 g, 1.0 mmol) was stirred at 0 °C for about 0.5 h to give a clear solution. Faint yellow crystals were obtained next day upon standing the reaction mixture at room temperature (750 mg, 53% yield based on the  $H_2L^1$ ). M. p. (sealed): 173 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the lack of locking signals for the paramagnetism of the complex. IR (KBr plate, cm<sup>-1</sup>): v 3047 (m), 2962 (s), 2870 (m), 1643 (s), 1541 (s), 1500 (s), 1413 (m), 1384 (m), 1363 (m), 1340 (m), 1307 (s), 1244 (m), 1182 (m), 1056 (m), 862 (m), 806 (m), 746 (m), 646 (m). Anal. Calcd for C<sub>66</sub>H<sub>98</sub>N<sub>4</sub>O<sub>6</sub>Si<sub>2</sub>Gd<sub>2</sub>: C, 56.05; H, 6.98; N, 3.96. Found: C, 56.07; H, 7.23; N, 4.15.

 $\{[\eta^1:(\mu_2-\eta^1:\eta^1)-2-(2,6-$ Preparation of <sup>1</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCO)Ind]Dy(CH<sub>2</sub>SiMe<sub>3</sub>)(THF)<sub>2</sub>}<sub>2</sub> (1b). A method similar to that for the preparation of complex 1a was used by treatment of a toluene (15.0 mL) solution of  $[Dy(CH_2SiMe_3)_3(THF)_2]$  (0.57 g, 1.0 mmol) and  $H_2L^1$  (0.32 g, 1.0 mmol) at 0 °C. Faint yellow crystals were obtained (670 mg, 47% yield based on the  $H_2L^1$ ). M. p. (sealed): 176 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the lack of locking signals for the paramagnetism of the complex. IR (KBr plate, cm<sup>-1</sup>): v 3047 (m), 2964 (s), 2870 (m), 1643 (s), 1541 (s), 1500 (s), 1413 (s), 1363 (m), 1307 (s), 1259 (m), 1240 (m), 1182 (m), 1058 (m), 821 (m), 806 (m), 746 (m), 648 (m). Anal. Calcd for C<sub>66</sub>H<sub>98</sub>N<sub>4</sub>O<sub>6</sub>Si<sub>2</sub>Dy<sub>2</sub>: C, 55.64; H, 6.93; N, 3.93. Found: C, 55.65; H, 7.13; N, 3.64.

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of  $\{[\eta^1:(\mu_2-\eta^1:\eta^1)-2-(2,6)\}$ Preparation that for the preparation of complex 1a was used by treatment of a toluene (15.0 mL) solution of [Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub>] (0.49 g, 1.0 mmol) and  $H_2L^1$  (0.32 g, 1.0 mmol) at 0 °C. Faint yellow crystals were obtained (600 mg, 47% yield based on the  $H_2L^1$ ). M. p. (sealed): 180 °C (dec.) under Ar. <sup>1</sup>H NMR (500 MHz,  $C_6D_6$ , 25 °C, TMS): δ 7.61 (d, J = 10.00 Hz, 1H, Ar-H), 7.56 (d, J = 5.00 Hz, 1H, Ar-H), 7.37-7.31 (m, 4H, indole-Ar-H), 7.06-7.03 (m, 1H, Ar-H), 6.18 (s, 1H, indole-Ar-H), 3.85 (s, 8H, THF), 3.67 (s, 2H, - $CHMe_2$ ), 1.36 (s, 8H, THF), 1.31 (d, J = 5.00 Hz, 6H,  $-CH(CH_3)_2$ ), 1.22 (d, J = 5.00 Hz, 6H, -CH(CH<sub>3</sub>)<sub>2</sub>), -0.04 (s, 9H, -Si(CH<sub>3</sub>)<sub>3</sub>), 0.34 (s, 2H, Y-CH<sub>2</sub>-). <sup>13</sup>C NMR (125 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C, TMS): δ 165.6 (-O-C=N-), 144.3, 144.1, 140.4, 138.4, 131.3, 124.6, 124.3, 122.6, 122.1, 118.7, 115.7, 108.0, 70.6 (-O-(CH<sub>2</sub>)<sub>2</sub>-, THF), 28.1 (-CHMe<sub>2</sub>), 25.4 (-(CH<sub>2</sub>)<sub>2</sub>-, THF), 25.1 (d, J<sub>Y-C</sub> = 50 Hz, Y-CH<sub>2</sub>-), 3.9 (-CH(CH<sub>3</sub>)<sub>2</sub>), 1.4 (-SiCMe<sub>3</sub>). IR (KBr plate, cm<sup>-1</sup>): v 3047 (w), 2962 (m), 2870 (w), 1645 (s), 1543 (s), 1498 (m), 1413 (m), 1307 (m), 1259 (m), 1242 (m), 1097 (m), 862 (m), 821 (m), 806 (m), 746 (s), 650 (m). Anal. Calcd for C<sub>66</sub>H<sub>98</sub>N<sub>4</sub>O<sub>6</sub>Si<sub>2</sub>Y<sub>2</sub>: C, 62.05; H, 7.73; N, 4.39. Found: C, 62.33; H, 7.58; N, 4.27.

 $\{[\eta^1:(\mu_2-\eta^1:\eta^1)-2-(2,6-$ Preparation of <sup>'</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCO)Ind]Er(CH<sub>2</sub>SiMe<sub>3</sub>)(THF)<sub>2</sub>}<sub>2</sub> (1d). A method similar to that for the preparation of complex 1a was used by (15.0 mL) treatment of a toluene solution of  $[Er(CH_2SiMe_3)_3(THF)_2]$  (0.57 g, 1.0 mmol) and  $H_2L^1$  (0.32 g, 1.0 mmol) at 0 °C. Pink crystals were obtained (731 mg, 51% yield based on the  $H_2L^1$ ). M. p. (sealed): 187 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the lack of locking signals for the paramagnetism of the complex. IR (KBr plate, cm<sup>-1</sup>): v 3047 (m), 2962 (s), 2868 (m), 1643 (s), 1541 (s), 1500 (s), 1413 (s), 1384 (m), 1363 (m), 1338 (m), 1307 (m), 1257 (m), 1242 (m), 1180 (m), 1056 (m), 1008 (w), 862 (m), 821 (m), 806 (m), 746 (s), 646 (m). Anal. Calcd for C<sub>66</sub>H<sub>98</sub>N<sub>4</sub>O<sub>6</sub>Si<sub>2</sub>Er<sub>2</sub>: C, 55.27; H, 6.89; N, 3.91. Found: C, 55.65; H, 7.16; N, 4.10.

 $\{[\eta^1:(\mu_2-\eta^1:\eta^1)-2-(2,6-$ Preparation of <sup>1</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCO)Ind]Yb(CH<sub>2</sub>SiMe<sub>3</sub>)(THF)<sub>2</sub>}<sub>2</sub> (1e). A method similar to that for the preparation of complex 1a was used by treatment of a toluene (15.0 mL) solution of  $[Yb(CH_2SiMe_3)_3(THF)_2]$  (0.58 g, 1.0 mmol) and  $H_2L^1$  (0.32 g, 1.0 mmol) at 0 °C. Deep red crystals were obtained (723 mg, 50% yield based on the  $H_2L^1$ ). M. p. (sealed): 195 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the lack of locking signals for the paramagnetism of the complex. IR (KBr plate, cm<sup>-1</sup>): v 3049 (w), 2962 (s), 2870 (w), 1643 (s), 1541 (s), 1502 (m), 1413 (s), 1363 (m), 1344 (m), 1307 (s), 1246 (s), 1182 (m), 1056 (s), 862 (s), 800 (m), 746 (s), 648 (m). Anal. Calcd for C<sub>66</sub>H<sub>98</sub>N<sub>4</sub>O<sub>6</sub>Si<sub>2</sub>Yb<sub>2</sub>: C, 54.83; H, 6.83; N, 3.88. Found: C, 54.75; H, 7.14; N, 3.64.

Preparation of  $\{[\eta^{1}:\eta^{1}-2-(2,6-Pr_{2}C_{6}H_{3}NHC=0)Ind-\eta^{1}:(\mu_{2} \eta^{1}:\eta^{1}:\eta^{1}-2-(2,6-Pr_{2}C_{6}H_{3}NCO)Ind]Y(THF)_{2}$  (1ca). A THF (15.0 mL) solution of [Y(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub>] (0.49 g, 1.0 mmol) and  $H_2L^1$  (0.64 g, 2.0 mmol) was stirred at room temperature for 3 h. The solvent was evaporated under reduced pressure. The residue was extracted with 10 mL *n*-hexane and 5 mL toluene.

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Faint yellow crystals were obtained at room temperature for several days. [799 mg, 50% yield based on the rare-earth metal complex  $Y(CH_2TMS)_3(THF)_2$ ]. M. p. (sealed): 187 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained, due to the poor solubility of the complex. IR (KBr plate, cm<sup>-1</sup>): v 3240 (m), 3061 (m), 2963 (m), 2928 (m), 2868 (m), 1645 (m), 1539 (m), 1504 (m), 1487 (m), 1472 (m), 1418 (m), 1362 (m), 1341 (m), 1310 (m), 1258 (s), 1246 (s), 1231 (s), 1180 (s), 1148 (s), 1121 (s), 1098 (s), 1057 (s), 1009 (s), 986 (s), 935 (s), 899 (s), 812 (s), 800 (s), 770 (s), 748 (m), 573 (s), 527 (s), 482 (s), 432 (s). Anal. Calcd for  $C_{92}H_{106}N_8O_6Y_2$ ·3C<sub>7</sub>H<sub>8</sub>: C, 72.54; H, 6.84; N, 5.99. Found: C, 72.38; H, 7.00; N, 5.90.

Preparation of  $\{[\eta^1:(\mu_2-\eta^1:\eta^1)-2-(2,6-Pr_2C_6H_3NCO)Ind]Y[\kappa^2-$ (N,N)(<sup>'</sup>PrN)<sub>2</sub>C(CH<sub>2</sub>SiMe<sub>3</sub>)](THF)<sub>2</sub> (1cb). A toluene (15.0 mL) solution of complex 1c (0.64 g, 0.50 mmol) and DIC (157  $\mu$ L, 1.00 mmol) was stirred at room temperature for 4 h. The solvent was evaporated under reduced pressure. The residue was extracted with 10 mL THF and 6 mL n-hexane. Colorless crystals were obtained upon standing the solution at -30 °C for several days (229 mg, 30% yield based on the complex 1c). M. p. (sealed): 138 °C (dec.) under Ar. <sup>1</sup>H NMR (500 MHz, THF- $d_8$ , 25 °C, TMS):  $\delta$  7.42 (d, J = 10.00 Hz, 1H, indole-Ar-H), 7.21 (s, 1H, indole-Ar-H), 6.91 (d, J = 5.00 Hz, 2H, indole-Ar-H), 6.58 (t, J = 10.00 Hz, 2H, Ar-H), 6.39 (t, J = 10.00 Hz, 1H, Ar-H), 6.16 (d, J = 10.00 Hz, 1H, indole-Ar-H), 3.54 (t, J = 10.00 Hz, 4H, THF), 1.71-1.69 (m, 4H, THF), 1.55 (s, 2H,  $-CH_2SiMe_3$ ), 0.94 (d, J = 5.00 Hz, 24H, -CH(CH<sub>3</sub>)<sub>2</sub>), 0.8-0.83 (m, 4H, -CHMe<sub>2</sub>), 0.04 (s, 9H, -Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, THF-d<sub>8</sub>, 25 °C, TMS): δ 171.4 (-O-C=N-), 153.4, 148.4, 147.5, 140.6, 131.9, 131.4, 128.4, 123.6, 123.4, 122.1, 120.9, 119.3, 118.4, 103.0, 68.0 (-O-(CH<sub>2</sub>)<sub>2</sub>-, THF) 32.3 (Ar-CHMe<sub>2</sub>), 29.3 (Ar-CH(CH<sub>3</sub>)<sub>2</sub>), 23.3 (-(CH<sub>2</sub>)<sub>2</sub>-, THF), 20.3 (N-CHMe2), 15.0 (N-CH(CH3)2), 14.2 (N-C-N), 1.2 (-SiCMe3). IR (KBr plate, cm<sup>-1</sup>): v 3048 (w), 2965 (w), 2870 (m), 1643 (w), 1541 (w), 1503 (w), 1487 (m), 1414 (m), 1385 (m), 1366 (m), 1339 (m), 1308 (m), 1242 (m), 1182 (s), 1128 (s), 1061 (s), 1011 (s), 982 (s), 937 (s), 901 (s), 833 (m), 824 (m), 806 (s), 768 (s), 746 (w), 648 (s), 569 (s), 529 (s), 486 (s), 428 (s), 419 (s), 399 (s). Anal. Calcd for C<sub>72</sub>H<sub>110</sub>N<sub>8</sub>O<sub>4</sub>Si<sub>2</sub>Y<sub>2</sub>: C, 62.41; H, 8.00; N, 8.09. Found: C, 62.57; H, 8.22; N, 7.91.

 $\{[\eta^1:(\mu_2-\eta^1:\eta^1)-2-(2,6-$ Preparation of <sup>1</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCO)Ind]Y[N(Me)CH<sub>2</sub>CH=CH<sub>2</sub>](THF)<sub>2</sub>}<sub>2</sub> (1cc). A toluene (15.0 mL) solution of complex 1c (0.64 g, 0.50 mmol) and N-Methylallylamine (96  $\mu$ L, 1.00 mmol) was stirred at room temperature for 4 h. The solvent was evaporated under reduced pressure. The residue was extracted with 10 mL THF and 9 mL n-hexane. Faint yellow crystals were obtained upon standing the solution at 0 °C for several days (249 mg, 40% yield based on the complex 1c). M. p. (sealed): 167 °C (dec.) under Ar. <sup>1</sup>H NMR (500 MHz, THF- $d_8$ , 25 °C, TMS):  $\delta$  7.31 (d, J = 5.00 Hz, 1H, Ar-H), 7.12 (s, 1H, Ar-H), 7.10 (d, J = 5.00 Hz, 1H, Ar-H), 7.08 (s, 1H, Ar-H), 7.03 (d, J = 5.00 Hz, 1H, Ar-H), 6.81 (t, J = 7.50 Hz, 1H, Ar-H), 6.57 (t, J = 7.50 Hz, 1H, Ar-H), 5.47 (s, 1H, indole-Ar-H), 4.93-4.89 (m, 2H, -CH=CH2), 4.35-4.33 (m, 1H, -CH=CH<sub>2</sub>), 3.51(t, J = 5.00 Hz, 8H, THF), 3.44-3.33 (m, 2H, -CHMe<sub>2</sub>), 3.09-3.00 (m, 2H, -NCH<sub>2</sub>-), 2.58 (s, 3H, -NCH<sub>3</sub>), 1.68-1.65 (m, 8H, THF), 1.06 (d, J = 10.00 Hz, 6H, -CH(CH<sub>3</sub>)<sub>2</sub>), 0.85 (d, J = 10.00 Hz, 6H, -CH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C NMR (125 MHz, THE,  $d_{8cl}$ 25<sub>nli</sub>C<sub>e</sub> TMS): δ 166.1 (-O-C=N-), 145.5, 144.4, D 40.9, 40.9, 40.9, 150.4 (-CH=2H<sub>2</sub>), 35.4 (-CH=2H<sub>2</sub>), 38.7 (N-CH<sub>2</sub>-), 36.4 (-CMe<sub>2</sub>), 32.5 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.5 (-(CH<sub>2</sub>)<sub>2</sub>-, THF), 1.2 (N-CH<sub>3</sub>). IR (KBr plate, cm<sup>-1</sup>): v 2963 (m), 2868 (m), 1645 (m), 1539 (w), 1504 (m), 1416 (m), 1362 (m), 1344 (m), 1310 (m), 1258 (m), 1240 (m), 1182 (s), 1144 (s), 1121 (s), 1057 (s), 1007 (s), 986 (s), 912 (s), 800 (s), 768 (s), 746 (m), 644 (s), 621 (s), 569 (s). Anal. Calcd for C<sub>66</sub>H<sub>92</sub>N<sub>6</sub>O<sub>6</sub>Y<sub>2</sub>: C, 63.76; H, 7.46; N, 6.76. Found: C, 63.62; H, 6.96; N, 6.49.

 $\{[\eta^1:(\mu_2-\eta^1:\eta^1)-2-(2,6-$ Preparation of <sup>'</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCO)Ind]Yb(C≡CPh)(THF)<sub>2</sub>}<sub>2</sub> (1ea). A THF (15.0 mL) solution of complex 1e (0.69 g, 0.50 mmol) and phenylacetylene (110  $\mu$ L, 1.00 mmol) was stirred at 60 °C for 12 h. The solvent was evaporated under reduced pressure. The residue was extracted with 10 mL n-hexane and 5 mL THF. Yellow crystals were obtained upon standing the solution at 0 °C for several days (258 mg, 35% yield based on the complex **1e**). M. p. (sealed): 107 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained, due to the lack of locking signals for the paramagnetism of the complex. IR (KBr plate, cm<sup>-1</sup>): v 1773 (s), 1751 (s), 1734 (s), 1719 (s), 1701 (s), 1684 (s), 1638 (m), 1618 (m), 1558 (s), 1541 (s), 1533 (s), 1508 (s), 1499 (s), 1491 (s), 1474 (s), 1458 (s), 1437 (s), 1400 (s), 1385 (s), 1364 (s), 1341 (s), 1308 (s), 1261 (s), 1094 (s), 1022 (s), 802 (s), 746 (s), 619 (s). Anal. Calcd for C<sub>74</sub>H<sub>86</sub>N<sub>4</sub>O<sub>6</sub>Yb<sub>2</sub>: C, 60.31; H, 5.88; N, 3.80. Found: C, 59.93; H, 5.62; N, 3.72.

Preparation of  $\{[\eta^{1}:(\mu_{2}-\eta^{1}:\eta^{1})-2-(2,6-$ <sup>1</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCO)Ind]Yb(CH<sub>2</sub>SiMe<sub>3</sub>)(Pyridine)(THF)}<sub>2</sub> (1eb). toluene (15.0 mL) solution of complex 1e (0.69 g, 0.50 mmol) and Pyridine (56  $\mu$ L, 1.00 mmol) was stirred at room temperature for 3 h. The solvent was evaporated under reduced pressure. The residue was extracted with 10 mL toluene and 5 mL n-hexane. Pale brown crystals were obtained standing the solution at 0 °C for several days (226 mg, 31% yield based on the complex 1e). M. p. (sealed): 127 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to lack of locking signals for the paramagnetism of the complex. IR (KBr plate, cm<sup>-1</sup>): v 2963 (m), 1641 (m), 1541 (m), 1508 (m), 1439 (m), 1414 (m), 1385 (m), 1346 (m), 1310 (m), 1248 (m), 1183 (s), 1148 (s), 1123 (s), 1059 (s), 1032 (s), 1007 (s), 935 (s), 860 (m), 799 (s), 746 (m), 702 (m), 650 (s), 617 (s), 571 (s). Anal. Calcd for C<sub>68</sub>H<sub>92</sub>N<sub>6</sub>O<sub>4</sub>Si<sub>2</sub>Yb<sub>2</sub>·0.5C<sub>7</sub>H8: C, 57.03; H, 6.43; N, 5.58. Found: C, 57.18; H, 6.16; N, 5.68.

# Preparation of ${[\eta^1:(\mu_2-\eta^1:\eta^1)-2-(2,6-i^2Pr_2C_6H_3NCO)Ind]Yb(CH_2SiMe_3)(\eta^1-(N)-C_3H_3N_2C_6H_5)(THF)}_2$

(1ec). A toluene (15.0 mL) solution of complex 1e (0.69 g, 0.50 mmol) and *N*-Phenylimidazole (126  $\mu$ L, 1.00 mmol) was stirred at room temperature for 3 h. The solvent was evaporated under reduced pressure. The residue was extracted with 10 mL toluene and 5 mL *n*-hexane. Red crystals were obtained upon standing the solution at 0 °C for several days (238 mg, 30% yield based on the complex 1e). M. p. (sealed): 151 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the lack of locking signals for the paramagnetism of the

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complex. IR (KBr plate, cm<sup>-1</sup>):  $\nu$  2961 (w), 2866 (m), 1641 (w), 1601 (w), 1541 (w), 1512 (w), 1416 (m), 1346 (m), 1308 (w), 1246 (m), 1180 (s), 1144 (s), 1119 (m), 1059 (m), 1007 (s), 988 (s), 964 (s), 928 (s), 912 (s), 860 (m), 748 (w), 692 (m), 658 (m), 523 (s). Anal. Calcd for C<sub>76</sub>H<sub>98</sub>N<sub>8</sub>O<sub>4</sub>Si<sub>2</sub>Yb<sub>2</sub>: C, 57.41; H, 6.21; N, 7.05. Found: C, 57.42; H, 5.88; N, 7.00.

Preparationof $\{[\eta^1:(\mu_2-\eta^1:\eta^1)-2-(2,6-i^2Pr_2C_6H_3NCO)Ind]Yb(CH_2SiMe_3)(DMAP)_2\}_2$  (1ed). Complex 1edcould be synthesized by the following two methods: path A, aTHF (10.0 mL) solution of complex 1e (0.69 g, 0.50 mmol) andDMAP (0.24 g, 2.0 mmol) was stirred at room temperature for1 min and stand overnight, then filtration.

Alternate path B, a toluene (15.0 mL) solution of Yb(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (0.58 g, 1.0 mmol) and DMAP (0.24 g, 2.0 mmol) was stirred at room temperature for 0.5 h, to the solution was added  $H_2L^1$  (0.32 g, 1.0 mmol), and the mixture was stirred at room temperature for 3 h, The solvent was evaporated under reduced pressure. The residue was extracted with 10 mL THF and 5 mL n-hexane. Red crystals were obtained upon standing the solution at 0 °C for several days (823 mg, 50% yield based on the complex 1e). M. p. (sealed): 112 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the lack of locking signals for the paramagnetism of the complex. IR (KBr plate,  $cm^{-1}$ ): v 1641 (m), 1609 (m), 1539 (m), 1506 (m), 1489 (s), 1447 (m), 1418 (m), 1383 (m), 1310 (s), 1260 (s), 1227 (m), 1182 (s), 1123 (s), 1105 (s), 1065 (s), 993 (m), 806 (m), 746 (s), 739 (s), 532 (m). Anal. Calcd for C<sub>78</sub>H<sub>106</sub>N<sub>12</sub>O<sub>2</sub>Si<sub>2</sub>Yb<sub>2</sub>·2THF: C, 57.70; H, 6.87; N, 9.39. Found: C, 58.09; H, 7.08; N, 9.02.

**Preparation of Yb(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(DMAP)<sub>2</sub> (3a).** A toluene (15.0 mL) solution of Yb(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (0.58 g, 1.0 mmol) and DMAP (0.24 g, 2.0 mmol) was stirred at room temperature for 0.5 h. The solvent was evaporated under reduced pressure. The residue was extracted with 10 mL *n*-hexane and 5 mL toluene. Yellow crystals were obtained upon standing the solution at -30 °C for several days. [475 mg, 70% yield based the rare-earth metal complex Yb(CH<sub>2</sub>TMS)<sub>3</sub>(THF)<sub>2</sub>]. M. p. (sealed): 100 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the lack of locking signals for the paramagnetism of the complex. IR (KBr plate, cm<sup>-1</sup>): *v* 1604 (w), 1537 (m), 1522 (m), 1447 (m), 1379 (m), 1225 (m), 1103 (s), 1069 (s), 989 (m), 945 (s), 808 (m), 750 (m), 540 (m), 530 (m). Anal. Calcd for C<sub>26</sub>H<sub>53</sub>N<sub>4</sub>Si<sub>3</sub>Yb: C, 45.99; H, 7.87; N, 8.25. Found: C, 45.08; H, 7.61; N, 8.61.

 $\{[\eta^1:(\mu_2-\eta^1:\eta^1):\eta^1-2-(2,6-$ Preparation of  ${}^{i}Pr_{2}C_{6}H_{3}NCO$  [Ind]  $_{2}[\eta^{1}:\eta^{1}-2-(2,6-{}^{i}Pr_{2}C_{6}H_{3}NCO)$  [Ind]  $Yb_{2}[\eta^{1}-(N)-$ C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>CH<sub>3</sub>]<sub>4</sub> (1ee). A toluene (15.0 mL) solution of  $Yb(CH_2SiMe_3)_3(THF)_2$ (0.58 g, 1.0 mmol) and N-Methylimidazole (159  $\mu$ L, 2.0 mmol) was stirred at room temperature for 2 h, then to the reaction mixture was added  $H_2L^1$  (0.32 g, 1.0 mmol). The reaction mixture was then stirred at room temperature for 3 h, The solvent was evaporated under reduced pressure. The residue was extracted with 10 mL THF and 2 mL n-hexane. Yellow crystals were obtained upon standing the solution at 0 °C for several days [733 mg, 45%

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yield based the rare-earth metal complex Yb(CH<sub>2</sub>T,MS)<sub>a</sub>(THF)<sub>a</sub>]. M. p. (sealed): 210 °C (dec.) under Ar. <sup>1</sup>H<sup>-</sup>NMR spectra of the complex were not obtained due to the lack of locking signals for the paramagnetism of the complex. IR (KBr plate, cm<sup>-1</sup>): *v* 1643 (m), 1541 (m), 1501 (s), 1414 (s), 1385 (s), 1364 (s), 1339 (s), 1308 (s), 1260 (s), 1240 (s), 1182 (s), 1082 (s), 920 (s), 822 (s), 806 (s), 768 (s), 746 (s), 739 (s). Anal. Calcd for C<sub>79</sub>H<sub>90</sub>N<sub>14</sub>O<sub>3</sub>Yb<sub>2</sub>·THF: C, 58.58; H, 5.80; N, 11.52. Found: C, 58.34; H, 5.82; N, 11.42.

 $\{[\eta^1:(\mu_2-\eta^1:\eta^1):\eta^1-2-(2,6-$ Preparation of <sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCO)Ind]<sub>2</sub>[ $\eta^1$ : $\eta^1$ -2-(2,6-<sup>i</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NCO)Ind]Yb<sub>2</sub>[ $\eta^1$ -(N)-C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>]<sub>4</sub>} (1ef). A toluene (15.0 mL) solution of Yb(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (0.58 g, 1.0 mmol) and N-Benzylimidazole (0.31 g, 2.0 mmol) was stirred at room temperature for 2 h, then to the solution was added  $H_2L^1$  (0.32 g, 1.0 mmol). The reaction mixture was stirred at room temperature for 3 h, The solvent was evaporated under reduced pressure. The residue was extracted with 10 mL THF and 2 mL n-hexane. Yellow crystals were obtained upon standing the solution at 0 °C for several days [773 mg, 40% yield based the rare-earth metal complex Yb(CH<sub>2</sub>TMS)<sub>3</sub>(THF)<sub>2</sub>]. M. p. (sealed): 113 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the lack of locking signals for the paramagnetism of the complex. IR (KBr plate, cm<sup>-1</sup>): v 1773 (s), 1751 (s), 1734 (s), 1719 (s), 1701 (s), 1684 (s), 1618 (m), 1578 (s), 1570 (s), 1558 (s), 1533 (s), 1508 (s), 1499 (s), 1458 (s), 1406 (s), 1385 (s), 1364 (s), 1308 (s), 1261 (s), 1231 (s), 1078 (s), 1030 (s), 802 (s), 746 (s), 737 (s), 710 (s), 662 (s), 627 (s), 617 (s). Anal. Calcd for  $C_{103}H_{106}N_{14}O_{3}Yb_{2}\cdot 4C_{7}H_{8}$ : C, 68.33; H, 6.04; N, 8.52. Found: C, 68.01; H, 6.40; N, 8.81.

Preparation of  $\{[\eta^1:(\mu_2-\eta^1:\eta^1):\eta^1-2-(2-$ <sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>NCO)Ind]Gd(CH<sub>2</sub>SiMe<sub>3</sub>)(THF)<sub>2</sub>}<sub>2</sub> (2a). A toluene (15.0 mL) solution of [Gd(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub>] (0.56 g, 1.0 mmol) and  $H_2L^2$  (0.29 g, 1.0 mmol) was stirred at room temperature for about several seconds to give a clear solution. Faint yellow crystals were obtained the next day upon standing the reaction solution overnight (762 mg, 55% yield based on the  $H_2L^2$ ). M. p. (sealed): 70 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the lack of locking signals for the paramagnetism of the complex. IR (KBr plate, cm<sup>-1</sup>): v 2955 (s), 1645 (m), 1626 (m), 1543 (m), 1508 (s), 1443 (s), 1414 (s), 1364 (s), 1341 (s), 1312 (s), 1263 (s), 1250 (s), 1196 (s), 1086 (s), 1051 (s), 984 (s), 853 (s), 829 (s), 762 (s), 746 (s). Anal. Calcd for C<sub>62</sub>H<sub>90</sub>N<sub>4</sub>O<sub>6</sub>Si<sub>2</sub>Gd<sub>2</sub>·2C<sub>7</sub>H<sub>8</sub>: C, 59.18; H, 6.93; N, 3.63. Found: C, 59.14; H, 6.96; N, 3.72.

**Preparation** of  $\{[\eta^1:(\mu_2-\eta^1:\eta^1):\eta^1-2-(2-t^3BuC_6H_4NCO)Ind]Dy(CH_2SiMe_3)(THF)_2\}_2$  (2b). A method similar to that for the preparation of complex 2a was used by treatment of a toluene (15.0 mL) solution of  $[Dy(CH_2SiMe_3)_3(THF)_2]$  (0.57 g, 1.0 mmol) and  $H_2L^2$  (0.29 g, 1.0 mmol) at room temperature. Faint yellow crystals were obtained the next day upon standing the solution at room temperature (657 mg, 48% yield based on the  $H_2L^2$ ). M. p. (sealed): 101 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the lack of locking signals for the paramagnetism of the complex. IR (KBr plate, cm<sup>-1</sup>): v

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2955 (s), 1645 (w), 1626 (m), 1545 (m), 1508 (m), 1443 (s), 1414 (s), 1364 (s), 1341 (s), 1312 (m), 1265 (s), 1250 (s), 1196 (s), 1148 (s), 1117 (s), 1086 (s), 1051 (s), 984 (s), 862 (s), 830 (s), 762 (s), 746 (s). Anal. Calcd for  $C_{62}H_{90}N_4O_6Si_2Dy_2$ : C, 54.41; H, 6.63; N, 4.09. Found: C, 54.20; H, 6.74; N, 4.35.

 $\{[\eta^1:(\mu_2-\eta^1:\eta^1):\eta^1-2-(2-$ Preparation of <sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>NCO)Ind]Y(CH<sub>2</sub>SiMe<sub>3</sub>)(THF)<sub>2</sub>}<sub>2</sub> (2c). A method similar to that for the preparation of complex 2a was used, consisting of the treatment of a toluene (15.0 mL) solution of  $[\text{Y}(\text{CH}_2\text{SiMe}_3)_3(\text{THF})_2]$  (0.49 g, 1.0 mmol) and  $\textbf{H}_2\textbf{L}^2$  (0.29 g, 1.0 mmol) at room temperature. Faint yellow crystals were obtained the next day upon standing the solution at room temperature (623 mg, 51% yield based on the  $H_2L^2$ ). M. p. (sealed): 65 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the poor solubility of the complex. IR (KBr plate, cm<sup>-1</sup>): v 2955 (s), 1645 (m), 1626 (m), 1543 (m), 1508 (m), 1443 (s), 1414 (s), 1364 (s), 1341 (s), 1312 (s), 1263 (s), 1250 (s), 1196 (s), 1148 (s), 1117 (s), 1086 (s), 1051 (s), 984 (s), 953 (s), 829 (s), 762 (s), 746 (s). Anal. Calcd for C<sub>62</sub>H<sub>90</sub>N<sub>4</sub>O<sub>6</sub>Si<sub>2</sub>Y<sub>2</sub>: C, 60.97; H, 7.43; N, 4.59. Found: C, 60. 91; H, 7.44; N, 4.43.

Preparation  $\{[\eta^1:(\mu_2-\eta^1:\eta^1):\eta^1-2-(2$ of <sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>NCO)Ind]Er(CH<sub>2</sub>SiMe<sub>3</sub>)(THF)<sub>2</sub>}<sub>2</sub> (2d). A method similar to that for the preparation of complex 2a was used, consisting of the treatment of a toluene (15.0 mL) solution of  $[Er(CH_2SiMe_3)_3(THF)_2]$  (0.57 g, 1.0 mmol) and  $H_2L^2$  (0.29 g, 1.0 mmol) at room temperature. Pink crystals were obtained the next day upon standing the solution at room temperature (758 mg, 55% yield based on the  $H_2L^2$ ). M. p. (sealed): 90 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the lack of locking signals for the paramagnetism of the complex. IR (KBr disk, cm<sup>-1</sup>): v 2955 (m), 1645 (w), 1626 (m), 1541 (w), 1508 (m), 1443 (s), 1414 (m), 1364 (s), 1341 (s), 1312 (m), 1250 (s), 1196 (s), 1148 (s), 1117 (s), 1088 (s), 1051 (s), 984 (s), 862 (s), 829 (s),762 (s), 746 (s). Anal. Calcd for C<sub>62</sub>H<sub>90</sub>N<sub>4</sub>O<sub>6</sub>Si<sub>2</sub>Er<sub>2</sub>: C, 54.04; H, 6.58; N, 4.07. Found: C, 53.85; H, 6.46; N, 4.10.

 $\{[\eta^1:(\mu_2-\eta^1:\eta^1):\eta^1-2-(2-$ Preparation of <sup>t</sup>BuC<sub>6</sub>H<sub>4</sub>NCO)Ind]Yb(CH<sub>2</sub>SiMe<sub>3</sub>)(THF)<sub>2</sub>}<sub>2</sub> (2e). A method similar to that for the preparation of complex 2a was used, consisting of the treatment of a toluene (15.0 mL) solution of  $[Yb(CH_2SiMe_3)_3(THF)_2]$  (0.58 g, 1.0 mmol) and  $H_2L^2$  (0.29 g, 1.0 mmol) at room temperature. Red crystals were obtained the next day upon standing the solution at room temperature (709 mg, 51% yield based on the  $H_2L^2$ ). M. p. (sealed): 76 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the lack of locking signals for the paramagnetism of the complex. IR (KBr plate, cm<sup>-1</sup>): v 2953 (s), 1645 (w), 1626 (m), 1541 (w), 1508 (m), 1443 (s), 1414 (m), 1364 (s), 1341 (s), 1312 (m), 1250 (s), 1194 (s), 1148 (s), 1117 (s), 1086 (s), 1051 (s), 984 (s), 862 (s), 829 (s), 802 (s), 762 (s), 746 (m). Anal. Calcd for C<sub>62</sub>H<sub>90</sub>N<sub>4</sub>O<sub>6</sub>Si<sub>2</sub>Yb<sub>2</sub>(-2THF): C, 52.02; H, 5.99; N, 4.50. Found: C, 51.81; H, 6.02; N, 4.16.

Preparation of { $[\eta^1:\eta^1-2-(2^{-t}BuC_6H_4NHC=O)Ind-\eta^1:(\mu_2-\eta^1:\eta^1):\eta^1-2-(2^{-t}BuC_6H_4NCO)Ind]Yb(THF)$ }2 (2ea). A THF (15.0 mL)

#### solution of [Yb(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub>] (0.58 g, 1.0 mmol) and H<sub>2</sub>L<sup>2</sup> (0.58 g, 2.0 mmol) was stirred at room lemperature for 37R. The solvent was evaporated under reduced pressure. The residue was extracted with 10 mL toluene and 5 mL *n*-hexane. Red crystals were obtained upon standing the solution at room temperature for several days (546 mg, 33% yield based on the H<sub>2</sub>L<sup>2</sup>). M. p. (sealed): 171 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the lack of locking signals for paramagnetism. IR (KBr plate, cm<sup>-1</sup>): *v* 2957 (m), 1647 (m), 1636 (m), 1618 (m), 1558 (m), 1541 (m), 1533 (m), 1508 (m), 1053(m), 860 (m), 746 (m), 669 (m), 617 (m). Anal. Calcd for C<sub>84</sub>H<sub>90</sub>N<sub>8</sub>O<sub>6</sub>Yb<sub>2</sub>·C<sub>7</sub>H<sub>8</sub>: C, 62.60; H, 5.66; N, 6.42. Found: C, 62.27; H, 6.04; N, 6.24.

**Preparation of**  $\{[\eta^1:(\mu_2-\eta^1:\eta^1):\eta^1-2-(2-^tBuC_6H_4NCO)Ind]Yb[κ^2-(N,O)-OC(CH_2SiMe_3)NC_6H_5](THF)\}_2$  (2eb). A toluene (15.0 mL) solution of complex 2e (0.69 g, 0.50 mmol) and Phenylisocyanate (109 μL, 1.00 mmol) was stirred at room temperature for 3 h. Red crystals were obtained upon standing the solution at room temperature for several days (356 mg, 48% yield based on the complex 2e). M. p. (sealed): 224 °C (dec.) under Ar. <sup>1</sup>H NMR spectra of the complex were not obtained due to the lack of locking signals for the paramagnetism of the complex. IR (KBr plate, cm<sup>-1</sup>): v 1647 (m), 1599 (m), 1541 (m), 1533 (m), 1499 (m), 1441 (m), 1420 (m), 1315 (m), 1250 (m), 1198 (s), 1142 (s), 1088 (s), 1053(s), 1007 (s), 988 (s), 849 (m), 748 (m), 692 (s). Anal. Calcd for C<sub>68</sub>H<sub>84</sub>N<sub>6</sub>O<sub>6</sub>Si<sub>2</sub>Yb<sub>2</sub>·1.5C<sub>7</sub>H<sub>8</sub>: C, 58.13; H, 5.97; N, 5.18. Found: C, 57.93; H, 5.93; N, 4.99.

**Isoprene Polymerization.** The procedures for isoprene polymerization catalyzed by these complexes were similar; a typical polymerization procedure is described as follow. A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged the desired amount of solvent, the organo-rare-earth alkyl complex, borate, alkyl aluminum, and isoprene. The mixture was stirred vigorously for the desired time, during which an increase of viscosity was observed. The reaction mixture was quenched be addition of 30 mL of acidified methanol. The polymer was coagulated, washed with methanol two times, and finally dried under vacuum to a constant weight.

**Crystal Structure Analyses of Complexes.** A suitable singlecrystal of each complex was mounted in a sealed capillary. Diffraction was performed on a Bruker SMART APEX II CCD area detector diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K,  $\varphi$  and  $\omega$  scan technique. An empirical absorption correction was applied using the SADABS program.<sup>28</sup> All structures were solved by direct methods, completed be subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations based on  $F^2$ using the SHELXTL program package<sup>29</sup> and Olex<sup>2</sup> program.<sup>30</sup> 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. Selected bond lengths and angles are

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listed in Table 1, and crystal data and details of the data collection and structure refinements are given in the ESI. All crystal structure diagrams were drawn by Ortep-3 program.<sup>31</sup>

## **Conflicts of interest**

There are no conflicts to declare.

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#### Notes and references

Published on 08 March 2019. Downloaded on 3/12/2019 3:46:56 AM

- X. Zhu, S. Zhou, S. Wang, Y. Wei, L. Zhang, F. Wang, S. Wang, Z. Feng, *Chem. Commun.*, 2012, 48, 12020-12022.
- 2 X. Zhu, S. Wang, S. Zhou, Y. Wei, L. Zhang, F. Wang, Z. Feng, L. Guo, X. Mu, *Inorg. Chem.*, 2012, **51**, 7134-7143.
- 3 (a) Z. Feng, X. Zhu, S. Wang, S. Wang, S. Zhou, Y. Wei, G. Zhang, B. Deng, X. Mu, *Inorg. Chem.*, 2013, **52**, 9549-9556. (b)
   L. Guo, S. Wang, Y. Wei, S. Zhou, X. Zhu, X. Mu, *Inorg. Chem.*, 2017, **56**, 6197-6207.
- 4 (a) G. Zhang, Y. Wei, L. Guo, X. Zhu, S. Wang, S. Zhou, X. Mu, *Chem. Eur. J.*, 2015, 21, 2519-2526. (b) G. Zhang, S. Wang, S. Zhou, Y. Wei, L. Guo, X. Zhu, L. Zhang, X. Gu, X. Mu, *Organometallics*, 2015, 34, 4251-4261. (c) G. Zhang, B. Deng, S. Wang, Y. Wei, S. Zhou, X. Zhu, Z. Huang, X. Mu, *Dalton Trans.*, 2016, 45, 15445-15456. (d) G. Zhang, S. Wang, X. Zhu, S. Zhou, Y. Wei, Z. Huang, X. Mu, *Organometallics*, 2017, 36, 3812-3822.
- 5 L. Guo, X. Zhu, G. Zhang, Y. Wei, L. Ning, S. Zhou, Z. Feng, S. Wang, X. Mu, J. Chen, Y. Jiang, *Inorg. Chem.*, 2015, **54**, 5725-5731.
- 6 X. Zhu, Y. Li, Y. Wei, S. Wang, S. Zhou, L. Zhang, Organometallics, 2016, **35**, 1838-1846.
- 7 (a) J. A. Broomhead, J. Evans, W. D. Grumley, M. J. Sterns, *Chem. Soc., Dalton Trans.*, 1977, 2, 173-176. (b) D. P. Fairlie, P. M. Angus, M. D. Fenn, W. G. Jackson, *Inorg. Chem.*, 1991, 30, 1564-1569. (c) W. Henderson, A. G. Oliver, B. K. Nicholson, *Inorg. Chim. Acta*, 2000, 298, 84-89. (d) A. L. Reznichenko, K. C. Hultzsch, *Organometallics*, 2010, 29, 24-27. (e) V. Mathrubootham, J. Thomas, R. Staples, J. McCraken, J. Shearer, E. L. Hegg, *Inorg. Chem.*, 2010, 49, 5393-5406. (f) M. W. Drover, J. A. Love, L. L. Schafer, *Chem. Soc. Rev.*, 2017, 46, 2913-2940.
- 8 (a) A. Bino, F. A. Cotton, W. Kaim, *Inorg. Chem.*, 1979, 18, 3030-3034. (b) K. J. Nelson, R. W. McGaff, D. R. Powell, *Inorg. Chim. Acta*, 2000, 304, 130-133. (c) F. A. Cotton, L. M. Daniels, J. P. Donahue, C. Y. Liu, C. A. Murillo, *Inorg. Chem.*, 2002, 41, 1354-1356. (d) W. Chen, K. Matsumoto, *Eur. J. Inorg. Chem.*, 2002, 2664-2670. (e) W. Chen, F. Liu, T. Nishioka, K. Matsumoto, *Eur. J. Inorg. Chem.*, 2003, 4234-4243. (f) W. Chen, F. Liu, K. Matsumoto, J. Autschbach, B. L. Guennic, T. Ziegler, M. Maliarik, J. Glaser, *Inorg. Chem.*, 2006, 45, 4526-4536. (g) W. Chen, F. Liu, D. Xu, K. Matsumoto, S. Kishi, M. Kato, *Inorg. Chem.*, 2006, 45, 5552-5560.
- 9 (a) S. Gambarotta, S. Strologo, C. Floriani, A. Chiesi-Villa, C. Guastini, *Inorg. Chem.*, 1985, 24, 654-660. (b) R. Lai, S. Mabille, A. Croux, S. L. Bot, *Polyhedron*, 1991, 10, 463-465. (c) S. U. Koschmieder, G. Wilkinson, B. Hussain-Bates, M. B. Hursthouse, *J. Chem. Soc.*, *Dalton Trans.*, 1992, 19-24. (d) S.

Liu, W.-H. Sun, Y. Zeng, D. Wang, W. Zhang, Y. Li, Organometallics, 2010, **29**, 2459-2464<sub>DOI</sub>: 10.1039/GDT005078

- X.-g. Zhou, L.-b. Zhang, M. Zhu, R.-f. Cai, L.-h. Weng, Organometallics, 2001, 20, 5700-5706.
   D.-H. Lee, J. H. Lee, B. K. Park, E. Y. Kim, Y. Kim, C. Kim, I.-M.
- LEE, J. H. LEE, J. H. LEE, B. K. Park, E. Y. KIM, Y. KIM, C. KIM, I.-M. Lee, Inorg. Chim. Acta, 2009, **362**, 5097-5102.
- 12 J. Jarusiewicz, Y. Choe, K. S. Yoo, C. P. Park, K. W. Jung, *J. Org. Chem.*, 2009, **74**, 2873-2876.
- 13 K. S. Yoo, J. O'Neill, S. Sakaguchi, R. Giles, J. H. Lee, K. W. Jung, J. Org. Chem., 2010, 75, 95-101.
- 14 Z. Huang, S. Wang, X. Zhu, Q. Yuan, Y. Wei, S. Zhou, X. Mu, *Inorg. Chem.* 2018, **57**, 15069-15078.
- (a) J. Sun, D. J. Berg, B. Twamley, *Organometallics*, 2008, 27, 683-690.
   (b) W. Yi, J. Zhang, M. Li, Z. Chen, X. Zhou, *Inorg. Chem.*, 2011, 50, 11813-11824.
- 16 (a) F. Yuan, Q. Shen, J. Sun, *Polyhedron*, 1998, **17**, 2009-2012.
  (b) F. Yuan, Q. Shen, J. Sun, *Chem. J. Chin. Univ.*, 2001, **22**, 1501-1505.
  (c) H. Zhou, H. Guo, Y. Yao, L. Zhou, H. Sun, H. Sheng, Y. Zhang, Q. Shen, *Inorg. Chem.*, 2007, **46**, 958-964.
- 17 Y. Wang, Q. Shen, L. Wu, Y. Zhang, J. Sun, *J. Organomet. Chem.*, 2001, **626**, 176-180.
- 18 (a) W. J. Evans, K. J. Forrestal, J. W. Ziller, *J. Am. Chem. Soc.*, 1998, **120**, 9273-9282. (b) W. J. Evans, R. N. R. Broomhall-Dillard, J. W. Ziller, *J. Organomet. Chem.*, 1998. **569**, 89-97.
- 19 R. Duchateau, E. A. C. Brussee, A. Meetsma, J. H. Teuben, Organometallics, 1997, 16, 5506-5516.
- 20 (a) H. Cheng, B. Zhao, Y. Yao, C. Lu, *Green Chem.*, 2015, 17, 1675-1682. (b) H. Cheng, Y. Xiao, C. Lu, B. Zhao, Y. Wang; Y. Yao, *New J. Chem.*, 2015, 39, 7667-7671. (c) C. Gong, H. Ding, C. Lu, B. Zhao, Y. Yao, *Dalton Trans.*, 2017, 46, 6031-6038.
- 21 J. M. Lauzon, P. Eisenberger, S.-C. Roşca, L. L. Schafer, ACS Catal., 2017, 7, 5921-5931.
- 22 S. Li, J. Cheng, Y. Chen, M. Nishiura, Z. Hou, *Angew. Chem. Int. Ed.*, 2011, **50**, 6360-6363.
- 23 M. Manßen, I. Töben, C. Kahrs, J.-H. Bölte, M. Schmidtmann, R. Beckhaus, *Organometallics*, 2017, **36**, 2973-2981.
- 24 (a) W.-X. Zhang, M. Nishiura, Z. Hou, J. Am. Chem. Soc., 2005, 127, 16788-16789. (b) A. G. M. Barrett, M. R. Crimmin, M. S. Hill, P. B. Hitchcock, S. L. Lomas, M. F. Mahon, P. A. Procopiou, K. Suntharalingam, Organometallics, 2008, 27, 6300-6306. (c) L. Xu, Y.-C. Wang, W.-X. Zhang, Z. Xi, Dalton Trans., 2013, 42, 16466-16469.
- (a) P. L. Diaconescu, Acc. Chem. Res., 2010, 43, 1352-1363. (b)
   C. T. Carver, B. N. Williams, K. R. Ogilby, P. L. Diaconescu, Organometallics, 2010, 29, 835-846. (c) X. Zhu, Y. Li, D. Guo,
   S. Wang, Y. Wei, S. Zhou, Dalton Trans., 2018, 47, 3947-3957.
- 26 G. Occhipinti, C. Meermann, H. M. Dietrich, R. Litlabø, F. Auras, K. W. Törnroos, C. Maichle-Mössmer, V. R. Jensen, R. Anwander, J. Am. Chem. Soc., 2011, 133, 6323-6337.
- 27 (a) G. Lanza, I. L. Fragalà, T. J. Marks, J. Am. Chem. Soc., 2000, 122, 12764-12777. (b) P. G. Hayes, W. E. Piers, M. Parvez, J. Am. Chem. Soc., 2003, 125, 5622-5623.
- 28 G. M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Dector Data; University of Göttingen: Germany, 1996.
- 29 (a) G. M. Sheldrick, SHELXTL 5.10 for Windows NT: Structure Determination Software Programs; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997. (b) G. M. Sheldrick, Acta Cryst., 2008, A64, 112-122. (c) G. M. Sheldrick, Acta Cryst., 2015, A71, 3-8. (d) Sheldrick, G. M. Acta Cryst., 2015, C71, 3-8.
- 30 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, J. Appl. Cryst., 2009, **42**, 339-341.
- 31 L. J. Farrugia, J. Appl. Cryst., 2012, 45, 849-854.