## **ORGANOMETALLICS**

# Synthesis and Reactivity of *NNNN*-Pincer Multidentate Pyrrolyl Rare-Earth-Metal Amido-Chloride or Dialkyl Complexes

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**ABSTRACT:** The *NNNNN*-pincer multidentate pyrrolyl rare-earth-metal amido-chloride complexes { $\eta^{1}$ : $\kappa^{3}$ -2,5-[CH<sub>3</sub>N-(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]<sub>2</sub>C<sub>4</sub>H<sub>2</sub>N}RECl[N(SiMe<sub>3</sub>)<sub>2</sub>] (RE = Y (2a), Sm (2b), Dy (2c), Er (2d), Yb (2e)) were synthesized by one step from reactions of [(Me<sub>3</sub>Si)<sub>2</sub>N]<sub>3</sub>RE( $\mu$ -Cl)Li(THF)<sub>3</sub> with {2,5-[CH<sub>3</sub>N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]<sub>2</sub>}C<sub>4</sub>H<sub>2</sub>NH (1). Reactions of compound 1 with RE(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> gave the rare-earth-metal dialkyl complexes { $\eta^{1}$ : $\kappa^{2}$ -2,5-[CH<sub>3</sub>N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]<sub>2</sub>C<sub>4</sub>H<sub>2</sub>N}RE(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> gave the rare-earth-metal dialkyl complexes { $\eta^{1}$ : $\kappa^{2}$ -2,5-[CH<sub>3</sub>N(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]<sub>2</sub>C<sub>4</sub>H<sub>2</sub>N}RE(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (RE = Y (3b), Dy (3c), Er (3d), Yb (3e), Lu (3f)). Further reactions of complexes 3 with dimethylaniline afforded rare-earth-metal diamido complexes bearing an *NNNNN*-pincer multidentate pyrrolyl ligand, but not rare-earth-metal analyses, and single-crystal X-ray diffraction. The pincer multidentate pyrrolyl rare-earth-metal dialkyl complexes showed high catalytic activities for the addition of amines to carbodiimides or isothiocyanate to afford the substituted guanidines and thioureas.

#### INTRODUCTION

Rare-earth-metal diamido or dialkyl complexes are potential precursors with the treatment of an appropriate borate compound such as [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] or [PhNMe<sub>2</sub>H][B- $(C_6F_5)_4$  to generate cationic monoamido or monoalkyl species, which have been demonstrated to be excellent catalysts of polymerization and copolymerization, as well as other catalytic transformations such as alkylative alumination and C-H alkylations.<sup>1</sup> Additionally, hydrogenolysis of the rareearth dialkyl complexes with H<sub>2</sub> will result in the formation of rare-earth polyhydride complexes showing novel features in both structure and reactivity.<sup>2</sup> Moreover, rare-earth dialkyl complexes have been demonstrated to afford elusive rare-earth terminal imido [RE=N] complexes through a subsequent intramolecular alkane elimination reaction of hybrid alkyl/ amido species, which were obtained via the elimination of an alkyl group when rare-earth dialkyl complexes were reacted with a primary amine.<sup>3</sup> In comparison with rare-earth-metal monoamido or monoalkyl complexes, rare-earth-metal diamido or dialkyl complexes have generally been more difficult to synthesize due to their facile ligand redistribution. Therefore, it is very important to develop new ancillary ligands to support the rare-earth diamido or dialkyl complexes.

Pincer-type ligands have attracted increasing attention in modern coordination chemistry, because they possess a controlled balance of stability and reactivity through modifications of the ligand.<sup>4</sup> Many typical pincer ligands have been widely applied in the synthesis of rare-earth-metal complexes due to their stability with the rare-earth metal.<sup>5</sup> Rare-earth-metal dialkyl complexes containing *PNP-*, *NNN-*, and *CPC-*pincer ligands have displayed a high catalytic activity

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toward the polymerization and copolymerization of olefins and dienes.<sup>6</sup> The CNC-pincer rare-earth-metal diamido complexes have displayed a high catalytic activity toward the C-H/P-H bond addition of terminal alkynes or a phosphine to give heterocumulenes.7 Mindiola and his co-workers demonstrated the existence of a scandium terminal imido complex with a PNP-pincer ancillary ligand by applying a combination of isotopic labeling and reactivity studies of scandium terminal imido intermediates that could promote intermolecular C-H bond activation.<sup>8</sup> Chen reported groundbreaking studies in this field on the isolation and structural characterization of the first rare-earth-metal terminal imido complex bearing an NNNtridentate  $\beta$ -diketiminato ligand.<sup>9</sup> Further, they developed the synthesis of a rare-earth-metal terminal imido complex with an NNNN-tetradentate  $\beta$ -diketiminato ligand without additional DMAP.<sup>10</sup> Moreover, they revealed the predicted very rich and diverse reactivity of the highly polarized Sc=N functionality.<sup>11</sup> Cui and co-workers have also successfully isolated a scandium terminal imido complex with an NPNPN-pincer ancillary ligand by use of a scandium alkyl amide precursor in the presence of DMAP, which was derived from the reaction of a scandium dialkyl complex with 2,6-diisopropylaniline. Pyrrole-based NNN-pincer ligands have also been applied in syntheses of rare-earth dialkyl complexes to exhibit specific selective living polymerization of isoprene and intramolecular C-H activation.<sup>13</sup> Attempting to increase the coordination atoms of pyrrole-based pincer ligands, we herein report the synthesis of NNNN-pincer multidentate pyrrolyl rare-earthmetal amido-chloride and dialkyl complexes and further reactions of rare-earth-metal dialkyl complexes with dimethylaniline, and their catalytic activities toward the addition of amines to carbodiimides or isothiocyanate have been examined.

#### RESULTS AND DISCUSSION

Synthesis of Pincer Multidentate Pyrrolyl Rare-Earth Amido-Chloride Complexes. Reactions of  $[(Me_3Si)_2N]_3RE(\mu$ -Cl)Li(THF)<sub>3</sub> with compound 1 in toluene afforded the unexpected pincer pyrrolyl rare-earth-metal amido-chloride complexes { $\eta^1$ : $\kappa^3$ -2,5-[CH<sub>3</sub>N-(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]<sub>2</sub>C<sub>4</sub>H<sub>2</sub>N}RECl[N(SiMe\_3)<sub>2</sub>] (RE = Y (2a), Sm (2b), Dy (2c), Er (2d), Yb (2e)) in one step (Scheme 1).





These types of rare-earth-metal amido-chloride complexes could also be prepared through reaction of ligands with  $Ln[N(SiMe_3)_2]_2Cl(THF)$ .<sup>14</sup> Complexes 2a-e are extremely sensitive to air and moisture, and they are soluble in THF, toluene, and *n*-hexane. All complexes were characterized by spectroscopic methods, elemental analyses, and single-crystal X-ray diffraction. Interestingly, the <sup>1</sup>H NMR spectrum of complex 2a exhibited two singlets (0.53 and 0.16 ppm) of the  $N(SiMe_3)_2$  group, integrating to 9 H each, and the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of complex 2a exhibited two singlets (6.2 and 5.3 ppm) of the  $N(SiMe_3)_2$  group; the observation of

inequivalent SiMe<sub>3</sub> groups was due to the steric crowding that suppressed the rotation of the Y–N bond. The reaction of  $[(Me_3Si)_2N]_3Y(\mu$ -Cl)Li(THF)<sub>3</sub> with compound 1 in  $d_8$ -toluene was followed by <sup>1</sup>H NMR spectroscopy, and one singlet (0.22 ppm) was observed in about 2 h, probably owing to the leaving of  $(Me_3Si)_2NLi$  (Figure S1 in the Supporting Information).

X-ray analyses revealed that complexes 2a-e had isostructural octahedral configurations, and a representative structure diagram of complex 2d is shown in Figure 1. In complexes 2a-



Figure 1. Representative molecular structure of complex 2d. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

**2e**, the rare-earth-metal ion adopted a six-coordinate heavily distorted tetragonal bipyramidal geometry in which the rareearth-metal ion was coordinated by four nitrogen atoms of the *NNNNN*-pincer multidentate pyrrolyl ligand in  $\eta^{1}$ : $\kappa^{3}$  fashions, chlorine, and the nitrogen atom of silylamine; however, one of the nitrogen atoms of the pincer ligand is uncoordinated to the rare-earth metal. The bond angles N(3)–RE(1)–N(4) (124–131°) and N(6)–RE(1)–Cl(1) (164–169°) in complexes **2a–e** reflect the heavily distorted tetragonal bipyramidal geometry.

The selected bond lengths and angles of complexes 2a-e are given in Table 1. In the rare-earth amido-chloride complexes 2a-e, the average bond lengths RE–N (2.470(2) Å for Y (2a), 2.519(2) Å for Sm (2b), 2.478(2) Å for Dy (2c), 2.452(3) Å for Er (2d), 2.438(3) Å for Yb (2e)) were consistent with the order of ionic radii of the rare-earth metal. Meanwhile, the bond length RE–N(1) was shorter than those of RE–N(2), -N(3), and -N(4) in complexes 2a-e, as expected due to the donation from the anionic pyrrolide being stronger than those from the neutral amino donors in the molecules.

Synthesis of Pincer Multidentate Pyrrolyl Rare-Earth Metal Dialkyl Complexes. Reactions of RE-(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> with compound 1 gave the rare-earthmetal dialkyl complexes { $\eta^1:\kappa^2-2, 5-[CH_3N-(CH_2CH_2)_2NCH_2]_2C_4H_2N$ }Sc(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (3a) and { $\eta^1:\kappa^3-2,5-[CH_3N(CH_2CH_2)_2NCH_2]_2C_4H_2N$ }RE(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (RE = Y (3b), Dy (3c), Er (3d), Yb (3e), Lu (3f)) (Scheme 2). Complexes 3a-f are extremely sensitive to air and moisture. They are soluble in THF, toluene, and *n*-hexane. All complexes were characterized by spectroscopic methods, elemental analyses, and single-crystal X-ray diffraction.

Table	1.	Selected	Bond	Lengths	(A)	and	Bond	Angle	es (d	leg)	of	Co	mplexes	2a-	-e
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	<b>2a</b> (Y)	<b>2b</b> (Sm)	<b>2c</b> (Dy)	<b>2d</b> (Er)	<b>2e</b> (Yb)
RE(1) - N(1)	2.269(2)	2.3003(13)	2.281(3)	2.240(2)	2.237(3)
RE(1)-N(2)	2.584(2)	2.641(2)	2.597(3)	2.548(3)	2.554(3)
RE(1) - N(3)	2.571(2)	2.633(2)	2.582(3)	2.552(3)	2.538(3)
RE(1)-N(4)	2.663(2)	2.707(2)	2.667(3)	2.674(2)	2.631(3)
RE(1)-N(6)	2.261(2)	2.314(2)	2.265(3)	2.248(2)	2.231(2)
RE(1)-Cl(1)	2.5769(8)	2.6481(8)	2.5863(10)	2.5567(9)	2.5411(9)
$RE(1)-N_{av}$	2.470(2)	2.519(2)	2.478(2)	2.452(3)	2.438(3)
N(1)-RE(1)-N(2)	65.57(8)	64.44(8)	65.36(11)	66.03(8)	66.25(10)
N(2)-RE(1)-N(3)	58.38(8)	57.44(8)	58.15(11)	59.06(11)	59.02(10)
N(3)-RE(1)-N(4)	167.34(7)	169.49(7)	167.64(10)	164.79(10)	165.92(10)
N(1)-RE(1)-N(4)	65.98(8)	64.92(7)	65.99(10)	67.06(7)	66.57(10)
N(6)-RE(1)-Cl(1)	125.90(6)	127.02(6)	125.45(7)	131.26(6)	124.46(7)

Scheme 2. Synthesis of Complexes 3a-f



X-ray diffraction revealed that the rare-earth-metal ion in complex 3a (Figure 2) adopted a five-coordinate trigonal-



Figure 2. Molecular structure of complex 3a. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

bipyramidal geometry and the NNNNN-pincer multidentate pyrrolyl ligand coordinated to the rare-earth metal in  $\eta^{1:\kappa^2}$ modes; the two nitrogen atoms of another N-methylpiperazine were uncoordinated to the rare-earth metal. The average bond length Sc(1)- $\sigma$ -C of 2.218(3) Å in complex 3a (Table 2) was comparable to those in NNN-tridentate pyrrolyl scandium complexes (2.222(5) and 2.225(5) Å).<sup>13</sup> The bond length Sc- $\sigma$ -N(1) (2.138(3) Å) in complex 3a was slightly longer than those of 2.087(4) and 2.079(2) Å in NNN-tridentate pyrrolyl scandium complexes<sup>13</sup> and was slightly shorter than that of 2.219 Å in pyrrolylaldiminato scandium complexes.<sup>15</sup>

However, in complexes 3b-f (a representative structure diagram of complex 3b is given in Figure 3), the rare-earthmetal ion adopted a six-coordinate distorted-tetragonalbipyramidal geometry. The NNNNn-pincer multidentate pyrrolyl ligand coordinated to the rare-earth metal in  $\eta^1:\kappa^3$ modes; one of the nitrogen atoms was uncoordinated to the rare-earth metal. Different from NNN-tridentate pyrrolyl rareeart-metal complexes, the coordination mode of the tridentate ligand could stabilize the Sc3+ ion but could not afford satisfactory steric shielding for the Ln<sup>3+</sup> ion; thus two molecules combined and redistributed into a dimer.<sup>13</sup> The selected bond distances and angles of complexes 3a-f are given in Table 2. The average lengths RE(1)-C of 2.407(4) Å in 3b, 2.419(3) Å in 3c, 2.383(8) Å in 3d, 2.364(8) Å in 3e, and 2.363(7) Å in 3f fell in a reasonable range when the difference in ionic radii of the rare-earth metals was considered. The average lengths RE(1)-C were comparable to those of NNN-tridentate pyrrolyl rare-earth complexes<sup>13</sup> and  $\beta$ diketiminato scandium complexes.<sup>16</sup>

**Reactivity of Pincer Multidentate Pyrrolyl Rare-Earth** Metal Dialkyl Complexes with Arylamine. In order to further explore the reactivity of pincer multidentate pyrrolyl rare-earth metal dialkyl complexes, reactions of complexes 3 with arylamine were studied. Reactions of complexes 3 with 1 equiv of  $2,6-Me_2C_6H_3NH_2$  afforded the rare-earth-metal diarylamido complexes 4a,b,d,f bearing an NNNNN-pincer multidentate pyrrolyl ligand (Scheme 3). Different from the case for a  $\beta$ -diketiminato ligand, <sup>9-11</sup> no rare-earth-metal imido complexes were obtained through proton abstraction even with additional DMAP as a Lewis base, although there was still an uncoordinated nitrogen of one piperazidine. Especially, there were still two uncoordinated nitrogens of one piperazidine in scandium complex 4a. In order to further determine the yields, complexes 4a,b,d,f as catalysts were synthesized by reactions of complexes 3 with 2 equiv of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> to afford the complexes in 76-88% yields. Complexes 4a,b,d,f were extremely sensitive to air and moisture. They were soluble in THF, slightly soluble in toluene, and insoluble in hexane. All complexes were characterized by spectroscopic methods, elemental analyses, and single-crystal X-ray diffraction.

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	3a (Sc)	<b>3b</b> (Y)	3c (Dy)	3d (Er)	3e (Yb)	3f (Lu)
RE(1)-N(1)	2.138(3)	2.274(4)	2.289(3)	2.263(7)	2.241(7)	2.238(6)
RE(1)-N(2)	2.306(3)	2.565(4)	2.579(3)	2.537(7)	2.522(7)	2.522(7)
RE(1)-N(3)	2.363(3)	2.532(3)	2.551(2)	2.525(6)	2.503(6)	2.499(7)
RE(1)-N(4)		2.690(3)	2.701(2)	2.679(6)	2.673(7)	2.675(7)
RE(1) - C(17)	2.200(3)	2.404(4)	2.416(3)	2.376(8)	2.360(8)	2.358(7)
RE(1) - C(21)	2.216(3)	2.407(5)	2.422(3)	2.390(7)	2.364(8)	2.367(8)
$RE(1)-N_{av}$	2.269(3)	2.5153(4)	2.53(3)	2.501(7)	2.4848(7)	2.4835(6)
N(1)-RE(1)-N(2)	74.96(11)	66.46(14)	66.42(10)	66.8(3)	67.5(2)	67.4(3)
N(2)-RE(1)-N(3)	63.42(11)	58.81(12)	58.67(9)	59.3(2)	58.9(2)	59.4(2)
N(3)-RE(1)-N(4)		169.93(12)	170.26(9)	169.3(2)	168.8(2)	168.3(2)
N(1)-RE(1)-N(4)		64.93(13)	64.68(9)	64.8(3)	65.5(2)	65.7(2)
N(3)-RE(1)-C(21)	91.68(10)	90.24(15)	90.55(10)	86.5(3)	86.6(3)	90.2(3)
N(1)-RE(1)-C(21)	103.50(10)	127.27(15)	128.03(11)	101.8(3)	127.5(3)	126.5(3)
N(1)-RE(1)-C(17)	112.88(10)	101.57(14)	101.21(11)	127.1(2)	101.3(3)	101.9(3)
N(2)-RE(1)-C(17)	112.07(11)	113.08(15)	112.64(10)	114.3(3)	113.7(3)	113.9(3)
N(3)-RE(1)-C(17)	100.34(11)	80.80(14)	86.74(10)	90.2(3)	89.6(3)	86.8(3)
C(21)-RE(1)-C(17)	111.84(11)	121.70(16)	121.00(12)	121.5(3)	121.6(3)	121.3(3)



**Figure 3.** Representative structure diagram of complex **3b**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Scheme 3. Synthesis of Complexes 4a,b,d,f



X-ray analyses revealed that complex **4a** (Figure 4) adopted a five-coordinate trigonal-bipyramidal geometry, and the



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Figure 4. Molecular structure of complex 4a. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

*NNNNN*- pincer multidentate pyrrolyl ligand coordinated to the rare-earth metal in  $\eta^{1}$ : $\kappa^{2}$  modes, leaving one piperazidine dangling without coordination. Complexes **4b**,**d**,**f** had isostructural six-coordinate distorted-tetragonal-bipyramidal geometries, and a representative structure diagram of complex **4b** is shown in Figure 5. X-ray analyses showed that RE<sup>3+</sup> was bound to four nitrogen atoms of the pyrrolyl ligand and two nitrogen atoms of the anilido fragments in complexes **4b**,**d**,**f**, and the *NNNNN*-pincer multidentate pyrrolyl ligand coordinated to the rare-earth metal in  $\eta^{1}$ : $\kappa^{3}$  modes. Selected bond lengths and angles of complexes **4a**,**b**,**d**,**f** are given in Table 3.

**Catalytic Hydroamination of Heterocumulenes.** The catalytic addition of an amide to carbodiimides or isothiocyanate has provided a straightforward and atomeconomical route to synthesis of guanidines and thioureas.<sup>17</sup> Rare-earth-metal complexes as catalysts for the hydroamination of heterocumulenes have been developed in recent years.<sup>18</sup> The previous studies showed that the reaction of the amines with rare-earth-metal amidates or alkylates gave the rare-earth-metal amido as an intermediate, which further went through an insertion of carbodiimide to intermediate to afford a metal



**Figure 5.** Representative molecular structure of complex **4b**. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

guanidinate species.<sup>19</sup> Therefore, NNNN-pincer pyrrolyl rare-earth-metal dialkyl complexes were reacted with an amide to afford the corresponding rare-earth-metal diamido complexes, which should also be able to serve as intermediates. The additions of aniline to N,N'-dicyclohexylcarbodiimide were first examined using 1 mol % of complex 3a in different solvents to afford the product in almost quantitative yields (entries 1-3, Table 4), indicating the solvent compatibility of the catalyst. It was found that complexes 3b-f could all highly catalyze the addition of aniline to  $N_{,}N'$ -dicyclohexylcarbodiimide (entries 4-8, Table 4). However, rare-earth amidochloride complexes 2a-e catalyzed the addition of aniline to N,N'-dicyclohexylcarbodiimide to give the product 7a in 81-85% yields over 6 h (entries 9-13, Table 4). Further optimizations for the guanylation of aniline were accomplished, affording the product 7a in 95% yield with 0.5 mol % of catalyst 3b under solvent-free conditions (entry 18, Table 4). Complex 4a as catalyst for the a guanylation of aniline provided the product 7a in a yield similar to that of complex 3a as the catalyst, indicating that the rare-earth-metal diamido complex was probably an intermediate of the catalytic reaction.

Table 4. Optimization	of the	Catalytic	Addition	of .	Aniline
to $CyN = C = NCy^{a}$					

			catalyst	HN-	Су
	Ph-NH	<sub>2</sub> + CyN=C=NCy -	rt	Ph-N=C	
	5a	6a	1	HN-	Су
				/a	
entry	catalyst	loading (mol %)	time (h)	solvent	yield (%) <sup>b</sup>
1	3a	1	2	toluene	99
2	3a	1	2	THF	99
3	3a	1	2	hexane	99
4	3b	1	2	toluene	99
5	3c	1	2	toluene	99
6	3d	1	2	toluene	99
7	3e	1	2	toluene	99
8	3f	1	2	toluene	99
9	2a	1	6	toluene	83
10	2b	1	6	toluene	87
11	2c	1	6	toluene	81
12	2d	1	6	toluene	83
13	2e	1	6	toluene	86
14	3b	0.5	2	toluene	95
15	3b	0.1	2	toluene	70
16	3b	1	1	toluene	99
17	3b	1	0.5	toluene	99
18	3b	1	0.5	solvent-free	99
<sup>a</sup> React	ion conc	litions: aniline (	1.0 mmol	), $CyN = C =$	=NCy (1.0
mmol)	. solvent	(2.0 mL). <sup>b</sup> Isolat	ed vield.		

Thus, complex **3b** was selected as the catalyst for the following experiments to examine the addition of various amines to heterocumulene under solvent-free conditions or in toluene (2.0 mL, to increase the solubility for solid amines), and the results are presented in Table 5. The results showed that the additions afforded the guanylation products 7b-j in excellent yields of 96-99% for various aromatic amines with electron-donating or electron-withdrawing groups (entries 2–10, Table 5). The catalytic system also worked excellently for addition of aliphatic amines to afford the corresponding compounds 7k-n (entries 11-14, Table 5). The addition of amines to N,N'-diisopropylcarbodiimide also gave the corresponding compounds 7o-r in high yields (entries 15-18, Table 5). Further expansion of the addition of amines to isothiocyanate also worked well to afford the substituted

	4a (Sc)	<b>4b</b> (Y)	<b>4d</b> (Er)	4f (Lu)
RE(1)-N(1)	2.1535(17)	2.2933(16)	2.276(3)	2.246(2)
RE(1)-N(2)	2.4098(18)	2.5776(16)	2.556(3)	2.523(2)
RE(1)-N(3)	2.4327(19)	2.5668(17)	2.548(3)	2.519(2)
RE(1)-N(4)		2.8058(16)	2.802(3)	2.806(2)
RE(1)-N(6)	2.0729(19)	2.2457(16)	2.216(2)	2.180(2)
RE(1) - N(7)	2.0562(17)	2.2244(15)	2.234(2)	2.202(2)
$RE(1)-N_{av}$	2.2250(19)	2.4523(17)	2.4387(3)	2.4127(2)
N(1)-RE(1)-N(2)	69.50(7)	65.24(6)	65.54(9)	66.34(8)
N(2)-RE(1)-N(3)	61.46(7)	58.28(5)	58.67(9)	59.37(7)
N(3)-RE(1)-N(4)		168.29(5)	167.82(8)	166.95(7)
N(1)-RE(1)-N(3)	126.22(7)	119.43(6)	120.03(9)	121.45(8)
N(1)-RE(1)-N(4)		65.06(5)	65.26(9)	65.49(7)
N(6)-RE(1)-N(7)	121.05(8)	122.32(6)	122.21(10)	121.93(9)
N(2)-RE(1)-N(6)	120.02(8)	115.54(6)	115.91(10)	116.79(8)
N(2)-RE(1)-N(7)	107.86(7)	107.96(6)	107.92(9)	107.70(8)

### Table 5. Catalytic Addition of Various Amines to Heterocumulenes by Complex $3b^{a}$

	D1D2NUL -		complex 3b (0.5 mol%	) X	R <sup>3</sup>
	- R'R-NH +	R N-C-A-	solvent-free, r.t., 2h	R <sup>1</sup> R <sup>2</sup> N	N H
	5	6		7	
enti	у	R <sup>1</sup> R <sup>2</sup> NH	R <sup>3</sup> /X	product	yield (%) <sup>b</sup>
1	PhNI	H <sub>2</sub>	Cy/NCy	7a	99
2	2-Me	C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	Cy/NCy	7b	99
3	3-Me	C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	Cy/NCy	7c	99
4	2,6-N	4e <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	Cy/NCy	7d	98
5	2,6- <sup>i</sup> F	Pr <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	Cy/NCy	7e	99
6	2-ClC	$C_6H_4NH_2$	Cy/NCy	7f	99
7	3-Cl0	$C_6H_4NH_2$	Cy/NCy	7 <b>g</b>	99
8 <sup>c</sup>	2,6-0	Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> NH <sub>2</sub>	Cy/NCy	7h	96
9 <sup>c</sup>	2-BrO	$C_6H_4NH_2$	Cy/NCy	7i	99
10	3,5-(	$(CF_3)_2C_6H_3N$	H <sub>2</sub> Cy/NCy	7j	99
11	PhCI	$H_2NH_2$	Cy/NCy	7k	99
12	CyN	H <sub>2</sub>	Cy/NCy	71	99
13	pyrro	olidine	Cy/NCy	7 <b>m</b>	97
14	CH <sub>2</sub>	$(CH_2CH_2)_2N$	JH Cy/NCy	7 <b>n</b>	94
15	PhNI	H <sub>2</sub>	$^{i}\mathrm{Pr}_{2}/\mathrm{N}^{i}\mathrm{Pr}_{2}$	7 <b>o</b>	99
16	2-Me	C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	$^{i}\mathrm{Pr}_{2}/\mathrm{N}^{i}\mathrm{Pr}_{2}$	7p	98
17	2-ClO	$C_6H_4NH_2$	$^{i}Pr_{2}/N^{i}Pr_{2}$	7 <b>q</b>	98
18	PhNI	$H_2$	4-MePh/S	7 <b>r</b>	95
19	2-Me	C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	4-MePh/S	7s	96
20	2-ClO	C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	4-MePh/S	7t	93
21	CyN	$H_2$	4-MePh/S	7 <b>u</b>	99
22	CyN	H <sub>2</sub>	<sup>t</sup> Bu/S	$7\mathbf{v}$	98

<sup>a</sup>Reaction conditions: complex **3b** (0.005 mmol), amine (1.0 mmol), heterocumulene (1.0 mmol), room temperature. <sup>b</sup>Isolated yields. <sup>c</sup>Reaction was run in toluene (2.0 mL) to increase the solubility for solid amines.

thioureas 7s-v in almost quantitative yields (entries 19–22, Table 5).

#### CONCLUSION

A series of rare-earth-metal complexes bearing an NNNNNpincer multidentate pyrrolyl ligand were synthesized and welldefined. Pincer multidentate pyrrolyl rare-earth-metal amidochloride complexes were synthesized via one-step reactions of  $[(Me_3Si)_2N]_3RE(\mu$ -Cl)Li(THF)<sub>3</sub> with the NNNN-pincer multidentate pyrrolyl ligand. Pincer multidentate pyrrolyl rare-earth-metal dialkyl complexes were synthesized through reactions of  $RE(CH_2SiMe_3)_3(THF)_2$  with the NNNN-pincer multidentate pyrrolyl ligand, and their reactivities with 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>NH<sub>2</sub> were examined to afford rare-earth-metal diarylamido complexes. No rare-earth-metal imido complexes were obtained even under the condition of additional DMAP, although there still were uncoordinated nitrogens in the ligand of rare-earth-metal complexes. Further, the NNNNN-pincer multidentate pyrrolyl rare-earth-metal dialkyl complexes exhibited high catalytic activities toward the addition of amines to carbodiimides or isothiocyanate for synthesis of the substituted guanidines and thioureas in quantitative yields.

#### EXPERIMENTAL SECTION

**General Remarks.** All syntheses and manipulations of air- and moisture-sensitive materials were performed under dry argon and an oxygen-free atmosphere using standard Schlenk techniques or in a glovebox. Solvents were refluxed and distilled over sodium/ benzophenone under argon prior to use.  $[(Me_3Si)_2N]_3RE(\mu-Cl)Li$ -

 $(THF)_3^{20}$  and RE $(CH_2SiMe_3)_3(THF)_2^{-21}$  were prepared according to the literature procedures. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for analyses of compounds were recorded on a Bruker AV-400 or 500 NMR spectrometer in  $C_6D_6$  for lanthanide complexes and in CDCl<sub>3</sub> for organic compounds. IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer.

Synthesis of Compound 1. To a solution of 1-methylpiperazine (5.0 mL, 45.0 mmol), 37% formaldehyde solution (3.65 mL, 45.0 mmol), and pyrrole (1.58 mL, 22.5 mmol) in ethanol (20.0 mL) was added dropwise glacial acetic acid. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was extracted with dichloromethane (50.0 mL × 3), and the extracts were dried over anhydrous Mg<sub>2</sub>SO<sub>4</sub> and filtered. The organic layer was concentrated under reduced pressure to provide the white solid 1 (5.64 g, 86% yield). Mp: 131–133 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.57 (s, 1H), 5.89 (s, 2H), 3.44 (s, 4H), 2.44 (br, 16H), 2.27 (s, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  128.2, 107.4, 55.5, 55.1, 53.0, 46.0. HRMS (ESI): calcd for C<sub>16</sub>H<sub>29</sub>N<sub>5</sub> [M + H<sup>+</sup>] 292.2496, found 292.2494.

**General Synthesis of Complexes 2a–e.** Under an argon atmosphere, an oven-dried 250.0 mL Schlenk flask equipped with a magnetic stir bar was charged with compound 1 (0.29 g, 1.00 mmol),  $[(Me_3Si)_2N]_3RE(\mu$ -Cl)Li(THF)<sub>3</sub> (1.00 mmol), and toluene (20.0 mL) at room temperature. The reaction mixture was stirred at 90 °C for 12 h, and the solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane/toluene (1/1), and crystals were obtained by cooling the solution to 0 °C for several days.

Complex 2a. Colorless crystals (0.50 g, 89% yield). Mp: 227–229 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  2935(s), 2850(s), 2809(s), 1452(w), 1339(s), 1282(m), 1157(s), 1012(s), 937(s), 449(m). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.30 (s, 2H), 4.12 (s, 4H), 3.72–2.68 (m, 10H), 2.38–1.95 (m, 12H), 0.53 (s, 9H), 0.16 (s, 9H). <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  134.6, 103.1, 59.7, 53.3, 49.2, 46.1, 6.2, 5.3. Anal. Calcd for C<sub>22</sub>H<sub>46</sub>ClN<sub>6</sub>Si<sub>2</sub>Y·C<sub>6</sub>H<sub>14</sub>: C, 50.85; H, 9.14; N, 12.71. Found: C, 50.41; H, 8.98; N, 12.89.

Complex **2b**. Pale yellow crystals (0.58 g, 81% yield). Mp: 235–237 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  2945(s), 2846(s), 2814(s), 1452(w), 1342(s), 1286(m), 1168(s), 1015(s), 924(s), 808(s). Anal. Calcd for C<sub>22</sub>H<sub>46</sub>ClN<sub>6</sub>Si<sub>2</sub>Sm: C, 41.51; H, 7.28; N, 13.20. Found: C, 41.33; H, 6.91; N, 13.12.

Complex 2c. Colorless crystals (0.62 g, 84% yield). Mp: 231–233 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  2945(s), 2852(s), 2810(s), 1638(w), 1455(s), 1352(m), 1282(s), 1245(s), 1154(s), 1012(s), 927(m). Anal. Calcd for C<sub>22</sub>H<sub>46</sub>ClDyN<sub>6</sub>Si<sub>2</sub>: C, 40.73; H, 7.15; N, 12.95. Found: C, 40.33; H, 7.04; N, 13.01.

Complex 2d. Pink crystals (0.48 g, 75% yield). Mp: 227–229 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  2952(s), 2839(s), 2811(s), 1455(w), 1345(s), 1295(m), 1248(s), 1147(s), 1009(s), 921(s), 826(m). Anal. Calcd for C<sub>22</sub>H<sub>46</sub>ClErN<sub>6</sub>Si<sub>2</sub>: C, 40.43; H, 7.09; N, 12.86. Found: C, 40.07; H, 7.22; N, 12.41.

Complex **2e**. Yellow crystals (0.59 g, 79% yield). Mp: 224–226 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  2942(s), 2815(s), 1455(w), 1345(s), 1279(m), 1147(s), 1053(s), 1006(s), 924(s), 804(m). Anal. Calcd for C<sub>22</sub>H<sub>46</sub>ClN<sub>6</sub>Si<sub>2</sub>Yb: C, 40.08; H, 7.03; N, 12.75. Found: C, 40.16; H, 7.08; N, 12.73.

**General Synthesis of Complexes 3a–f.** Under an argon atmosphere, an oven-dried 50.0 mL Schlenk flask equipped with a magnetic stir bar was charged with compound 1 (0.29 g, 1.00 mmol), RE(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (1.00 mmol), and THF (20.0 mL) at room temperature. The reaction mixture was stirred at room temperature for 12 h, and the solvent was evaporated under reduced pressure. The residue was extracted with *n*-hexane (10.0 mL), and the crystals were obtained by cooling the solution to 0 °C for several days.

Complex **3a**. Colorless crystals (0.31 g, 60% yield). Mp: 98–99 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  2941 (s), 2798 (s), 1455 (s), 1345(m), 1287 (w), 1110(m), 1011 (s), 813(s). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.25 (s, 2H), 3.69 (br, 4H), 3.08–2.51 (m, 16H), 2.17 (s, 6H), 0.22 (s, 18H), 0.20 (s, 4H). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  137.5, 107.9, 57.9, 53.0, 52.5, 46.2, 41.9, 4.4. Anal. Calcd for C<sub>24</sub>H<sub>50</sub>N<sub>5</sub>ScSi<sub>2</sub>: C, 56.54; H, 9.89; N, 13.74. Found: C, 56.63; H, 9.88; N, 13.27.

*Complex* **3b**. Pale yellow crystals (0.35 g, 63% yield). Mp: 169–171 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  2938 (s), 2797 (s), 1452 (s), 1345 (m), 1279 (w), 1106 (m), 1015 (s), 811(s). <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.28 (s, 2H), 3.76 (s, 4H), 3.24 (s, 4H), 2.63–2.26 (m, 8H), 2.09 (s, 6H), 1.82 (s, 4H), 0.26 (s, 18H), -0.64 (d, *J* = 2.8 Hz, 4H). <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  134.1, 104.3, 56.4, 50.9, 50.3, 45.6, 32.1 (*J*<sub>Y-C</sub> = 47.5 Hz), 5.2. Anal. Calcd for C<sub>24</sub>H<sub>50</sub>N<sub>5</sub>Si<sub>2</sub>Y: C, 52.05; H, 9.10; N, 12.65. Found: C, 52.06; H, 9.02; N, 12.38.

*Complex* **3c**. Pale yellow crystals (0.41 g, 66% yield). Mp: 177–179 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  2937(s), 2800(s), 1459(s), 1345(m), 1286(w), 1160 (m),1009(s), 921(s), 814(s). Anal. Calcd for C<sub>24</sub>H<sub>50</sub>DyN<sub>5</sub>Si<sub>2</sub>: C, 45.95; H, 8.03; N, 11.16. Found: C, 45.59; H, 8.10; N, 11.16.

Complex 3d. Pink crystals (0.38 g, 60% yield). Mp: 172–174 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  2945(s), 2807(s), 1455(s), 1345(m), 1260(w), 1150 (m), 1015(s), 808(s). Anal. Calcd for C<sub>24</sub>H<sub>50</sub>ErN<sub>5</sub>Si<sub>2</sub>: C, 45.60; H, 7.97; N, 11.08. Found: C, 45.71; H, 7.58; N, 10.92.

Complex **3e**. Yellow crystals (0.36 g, 56% yield). Mp: 165–167 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  2954(s), 2786(s), 1588(s), 1449(m), 1339(w), 1260(m), 921(s), 792(s). Anal. Calcd for C<sub>24</sub>H<sub>50</sub>N<sub>5</sub>Si<sub>2</sub>Yb: C, 45.19; H, 7.90; N, 10.98. Found: C, 44.88; H, 8.18; N, 10.81.

*Complex 3f.* Colorless crystals (0.45 g, 70% yield). Mp: 102–104 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  2937(s), 2797(s), 1455(s), 1345(m), 1285(w), 1102(m), 1010(s), 810(s). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  6.28 (s, 2H), 3.79 (s, 4H), 3.32–2.26 (m, 16H), 2.09 (s, 6H), 0.24 (s, 18H), -0.85 (s, 4H). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  134.7, 104.6, 55.8, 50.8, 50.1, 45.5, 38.1, 5.4. Anal. Calcd for C<sub>24</sub>H<sub>50</sub>N<sub>5</sub>Si<sub>2</sub>Lu: C, 45.05; H, 7.88; N, 10.95. Found: C, 45.15; H, 7.77; N, 10.94.

**General Synthesis of Complexes 4a,b,d,f.** Under an argon atmosphere, an oven-dried 50.0 mL Schlenk flask equipped with a magnetic stir bar was charged with complex **3a** (0.25 g, 0.50 mmol), **3b** (0.28 g, 0.50 mmol), **3d** (0.32g, 0.50 mmol), or **3f** (0.32 g, 0.50 mmol) in toluene (2.0 mL) was added dropwise into a solution of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> (123.0  $\mu$ L, 1.00 mmol) in toluene (3.0 mL) at room temperature. The reaction mixture was stirred at room temperature for 6 h, and solvent was evaporated under reduced pressure. The residue was extracted with THF/*n*-hexane (1/1), and the crystals were obtained by cooling the solution to 0 °C for several days. The yields of complexes **4a,b,d,f** were based on the corresponding complexes **3** with 2 equiv of 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>.

*Complex* **4a**. Colorless crystals (0.21 g, 76% yield). Mp: 123–125 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  3385(s), 2936(s), 2796(s), 1591(s), 1455(s), 1284(w), 1146(m), 1010(s), 808(s). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.14–7.09 (m, 4H), 6.29 (t, *J* = 7.2, 2H), 6.31 (s, 2H), 4.41 (s, 2H), 3.63 (s, 4H), 3.05 (s, 4H), 2.11–2.39 (m, 24 H), 1.83 (s, 6H). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  153.9, 135.4, 128.9, 122.0, 115.5, 104.3, 57.5, 55.3, 52.3, 45.1, 20.0. Anal. Calcd for C<sub>32</sub>H<sub>48</sub>ScN<sub>7</sub>· C<sub>4</sub>H<sub>8</sub>O: C, 66.74; H, 8.71; N, 15.13. Found: C, 66.83; H, 8.37; N, 15.75.

*Complex* **4b**. Colorless crystals (0.26 g, 87% yield). Mp: 141–143 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  3386(s), 2937(s), 2797(s), 1591(s), 1456(s), 1269(w), 1125(m), 1011(s), 806(s). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.13-7.10 (m, 4H), 6.68 (t, *J* = 7.0 Hz, 2H), 6.31 (s, 2H), 4.41 (s, 2H), 3.63 (s, 4H), 3.04 (s, 4H), 2.38–1.88 (m, 21H), 1.88 (s, 3H), 1.83 (s, 6H). <sup>13</sup>C NMR (101 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  143.3, 128.8, 128.6, 121.4, 118.2, 107.6, 56.0, 55.6, 53.5, 46.2, 17.6. Anal. Calcd for C<sub>32</sub>H<sub>48</sub>YN<sub>7</sub>: C, 62.02; H, 7.81; N, 15.82. Found: C, 61.63; H, 7.84; N, 15.78.

Complex 4d. Pink crystals (0.30 g, 88% yield). Mp: 121–123 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  3386(s), 2937(s), 2796(s), 1590(s), 1456(s), 1278(w), 1125(m), 1011(s), 805(s). Anal. Calcd for  $C_{32}H_{48}ErN_7$ : C, 55.06; H, 6.93; N, 14.05. Found: C, 54.83; H, 7.16; N, 13.63.

*Complex* **4f.** Colorless crystals (0.28 g, 81% yield). Mp: 123–125 °C. IR (KBr pellets, cm<sup>-1</sup>):  $\nu$  3385(s), 2937(s), 2796(s), 1591(s), 1456(s), 1278(w), 1126(m), 1010(s), 806(s). <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.14–7.11 (m, 4H), 6.69 (t, *J* = 7.5 Hz, 2H), 6.34 (s, 2H), 4.01 (s, 2H), 3.66 (s, 4H), 3.06 (s, 4H), 2.55–1.90 (m, br, 24H), 1.83 (s, 6H). <sup>13</sup>C NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  155.9, 135.3, 128.3, 121.5, 114.4, 104.9, 55.6, 53.5, 52.0, 46.2, 44.9, 20.1, 17.7. Anal. Calcd for

 $\rm C_{32}H_{48}LuN_{7}:$  C, 54.46; H, 6.86; N, 13.89. Found: C, 54.12; H, 6.62; N, 13.76.

X-ray Crystallography. Suitable crystals of complexes 2a–e, 3a– f, and 4a,b,d,f were each mounted in a sealed capillary. Diffraction was performed on a Burker SMART CCD area detector diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). An empirical absorption correction was applied by using the SADABS program. All 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. All hydrogen atoms were refined using a riding model. See the Supporting Information for crystallographic parameters and data collection and refinement information.

General Procedure for the Catalytic Addition of Amine to Carbodiimide. Under an argon atmosphere, an oven-dried 25.0 mL Schlenk flask equipped with a magnetic stir bar was charged with complex 2b (3.20 mg, 0.005 mmol), the aniline (98.0  $\mu$ L, 1.0 mmol), and *N*,*N'*-dicyclohexylcarbodiimide (206.30 mg, 1.0 mmol) and the resulting mixture was stirred either under solvent-free conditions or in toluene (2.0 mL) for 2 h. The reaction mixture was then hydrolyzed with water (0.5 mL) and extracted with dichloromethane (10.0 mL × 3), and the extracts were dried over anhydrous MgSO<sub>4</sub> and filtered. After the solvent was removed under reduced pressure, the final product could be obtained by washing the crude product with 10.0 mL of diethyl ether.

General Procedure for the Catalytic Addition of Amines to Isothiocyanate. Under an argon atmosphere, an oven-dried 25.0 mL Schlenk flask equipped with a magnetic stir bar was charged with complex 2b (3.20 mg, 0.005 mmol), the aniline (98.0  $\mu$ L, 1.0 mmol), and 4-methylphenyl isothiocyanate (146.0  $\mu$ L, 1.0 mmol) and the resulting mixture was stirred under solvent-free conditions for 2 h. The reaction mixture was then hydrolyzed with water (0.5 mL) and extracted with dichloromethane (10.0 mL × 3), and the extracts were dried over anhydrous MgSO<sub>4</sub> and filtered. The solvent was removed under reduced pressure, and the final product was obtained.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00606.

Full experimental details, characterization data for compounds 7a-v, and crystallographic data and refinements for complexes 2a-e, 3a-f, and 4a,b,d,f (PDF)

#### Accession Codes

CCDC 2025788–2025802 contain the supplementary crystallographic data for this paper. These data can be obtained free 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.

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#### Notes

The authors declare no competing financial interest.

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#### ■ ABBREVIATIONS

Cy, cyclohexane

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