Selective Formation of Homoleptic and Heteroleptic 2,5-Bis(*N*-aryliminomethyl)pyrrolyl Yttrium Complexes and Their Performance as Initiators of ϵ-Caprolactone Polymerization

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Tridentate 2,5-bis(*N*-aryliminomethyl)pyrroles (**1a**, aryl = 4-methoxylphenyl; **1b**, aryl = 4-methylphenyl; **1c**, aryl = 2-methylphenyl; **1d**, aryl = 2,6-dimethylphenyl; **1e**, aryl = 2,6-diisopropylphenyl) have been prepared, and their reactions with a homoleptic $Y\{N(SiMe_3)_2\}_3$ (**2**) have been investigated. The number of pyrrolyl ligands introduced to an yttrium atom can be controlled by varying the bulkiness of the ligand to give mono(pyrrolyl) (**3**), bis(pyrrolyl) (**4**), or tris(pyrrolyl) complexes (**5**) upon aminolysis. When bulky ligands such as **1d** and **1e** were used, a mono(pyrrolyl) complex $Y(Xyl_2\text{-pyr})\{N(SiMe_3)_2\}_2$ (**3d**, Xyl_2-pyr = 2,5-bis{*N*-(2,6-dimethylphenyl)iminomethyl}pyrrolyl) and a bis(pyrrolyl) complex $Y(DIP_2\text{-pyr})_2\{N(SiMe_3)_2\}$ (**4e**, DIP_2-pyr = 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl) were predominantly obtained, respectively, with the release of hexamethyldisilazane. Both complexes adopt five-coordination geometries, a distorted trigonal bipyramidal mode for **3d** and a distorted square-pyramidal one for **4e**, in which the *N*,*N*′-bidentate coordination of **1e** to the yttrium atom was found in solution and the solid state presumably due to the bulkiness of the isopropyl substituents. In the case of *p*-substituted ligands, **1a** and **1b**, we obtained homoleptic tris(pyrrolyl) yttrium complexes **5a** and **5b**, respectively. The complex **5a** has three *N*,*N*′,*N*″-tridentate pyrrolyl ligands, and the yttrium center adopts a three-face-centered trigonal prismatic mode of nine-coordination, while we found the eight-coordinated, square-antiprismatic geometry for **5b** with two *N*,*N*′,*N*″-tridentate and one *N*,*N*′-bidentate pyrrolyl ligand. Thus, we demonstrated that the yttrium atom was able to have a five-, eight-, and nine-coordination number, depending on the congestion by the bis(aryliminomethyl)pyrrolyl ligands. We also found that these newly prepared mono(pyrrolyl) (**3d**) and bis(pyrrolyl) (**4e**) complexes catalyzed polymerization of ϵ-caprolactone and that complex **4e** acted as a single-site catalyst to give a polyester with a narrow molecular weight distribution ($M_w/M_n = 1.2$).

Introduction

Recent development of organolanthanide chemistry enables us to design the ligand environments of lanthanide complexes for efficient or selective catalysts.[1,2] In the past two decades, extensive studies directed to organic transformation reactions[3−7] and polymerizations[8−15] have been carried out using metallocene and half-metallocene complexes of lanthanide and group 3 metals. As tunable ancillary ligands, nitrogen-based polydentate ligands[16] are anticipated to be alternatives of cyclopentadienyl-based ligands in organolanthanide and yttrium chemistry. For example, benzamidinates,[17] β-diketiminates,[18] aminotroponiminates,[19] diamidoligands,[20] and oligopyrrolyl ligands[21,22] have been utilized for preparing lanthanide and yttrium complexes. We have been interested in the pyrrolyl derivatives as nitrogen-based polydentate ancillary ligands for early transition metals, and we and the other group prepared 2-(*N*-aryliminomethyl)pyrrolyl complexes of group 4 metals as catalyst precursors for ethylene polymerization.[23,24] As an extension of our continuous interest in the

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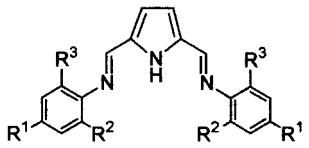
Chart 1



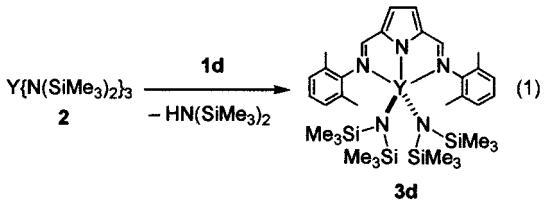
1a: R^1 = MeO; R^2 = H, R^3 = H (An_2-pyrH)
1b: R^1 = Me; R^2 = H, R^3 = H (p-Tol_2-pyrH)
1c: R^1 = H; R^2 = Me, R^3 = H (o-Tol_2-pyrH)
1d: R^1 = H; R^2 = Me, R^3 = Me ([Xyl_2-pyrH)
1e: R^1 = H; R^2 = ^{i}Pr, R^3 = ^{i}Pr (DIP_2-pyrH)

pyrrolyl ligand system, we prepared tridentate bis(iminomethyl)pyrrolyl ligands (Chart 1) and their yttrium complexes. In this paper we report the selective formation of homoleptic and heteroleptic pyrrolyl complexes of yttrium, whose unique coordination modes have been elucidated by crystallographic studies. Furthermore, we demonstrate that the heteroleptic pyrrolyl complexes have a capability to polymerize ϵ-caprolactone to give polyesters with narrow molecular weight distributions.

Results and Discussion

Synthesis and Characterization of 2,5-Bis(*N*-aryliminomethyl)pyrrolyl Complexes of Yttrium.

Tridentate ligands, 2,5-bis(*N*-aryliminomethyl)pyrroles **1a**−**e** (Chart 1), were prepared by condensation reaction of 2,5-diformylpyrrole with 2 equiv of the corresponding aniline derivative. A series of yttrium complexes having the tridentate ligand was conveniently obtained by amine elimination reaction starting from a homoleptic triamido complex $Y\{N(SiMe_3)_2\}_3$ (**2**). Three kinds of yttrium complexes, heteroleptic mono(pyrrolyl) (**3**) and bis(pyrrolyl) (**4**) complexes and homoleptic tris(pyrrolyl) complexes (**5**), are possible; however, the number of pyrrolyl ligands bound to the yttrium atom can be controlled in some cases by changing the congestion of two aromatic rings of the ligand. Treatment of **2** with 1 equiv of 2,5-bis{*N*-(2,6-dimethylphenyl)iminomethyl}-pyrrole (**1d**) in toluene predominantly afforded a yellow, air and moisture sensitive yttrium mono(pyrrolyl) complex, $Y(Xyl_2\text{-pyr})\{N(SiMe_3)_2\}_2$ (**3d**, Xyl_2-pyr = 2,5-bis{*N*-(2,6-dimethylphenyl)iminomethyl}pyrrolyl) in 82% yield along with the release of hexamethyldisilazane (eq 1). Complex **3d** was found to be inert to further reaction with **1d** even at elevated temperature (50 °C).



(1)

3d

The ^{1}H NMR spectrum of **3d** in benzene-d_6 consisted of a singlet resonance close to δ 0 due to $N(SiMe_3)_2$ and one set of signals due to the pyrrolyl ligand in an exact 2:1 ratio. The resonance of the pyrrolyl ring proton appeared in the olefinic region (δ 6.54), suggesting that the pyrrolyl anion coordinated in an η^1-*N*-coordination fashion to a yttrium metal. The singlet signal due to the imino proton was observed in slightly higher field (δ 7.34) compared with that of the free ligand **1d** (δ 7.55). In the ^{13}C NMR spectrum of **3d**, the resonance of the imino carbon was observed in lower field (δ 164.9)

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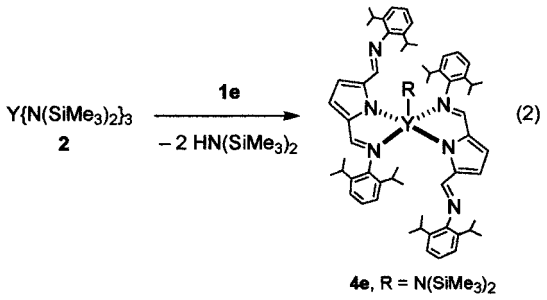
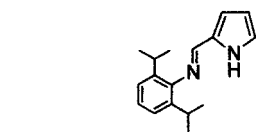
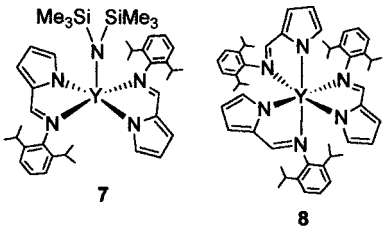
than that of **1d** (δ 152.0). These findings indicate that the pyrrolyl ligand coordinated to the yttrium metal in a tridentate *N*,*N*′,*N*″-meridional fashion, as confirmed by X-ray analysis (vide infra).

In the case of the much bulkier ligand **1e**, a bis(pyrrolyl) complex Y(DIP$_2$-pyr)$_2${N(SiMe$_3$)$_2$} [**4e**, DIP$_2$-pyr = 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}-pyrrolyl] formed selectively regardless of the molar ratio of **1e** and **2**, and hence a maximum yield was obtained when **2** was treated with 2 equiv of **1e** (eq 2). The two

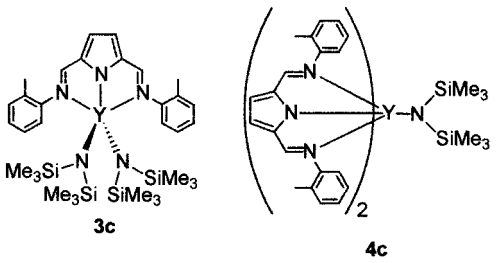


bulky pyrrolyl ligands of **4e** coordinated to the yttrium metal as *N*,*N*′-bidentate ones, as revealed by the ^{1}H NMR spectrum; one imino proton was observed at higher field (δ 7.37) and the other at lower field (δ 8.21) compared with that of the free ligand (δ 7.81), indicating that one of the two N=CH moieties coordinated to the yttrium atom and the other is free from coordination. The pyrrolyl ring protons were accordingly observed as an ABq pattern (δ 6.18 for 3-pyr and δ 5.62 for 4-pyr) with a coupling constant (3.7 Hz). This complexation was further supported by a 2D ^{1}H−^{1}H NOESY measurement: the proton of the imino group bound to the metal center correlated with the neighboring pyrrolyl ring proton, while the proton of the noncoordinating imino group correlated with the SiMe$_3$ group of the amido ligand instead of the pyrrolyl proton. The number of ligands coordinated to the metal was thus controlled to be two, as a result of the steric congestion of **1e**, whose two bulky arylimino moieties prevented the tridentate *N*,*N*′,*N*″-coordination. It is noteworthy that one bulky arylimino substituent was not enough to keep the complexation found for **4e**. When **2** reacted with 2 equiv of an iminopyrrolyl ligand, 2-{*N*-(2,6-diisopropylphenyl)-iminomethyl}pyrrole (**6**, DIP-pyrH) instead of **1e**, we obtained a mixture of a bis(pyrrolyl) complex Y(DIP-pyr)$_2${N(SiMe$_3$)$_2$} (**7**) and a homoleptic complex Y(DIP-pyr)$_3$ (**8**); the latter complex was obtained quantitatively upon treating **2** with 3 equiv of **6**.

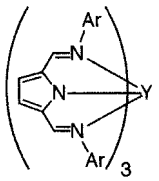




In sharp contrast to **1d** and **1e**, complexation of 2,5-bis{*N*-(2-methylphenyl)iminomethyl}pyrrole (**1c**, *o*-Tol$_2$-pyrH) to a yttrium atom could not be controlled. Reaction of **1c** with 1 equiv of **2** in toluene gave a 4:1 mixture of a mono(pyrrolyl) complex, Y(*o*-Tol$_2$-pyr)-{N(SiMe$_3$)$_2$}$_2$ (**3c**), and a bis(pyrrolyl) complex, Y(*o*-Tol$_2$-pyr)$_2${N(SiMe$_3$)$_2$} (**4c**), from which we isolated **3c** after recrystallization. Unlike the complex **4e**, although **4c** was characterized only by NMR spectroscopy, both of the two pyrrolyl ligands of **4c** coordinated to the yttrium metal in an *N*,*N*′,*N*″-meridional fashion.



Much less bulky tridentate pyrrolyl ligands having *p*-substituted phenyl groups, 2,5-bis(4-methoxylphenyliminomethyl)pyrrole (**1a**, An$_2$-pyrH) and 2,5-bis(4-methylphenyliminomethyl)pyrrole (**1b**, *p*-Tol$_2$-pyrH), led to the formation of homoleptic tris(pyrrolyl) complexes, Y(An$_2$-pyr)$_3$ (**5a**) and Y(*p*-Tol$_2$-pyr)$_3$ (**5b**), respectively. In all cases when 1 or 2 equiv of **1a** and **1b** per **2** was used, small amounts of the corresponding mono(pyrrolyl) and bis(pyrrolyl) complexes were contaminated, but the reaction of **2** with 3 equiv of **1a** and **1b** gave, respectively, **5a** and **5b** in quantitative yields. The ^{1}H NMR spectra of **5a** and **5b** displayed a symmetric signal pattern of the pyrrolyl ligand with a higher chemical shift value of the imino proton compared with that of the free ligand (δ 7.90 for **1a** and δ 7.60 for **5a**; δ 8.02 for **1b** and δ 7.57 for **5b**). The ^{13}C NMR spectra of these complexes also displayed a single resonance due to the imino carbon at lower field (δ 160.2 for **5a** and δ 160.4 for **5b**). The high-field shift of N=C*H* in the ^{1}H NMR spectrum and low-field shift of N=*C*H in the ^{13}C NMR spectrum indicate all imino groups coordinate to the metal center, and hence the yttrium atom adopts a nine-coordination geometry in solution, which is not often observed for the yttrium atom.



5a: Ar = C$_6$H$_4$-OMe-*p*
5b: Ar = C$_6$H$_4$-Me-*p*

Description of Structures. The structures of heteroleptic complexes **3d** and **4e** and homoleptic complexes **5a** and **5b** were characterized by crystallographic studies. Figure 1 shows the crystal structure of **3d**, and its selected bond distances and angles are listed in Table 1. The yttrium center of **3d** has a distorted trigonal bipyramidal geometry; two nitrogen atoms of two amido N(SiMe$_3$)$_2$ groups and one nitrogen atom of the pyrrolyl skeleton occupied equatrial positions, the planarity

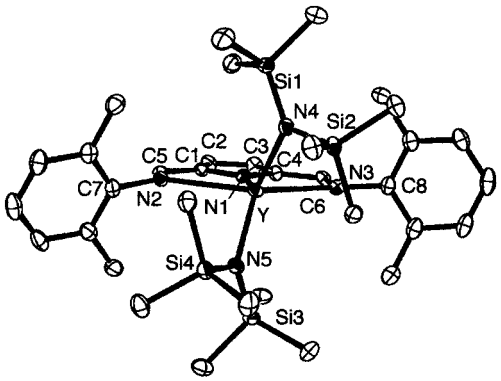


Figure 1. Molecular structure of **3d**. Hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances and Angles for 3d

	Bond Distances (Å)		
Y−N1	2.288(3)	C1−C2	1.403(5)
Y−N2	2.707(3)	C2−C3	1.386(6)
Y−N3	2.776(3)	C3−C4	1.409(5)
Y−N4	2.254(3)	C1−C5	1.425(5)
Y−N5	2.246(3)	C4−C6	1.431(5)
N1−C1	1.358(5)	N2−C5	1.295(5)
N1−C4	1.359(5)	N3−C6	1.295(5)
	Bond Angles (deg)		
N1−Y−N2	65.2(1)	Y−N1−C1	125.8(2)
N1−Y−N3	63.9(1)	Y−N1−C4	127.6(3)
N1−Y−N4	118.2(1)	C1−N1−C4	106.6(3)
N1−Y−N5	119.9(1)	Y−N2−C5	110.8(2)
N2−Y−N3	129.1(1)	Y−N2−C7	134.1(2)
N2−Y−N4	113.8(1)	C5−N2−C7	113.8(3)
N2−Y−N5	89.0(1)	Y−N3−C6	110.7(3)
N3−Y−N4	90.5(1)	Y−N3−C8	133.8(2)
N3−Y−N5	116.1(1)	C6−N3−C8	114.4(3)
N4−Y−N5	121.9(1)		

around the yttrium atom being revealed by the sum of three angles (360°), while two nitrogen atoms of two imino groups were placed at two apical positions with the angle N2−Y−N3 (129.1(1)°) much deviated from 180° owing to the chelating ligation of **1d**. Two phenyl rings in **3d** are oriented perpendicular to the plane of the pyrrolyl moiety. The bond distance of Y−N(pyrrolyl) (Y−N1 = 2.288(3) Å) is comparable with that of the lutetium−pyrrolyl complex, $LuCp_2(C_4H_4N)(THF)$ (2.289(4) Å),[25] on taking into account the difference of ionic radii of metals. The metal−imino nitrogen bond distances (Y−N2 = 2.707(3) Å and Y−N3 = 2.776(3) Å) are longer than the Y−N1 distance. The bond distances of Y−N(amido) (Y−N4 = 2.254(3) Å and Y−N5 = 2.246(3) Å) are comparable with those found for bis(amido) yttrium complexes, $Y\{N(SiMe_3)_2\}_2\{OSi^tBu(2\text{-}C_6H_4(CH_2NMe_2))_2\}$ (2.237(9) Å)[26] and $Y\{N(SiMe_3)_2\}_2\{N\text{-isopropyl-}2\text{-(isopropylamino)troponiminato}\}$ (2.236(3) Å).[19b]

Complex **4e** adopts a square-pyramidal geometry where four corners of the square plane are occupied by the four nitrogen atoms (N1, N2, N4, and N5) of two bidentate pyrrolyl ligands and an amido ligand is capped, as illustrated in Figure 2, and selected bond distances and bond angles of **4e** are listed in Table 2. The yttrium atom deviates from an equatrial N_4-plane by 1.036(2) Å to approach toward the capped amido ligand. The most remarkable feature of **4e** is that two bis(imino)pyrrolyl ligands **1e** coordinate in an *N*,*N*′-fashion to the yttrium atom. This dissymmetric coordination of the ligand is a consequence of the steric bulkiness induced by the 2,6-diisopropylphenyl groups. The noncoordinated imino moieties are situated opposite each other to minimize the steric congestion, being in good accordance with a NOESY measurement. The bond distances of Y−N(pyrroly) (Y−N1 = 2.347(4) Å and Y−N4 = 2.355(4) Å) are longer by 0.06 Å than that found for **3d** (2.288(3) Å). On the other hand, the bond distances of Y−N(imino) (Y−N2 = 2.437(5) Å and Y−N5 = 2.449(5) Å) are shorter than those of **3d** (2.707(3) and 2.776(3) Å). The distances of imino linkages (N2−C5 = 1.315(6) Å and N5−C13 = 1.290(6) Å) are substantially longer than those of free ones (N3−C6 = 1.270(6) Å and N6−C14 = 1.264(6) Å). The bond distance of Y−N(amido) (Y−N7 = 2.204(4) Å) is comparable with that of metallocene complexes $Cp^*_2Y\{N(SiMe_3)_2\}$ (2.274(5) and 2.253(5) Å)[27] and $(R)\text{-}(\eta^5\text{-}C_5H_4)Si(Me_2)[\eta^5\text{-}(-)\text{-menthyl-}(C_5H_3)]Y\{N(SiMe_3)_2\}$ (2.281(8) and 2.211(8) Å)[28] and a half-metallocene amido complex, $[(\eta^5\text{-}C_5Me_4)Si(Me_2)\text{-}\eta'\text{-}N\text{-}^tBu]Y\{N(SiMe_3)_2\}$ (2.184(7) Å).[29]

The molecular structures of the tris(pyrrolyl) complexes **5a** and **5b** are shown in Figures 3 and 4, respectively, and their selected bond lengths and angles are listed in Tables 3 and 4. Complex **5a** crystallized in cubic space group *Ia*3 and has a C_3-axis passing through a yttrium atom. The yttrium atom is accordingly surrounded with nine nitrogen atoms of three tridentate *N*,*N*′,*N*″-ligands and adopts a three-face-centered trigonal prismatic mode of nine-coordination, where the two pairs N2, N2′, and N2″ and N3, N3′, and N3″ are located at the three corners of each triangle, and N1, N1′, and N1″ occupy three face-centered positions. This is a quite rare coordination number for the yttrium atom, though many hydrated salts of the lanthanide elements, which have much larger ionic radii, adopt the same geometry. The bond distances of Y−N(imino) (Y−N2 = 2.737(2) Å and Y−N3 = 2.758(3) Å) are similar to that found for **3d**, but the bond distance of Y−N(pyrrolyl) (Y−N1 = 2.340(2) Å) is slightly longer than that of **3d**.

On the other hand, the solid-state structure of **5b**, despite its solution behavior is quite similar to **5a**, and proved to have an eight-coordination number and a square-antiprismatic arrangement around the yttrium atom, where one pyrrolyl ligand attaches in a bidentate *N*,*N*′-fashion to the yttrium atom and the others coordinate to the yttrium atom as meridional tridentate ligands. The bond distances of Y−N (tridentate pyrrolyl) (Y−N1 = 2.309(5) Å and Y−N4 = 2.306(5) Å) are shorter than that of Y−N(bidentate pyrrolyl) (Y−N7 = 2.401(6) Å). The bond distances of Y−N(imino) in the tridentate parts (Y−N2 = 2.667(5) Å, Y−N3 = 2.652(5) Å, Y−N5 = 2.652(5) Å, and Y−N6 = 2.716(5) Å) are longer than that of the bidentate one (Y−N8 = 2.484(5) Å).

Polymerization of ϵ-Caprolactone Catalyzed by Pyrrolyl Complexes of Yttrium. Mono(pyrrolyl) **3d**

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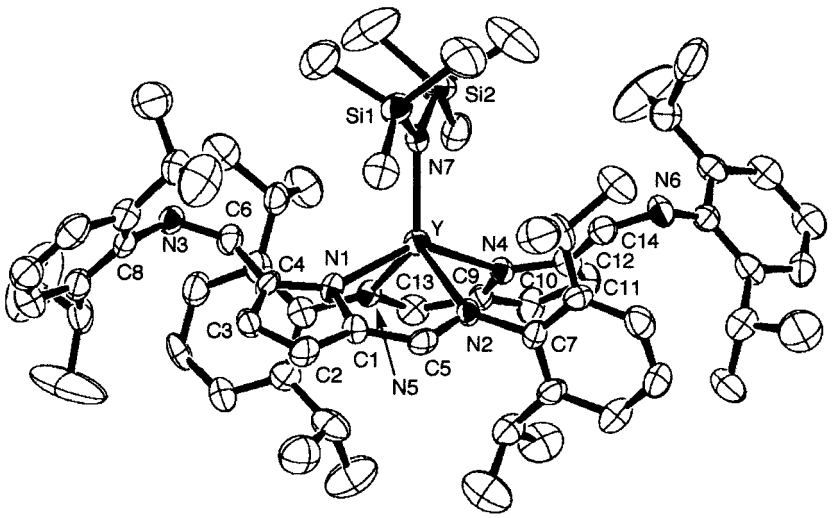

Figure 2. Molecular structure of **4e**. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Distances and Angles for 4e

	Bond Distances (Å)		
Y−N1	2.347(4)	N2−C5	1.315(6)
Y−N2	2.437(5)	N3−C6	1.270(6)
Y−N4	2.355(4)	N4−C9	1.365(6)
Y−N5	2.449(5)	N4−C12	1.374(6)
Y−N7	2.204(4)	C9−C10	1.394(7)
N1−C1	1.368(6)	C10−C11	1.384(7)
N1−C4	1.352(6)	C11−C12	1.392(7)
C1−C2	1.375(6)	C9−C13	1.429(7)
C2−C3	1.358(7)	C12−C14	1.456(8)
C3−C4	1.371(7)	N5−C13	1.290(6)
C1−C5	1.421(7)	N6−C14	1.264(6)
C4−C6	1.453(7)		
	Bond Angles (deg)		
N1−Y−N2	73.2(2)	Y−N1−C4	142.8(4)
N4−Y−N5	71.6(1)	C1−N1−C4	104.5(5)
N1−Y−N5	87.0(1)	Y−N2−C5	110.2(4)
N2−Y−N4	87.4(1)	Y−N2−C7	132.9(4)
N1−Y−N7	110.1(1)	C5−N2−C7	116.1(5)
N4−Y−N7	108.9(1)	Y−N4−C9	113.7(4)
N1−Y−N4	141.0(1)	Y−N4−C12	141.3(4)
N2−Y−N5	116.5(1)	C9−N4−C12	104.2(5)
N2−Y−N7	121.4(2)	Y−N5−C13	112.0(4)
N5−Y−N7	122.2(2)	Y−N5−C15	131.0(3)
Y−N1−C1	112.1(3)	C13−N5−C15	116.7(5)

and bis(pyrrolyl) **4e** complexes were found to catalyze polymerization of ϵ-caprolactone, which was consumed within 10 min (Table 5), while homoleptic pyrrolyl complexes **5a** and **5b** had no activity (entries 5 and 6), suggesting that a Y−N(pyrrolyl) bond did not have any ability to initiate the polymerization. The bis(pyrrolyl) complex **4e**, which has one Y−N(amido) bond, gave the poly(ϵ-caprolactone) with narrow polydispersity (M_w/M_n = 1.3) (entry 1), and the polymer using the mono(pyrrolyl) complex **3d**, which has two Y−N(amido) bonds, was inferior in its polydispersity (M_w/M_n = 2.0) (entry 3), indicating that the number of Y−N(SiMe$_3$)$_2$ bonds significantly affected molecular weight distributions. The spectral characterization of the polymers showed the presence of a terminal bis(trimethylsilyl)amide group, which was derived from a nucleophilic attack at the lactone-carbon atom followed by acyl−oxygen bond cleavage. These observations are consistent with the reported polymerization of ϵ-caprolactone using the homoleptic complex **2**, which gave poly(ϵ-caprolactone) with a very broad polydispersity (M_w/M_n = 2.9).[30]

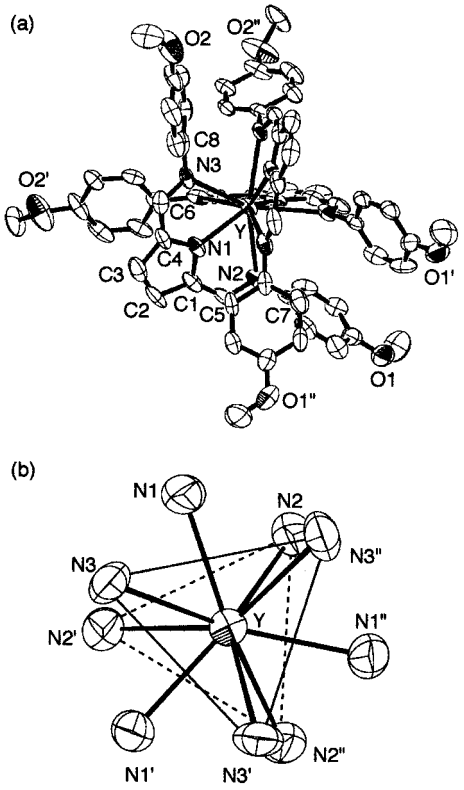

Figure 3. (a) Molecular structure of **5a**. Hydrogen atoms are omitted for clarity. (b) Schematic drawing of the three-face-centered trigonal prismatic geometry of the yttrium atom.

Polymerization at 0 °C resulted in the polymer having a rather narrower molecular weight distributions (entries 2 and 4; M_w/M_n = 1.2 for **4e** and M_w/M_n = 1.6 for **3d**).

Conclusion

Several heteroleptic and homoleptic 2,5-bis(*N*-arylliminomethyl)pyrrolyl complexes of yttrium have been prepared by aminolysis of Y{N(SiMe$_3$)$_2$}$_3$ with the corresponding pyrrolyl ligand. We found that the number of pyrrolyl ligands coordinated to a yttrium metal can be controlled by changing the substituent(s) on aryl

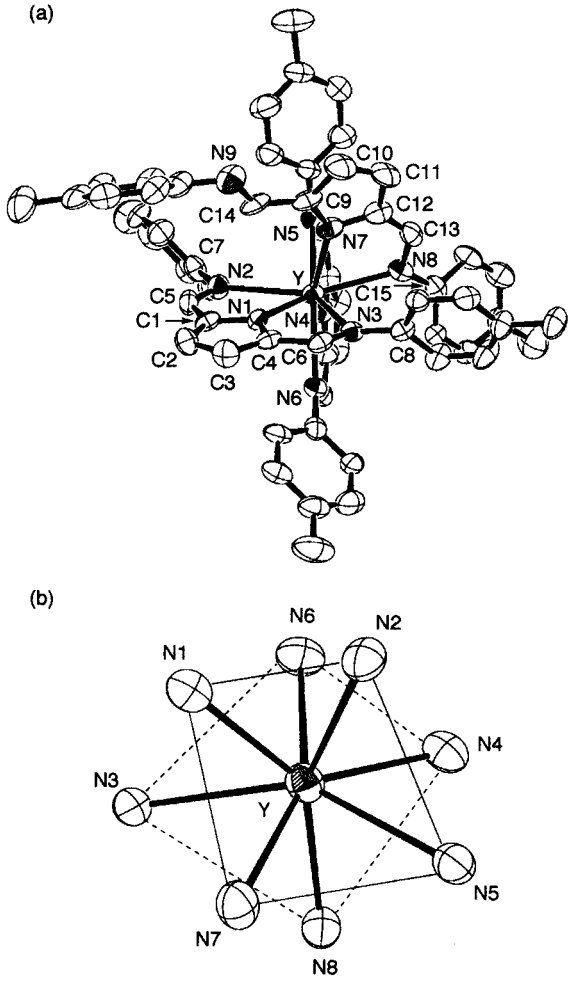

Figure 4. (a) Molecular structure of **5b**. Hydrogen atoms are omitted for clarity. (b) Schematic drawing of the square-antiprismatic geometry of the yttrium atom.

Table 3. Selected Bond Distances and Angles for 5a[a]

Bond Distances (Å)			
Y−N1	2.340(2)	C2−C3	1.341(4)
Y−N2	2.737(2)	C3−C4	1.410(4)
Y−N3	2.758(3)	C1−C5	1.418(4)
N1−C1	1.346(3)	C4−C6	1.424(4)
N1−C4	1.357(4)	N2−C5	1.299(3)
C1−C2	1.417(4)	N3−C6	1.283(3)
Bond Angles (deg)			
N1−Y−N1′	119.965(4)	Y−N1−C4	126.3(2)
N1−Y−N2	63.15(8)	C1−N1−C4	106.1(3)
N1−Y−N2′	75.51(8)	Y−N2−C5	111.8(2)
N1−Y−N2″	137.72(9)	Y−N2−C7	131.0(2)
N1−Y−N3	63.71(8)	C5−N2−C7	117.2(3)
N1−Y−N3′	136.91(8)	Y−N3−C6	111.2(2)
N1−Y−N3″	71.05(8)	Y−N3−C8	130.9(2)
Y−N1−C1	127.6(2)	C6−N3−C8	116.5(3)

[a] Atoms with primes and double-primes are crystallographically equivalent to those having the same number without primes.

rings of the pyrrolyl ligand, resulting in the selective formation of a mono(pyrrolyl) complex **3d**, a bis(pyrrolyl) complex **4e**, and homoleptic tris(pyrrolyl) complexes **5a** and **5b**. Of particular interest is the diversity of the coordination mode; a distorted trigonal bipyramidal geometry and a distorted square-pyramidal one were observed for **3d** and **4e**, respectively, and the homoleptic complexes **5a** and **5b** were found to have rare structures with eight- and nine-coordination numbers, a three-face-centered trigonal prismatic structure for **5a** and a square-antiprismatic one for **5b**. Moreover, the mono(pyrrolyl) and bis(pyrrolyl) complexes **3d** and **4e** were found to be catalysts for polymerization of ϵ-caprolactone to give polyesters with narrow polydispersities (M_w/M_n = 1.6 for **3d**, M_w/M_n = 1.2 for **4e**). Thus, the complex **4e** acted as a single site initiator of ϵ-caprolactone polymerization. The unique complexation of tridentate pyrrolyl ligands to other metals and their catalytic performance will be described in a subsequent paper.

Table 4. Selected Bond Distances and Angles for 5b

Bond Distances (Å)			
Y−N1	2.309(5)	C1−C5	1.427(9)
Y−N2	2.667(5)	C4−C6	1.439(9)
Y−N3	2.652(5)	N2−C5	1.308(8)
Y−N4	2.306(5)	N3−C6	1.300(7)
Y−N5	2.652(5)	N7−C9	1.389(8)
Y−N6	2.716(5)	N7−C12	1.354(8)
Y−N7	2.401(6)	C9−C10	1.395(9)
Y−N8	2.484(5)	C10−C11	1.40(1)
N1−C1	1.375(7)	C11−C12	1.405(10)
N1−C4	1.370(7)	C9−C13	1.383(9)
C1−C2	1.387(8)	C12−C14	1.444(10)
C2−C3	1.395(9)	N8−C13	1.309(8)
C3−C4	1.383(9)	N9−C14	1.275(8)
Bond Angles (deg)			
N1−Y−N2	64.3(2)	N5−Y−N6	127.7(2)
N1−Y−N3	64.2(2)	N5−Y−N7	77.0(2)
N1−Y−N4	132.9(2)	N5−Y−N8	75.2(2)
N1−Y−N5	132.0(2)	N6−Y−N7	152.8(2)
N1−Y−N6	83.4(2)	N6−Y−N8	102.2(2)
N1−Y−N7	86.5(2)	N7−Y−N8	70.5(2)
N1−Y−N8	140.0(2)	Y−N1−C1	127.3(4)
N2−Y−N3	128.4(2)	Y−N1−C4	126.8(4)
N2−Y−N4	83.4(2)	C1−N1−C4	105.7(5)
N2−Y−N5	77.8(2)	Y−N2−C5	113.2(4)
N2−Y−N6	91.5(2)	Y−N2−C7	130.9(4)
N2−Y−N7	106.7(2)	C5−N2−C7	115.9(5)
N2−Y−N8	152.7(2)	Y−N3−C6	114.4(4)
N3−Y−N4	131.9(2)	Y−N3−C8	127.2(4)
N3−Y−N5	145.4(2)	C6−N3−C8	116.1(6)
N3−Y−N6	79.0(2)	Y−N7−C9	113.6(4)
N3−Y−N7	73.9(2)	Y−N7−C12	140.7(5)
N3−Y−N8	77.8(2)	C9−N7−C12	105.7(6)
N4−Y−N5	64.7(2)	Y−N8−C13	111.6(5)
N4−Y−N6	63.3(2)	Y−N8−C15	127.2(4)
N4−Y−N7	137.4(2)	C13−N8−C15	120.4(6)
N4−Y−N8	82.0(2)		

Table 5. Polymerization of ϵ-Caprolactone Catalyzed by Yttrium−Pyrrolyl Complexes[a]

entry	catalyst	temp (°C)	time (min)	yield[c]	M_n[d] (%)	M_w/M_n[d]
1	**4e**	20	5	99	58 700	1.3
2	**4e**	0	5	99	61 300	1.2
3	**3d**	20	5	99	42 000	2.0
4	**3d**	0	5	71	66 000	1.6
5	**5a**	20	300	trace		
6	**5b**	20	300	trace		
$Y\{N(SiMe_3)_2\}_3$[b]		20	90	65	524 000	2.9

[a] General conditions: in toluene, [Y] = 20 mM, S/C = 100. [b] Ref 30. [c] Yield = weight of polymer obtained/weight of monomer used. [d] Measured by GPC calibrated with standard polystyrene samples.

Experimental Section

General Procedures. All manipulations involving air- and moisture-sensitive yttrium complexes were carried out using standard Schlenk techniques under argon. Hexane, THF, and toluene were dried and deoxygenated by distillation over sodium benzophenone ketyl under argon. Benzene-d_6 was distilled from Na/K alloy and thoroughly degassed by trap-to-

trap distillation before use. ϵ-Caprolactone was purchased and purified before use. 2-{*N*-(2,6-Diisopropylphenyl)iminomethyl}-pyrrole (**6**),[23] Y{N(SiMe$_2$)$_2$}$_3$ (**2**),[29] and 2,5-diformylpyrrole[31] were prepared according to the literature.

The ^{1}H (500, 400, 300, and 270 MHz) and ^{13}C (125, 100, 75, and 68 MHz) NMR spectra were measured on a Varian Unity Inova-500, a JEOL JNM-AL400, a Varian Mercury-300, or a JEOL GSX-270 spectrometer. When benzene-d_6 was used as the solvent. The spectra were referenced to the residual solvent protons at δ 7.20 in the ^{1}H NMR spectra and to the residual solvent carbons at δ 128.0 in the ^{13}C NMR spectra. Assignments for ^{1}H and ^{13}C NMR peaks for some complexes were aided by 2D ^{1}H−^{1}H COSY, 2D ^{1}H−^{1}H NOESY, 2D ^{1}H−^{13}C HMQC, and 2D ^{1}H−^{13}C HMBC spectra. Elemental analyses were recorded by a Perkin-Elmer 2400 at the Faculty of Engineering Science, Osaka University. The gel permeation chromatographic analyses were carried out at 40 °C using a Shimadzu LC-10A liquid chromatograph system and a RID-10A refractive index detector, equipped with a Shodex KF-806L column, which was calibrated versus commercially available polystyrene standards (SHOWA DENKO). All melting points were measured in sealed tubes under argon atmosphere and were not corrected.

Preparation of 2,5-Bis(aryliminomethyl)pyrroles: 2,5-Bis{*N*-(4-methoxyphenyl)iminomethyl}pyrrole (1a). A solution of *p*-anisidine (1.00 g, 8.12 mmol) in ethanol (20 mL) was added to a solution of 2,5-diformylpyrrole (0.50 g, 4.06 mmol) in ethanol (20 mL) at room temperature. After the mixture was stirred for 2 h at room temperature, a yellow slurry was formed. The resulting yellow powder was collected by filtration, washed with cold ethanol and hexane, and then dried under vacuum. Yield: 1.18 g (3.55 mmol, 87%), mp 223−232 °C (dec). ^{1}H NMR (C_6D_6, 35 °C): δ 3.38 (s, 6H, OCH_3), 6.50 (s, 2H, 3,4-pyr), 6.84 (d, 4H, *m*-C_6H_4), 7.18 (d, 4H, *o*-C_6H_4), 8.04 (s, 2H, N=C*H*), 10.32 (br s, 1H, N*H*). ^{13}C NMR ($CDCl_3$, 35 °C): δ 55.6 (q, $^1J_{C-H}$ = 144 Hz, O*C*H$_3$), 114.5 (d, $^1J_{C-H}$ = 158 Hz, *m*-C_6H_4), 116.0 (d, $^1J_{C-H}$ = 166 Hz, 3,4-pyr), 122.0 (d, $^1J_{C-H}$ = 158 Hz, *o*-C_6H_4), 134.0 (s, 2,5-pyr), 144.3 (s, *ipso*-C_6H_4), 146.7 (d, $^1J_{C-H}$ = 161 Hz, N=*C*H), 158.2 (s, *p*-C_6H_4). EI-MS: *m*/*z* 333 (M^+, base peak), 318 [$(M - CH_3)^+$]. Anal. Calcd for $C_{20}H_{19}N_3O_2$: C, 72.05; H, 5.74; N, 12.60. Found: C, 71.78; H, 5.87; N, 12.58.

2,5-Bis{*N*-(4-methylphenyl)iminomethyl}pyrrole (1b): 54% yield, mp 197−198 °C. ^{1}H NMR (C_6D_6, 35 °C): δ 2.19 (s, 6H, CH_3), 6.47 (s, 2H, 3,4-pyr), 7.05 (d, 4H, *m*-C_6H_4), 7.14 (d, 4H, *o*-C_6H_4), 8.02 (s, 2H, N=C*H*), 10.33 (br s, 1H, NH). ^{13}C NMR (C_6D_6, 35 °C): δ 21.2 (q, $^1J_{C-H}$ = 126 Hz, CH_3), 116.1 (d, $^1J_{C-H}$ = 171 Hz, 3,4-pyr), 121.4 (d, $^1J_{C-H}$ = 158 Hz, *o*-C_6H_4), 130.0 (d, $^1J_{C-H}$ = 158 Hz, *m*-C_6H_4), 134.5 (s, 2.5-pyr), 135.7 (s, *p*-C_6H_4), 147.6 (d, $^1J_{C-H}$ = 161 Hz, N=*C*H), 149.3 (s, *ipso*-C_6H_4). EI-MS: *m*/*z* 301 (M^+, base peak). Anal. Calcd for $C_{20}H_{19}N_3$: C, 79.70; H, 6.35; N, 13.94. Found: C, 79.57; H, 6.30; N, 13.87.

2,5-Bis{*N*-(2-methylphenyl)iminomethyl}pyrrole (1c): 60% yield, mp 107−108 °C. ^{1}H NMR ($CDCl_3$, 35 °C): δ 2.38 (s, 6H, CH_3), 6.70 (s, 2H, 3,4-pyr), 6.94 (d, 2H, C_6H_4), 7.12 (t, 2H, C_6H_4), 7.21 (t, 2H, C_6H_4), 7.23 (d, 2H, C_6H_4), 8.22 (s, 2H, N=C*H*), 10.15 (br s, 1H, NH). ^{13}C NMR ($CDCl_3$, 35 °C): δ 18.2 (q, $^1J_{C-H}$ = 127 Hz, CH_3), 116.5 (d, $^1J_{C-H}$ = 173 Hz, 3,4-pyr), 117.7 (d, $^1J_{C-H}$ = 157 Hz, C_6H_4), 125.9 (d, $^1J_{C-H}$ = 160 Hz, C_6H_4), 126.9 (d, $^1J_{C-H}$ = 160 Hz, C_6H_4), 130.5 (d, $^1J_{C-H}$ = 158 Hz, C_6H_4), 132.3 (s, 2.5-pyr), 134.2 (s, 2-C_6H_4), 148.6 (d, $^1J_{C-H}$ = 163 Hz, N=*C*H), 150.7 (s, 1-C_6H_4). EI-MS: *m*/*z* 301 (M^+, base peak), 286 [$(M - CH_3)^+$]. Anal. Calcd for $C_{20}H_{19}N_3$: C, 79.70; H, 6.35; N, 13.94. Found: C, 79.51; H, 5.98; N, 14.09.

2,5-Bis{*N*-(2,6-dimethylphenyl)iminomethyl}pyrrole (1d). In a 100 mL round-bottom flask, 2,5-diformylpyrrole (600 mg, 4.87 mmol) and 2.1 equiv of 2,6-dimethylaniline (1.26 mL, 10.2 mmol) were dissolved in toluene (30 mL) at room temperature. After two drops of formic acid was added to the solution, the mixture was refluxed for 12 h using a water separator. After cooling, the solvent was evaporated to dryness. The resulting yellow oil was purified by column chromatography on silica gel (hexane/AcOEt = 10:1) to give **1d** as yellow powders. Yield: 1.11 g (3.37 mmol, 69%), mp 139−140 °C. ^{1}H NMR ($CDCl_3$, 35 °C): δ 2.19 (s, 12H, CH_3), 6.68 (s, 2H, 3,4-pyr), 6.96 (t, $^3J_{H-H}$ = 7.5 Hz, 2H, *p*-C_6H_3), 7.07 (d, $^3J_{H-H}$ = 7.5 Hz, 4H, *m*-C_6H_3), 8.05 (s, 2H, N=C*H*), 10.24 (br s, 1H, NH). ^{13}C NMR ($CDCl_3$, 35 °C): δ 18.4 (q, $^1J_{C-H}$ = 128 Hz, CH_3), 116.1 (d, $^1J_{C-H}$ = 173 Hz, 3,4-pyr), 123.8 (d, $^1J_{C-H}$ = 159 Hz, *p*-C_6H_3), 127.4 (s, *o*-C_6H_3), 128.1 (d, $^1J_{C-H}$ = 153 Hz, *m*-C_6H_3), 133.4 (s, 2.5-pyr), 150.6 (s, *ipso*-C_6H_3), 152.0 (d, $^1J_{C-H}$ = 163 Hz, N=*C*H). EI-MS: *m*/*z* 329 (M^+, base peak), 314 $(M - CH_3)^+$. Anal. Calcd for $C_{22}H_{23}N_3$: C, 80.21; H, 7.04; N, 12.75. Found: C, 80.19; H, 6.70; N, 12.80.

2,5-Bis{*N*-(2,6-diisopropylphenyl)iminomethyl}-pyrrole (1e).[24b] A solution of 2,6-diisopropylaniline (9.19 mL, 48.7 mmol) in methanol (10 mL) was added to a solution of 2,5-diformylpyrrole (3.00 g, 24.4 mmol) in methanol (20 mL) at room temperature. After a few drops of acetic acid was added, the reaction mixture was stirred for 4 h at 10 °C. The resulting yellow precipitate was collected by filtration and then was dried under vacuum. Recrystallization from hexane gave **1e** (4.77 g, 10.8 mmol, 44%), mp 206−208 °C (dec). ^{1}H NMR (C_6D_6, 35 °C): δ 1.14 (d, 24H, CH*Me*$_2$), 3.08 (sept, 4H, C*H*Me$_2$), 6.44 (s, 2H, 3,4-pyr), 7.17 (m, 6H, C_6H_3), 7.81 (s, 2H, N=C*H*), 10.48 (br s, 1H, NH). ^{13}C NMR (C_6D_6, 35 °C): δ 23.9 (q, $^1J_{C-H}$ = 125 Hz, CH*Me*$_2$), 28.5 (d, $^1J_{C-H}$ = 129 Hz, *C*HMe$_2$), 116.2 (d, $^1J_{C-H}$ = 172 Hz, 3,4-pyr), 123.4 (d, $^1J_{C-H}$ = 155 Hz, *m*-C_6H_3), 124.8 (d, $^1J_{C-H}$ = 159 Hz, *p*-C_6H_3), 134.0 (s, 2,5-pyr), 138.2 (s, *o*-C_6H_3), 149.4 (s, *ipso*-C_6H_3), 151.8 (d, $^1J_{C-H}$ = 163 Hz, N=*C*H). EI-MS: *m*/*z* 441 (M^+), 426 [$(M - CH_3)^+$], 398 [$(M - CHMe_2)^+$, base peak]. Anal. Calcd for $C_{30}H_{39}N_3$: C, 81.59; H, 8.90; N, 9.51. Found: C, 81.23; H, 9.20; N, 9.46.

Synthesis of Y(*o*-Tol$_2$-pyr){N(SiMe$_3$)$_2$}$_2$ (3c). A solution of 2,5-di{*N*-(2-methylphenyl)iminomethyl}pyrrole (**1c**) (130 mg, 0.433 mmol) in toluene (3 mL) was added to a toluene solution (3 mL) of **2** (247 mg, 0.433 mmol) cooled at −50 °C. The reaction mixture was allowed to warm to room temperature and stirred further for 4 h. After removal of insoluble products by centrifugation, all volatiles were removed in vacuo. The ^{1}H NMR spectrum of the resulting yellow crystalline solid showed signals due to a complex bis(pyrrolyl) complex **3c** and a bis(pyrrolyl) complex Y(*o*-Tol$_2$-pyr)$_2${N(SiMe$_3$)$_2$} (**4c**) in 4:1 ratio. Recrystallization from a toluene/hexane mixture gave analytically pure yellow crystals of **3c** (160 mg, 0.225 mmol, 52% yield), mp 199−205 °C (dec). **3c**: ^{1}H NMR (C_6D_6, 35 °C): δ 0.22 (s, 36H, SiMe$_3$), 2.30 (s, 6H, C_6H_4-CH_3), 6.56 (s, 2H, 3,4-pyr), 7.03 (t, 2H, 4-C_6H_4), 7.07 (d, 2H, 3-C_6H_4), 7.15 (t, 2H, 5-C_6H_4), 7.39 (d, 2H, 6-C_6H_4), 7.45 (s, 2H, N=CH). ^{13}C NMR (C_6D_6, 35 °C): δ 5.4 (q, $^1J_{C-H}$ = 117 Hz, SiMe$_3$), 19.8 (q, $^1J_{C-H}$ = 127 Hz, C_6H_4-*C*H$_3$), 118.8 (d, $^1J_{C-H}$ = 170 Hz, 3,4-pyr), 124.4 (d, $^1J_{C-H}$ = 156 Hz, 6-C_6H_4), 125.7 (d, $^1J_{C-H}$ = 159 Hz, 5-C_6H_4), 126.8 (d, $^1J_{C-H}$ = 159 Hz, 4-C_6H_4), 131.1 (d, $^1J_{C-H}$ = 158 Hz, 3-C_6H_4), 131.9 (s, 2-C_6H_4), 142.1 (s, 2,5-pyr), 151.1 (s, 1-C_6H_4), 163.8 (d, $^1J_{C-H}$ = 167 Hz, N=CH). Anal. Calcd for $C_{32}H_{54}N_5Si_4Y$: C, 54.13; H, 7.67; N, 9.86. Found: C, 54.30; H, 7.35; N, 9.59.

4c: ^{1}H NMR (C_6D_6, 35 °C): δ 0.13 (s, 18H, SiMe$_3$), 1.78 (s, 12H, Ar-CH_3), 6.55 (s, 4H, 3.4-pyr), 6.75−7.17 (m, 12H, 3,4,5-C_6H_4), 7.40 (s, 4H, 6-C_6H_4), 7.49 (s, 4H, N=CH).

Preparation of Y(Xyl$_2$-pyr){N(SiMe$_3$)$_2$}$_2$ (3d). A solution of 2,5-bis{*N*-(2,6-dimethylphenyl)iminomethyl}pyrrole (**1d**) (127 mg, 0.384 mmol) in toluene (2 mL) was added to a solution of **2** (219 mg, 0.384 mmol) in toluene (2 mL) at room temperature. The reaction mixture was stirred for 2 h at 60 °C to liberate hexamethyldisilazane, detected by GC−MS and ^{1}H NMR spectroscopy. After insoluble products were separated

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by centrifugation, the supernatant toluene solution was concentrated to ca. 1.5 mL to give a yellow suspension, which was recrystallized from toluene to give yellow crystals of **3d** (232 mg, 82% yield), mp 210−215 °C (dec). ^{1}H NMR (C_6D_6, 35 °C): δ 0.23 (s, 36H, $SiMe_3$), 2.33 (s, 12H, Ar−CH_3), 6.54 (s, 2H, 3,4-pyr), 7.00 (s, 6H, C_6H_3), 7.34 (s, 2H, N=CH). ^{13}C NMR (C_6D_6, 35 °C): δ 5.5 (q, $^1J_{C-H}$ = 117 Hz, $SiMe_3$), 21.7 (q, $^1J_{C-H}$ = 127 Hz, Ar-*C*H_3), 119.1 (d, $^1J_{C-H}$ = 170 Hz, 3,4-pyr), 125.9 (d, $^1J_{C-H}$ = 160 Hz, *p*-C_6H_3), 129.1 (d, $^1J_{C-H}$ = 159 Hz, *m*-C_6H_3), 130.3 (s, *o*-C_6H_3), 142.0 (s, 2,5-pyr), 151.2 (s, *ipso*-C_6H_3), 164.9 (d, $^1J_{C-H}$ = 164 Hz, N=CH). Anal. Calcd for $C_{34}H_{58}N_5Si_4Y$: C, 55.23; H, 7.92; N, 9.49. Found: C, 55.27; H, 7.33; N, 9.52.

Preparation of Y(DIP$_2$-pyr)$_2${N(SiMe$_3$)$_2$} (4e). To a solution of **2** (384 mg, 0.674 mmol) in toluene (2.5 mL) at room temperature was added a solution of 2,5-bis{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrole (**1e**) (672 mg, 1.35 mmol) in toluene (2.5 mL). The reaction mixture was stirred for 12 h at 60 °C. The resulting yellow microcrystals were washed with a small amount of cold hexane. These microcrystals (737 mg, 0.652 mmol, 97%) were recrystallized from a mixture of toluene and hexane to give analytically pure yellow crystals of **4e** (598 mg, 78% yield), mp 205−210 °C (dec). ^{1}H NMR (C_6D_6, 35 °C): δ 0.30 (s, 18H, $SiMe_3$), 0.45 (d, 6H, CH*Me*$_2$ (noncoordinated)), 1.01 (d, 6H, CH*Me*$_2$ (noncoordinated)), 1.15 (d, 6H, CH*Me*$_2$ (coordinated)), 1.18 (d, 6H, CH*Me*$_2$ (coordinated)), 1.19 (d, 6H, CH*Me*$_2$ (noncoordinated)), 1.28 (d, 6H, CH*Me*$_2$ (coordinated)), 1.30 (d, 6H, CH*Me*$_2$ (noncoordinated)), 1.77 (d, 6H, CH*Me*$_2$ (coordinated)), 2.31 (sept, 2H, C*H*Me$_2$ (noncoordinated)), 2.68 (sept, 2H, C*H*Me$_2$ (noncoordinated)), 3.13 (sept, 2H, C*H*Me$_2$ (coordinated)), 3.62 (sept, 2H, C*H*Me$_2$ (coordinated)), 5.62 (d, $^3J_{H-H}$ = 3.7 Hz, 2H, 4-pyr), 6.18 (d, $^3J_{H-H}$ = 3.7 Hz, 2H, 3-pyr), 7.20 (m, 12H, C_6H_3), 7.37 (s, 2H, N=CH (coordinated)), 8.21 (s, 2H, N=CH (noncoordinated)). ^{13}C NMR (C_6D_6, 35 °C): δ 5.0 (q, $^1J_{C-H}$ = 118 Hz, $SiMe_3$), 21.9, 22.4, 23.3, 23.5, 23.8, 24.6, 25.9, and 26.1 (q, $^1J_{C-H}$ = 121−126 Hz, CH*Me*$_2$), 27.4, 27.9, 29.6, and 30.2 (q, $^1J_{C-H}$ = 127−129 Hz, C*H*Me$_2$), 117.2 (d, $^1J_{C-H}$ = 174 Hz, 4-pyr), 122−128 (d, $^1J_{C-H}$ = 157−159 Hz, six sets of *p*- and *m*-C_6H_3), 125.8 (d, $^1J_{C-H}$ = 172 Hz, 3-pyr), 134.9 (s, 5-pyr), 135.4, 137.1, 141.0, and 141.4 (s, *o*-C_6H_3), 144.7 (s, *ipso*-C_6H_3), 146.7 (s, 2-pyr), 148.5 (s, *ipso*-C_6H_3), 153.7 (d, $^1J_{C-H}$ = 170 Hz, N=CH (noncoordinated)), 165.9 (d, $^1J_{C-H}$ = 164 Hz, N=CH (coordinated)). Anal. Calcd for $C_{66}H_{94}N_7Si_2Y$: C, 70.12; H, 8.38; N, 8.67. Found: C, 69.94; H, 8.41; N, 8.54. FAB-MS: *m*/*z* 969 [{M − N(SiMe$_3$)$_2$}$^+$], 883 [{M − N(SiMe$_3$)$_2$ − ^{i}Pr$_2$}$^+$].

Preparation of Y(An$_2$-pyr)$_3$ (5a). A mixture of 2,5-di{*N*-(4-methoxyphenyl)iminomethyl}pyrrole (**1a**, 526 mg, 1.58 mmol) and **2** (300 mg, 0.526 mmol) in toluene (4 mL) was stirred for 2 h at 60 °C. Supernatant liquid was concentrated in vacuo, and then the resulting yellow microcrystals were washed with a small amount of cold hexane. The microcrystals (544 mg, 0.501 mmol, 95%) were recrystallized from a mixture of toluene and hexane to give analytically pure yellow crystals of **5a** (463 mg, 81% yield), mp 150−153 °C (dec). ^{1}H NMR (C_6D_6, 35 °C): δ 3.37 (s, 18H, OCH_3), 6.31 (d, 12H, *o*-C_6H_4), 6.58 (s, 6H, 3,4-pyr), 6.76 (d, 12H, *m*-C_6H_4), 7.61 (s, 6H, N=CH). ^{13}C NMR (C_6D_6, 35 °C): δ 55.2 (q, $^1J_{C-H}$ = 143 Hz, O*C*H_3), 113.6 (d, $^1J_{C-H}$ = 158 Hz, *m*-C_6H_4), 116.9 (d, $^1J_{C-H}$ = 168 Hz, 3,4-pyr), 123.5 (d, $^1J_{C-H}$ = 159 Hz, *o*-C_6H_4), 143.0 (s, 2,5-pyr), 146.9 (s, *ipso*-C_6H_4), 157.6 (s, *p*-C_6H_4), 160.2 (d, $^1J_{C-H}$ = 161 Hz, N=CH). Anal. Calcd for $C_{60}H_{54}N_9O_6Y$: C, 66.36; H, 5.01; N, 11.61. Found: C, 66.75; H, 5.36; N, 11.21.

In the case of 1:1 reaction, the signals due to bis(pyrrolyl) complex Y(*p*-An$_2$-pyr)$_2${N(SiMe$_3$)$_2$} (**4a**) were observed together with **5a** and its content was estimated to be 16%. **4a**: ^{1}H NMR (C_6D_6, 35 °C): δ 0.11 (s, 18H, $SiMe_3$), 3.30 (s, 18H, OCH_3), 6.68 (d, 8H, *m*-C_6H_4), 6.79 (s, 4H, 3,4-pyr), 6.84 (br, 8H, *o*-C_6H_4), 7.91 (br s, 4H, N=CH). ^{13}C NMR (C_6D_6, 35 °C): δ 4.9 (q, $^1J_{C-H}$ = 116 Hz, $SiMe_3$), 55.1 (q, $^1J_{C-H}$ = 143 Hz, O*C*H_3), 114.0 (d, $^1J_{C-H}$ = 160 Hz, *m*-C_6H_4), 118.3 (d, $^1J_{C-H}$ = 167 Hz, 3,4-pyr), 123.6 (d, $^1J_{C-H}$ = 160 Hz, *o*-C_6H_4), 143.7 (s, 2,5-pyr), 145.0 (s, *ipso*-C_6H_4), 158.3 (s, *p*-C_6H_4), 158.4 (br, $^1J_{C-H}$ = 161 Hz, N=CH).

Synthesis of Y(*p*-Tol$_2$-pyr)$_3$ (5b). A mixture of 2,5-di{*N*-(4-methylphenyl)iminomethyl}pyrrole (**1b**, 414 mg, 1.374 mmol) and **2** (261 mg, 0.458 mmol) in toluene (6 mL) at room temperature was stirred for 2 h at 60 °C. Yellow precipitates (423 mg, 93%) were recrystallized from a mixture of toluene and hexane to give analytically pure yellow crystals of **5b** (340 mg, 0.344 mmol, 75% yield), mp 156−162 °C (dec). ^{1}H NMR (C_6D_6, 35 °C): δ 2.17 (s, 18H, CH_3), 6.24 (d, 12H, *o*-C_6H_4), 6.56 (s, 6H, 3,4-pyr), 6.93 (d, 12H, *m*-C_6H_4), 7.57 (s, 6H, N=CH). ^{13}C NMR (C_6D_6, 35 °C): δ 21.1 (q, $^1J_{C-H}$ = 126 Hz, *C*H_3), 116.9 (d, $^1J_{C-H}$ = 168 Hz, 3,4-pyr), 122.5 (d, $^1J_{C-H}$ = 159 Hz, *o*-C_6H_4), 128.7 (d, $^1J_{C-H}$ = 158 Hz, *m*-C_6H_4), 133.9 (s, *p*-C_6H_4), 143.0 (s, 2,5-pyr), 151.1 (s, *ipso*-C_6H_4), 160.4 (d, $^1J_{C-H}$ = 161 Hz, N=CH). Anal. Calcd for $C_{60}H_{54}N_9Y$: C, 72.79; H, 5.50; N, 12.73. Found: C, 72.64; H, 5.89; N, 13.03.

In the case of 1:1 reaction, the signals due to bis(pyrrolyl) complex Y(*p*-Tol$_2$-pyr)$_2${N(SiMe$_3$)$_2$} (**4b**) were observed and its content was estimated to be 13%. **4b**: ^{1}H NMR (C_6D_6, 35 °C): δ 0.09 (s, 18H, $SiMe_3$), 2.08 (s, 12H, CH_3), 6.79 (s, 4H, 3,4-pyr), 6.86 (br, 16H, C_6H_4), 7.91 (s, 4H, N=CH). ^{13}C NMR (C_6D_6, 35 °C): δ 4.8 (q, $^1J_{C-H}$ = 117 Hz, $SiMe_3$), 21.0 (q, $^1J_{C-H}$ = 126 Hz, CH_3), 118.5 (d, $^1J_{C-H}$ = 167 Hz, 3,4-pyr), 122.5 (d, $^1J_{C-H}$ = 159 Hz, *o*-C_6H_4), 129.2 (d, $^1J_{C-H}$ = 158 Hz, *m*-C_6H_4), 135.2 (s, *p*-C_6H_4), 143.8 (s, 2,5-pyr), 149.3 (s, *ipso*-C_6H_4), 162.1 (d, $^1J_{C-H}$ = 166 Hz, N=CH).

Preparation of Y(DIP-pyr)$_3$ (7) and Y(DIP-pyr)$_2${N(SiMe$_3$)$_2$} (8). A solution of **2** (400 mg, 0.702 mmol) in toluene (2 mL) was cooled at −50 °C, and then a solution of 2-{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrole (**6**, 357 mg, 1.40 mmol) in toluene (2 mL) was added. The resulting mixture was allowed to warm to room temperature and then stirred further for 4 h at 50 °C. After insoluble products were separated by centrifugation, all volatiles were removed in vacuo. The ^{1}H NMR spectrum of the resulting white microcrystals showed signals due to a homoleptic complex, Y(DIP-pyr)$_3$ (**7**), and a bis(pyrrolyl) complex, Y(DIP-pyr)$_2${N(SiMe$_3$)$_2$} (**8**), in 57:43 ratio.

7: ^{1}H NMR (400 MHz, C_6D_6, 35 °C): δ 0.61 (d, 9H, CH*Me*$_2$), 0.89 (d, 9H, CH*Me*$_2$), 0.93 (d, 9H, CH*Me*$_2$), 0.94 (d, 9H, CH*Me*$_2$), 2.44 (sept, 3H, C*H*Me$_2$), 2.85 (sept, 3H, C*H*Me$_2$), 6.40 (dd, $^3J_{H-H}$ = 1.6 and 3.6 Hz, 3H, 4-pyr), 6.84 (d, 3H, 3-pyr), 6.89 (br s, 3H, 5-pyr), 7.06 (m, 9H, C_6H_3), 7.63 (s, 3H, N=CH). ^{13}C NMR (100 MHz, C_6D_6, 35 °C): δ 22.9, 23.4, 26.0, and 26.4 (q, $^1J_{C-H}$ = 123−126 Hz, CH*Me*$_2$), 28.5 and 29.0 (d, $^1J_{C-H}$ = 128 Hz, *C*HMe$_2$), 113.8 (d, $^1J_{C-H}$ = 168 Hz, 4-pyr), 123.5 (d, $^1J_{C-H}$ = 168 Hz, 3-pyr), 124−127 (d, $^1J_{C-H}$ = 157−159 Hz, *p*- and *m*-C_6H_3), 136.6 (s, *o*-C_6H_3), 140.3 (d, $^1J_{C-H}$ = 172 Hz, 5-pyr), 143.1 (s, 2-pyr), 147.2 (s, *ipso*-C_6H_3), 164.3 (d, $^1J_{C-H}$ = 161 Hz, N=*C*H).

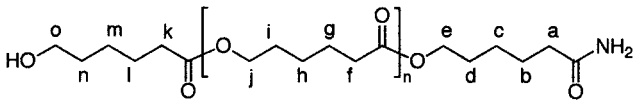
8: ^{1}H NMR (400 MHz, C_6D_6, 35 °C): δ 0.21 (s, 18H, $SiMe_3$), 0.59 (d, 3H, CH*Me*$_2$), 0.99 (d, 3H, CH*Me*$_2$), 1.05 (d, 6H, CH*Me*$_2$), 1.11 (d, 6H, CH*Me*$_2$), 1.25 (d, 3H, CH*Me*$_2$), 1.58 (d, 3H, CH*Me*$_2$), 2.90 (sept, 2H, C*H*Me$_2$), 3.71 (sept, 2H, C*H*Me$_2$), 6.40 (dd, $^1J_{H-H}$ = 2.0 and 3.6 Hz, 2H, 4-pyr), 6.19 (br s, 2H, 5-pyr), 6.63 (d, 2H, 3-pyr), 7.07 (m, 6H, C_6H_3), 7.74 (s, 2H, N=CH). ^{13}C NMR (100 MHz, C_6D_6, 35 °C): δ 4.9 (q, $^1J_{C-H}$ = 117 Hz, $SiMe_3$), 22.4, 22.8, 24.1, 25.7, 26.4, and 26.5 (q, $^1J_{C-H}$ = 123−126 Hz, CH*Me*$_2$), 29.3 and 29.6 (d, $^1J_{C-H}$ = 128 Hz, C*H*Me$_2$), 113.4 (d, $^1J_{C-H}$ = 168 Hz, 4-pyr), 123.7 (d, $^1J_{C-H}$ = 168 Hz, 3-pyr), 124−127 (d, $^1J_{C-H}$ = 157−159 Hz, *p*- and *m*-C_6H_3), 136.6 (s, *o*-C_6H_3), 138.4 (d, $^1J_{C-H}$ = 173 Hz, 5-pyr), 141.7 (s, 2-pyr), 146.2 (s, *ipso*-C_6H_3), 163.2 (d, $^1J_{C-H}$ = 162 Hz, N=*C*H).

Recrystallization from a mixture of toluene and hexane gave analytically pure colorless crystals of **7** in 34% yield, mp 190−198 °C (dec). Anal. Calcd for $C_{51}H_{63}N_6Y$: C, 72.15; H, 7.48; N, 9.90. Found: C, 71.92; H, 7.72; N, 10.00.

Polymerization of ϵ-Caprolactone. In a typical reaction, to a solution of **4e** (13.3 mg, 0.0118 mmol) in toluene (0.59 mL, to generate 20 mM solution) was added ϵ-caprolactone

(100 equiv, 0.131 mL, 1.18 mmol) at 0 °C. The yellow solution was stirred for 5 min at 0 °C. The polymerization was terminated by the addition of methanol and aqueous hydrogen chloride. The resulting white polymer was collected by filtration and dried in vacuo at 60 °C. The yield of poly(ϵ-caprolactone) was found to be quantitative. The resulting poly(ϵ-caprolactone) was analyzed by means of gel permeation chromatography.

Characterization of poly(ϵ-caprolactone). Complex **4e** (5.0 mg, 4.4 μmol) and 30 equiv of ϵ-caprolactone (15 mg, 0.133 mmol) were dissolved in 0.58 mL of toluene-d_8 at 0 °C in a 5φ mm NMR tube. After polymerization was complete the ^{1}H NMR spectrum showed signals due to a terminal *N*,*O*-bis(trimethylsilyl)amide group of poly(ϵ-caprolactone). ^{1}H NMR (toluene-d_8, 35 °C): δ −0.26 (s, $SiMe_3$), 0.27 (s, $SiMe_3$), 1.18 (m, $COCH_2CH_2CH_2CH_2CH_2O$), 1.44 (m, $COCH_2CH_2CH_2CH_2CH_2O$), 1.52 (m, $COCH_2CH_2CH_2CH_2CH_2O$), 2.10 (t, $COCH_2CH_2CH_2CH_2CH_2O$), 3.97 (t, $COCH_2CH_2CH_2CH_2CH_2O$). Poly(ϵ-caprolactone) with M_n = 16 400 exhibited an end-group signal of NH_2 by hydrolysis of the terminal *N*,*O*-bis(trimethylsilyl)-amide group, $-C(OSiMe_3)=NSiMe_3$. ^{1}H NMR (500 MHz, $CDCl_3$, 50 °C): δ 1.31 (m, Hh), 1.31 (m, Hm), 1.38 (m, Hc), 1.45 (m, Hn), 1.55 (m, Hd), 1.55 (m, Hg), 1.55 (m, Hi), 1.55 (m, Hl), 1.70 (m, Hb), 2.23 (t, Hf), 2.23 (t, Hk), 2.28 (t, Ha), 3.65 (br s, Ho), 4.00 (t, Hj), 4.24 (t, He).



Crystallographic Data Collections and Structure Determination of 3d, 4e, 5a, and 5b. Crystals of **3d**, **4e**, **5a**, and **5b** suitable for X-ray diffraction studies were sealed in glass capillaries under an argon atmosphere and were mounted on a Rigaku RAXIS-RAPID imaging plate diffractometer for data collection using Mo Kα (graphite monochromated, λ = 0.71069) radiation. Crystal data and data statistics are summarized in Table 6. Each indexing was performed from two oscillations. The camera radius was 127.40 mm. Readout was performed in the 0.100 mm pixel mode. A symmetry-related absorption correction using the program ABSCOR[32] was applied. Each data was corrected for Lorentz and polarization effects.

The structures of complex **3d**, **4e**, and **5a** were solved by the direct method (SHELXS-97)[33] and expanded using Fourier techniques (DIRDIF-94).[34] The structure of complex **5b** was solved by the heavy-atom Patterson method (PATTY-94)[34] and expanded using Fourier techniques (DIRDIF-94).[34] The non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method. Hydrogen atoms were placed at calculated positions (C−H = 0.95 Å) and kept fixed. Measured nonequivalent reflections were used for the structure determination. In the subsequent refinement, the function $\sum w(F_o^2 - F_c^2)^2$ was minimized, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. The agreement indices are defined as $R1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ and $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum(wF_o^4)]^{1/2}$. All calculations were performed using the teXsan crystallographic software package, and illustrations were drawn by ORTEP. The quality of the crystals of **4e** was not good presumably due to the presence of solvent molecules. The absolute structure parameter (Flack parameter, χ) of **3d** was found to be −0.005(5).

(32) Higashi, T. *Program for Absorption Correction*; Rigaku Corporation: Tokyo, Japan, 1995.

(33) Sheldrick, G. M. *Program for the Solution of Crystal Structures*; University of Goettingen: Germany, 1997.

(34) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-94 program system, Technical Report of the Crystallography Laboratory*; University of Nijmegan: The Netherlands, 1994.

Table 6. Crystal Data and Data Collection Parameters of 3d, 4e, 5a, and 5b

	3d	**4e**·0.5(hexane)
formula	$C_{34}H_{58}N_5Si_4Y$	$C_{69}H_{101}N_7Si_2Y$
fw	738.12	1173.68
cryst syst	orthorhombic	monoclinic
space group	$Pna2_1$ (No. 33)	$P2_1/n$ (No. 14)
a, Å	17.6103(5)	13.8792(4)
b, Å	13.4670(4)	26.8160(7)
c, Å	16.7900(5)	19.2282(5)
α, deg		
β, deg		102.3942(8)
γ, deg		
V, Å^3	3981.9(2)	6989.6(3)
Z	4	4
no. of reflns for cell determ (2θ range)	30 314 (3.8−55.0°)	70 142 (3.3−55.0°)
D_{calcd}, g/cm^{-3}	1.231	1.115
F(000)	1568.00	2524.00
μ[Mo Kα], cm^{-1}	16.10	9.12
T, K	100(1)	213(1)
cryst size, mm	0.70 × 0.64 × 0.61	0.24 × 0.20 × 0.16
no. of images	78	185
total oscillation angles (deg)	232.0	370.0
exposure time (min per deg)	0.30	0.7
$2\theta_{min}$, $2\theta_{max}$, deg	5.0, 55.0	5.0, 55.0
no. of reflns measd (total)	36 755	89 811
no. of refl. measd (unique)	8982 (R_{int} = 0.111)	15978 (R_{int} = 0.202)
no. of variables	396	697
R1, wR2 (all data)	0.060, 0.124	0.233, 0.099
R ($I > 2.0\sigma(I)$)	0.051	0.057
GOF on F^2	1.03	0.52
Δ, e Å^{-3}	0.48, −0.51	1.54, −2.16

	5a	**5b**·1.5(toluene)
formula	$C_{60}H_{54}N_9O_6Y$	$C_{70.50}H_{66}N_9Y$
fw	1086.05	1128.26
cryst syst	cubic	triclinic
space group	*Ia*3 (No. 206)	*P*1 (No. 2)
a, Å	27.6372	15.4867(2)
b, Å	27.6372	16.2113(5)
c, Å	27.6372	13.7190(3)
α, deg		98.023(3)
β, deg		91.686(2)
γ, deg		62.368(2)
V, Å^3	21109.7	3019.1(1)
Z	16	2
no. of reflns for cell determ (2θ range)	77 367 (3.6−55.0°)	13 289(3.8−55.0°)
D_{calcd}, g/cm^{-3}	1.367	1.241
F(000)	9024.00	1182.00
μ[Mo Kα], cm^{-1}	11.68	10.17
T, K	213(1)	213(1)
cryst size, mm	0.32 × 0.30 × 0.26	0.28 × 0.22 × 0.14
no. of images	111	74
total oscillation angles (deg)	222.0	222.0
exposure time (min per deg)	0.70	1.20
$2\theta_{min}$, $2\theta_{max}$, deg	5.0, 55.0	5.0, 55.0
no. of reflns measd (total)	90 311	25 537
no. of reflns measd (unique)	10 672 (R_{int} = 0.101)	13 247 (R_{int} = 0.095)
no. of variables	251	694
R1, wR2 (all data)	0.136, 0.053	0.219, 0.185
R ($I > 2.0\sigma(I)$)	0.047	0.110
GOF on F^2	0.52	0.98
Δ, e Å^{-3}	3.30, −1.77	1.43, −1.69

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Supporting Information Available: Tables of atomic parameters, thermal displacement parameters, bond lengths, and bond angles for **3d**, **4e**, **5a**, and **5b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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