Organolanthanide-Based Coordination and Insertion Reactivity of the Anion Formed by Deprotonation of ϵ-Caprolactam

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Methods to incorporate the strong ligation capacity of ϵ-caprolactam into monoanionic ligands suitable for electropositive metals such as yttrium are described. ϵ-Caprolactam, $HN(CH_2)_5C{=}O$, is deprotonated by $(C_5H_4Me)_2Y[N(SiMe_3)_2]$ to form the dimeric complex $[(C_5H_4Me)_2Y(\mu\text{-}NC_6H_{10}O)]_2$, **1**. Each caprolactamate anion, $(NC_6H_{10}O)^-$, forms one Y−N bond and coordinates to both yttrium centers via a bridging oxygen such that yttrium has a formal coordination number of nine. ϵ-Caprolactam is also deprotonated by $(C_5Me_5)_2Y(C_3H_5)(THF)$, to form the monomeric, pentamethylcyclopentadienyl analogue $(C_5Me_5)_2Y(NC_6H_{10}O)$, **2**, in which the caprolactamate anion chelates the formally eight-coordinate yttrium. CO_2 inserts into the Ln−N bond in **2** to form $[(C_5Me_5)_2Y(\mu\text{-}O_2CNC_6H_{10}O)]_2$, **3**. The tridentate monoanionic $(O_2CNC_6H_{10}O)^-$ ligand forms an eight-membered $YOCOYOCO$ ring via carboxylate oxygen atoms and also coordinates to each yttrium center via the oxygen originating from ϵ-caprolactam. Phenyl isocyanate inserts into the Y−N bond of **2** to form $(C_5Me_5)_2Y[(\mu^2\text{-}OC(NPh)NC_6H_{10}O)]$, **4**, which contains a planar $YOCNCO$ ring and eight-coordinate yttrium. *tert*-Butyl isocyanide does not undergo insertion chemistry with **2**, but instead forms the adduct $(C_5Me_5)_2Y(NC_6H_{10}O)(CNCMe_3)$, **5**.

Introduction

Recent studies of the coordination chemistry of ϵ-caprolactam in lanthanide complexes have revealed that this is a powerful ligand capable of displacing anions from the metal to make cationic complexes such as $[Pr(C_6H_{11}NO)_7]^{+3}$,[1] $[Pr(C_6H_{11}NO)_6Cl]^{+2}$,[2] and $[Eu(C_6H_{11}NO)_4Cl_2]^+$.[2] To determine if this strong ligation capacity could be incorporated into an anionic ligand which could provide charge balance in neutral complexes of electropositive metals, we have examined the coordination chemistry and reactivity of the anion obtained by deprotonating ϵ-caprolactam. Although this $(C_6H_{10}NO)^-$ caprolactamate anion is well known as a component in the anionic ring-opening polymerization of ϵ-caprolactam to form nylon-6,[3,4] prior to this study it had been structurally characterized in only two metal complexes: $[(C_5H_5)_2Ti(NC_6H_{10}O)]$[5] and $[O[Si(^iPr)_2N(C_5H_3NMe)]_2Ti(NMe_2)(NC_6H_{10}O)]$.[6] The ϵ-caprolactam anion in both cases formed monomeric complexes in which the metal is chelated by the nitrogen and oxygen donor atoms. However, recently while this work was in progress, it was discovered that the ϵ-caprolactamate anion can also bridge between two lanthanide metals: the X-ray crystal structure of $[(C_5H_4Me)_2Yb(\mu\text{-}NC_6H_{10}O)]_2$[7] was reported along with synthetic information on Er and Y analogues.

We report here our initial studies of the coordination chemistry of this ligand with yttrium as a representative of the late lanthanides. Two different coordination modes of the resonance-stabilized ϵ-caprolactam anion are found depending on the ancillary ligation around the metal: chelating and bridging (Figure 1). In addition, we report the insertion reactivity of this anion with CO_2, PhNCO, and Me_3CNC.[8−11]

Experimental Section

General Procedures. The chemistry described below was performed under nitrogen with rigorous exclusion of air and water using Schlenk, vacuum line, and glovebox techniques. Solvents were purified and dried over sodium or potassium benzophenone ketyl or over sodium/potassium alloy. $[(C_5H_4Me)_2Y(\mu\text{-}Cl)]_2$ was prepared according to the literature.[12] $(C_5Me_5)_2Y(C_3H_5)(THF)$ was prepared as a yellow solid in 77% yield

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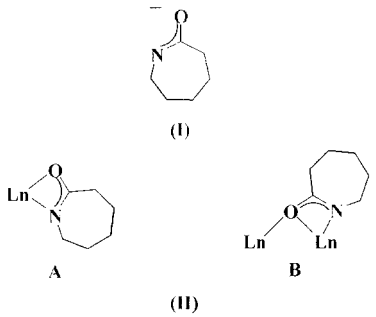

Figure 1. Delocalization in the caprolactamate anion (I) and two possible binding modes (II).

following literature procedures[13] from the reaction of $(C_5Me_5)_2YCl_2K(THF)_2$[14] (0.96 g, 1.6 mmol) with $ClMg(CH_2CHCH_2)$ (0.78 mL, 1.6 mmol) in THF. Research grade CO_2 was purchased from Airgas and used without further purification. Phenyl isocyanate and *tert*-butyl isocyanide were purchased from Aldrich, dried over activated 3 Å molecular sieves, and put through three freeze−pump−thaw cycles before use. ^1H and ^{13}C NMR spectra were obtained on an Omega 500 MHz or a Bruker DRX-400 MHz spectrometer at 25 °C. X-ray crystallographic data were obtained on a Bruker CCD platform diffractometer. IR spectra were taken on thin films obtained from benzene solutions (except where noted) using an ASI ReactIR 1000 spectrometer. Complexometric analyses were obtained as previously described.[15] Complete elemental analyses were performed by Desert Analytics.

Synthesis of $(C_5H_4Me)_2Y[N(SiMe_3)_2]$. In a glovebox, $NaN(SiMe_3)_2$ (1.5 g, 8.0 mmol) was added to a stirred slurry of $[(C_5H_4Me)_2Y(\mu\text{-Cl})]_2$ (2.3 g, 8.1 mmol) in 10 mL of THF, and the mixture was stirred for 12 h. The solvent was removed by rotary evaporation to give a white solid. Hexanes were added, and the slurry was heated to boiling. The hot slurry was centrifuged, and the colorless solution was collected and cooled to room temperature followed by removal of solvent by rotary evaporation to yield $(C_5H_4Me)_2Y[N(SiMe_3)_2]$ (2.0 g, 63%). Anal. Calcd for $C_{18}H_{32}NSi_2Y$: Y, 21.8. Found: Y, 22.2. ^1H NMR (C_6D_6): δ 6.01 (m, 4H), 5.86 (m, 4H), 2.08 (s, 6H), 0.07 (s, 18H). ^{13}C NMR (C_6D_6): δ 113.9 (C_5H_4Me), 112.3 (C_5H_4Me), 15.3 (C_5H_4Me), 3.1 ($SiMe_3$). IR: 2949 s, 2899 s, 1478 w, 1243 s, 1019 s, 869 m, 834 s, 807 m, 772 m cm^{-1}.

Synthesis of $[(C_5H_4Me)_2Y(\mu\text{-}NC_6H_{10}O)]_2$, 1. In a glovebox, ϵ-caprolactam (0.55 g, 4.8 mmol) was added to a stirring, colorless solution of $(C_5H_4Me)_2Y[N(SiMe_3)_2]$ (2.0 g, 4.9 mmol) in 10 mL of hexanes. A white solid immediately precipitated, and the solution was stirred for 12 h. Removal of solvent by rotary evaporation yielded **1** as a white solid (1.6 g, 87%). Crystals suitable for X-ray diffraction were grown in toluene at room temperature as colorless blocks. Anal. Calcd for $C_{36}H_{48}N_2O_2Y_2$: Y, 12.4. Found: Y, 13.0. Isopiestic molecular weight (in THF vs $(C_5H_5)_2Fe$): Calcd for $C_{36}H_{48}N_2O_2Y_2$: 719. Found: 710. ^1H NMR (C_6D_6): δ 6.02 (dd, 2H, J_{H-H} = 5 Hz, J_{H-H} = 3 Hz), 5.95 (dd, 2H, J_{H-H} = 5 Hz, J_{H-H} = 3 Hz), 5.90 (dd, 2H, J_{H-H} = 4.5 Hz, J_{H-H} = 2 Hz), 5.84 (dd, 2H, J_{H-H} = 4.8 Hz, J_{H-H} = 2 Hz), 2.92 (m, 2H), 2.21 (s, 6H), 2.08 (m, 2H), 1.42 (m, 4H), 1.32 (m, 2H). ^{13}C NMR (C_6D_6): δ 180.8 (*C*O), 121.7 ($C_5H_4CH_3$), 111.9 ($C_5H_4CH_3$), 111.0 ($C_5H_4CH_3$), 110.4 ($C_5H_4CH_3$), 109.7 ($C_5H_4CH_3$), 48.8 (CH_2), 38.0 (CH_2), 32.6 (CH_2), 30.1 (CH_2), 24.8 (CH_2), 17.0 (C_5H_4Me). IR: 2922 s, 2853 s, 1664 s, 1606 m, 1556 w, 1478 w, 1436 w, 1386 m, 1347 w, 1305 w, 1278 m, 1258 s, 1235 w, 1204 m, 1154 w, 1127 m, 1085 m, 1031 s, 984 m, 961 m, 930 w, 830 s, 803 m, 760 s cm^{-1}.

Synthesis of $(C_5Me_5)_2Y(NC_6H_{10}O)$, 2. In a glovebox, ϵ-caprolactam (0.24 g, 2.1 mmol) was added to a yellow solution of $(C_5Me_5)_2Y(C_3H_5)(THF)$ (1.0 g, 2.1 mmol) in 10 mL of benzene, which turned clear upon addition. The reaction was stirred for 12 h, and removal of solvent by rotary evaporation gave a white solid (1.8 g, 88%). Colorless crystals of **2** suitable for X-ray diffraction were grown in hexanes/toluene (80:20) at room temperature. Anal. Calcd for $C_{26}H_{40}NOY$: Y, 18.9. Found: Y, 18.2. ^1H NMR (C_6D_6): δ 2.93 (m, 2H), 2.32 (m, 2H), 1.94 (s, 30H), 1.47 (m, 4H), 1.41 (m, 2H). ^{13}C NMR (C_6D_6): δ 182.4 (*C*O), 116.7 (C_5Me_5), 47.1 (CH_2), 37.7 (CH_2), 32.0 (CH_2), 30.5 (CH_2), 24.0 (CH_2), 11.2 (C_5Me_5). IR: 2961 s, 2922 s, 2856 s, 1656 s, 1575 w, 1532 m, 1444 s, 1409 w, 1378 w, 1351 w, 1262 s, 1200 m, 1150 w, 1123 m, 1089 s, 1019 s, 799 s cm^{-1}.

Synthesis of $[(C_5Me_5)_2Y(\mu\text{-}O_2CNC_6H_{10}O)]_2$, 3. A flask fitted with a high-vacuum greaseless stopcock, which contained **2** (290 mg, 0.62 mmol) in 10 mL of benzene, was attached to a high-vacuum line and freeze−pump−thawed three times. Excess CO_2 at 1 atm was admitted to the flask, and within 1 h, colorless crystalline solids appeared. After 3 h, the flask was evacuated to the pressure of the solvent and returned to the glovebox, where solvent was decanted to leave **3** as a colorless crystalline solid (264 mg, 89%). Anal. Calcd for $C_{54}H_{80}N_2O_6Y_2$: C, 62.91; H, 7.82; N, 2.72. Found: C, 62.92; H, 7.99; N, 2.97. ^1H NMR (C_5D_5N): δ 4.17 (m, 2H), 2.82 (m, 2H), 1.82 (s, 30H), 1.58 (br, 6H, $\Delta\nu_{1/2}$ = 29.1 Hz). ^{13}C NMR (C_5D_5N): δ 187.7 (*C*O), 180.3 (*C*O), 128.3 (C_5Me_5), 45.7 (CH_2), 39.9 (CH_2), 31.3 (CH_2), 29.0 (CH_2), 28.0 (CH_2), 11.3 (C_5Me_5). IR (thin film from THF): 2926 s, 2856 s, 1695 s, 1637 s, 1455 m, 1378 w, 1309 w, 1258 m, 1227 w, 1173 w, 1143 w, 1089 s, 1023 s, 973 w, 857 w, 803 s cm^{-1}.

Synthesis of $(C_5Me_5)_2Y(PhNCOC_6H_{10}NO)$, 4. In a glovebox, PhNCO (27 mg, 0.23 mmol) was slowly added to a stirring solution of **2** (109 mg, 0.23 mmol) in 10 mL of benzene. Upon addition, the solution developed a yellow color. After the reaction was stirred for 12 h, the solvent was removed by rotary evaporation to leave **4** as a yellow powder (134 mg, 98%). Crystals of **4** were grown from a hexanes/toluene mixture (90:10) at −32 °C. Anal. Calcd for $C_{33}H_{45}N_2O_2Y$: C, 67.11; H, 7.68; N, 4.74. Found: C, 66.78; H, 7.97; N, 4.49. ^1H NMR (C_6D_6): δ 7.50 (d, 2H, J_{H-H} 10 Hz), 7.34 (t, 2H, J_{H-H} 10 Hz), 7.02 (t, 1H, J_{H-H} 10 Hz), 4.07 (m, 2H), 2.14 (m, 2H), 1.90 (s, 30H), 1.55 (br, 2H), 1.36 (br, 2H), 1.23 (br, 2H). ^{13}C NMR (C_6D_6): δ 180.3 (*C*O), 151.7 (*C*O), 149.9 (C_6H_5), 128.4 (C_6H_5), 124.6 (C_6H_5), 122.1 (C_6H_5), 116.9 (C_5Me_5) 48.2 (CH_2), 40.3 (CH_2), 28.7 (CH_2), 27.5(CH_2), 23.0 (CH_2), 11.4 (C_5Me_5). IR: 2934 m, 2910 m, 2860 m, 1640 s, 1590 s, 1548 w, 1502 w, 1447 m, 1309 m, 1258 w, 1170 w, 1139 w, 1085 w, 1023 w, 977 w, 820 w, 753 w cm^{-1}.

Synthesis of $(C_5Me_5)_2Y(NC_6H_{10}O)(CNCMe_3)$, 5. In a glovebox, $CNCMe_3$ (0.05 mL, 1.06 mmol) was added to a white slurry of **2** (0.50 g, 1.06 mmol) in 5 mL of hexanes. The slurry immediately became clear, and the reaction was stirred for 1 h. Solvent was removed by rotary evaporation to give **5** as a colorless solid (0.48 g, 92%). X-ray quality crystals were obtained by concentrating a toluene solution of **5** and storing it overnight at −35 °C. Anal. Calcd for $C_{31}H_{49}N_2OY$: Y, 16.0. Found: Y, 15.2. ^1H NMR (C_6D_6): δ 2.98 (m, 2H), 2.38 (m, 2H), 2.10 (s, 30H), 1.53 (b, 6H, $\Delta\nu_{1/2}$ = 30.4 Hz), 0.91 (s, 9H). ^{13}C NMR (C_6D_6): δ 180.3 (*C*O), 150.7 (*C*NCMe$_3$), 114.6 (C_5Me_5) 55.2 (CN*C*Me$_3$), 47.5 (CH_2), 38.1 (CH_2), 32.0 (CH_2), 31.0 (CH_2), 29.5 (CNC*Me*$_3$), 24.3 (CH_2), 11.7 (C_5Me_5). IR: 2904 m, 2858 m, 2186 m, 1637 s, 1545 s, 1444 s, 1375 m, 1205 m, 1128 w, 1089 w, 1027 w, 811 w, 703 w cm^{-1}.

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5H_4Me)_2Y(\mu\text{-}NC_6H_{10}O)]_2$, 1. A colorless crystal of approximate dimensions 0.23 × 0.26 × 0.27 mm was

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mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[16] program package was used to determine the unit-cell parameters and for data collection (30 s/frame scan time for a hemisphere of diffraction data). The raw frame data were processed using SAINT[17] and SADABS[18] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[19] program. The diffraction symmetry was 2/*m*, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[20] for neutral atoms were used throughout the analysis. The molecule was a dimer that was located about an inversion center. Hydrogen atoms were located from a difference Fourier map and refined (*x*,*y*,*z* and U_{iso}). At convergence, wR2 = 0.0580 and GOF = 1.104 for 287 variables refined against 3926 unique data (as a comparison for refinement on *F*, R1 = 0.0246 for those 3572 data with $I > 2.0\sigma(I)$). Subsequent complexes were handled as described for **1**.

$(C_5Me_5)_2Y(C_6H_{10}NO)$, 2. The space group was determined to be $P2_1/n$, and the pentamethylcyclopentadienyl ligand defined by atoms C(11)−C(20) was disordered. The pentamethylcyclopentadienyl was included using multiple components with partial site-occupancy factors. At convergence, wR2 = 0.1585 and GOF = 1.066 for 252 variables refined against 4191 data (0.85 Å resolution). As a comparison for refinement on *F*, R1 = 0.0536 for those 3299 data with $I > 2.0\sigma(I)$.

$[(C_5Me_5)_2Y(\mu\text{-}O_2CNC_6H_{10}O)]_2$, 3. The space group was determined to be $P2_1/c$, and the molecule was located about an inversion center. There was one molecule of toluene solvent present per formula unit. The toluene molecule was disordered and included using multiple components with partial site-occupancy factors. At convergence, wR2 = 0.1495 and GOF = 1.009 for 330 variables refined against 6838 data. As a comparison for refinement on *F*, R1 = 0.0537 for those 4016 data with $I > 2.0\sigma(I)$.

$(C_5Me_5)_2Y(PhNCOC_6H_{10}NO)$, 4. The space group was determined to be $P2_1/c$. Hydrogen atoms were either located from a difference Fourier map and refined (*x*,*y*,*z* and U_{iso}) or included using a riding model. At convergence, wR2 = 0.0971 and GOF = 1.034 for 423 variables refined against 7474 unique data (as a comparison for refinement on *F*, R1 = 0.0367 for those 5628 data with $I > 2.0\sigma(I)$).

$(C_5Me_5)_2Y(NC_6H_{10}O)(CNCMe_3)$, 5. The space group was determined to be $P2_1/n$, and the pentamethylcyclopentadienyl ligand defined by atoms C(11)−C(15) exhibited rotational disorder. The disorder was modeled using two components for each atom with site-occupancy factors of 0.60 for the major component and 0.40 for the minor component. At convergence, wR2 = 0.1422 and GOF = 1.020 for 306 variables refined against 7415 unique data (as a comparison for refinement on *F*, R1 = 0.0550 for those 4911 data with $I > 2.0\sigma(I)$).

Results

$[(C_5H_4Me)_2Y(\mu\text{-}NC_6H_{10}O)]_2$, 1. Addition of ϵ-caprolactam to $(C_5H_4Me)_2Y[N(SiMe_3)_2]$ in hexanes generates a white solid, **1**, which has a ^{1}H NMR spectrum containing peaks consistent with an ϵ-caprolactam moiety lacking the resonance of the NH proton. A single

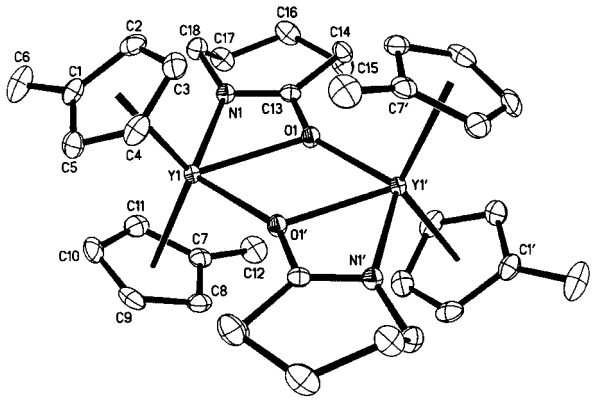

Figure 2. Thermal ellipsoid plot of $[(C_5H_4Me)_2Y(\mu\text{-}NC_6H_{10}O)]_2$, **1**, drawn at the 50% probability level with hydrogen atoms omitted for clarity.

$C_5H_4\mathit{Me}$ methyl resonance is observed for **1**, but four separate ring proton signals are observed for the $(C_5H_4Me)_2Y$ unit. The IR spectrum lacked the NH stretch of ϵ-caprolactam and differed from coordinated ϵ-caprolactam-lanthanide complexes in the ν_{CO} region. Although the spectroscopic data showed that a new product had formed cleanly, definitive identification required an X-ray crystallographic study. **1** was found to be the dimer, $[(C_5H_4Me)_2Y(\mu\text{-}NC_6H_{10}O)]_2$, in the solid state as shown in Figure 2. Evidently, deprotonation of the NH proton of ϵ-caprolactam was cleanly effected by the yttrium amide precursor, giving **1** in 88% yield according to eq 1. Isopiestic solution molecular weight studies of **1** in THF vs ferrocene indicated that the complex exists as a dimer in solution as well.

$$2(C_5H_4Me)_2Y[N(SiMe_3)_2] + 2HNC_6H_{10}O \xrightarrow{\text{hexanes}} \mathbf{1} + 2HN(SiMe_3)_2 \quad (1)$$

Dimeric **1** is isomorphous with the recently published Yb/ϵ-caprolactamate complex $[(C_5H_4Me)_2Yb(\mu\text{-}NC_6H_{10}O)]_2$.[7] It is presumably identical with the yttrium analogue reported in that paper. In **1**, each bis(methylcyclopentadienyl)yttrium metallocene moiety is ligated by the nitrogen of the deprotonated ϵ-caprolactam and the two metallocenes are connected by bridging oxygen atoms. Each yttrium is formally nine-coordinate. The 2.388 and 2.393 Å Y−C (ring centroid) distances and the 127° (ring centroid)−Y−(ring centroid) angle are in the normal range for yttrium metallocenes with this degree of ring substitution.[12,21] The 3.908 Å Y···Y separation is longer than the 3.664(1) Å distance in $[(C_5H_4Me)_2Y(\mu\text{-}H)(THF)]_2$,[12] which is consistent with the larger size of the bridging ligand in **1**.

The Y-caprolactamate bond distances as well as the distances within the caprolactamate anion, Table 2,

(16) *SMART Software Users Guide*, Version 4.21; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1997.
(17) *SAINT Software Users Guide*, Version 4.05; Bruker Analytical X-Ray Systems, Inc.: Madison, WI, 1997.
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Table 1. Experimental Data for the X-ray Diffraction Studies of $[(C_5H_4Me)_2Y(\mu\text{-}NC_6H_{10}O)]_2$, 1, $(C_5Me_5)_2Y(C_6H_{10}NO)$, 2, $[(C_5Me_5)_2Y(\mu\text{-}O_2CNC_6H_{10}O)]_2$, 3, $(C_5Me_5)_2Y(PhNCOC_6H_{10}NO)$, 4, and $(C_5Me_5)_2Y(NC_6H_{10}O)(CN^tBu)$, 5

	1	2	3	4	5
formula	$C_{36}H_{48}N_2O_2Y_2$	$C_{26}H_{40}NOY$	$C_{66}H_{92}N_2O_6Y_2$	$C_{33}H_{45}N_2O_2Y$	$C_{31}H_{49}N_2OY$
fw	718.58	471.50	1123.15	590.62	554.63
temp (K)	158	158	163	163	162
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/n$
a (Å)	12.2124(6)	8.6069(7)	10.8178(14)	10.0802(6)	10.5610(11)
b (Å)	11.1331(5)	21.0692(16)	14.9661(19)	20.5779(13)	18.4443(19)
c (Å)	12.7269(6)	13.587(10)	17.994(2)	15.0401(9)	16.4911(17)
β (deg)	107.3940(10)	90.7210(10)	105.264(2)	98.5670(10)	106.588(2)
V (Å^3)	1651.25(13)	2463.7(3)	2810.5(6)	3084.9(3)	3078.6(6)
Z	2	4	2	4	4
ρ_{calcd} (Mg/m^3)	1.445	1.271	1.327	1.272	1.197
μ (mm^{-1})	3.530	2.383	2.106	1.921	1.918
final R1 [$I>2\sigma(I)$]	0.0246	0.0536	0.0537	0.0367	0.0550
final wR2 (all data)	0.0580	0.1499	0.1206	0.0971	0.142

Table 2. Selected Bond Distances (Å) for $[(C_5H_4Me)_2Y(\mu\text{-}NC_6H_{10}O)]_2$, 1, $(C_5Me_5)_2Y(C_6H_{10}NO)$, 2, $[(C_5Me_5)_2Y(\mu\text{-}O_2CNC_6H_{10}O)]_2$, 3, $(C_5Me_5)_2Y(PhNCOC_6H_{10}NO)$, 4, and $(C_5Me_5)_2Y(NC_6H_{10}O)(CN^tBu)$, 5

	1	2	3	4	5
Y−(C_5Me_5 ring centroid)	2.391	2.360	2.424	2.363	2.409
Y−O	Y(1)−O(1) 2.3961(12) Y(1)−O(1′) 2.2990(12)	2.288(3)	Y(1)−O(1) 2.287(3) Y(1)−O(2) 2.359(3) Y(1)−O(3) 2.392(3)	Y(1)−O(1) 2.2528(14) Y(1)−O(2) 2.1733(14)	2.326(3)
Y−N	2.4116(14)	2.362(4)			2.391(3)
C−N	C(13)−N(1) 1.296(2)	C(21)−N(1) 1.280(6)	C(22)−N(1) 1.362(5)	C(21)−N(1) 1.345(3)	C(26)−N(1) 1.303(5)
O−C	C(13)−O(1) 1.323(2)	C(21)−O(1) 1.309(5)	C(22)−O(2) 1.247(5)	C(21)−O(1) 1.258(2)	C(26)−O(1) 1.302(5)

suggest that the anionic charge is delocalized in **1**, as shown in Figure 1. The 2.4116(14) Å Y(1)−N(1) distance is similar to that in the ytterbium analogue, which has an Yb−N distance of 2.374(4) Å,[7] when the difference in the metal sizes is taken into consideration.[22] Similar to $[(C_5H_4Me)_2Yb(\mu\text{-}NC_6H_{10}O)]_2$, the metal−nitrogen bond in **1** is slightly longer then the Y−N bond distances in $(C_5Me_5)_2Y[N(SiMe_3)_2]$[23] and $(C_5Me_4Et)_2Y[N(SiMe_3)_2]$,[24] which range from 2.324(7) to 2.39(1) Å, but it is shorter than dative Y←NR_3 interactions in the complexes $(C_5H_5)_2Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)$[25] and $(C_5Me_5)Y(C_6H_4\text{-}2\text{-}CH_2NMe_2)_2$,[26] which range from 2.43(2) to 2.588(5) Å. The 2.396(1) Å Y(1)−O(1) and 2.2990(12) Å Y(1′)−O(1) distances in **1** are also similar to the analogous distances seen in $[(C_5H_4Me)_2Yb(\mu\text{-}NC_6H_{10}O)]_2$, 2.370(3) and 2.277(3) Å, which show that the caprolactamate anion makes a longer bond to the metal to which it is chelated than to the other metal. These Y−O distances in **1** are longer than the bridging metal−oxygen distances in the dimeric ytterbium butoxide $[(C_5H_5)_2Yb(\mu\text{-}OBu)]_2$, 2.190(5) and 2.207(6) Å,[27] and the dimeric yttrium methoxide $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OMe)]_2$, 2.217(3) and 2.233(3) Å,[28] but they are shorter than the 2.460(8) Å dative Y−O distance found in nine-coordinate $[(C_5H_4Me)_2Y(\mu\text{-}H)(THF)]_2$.[12] The 1.323(2) Å C(13)−O(1) distance is longer than the C═O bond found in neutral ϵ-caprolactam (1.242(2) Å),[29] while the 1.296(2) Å N(1)−C(13) distance is shorter than the analogous N−C bond in ϵ-caprolactam (1.327(2) Å). Consistent with the delocalization displayed by these bond distances, the Y(1), N(1), C(13), and O(1) atoms are coplanar to within 0.0219 Å.

$(C_5Me_5)_2Y(NC_6H_{10}O)$, 2. The synthesis of a pentamethylcyclopentadienyl analogue of **1** was explored in order to examine how different ancillary environments would effect the coordination of the ϵ-caprolactam anion. Unlike **1**, however, $(C_5Me_5)_2Y[N(SiMe_3)_2]$ does not react as readily with ϵ-caprolactam in hexanes. After stirring overnight, 90% of the starting material remains. To circumvent this low reactivity, $(C_5Me_5)_2Y(C_3H_5)(THF)$ was employed since it has been recently reported that lanthanide allyls are convenient and reactive starting materials.[13]

Addition of ϵ-caprolactam to $(C_5Me_5)_2Y(C_3H_5)(THF)$ in benzene causes an immediate color change from dark yellow to colorless. **2** was isolated from the reaction in high yield as a white solid. The ^{1}H NMR spectrum contained resonances similar to those of the caprolactamate in **1**. Unlike **1**, however, the C_5Me_5 rings displayed a single resonance at 1.94 ppm and the IR spectrum contained a different pattern in the ν_{CO} region. X-ray crystallographic analysis identified **2** as $(C_5Me_5)_2Y(NC_6H_{10}O)$ and showed that it exists as a monometallic species in the solid state, Figure 3. As has been

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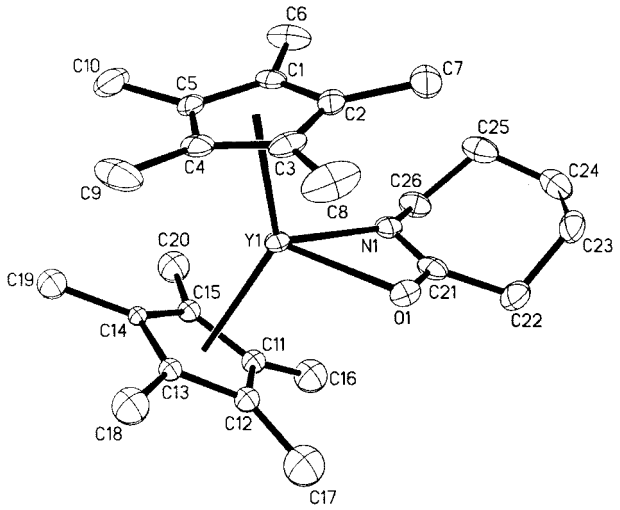

Figure 3. Thermal ellipsoid plot of $(C_5Me_5)_2Y(C_6H_{10}NO)$, **2**, drawn at the 30% probability level with hydrogen atoms omitted for clarity.

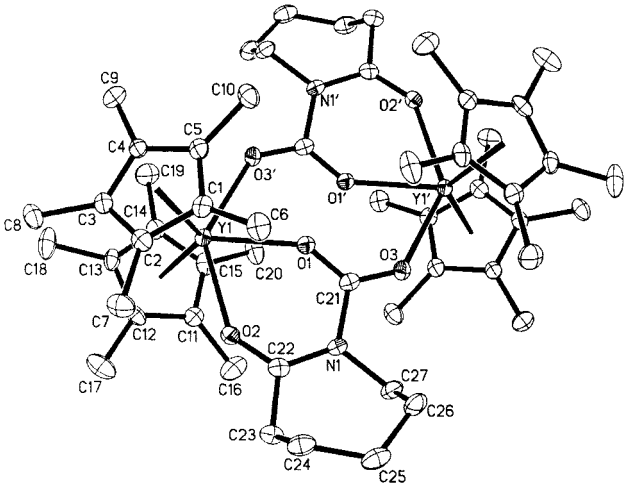

Figure 4. Thermal ellipsoid plot of $[(C_5Me_5)_2Y(\mu\text{-}O_2CNC_6H_{10}O)]_2$, **3**, drawn at the 30% probability level with hydrogen atoms omitted for clarity.

discussed previously,[30] formation of bridged structures with the $(C_5Me_5)_2Y$ unit is disfavored by the steric crowding that arises with this combination of a large ancillary ligand and a small metal. Hence, a monomeric structure is quite reasonable. Equation 2 summarizes the deprotonation reaction which occurs in >80% yield.

$$(C_5Me_5)_2Y(C_3H_5)(THF) + HNC_6H_{10}O \xrightarrow[-THF]{\text{benzene}} \mathbf{2} + C_3H_6 \quad (2)$$

Complex **2** has normal metrical parameters in the bis(pentamethylcyclopentadienyl) portion of the molecule[31] and there appears to be charge delocalization in the caprolactamate anion as in **1**: as shown in Table 2, the Y−N, Y−O, C−O, and C−N distances in **2** are similar to those in **1**. The YNCO ring is planar to within 0.025 Å.

Carbon Dioxide Insertion Activity. To examine if insertion chemistry would occur with the caprolactamate anion, **1** and **2** were reacted with CO_2, a substrate that has the capacity to insert to form stable carboxylate products.[8] When **1** was put under an atmosphere of CO_2 at ambient temperature for 24 h, no reaction was observed. However, when **2** is left unstirred under an atmosphere of CO_2 for 3 h, a white crystalline solid, **3**, precipitates from the colorless solution. The resultant solid is soluble in coordinating solvents such as pyridine and moderately soluble in THF, but it is only slightly soluble in arenes.

Although the NMR spectrum of **3** indicated that a new product had formed cleanly and a carboxylate peak was observed at 187.7 ppm in the ^{13}C NMR spectrum, X-ray crystallography was necessary for complete characterization. Complex **3** was found to be the dimer $[(C_5Me_5)_2Y(\mu\text{-}O_2CNC_6H_{10}O)]_2$, Figure 4. The structural data revealed that CO_2 had inserted into the Y−N bond in **2** to form an ϵ-caprolactam-substituted carboxylate anion in which both carboxylate oxygens as well as the ϵ-caprolactam oxygen coordinate to yttrium, eq 3. The

$$2\ \mathbf{2} + 2\ CO_2 \xrightarrow{\text{benzene}} \mathbf{3} \quad (3)$$

carboxylate unit bridges the two yttrium atoms through both oxygen atoms, while the other oxygen in the newly formed ligand chelates to just one metal to give a formal coordination number of 9 to each yttrium metal. The average Y−O carboxylate distance, 2.339(3) Å, is similar to analogous distances in other organoyttrium CO_2 insertion products (2.30−2.35 Å).[32,33] The other Y−O distance in **3**, 2.359(3) Å, is shorter then common dative Y−O(THF) bond lengths in $(C_5Me_5)_2Y(CH_3)(THF)$[34] and

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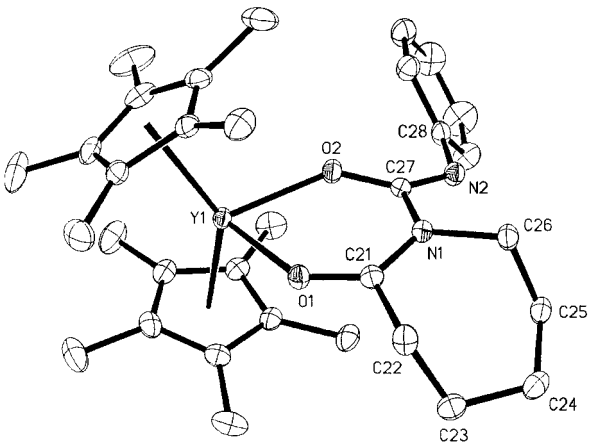


Figure 5. Thermal ellipsoid plot of $(C_5Me_5)_2Y(PhNCOC_6H_{10}NO)$, **4**, drawn at the 30% probability level with hydrogen atoms omitted for clarity.

$(C_5Me_5)_2YCl(THF)$,[35] which range from 2.435(8) to 2.466(7) Å, but it is similar to the Y−O(ϵ-caprolactam) bond lengths found in $[Pr(C_6H_{11}NO)_6Cl]^{2+}$ and $[Eu(C_6H_{11}NO)_4Cl_2]^+$, 2.418(3) and 2.315(18) Å,[2] respectively, when metal radial size is taken into consideration. [22]

Charge delocalization is substantially diminished in the ϵ-caprolactam ring in **3**, as measured by the relatively short 1.247(5) Å C(22)−O(2) and long 1.362(5) Å C(22)−N(1) bonds, both of which are similar to the analogous distances in free ϵ-caprolactam. The 1.250(5) Å C(21)−O(3) and 1.244(5) Å C(21)−O(1) carboxylate distances are similar to those in other carboxylate-bridged lanthanide complexes.[36,37] These distances indicate that the new anionic ligand formed by this insertion can be viewed as an ϵ-caprolactam-substituted carboxylate.

Phenyl Isocyanate Insertion Activity. Since isocyanates are electronic analogues of carbon dioxide, the insertion chemistry of phenyl isocyanate with both **1** and **2** was also examined. As in the case of the CO_2 reactions, **1** did not react with PhNCO, while addition of PhNCO to **2** immediately causes a color change to yellow. A new product, **4**, can be isolated that displays downfield shifts of the phenyl isocyanate protons in the ^1H NMR spectrum. In the ^{13}C NMR of **4**, the carbonyl chemical shift also moves downfield from a value of 133.7 ppm for free PhNCO to 149.9 ppm.

To determine the coordination geometry around yttrium in the new product, **4** was studied by X-ray analysis, Figure 5. PhNCO inserts into the caprolactamate Y−N bond of **2** to form a new anion, as shown in eq 4. The $(PhNCONC_6H_{10}O)^-$ anion chelates yttrium with both oxygen atoms forming a monometallic eight-coordinate complex. The 2.1733(14) Å Y(1)−O(2) distance involving the PhNCO-derived oxygen is shorter than the Y−O length in the only other yttrium amide

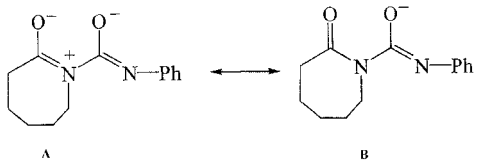
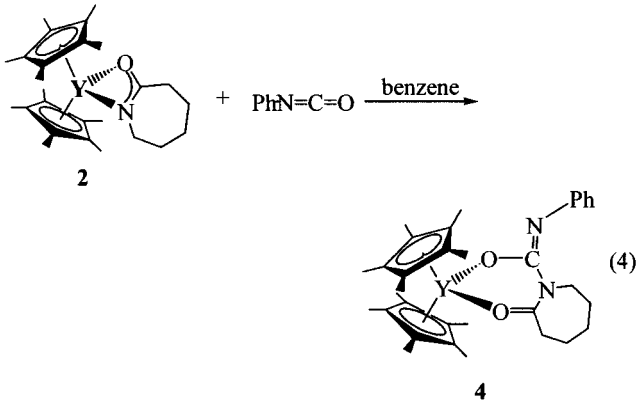


Figure 6. Resonance structures of the anion obtained by phenyl isocyanate insertion into caprolactamate.

phenyl isocyanate insertion product in the literature, $[(C_5H_4CH_3)_2Y(OCN(^iPr)_2NPh)]$, 2.285(2) Å.[38] The other Y(1)−O(1) distance of 2.2528(14) Å, which involves the ϵ-caprolactam-derived oxygen, is comparable to the analogous lengths seen in **1** and **2**.



The Y(1)−O(2)−C(27)−N(1)−C(21)−O(1) ring is planar to within 0.069 Å, and the C−O and C−N bond distances suggest charge delocalization as shown in Figure 6. The C(21)−O(1) and C(27)−O(2) distances of 1.258(2) and 1.283(2) Å, respectively, are between the 1.192−1.256 Å range of $C(sp^2)$═O and the 1.293−1.407 Å range of $C(sp^2)$−O distances.[39] The 1.345(3) Å bond of C(21)−N(1) also lies between the typical 1.279−1.329 Å $C(sp^2)$═N distance and 1.321−1.416 Å range of $C(sp^2)$−N.[9] The short C(27)−N(2) bond distance of 1.277(3) Å lies in the range of $C(sp^2)$═N and results in a long C(27)−N(1) bond of 1.465(3) Å, which suggests that resonance B is favored. PhNCO insertion into the Y−N bond forms an ϵ-caprolactam-substituted amidate ligand, in which the ϵ-caprolactam carbonyl oxygen chelates to the yttrium.

$(C_5Me_5)_2Y(NC_6H_{10}O)(CN^tBu)$, 5. In addition to the reactions of CO_2 and PhNCO, the reactivity of **1** and **2** with *tert*-butyl isocyanide was examined. Consistent with the previous examples, **1** did not react with *tert*-butyl isocyanide. However, when CN^tBu is added to a hexanes solution of **2**, a new product, **5**, is obtained, which displayed a new CN^tBu resonance in the ^1H NMR spectrum. The IR spectrum contained an absorbance at 2186 cm^{-1} that is similar to the 2180 cm^{-1} ν_{CN} absorption of the isocyanide adduct $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-}O)$.[40] The ν_{CO} stretch at 1637 cm^{-1} is similar to that observed in **2**. This suggested that simple adduct formation could have taken place according to eq 5. This

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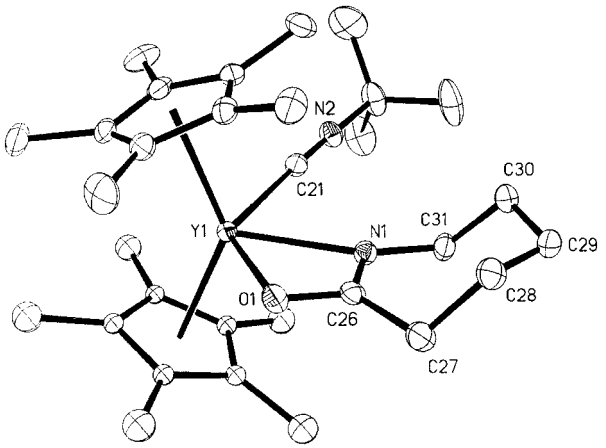
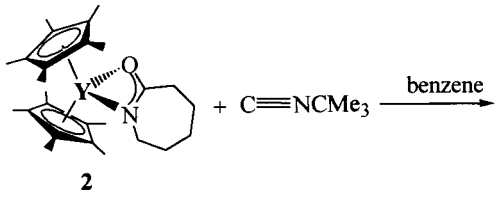


Figure 7. Thermal ellipsoid plot of $(C_5Me_5)_2Y(NC_6H_{10}O)(CN^tBu)$, **5**, drawn at the 30% probability level with hydrogen atoms omitted for clarity.

was also suggested by the ^{13}C NMR spectrum: the 150 ppm shift of the Me_3CNC carbon in **5** was very similar to the shift of 156.2 in free *tert*-butyl isocyanide. To determine how the coordination of isocyanide affected the binding mode of the caprolactamate anion, **5** was characterized by X-ray crystallography.



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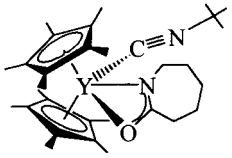

5 (5)

As shown in Figure 7, *tert*-butyl isocyanide coordinates to yttrium but does not insert into the Y−N bond. The binding mode of the caprolactamate anion is not changed by the additional ligand, but the yttrium caprolactamate bond distances lengthen to Y−O(1) 2.326(3) Å and Y−N(1) 2.391(3) Å compared to those in **2**, 2.289(3) and 2.360(3) Å, respectively. The Y(1)−C(21) ($CNCMe_3$) distance of 2.578(4) is comparable to that in the samarium isocyanide adducts $[(C_5Me_5)_2Sm(CNCMe_3)]_2(\mu\text{-O})]$ and $[(C_5Me_5)_2Sm(\mu\text{-CN})(CNC_6H_{11})]_3$,[41] 2.64(1) and 2.67(2) Å, respectively, when the differences in metal sizes are taken into account.[22]

Discussion

ϵ-Caprolactam can be deprotonated by amide and allyl functionalities in yttrium metallocene complexes to form the $(NC_6H_{10}O)^-$ caprolactamate anion. This deprotonation reaction is sensitive to the ancillary ligands in the yttrium metallocene, since the $[N(SiMe_3)_2]^-$ anion will accomplish this deprotonation in $(C_5H_4Me)_2Y[N(SiMe_3)_2]$, but not in $(C_5Me_5)_2Y[N(SiMe_3)_2]$. In the bis(pentamethylcyclopentadienyl) system, a more reactive ligand was needed to form the caprolactamate. The conveniently made[13] allyl complex $(C_5Me_5)_2Y(C_3H_5)(THF)$ had the necessary reactivity.

The coordination mode of the caprolactamate ligand with yttrium also apparently depends on the size of the ancillary ligand set. Hence, with a bis(methylcyclopentadienyl) ligand set, the caprolactamate functions as a bridging ligand, Figure 2, which connects two metal centers via bridging oxygen and provides extra coordination via the nitrogen donor atom. Interestingly, in $(C_5H_4Me)_2Y(THF)\{OC[N(^iPr_2)]NPh\}$, which has a similar, but noncyclic OCN unit, coordinated to the same $(C_5H_4Me)_2Y$ metallocene fragment, a monomeric THF adduct is isolated from THF. Complex **1** evidently prefers an unsolvated dimeric form since crystallization of **1** prepared in THF gives the unsolvated dimer. With larger ancillary ligands, namely, the common bis(pentamethylcyclopentadienyl) ligand set, the caprolactamate adopts a chelating binding mode, Figure 3, as previously observed in the titanium complexes $[(C_5H_5)_2Ti(NC_6H_{10}O)]$[5] and $[O[Si(^iPr)_2N(C_5H_3NMe)]_2Ti(NMe_2)(NC_6H_{10}O)]$.[6]

The ancillary ligand set apparently affects not only the synthesis and structure but also the reactivity. Insertion chemistry was not observed with $[(C_5H_4Me)_2Y(NC_6H_{10}O)]_2$, **1**, under ambient conditions, whereas $(C_5Me_5)_2Y(NC_6H_{10}O)$, **2**, was reactive with several substrates under analogous conditions. It has been reported elsewhere, however,[7] that the $[(C_5H_4Me)_2Ln(NC_6H_{10}O)]_2$ (Ln = Yb, Er, Y) complexes polymerize ϵ-caprolactone at or above 60 °C. The limited reactivity of **1** may be related to the fact that **1** displays a dimeric molecular weight even in THF. The caprolactamate anion may form a particularly strong dimeric structure when this is sterically possible, and this may be less reactive. Hence, heating these dimers may be necessary to form monomers that can participate in insertion chemistry.

The reactivity of **2** with CO_2 and PhNCO shows that the Y−N part of the caprolactamate anion is most susceptible to insertion. The structure of the isocyanide adduct, **5**, suggests that prior coordination of the insertion substrate to yttrium is sterically possible.

The structures of the CO_2 and PhNCO insertion products demonstrate that this type of reaction can be used to generate new types of anionic ligands incorporating the strong bonding of ϵ-caprolactam. For example, $[(C_5Me_5)_2Y(O_2CNC_6H_{10}O)]_2$, **3**, adopts a structure in which the ϵ-caprolactam-derived oxygen of the newly formed $(O_2CNC_6H_{10}O)^-$ anion still coordinates to yttrium. The alternative structure, in which the ϵ-caprolactam moiety is a noncoordinating substitutent attached to the carboxylate, is not observed. In the case of $(C_5Me_5)_2Y(PhNCONC_6H_{10}O)$, **4**, the $(PhNCONC_6H_{10}O)^-$ formed by insertion is formally analogous to an acetylacetonate ligand, Figure 6, but involves heteroatoms and the cyclic component of a ϵ-caprolactam. Hence, the caprolactamate anion can be used to construct more complex bridging polydentate monoanionic ligand structures in which the powerful ligating ability of ϵ-caprolactam can be utilized.

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Conclusion

ϵ-Caprolactam can be readily deprotonated by organoyttrium complexes to provide access to a chelating monoanion that has variable coordination modes depending on the ancillary ligands. The amide component of the caprolactamate ligand is susceptible to insertion chemistry with some substrates again depending on the ancillary ligand coordination. Insertion chemistry with the caprolactamate anion can provide a route to new types of polydentate anionic ligands that contain ϵ-caprolactam components. These new ligands, as well as the caprolactamate, incorporate the strong binding ability of caprolactam into an anionic ligand that can charge balance the cationic metal center in complexes of electropositive metals such as yttrium and lanthanide metals.

Acknowledgment. For support of this research, we thank the Division of Chemical Sciences of the Office of Basic Energy Sciences of the Department of Energy. We also thank Dr. Matthew Johnston for crystallographic assistance.

Supporting Information Available: This material is available in the form of a CIF file for the structures reported herein via the Internet at http://pubs.acs.org.

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