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Syntheses of $\{(MeC_5H_4)_2Ln(THF)[O{\cdots}CN(i\text{-}Pr)_2{\cdots}NPh]\}$ (Ln = Y, Er, Yb) and the X-ray Crystal Structure of the Yttrium Complex: The Active Species for Polymerization of Phenyl Isocyanate by (Diisopropylamido)bis(methylcyclopentadienyl)lanthanides

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Isocyanates are not only the useful reagents in organic synthesis but also important monomers in polymer chemistry. Due to the formal electronic analogy with carbon dioxide, they have been used as models in the study of insertion of carbon dioxide into a metal−carbon bond.[1] Although insertion reactions of isocyanates into transition-metal−ligand bonds are well-documented,[2] no such reactivity has been reported for organolanthanide complexes to our knowledge. Due to our interest in the synthesis and chemistry of organolanthanide amides, we investigated the synthesis of lanthanocene isopropylamide and its reactivity toward phenyl isocyanate. It has been found that (diisopropylamido)bis(methylcyclopentadienyl)lanthanides $(MeC_5H_4)_2LnN(i\text{-}Pr)_2(THF)$ (Ln = Y (**1**), Er (**2**),Yb (**3**)) are able to polymerize phenyl isocyanate at 30 °C. A study of the polymerization mechanism led to isolation of the insertion products of the first monomer into the Ln−N σ bond of complexes **1**−**3**, $\{(MeC_5H_4)_2Ln(THF)[O{\cdots}CN(i\text{-}Pr)_2{\cdots}NPh]\}$ (Ln = Y (**4**), Er (**5**), Yb (**6**)). Complexes **4**−**6** also show good catalytic activity for PhNCO polymerization. The X-ray crystal structure determination of complex **4** shows that the yttrium atom is η^5-bonded to two methylcyclopentadienyl rings and coordinated by one tetrahydrofuran and one bidentate ligand with nitrogen and oxygen atoms. In this article, we would report the results of these studies.

Experimental Section

The chemistry described below was performed under pure argon with rigorous exclusion of air and water using Schlenk techniques. Solvents were dried and freed of oxygen by refluxing over Na or sodium benzophenone ketyl and distilled under argon prior to use. Anhydrous $LnCl_3$ was made according to the literature procedures.[3] $LiN(i\text{-}Pr)_2$ was obtained by the reaction of $HN(i\text{-}Pr)_2$ with n-BuLi in a solution of THF and hexane.

Melting point temperatures were determined in sealed argon-filled capillaries and are uncorrected. Metal analyses were carried out by complexometric titration. Carbon, hydrogen, and nitrogen analyses were performed by direct combustion. The IR spectra were recorded on a Perkin-Elmer 983 spectrometer. ^1H NMR spectra were obtained with a Bruker AM-300 apparatus. Electron ionization mass spectra (EIMS) were determined on a HP5989 A spectrometer.

$(MeC_5H_4)_2YN(i\text{-}Pr)_2(THF)$, 1. To a slurry of YCl_3 (3.72 g, 19.06 mmol) in 30 mL of THF, 31.64 mL of a solution of MeC_5H_4Na (38.12 mmol) in THF was added. The mixture was stirred at room temperature for 48 h. After centrifugation, the THF was completely removed and the oily residue was extracted with 50 mL of toluene. Then the toluene extracts (49 mL, 14.15 mmol) were cooled to 0 °C. Twenty milliliters of a solution of $LiN(i\text{-}Pr)_2$ (14.20 mmol) in toluene was added from a syringe. The mixture was stirred for 1 h at 0 °C and then for another 48 h at room temperature. After centrifugation, the toluene was pumped off and the solids were extracted with diethyl ether. When the extracts were concentrated and cooled to −20 °C, colorless crystals were formed. Yield: 3.59 g (44.7%). Anal. Calcd for $C_{22}H_{36}ONY$: C, 61.21; H, 8.72; N, 3.15; Y, 20.67. Found: C, 61.51; H, 9.01; N, 3.32; Y, 21.07. IR (KBr pellet, cm^{-1}): 2965 (s), 1617 (m), 1523 (m), 1380 (m), 1178 (w), 1073 (w), 901 (w), 619 (s).

$(MeC_5H_4)_2ErN(i\text{-}Pr)_2(THF)$, 2. This compound was prepared from 3.45 g of $ErCl_3$ (12.61 mmol), 25.22 mmol of MeC_5H_4Na, and 20 mL of a solution of $LiN(i\text{-}Pr)_2$ (10.70 mmol) in toluene using the procedure described above. Pink crystals were obtained. Yield: 3.12 g (49.5%). Anal. Calcd for $C_{22}H_{36}ONEr$: C, 51.57; H, 7.24; N, 2.65; Er, 34.01. Found: C, 51.81; H, 7.27; N, 2.80; Er, 34.23. IR (KBr pellet, cm^{-1}): 2965 (s), 1628 (m), 1523 (m), 1379 (m), 1168 (w), 1049 (w), 901 (m), 736 (m), 677 (s), 614 (s).

$(MeC_5H_4)_2YbN(i\text{-}Pr)_2(THF)$, 3. This complex was prepared from 3.54 g of $YbCl_3$ (12.67 mmol), 25.34 mmol of MeC_5H_4Na, and 20 mL of a solution of $LiN(i\text{-}Pr)_2$ (10.80 mmol) in toluene using the procedure described above. Dark green crystals were isolated. Yield: 2.80 g (43.7%). Anal. Calcd for $C_{22}H_{36}ONYb$: C, 52.20; H, 7.18; N, 2.77; Yb, 34.19. Found: C, 52.52; H, 7.52; N, 2.82; Yb, 34.02. IR (KBr pellet, cm^{-1}): 2965 (s), 1626 (m), 1523 (m), 1380 (m), 1178 (w), 1074 (w), 901 (w), 602 (s), 568 (s).

$\{(MeC_5H_4)_2Y(THF)[O{\cdots}CN(i\text{-}Pr)_2{\cdots}NPh]\}$, 4. Phenyl isocyanate (0.63 mL, 5.82 mmol) was added to a toluene (30 mL) solution of $(MeC_5H_4)_2YN(i\text{-}Pr)_2(THF)$ (2.45 g, 5.82 mmol). The resulting colorless solution was stirred at room temperature for 24 h. After the clear solution was concentrated, colorless crystals were obtained at −10 °C. Yield: 1.59 g (50.7%). Mp = 133−136 °C. Anal. Calcd for $C_{29}H_{41}O_2N_2Y$: C, 64.67; H, 7.69; N, 5.20; Y, 16.51. Found: C, 64.82; H, 7.71; N, 5.27; Y, 16.85. IR (KBr pellet, cm^{-1}): 3450 (m), 3334 (m), 3064 (w), 2971 (s), 2933 (m), 2879 (w), 1644 (s), 1600 (m), 1528 (s), 1500 (s), 1443 (s), 1374 (m), 1335 (s), 1243 (m), 1150 (s), 1057 (m), 895 (w), 818 (w), 756 (s), 695 (m), 602 (m), 509 (w). ^1H NMR(C_6D_6, 300 MHz, 25 °C): δ 7.00−7.30 (m, 5H, Ph), 6.10 (s, 8H, MeC_5H_4), 3.65 (s, 4H, THF), 3.50 (m, 2H, $N(i\text{-}Pr)_2$), 2.35 (s, 6H, MeC_5H_4), 1.35 (s, 4H, THF), 1.15 (s,12H, $N(i\text{-}Pr)_2$). MS (70 eV): *m/z* 466 (5, M^+ − THF), 423 (10, M^+ − THF −

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Table 1. Experimental Data for the X-ray Diffraction Study of Complex 4

formula	$C_{29}H_{41}YO_2N_2$
fw	538.56
temp (K)	193
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a (Å)	11.259(2)
b (Å)	15.209(8)
c (Å)	8.516(2)
β (deg)	90.99(2)
V (Å^3)	1400.3(9)
Z	2
D(calcd) (Mg/M^3)	1.277
diffractometer	Rigaku AFC7R
radiation	Mo Kα ($\lambda = 0.710\ 69$ Å)
scan type	$\omega-2\theta$
scan range (deg)	$1.05 + 0.30 \tan \theta$
scan speed (deg min^{-1}, in ω)	16.0
2θ range (deg)	18.3−21.4
(Mo Kα) (cm^{-1})	21.11
no. of reflns collected	4085
no. of obs ($I > 3.00\alpha(I)$)	3240
no. of variables	308
R	0.038
R_w	0.048
goodness of fit	1.98

CHMe$_2$), 387 (10, M$^+$ − THF − MeC$_5$H$_4$), 247 (10, M$^+$ − THF − NPhCN(i-Pr)$_2$O).

$\{(MeC_5H_4)_2Er(THF)[O\overset{\cdots}{-}CN(i\text{-}Pr)_2\overset{\cdots}{-}NPh]\}$, 5. Following the above procedure, phenyl isocyanate (0.53 mL, 4.90 mmol) was added to a toluene (30 mL) solution of (MeC$_5$H$_4$)$_2$ErN(i-Pr)$_2$(THF) (2.45 g, 4.90 mmol). The resulting solution was stirred at room temperature for 24 h. After the clear solution was concentrated, pink crystals were formed. Yield: 1.76 g (58.3%). Mp = 130−135 °C. Anal. Calcd for $C_{29}H_{41}O_2N_2Er$: C, 56.46; H, 6.71; N, 4.54; Er, 27.11. Found: C, 56.73; H, 6.79; N, 4.60; Er, 27.46. IR (KBr pellet, cm^{-1}): 3450 (m), 3064 (w), 2970 (s), 2933 (m), 2879 (w), 1636 (s), 1600 (m), 1528 (s), 1500 (m), 1451 (s), 1374 (m), 1335 (s), 1250 (m), 1150 (s), 1057 (m), 895 (w), 749 (s), 695 (m), 602 (m), 509 (w). MS (70 eV): *m/z* 544 (60, M$^+$ − THF), 501 (100, M$^+$ − THF − CHMe$_2$), 465 (50, M$^+$ − THF − MeC$_5$H$_4$), 325 (50, M$^+$ − THF − NPhCN(i-Pr)$_2$O).

$\{(MeC_5H_4)_2Yb(THF)[O\overset{\cdots}{-}CN(i\text{-}Pr)_2\overset{\cdots}{-}NPh]\}$, 6. Following the above procedure, phenyl isocyanate (0.48 mL, 4.44 mmol) was added to a toluene (30 mL) solution of (MeC$_5$H$_4$)$_2$YbN(i-Pr)$_2$(THF) (2.24 g, 4.44 mmol). The resulting solution was stirred at room temperature for 24 h. After the clear solution was concentrated, red crystals were isolated. Yield: 1.25 g (45.1%). Mp = 120−125 °C. Anal. Calcd for $C_{29}H_{41}O_2N_2Yb$: C, 55.93; H, 6.65; N, 4.50; Yb, 27.79. Found: C, 56.11; H, 6.70; N, 4.58; Yb, 28.03. IR (KBr pellet, cm^{-1}): 3450 (m), 3288 (m), 3064 (w), 2971 (s), 2933 (m), 2879 (w), 1636 (s), 1600 (m), 1528 (s), 1505 (m), 1450 (w), 1374 (m) , 1335 (s), 1250 (m), 1150 (s), 1057 (m), 895 (w), 749 (s), 695 (m), 602 (m), 502 (w). MS (70 eV): *m/z* 550 (5, M$^+$ − THF), 507 (5, M$^+$ − THF − CHMe$_2$), 471 (5, M$^+$ − THF − MeC$_5$H$_4$), 331 (5, M$^+$ − THF − NPhCN(i-Pr)$_2$O).

X-ray Data Collection, Structure Determination, and Refinement for Complex 4. A colorless crystal of approximate dimensions 0.20 × 0.20 × 0.30 mm was mounted in a thin-walled glass capillary for X-ray structure analysis. Diffraction data were collected on Rigaku AFC7R diffractometer using graphite- monochromated Mo Kα ($\lambda = 0.710\ 69$ Å) radiation. During the course of the collection of the intensity data, no significant decays were observed. The intensity was corrected for Lorentz−polarization effects and empirical absorption. A summary of the crystallographic data is given in Table 1.

The structure was solved by the heavy-atom method. The coordinates of the Y atom derived from Patterson analysis were used to calculate the Fourier map. Successive Fourier syntheses gave the coordinates of all non-hydrogen atoms refined by the block-diagonal least-squares method. H atoms were placed in calculated positions and assigned isotropic thermal parameters. Further refinement led to final convergence at $R = 0.038$. All calculations were performed on an IRIS INDIGO computer using DIRDIF 92 programs.

Results and Discussion

Syntheses of (MeC$_5$H$_4$)$_2$LnN(i-Pr)$_2$(THF) (Ln = Y (1), Er (2), Yb (3)). In recent years, organolanthanide amides have received a great deal of attention. These complexes were prepared by two main routes: (1) the ionic metathesis of alkali metal amides with lanthanocene chlorides;[4−11] (2) the metalation of various amines by lanthanocene alkyl or hydride precursors.[8,12−15] The neutral and ionic organolanthanide complexes with N(SiMe$_3$)$_2$,[7−11,16] NPh$_2$,[14] NMe$_2$,[12,13] and NH$_2$[4,12,17,18] as ligands were published. Recently, we reported the preparation and molecular structures of some anionic lanthanocene diphenylamides by the ionic metathesis route.[19−22] Attempts to isolate the neutral lanthanocene diphenylamides were unsuccessful. Using the same strategy, however, we obtained the desired neutral (diisopropylamido)bis(methylcyclopentadienyl)lanthanides (MeC$_5$H$_4$)$_2$LnN(i-Pr)$_2$(THF) (Ln = Y(**1**), Er (**2**), Yb (**3**)), as shown in the following equations:

$$\mathrm{LnCl_3 + 2MeC_5H_4Na \xrightarrow{THF} (MeC_5H_4)_2LnCl(THF) + NaCl}$$

$$\mathrm{(MeC_5H_4)_2LnCl(THF) + LiN(i\text{-}Pr)_2 \xrightarrow{toluene} (MeC_5H_4)_2LnN(i\text{-}Pr)_2(THF) + LiCl}$$
$$(\mathrm{Ln = Y}\ (\mathbf{1}),\ \mathrm{Er}\ (\mathbf{2}),\ \mathrm{Yb}\ (\mathbf{3}))$$

Complexes **1**−**3** were characterized by elemental analysis and IR. Unfortunately, their crystal structures have not been solved yet by X-ray analysis due to poor crystalline quality. Nevertheless, their formation can be confirmed further by the structural characterization of the product formed via their reaction with phenyl

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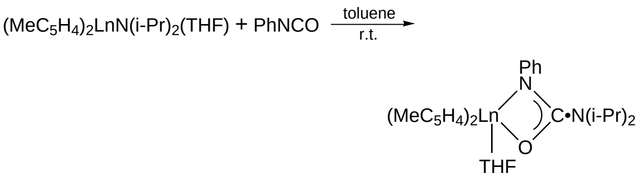
isocyanate (vide infra). Complexes **1**−**3** are extremely sensitive to air and moisture. They are soluble in THF and toluene but not in hexane.

Reactivity of Complexes 1−3 to Phenyl Isocyanate: Syntheses of $\{(MeC_5H_4)_2Ln(THF)[O\overset{\cdots}{-}CN(i\text{-}Pr)_2\overset{\cdots}{-}NPh]\}$ (Ln = Y (4), Er (5), Yb (6)). Like organolanthanide species containing Ln−C or Ln−H σ bonds, the organolanthanide amides also exhibit high reactivity. For example, they are able to activate small molecules such as CO and olefins. Organolanthanide amides react with CO to give the insertion product $[(C_5Me_5)_2Sm]_2$ $[(PhN)OCCO(NPh)]$,[23] with aminoolefins to yield the corresponding heterocycles,[15] with methyl methacrylate (MMA) to lead to MMA polymerization.[24] In order to explore their chemistry further, we tested their reactivity with phenyl isocyanate. The preliminary experiments show that complexes **1**−**3** can exhibit good catalytic activity for PhNCO polymerizations. When 300 equiv of phenyl isocyanate was added to $(MeC_5H_4)_2LnN(i\text{-}Pr)_2(THF)$ at 30 °, the polymerization took place rapidly. After 5 h, two products, the methanol insoluble fraction (39% yield) and the methanol soluble fraction (61% yield), were obtained. As we know, the methanol insoluble fraction is not soluble in normal solvents. This prevents us from further charaterizing this product. The work with alkyl isocyanates is now proceeding. In order to get further insight into the initiation mechanism, we have tried the stoichiometric reactions (1:1) between $(MeC_5H_4)_2LnN(i\text{-}Pr)_2(THF)$ (Ln = Y (**1**), Er (**2**), Yb (**3**)) and PhNCO at room temperature. At last, we succeeded in isolating the first PhNCO monomer insertion products into precatalysts $\{(MeC_5H_4)_2Ln(THF)[O\overset{\cdots}{-}CN(i\text{-}Pr)_2\overset{\cdots}{-}NPh]\}$ (Ln = Y (**4**), Er (**5**), Yb (**6**)) as crystals.



[Ln = Y (**4**), Er (**5**), Yb (**6**)]

Complexes **4**−**6** were characterized by elemental analysis, IR, ^1H NMR (for **4**), and MS. Their bonding mode was proven by the X-ray analysis on complex **4**. Complexes **4**−**6** are slightly sensitive to air and moisture and thermally stable. Their melting points are at about 130 °C. These complexes show good activity for polymerization of PhNCO. When 300 equiv of PhNCO was added to complex **4** at 30 °C, the polymerization occurred immediately and the yellow solid polymers precipitated concomitantly. After work-up, the polymers, 43% of the methanol insoluble fraction and 57% of the methanol soluble fraction, were obtained. In comparison with the results obtained by precatalyst **1**, it is reasonable that these isolated complexes may be considered to be the real active species for polymerization of phenyl isocyanate. It is noticed that the behavior of complexes **1**−**3** with PhNCO is quite similar to that of $CpTiCl_2(NMe_2)$, which is also a good catalyst for isocyanate polymerizations,[25] but completely different from that of Cp_2ZrMe_2.[1] The reaction of Cp_2ZrMe_2 with PhNCO can only proceed to the first insertion step. That is to say that the reaction gives only $\{Cp_2Zr(Me)[O\overset{\cdots}{-}C(Me)\overset{\cdots}{-}NPh]\}$ but not an isocyanate polymer.[1]

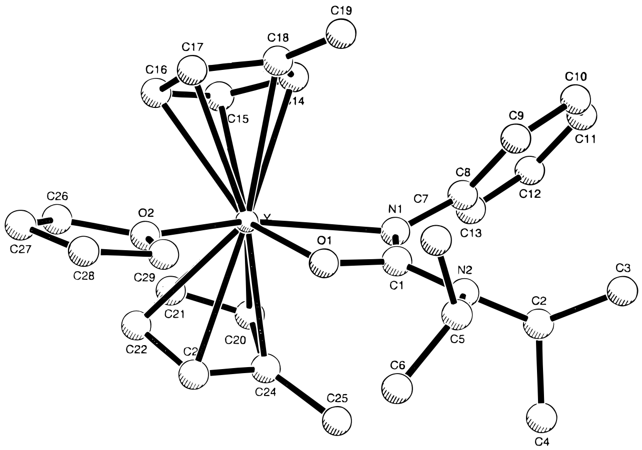


Figure 1. ORTEP diagram of the molecular structure of $\{(MeC_5H_4)_2Y(THF)[O\overset{\cdots}{-}CN(i\text{-}Pr)_2\overset{\cdots}{-}NPh]\}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complex 4

Bond Distances			
Y−N(1)	2.401(2)	Y−O(1)	2.285(2)
Y−O(2)	2.473(3)	Y−C(14)	2.673(4)
Y−C(15)	2.666(4)	Y−C(16)	2.657(4)
Y−C(17)	2.673(4)	Y−C(18)	2.689(4)
Y−C(20)	2.668(5)	Y−C(21)	2.662(5)
Y−C(22)	2.667(6)	Y−C(23)	2.683(6)
Y−C(24)	2.701(5)	O(1)−C(1)	1.297(4)
C(1)−N(1)	1.323(5)	N(1)−C(8)	1.416(5)
C(1)−N(2)	1.362(5)		
Bond Angles			
O(1)−Y−N(1)	55.96(9)	O(2)−Y−O(1)	74.18(9)
O(2)−Y−N(1)	129.80(10)	O(1)−C(1)−N(1)	114.3(3)
Y−O(1)−C(1)	97.8(2)	Y−N(1)−C(1)	91.7(2)
Cent(1)−Y−Cent(2)	127.51		

X-ray Crystal Structure of Complex 4. Complex **4** crystallizes from concentrated toluene at −20 °C in the triclinic space group *P*1 (No. 2). The ORTEP diagram of the crystal structure of complex **4** is given in Figure 1. Selected bond lengths and angles are given in Table 2. The X-ray structure shows complex **4** as a discrete monomer with the yttrium atom η^5-bonded to two methylcyclopentadienyl rings and coordinated by one tetrahydrofuran and one bidentate ligand. The coordination number of the central metal Y is nine.

The N1−C1 distance (1.323(5) Å) in complex **4** is slightly but significantly longer than the value accepted for a $N(sp^2){=}C(sp^2)$ double bond (1.26 Å), and the O1−C1 distance (1.297(4) Å) is slightly but significantly shorter than that observed for the $O{-}C(sp^2)$ single bond (1.324(6) Å) in $[(MeC_5H_4)_2Y\ \mu\text{-}OCH{=}CH_2)]_2$.[26] These bond parameters indicate some electronic delocalization over the O1−C1−N1 unit. The values of the N1−C8 and C1−N2 distances (Table 2) correspond well to single bonds. The O1, C1, N1, and N2 atoms are coplanar within experimental error.

The Y−N1 distance in complex **4**, 2.401(3) Å, is much longer than the 2.253(5) and 2.274(5) Å distance in

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$(C_5Me_5)_2YN(SiMe_3)_2$.[7] The latter was thought to be unusually short due to a dative π-interaction between the lone pair of electrons on nitrogen and the yttrium metal. However, the Y−N1 distance in complex **4** is clearly shorter than a typical $R_3N{:} \rightarrow Y$ donor bond distance (2.47−2.63 Å).[27] Therefore, the Y−N1 distance is intermediate between a $Y-NR_2$ bond and a $Y \leftarrow{:}\ NR_3$ donor bond. The Y−O1 bond in complex **4**, 2.285(2) Å, is much longer than the Sm−O(Ar) bond, 2.151(7) Å in $[Sm(OAr)_3(THF)](THF)$[28] after the substraction of the estimated difference (ca. 0.18 Å) for four-coordinate Sm^{3+} and nine-coordinate Y^{3+},[29] even longer than the $Y-\mu$-OR bonds (2.217(3) and 2.233(3) Å) in $[(C_5H_4SiMe_3)_2Y(\mu\text{-}OMe)]_2$[30] but much shorter than the Y−O2(THF) donor bond, 2.473(3) Å in complex **4**. Hence, the anion $[O\overset{--}{-}CN(i\text{-}Pr)_2\overset{--}{-}NPh]^-$ bonds to the yttrium atom via a partial single bond, partial donor bond interaction with N1 and O1 atoms.

The most closely related organolanthanide species that can be compared to complex **4** is $[(C_5Me_5)_2Sm]_2$-[(PhN)OCCO(NPh)] (7),[23] which has a Sm−N distance of 2.49(1) Å and a Sm−O bond length of 2.30(1) Å. After corrections are made from the difference (0.004 Å) in the ionic radii for nine-coordinate Y^{3+} and eight-coordinate Sm^{3+},[29] the distance of Y−N1 in complex **4** is much shorter than that of Sm−N in complex **7**, but the Y−O1 bond length in complex **4** is similar to the Sm−O bond length in complex **7**. This indicates that complex **4** has a much stronger Y−N1 bond.

The Y−N1 and Y−O1 bond distances in complex **4** are also compared with the closest structurally related zirconium(IV) complex $\{Cp_2Zr(Me)[O\overset{--}{-}C(Me)\overset{--}{-}NPh]\}$ (8),[1] which has a Zr−N distance of 2.297(4) Å and a Zr−O distance of 2.298(4) Å. Both the Y−N1 and Y−O1 bond distances in complex **4** are shorter than the corresponding Zr−N and Zr−O bond lengths in complex **8** when corrections are made from the difference (0.185 Å) in the ionic radii for nine-coordinate Y^{3+} and Zr^{4+}.[29] This also shows that the yttrium atom is more tightly bonded to a bidentate ligand with N1 and O1 atoms in complex **4**.

The average yttrium cyclopentadienyl carbon distance in complex **4**, 2.674(5) Å, is similar to that found in other trivalent yttrium complexes: $[(C_5H_5)_2Y(\mu\text{-}CH_3)]_2$ (**9**),[31] 2.66(2) Å; $[(CH_3C_5H_4)_2Y(\mu\text{-}H)(THF)]_2$ (**10**)[32] 2.69(2) Å; $[(C_5H_5)_2Y(\mu\text{-}\eta^2\text{-}HC{=}NCH_3)]_2$ (**11**)[33] 2.68 Å; $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ (**12**)[26] 2.651 Å. The (ring centroid)−Y−(ring centroid) angle in complex **4**, 127.5°, is also similar: **9**, 128.9°; **10**, 127.5°; **11**, 127.2°; **12**, 128.1°.

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Supporting Information Available: Tables of atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, torsion angles, and least-squares planes and a diagram of complex **4** (28 pages). Ordering information is given on any current masthead page.

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