An Yttrium-Based System to Evaluate Lewis Base Coordination to an Electropositive Metal in a Metallocene Environment

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The unsolvated bimetallic yttrium complex $(C_5Me_5)_2Y(\mu\text{-}Cl)Y(C_5Me_5)_2Cl$ (**1**) provides a convenient platform upon which to compare the coordination chemistry of oxygen-donor ligands and monomers with Lewis acidic metal ions. Reaction of **1** with 2 equiv of oxygen-containing substrates formed the monomeric complexes $(C_5Me_5)_2YCl(L)$ (L = THF (**2**), benzophenone (**3**), methyl methacrylate (**4**), ϵ-caprolactone (**5**), hexamethylphosphoramide (**6**), ϵ-caprolactam (**7**), 1-methyl-2-pyrrolidinone (**8**), *N*,*N*′-dimethylpropyleneurea (**9**)). Each of these readily crystallize, which allows comparison of the Y−O interaction in the solid state. The X-ray data show that the numerical values of the measured Y−O lengths decrease in the order THF > benzophenone > methyl methacrylate > ϵ-caprolactone > hexamethylphosphoramide > ϵ-caprolactam > 1-methyl-2-pyrrolidinone > *N*,*N*′-dimethylpropyleneurea, although these bond lengths span only a short range and some are the same within experimental error. In the case of ϵ-caprolactam, a bis adduct, $(C_5Me_5)_2YCl(\epsilon\text{-caprolactam})_2$ (**10**), can be isolated from the reaction of **1** and excess ϵ-caprolactam. ^{1}H NMR spectroscopy indicates that $(C_5Me_5)_2YCl(L)/L'$ ligand displacement reactions in solution with **2**−**9** follow a trend consistent with the bond lengths except for $(C_5Me_5)_2YCl(\epsilon\text{-caprolactam})$ (**7**), in which L participates in hydrogen bonding to the chloride.

Introduction

The large, electropositive, oxophilic yttrium and lanthanide metal ions frequently form complexes with oxygen-donor ligands. Commonly this involves oxygen-containing solvents such as THF,[1−4] diethyl ether, and dimethoxyethane (DME), but it has also been shown that polymerizable monomers such as ϵ-caprolactone[5,6] and ϵ-caprolactam[7,8] can form strongly bound adducts with the lanthanides. Although there are many examples of crystallographically characterized yttrium and lanthanide metal complexes of oxygen-donor ligands, less information is available on solid-state and solution interactions of oxygen-containing polymerizable monomers. Data on the hierarchy of coordination strengths of oxygen-donor ligands would aid in choosing the proper solvents for reactions involving oxygen-containing monomers and in copolymerization systems. It would also be useful to have details of the site of coordination and binding preference of monomers that contain several potential oxygen donors in a polyfunctional substrate.

We report here our attempts to develop a system that can be conveniently used to evaluate the relative donor capacity of oxygen-containing substrates to metals such as yttrium and the lanthanides in typical organometallic environments. Our data suggest that $(C_5Me_5)_2Y(\mu\text{-}Cl)Y(C_5Me_5)_2Cl$ (**1**) is appropriate for this purpose, since it is readily synthesized[9] and diamagnetic and it reacts in high yield with oxygen donor complexes, L, to make $(C_5Me_5)_2YCl(L)$ adducts. The adducts crystallize to give one of the more common types of organometallic coordination environments: i.e., one involving two $(C_5Me_5)^-$ ligands, an anionic ligand $(Cl)^-$, and a neutral donor ligand. This system allows solid-state evaluation of the Lewis acid−base interaction and competitive binding studies via ^{1}H NMR spectroscopy. The coordination chemistry of **1** with eight oxygen-containing substrates is reported here.

Experimental Section

All of the compounds described below were handled under nitrogen with rigorous exclusion of air and water using standard Schlenk, vacuum line, and glovebox techniques. Solvents were prepared, and physical measurements were obtained as previously described.[10] ϵ-Caprolactone, methyl methacrylate (MMA), *N*,*N*′-dimethylpropyleneurea (DMPU), 1-methyl-2-pyrrolidinone (MPU), and hexamethylphosphora-

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mide (HMPA) were purchased from Aldrich, dried over activated 3A molecular sieves, and degassed with three freeze−pump−thaw cycles before use. ϵ-Caprolactam was purchased from Aldrich and sublimed before use. Benzophenone was purchased from Fisher and used as received. $(C_5Me_5)_2YCl(\mu\text{-}Cl)Y(C_5Me_5)_2$ (**1**) was prepared as previously described.[9] $(C_5Me_5)_2YCl(THF)$[1] was synthesized by a modified procedure as described below. ^1H and ^{13}C NMR spectra were obtained on an Omega 500 MHz or a GN 500 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. Complexometeric analyses were obtained as previously described.[11]

Typical Procedure for the Synthesis of $(C_5Me_5)_2YCl(L)$. Preparation of $(C_5Me_5)_2YCl(THF)$ (2). In a glovebox, THF (14 mg, 0.20 mmol) in 5 mL of benzene was added to a slurry of **1** (30 mg, 0.038 mmol) in about 1 mL of benzene. The slurry instantly became a colorless solution. After 1 h of stirring, the solvent was removed by rotary evaporation and the white solid, **2**, was obtained (35 mg, 80%) and identified by ^1H NMR spectroscopy.[1]

$(C_5Me_5)_2YCl(L)$ (L = Benzophenone (3), MMA (4), ϵ-Caprolactone (5), HMPA (6), ϵ-Caprolactam (7), 1-Methyl-2-pyrrolidinone (8), DMPU (9)). 3−9 were prepared as described for **2**. Reagents, yields, and spectroscopic data for individual samples are given below.

$(C_5Me_5)_2YCl$(benzophenone) (3). A dark red solid (40 mg, 91%) was isolated from benzophenone (14 mg, 0.08 mmol) and **1** (30 mg, 0.038 mmol). Anal. Calcd for $C_{33}H_{40}ClOY$: Y, 15.4. Found: Y, 15.1. ^1H NMR (C_6D_6): δ 7.76 (b, 4H, $\Delta\nu_{1/2} = 100$ Hz), 7.10 (m, 2H), 7.04 (m, 4H), 2.04 (s, 30H). ^{13}C NMR (C_6D_6): δ 206.6 (*C*O), 135.1 (*o*-*C*), 132.3 (*m*-*C*), 129.3 (*p*-*C*), 117.8 (C_5Me_5), 11.8 (C_5Me_5). IR: 3059 w, 2912 s, 2858 s, 1614 s, 1568 s, 1444 s, 1328 s, 1290 s, 1159 m, 1081 s, 1027 s, 942 m, 803 m, 703 s cm^{-1}. UV−vis (hexanes; λ_{max}, nm (ϵ, M^{-1}cm^{-1})): 457 (1460).

$(C_5Me_5)_2YCl$(MMA) (4). A yellow solid was isolated (50 mg, 94%) from MMA (10 mg, 0.10 mmol) and **1** (43 mg, 0.054 mmol). Anal. Calcd for $C_{25}H_{38}ClO_2Y$: Y, 18.0. Found: Y, 18.2. ^1H NMR (C_6D_6): δ 6.19 (m, 1H), 5.20 (m, 2H), 3.56 (s, 3H), 2.02 (s, 30H), 1.56 (s, 3H). ^{13}C NMR (C_6D_6): δ 175.5 (*C*O),-134.7 (C*C*=C), 131.8 (*C*H$_2$), 117.6 (C_5Me_5), 56.8 (O*C*H$_3$), 17.8 (*C*H$_3$), 11.7 (C_5Me_5). IR: 2920 vs, 2858 vs, 1661 s, 1630 s, 1560 m, 1444 s, 1375 m, 1328 s, 1259 s, 1089 s, 1020 vs, 803 vs cm^{-1}.

$(C_5Me_5)_2YCl(\epsilon$-Caprolactone) (5). A white solid (49 mg, 94%) was obtained from the reaction between **1** (40 mg, 0.051 mmol) and ϵ-caprolactone (12 mg, 0.11 mmol). Anal. Calcd for $C_{26}H_{40}ClO_2Y$: Y, 17.5. Found: Y, 17.9. ^1H NMR (C_6D_6): δ 3.35 (m, 2H), 2.40 (m, 2H), 2.09 (s, 30H), 1.22 (m, 2H), 0.95 (m, 4H). ^{13}C NMR (C_6D_6): δ 185.7 (*C*O), 117.2 (C_5Me_5), 33.4 (*C*H$_2$), 31.9 (*C*H$_2$), 28.2 (*C*H$_2$), 28.1 (*C*H$_2$), 22.7 (*C*H$_2$), 11.5 (C_5Me_5). IR: 2904 s, 2866 s, 1688 vs, 1437 m, 1359 m, 1305 m, 1259 m, 1189 m, 1097 m, 1043 m, 803 w, 703 w cm^{-1}.

$(C_5Me_5)_2YCl$(HMPA) (6). A white solid (68 mg, 93%) was obtained from HMPA (23 mg, 0.12 mmol) and **1** (50 mg, 0.063 mmol). Anal. Calcd for $C_{26}H_{66}ClN_3OPY$: Y, 15.0. Found: Y, 15.3. ^1H NMR (C_6D_6): δ 2.18 (s, 30H), 2.18 (d, 18H, $J = 10$ Hz). ^{13}C NMR (C_6D_6): δ 117.0 (C_5Me_5), 37.4 (*C*H$_2$, $J_{C-P} = 20$ Hz), 12.0 (C_5Me_5). IR: 2920 s, 2858 s, 1591 w, 1444 m, 1305 s, 1189 s, 1128 vs, 989 vs, 757 w cm^{-1}.

$(C_5Me_5)_2YCl(\epsilon$-caprolactam) (7). A white solid (68 mg, 94%) was isolated from ϵ-caprolactam (16 mg, 0.14 mmol) and **1** (56 mg, 0.071 mmol) in 15 mL of benzene. Anal. Calcd for $C_{26}H_{41}ClNOY$: Y, 17.5. Found: Y, 18.0. ^1H NMR (C_6D_6): δ 8.67 (br, 1H, $\Delta\nu_{1/2} = 28$ Hz), 2.30 (m, 2H), 2.08 (s, 30H), 1.90 (m, 2H), 1.17 (m, 2H), 1.08 (m, 2H), 0.88 (m, 2H). ^{13}C NMR (C_6D_6): 181.9 (*C*O), 117.0 (C_5Me_5), 42.5 (*C*H$_2$), 36.4 (*C*H$_2$), 30.0 (*C*H$_2$), 28.3 (*C*H$_2$), 22.6 (*C*H$_2$), 11.4 (C_5Me_5). IR: 3205 m, 2927 s, 2858 s, 1630 vs, 1498 m, 1437 s, 1359 m, 1259 m, 1205 m, 1089 s, 1020 s, 803 s cm^{-1}.

$(C_5Me_5)_2YCl$(1-methyl-2-pyrrolidinone) (8). A white solid (47.6 mg, 96%) was obtained from 1-methyl-2-pyrrolidinone (10 mg, 0.10 mmol) and **1** (40 mg, 0.05 mmol). Anal. Calcd for $C_{25}H_{39}ClNOY$: Y, 18.0. Found: Y, 17.5. ^1H NMR (C_6D_6): δ 2.25 (s, 3H), 2.11 (s, 30H), 1.64 (m, 2H), 1.42 (m, 2H), 0.98 (m, 2H). ^{13}C NMR (C_6D_6): δ 176.6 (*C*O), 116.6 (C_5Me_5), 49.9 (*C*H$_2$), 31.5 (*C*H$_2$), 30.2 (*C*H$_2$), 17.4 (*C*H$_3$), 1164 (C_5Me_5). IR: 2904 s, 1645 vs, 1514 m, 1444 m, 1313 m, 1259 m, 1112 m, 1027 m, 803 w, 765 w cm^{-1}.

$(C_5Me_5)_2YCl$(DMPU) (9). A white solid (54 mg, 90%) was isolated from DMPU (15 mg, 0.12 mmol) and **1** (45 mg, 0.056 mmol). Anal. Calcd for $C_{26}H_{42}ClN_2OY$: Y, 17.0. Found: Y, 16.8. ^1H NMR (C_6D_6): δ 2.82 (s, 3H), 2.45 (s, 3H), 2.22 (m, 2H), 2.18 (m, 2H), 2.15 (s, 30H), 0.91 (m, 2H). ^{13}C NMR (C_6D_6): δ 157.3 (*C*O), 116.7 (C_5Me_5), 47.6 (*C*H$_2$), 47.0 (*C*H$_2$), 38.3 (*C*H$_3$), 36.6 (*C*H$_3$), 20.6 (*C*H$_2$), 11.8 (C_5Me_5). IR: 2920 s, 2858 s, 1576 vs, 1413 w, 1321 w, 1259 s, 1020 vs, 905 w, 865 w, 766 vs cm^{-1}.

$(C_5Me_5)_2YCl(\epsilon$-caprolactam)$_2$ (10). The reaction of excess ϵ-caprolactam (60 mg, 0.53 mmol) with **1** (70 mg, 0.089 mmol) gave a white solid which crystallized with one caprolactam in the lattice, $(C_5Me_5)_2YCl(\epsilon\text{-caprolactam})_2\cdot$(caprolactam) (125 mg, 96%). Anal. Calcd for $C_{38}H_{63}ClN_3O_3Y$: Y, 12.1. Found: Y, 12.3. ^1H NMR (C_6D_6): δ 8.17 (b, 3H, $\Delta\nu_{1/2} = 49$ Hz), 2.50 (m, 6H), 2.14 (m, 6H), 2.11 (s, 30H), 1.30 (m, 6H), 1.15 (m, 6H), 1.03 (m, 6H). ^{13}C NMR (C_6D_6): δ 179.5 (*C*O), 116.5 (C_5Me_5), 42.4 (*C*H$_2$), 36.8 (*C*H$_2$), 30.4 (*C*H$_2$), 29.5 (*C*H$_2$), 23.2 (*C*H$_2$), 11.7 (C_5Me_5). IR: 3290 w, 3205 m, 3051 w, 2927 s, 2858 s, 1637 vs, 1483 m, 1437 m, 1359 m, 1197 m, 1120 m, 1020 m, 981 w, 811 m cm^{-1}.

X-ray Data Collection, Structure Determination, and Refinement. $(C_5Me_5)_2YCl$(benzophenone) (3). Complexes **3−10** were handled as described in detail here for **3**, except for the specific comments which follow. A red crystal of approximate dimensions 0.15 × 0.28 × 0.49 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[12] program package was used to determine the unit-cell parameters and for data collection (20 s/frame scan time for a sphere of diffraction data). The raw frame data were processed using SAINT[13] and SADABS[14] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[15] program. The diffraction symmetry was 2/*m*, and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$, which was later determined to be correct. Details are given in Table 1.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. Analytical scattering factors[16] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

$(C_5Me_5)_2YCl(\epsilon$-caprolactone) (5). The pentamethylcyclopentadienyl and caprolactone ligands exhibited a high degree of thermal motion. The ring defined by C(11)−C(15) was refined with isotropic thermal parameters using multiple components with partial site-occupancy factors (0.60/0.40 major/minor components). The disordered atoms of the caprolactone ligand were also handled in this manner. It was necessary to include bond distance constraints for this ligand.

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Table 1. Summary of Crystallographic Data for $(C_5Me_5)_2YCl(L)$ (L = THF (2), Benzophenone (3), Methyl Methacrylate (4), ϵ-Caprolactone (5), Hexamethylphosphoramide (6), ϵ-Caprolactam (7), 1-Methyl-2-pyrrolidinone (8), *N*,*N*′-Dimethylpropyleneurea (9)) and $(C_5Me_5)_2YCl(\epsilon\text{-caprolactam})_2$ (10)

	3	4	5	6	7	8	9	10
formula	$C_{33}H_{40}ClOY$	$C_{25}H_{38}ClNO_2Y$	$C_{26}H_{40}ClO_2Y$	$C_{26}H_{48}ClN_3OPY$	$C_{26}H_{41}ClNOY$	$C_{25}H_{39}ClNOY$	$C_{26}H_{42}ClN_2OY$	$C_{32}H_{52}ClN_2O_2Y{\cdot}C_6H_{11}NO$
fw	577.01	494.91	508.94	574.00	507.96	493.93	522.98	734.27
temp (K)	158	163(2)	158(2)	158(2)	163(2)	173(2)	163(2)	163(2)
cryst syst	monoclinic	orthorhombic	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	*Pbca*	*Pbca*	$P2_1/c$	*Pbca*	*Pn*	$P2_1/c$	$P2_1/c$
a (Å)	13.0017(15)	16.4172(8)	17.6071(10)	10.1251(8)	17.4491(8)	10.4464(7)	9.4446(4)	18.3535(14)
b (Å)	10.7469(12)	14.9659(7)	15.7221(9)	19.0600(16)	15.5408(7)	9.7393(6)	17.3668(7)	16.4063(12)
c (Å)	21.515(2)	20.5069(10)	18.8986(10)	15.3784(13)	19.1854(9)	12.3895(8)	16.3932(7)	12.7998(9)
β (deg)	98.192(2)	90	90	95.996(2)	90	93.7970(10)	91.8030(10)	92.1630(10)
V (Å^3)	2975.6(6)	5038.5(4)	5231.5(5)	2951.6(4)	5202.6(4)	1257.75(14)	2687.52(19)	3851.4(5)
Z	4	8	8	4	8	2	4	4
ρ_{calcd} (Mg/m^3)	1.288	1.305	1.292	1.292	1.297	1.304	1.293	1.266
μ (mm^{-1})	2.072	2.438	2.350	2.142	2.361	2.440	2.288	1.621
final R1 ($I > 2\sigma(I)$)	0.0546	0.0335	0.0560	0.0629	0.0583	0.0449	0.0266	0.0505
final wR2 (all data)	0.1406	0.0849	0.1466	0.1829	0.1362	0.1094	0.0675	0.1428

$(C_5Me_5)_2YCl(\epsilon\text{-caprolactam})$ (7). Hydrogen atom H(1) was located from a difference Fourier map and refined (*x*, *y*, *z*, and U_{iso}). The remaining hydrogen atoms were included using a riding model.

$(C_5Me_5)_2YCl$(1-methyl-2-pyrrolidinone) (8). The absolute structure was assigned by refinement of the Flack parameter.[16]

$(C_5Me_5)_2YCl$(DMPU) (9). Hydrogen atoms were located from a difference Fourier map and refined (*x*, *y*, *z*, and U_{iso}).

$(C_5Me_5)_2YCl(\epsilon\text{-caprolactam})_2$ (10). There was one solvent molecule of ϵ-caprolactam present per formula unit. The solvent exhibited high thermal motion, but a suitable disorder model could not be established. The largest difference peak was 1.7 e/Å^3. The solvent was included using SAME and EADP constraints in SHELXTL.[15]

Results

Synthesis of $(C_5Me_5)_2YCl(L)$ Complexes. $(C_5Me_5)_2Y(\mu\text{-Cl})Y(C_5Me_5)_2Cl$ (**1**) reacts readily with oxygen donor Lewis bases to form the monometallic adducts $(C_5Me_5)_2YCl(L)$ (L = THF[1] (**2**), benzophenone (**3**), methyl methacrylate (MMA; **4**), ϵ-caprolactone (**5**), hexamethylphosphoramide (HMPA; **6**), ϵ-caprolactam (**7**), 1-methyl-2-pyrrolidinone (MPU; **8**), *N*,*N*′-dimethylpropyleneurea (DMPU; **9**)), according to eq 1. In each case the

$$(C_5Me_5)_2Y(\mu\text{-Cl})Y(C_5Me_5)_2Cl + 2L \rightarrow \underset{\mathbf{1}}{} \quad 2(C_5Me_5)_2YCl(L) \quad (1)$$
$$\mathbf{2-9}$$

L = THF (**2**), benzophenone (**3**), MMA (**4**), ϵ-caprolactone (**5**), HMPA (**6**), ϵ-caprolactam (**7**), MPU (**8**), DMPU (**9**)

reaction can be carried out with a stoichiometric amount of L and the yield is high (>80%). Complexes **2** and **5**−**9** are isolable as white crystalline solids, $(C_5Me_5)_2YCl$(MMA) (**4**) is yellow, and $(C_5Me_5)_2YCl$(benzophenone) (**3**) is a dark red solid due to a broad absorption with a maximum at $\lambda = 457$ nm with $\epsilon = 1500$ M^{-1} cm^{-1}. Color changes due to benzophenone coordination have been observed previously with organoaluminum complexes.[17]

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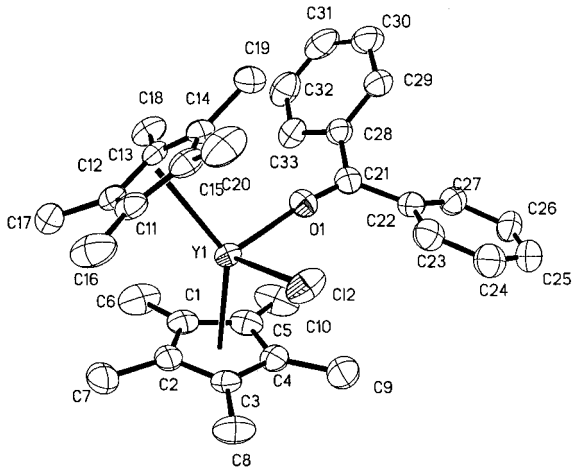


Figure 1. Molecular structure of $(C_5Me_5)_2YCl$(benzophenone) (**3**) with probability ellipsoids drawn at the 50% level.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes $(C_5Me_5)_2YCl(L)$[1] (2−9) and $(C_5Me_5)_2YCl(\epsilon\text{-caprolactam})_2$ (10)

complex	Ln−(C_5Me_5 ring centroid)	(ring centroid)−metal−(ring centroid)	Ln−O	diff in Y−O length, complex ***N*** − complex ***N*** − 1	Ln−Cl
2[1]	2.382 2.379	136.2	2.410(7)		2.579(3)
3	2.376 2.384	138.0	2.312(2)	0.098	2.576(1)
4	2.386 2.382	137.2	2.306(2)	0.006	2.590(1)
5	2.367 2.361	137.4	2.263(3)	0.043	2.565(1)
6	2.401 2.422	134.0	2.255(3)	0.008	2.588(1)
7	2.377 2.379	137.0	2.249(3)	0.006	2.606(1)
8	2.382 2.384	136.4	2.233(3)	0.016	2.600(1)
9	2.396 2.394	136.9	2.218(1)	0.015	2.6022(4)
10	2.425 2.435	138.3	2.346(2) 2.348(2)		2.758(1)

Structural Comparisons on the $(C_5Me_5)_2YCl(L)$ Complexes. Table 2 presents structural information on **3**−**9**, which are shown in Figures 1−8, as well as $(C_5Me_5)_2YCl$(THF) (**2**).[1] In all of these complexes, the Lewis

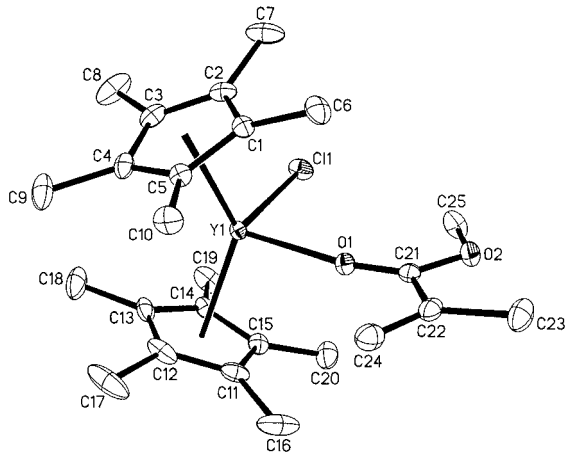


Figure 2. Molecular structure of $(C_5Me_5)_2YCl(MMA)$ (**4**) with probability ellipsoids drawn at the 50% level.

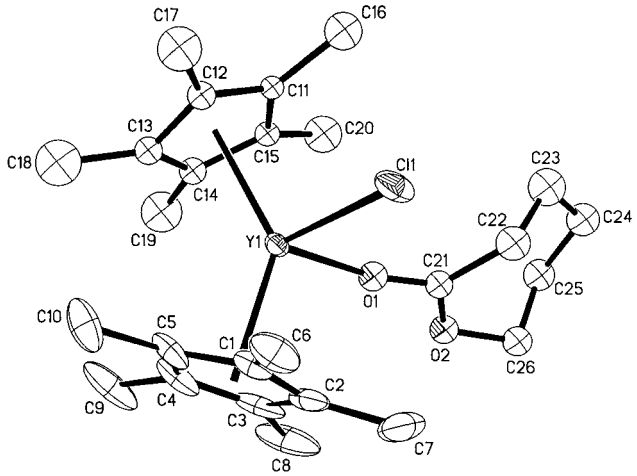


Figure 3. Molecular structure of $(C_5Me_5)_2YCl(\epsilon$-caprolactone) (**5**) with probability ellipsoids drawn at the 30% level. Disorder in the caprolactone and the C(11)−C(15) ring is not shown.

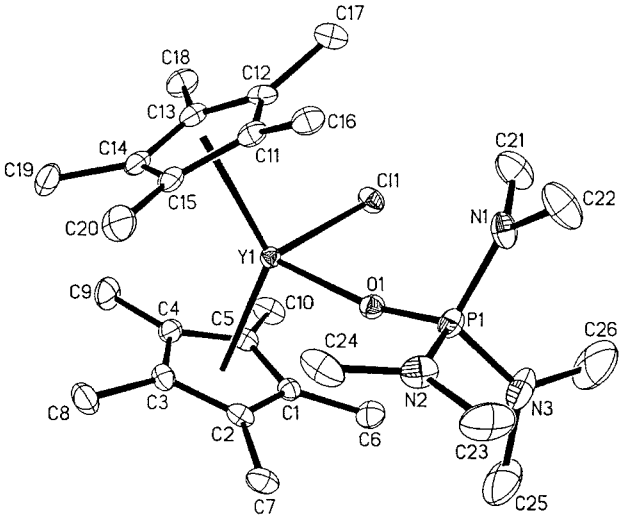


Figure 4. Molecular structure of $(C_5Me_5)_2YCl(HMPA)$ (**6**) with probability ellipsoids drawn at the 50% level.

base coordinates to yttrium via a single oxygen atom. Hence, in **5** (Figure 3), ϵ-caprolactone coordinates as an η^1 ligand through the carbonyl oxygen despite the presence of an adjacent oxygen donor atom next to the carbonyl oxygen. This is consistent with the only other

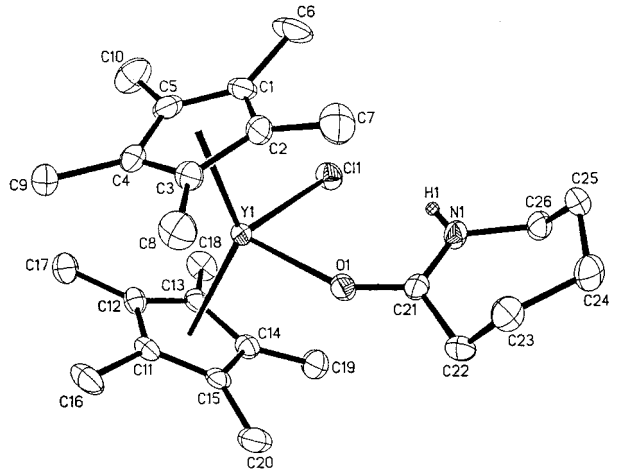


Figure 5. Molecular structure of $(C_5Me_5)_2YCl(\epsilon$-caprolactam) (**7**) with probability ellipsoids drawn at the 50% level.

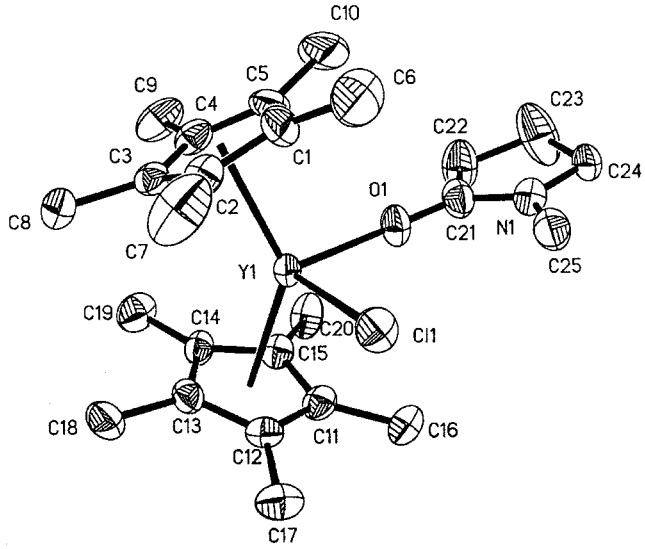


Figure 6. Molecular structure of $(C_5Me_5)_2YCl(MPU)$ (**8**) with probability ellipsoids drawn at the 50% level.

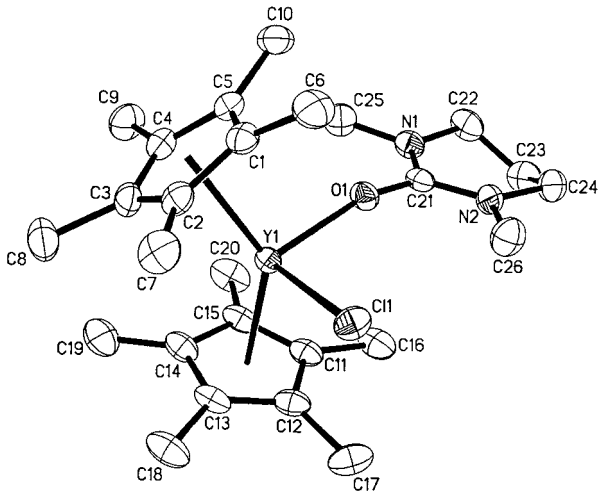


Figure 7. Molecular structure of $(C_5Me_5)_2YCl(DMPU)$ (**9**) with probability ellipsoids drawn at the 50% level.

ϵ-caprolactone/yttrium complex reported in the literature: *mer*-$YCl_3(\epsilon$-caprolactone$)_3$.[5] The η^1 binding mode of ϵ-caprolactam in **7** (Figure 5) is similar to that found in $[Pr(C_6H_{11}NO)_7]^{3+}$,[7] $[Pr(C_6H_{11}NO)_6Cl]^{2+}$,[8] and [Eu-

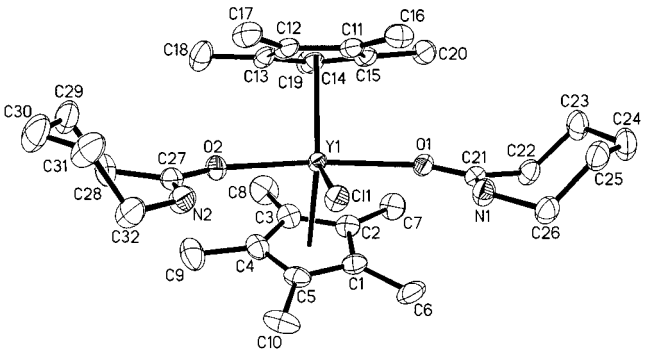
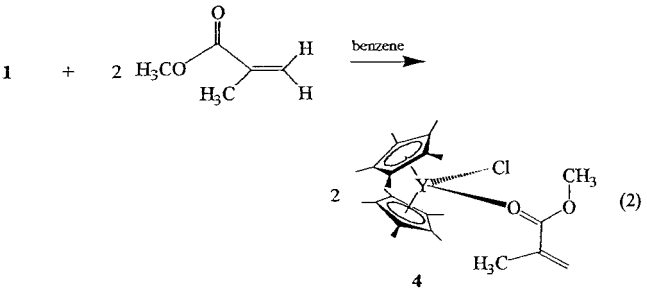


Figure 8. Molecular structure of $(C_5Me_5)_2YCl(\epsilon\text{-caprolactam})_2$ (**10**) with probability ellipsoids drawn at the 50% level.

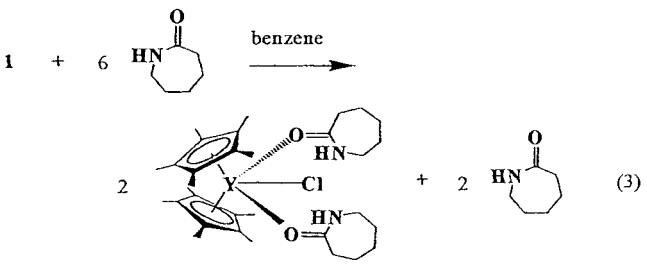
$(C_6H_{11}NO)_4Cl_2]^+$.[8] The other substituted "lactam type" molecules, the 1-methyl-2-pyrrolidinone adduct **8** (Figure 6) and the *N*,*N*′-dimethylpropyleneurea adduct **9** (Figure 7), also adopt η^1 binding modes. Methyl methacrylate coordinates to the metal center in **4** only through the carbonyl oxygen. The other oxygen and the adjacent vinyl group point away from the metal (eq 2,



(2)

Figure 2). The η^1 binding mode of HMPA (Figure 4) is typical of that seen in other trivalent lanthanide/HMPA complexes such as $[TmI_2(HMPA)_4]I(pyridine)_5$.[18]

Since each complex has a single Y−O(donor atom) bond length, this series can be used to compare the first approach of these ligands to a trivalent Lewis acidic metal center in a metallocene coordination environment. It might be assumed that coordination through a single donor atom would necessarily occur because the $(C_5Me_5)_2YCl$ moiety only has room for one more ligand. However, isolation of $(C_5Me_5)_2YCl(C_6H_{11}NO)_2$ (**10**) (Figure 8) shows that this is not the case. Reaction of **1** with excess ϵ-caprolactam gives a bis adduct (eq 3). Complex



(3)

10

10 crystallizes with one molecule of ϵ-caprolactam in the lattice. The NMR spectrum of this system indicates that in solution, this lattice caprolactam exchanges with the solvated caprolactam.

As shown in Table 2, complexes **2**−**9** have similar structural parameters in the metallocene part of the molecules. Hence, the (C_5Me_5 ring centroid)−yttrium−(C_5Me_5 ring centroid) angles fall in a narrow 134−138° range, as do the Y−(C_5Me_5) ring centroid distances, at 2.36−2.43 Å. The Y−Cl distances, which sometimes can be more variable in a series,[1] are also quite regular: 2.565(1)−2.606(1) Å.

In contrast to the similar structural parameters of the $(C_5Me_5)_2YCl$ parts of these molecules, the Y−O distances are more variable with distances ranging from 2.218(1) to 2.410(7) Å. Since this range is not extremely large and since some of the differences between the ligands are within the error limits, care must be taken in using these data. However, these results do show that these oxygen donors approach yttrium at slightly different distances, despite the relatively uniform $(C_5Me_5)_2$-YCl components.

The longest of the Y−O distances, 2.410(7) Å, is found in the THF adduct **2**.[1] Since THF is a common solvent in organometallic yttrium chemistry, this provides a good reference point. The next longest bond lengths are the 2.312(2) Å distance found in the benzophenone adduct **3** and the 2.306(2) Å distance in the methyl methacrylate complex **4**. Structural data on lanthanide coordination complexes of MMA have not been reported to our knowledge, but the yellow terbium benzophenone complex $Tb[N(SiMe_3)_2]_3$(benzophenone) has a Tb−O distance of 2.305(9) Å.[19] This distance is comparable to the Y−O distance in **3**, since terbium is approximately 0.02 Å larger than yttrium.[20] An yttrium benzophenone complex has also been synthesized, $Y[N(SiMe_3)_2]_3$-(benzophenone),[19] but it was not structurally characterized and, unlike **3**, did not display absorption in the visible region.

ϵ-Caprolactone, the precursor to a biodegradable polylactone,[21] forms the next smallest Y−O bond in this series, which is 2.263(3) Å in **5**. This distance is similar to the 2.269(2)−2.296(3) Å range of distances found in *mer*-$YCl_3(\epsilon\text{-caprolactone})_3$[5] despite the difference in formal coordination number, 6 vs 8 in **5**.

The next smallest Y−O distance of 2.255(3) Å was found with hexamethylphosphoramide (HMPA), which was examined since it has been utilized extensively as a strong donor to increase the reduction potential of Sm(II) in SmI_2.[22−25] The 2.255(3) Å Y−O(HMPA) distance in **6** is reasonable compared to trivalent Tm−O(HMPA) distances of 2.189(4) Å in $[TmI_2(HMPA)_4]I(pyridine)_5$ and 2.198(6) Å in $\{[TmI(HMPA)_4(pyridine)][I]_2\}$,[18] when radial sizes are taken into consideration.[20]

ϵ-Caprolactam, the precursor to nylon-6,[26] forms the next Y−O bond in the decreasing order, the 2.249(3) Å

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Y−O bond in **7**. This distance is shorter than the distances found in cationic $[Pr(C_6H_{11}NO)_6Cl]^{2+}$ and $[Eu(C_6H_{11}NO)_4Cl_2]^+$, 2.418(3) and 2.315(18) Å, respectively,[8] when metal size is taken into account.[20] The 2.58(6) Å NH···Cl and 3.328(5) Å N···Cl distances found in **7** are appropriate for hydrogen bonding compared to analogous distances in, for example, ϵ-caprolactam hydrochloride[27] and the tris(pyrazolyl)hydroborate {[HB(3-Bu^{t}pzH)$_3$]Cl}[AlCl$_4$].[28]

The shortest of the Y−O distances observed were from 1-methyl-2-pyrrolidinone (MPU), 2.233(3) Å in **8**, and *N*,*N*′-dimethylpropyleneurea (DMPU), 2.218(1) Å in **9**. MPU was included to examine the effect on binding of replacing an N−H functionality in **7** with N−Me. DMPU has been explored in lanthanide chemistry as a possible replacement for carcinogenic HMPA in Sm(II) reduction chemistry.[29,30]

The structure of $(C_5Me_5)_2YCl(\epsilon\text{-caprolactam})_2$ (**10**) is similar to those of **2**−**9** in the metallocene region but different in the other distances. The 138.3° centroid−metal−centroid angle and 2.425 and 2.435 Å Y−(C_5Me_5) ring centroid distances in **10** are near the ranges found in **2**−**9,** 134−138° and 2.36−2.43 Å, respectively (Table 2). The most striking difference in **10** is the 2.7576(9) Å Y−Cl distance, which is substantially larger than the 2.565(1)−2.606(1) Å distances in **2**−**9**. This unusually long distance is probably due to hydrogen bonding, since the chloride anion is located between *two* ϵ-caprolactam molecules at distances appropriate for this type of interaction. The N···Cl distances of 3.161(3) and 3.174(3) Å are shorter than the analogous distance in **7**, 3.328(5) Å. The 2.348(2) and 2.346(2) Å Y−O(ϵ-caprolactam) distances are also longer that the 2.249(3) Å distance in **7** (nine-coordinate yttrium is 0.056 Å larger than eight-coordinate yttrium).[20]

In summary, numerical values of the Y−O distances in **2**−**9** decrease in the order THF, benzophenone, MMA, ϵ-caprolactone, HMPA, ϵ-caprolactam, MPU and DMPU. The THF−benzophenone difference is the largest at 0.098 Å, and the benzophenone−MMA and HMPA−ϵ-caprolactam differences (0.006 Å) are the smallest (Table 2). The other differences are in the range 0.008−0.043 Å.

For the complexes of ligands containing carbonyl moieties, **3**−**5** and **7**−**9**, the Y−O distances were compared with Y−O−C angles. As shown by the following sequence, which decreases in order of Y−O distance, there is no correlation: **3**, benzophenone, 169.8(3)°; **4**, MMA, 170.44(17)°; **5**, ϵ-caprolactone, 156.5(3)°; **7**, ϵ-caprolactam, 146.5(3)°; **8**, MPA, 171.6(3)°; **9**, DMPU, 163.58(11)°.

Ligand Displacement Reactions of $(C_5Me_5)_2YCl(L)$ Complexes. To determine if the solid-state Y−O bond lengths correlated with solution behavior, each (C_5Me_5)$_2$YCl(L) yttrium adduct was reacted with an equimolar amount of the neutral donor that had the next shorter Y−O bond (eq 4). The reactions were monitored

$$(C_5Me_5)_2YCl(L) + L' \rightarrow 2(C_5Me_5)_2YCl(L') + L \qquad (4)$$

by ^{1}H NMR spectroscopy in C_6D_6 to determine if the ligand with the shorter Y−O bond would displace the ligand with a longer Y−O bond.

Addition of benzophenone to (C_5Me_5)$_2$YCl(THF) (**2**) instantaneously forms a dark red solution of **3**. The ^{1}H NMR spectrum indicated complete displacement of THF by benzophenone to form (C_5Me_5)$_2$YCl(benzophenone) (**3**): the 2.20 ppm C_5Me_5 shift of **2** is absent, the 2.04 ppm shift of **3** is the only peak in the C_5Me_5 region, and free THF is observed in the spectrum. Additional reactions were initially done with **2** to confirm the generality of this result: THF was also displaced by MMA and ϵ-caprolactone to form (C_5Me_5)$_2$YCl(MMA) (**4**), and (C_5Me_5)$_2$YCl(ϵ-caprolactone) (**5**), respectively. All of these displacements formed products with shorter Y−O bonds.

However, when MMA is added to (C_5Me_5)$_2$YCl(benzophenone) (**3**), the red color of **3** persists. Since the C_5Me_5 chemical shifts of **3** and (C_5Me_5)$_2$YCl(MMA) (**4**) are similar, 2.04 and 2.02 ppm, respectively, the reaction was monitored by observing MMA resonances. No displacement was observed: only free MMA was found in the ^{1}H NMR spectrum. In this case, the reverse reaction of yellow (C_5Me_5)$_2$YCl(MMA) (**4**) with benzophenone occurs quickly to form a dark red solution containing only **3** and free MMA by ^{1}H NMR spectroscopy. These solution data suggest a preference for benzophenone coordination over MMA, although (C_5Me_5)$_2$YCl(MMA) has a numerically smaller Y−O value (2.306(2) Å) than (C_5Me_5)$_2$YCl(benzophenone (2.312(2) Å).

When (C_5Me_5)$_2$YCl(benzophenone) is reacted with ϵ-caprolactone, the dark red color dissipates instantaneously to form a colorless solution. By ^{1}H NMR spectroscopy, benzophenone is displaced by ϵ-caprolactone to form (C_5Me_5)$_2$YCl(ϵ-caprolactone) (**5**). Similarly, when (C_5Me_5)$_2$YCl(MMA) (**4**) is reacted with ϵ-caprolactone, the yellow color immediately dissipates and only **5** is observed by ^{1}H NMR.

Reactions of HMPA with (C_5Me_5)$_2$YCl(ϵ-caprolactone) (**5**), ϵ-caprolactam with (C_5Me_5)$_2$YCl(HMPA) (**6**), and DMPU with (C_5Me_5)$_2$YCl(MPU) (**8**) occur quickly and are complete as soon as the ^{1}H NMR spectrum can be obtained. In each case ligand displacement occurs to form a complex with a shorter bond to yttrium. However, the trend between Y−O metal distance and solution displacement is not observed with (C_5Me_5)$_2$YCl(ϵ-caprolactam) (**7**), as neither MPU nor DMPU displace ϵ-caprolactam from **7**. The extra stability of **7** is consistent with its hydrogen-bonded structure.

IR and ^{13}C NMR Spectroscopy of the Carbonyl-Containing Complexes. The $\Delta\nu_{CO}$ stretching frequencies and ^{13}C NMR shifts of the carbonyl carbon in compounds **3**−**5** and **7**−**9** were examined to see if the shift observed from the free ligands correlated with the Y−O bond distances and ligand displacement data. As shown in Table 3, these data do not correlate exactly with the Y−O bond lengths or the displacement reactivity. The IR data show that the complexes with the shortest Y−O distances, **8** and **9**, have the largest differences in $\Delta\nu_{CO}$ between complexed and free ligand,

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Table 3. Carbonyl Stretching Frequencies (cm^{-1}) and ^{13}C NMR Shifts (ppm) for the Free Ligands and $(C_5Me_5)_2YCl(L)$ Complexes 3−5 and 7−9, Listed in Order of Decreasing Y−O Distance

		IR, cm^{-1}			NMR, ppm		
complex	ligand (L)	free L	complexed L	diff	free L	complexed L	diff
3	benzophenone	1684	1614	70	195.7	206.6	10.9
4	methyl methacrylate	1748	1661	87	167.2	175.5	8.3
5	ϵ-caprolactone	1772	1688	84	175.0	185.7	10.7
7	ϵ-caprolactam	1713	1630	83	177.0	181.9	4.9
8	1-methyl-2-pyrrolidinone	1738	1645	93	173.7	176.6	2.9
9	*N*,*N*′-dimethyl-propyleneurea	1687	1576	111	156.3	157.3	1

but the other ligands do not follow a regular order and the differences in stretching frequencies are in a small range. The ^{13}C NMR data show that complexes **8** and **9** have the smallest differences between free and complexed ligand and that the carbonyl complex with the longest Y−O bond, **3**, has the largest difference, but the value for the MMA complex **4** is out of order.

Discussion

Although a few oxygen-donor complexes of yttrium permethylmetallocenes of general formula $(C_5Me_5)_2YX(L)$ (X = monoanionic ligand, L = oxygen donor ligand) have been structurally characterized prior to this study, e.g. $(C_5Me_5)_2YCl(THF)$,[1] $(C_5Me_5)_2Y(CH_3)(THF)$,[31] $(C_5Me_5)_2Y(C_6H_3Me_2\text{-}2,6)C{=}N(C_6H_3Me_2\text{-}3,5)(THF)$,[32] and $(C_5Me_5)_2Y(CH_2Ph)(THF)$,[33] all involve only L = THF. Adducts of reactive polymerizable substrates such as ϵ-caprolactone and methyl methacrylate would be more difficult to isolate, since these substrates can react with yttrium alkyl bonds.[34,35] The chloride complex $(C_5Me_5)_2Y(\mu\text{-}Cl)Y(C_5Me_5)_2Cl$ (**1**) appears to be a good system with which to evaluate the coordination chemistry of Lewis bases, since polymerizable substrates do not react under ambient conditions. A variety of adducts can be synthesized in high yield, and suitable crystals can be obtained such that metrical data on coordination chemistry can be obtained.

Although this survey has focused on polymerizable substrates and typical lanthanide oxygen donor base adducts, the results suggest that **1** could be used more generally as a route to make crystalline adducts of a variety of oxygen donor molecules. For example, if the absolute configuration of an organic ether or ester was needed and the molecule did not crystallize on its own, adduct formation with **1** could provide the needed structural information. This could prove to be a valuable aspect of this system.

In each case reported here, the oxygen-containing adduct binds only through a single oxygen such that the Y−O bond lengths can be compared. Since the Y−O distances span only a short range and since several are within the experimental error limits, it was unclear if these data would be useful in predicting chemical reactivity. Surprisingly, there is a rough correlation between the solution displacement chemistry and the solid-state data.

Hence, bases that form complexes with shorter Y−O distances will displace bases that form complexes with longer Y−O distances, with two exceptions. The first is the benzophenone/MMA pair, which differ in measured Y−O distances by only 0.006 Å, a difference too small upon which to make a prediction. The other exception is that the ϵ-caprolactam in complex **7** cannot be easily displaced by bases which form shorter Y−O bonds. This too can be rationalized, in this case, by the fact that ϵ-caprolactam forms a hydrogen bond to the chloride, which provides extra stabilization. Hence, this $(C_5Me_5)_2Y(\mu\text{-}Cl)Y(C_5Me_5)_2Cl/(C_5Me_5)_2YCl(L)$ system can be used not only to examine Y−O bonding but also to examine the influence of hydrogen bonding.

This study also showed that the $(C_5Me_5)_2YCl$ coordination envirnoment is flexible enough to accommodate two base adducts, as shown in $(C_5Me_5)_2YCl(\epsilon\text{-caprolactam})_2$ (**10**). In this case, two N−H···Cl hydrogen bonds resulted in a rather long Y−Cl bond. Hence, hydrogen bonding of this type can be used to destabilize certain metal−ligand bonds in metallocene complexes of this type.

Attempts to correlate $\Delta\nu_{CO}$ carbonyl stretching frequencies or ^{13}C NMR shifts of carbonyl carbons with the displacement reactivity were not as successful. Hence, the bond length data appear to be the best available predictors of displacement reactivity. As long as it is realized that small differences in Y−O bond lengths may not give predictable results and additional sources of stabilization can interfere with correlations, the length of the Y−donor atom interactions in the $(C_5Me_5)_2YCl(L)$ system can be useful in estimating the relative ability of different ligands to coordinate. In any case, it is a good system to evaluate ligand binding modes in a metallocene environment.

Conclusion

$(C_5Me_5)_2Y(\mu\text{-}Cl)Y(C_5Me_5)_2Cl$ provides an effective means for the comparative evaluation of ligand donor ability in typical organoyttrium and organolanthanide complexes. It is a readily synthesized, diamagnetic complex which forms crystalline adducts, $(C_5Me_5)_2YCl(L)$, in high yield. The Y−O bond distances correlate with the substitution reactivity of this class of complexes and allow examination of hydrogen-bonding effects. This approach should be readily extendable to other ligands and substrates to provide data on their binding and structure as well as a larger body of data which allows direct comparisons in a metallocene system.

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Supporting Information Available: Tables giving X-ray crystallographic data for complexes **3**−**10**; these data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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