89SR189035 with the U.S. Department of Energy.

Supplementary Material Available: A listing of 2θ values, *d* spacings, line intensities, and *hkl* indices for α-$FeF_3 \cdot 3H_2O$ and "$FeF_2 \cdot 4H_2O$" (3 pages). Ordering information is given on any current masthead page.

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Structural Diversity in Bis(pentamethylcyclopentadienyl)yttrium Chloride Complexes: Cocrystallization of [$(C_5Me_5)_2Y(\mu$-$Cl)_2Li(THF)_2$] and [$(C_5Me_5)_2YCl(\mu$-$Cl)Li(THF)_3$]

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Introduction

The organometallic chemistry of trivalent lanthanide and yttrium complexes is dominated by complexes containing two C_5Me_5 rings and a third anionic ligand.[1] Due to the large size and electrophilic nature of these metals, complexes of the formula $(C_5Me_5)_2LnZ$ (Ln = lanthanide or yttrium; Z = monodentate monoanionic ligand) generally bind an additional ligand and exist as base adducts of formula $(C_5Me_5)_2Ln(Z)(L)$ (L = electron pair donor). In the ionic metathesis reactions commonly used to prepare these complexes, e.g., eqs 1 and 2 (M = alkali metal),

$$LnCl_3 + 2MC_5Me_5 \rightarrow (C_5Me_5)_2LnCl(L) + 2MCl \quad (1)$$

$$(C_5Me_5)_2LnCl(L) + LiZ \rightarrow (C_5Me_5)_2Ln(Z)(L) + LiCl \quad (2)$$

the alkali metal halide byproducts can provide the additional ligand, L, and adducts such as $(C_5Me_5)_2LnCl_2M(ether)_x$ or $(C_5Me_5)_2LnZClLi(ether)_x$ are commonly observed. Indeed, the first (pentamethylcyclopentadienyl)lanthanide complexes to be isolated were of this type.[2-4]

Numerous examples of alkali metal adducts of general formula $(C_5Me_5)_2LnZ_2M(ether)_x$ have been reported.[2-35] In general, these compounds are considered to have two ether molecules of solvation and two doubly-bridging Z ligands, i.e., $(C_5Me_5)_2Ln(\mu$-$Z)_2M(ether)_2$, which is consistent with the initial crystallographic data obtained on these complexes.[6,7,9,13,15,16,19,20,24,28-30] However, variations in the amount of ether present in these complexes have been observed, both in elemental analytical data and in recent X-ray crystallographic studies. For example, a monosolvated complex, $[(C_5Me_5)_2Ce(\mu_3$-$Cl)_2K(THF)]_n$, has been reported,[25] in which the alkali metal achieves five-coordination by interacting with chloride ligands of three different monomer units. The monosolvate $(C_5Me_5)_2Y(\mu$-$C{\equiv}CCMe_3)_2Li(THF)$, is not similarly oligomerized.[30] In this case, the steric bulk of two bridging

Table I. Experimental Data for the X-ray Diffraction Study

formula	$C_{60}H_{100}Li_2O_5Cl_4Y_2$
fw	1234.9
temp	173 K
crystal system	monoclinic
space group	$P2_1/c$ (C_{2h}^5; No. 14)
a	14.622 (2) Å
b	29.314 (5) Å
c	15.157 (2) Å
β	90.055 (13)°
V	6497 (2) Å^3
Z	4
D_{calcd}	1.263 Mg/m^3
diffractometer	Siemens P3 (R3m/V system)
radiation	Mo Kα ($\bar{\lambda}$ = 0.710730 Å)
monochromator	highly oriented graphite
data collected	$+h,+k,\pm l$
scan type	ω
scan width	1.1°
scan speed	3.0° min^{-1} (in ω)
2θ range	4.0-45.0°
μ(Mo Kα)	1.995 mm^{-1}
abs cor	semiempirical (ψ-scan method)
no. of reflns collected	9164
no. of unique reflns with $\lvert F_o \rvert > 0$	7370
no. of reflns with $\lvert F_o \rvert > 3.0\sigma(\lvert F_o \rvert)$	5649
no. of variables	659
R_F; R_{wF}	7.1%; 7.2%
goodness of fit	1.21

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$C{\equiv}CCMe_3$ ligands appears to prevent formation of a disolvate. Also cited in the literature[10] is the existence of crystallographic data on a trisolvated complex, $(C_5Me_5)_2YbMe(\mu\text{-}Me)Li(THF)(Et_2O)_2$.

Since $(C_5Me_5)_2LnZ_2M(ether)_x$ complexes are so common and so readily formed, their degree of solvation and the accompanying structural consequences should be well-defined. We report here an X-ray crystallographic study which shows that the disolvated and trisolvated forms are similar when Ln = Y, Z = Cl, M = Li, and ether = THF and that they cocrystallize in a single crystal.

Experimental Section

The complexes isolated below were handled under nitrogen with rigorous exclusion of air and water through the use of Schlenk, vacuum-line, and glovebox techniques. Solvents were dried and physical measurements were obtained as previously described.[36] $(C_5Me_5)_2YCl(THF)$ was prepared from NaC_5Me_5 and YCl_3 according to the literature.[21] $LiOCMe_3$ was prepared in THF by the stoichiometric reaction of *n*-BuLi with Me_3COH distilled from CaH_2.

$[(C_5Me_5)_2Y(\mu\text{-}Cl)_2Li(THF)_2]$ (1a) and $[(C_5Me_5)_2YCl(\mu\text{-}Cl)Li(THF)_3]$ (1b). In a glovebox, a 250-mL Schlenk flask was charged with $LiOCMe_3$ (0.26 g, 3.25 mmol) in 50 mL of toluene. $(C_5Me_5)_2YCl(THF)$ (0.50 g, 1.08 mmol) was slowly added, and the mixture was stirred for 30 min. The flask was fitted with a reflux condenser, attached to a double-manifold Schlenk line and heated at reflux for 18 h. After removal of the solvent in vacuo, the pale yellow powder was washed with hexanes. An off-white powder (0.545 g) was isolated by extraction with toluene, followed by solvent removal. ^1H NMR (toluene-d_8, 20 °C): $\delta = 1.72$ (1 H, s), 1.68 (5 H, s), 1.47 (5 H, s), 1.30 (5 H, s). Pale yellow crystals obtained from toluene at −30 °C displayed the same ^1H NMR spectrum. The spectrum was invariant over the temperature range 0–80 °C.

X-ray Data Collection, Structure Determination, and Refinement for $[(C_5Me_5)_2Y(\mu\text{-}Cl)_2Li(THF)_2]$ (1a) and $[(C_5Me_5)_2YCl(\mu\text{-}Cl)Li(THF)_3]$ (1b). A pale yellow-gold crystal of approximate dimensions 0.23 × 0.40 × 0.43 mm was immersed in Paratone-N, mounted on a glass fiber, and transferred to the Siemens P3 automated four-circle diffractometer equipped with a modified LT-2 low-temperature system. The determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix was carried out by previously described methods similar to those of Churchill.[37] Intensity data were collected at 173 K using an ω-scan technique with Mo Kα radiation under the conditions described in Table I. All 9164 data were corrected for absorption and for Lorentz and polarization effects and were placed on an approximately absolute scale. Axial photographs were carefully examined for symmetry, since all three angles were approximately 90°. The diffraction symmetry was determined to be $2/m$. The systematic extinctions observed were $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$. The centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14) is therefore uniquely defined.

All crystallographic calculations were carried out using either our locally modified version of the UCLA Crystallographic Computing Package[38] or the SHELXTL PLUS program set.[39] The analytical scattering factors for neutral atoms were used throughout the analysis;[40a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[40b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(|F_o|) + 0.0015(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d(C\text{–}H) = 0.96$ Å and $U(iso) = 0.08$ Å^2. There are two different independent molecules in the asymmetric unit ($Z = 4$); see Figures 1 and 2. Refinement of positional and thermal parameters led to convergence with $R_F = 7.1\%$, $R_{wF} = 7.2\%$, and GOF = 1.21 for 659 variables refined against those 5649 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier synthesis showed no significant features, $\rho(max) = 0.57$ e Å^{-3}.

Results

As part of a study of mixed-ligand $C_5Me_5/OCMe_3$ complexes, we carried out a reaction of $(C_5Me_5)_2YCl(THF)$ with 3 equiv of $LiOCMe_3$ in toluene at reflux, which gave a mixture of products. Crystallization of the toluene extract of this reaction mixture gave single crystals which were unusual in that two different forms of the $[(C_5Me_5)_2YCl_2]^-$ moiety cocrystallized in the same unit cell: $[(C_5Me_5)_2Y(\mu\text{-}Cl)_2Li(THF)_2]$ (1a) and $[(C_5Me_5)_2YCl(\mu\text{-}Cl)Li(THF)_3]$ (1b) (see below). Evidently, some ligand exchange occurs in this reaction, which allows incorporation of LiCl into the starting material. However, attempts to synthesize these crystals directly from $(C_5Me_5)_2YCl(THF)$ and LiCl in refluxing toluene/THF have been unsuccessful.

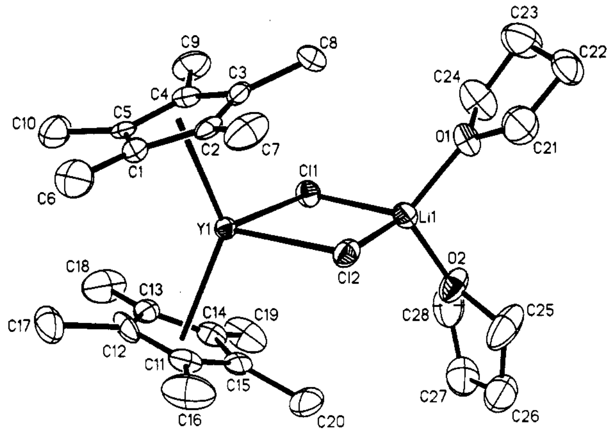

Figure 1. ORTEP diagram of $(C_5Me_5)_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (1a) with the probability ellipsoids drawn at the 40% level.

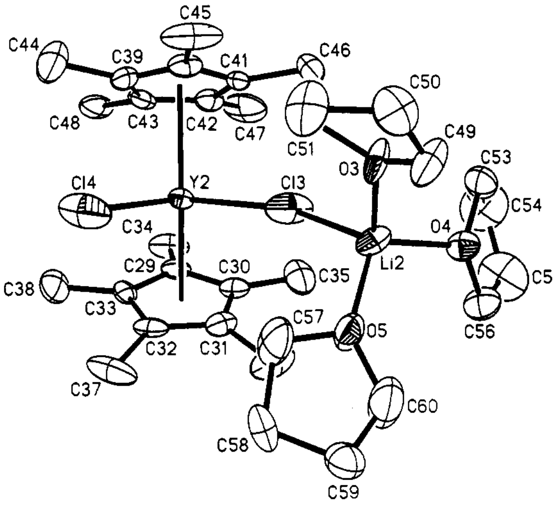

Figure 2. ORTEP diagram of $(C_5Me_5)_2YCl(\mu\text{-}Cl)Li(THF)_3$ (1b) with the probability ellipsoids drawn at the 40% level.

Figure 1 shows one molecule, $(C_5Me_5)_2Y(\mu\text{-}Cl)_2Li(THF)_2$ (1a), which has the traditionally expected structure containing two bridging halide ligands and an alkali metal bound by two solvate molecules. Figure 2 shows the second molecule in the unit cell, $(C_5Me_5)_2YCl(\mu\text{-}Cl)Li(THF)_3$ (1b), which contains a terminal chloride ligand, a single bridging chloride, and a trisolvated alkali metal. Packing diagrams show that 1a and 1b are well separated from each other.

In both 1a and 1b, the yttrium atoms are surrounded by four ligands in the typical distorted tetrahedral arrangement. The Cl–Y–Cl angle in 1b opens to 95.4 (1)° compared to 84.8 (1)° in 1a, since the two chloride ligands in 1b are not both constrained to bridge to lithium. Z–Ln–Z angles of 82–87° are typical in eight-coordinate complexes of the type $(C_5R_5)_2Ln(\mu\text{-}Z)_2ML_2$.[8] The C_5Me_5 rings in 1b are almost exactly staggered with a twist angle[41] of 35.6° compared to 36° for a perfectly staggered arrangement. In 1a, the corresponding twist angle is 25.3°. This

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(41) The twist angle is defined as the average of the five smallest dihedral angles formed between the ten planes which consist of a ring carbon atom and the two centroids.

suggests that the metal center is more sterically constrained in **1a**, as would be expected.[7] However, the yttrium–C(C_5Me_5) average distances, 2.66 (2) Å in **1a** and 2.67 (1) Å in **1b**, are indistinguishable.

The terminal Y–Cl bond length in **1b**, 2.575 (3) Å, is very close to the terminal Y–Cl bond distances in $(C_5Me_5)_2YCl(THF)$ (**2**), 2.579 (3) Å,[31] and $(C_5Me_5)_2Y(\mu\text{-}Cl)YCl(C_5Me_5)_2$ (**3**), 2.579 (6) Å.[25] The Y–(μ-Cl) distances in **1a** and **1b**, 2.650 (4) and 2.620 (3) Å, are longer than the terminal lengths, as expected. However, these distances are closer to the 2.640 (5) Å bridging bond length for the seven-coordinate metal center in **3**, $(C_5Me_5)_2\mathit{Y}(\mu\text{-}\mathit{Cl})YCl(C_5Me_5)_2$, than the 2.776 (5) Å length for the analogous eight-coordinate yttrium in **3**, $(C_5Me_5)_2Y(\mu\text{-}\mathit{Cl})\mathit{Y}Cl(C_5Me_5)_2$.

The bridging lithium–chloride bond distance in **1a**, 2.374 (16) Å, is near the normal range of 2.39–2.41 Å found in $(C_5Me_5)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**4**),[7] $(C_5H_4SiMe_3)_2Yb(\mu\text{-}Cl)_2Li(OEt_2)_2$ (**5**),[7] and $[C_5H_3(SiMe_3)_2]_2Nd(\mu\text{-}Cl)_2Li(THF)_2$ (**6**).[6] The 2.297 (16) Å Li–Cl distance in **1b**, in which only one anionic ligand is attached to lithium, is somewhat shorter. The average Li–O(THF) distances are not markedly different in **1a** and **1b**, 1.90 (1) and 1.91 (1) Å, respectively, and are similar to the 1.93 (3) Å distance in **6**.[7]

Discussion

The cocrystallization of both disolvated and trisolvated $(C_5Me_5)_2YCl_2Li(THF)_x$ complexes is unusual. Generally, crystallization of a complex results in the most energetically preferred geometry available for the prevailing set of crystallization conditions. The crystallization of a complex in two different forms in the same unit cell suggests that the factors leading to the formation of these two species are very similar. A classic case of this phenomenon is the X-ray crystal structure of $[Cr(H_2NCH_2CH_2NH_2)_3][Ni(CN)_5](H_2O)_{1.5}$, in which both square pyramidal and trigonal bipyramidal $[Ni(CN)_5]^{3-}$ units are found in the same unit cell.[42] The similarity in energies of these two different five-coordinate geometries is well established.[43]

In this case, the observation that both di- and trisolvated complexes can cocrystallize suggests that both of these forms are readily available to $(C_5Me_5)_2LnZ_2M(ether)_x$ complexes. Given the differences in reactivity between terminal and bridging ligands in organolanthanide complexes,[44] this could have significant implications in reaction chemistry if both forms are available in solution. Specifically, the presence of a small amount of coordinating solvent, which might be expected to reduce reactivity by occupying a vacant coordination site on a lanthanide metal center, may actually enhance reactivity by generating a terminal ligand via a $(C_5R_5)_2Ln(\mu\text{-}Z)_2M(ether)_2$ to $(C_5R_5)_2LnZ(\mu\text{-}Z)M(ether)_3$ process. In such a case, a small amount of an ether in an arene or alkane solvent could change the reactivity from that found in a rigorously ether-free solvent and could lead to variations in reactivity depending on solvent purity.

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Supplementary Material Available: ORTEP diagrams showing top views of **1a** and **1b**, tables of complete crystallographic data, positional parameters, bond distances and angles, and thermal parameters (18 pages); a listing of structural factor amplitudes (23 pages). Ordering information is given on any current masthead page.

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Additions and Corrections

1989, Volume 28

Carl R. Steffan, Andreja Bakac,* and James H. Espenson*: Quenching of the Doublet Excited State of Tris(polypyridine)chromium(III) Ions by Oxalate Ions: An Example of Irreversible Electron Transfer.

Page 2995. The half-reaction in eq 14, with $E°_{14} = 0.60$ V, should read

$$CO_2 + CO_2^{\bullet -} + e^- = C_2O_4^{2-} \qquad (14)$$

Since K for $CO_2 + CO_2^{\bullet -} \rightleftharpoons C_2O_4^{\bullet -}$ is unknown, the value of $E°$ for $C_2O_4^{\bullet -} + e^- = C_2O_4^{2-}$ cannot be rigorously calculated from known data, but an estimate of 1.7 V has been made (Neshvad, G.; Hoffman, M. Z. *J. Phys. Chem.* **1989**, *93*, 2445. See also: Hoffman, M. Z.; Prasad, D. R. *J. Photochem. Photobiol., A* **1990**, *54*, 197).—James H. Espenson