The spectra were usually acquired from concentrated solutions in pure C_6D_6. Where photolyses to silaethylenes were involved, NMR tubes were sealed under an argon atmosphere. ^{13}C spectra were acquired on a Varian CFT 20, a Bruker WM-250 instrument, or more usually on the Bruker WH-400 spectrometer operating in the FT mode at a frequency of 100.62 MHz, operated by the Southwestern Ontario NMR Centre located at the University of Guelph, Guelph, Ontario. The spectra were run with level decoupling with the decoupler set at low power between acquisitions in order to obtain proton–^{13}C NOE. Moderately long delays (~30 s) were allowed between pulses, especially when the carbonyl-carbon was being studied. C_6D_6 was used as internal lock and internal chemical shift callibration for ^{13}C.

^{29}Si spectra were obtained on the same Bruker WH-400 spectrometer operating at a frequency of 79.495 MHz in the FT mode. The chemical shifts are reported relative to the silicon resonance of Me_4Si, used as an external reference. All of the spectra were obtained by using a gated decoupling sequence in which the protons were broad-band decoupled only during acquisition of the silicon free induction decay. This results in the complete suppression of the nuclear Overhauser enhancement. In the cases where no relaxation agent was added, spectra were accumulated by using approximately a 30° pulse width and approximately a 1-min relaxation delay between pulses. In some of the spectra Gaussian multiplication was employed to provide resolution enhancement.

Acknowledgment. We are grateful to Drs. R. K. M. R. Kallury, B. Behnam, L. Yau, and Y.-M. Chang for supplying some of the compounds, to Dr. R. E. Lenkinski and Bruce MacDonald of the SW Regional NMR Centre for assistance and advice, and to Mrs. Brigitte Gutekunst for technical assistance. This research was supported financially by the Natural Sciences and Engineering Research Council of Canada.

Registry No. $(Me_3Si)_3SiCOCMe_3$, 69397-47-3; $(Me_3Si)_3SiCOCEt_3$, 72214-49-4; $(Me_3Si)_3SiCO$(1-methyl-1-cyclohexyl), 81671-42-3; $(Me_3Si)_3SiCO$(1-bicyclo[2.2.2]octyl), 81671-43-4; $(Me_3Si)_3SiCO$(1-adamantyl), 72189-53-8; $(Me_3Si)_3SiCOPh$, 60154-95-2; $(Me_3Si)_3SiCOC_6H_4$-*p*-OMe, 81671-44-5; $(Me_3Si)_3SiCOC_6H_4$-*o*-OMe, 81671-45-6; $(Me_3Si)_3SiCOCF_3$, 81671-46-7; $(Me_3Si)_3SiCOC_6F_5$, 81671-47-8; $(Me_3Si)_3SiCOOH$, 70096-33-2; $(Me_3Si)_3SiCOOSiPh_3$, 81671-48-9; $(Me_3Si)_3SiSiMe_3$, 4098-98-0; $Ph_3SiCOMe$, 4916-42-1; $Me_3SiCOMe$, 13411-48-8; $Me_3SiCOPh$, 5908-41-8; $Et_3SiCOPh$, 63935-93-3; $Ph_3SiCOPh$, 1171-49-9; $(Me_3Si)_2Si{=}C(OSiMe_3)(CMe_3)$, 81671-49-0; $(Me_3Si)_2Si{=}C(OSiMe_3)(CEt_3)$, 81671-50-3; $(Me_3Si)_2Si{=}C(OSiMe_3)$(1-methyl-1-cyclohexyl), 81671-51-4; $(Me_3Si)_2Si{=}C(OSiMe_3)$(1-adamantyl), 72189-54-9.

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Crystal and Molecular Structure of Cyclopentadienylerbium Dichloride Tris(tetrahydrofuranate), $(C_5H_5)ErCl_2(THF)_3$

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The nature of the $(C_5H_5)LnCl_2(THF)_3$ compounds has been investigated by an X-ray structural determination of the Ln = Er complex. The compound crystallizes in the monoclinic space group $P2_1/n$ with four molecules in a unit cell of dimensions a = 7.822 (2) Å, b = 17.096 (4) Å, c = 15.162 (3) Å, and β = 95.80 (2)°. Least-squares refinement of the 208 variables led to a value for the conventional R index (on F) of 0.029 for 4207 independent reflections having $2\theta_{MoK\bar{\alpha}} < 58.7°$ and $I > 3\sigma(I)$. Although this complex is formally eight coordinate, octahedral is a simple and accurate description of the erbium(III) coordination sphere with the C_5H_5–Er interaction formally considered to occupy a single polyhedral vertex; the THF ligands have a meridional disposition and the chloride ligands occupy trans sites on this octahedron. The Er–C and Er–Cl bond distances average 2.667 (3) and 2.617 (2) Å, respectively. Two different Er–O bond distances were observed, averaging 2.358 (3) Å cis to the cyclopentadienyl ligand and 2.452 (4) Å trans to the cyclopentadienyl ligand. The major distortion observed in the structure involves a 0.54 Å displacement of the erbium atom out of the equatorial plane toward the cyclopentadienyl ligand. A number of comparisons are made to $(\eta^5\text{-}CH_3C_5H_4)UCl_3(THF)_2$ and other related structures.

While organolanthanide complexes containing cyclooctatetraene, cyclopentadienyl, π-allylic and σ-allyl ligands, among others, have been well established stoichiometrically,[3] structural progress has naturally lagged somewhat behind.[4] For the specific class of trivalent organolanthanides containing the cyclopentadienyl ligand as the only anionic carbon-bound ligand, structures have been reported for $(C_5H_5)_3Sm$,[5] $(C_9H_7)_3Sm$[6] (C_9H_7 = indenyl), $[(CH_3C_5H_4)_3Nd]_4$,[7] $(C_5H_5)_3Pr(CNC_6H_{11})$,[8] $(C_5H_5)_3Gd(THF)$,[9] $[(C_5H_5)_3Yb]_2(C_4H_4N_2)$[10] ($C_4H_4N_2$ = pyrazine), and

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(1) (a) Crystalytics Co. (b) The University of Nebraska. (c) University of Utah.

(2) Camille and Henry Dreyfus Teacher-Scholar.

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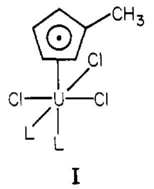
$[(CH_3C_5H_4)_2YbCl]_2$,[11] with the first compound forming an unusually associated polymeric structure in the solid state. Not surprisingly, the size of the lanthanide metal has a pronounced influence on the structural makeup of these compounds. Thus the larger lanthanides (Ce–Nd) only form tricyclopentadienyl complexes, while smaller lanthanides (Sm–Lu) form both tri-, di-, and monocyclopentadienyl compounds.[12,13] To date, no structural information has been provided for the monocyclopentadienyl complexes, which until recently were only known in the form $(C_5H_5)LnCl_2(THF)_3$ (Ln = Sm–Lu; THF = tetrahydrofuran).[13,14]

We were therefore interested in establishing the structures of this final class. In addition, the stoichiometry is formally quite similar to that observed in $(\eta^5\text{-}CH_3C_5H_4)UCl_3(THF)_2$,[15] I, suggesting that the two structural types might be related. Indeed, a direct application of the factors judged responsible for the observed *mer,cis*-$(\eta^5\text{-}CH_3C_5H_4)UCl_3(THF)_2$ structure leads to the prediction that a complex of stoichiometry $(C_5H_5)MCl_2(THF)_3$ should adopt a *mer,trans* structure as in II, rather than a *mer,cis*-III or *fac*-IV geometry. The structural investigation reported herein for $(\eta^5\text{-}C_5H_5)ErCl_2(THF)_3$ (1) has confirmed this expectation.



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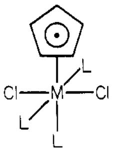
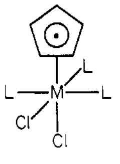
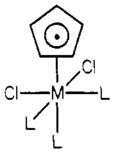


mer,trans-II



mer,cis-III



fac-IV

Experimental Section

The preparation and handling of all organometallics was necessarily carried out in an atmosphere of prepurified nitrogen, with rigorous exclusion of air and moisture. Sample manipulations were by Schlenk methods or in a glovebox. All solvents were thoroughly dried in a manner appropriate to each and were distilled under nitrogen immediately prior to use. Commercial anhydrous $ErCl_3$ was freed of final traces of water by overnight reflux with thionyl chloride.

Synthesis and Crystallization of $(\eta^5\text{-}C_5H_5)ErCl_2(THF)_3$. This compound was prepared in a manner similar to that previously reported.[13] A 1.70-g (19.3-mmol) sample of NaC_5H_5[16] was added with stirring to a slurry of 5.48 g (20.0 mmol) of $ErCl_3$ in 130 mL of THF. After 3 days, a pink solution was obtained with a great deal of product present in precipitated form. An extra 100 mL of THF was added, and the solution was heated to ca. 60 °C. After all of the product had dissolved, the solution was filtered through a coarse frit and cooled to −20 °C, producing a large mass of crystalline compound. X-ray quality crystals were obtained by preparing a concentrated solution of the compound in THF at ca. 70–80 °C and allowing it to cool slowly to room temperature by gradually decreasing the heat applied by an oil bath. A number of the crystals obtained were mounted in glass capillaries under a nitrogen atmosphere partially saturated with THF.

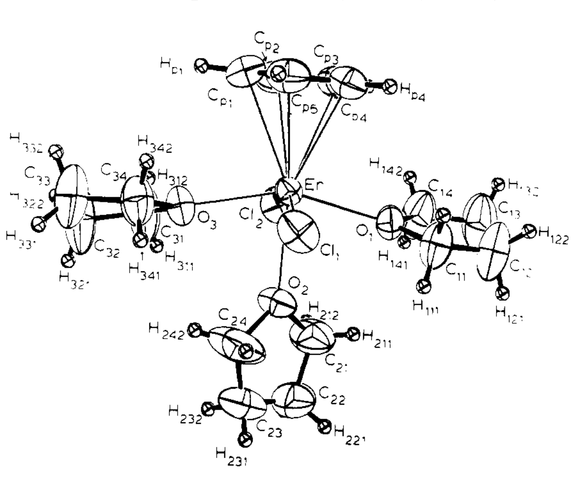


Figure 1. Perspective ORTEP drawing of the solid-state structure for $(\eta^5\text{-}C_5H_5)ErCl_2(OC_4H_8)_3$ (1). All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of their electron density. Hydrogen atoms are depicted at their idealized positions by arbitrarily small spheres which are in no way representative of their true thermal motion. The labeling scheme is described in ref 23.

X-ray Crystallographic Study of $(\eta^5\text{-}C_5H_5)ErCl_2(THF)_3$. Single crystals of $(\eta^5\text{-}C_5H_5)ErCl_2(THF)_3$, obtained as described above, are monoclinic, space group $P2_1/n$ (a special setting of $P2_1/c$—C_{2h}^5, no. 14)[17] with a = 7.822 (2) Å, b = 17.096 (4) Å, c = 15.162 (3) Å, β = 95.80 (2)°, V = 2017 Å^3, and Z = 4 (ρ_{calcd} = 1.711 g cm^{-3}; μ_a(Mo K$\bar{\alpha}$)[18a] = 4.49 mm^{-1}) at 20 °C. A crystal having the shape of a rectangular parallelepiped with dimensions of 0.16 × 0.31 × 1.00 mm was sealed under nitrogen in a thin-walled glass capillary and aligned on a computer-controlled Nicolet P$\bar{1}$ autodiffractometer with its long dimension nearly parallel to the phi axis of the instrument. Intensity measurements utilized graphite-monochromated Mo K$\bar{\alpha}$ radiation (λ = 0.710 73 Å) and 1° wide ω scans with a 4° takeoff angle and a normal-focus X-ray tube. With use of a 1.2-mm diameter collimator, data were collected as previously described[15] in three concentric shells of 2θ out to 58.7° (1.2 Cu K$\bar{\alpha}$ sphere equivalents) with fixed scan rates of 2.0 or 3.0°/min.

A total of 5536 reflections were collected, of which 4207 independent reflections were judged above background [$I > 3\sigma(I)$], and utilized in subsequent calculations. An empirical absorption correction was applied by using psi scan data for eight reflections having 2θ values between 8 and 39°; the relative transmission factors ranged from 0.55 to 1.00. The function minimized in full-matrix least-squares refinements was $\sum w(|F_o| - |F_c|)^2$ with the final empirical weights[19] ($w = 1/\sigma^2$) assigned by the method of Cruikshank.[20] The atomic scattering factors and anomalous dispersion terms for erbium and chlorine were taken from recent tabulations.[18b,c]

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(19) Empirical weights were calculated from the equation $\sigma = \sum_0^3 a_n|F_o|^n = 1.33 - (1.88 \times 10^{-2})|F_o| + (3.11 \times 10^{-4})|F_o|^2 - (7.82 \times 10^{-7})|F_o|^3$, the a_n being coefficients derived from the least-squares fitting of the curve $||F_o| - |F_c|| = \sum_0^3 a_n|F_o|^n$ where F_c values were calculated from the fully-refined model using unit weighting with 4207 independent reflections having $2\theta_{MoK\bar{\alpha}} < 58.7°$ and $I > 3\sigma(I)$.

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Table I. Positional and Thermal Parameters for Nonhydrogen Atoms in Crystalline $(\eta^5\text{-}C_5H_5)ErCl_2(OC_4H_8)_3$[a]

atom	fractional coordinates			anisotropic parameters,[c] Å^3					
type[b]	10^4x	10^4y	10^4z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Er	558.2 (2)	503.0 (1)	2657.3 (1)	2.75 (1)	3.45 (1)	2.92 (1)	−0.17 (1)	0.15 (1)	0.07 (1)
Cl_1	−2002 (1)	178 (1)	3577 (1)	3.69 (4)	7.11 (7)	4.16 (5)	−0.71 (5)	0.97 (4)	0.02 (5)
Cl_2	2517 (2)	297 (1)	1373 (1)	4.61 (5)	6.42 (7)	4.28 (5)	−0.06 (5)	1.47 (4)	0.29 (5)
O_1	2057 (4)	−542 (2)	3386 (2)	3.4 (1)	4.7 (1)	4.1 (1)	0.0 (1)	−0.0 (1)	1.1 (1)
O_2	−785 (4)	−632 (2)	1878 (3)	3.7 (1)	5.0 (2)	5.6 (2)	−0.6 (1)	0.2 (1)	−1.6 (1)
O_3	−1518 (4)	1080 (2)	1614 (2)	3.8 (1)	5.7 (2)	3.6 (1)	1.0 (1)	−0.0 (1)	0.5 (1)
C_{11}	1498 (9)	−987 (4)	4115 (4)	6.8 (3)	6.2 (3)	4.8 (3)	1.3 (3)	1.3 (2)	1.9 (2)
C_{12}	2929 (12)	−1506 (5)	4421 (5)	9.8 (5)	8.8 (5)	7.4 (4)	3.2 (4)	1.6 (4)	4.1 (4)
C_{13}	4405 (10)	−1250 (6)	3986 (6)	6.0 (4)	11.3 (6)	10.0 (5)	2.7 (4)	−0.2 (4)	4.1 (5)
C_{14}	3812 (8)	−769 (5)	3263 (6)	3.5 (2)	8.0 (4)	11.2 (5)	1.3 (2)	0.7 (3)	3.9 (4)
C_{21}	70 (10)	−1335 (4)	1684 (5)	7.6 (4)	6.2 (3)	8.0 (4)	0.1 (3)	−0.1 (3)	−3.2 (3)
C_{22}	−1181 (12)	−1874 (4)	1237 (5)	9.6 (5)	5.7 (3)	7.5 (4)	−1.4 (3)	−0.4 (4)	−1.3 (3)
C_{23}	−2712 (14)	−1441 (6)	1094 (9)	10.5 (6)	6.8 (5)	17.4 (9)	−3.0 (4)	−6.7 (6)	−1.0 (5)
C_{24}	−2540 (10)	−735 (6)	1585 (8)	5.0 (3)	9.8 (5)	14.9 (8)	−1.3 (3)	−1.8 (4)	−5.4 (5)
C_{31}	−1268 (10)	1234 (6)	703 (4)	7.6 (4)	13.3 (7)	4.1 (3)	4.7 (4)	1.1 (2)	2.4 (3)
C_{32}	−2835 (12)	1598 (7)	302 (5)	10.7 (6)	15.6 (8)	4.8 (3)	7.2 (6)	0.1 (3)	2.6 (4)
C_{33}	−3746 (10)	1889 (5)	1019 (6)	7.4 (4)	10.2 (5)	8.0 (4)	4.7 (4)	1.1 (3)	2.7 (4)
C_{34}	−3129 (7)	1429 (4)	1805 (4)	4.7 (2)	7.3 (3)	5.5 (3)	2.4 (2)	0.4 (2)	0.5 (3)
C_{p1}	939 (9)	2033 (3)	2987 (5)	6.9 (3)	3.4 (2)	6.7 (3)	−0.7 (2)	−0.1 (3)	−0.3 (2)
C_{p2}	2537 (9)	1773 (4)	2795 (5)	6.7 (3)	4.9 (3)	6.9 (3)	−2.3 (2)	1.6 (3)	−0.6 (2)
C_{p3}	3185 (8)	1292 (4)	3487 (5)	4.5 (2)	5.9 (3)	8.2 (4)	−1.0 (2)	−0.9 (3)	−1.8 (3)
C_{p4}	1955 (9)	1247 (4)	4097 (4)	7.2 (3)	5.0 (3)	4.6 (2)	−1.0 (2)	−0.9 (2)	−0.9 (2)
C_{p5}	569 (8)	1705 (3)	3780 (4)	6.0 (3)	4.9 (3)	5.8 (3)	−0.5 (2)	0.7 (2)	−1.6 (2)

[a] Numbers in parentheses are the estimated standard deviation for the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] The form of the anisotropic temperature factor is $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

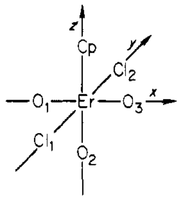
The location of the erbium atom was determined from a Patterson synthesis. Following refinement of the erbium atom (R_1[21] = 0.238), all remaining nonhydrogen atoms were located on a difference Fourier map. Unit-weighted (w = 1) isotropic least-squares refinement for the nonhydrogen atoms converged to R_1[21] = 0.051 and R_2[21] = 0.054 for 2036 independent reflections having $2\theta_{MoK\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$; anisotropic refinement gave $R_1 = 0.027$ and $R_2 = 0.032$. Hydrogen atoms were then placed in fixed idealized positions (C–H = 0.95 Å), and anisotropic refinement of all nonhydrogen atoms with the more complete ($2\theta_{MoK\bar{\alpha}} < 58.70$) data set led to $R_1 = 0.029$ and $R_2 = 0.035$ for 4207 reflections having $I > 3\sigma(I)$. A final difference Fourier map revealed no significant (>0.49 e$^-$/Å^3) peaks away from the erbium atom location. Since a careful examination of the final F_o and F_c values[22] indicated the absence of extinction effects, extinction corrections were not made.

All calculations were performed on a Data General Eclipse S-200 computer with 64K of 16-bit words, a floating-point processor for 32- and 64-bit arithmetic, and versions of the Nicolet E-XTL interactive crystallographic software package as modified at Crystalytics Co.

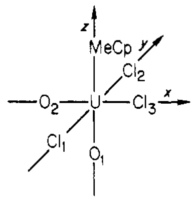
Results and Discussion

The solid-state structural result[23] depicted in Figure 1 has confirmed the discrete monomeric nature of $(\eta^5\text{-}C_5H_5)ErCl_2(THF)_3$ (**1**). The Er(III) ion is coordinated by two chloride ions, three THF oxygen atoms, and a η^5-bonded cyclopentadienyl ligand. The final positional and thermal parameters for nonhydrogen atoms of **1**, obtained from the last cycle of empirically weighted full-matrix least-squares refinement, are given with estimated standard deviations in Table I. Calculated positions for hydrogen atoms of **1** are given in Table II.[22] Structural parameters which characterize the coordination group of **1** are presented in Table III, and bond lengths and angles for nonhydrogen ligand atoms are given in Table IV.[22] Least-squares mean planes and atomic displacements therefrom are given for structurally significant groupings of atoms[23] along with selected dihedral angles in Table V.

While the formal coordination number of the erbium(III) ion in **1** is eight,[24] the parameters listed in Table III indicate a pseudooctahedral coordination geometry if the η^5-bonded C_5H_5 ligand is regarded as occupying a single polyhedral vertex. To simplify discussion of the bonding parameters, it is convenient to define a coordinate system with the erbium atom formally located at the origin. A similar scheme was helpful in describing the geometry of the related $(\eta^5\text{-}CH_3C_5H_4)UCl_3(THF)_2$ complex.[15] The coordinate systems for both compounds are indicated in V and VI, respectively (Cp = $\eta^5\text{-}C_5H_5$, MeCp = $\eta^5\text{-}CH_3C_5H_4$).



V



VI

The ligand complement in structure V can be derived from VI by replacement of the Cl_3 atom by the O_3 atom. With $(\eta^5\text{-}CH_3C_5H_4)UCl_3(THF)_2$, **2**, being a sterically crowded species[15] even though it is formally only eight-coordinate,[24] the replacement of Cl_3 in **2** by a THF oxygen to give **1** should not only produce a more symmetrical molecule but also one which is sterically less crowded since the van der Waals diameter[25] of chlorine is 0.8 Å larger than that of

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[21] The R values are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, where w is the weight given each reflection. The function minimized is $\sum w(|F_o| - K|F_c|)^2$ where K is the scale factor.

[22] See paragraph at end of paper regarding supplementary material.

[23] The numbering scheme used to designate atoms of $(\eta^5\text{-}C_5H_5)ErCl_2(THF)_3$, **1**, is as follows. Atoms of different THF ligands are differentiated by a first numerical subscript (1, 2, or 3) and those of the cyclopentadienyl ligand are designated by a subscripted p. Nonhydrogen atoms of the same element within the same ligand are differentiated by a (second) numerical subscript. Hydrogen atoms have the same two subscripts as the carbon atom to which they are covalently bonded; whenever necessary, a third (numerical) subscript is used to distinguish between hydrogens bonded to the same carbon.

[24] Assuming the $\eta^5\text{-}C_5H_5$ ligand occupies three coordination sites.

[25] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; p 260.

Table III. Bond Lengths, Polyhedral Edge Lengths, and Bond Angles Subtended at the Er(III) Atom in the Coordination Group of $(\eta^5\text{-}C_5H_5)ErCl_2(OC_4H_8)_3$ [a]

parameter[b]	value	av[c]	parameter[b]	value	av[c]
		Distances, Å			
$Er-C_{p1}$	2.674 (5)	2.667 (6, 3, 7, 5)	$C_g\cdots Cl_1$[d]	3.900 (3)	3.909 (3, 9, 9, 2)
$Er-C_{p2}$	2.663 (7)		$C_g\cdots Cl_2$[d]	3.918 (3)	
$Er-C_{p3}$	2.665 (7)		$C_g\cdots O_1$[d]	3.684 (3)	3.699 (3, 15, 15, 2)
$Er-C_{p4}$	2.664 (6)		$C_g\cdots O_3$[d]	3.714 (3)	
$Er-C_{p5}$	2.668 (6)		$Cl_1\cdots O_2$	3.156 (4)	3.173 (4, 17, 17, 2)
$Er-Cl_1$	2.613 (1)	2.617 (1, 4, 4, 2)	$Cl_2\cdots O_2$	3.190 (4)	
$Er-Cl_2$	2.620 (1)		$Cl_1\cdots O_1$	3.444 (4)	3.439 (4, 23, 42, 4)
$Er-O_1$	2.350 (3)	2.358 (3, 8, 8, 2)	$Cl_1\cdots O_3$	3.407 (4)	
$Er-O_3$	2.365 (3)		$Cl_2\cdots O_1$	3.424 (4)	
$Er-O_2$	2.452 (3)		$Cl_2\cdots O_3$	3.481 (4)	
$Er-C_g$[d]	2.389 (3)		$O_1\cdots O_2$	3.028 (5)	3.015 (5, 13, 13, 2)
			$O_2\cdots O_3$	3.002 (5)	
		Angles, Deg			
C_gErO_2[d]	179.3 (1)		Cl_1ErO_1	87.7 (1)	87.3 (1, 7, 11, 4)
C_gErCl_1[d]	102.4 (1)	102.5 (1, 3, 5, 14)	Cl_1ErO_3	86.2 (1)	
C_gErCl_2[d]	102.8 (1)		Cl_2ErO_1	86.9 (1)	
C_gErO_1[d]	102.0 (1)		Cl_2ErO_3	88.4 (1)	
C_gErO_3[d]	102.8 (1)		Cl_1ErO_2	77.0 (1)	77.5 (1, 5, 6, 4)
Cl_1ErCl_2	154.85 (4)		Cl_2ErO_2	77.9 (1)	
O_1ErO_3	155.18 (11)		O_1ErO_2	78.1 (1)	
			O_2ErO_3	77.1 (1)	

[a] The number in parentheses following an individual entry is the estimated standard deviation in the last significant digit. [b] Atoms are labeled in agreement with Figure 1 and Tables I–II. [c] See ref 29. [d] C_g refers to the center-of-gravity for the five carbon ring of the cyclopentadienyl ligand.

Table V. Atomic Displacements from Various Mean Planes of $(\eta^5\text{-}C_5H_5)ErCl_2(OC_4H_8)_3$

Equations of Mean Planes[a]

I	cyclopentadienyl ligand	$2.923x + 13.475y + 6.803z = 5.040$
II	xy coordination plane	$2.885x + 13.624y + 6.651z = 2.076$
III	xz coordination plane	$-5.866x - 0.801y + 11.102z = 2.593$
IV	yz coordination plane	$-4.184x + 10.415y - 8.012z = -1.839$

atom type	displacement,[b] Å from			
	plane I	plane II	plane III	plane IV
Er	−2.391	0.538	−0.011*	0.000*
Cl_1	−2.952	−0.032*	2.538	−0.004*
Cl_2	−2.970	−0.031*	−2.569	−0.004*
O_1	−2.865	0.032*	0.003*	−2.299
O_2	−4.843	−1.914	0.002*	0.005*
O_3	−2.930	0.032*	0.003*	2.306
C_g[c]	−0.002	2.927	0.003*	0.003*
C_{p1}	0.007*	2.952	0.010	1.171
C_{p2}	−0.007*	2.931	−1.120	0.385
C_{p3}	0.005*	2.923	−0.694	−0.941
C_{p4}	0.000*	2.912	0.708	−0.963
C_{p5}	−0.004*	2.926	1.133	0.348

[a] Monoclinic coordinates. Angles between planes are as follows: I–II, 0.83°; I–III, 89.69°; I–IV, 89.66°; II–III, 89.90°; II–IV, 89.54°; III–IV, 89.21°. [b] Atoms used to calculate the planes have their displacements designated by an asterisk. [c] C_g is defined in Table III.

oxygen. The data in Tables III and V are totally consistent with these expectations. First it should be noted that the trans C_g–M–O[26] angle is much closer to 180° in 1 than in 2 (179.3° vs. 175.0°) and the "equatorial" C_g–M–L and L–M–L angles are much more regular in 1 than in 2. As the data in Table V indicate, each set of four coordinated atoms which determine the idealized xy, xz, and yz planes in 1 are quite coplanar (to within 0.032 Å)—considerably more so than similar groupings in 2. These three coordination planes are also very close to being mutually perpendicular, with interplanar angles ranging from 89.2 to 89.9°. Thus if the local symmetry of the cyclopentadienyl ligand is ignored, the coordination polyhedron of 1 is seen to approximate rather closely its maximum possible symmetry of C_{2v}.

While the erbium(III) ion virtually residues in the xz and yz planes, it is displaced by 0.54 Å from the xy plane. As in 2, this clearly results from steric repulsions between the large cyclopentadienyl ligand and the four "equatorial"ligands in the xy coordination plane. Similar respective displacements of the metal atom by 0.47 and 0.5 Å have been observed in the structures of 2 and $(C_6H_6)U(AlCl_4)_3$.[15,27] That the cyclopentadienyl ligand occupies the largest area on the coordination sphere can readily be seen by a comparison of polyhedral edge lengths in Table III, as well as from the rather large cis C_g–U–O and C_g–U–Cl angles which range from 102.0 (1) to 102.8 (1)° or the cis O_2–U–O and O_2–U–Cl angles which fall in the range 77.0 (1)–78.1 (1)°. Even with this distortion, however, two $C_p\cdots Cl$ contacts are less than the sum of the respective van der Waals radii (1.7 and 1.8 Å, respectively[25]): $Cl_1\cdots C_{p5}$ = 3.291 (4) Å and $Cl_2\cdots C_{p2}$ = 3.319 (7) Å.

Simple steric considerations such as these appear to be instrumental in determining the stereochemistry of the coordination sphere. With the four ligands in the xy plane being forced down toward the ligand on the negative z axis, the most stable configuration should result when the coordination site trans to the bulky cyclopentadienyl ligand is occupied by the smallest coordinated atom—in this case, a THF oxygen atom. As previously discussed,[15] having a chloride ligand opposite to the cyclopentadienyl ligand would bring about extreme $Cl\cdots Cl$ nonbonded contacts (ca. 3.3 Å), in the absence of a great deal of change in bonding

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(26) C_g refers to the center-of-gravity for the five-membered ring of the cyclopentadienyl ligand.

(27) Cesari, M.; Pedretti, U.; Zazzeta, A.; Lugli, G.; Marconi, W. *Inorg. Chim. Acta* 1971, 5, 439.

parameters (particularly lengthening of the metal–ligand bonds). Thus, a *mer*,cis isomer (III) would not seem likely. The facial isomer (IV) would involve two adjacent THF ligands in the *xy* plane. Because of the disk shape of the cyclopentadienyl ligand, these two THF ligands would necessarily be required to be nearly parallel to the cyclopentadienyl ligand. Such an orientation would bring about severe H···H contacts between the two adjacent THF ligands. Thus, the most likely disposition of ligands on the coordination sphere would involve the observed *mer,trans* configuration (II).

Having demonstrated that the molecular configuration observed for **1** is the one which would be predicted from steric considerations, attention can now be focused on the more subtle aspects of the coordination geometry. A structural comparison of metal–ligand bond lengths for **1** and **2** has been greatly facilitated by the choice of erbium as the lanthanide metal, since the eight-coordinate Er(III) ion possesses an ionic radius (1.004 Å) virtually identical with that of the eight-coordinate U(IV) ion (1.00 Å).[28]

While the average metal–ligand bond lengths for Cl in **1** and **2** are quite comparable (2.617 (1, 4, 4, 2) Å[29] in **1** and 2.623 (3, 6, 9, 3) Å[29] in **2**), those for the remaining ligands are not. This would seem to indicate that the metal–chloride linkages contribute most to the bonding of the two complexes and is consistent with a high degree of ionic character. The Er–C bonds in **1** form an equivalent set with an average length of 2.667 (6, 3, 7, 5) Å which is 0.053 Å shorter than the 2.730 (14, 11, 28, 5) Å average length observed for the U–C bonds in **2**. While the U–O bonds in **2** are equivalent with an average length of 2.450 (8, 1, 1, 2) Å, the Er–O bonds are of two distinct types: one long "axial" (*z* axis) bond with a length of 2.452 (4) Å and two shorter "equatorial" (*xy* plane) bonds with the average length being 2.358 (3, 8, 8, 2) Å. The observation of shorter average metal–carbon and metal–oxygen bonds in **1** than **2** is consistent with **1** having the less congested coordination sphere (vide supra). Therefore the present comparisons serve to demonstrate the necessity of taking into account ligand–ligand repulsive interactions[30,31] in any scheme which is to accurately predict bond distances in ionic organometallic systems with sterically demanding ligands. Similar dependencies of coordination parameters on steric crowding have also been observed in the bis(pentamethylcyclopentadienyl) actinide series.[32]

Besides a general correlation of average metal–ligand bond lengths in **1** and **2** with the amount of steric crowding on their coordination spheres, it can be shown that each difference in metal–ligand bond lengths is associated with specific structural alterations. The metrical parameters for **2**[15] indicated considerable steric crowding in the *xy* and *yz* planes and somewhat less crowding in the *xz* plane. Since the Cl_3 ligand in **2** occupies a site in the *xy* plane and is replaced by a less bulky THF oxygen atom (O_3) in **1**, it is particularly noteworthy that the axial Er–O bond in **1** is in length nearly identical with the two U–O bonds in **2** and even 0.094 Å longer than the two equatorial Er–O bonds. Presumably the axial Er–O bond in **1** is stretched relative to the equatorial ones. The presence of short O···Cl contacts for O_2 but not O_1 and O_3 is consistent with this hypothesis; the 3.156 (4)-Å $O_2\cdots Cl_1$ and 3.190 (4)-Å $O_2\cdots Cl_2$ contacts are both less than the minimum van der Waals separation[25] of 3.20 Å. Replacement of Cl_3 in **2** by a THF oxygen would not only reduce "tension" in the *xy* plane but would also allow the metal to move closer to the *yz* plane. These factors would combine to permit shorter (and more normal) equatorial metal–oxygen bonds in **1** than **2**. Indeed, examination of the Ln–O bond distances in the eight-coordinate $(C_5H_5)_2Lu(t\text{-}C_4H_9)(THF)$[33] and ten-coordinate $(C_5H_5)_3Gd(THF)$ structures[9] (2.31 (2) and 2.494 (7) Å, respectively) leads to predicted, eight-coordinate Er–O bond distances of 2.34 and 2.33 Å, respectively, suggesting that the shorter Er–O bond distances here are more normal. A similar situation can be found in the structure of *mer*-$ScCl_3(THF)_3$, where two Sc–O distances averaged 2.156 (7, 9, 9, 2) Å and the third Sc–O distance was 2.236 (8) Å.[34]

Both U–O bonds in **2** appear to be stretched; the axial oxygen engages in close contacts of 3.212 (9) Å with Cl_1 and 3.204 (8) Å with Cl_2 while the equatorial oxygen is only 3.05 (2) Å away from a ring carbon of the methylcyclopentadienyl ligand. This latter contact likely is due to the orientation of the methylcyclopentadienyl ligand which results from the methyl group locking itself between Cl_2 and Cl_3. Such an orientation is not imposed for the unsubstituted cyclopentadienyl ligand in **1** and there are no close contacts involving oxygen atoms in the *xy* plane.

Steric factors also appear to be responsible for the elongation of the metal–carbon bonds in **2** relative to **1**. While both molecules contain short cyclopentadienyl ring C···Cl contacts (3.319 (7) Å for $C_{p2}\cdots Cl_2$ and 3.291 (6) Å for $C_{p5}\cdots Cl_1$ in **1**; 3.43 (2) Å for $C_{p2}\cdots Cl_3$, 3.35 (1) Å for $C_{p3}\cdots Cl_1$, and 3.32 (2) Å for $C_{p5}\cdots Cl_2$ in **2**), the cyclopentadienyl ligand in **2** also has two short contacts averaging 3.64 (2, 2, 2, 2) Å between the carbon atom of its methyl substituent and Cl_2 and Cl_3 (a contact distance of at least 3.80 Å would be expected on the basis of a 2.00-Å van der Waals radius for a methyl group[25]). In addition, the orientation thus imposed on the cyclopentadienyl ligand with respect to the ligands in the uranium *xy* coordination plane also resulted in a short $C_4\cdots O_2$ distance of 3.05 (2) Å. The presence of longer metal–carbon distances in **2** relative to **1** can be reasonably attributed to the combination of these contacts. Indeed, the presence of the methyl group in **2** also served to preferentially expand the Cl_2–U–Cl_3 angle as well as increase the tilt between the cyclopentadienyl ring and the *xy* coordination plane (3.75° compared to 0.83° in **1**).

The average Er–C bond distance of 2.667 (6, 3, 7, 5) Å in **1** compares reasonably well with that of 2.63 (1) Å for $(C_5H_5)_2Lu(t\text{-}C_4H_9)(THF)$ if the differences in metal ionic radii are taken into account. Comparisons with most other organolanthanides suggest, however, that the average Er–C bond length is slightly long (e.g., the ten-coordinate complexes: $(C_5H_5)_3Pr(CNC_6H_{11})$, Pr–C = 2.78 (1) Å; $(C_5H_5)_3Gd(THF)$, Gd–C = 2.74 (1) Å; $[(C_5H_5)_3Yb]_2(C_4H_4N_2)$, Yb–C = 2.68 (1) Å). Although reasonably good agreement is observed by using the 1.64-Å ionic radius for the cyclopentadienyl ligand[4c] (predicting an Er–C distance of 2.644 Å), the average Er–C bond distance of 2.667 Å in **1**

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[28] Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

[29] The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the average value.

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differs greatly from what would be predicted (2.724 and 2.604 Å, respectively) based on the U–C and Yb–C bond distances observed in the also eight-coordinate $(CH_3C_5H_4)UCl_3(THF)_2$ and $[(CH_3C_5H_4)_2YbCl]_2$ complexes (U–C = 2.720 Å and Yb–C = 2.585 Å). It is thus clear that metal–ligand bond distances in these compounds are highly dependent on the nature and severity of interligand contacts on the coordination sphere. The metal–carbon and metal–oxygen distances in **1** and **2** seem to be much more sensitive to the presence of nonbonded contacts than do the metal–chlorine distances. The average Er–Cl bond length of 2.617 (1, 4, 4, 2) Å in **1** is quite comparable to the average U–Cl bond length of 2.623 (3, 6, 9, 3) Å in **2**[15] as well as the U–Cl bond lengths of 2.599 (9, 2, 2, 2) Å in $[(C_2B_9H_{11})_2UCl_2]^{2-}$, 2.627 (2) Å in $(C_6H_5CH_2C_5H_4)_3UCl$ and 2.593 (3) Å in $(C_9H_7)_3UCl$.[35–37]

In summary, the results of this study indicate that the stereochemistry of the metal coordination sphere in monocyclopentadienyl lanthanide or actinide complexes can often be readily predicted in a strenghtforward fashion and that steric factors can have a pronounced effect on metal–ligand bond lengths in organometallic complexes of the f elements. Although little use has been made to date of the monocyclopentadienyl lanthanide or actinide complexes for more involved chemistry, there is little doubt that their easily modified coordination spheres will eventually provide a rich source of new chemistry. Finally, the possibility should be considered that related structures may well be found for large early transition-metal compounds which have the electronic capabilities to absorb the large numbers of electrons donated by such a ligand complement.[38]

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Supplementary Material Available: Table II (a listing of calculated coordinates for the hydrogen atoms), Table IV (bond lengths and angles for nonhydrogen ligand atoms), and a table of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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Rhodium and Molybdenum Complexes as Catalysts for Conversion of Nitrobenzene and Aliphatic Alcohols to Alkylquinolines

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Nitrobenzene reacts with ethanol and higher alcohols to form 2-methyl- or 2,3-dialkylquinolines, respectively. The reaction is catalyzed by rhodium or molybdenum complexes. The best yields and conversions are obtained in the presence of about equimolar mixtures of rhodium and molybdenum at ~180 °C. This latter system represents a convenient and practical synthesis of alkylquinolines. The probable reaction mechanism is discussed.

The well-known transition metal catalyzed reduction of nitrobenzene by carbon monoxide has been suggested to involve nitrene-type intermediates.[1] In order to allow the chemistry of the intermediate to be observed and prevent its trapping by carbon monoxide, we were interested in nitrobenzene deoxygenation by carbon monoxide present at low partial pressure. In this context we were intrigued by the reports[2] that a combination of group 8 metal carbonyls, such as chlorocarbonylrhodium(I) dimer (**1**) or tetrabutylammonium trichlorocarbonylpalladate (**2**), with Lewis acids, represented by molybdenum pentachloride, vanadium tri- and tetrachlorides, or titanium tetrachloride, allows reduction of nitro atomatics at ~100 kPa (1 atm) of CO and 100 °C. Interestingly, application of a similar catalyst system to reduction of nitrobenzene in alcoholic media resulted in formation of alkylquinolines instead of the expected carbamates. After our study was finished Watanabe and co-workers[3] published their account of a low-yield alkylquinoline formation from nitrobenzene and alcohols in the presence of tris(triphenylphosphine)dichlororuthenium(II). This prompted us to reveal our independent work which represents the first practical and moderate to high-yield synthesis of alkyl quinolines from nitrobenzene and extends the list of potential catalysts to rhodium and molybdenum.

Results and Discussion

Initially we examined the reduction of nitrobenzene under conditions similar to those employed by Schwetlick

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