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Synthetic and Structural Studies of Pentamethylcyclopentadienyl Complexes of Lanthanum and Cerium

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The proper choice of halide coligands permits the synthesis of pentamethylcyclopentadienyl complexes of cerium and lanthanum containing either one or two C_5Me_5 rings. Thus, $CeCl_3$ can be readily converted to the bis(ring) ionic compound $[Li(ether)_2][(C_5Me_5)_2CeCl_2]$ (1) while mono(ring) compounds are less readily available. However, the mono(ring) iodide derivatives $(C_5Me_5)LnI_2(THF)_3$ (Ln = La, Ce) are prepared in high yield from $LnI_3(THF)_x$ (the syntheses of which are also reported). Crystallography on the cerium analogue indicated a monomeric compound with a pseudooctahedral *mer,trans* geometry. Crystal data: space group $P2_1/n$, $a = 18.465$ (5) Å, $b = 17.217$ (4) Å, $c = 17.738$ (5) Å, $V = 5370.02$ Å^3, $Z = 8$. These mono(ring) compounds undergo ready loss of THF ligands in either the solid state or the solution but show no tendency to form ionic $[(C_5Me_5)LnI_3][K(ether)]$ under the conditions employed in the syntheses.

Recent studies on organometallic compounds of the lanthanide metals have shown them to be active in such important processes as C–H activation,[2] alkene and alkyne reduction,[3-5] alkene polymerization,[4-6] and carbonyl activation.[7,8] Much of this work has involved the use of the smaller, later lanthanide metals which are tolerant of a variety of ligation spheres. As such, Cp_3Ln, Cp_2LnX, and $CpLnX_2$ derivatives (X = halide, alkyl, etc.) are often readily available.[9] The early lanthanides, lanthanum and cerium, have received less attention, but some organolanthanum[4,10-14] and -cerium[11,12,17-22] compounds have been described. In general, these metals require more bulky ligand sets to achieve stable configurations. This notion has been set forth in quantitative fashion by using the "solid angle sum rule"[23] to estimate the degree of steric saturation in organo-f-element complexes. This concept was shown to correctly predict the stability of trigonal-bipyramidal species $(C_5H_5)_3M(NCR)_2$ for M = Ce and La.[17] Since these metals are too large to form bis- or mono(cyclopentadienyl) complexes, several approaches have been used to prepare stable compounds with fewer than three aromatic rings ligated. These include the use of bulkier ligands such as cyclooctatetraenyl dianion, which leads to formation of bis(ring) compounds $[(COT)_2Ce][K(diglyme)]$ and $(COT)_2Ce$[20,22] (the latter, a rare example of a Ce(IV) organometallic), as well as the mono(ring) dimer $[(COT)Ce(THF)_2(\mu\text{-}Cl)]_2$.[19] Similarly, heptamethylindenyl ligands (Hmi) have allowed the preparation of $(Hmi)_3Ce$, $(Hmi)_2CeCl$, and $(Hmi)CeCl_2$.[12] In seeking bis(cyclopentadienyl) analogues, Qian et al.[16] and John and Tsutsui[11] have shown that linking the two cyclopentadienyl rings with a polymethylene bridge allows the preparation of several compounds of general formula $[(C_5H_4)_2(CH_2)_x]Ln(Cl)(THF)$, while Lappert and Atwood[14] have reported the preparation of several bis(ring) lanthanides incorporating the bulky $[C_5H_3(SiMe_3)_2]$ ring into dimeric $\{[C_5H_3(SiMe_3)_2]_2Ln(\mu\text{-}Cl)\}_2$. Finally, there have been recent reports of early lanthanide pentamethylcyclopentadienyl compounds such as $[(C_5Me_5)_2LnCl_2]^-$[4,13,24] and derivatives (Ln = La, Pr, Nd); similar compounds are well-known for later lanthanides.[9] We have been interested in the relationship between lanthanide ion size and the stability of various complex geometries and have focused our attention

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on the preparation of lanthanum and cerium organometallics containing pentamethylcyclopentadienyl ligands. We report herein the results of our studies on these larger lanthanide metals, in which we have prepared both bis(ring) and the more sterically accessible mono(ring) compounds. We find that the preparation and isolation of these latter compounds is facilitated by using large coligands to stabilize the desired complexes.

Experimental Section

Proton NMR spectra were obtained on a Varian XL-200 or XL-400 FTNMR. Infrared spectra were determined by using an O-ring sealed airtight holder on a Perkin-Elmer M1500 FTIR instrument. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

All manipulations were carried out under an atmosphere of nitrogen or argon; both gases were dried and deoxygenated by passage through columns of BASF catalyst and Linde 4A molecular sieves. Solutions were handled by using Schlenk methods in glassware equipped with Solv-Seal joints, while solid transfers were performed in a Vacuum Atmospheres Corp. glovebox. Toluene, benzene, diethyl ether, dimethoxyethane, and tetrahydrofuran (Baker) were distilled from sodium benzophenone ketyl under nitrogen. Cerium and lanthanum metal chips were purchased from Alfa and handled under inert atmosphere. Anhydrous cerium and lanthanum chlorides were purchased from Aldrich and heated under vacuum prior to use. Pentamethylcyclopentadiene was purchased from Aldrich or prepared via literature procedures[25] and metalated by using n-BuLi or KH in tetrahydrofuran.

Molecular weight studies were carried out by using the Signer isothermal distillation method in an apparatus built locally. Known amounts of the unknown sample (usually ca. 100 mg) were added to one arm of the apparatus, and known amounts of ferrocene were added to the other. THF solvent (ca. 3 mL) was added to each side, and the system evaculated, closed off, and allowed to come to equilibrium. This latter process usually took 2–3 days, and we note the importance of isolating the system from drafts, extraneous heat sources, etc.

$[Li(Et_2O)_2][(C_5Me_5)_2CeCl_2]$ (1). In the glovebox, 0.5 g (2 mmol) of $CeCl_3$ and 0.58 g (2.1 mmol) of $(C_5Me_5)Li$ were added to a Schlenk apparatus equipped with reflux condensor and gas inlet. THF (50 mL) was added and the resulting suspension refluxed for 48 h. Upon cooling, the THF was removed in vacuo and the resulting residue extracted with toluene. The toluene was removed in vacuo and the compound dissolved in a minimum volume of diethyl ether. Cooling resulted in the precipitation of highly air- and moisture-sensitive yellow cubes (55%). IR (Nujol): 1300 (w), 1190 (w), 1158 (m), 1100 (s), 1165 (s), 1025 (m), 905 (w), 795 (w) cm^{-1}. ^1H NMR (THF-d_8): 3.99 ppm (br s, fwhm = 0.1 ppm; 200 MHz), as well as signals for free diethyl ether.

$[(C_5Me_5)CeCl_2(THF)_x]_y$ (2). A suspension of 1.1 g (4.46 mmol) of $CeCl_3$ in 75 mL of THF was refluxed for 12 h (this enhances the reaction, presumably by converting oligomeric $CeCl_3$ to a more soluble form). After the solution was cooled, 0.62 g (4.46 mmol) of $(C_5Me_5)K$ was added via addition tube under nitrogen. This gave rise to a yellow color, and the suspension was refluxed another 12 h. Solvent was removed in vacuo and the residue extracted with toluene. The toluene was removed in vacuo, and ca. 5 mL of THF was added to dissolve the solid. Hexane was then added slowly to precipitate the yellow solid. This was filtered and dried in vacuo (45%). IR (Nujol): 1039 (s), 893 (m), 840 (w) cm^{-1}.

$LaI_3(THF)_x$. In the glovebox, 2.2 g (15.8 mmol) of lanthanum metal chips was washed with dry THF several times and then immersed in 60 mL of THF. On the Schlenk line, 10.2 mL (19.9 g, 127 mmol) of degassed iodoethane was added via syringe and the resulting suspension refluxed for 24 h. The volume of THF was reduced in vacuo, and the crude solid (containing product and traces of unreacted lanthanum metal) was filtered and dried in vacuo. This solid was transferred to a Soxhlet extractor in the glovebox and extracted with THF under nitrogen for 5 days. The resulting solution was concentrated and cooled, and the colorless, air-sensitive crystals were filtered and dried in vacuo (10.2 g, 88%). IR (Nujol): 1170 (w), 1012 (s), 920 (w), 853 (s), 832 (m) cm^{-1}. Anal. Calcd for $C_{16}H_{32}I_3O_4La$ (x = 4): C, 23.79; H, 3.96. Found: C, 23.37; H, 3.62. Colorless $CeI_3(THF)_x$ was prepared in an identical manner (93% yield) and exhibited an identical IR spectrum.

Table I. Crystal Data for $(C_5Me_5)CeI_2(THF)_3$ (4)

empirical formula	$CeC_{22}H_{39}O_3I_2$
color of cryst	yellow
Cryst dimens, (mm)	0.14 × 0.14 × 0.19
space group	$P2_1/n$
cell dimens (at −160 °C; 30 reflections)	
a, Å	18.465 (5)
b, Å	17.217 (4)
c, Å	17.738 (5)
β, deg	107.76 (1)
Z (molecules/cell)	8
V, Å^3	5370.02
d(calcd), g/cm^3	1.844
wavelength, Å	0.71069
mol wt	745.48
Linear abs coeff, cm^{-1}	40.165
total no. of reflctns collected (6° ≤ 2θ ≤ 45°)	8689
no. of unique intensities	7053
no. of $F > 3\sigma(F)$	6370
final residuals	
$R(F)$	0.0546
$R_w(F)$	0.0564
goodness of fit for last cycle	1.168
max Δ/σ for last cycle	0.05

$(C_5Me_5)LaI_2(THF)_3$ (3). Under nitrogen, 6.8 g (9.2 mmol) of $LaI_3(THF)_x$ was stirred in 200 mL of THF and 1.8 g (10.3 mmol) $(C_5Me_5)K$ added. The resulting suspension was refluxed under argon for 16 h, after which time the THF was removed in vacuo and the residue extracted with toluene (ca. 200 mL). The toluene was removed in vacuo and the residue dissolved in THF (ca. 15 mL). The solution was immersed in an ice bath and the volume of THF reduced slowly to ca. 1–2 mL (if the solid is evacuated to dryness, ligated THF is removed with loss of crystallinity); 15 mL of ether was added and the crystals were filtered and allowed to dry at atmospheric pressure in the glovebox (78.8%). ^1H NMR (C_6D_6): 3.64 (mult, THF), 2.39 (s, C_5Me_5), 1.39 ppm (m, THF). IR (Nujol): 1310 (w), 1170 (w), 923 (w), 862 (s) cm^{-1}. Prolonged evacuation results in a colorless powder, with most of the THF removed. Analyses of the latter material indicated retention of some THF. Anal. Calcd for $C_{10}H_{15}I_2La$ ($[(C_5Me_5)LaI_2]_x$): C, 22.74; H, 2.84. Found: C, 24.71; H, 3.56. The cerium analogue 4 was prepared similarly and isolated as yellow-green cubes in an 81% yield.

X-ray Crystallography. A suitable crystal of 4 was cleaved from a larger sample and placed in the cold stream (−160 °C) of the goniostat by using standard inert-atmosphere techniques. A systematic search of a limited hemisphere of reciprocal space located a set of diffraction maxima with monoclinic symmetry and systematic absences corresponding to the unique space group $P2_1/n$. Data were collected over the range 6° ≤ 2θ ≤ 45°; parameters are given in Table I. The structure was solved by a combination of direct methods (MULTAN78) and Fourier techniques, and refined by full-matrix least squares. Many of the hydrogen atom positions were visible in a difference Fourier phased on the non-hydrogen parameters. The positions of all hydrogens were calculated and placed in fixed idealized (d(C–H) = 0.95 Å) positions for the final cycles. The hydrogen atoms were assigned a thermal parameter of 1 + B_{iso} of the carbon atom to which they were bound. A final difference Fourier was essentially featureless, the largest peak being 0.70 e/Å^3.

There are two independent molecules in the assymetric unit cell. These differ primarily in the conformation of one equatorial THF ligand (rotation about the Ce–O axis). We discuss the data for molecule A in the text; data for B are included as supplementary material.

Results and Discussion

As a logical starting point in our studies of pentamethylcyclopentadienyl complexes of the early lanthan-

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ides, we sought to prepare the bis(pentamethylcyclopentadienyl) derivative of cerium. The lanthanum derivative was at first reported to be available in only ca. 10% yield,[10a] but in a recent report this preparation has been improved substantially.[4] The reaction of cerium(III) chloride with $(C_5Me_5)M$ (M = Li, K) in refluxing tetrahydrofuran results in the production of the yellow salt $[M(THF)_2][(C_5Me_5)_2CeCl_2]$ (eq 1). While the reactions

$$CeCl_3 + 2(C_5Me_5)M \xrightarrow[THF]{} [M(THF)_2][(C_5Me_5)_2CeCl_2] + 2MCl \quad (1)$$

with either $(C_5Me_5)Li$ or $(C_5Me_5)K$ appear to proceed with comparable facility, the potassium-containing product is less soluble in toluene and hence more difficult to extract from the product mixture. The lithium salt was readily recrystallized from diethyl ether to yield the ether solvated $[Li(Et_2O)_2][(C_5Me_5)_2CeCl_2]$ (**1**) as large yellow cubes. This highly air- and moisture-sensitive compound is readily soluble in ethers and aromatic hydrocarbons, but only sparingly soluble in hexane. In seeking a convenient analytical tool for the identification of **1**, we chose to investigate the proton NMR spectrum of this paramagnetic (Ce(III), $4f^1$ configuration) complex. In addition to resonances for free diethyl ether (liberated in the THF-d_8 NMR solvent), the spectrum contained a singlet for the ring methyls at 3.99 ppm. The signal was broadened substantially by the paramagnetic metal center, with an observed full-width-at-half-maximum of ca. 0.1 ppm (19 Hz, 200 MHz field, 25 °C).

Because of the limited information content of the spectral data, we obtained crystallographic verification of the proposed structure. While this work was in progress, Rausch, Atwood, and co-workers reported crystallographic data which were identical with those we obtained.[15] These results showed the familiar bent metallocene structure with a solid-state association of the lithium counterion via chloride bridges. Noteworthy is the unusual relationship of the two C_5Me_5 rings in this compound; the ring methyls have adopted an eclipsed arrangement in the solid state. Watson has noted a similar situation in $[Li(Et_2O)_2][(C_5Me_5)_2YbI_2]$; in the corresponding chloride $[Li(Et_2O)_2][(C_5Me_5)_2YbCl_2]$, the rings adopted the more familiar staggered conformation.[26] This eclipsing interaction in the former compound was logically attributed to the steric congestion introduced by the combination of large iodide and small Yb(III) centers. In compound **1** the sterics would seem to be less important since it contains the large Ce(III) and small (relative to iodide) chloride centers.

One means by which the relative strength of metal–Cp bonds is assessed is via the metathesis reaction exemplified by eq 2, reported by Wilkinson in 1956.[18] Although this

$$2Cp_3Ce + 3FeCl_2 \rightarrow 3Cp_2Fe + 2CeCl_3 \quad (2)$$

process is driven by the production of a stronger Cp–M linkage, the formation of $CeCl_3$ ($\Delta H_f = -252.8$ kcal/mol)[27] also serves as a reasonable driving force. We carried out a related reaction between compound **1** and $[CpCo(NCMe)_3][BF_4]_2$,[28] which has no readily available halide ligands to exchange for C_5Me_5 ligands. Mixing the two compounds resulted in rapid production of the mixed cobaltocenium ion $[(C_5H_5)(C_5Me_5)Co][BF_4]$ (in low isolated yield) and unidentified cerium-containing decomposition products. Thus, even in the absence of Ce–Cl bond formation as a driving force, the (C_5Me_5)–Ce linkage in this bis(ring) compound is readily severed.

With the availability of **1**, we were encouraged to attempt preparation of a monomeric mono(ring) compound in the belief that it would prove more sterically accessible. Mono(cyclopentadienyl) analogues have been prepared for a number of lanthanides,[29] and the erbium derivative has been structurally characterized.[30] However, it has been noted that analogous compounds are largely inaccessible for the early lanthanides;[30] even with the larger cyclooctatetraenyl ring the corresponding mono(ring) compound $[(COT)Ce(THF)_2(\mu\text{-}Cl)]_2$ is dimeric.[19] Initial efforts toward the desired C_5Me_5 compound involved the reaction of $CeCl_3$ with limiting quantities (0.9 molar ratio) of $(C_5Me_5)Li$. The reaction appeared to proceed as in eq 3,

$$CeCl_3 + (C_5Me_5)Li \rightarrow \underset{\mathbf{2}}{[(C_5Me_5)CeCl_2(THF)_x]_y} \quad (3)$$

with formation of **2**. This paramagnetic product, which was produced in only 20% yield, exhibited no ^1H NMR evidence for the C_5Me_5 ring of **2**; however, NMR did serve to indicate the absence of **1**. The identification of **2** was based largely on its IR spectrum, which was identical with that obtained for an authentic mono(C_5Me_5) compound (**3**; vide infra). As further (chemical) evidence of this formulation, and in search of a higher yield synthesis, we sought to prepare **2** from **1** as shown in eq 4. This con-

$$[Li(ether)_2][(C_5Me_5)_2CeCl_2] + CeCl_3 \rightarrow \mathbf{2} + LiCl \quad (4)$$

proportionation route is useful for the preparation of both titanium compounds of general formula $(C_5R_5)TiCl_3$ (R = H, Me) from the $(C_5R_5)_2TiCl_2$ derivatives[31] but does not proceed for either zirconium analogue.[31,32] For cerium this reaction does yield **2** as the only identifiable organometallic product. While the yield is improved somewhat, it is still only ca. 45%; after the 55% yield for production of **1** is factored in, the route of eq 4 is only slightly better than the route of eq 3. (Both yield **2** in overall 20–25% yield based on $CeCl_3$ or $(C_5Me_5)Li$ initially used. We have subsequently improved the yield to ca. 45%; details are given in the Experimental Section.) Nonetheless, the conproportionation reaction (eq 4) is consistent with the claim that **2** is a mono(ring) product.

To determine if **2** is indeed the monomeric species sought, we pursued crystallographic verification of its structure. While it proved possible to grow crystals from a THF/ether mixture, these cracked immediately upon removal from the liquid. This is attributed to ready loss of either cerium-bound or lattice THF molecules, and we note that **2** shows no evidence of THF content if it is subjected to prolonged evacuation. As an alternative to crystallographic verification, the molecular weight of **2** was determined in THF solution via the Signer isothermal distillation method.[33] These determinations indicated a monomeric formulation for **2** in this solvent. Unfortunately, we were unable to perform such studies in other

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solvents because **2** precipitates before equilibrium is reached. We interpret these data as resulting from a monomer–oligomer equilibrium (eq 5) which equilibrates

$$y(C_5Me_5)CeCl_2(THF)_3 \rightleftharpoons [(C_5Me_5)CeCl_2(THF)_x]_y + y(3 - x)THF \quad (5)$$

rather slowly at room temperature. Thus, while **2** is monomeric in THF, it loses ligated THF and oligomerizes in other solvents. After being stirred in toluene (ca. 2–3 h), the oligomeric **2** precipitates and is found to dissolve in THF only after several hours of stirring. This ready loss of ligated THF has been observed by Raymond in the aforementioned $[(COT)Ce(THF)_2(\mu\text{-}Cl)]_2$, which was found to lose THF upon evacuation.[19] We have also attempted to prepare a diamagnetic lanthanum analogue so as to pursue NMR studies. This system behaves in a manner similar to the cerium compounds discussed above, with NMR indicating the isolation of two products in a 3:2 ratio (by integration of the C_5Me_5 resonances, which are found at 2.04 and 2.00 ppm in THF-d_8). We have been unable to separate these, and we tentatively suggest that the two products are the components of an equilibrium similar to that represented in eq 5. However, this cannot be driven to the left even in neat THF, perhaps because the larger size of the lanthanum nucleus favors aggregation. While we are unable to exclude rigorously an alternative explanation involving the presence of ionic $[Li(ether)][(C_5Me_5)LnCl_3]$ as one component of the mixture, comparison of the IR data for this system with the spectrum of **3** (vide infra) suggests the explanation given above.

Reasoning that increased steric bulk was required to stabilize monomeric mono(ring) compounds, we sought to replace the chlorides in **2** with larger halides. This required the availability of anhydrous lanthanide salts of these other halides. Attempts at drying commercially available $LnI_3{\cdot}9H_2O$ by heating in vacuo result in partial hydrolysis to polymeric oxoiodide $(LnOI)_n$; while the iodides can be dried with ammonium iodide at elevated temperatures,[34] we sought instead to prepare the iodides under anhydrous conditions. As such, we employed a variation of the methods of Namy et al. (who prepared THF solutions of SmI_2 and YbI_2 from the metals and diiodoethane),[35a] and of Evans et al. (who found that lanthanum and cerium metal reacted with iodoethane at room temperature to give mixtures of metal alkyls and halides).[35b] Indeed, metal chips react readily with various alkyl iodides in THF solution; moreover, there is no need to activate the metal in any way. For convenience, the syntheses (eq 6) are carried

$$2Ln + 6C_2H_5I \xrightarrow[THF]{} 2LnI_3(THF)_x + 3C_2H_4 + 3C_2H_6 \quad (6)$$

out with excess ethyl iodide, which can be easily removed in vacuo. Under these conditions (refluxing THF) we see no evidence for the presence of metal alkyls.[35b] After Soxhlet extraction, the iodides are readily isolated as colorless, crystalline THF solvates in ca. 80–90% yield (based on metal added, nearly all of which is consumed). These species are quite sensitive to atmospheric moisture but are indefinitely stable under nitrogen. Elemental analyses on the crystalline compounds suggest a value for x of 4 but do not distinguish between alternate formulations $LnI_3(THF)_4$ and $LnI_3(THF)_3{\cdot}(THF)$. We suspect the latter by analogy with the $MCl_3(THF)_3$ compounds of the early transition metals;[36] moreover, the IR spectra reported for the transition-metal complexes are nearly identical with those we obtain for $LnI_3(THF)_x$. The advantage of these species vs. the unsolvated, presumably oligomeric, anhydrous salts is that the solvates are reasonably soluble in organic solvents and less prone to undergo disproportionation reactions upon replacement of the halides with organic moieties.[36]

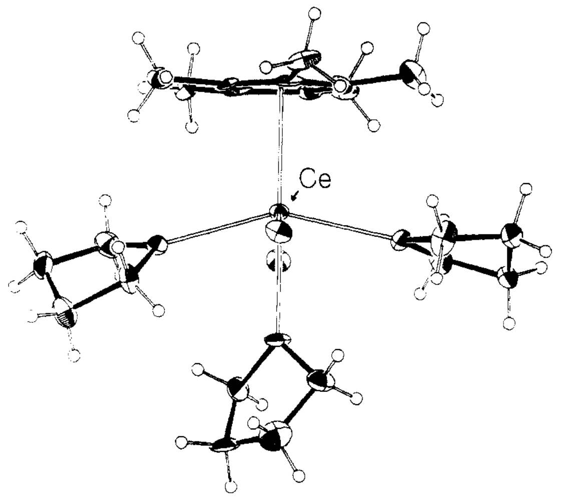

Figure 1. ORTEP drawing of $(C_5Me_5)CeI_2(THF)_3$ (**4**) with a view along the I–Ce–I containing plane.

In a related context, we note that $CeCl_3$ has proven highly effective in mediating the addition of alkyl Grignards and lithium reagents to ketones and enones.[37–44] Specifically, use of $CeCl_3$ precludes ketone enolization and 1,4 addition to enones, while cerium(III) iodide is effective in coupling α-haloketones with aldehydes. Many of the experimental methods call for prolonged stirring of the anhydrous $CeCl_3$ in THF; in the coupling reactions, cerium(III) iodide was generated from cerium metal and I_2 in THF solution.[42] Since we have isolated our crystalline THF adducts from a related reaction, we suggest that similar adducts are probably precursors in the important synthetic reactions.

The anhydrous iodides undergo ready reaction with $(C_5Me_5)K$ as depicted in eq 7. The products are extracted

$$LnI_3(THF)_x + (C_5Me_5)K \rightarrow \underset{\substack{\mathbf{3},\ Ln\ =\ La \\ \mathbf{4},\ Ln\ =\ Ce}}{(C_5Me_5)LnI_2(THF)_3} \quad (7)$$

from KI in toluene and crystallized from THF/ether as large, colorless (**3**) or yellow-green (**4**) cubes. These crystals do not show the tendency to lose THF that compound **2** does, but when subjected to prolonged evacuation, the THF ligands are removed to give a compound best for-

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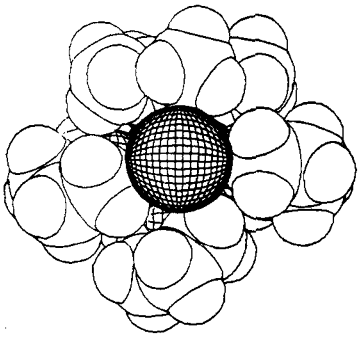

Figure 2. Space-filling model of 4 with a perspective similar to that in Figure 1. Cross-hatching indicates the iodide on the near side of the molecule.

mulated as $[(C_5Me_5)LnI_2(THF)_x]_y$ (with $x < 1$), as indicated by elemental analysis. As a precaution, crystals for X-ray diffraction were dried at atmospheric pressure in the glovebox to avoid THF loss. As with compound 2, prolonged stirring in toluene causes precipitation. Attempts to obtain NMR spectra for 3 in C_6D_6 were hampered by this problem; the solutions showed evidence of liberated THF, but no evidence for the La-bound C_5Me_5 group (a colorless precipitate was evident). In THF-d_8 no precipitation occurred and the spectrum showed signals for proteo-THF as well as C_5Me_5.

To confirm the stoichiometry and assign the geometry of these compounds, crystallographic studies were performed on the cerium analogue 4. As noted in the Experimental Section, the compound crystallized with two independent molecules in the unit cell. These differ only in the orientation of one of the equatorial THF ligands, the difference corresponding to a rotation about the Ce–O bond. The solid-state structure of one of the molecules is depicted in Figure 1, which gives a view of the molecule along the I–Ce–I plane. As is evident, the molecule is monomeric in the solid state with the Ce(III) ion coordinated by two iodide ions, three THF oxygen atoms, and the η^5-C_5Me_5 group. While the latter can be considered to occupy three coordination sites (giving a coordination of eight), the geometry of a species like 4 is usually described as pseudooctahedral with the ring occupying a single site. Within the latter framework, the compound can be identified as the *mer,trans* isomer. This is the expected isomer based on steric considerations advanced by Ernst et al. in their discussion of the structure of $(C_5H_4Me)UCl_3(THF)_2$.[45] They note that the equatorial groups tend to bend away from the bulky five-membered ring and toward the group in the position trans to the ring. As such, this position is expected to contain the smaller THF oxygen atom rather than the large halide, as is indeed observed for 4. The steric interaction between the ring and the equatorial groups is readily apparent from Figure 2, from which it is clear that the C_5Me_5 methyls are bent away from the rest of the molecule. Likewise, the equatorial groups are not situated 180° apart as would be expected in a perfect octahedron. As shown in Table II, the trans equatorial THF oxygens form an O–Ce–O angle of 152.93 (25)° while the iodides form an I–Ce–I angle of 152.18 (3)°. It is of interest to compare these values to the analogous angles in the closely related *mer,trans*-$(C_5H_5)ErCl_2(THF)_3$, for which the O–Er–O angle is 155.18 (11)° and the Cl–Er–Cl angle is 154.85 (4)°.[30] The similarity of these angles for the cerium and erbium compounds suggest that the larger C_5Me_5 and iodide ligands in 4 compensate well for the larger (relative to erbium) cerium ionic radius, a point illustrated by the space-filling drawing in Figure 2. In this regard it is interesting to note that these reactions with $(C_5Me_5)K$ (eq 7) show no tendency toward formation of ionic $[(C_5Me_5)LnI_3][K(ether)]$, even though Watson has observed formation of the ytterbium compound $[(C_5Me_5)YbI_3][Li(ether)]$.[26] This must reflect the fact that the lattice bonding in LiI is too weak to cause precipitation; we have seen that reaction of (C_5Me_5)*Li* with $CeI_3(THF)_x$ results in a yellow product without precipitation of LiI, but we have not characterized this species.

Table II. Selected Bond Lengths (Å) and Angles (deg) for $(C_5Me_5)CeI_2(THF)_3$[a,b]

	Bond Distances		
Ce–Cp	2.523 (13)	Ce–O(ax)	2.540 (8)
		Ce–O(eq)	2.511 (8)
Ce–C_4	2.749 (13)		2.566 (8)
Ce–C_5	2.785 (11)	Ce–I	3.2269 (12)
Ce–C_6	2.807 (12)		3.1733 (12)
Ce–C_7	2.844 (14)		
Ce–C_8	2.799 (12)		
	Bond Angles		
I–Ce–I	152.18 (3)	O(eq)–Ce–O(eq)	152.93 (25)
Cp–Ce–I	103.24 (8)	Cp–Ce–O(eq)	103.83 (26)
	104.57 (10)		103.14 (24)
I–Ce–O(ax)	75.41 (18)	Cp–Ce–O(ax)	179.79 (24)
	76.78 (18)		

[a] Subscripts indicate the specific atom referred to, with Cp referring to the C_5Me_5 center of gravity and the five carbons labelled as atoms 4–8. The notations ax (axial) and eq (equatorial) refer to groups which are trans and cis, respectively, to the C_5Me_5 ring. Number in parentheses is the standard deviation in the last significant digit.

In summary, we note that the steric demands of the ancillary ligands is critically important in determining the stability of monomeric pentamethylcyclopentadienyl complexes of the early lanthanides. From $LnCl_3$ (Ln = La, Ce) the bis(ring) compounds $[(C_5Me_5)_2LnCl_2][Li(ether)]$ are readily available, while the mono(ring) compounds appear as monomer–oligomer mixtures. Conversely, the anhydrous iodide complexes $LnI_3(THF)_x$ give rise to the mono(ring) compounds *mer,trans*-$(C_5Me_5)LnI_2(THF)_3$. We find the latter particularly interesting since there are relatively few examples of mono(ring) compounds of the larger lanthanides. If the THF ligands are considered labile (they are readily removed upon evacuation or dissolution of the compounds in another solvent), the molecules can be seen to have several potential coordination sites available along one hemisphere. As such, we expect them to be useful in the preparation of new derivatives and are pursuing studies of their organometallic and coordination chemistry.

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Registry No. 1, 102307-94-8; 3, 105472-88-6; 4, 105472-89-7; $(C_5Me_5)CeCl_2(THF)_2$, 105472-87-5; $LaI_3(THF)_4$, 105472-90-0; $CeI_3(THF)_4$, 105472-91-1.

Supplementary Material Available: BMFIT drawings of the two molecules and tables of crystal data, least-squares planes, positional and thermal parameters, and selected bond lengths and angles for 4 (15 pages); a listing of observed and calculated structure factors for 4 (17 pages). Ordering information is given on any current masthead page.

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