

Synthesis and X-ray Crystal Structure of an Unusual Oligomeric Bis(pentamethylcyclopentadienyl) Halide Complex of Cerium: $[(C_5Me_5)_2CeCl_2K(THF)]_n$

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The reaction of $CeCl_3$ with 2 equiv of KC_5Me_5 generates the oligomeric complex $[(C_5Me_5)_2CeCl_2K(THF)]_n$, which recrystallizes from THF under hexane diffusion in the space group Cc with unit-cell constants $a = 11.384$ (4) Å, $b = 28.875$ (8) Å, $c = 8.655$ (5) Å, $\beta = 100.75$ (6)°, $V = 2795.04$ Å³, and $Z = 4$ with $D_{calc} = 1.41$ g cm⁻³. Least-squares refinement on the basis of 1867 observed reflections led to a final R value of 0.024. The complex consists of $(C_5Me_5)_2Ce(\mu-Cl)_2K(THF)$ monomer units that oligomerize via additional interunit Cl to K coordination. The oligomerization generates five-coordinate potassium ions (four Cl ligands plus one THF) and μ_3-Cl ions. Each cerium ion is surrounded by two C_5Me_5 ligands and two Cl ligands in a roughly tetrahedral arrangement with average Ce-C(ring) and Ce-Cl distances of 2.79 (2) and 2.777 (1) Å, respectively. $[(C_5Me_5)_2CeCl_2K(THF)]_n$ may be sublimed at 195 °C and 4×10^{-6} Torr to give an orange toluene insoluble material. This orange material forms $(C_5Me_5)_2CeCl(THF)$ upon extraction with THF. The latter complex crystallizes from THF in space group $P1$ with unit-cell constants $a = 8.578$ (3) Å, $b = 17.448$ (7) Å, $c = 18.707$ (6) Å, $\alpha = 62.69$ (2)°, $\beta = 89.31$ (3)°, $\gamma = 89.03$ (3)°, and $V = 2487.5$ Å³.

One of the guiding concepts that has been useful in developing the organometallic chemistry of the lanthanide elements is the correlation of stability with steric saturation.²⁻⁶ Complexes in which the coordination environment of the metal is completely filled by ligands are, in general, most stable and readily isolable. Many of the early studies of organolanthanide chemistry have involved the smaller later elements in the series, Er-Lu, because steric saturation can be more readily achieved with these smaller metals.

As an example, the bis(cyclopentadienyl) halide complexes $[(C_5H_5)_2LnCl]_2$ are known only for $Ln = Sm-Lu$.⁷⁻¹⁰ For the larger metals, La-Nd, the $(C_5H_5)_2Cl$ ligand set does not sterically saturate the metal coordination environment and $[(C_5H_5)_2LnCl]_2$ complexes of these metals are thought to redistribute their ligands to form the more sterically saturated $(C_5H_5)_3Ln$ complexes.^{7,11} Only recently has a $(C_5H_5)_2NdCl$ derivative been characterized in a higher coordinate solvated form: $[(C_5H_5)_2Nd(\mu-Cl)(THF)]_2$.¹² Since $[(C_5H_5)_2LnCl]_2$ complexes are important precursors to lanthanide alkyl and hydride species,^{2,8-11,13} their absence has limited development of this type of chemistry with the early lanthanides.

In terms of cost and abundance, it was somewhat unfortunate that the early lanthanides were not so chemically accessible. The elements La through Nd are far more abundant in the earth's crust than the later lanthanides,¹⁴ and commercial mining operations naturally produce much more of the salts of the early lanthanide metals than of the late lanthanides.^{15,16}

Recently, however, progress has been made in early lanthanide organometallic chemistry by using sterically bulkier ligands. Specifically, when the size of the cyclopentadienyl ring is increased or when bridged dicyclopentadienyl units are used, $(C_5R_5)_2LnX$ derivatives (X = halide) have been obtainable for $Ln = La-Nd$.¹⁷⁻²⁸ The X-ray crystal structures of some of these complexes have been reported including $\{[1,3-(Me_3Si)_2C_5H_3]_2Pr(\mu-Cl)_2\}_2$,²⁰ $[1,3-(Me_3Si)_2C_5H_3]_2Nd(\mu-Cl)_2Li(THF)_2$,²¹ $\{[1,3-(Me_3Si)_2C_5H_3]_2NdCl_2\}(AsPh_4)_2$,²² $(C_5Me_5)_2Pr(\mu-Cl)_2Na(DME)_2$,²⁵ and $(C_5Me_5)_2Ce(\mu-Cl)_2Li(Et_2O)_2$.^{26,27}

Cerium is one of the most important of the early lanthanides, not only because of its abundance and com-

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mercial importance but also because it has two accessible oxidation states. In the course of preparing some bis-(pentamethylcyclopentadienyl) halide starting materials of cerium, we have obtained the crystal structure of an unusual oligomerized form of the $(C_5Me_5)_2CeCl_2^-$ anion. We report here the details of this remarkable structure which may derive from a $[(C_5Me_5)_2CeCl_2K(THF)_2]$ complex by solvent loss. Such desolvation often leads to insoluble products. In this case, it appears that we have trapped a desolvated species as it starts to oligomerize and become insoluble. This system shows the importance of the coordination environment of the alkali metal to oligomerization processes for complexes of this type.

Experimental Section

The complexes described below are extremely air- and moisture-sensitive. Therefore, all syntheses and subsequent manipulations of these compounds were conducted with the rigorous exclusion of air and water by using Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques.

Materials. Toluene, hexane, and THF were distilled from sodium benzophenone ketyl. C_6D_6 and THF- d_8 were vacuum transferred from sodium. Anhydrous cerium trichloride was prepared from the hydrate (Research Chemicals, Phoenix, AZ) by the method of Taylor and Carter.²⁹ KC_5Me_5 was prepared from C_5Me_5H (Strem) by using KH in THF.

Physical Measurements. Infrared spectra were obtained as previously described.³⁰ 1H NMR spectra were recorded by using a Bruker 250 MHz spectrometer and were referenced to residual β -methylene protons in C_6D_6O (δ 1.79). ^{13}C NMR spectra were obtained on a General Electric GN 500-MHz spectrometer, and assignments were made by using DEPT 45 experiments.³¹ All shifts are reported in parts per million. Room-temperature magnetic moments were obtained on a 250-MHz Bruker NMR spectrometer and calculated by using the Evans method.³² Complexometric titrations were obtained as previously described.³³ Molecular weight determination was done by using the Signer method.³³ Sublimation was carried out by using an apparatus described previously.³⁴

$[(C_5Me_5)_2CeCl_2K(THF)]_n$. In the glovebox, anhydrous $CeCl_3$ (375 mg, 1.52 mmol) was suspended in THF (25 mL). To this stirred suspension was added KC_5Me_5 (529 mg, 3.04 mmol). The mixture began to turn yellow immediately and was stirred for 24–48 h. The mixture was filtered to remove KCl, and the solvent was removed from the filtrate by rotary evaporation. The product, obtained as a yellow powder in 80% yield (643 mg), forms a yellow-green solution in THF and is slightly soluble in toluene in which it forms a yellow solution. Anal. Calcd for $CeC_{24}H_{38}Cl_2KO$: Ce, 23.6. Found: Ce, 25.0. Magnetic susceptibility: $\chi_m = 2560 \times 10^{-6}$ cgs; $\mu_{eff} = 2.48 \mu_B$. 1H NMR (THF- d_8): δ 4.03 (s br, $\Delta\nu_{1/2} = 20$ Hz). ^{13}C NMR (THF- d_8): δ 13.7 ($C_5(CH_3)_5$), no ring carbon resonance was observed. IR (KBr): 2880 (s), 1430 (m), 1370 (m), 1160 (w), 1040 (s), 885 (w) cm^{-1} . Crystals suitable for X-ray diffraction were obtained from a mixture of THF/hexane.

$(C_5Me_5)_2CeCl(THF)$. In the glovebox, a sample of $[(C_5Me_5)_2CeCl_2K(THF)]_n$ (206 mg, 0.348 mmol) was placed in a sublimation tube. This tube was removed from the glovebox, attached to a high vacuum line, and surrounded by a tube furnace. When the pressure was 4×10^{-5} Torr or less, the temperature of the tube was slowly raised to 195 °C. An orange product sublimed (126 mg) and a colorless powder that was insoluble in THF re-

Table I. Crystal Data For $[(C_5Me_5)_2CeCl_2K(THF)]_n$

formula	$CeKCl_2C_{24}H_{38}O$
fw	592.70
space group	Cc
cell constants	
<i>a</i> , Å	11.384 (4)
<i>b</i> , Å	28.875 (8)
<i>c</i> , Å	8.655 (5)
β , deg	100.75 (6)
<i>V</i> , Å ³	2795.04
molecules/unit cell	4
<i>D</i> (calcd), g cm ⁻³	1.41
μ (calcd), cm ⁻¹	19.96
radiatn	Mo K α
max cryst dimens, mm	0.20 × 0.12 × 0.25
scan width	0.80 + 0.20 tan θ
std reflectns	200, 040, 002
decay of stds	±2%
reflectns measd	1867
2 θ range, deg	2–44
obsd reflectns	1707
no. of parameters varied	258
GOF	0.86
<i>R</i>	0.024
<i>R</i> _w	0.029

mained in the bottom of the tube. The orange product, which is probably $[(C_5Me_5)_2CeCl]_n$, is insoluble in hexane and toluene. It dissolves in THF to form $(C_5Me_5)_2CeCl(THF)$ (146 mg, 80%), which is soluble in toluene and slightly soluble in hexane. Anal. Calcd for $C_{24}H_{38}CeClO$: Ce, 27.0. Found: Ce, 27.9. Isopiestic molecular weight: calcd, 593; found, 560. This material crystallizes from THF in space group $P\bar{1}$ with unit-cell constants $a = 8.578$ (3) Å, $b = 17.448$ (7) Å, $c = 18.707$ (6) Å, $\alpha = 62.69$ (2)°, $\beta = 89.31$ (3)°, $\gamma = 89.03$ (3)°, and $V = 2487.5$ Å³. The complex is isostructural with $(C_5Me_5)_2YCl(THF)$,³⁵ $(C_5Me_5)_2SmCl(THF)$,³⁶ and $(C_5Me_5)_2LuCl(THF)$.³⁶ Magnetic susceptibility: $\chi_m = 2090 \times 10^{-6}$ cgs; $\mu_{eff} = 2.24 \mu_B$. 1H NMR (THF- d_8): δ 4.40 (s br, $\Delta\nu_{1/2} = 25$ Hz). The 1H NMR spectrum in benzene- d_6 contains resonances with line widths of approximately 400 Hz. This makes it difficult to accurately assign shift values. In addition, the 1H NMR spectra are concentration-dependent. A sample, 40 mM in C_6D_6 , has broad resonances at 3.88 and –6.87 ppm. A sample of $(C_5Me_5)_2CeCl(THF)$ was taken up in THF- d_8 , and the solvent was removed. The 1H NMR spectrum in C_6D_6 exhibited only the δ 3.88 resonance. ^{13}C NMR (THF- d_8): δ 14.2 (s, $(C_5(CH_3)_5)$), no ring carbon resonance was observed. Crystals of $(C_5Me_5)_2CeCl(THF)$ sent for complete elemental analysis (Analytische Laboratorien, Engelskirchen, Germany) analyzed for the unsolvated species and presumably lost THF during the handling and drying process prior to analysis. Anal. Calcd for $CeC_{20}H_{30}Cl$: Ce, 31.42; C, 53.86; H, 6.78; Cl, 7.95. Found: Ce, 30.15; C, 54.69; H, 7.18; Cl, 7.93. Consistent with this, samples of $(C_5Me_5)_2CeCl(THF)$ change when placed under vacuum (2×10^{-5} Torr) at room temperature and are no longer very soluble in benzene. No signals were observed in the 1H NMR spectrum of a sample prepared from this material in C_6D_6 .

X-ray Crystallography of $[(C_5Me_5)_2CeCl_2K(THF)]_n$. A single crystal measuring 0.20 × 0.12 × 0.25 mm was sealed under N_2 in a thin-walled glass capillary. Final lattice parameters as determined from a least-squares refinement of $((\sin \theta)/\lambda)^2$ values for 25 reflections ($\theta > 18^\circ$) accurately centered on the diffractometer are given in Table I. Data were collected on an Enraf-Nonius CAD-4 diffractometer by the θ – 2θ scan technique. This method has been previously described.³⁷ A summary of data collection parameters is given in Table I. The intensities were corrected for Lorentz, polarization, and absorption effects. For the latter, an empirical method similar to that of Churchill was employed.³⁸

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Table II. Final Fractional Coordinates for $[(C_5Me_5)_2CeCl_2K(THF)]_n$

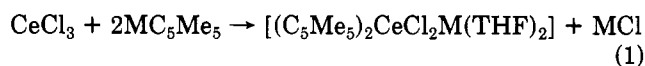
atom	x/a	y/b	z/c	$U(eq\text{v}), \text{\AA}^2$
Ce	0.0000	0.12971 (1)	0.7500	0.035 (3)
K	-0.1359 (2)	-0.01665 (8)	0.7014 (3)	0.057 (13)
Cl (1)	-0.0273 (3)	0.06219 (9)	0.5178 (3)	0.058 (13)
Cl(2)	-0.1433 (3)	0.07431 (9)	0.9007 (3)	0.056 (3)
Cp(1)	0.243 (1)	0.1544 (4)	0.840 (1)	0.048 (12)
Cp(2)	0.2432 (9)	0.1082 (4)	0.784 (1)	0.052 (5)
Cp(3)	0.1977 (9)	0.0786 (3)	0.889 (1)	0.043 (6)
Cp(4)	0.1719 (9)	0.1066 (4)	1.013 (1)	0.049 (9)
Cp(5)	0.198 (1)	0.1533 (4)	0.979 (2)	0.057 (3)
Cp(6)	-0.155 (2)	0.2033 (5)	0.763 (1)	0.088 (26)
Cp(7)	-0.057 (1)	0.2224 (4)	0.702 (2)	0.075 (27)
Cp(8)	-0.063 (1)	0.2049 (5)	0.553 (2)	0.086 (22)
Cp(9)	-0.159 (1)	0.1769 (5)	0.515 (2)	0.075 (4)
Cp(10)	-0.219 (1)	0.1759 (5)	0.642 (2)	0.073 (29)
Me(1)	0.300 (1)	0.1960 (5)	0.769 (2)	0.093 (36)
Me(2)	0.293 (1)	0.0931 (5)	0.641 (2)	0.079 (14)
Me(3)	0.190 (1)	0.0265 (4)	0.882 (2)	0.075 (26)
Me(4)	0.131 (1)	0.0889 (6)	1.162 (1)	0.086 (48)
Me(5)	0.195 (1)	0.1951 (5)	1.091 (2)	0.090 (8)
Me(6)	-0.197 (3)	0.2136 (9)	0.912 (2)	0.236 (108)
Me(7)	0.020 (3)	0.2613 (5)	0.783 (5)	0.197 (145)
Me(8)	0.028 (2)	0.2166 (8)	0.437 (3)	0.194 (22)
Me(9)	-0.203 (2)	0.1536 (7)	0.353 (2)	0.147 (61)
Me(10)	-0.336 (1)	0.1530 (9)	0.655 (4)	0.222 (138)
O	-0.370 (1)	-0.0387 (4)	0.657 (1)	0.118 (20)
C(1)	-0.431 (2)	-0.0757 (7)	0.572 (2)	0.123 (21)
C(2)	-0.514 (2)	-0.0936 (7)	0.675 (3)	0.132 (54)
C(3)	-0.529 (3)	-0.054 (1)	0.777 (3)	0.179 (31)
C(4)	-0.436 (3)	-0.019 (1)	0.763 (4)	0.211 (46)

Calculations were carried out with the SHELX system of computer programs.³⁹ Neutral atom scattering factors for Ce, K, O, and C were taken from Cromer and Waber,⁴⁰ and the scattering for cerium was corrected for the real and imaginary components of anomalous dispersion using the table of Cromer and Liberman.⁴¹ Scattering factors for H were from ref 42.

Systematic absences allow the choice of the centrosymmetric space group $C2/c$ or the noncentrosymmetric Cc . Structural solution and refinement was attempted in $C2/c$, but an appropriate structural model could not be derived. Solution of the structure in Cc proceeded successfully. The position of the cerium atom was revealed by inspection of a Patterson map, and the remaining non-hydrogen atoms were located on subsequent difference Fourier maps. Least-squares refinement with isotropic thermal parameters led to $R = \sum ||F_o| - |F_c|| / \sum |F_o| = 0.080$. Refinement of the non-hydrogen atoms with anisotropic thermal parameters led to final agreement factors of $R = 0.024$ and $R_w = 0.029$. Hydrogen atoms could not be located. A final difference Fourier showed no feature greater than $0.8 \text{ e}/\text{\AA}^3$. The weighting scheme was based on unit weights; no systematic variation of $w(|F_o| - |F_c|)$ vs $|F_o|$ or $(\sin \theta)/\lambda$ was noted. The final values of the positional parameters are given in Table II.

Results and Discussion

Synthesis. $CeCl_3$ has been reported to react with 2 equiv of KC_5Me_5 or LiC_5Me_5 in THF to form $[(C_5Me_5)_2CeCl_2M(THF)_2]$ according to eq 1 ($M = Li, K$).²⁶⁻²⁸ The lithium derivative can be recrystallized from



Et_2O to form $(C_5Me_5)_2Ce(\mu-Cl)_2Li(Et_2O)_2$ which has been

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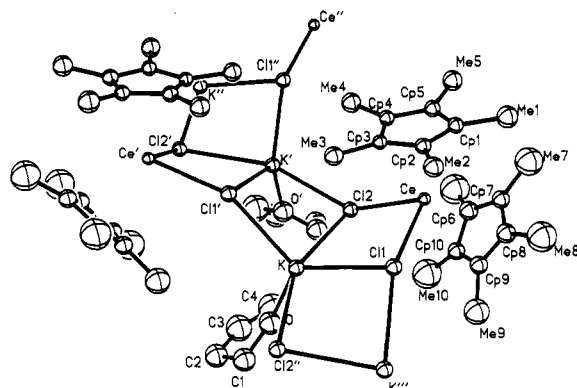


Figure 1. ORTEP diagram of two repeating units of $[(C_5Me_5)_2CeCl_2K(THF)]_n$ plus additional potassium, chloride, and cerium ions that complete the coordination spheres of the K and K' positions.

crystallographically characterized by two laboratories.^{26,27} The potassium derivative is reported to be less soluble and more difficult to extract from the product mixture in eq 1.²⁷ In our hands, removal of THF from this product by rotary evaporation gives a product with less than two THF ligands per molecule. Recrystallization from THF/hexane gives single crystals of the monosolvate $[(C_5Me_5)_2CeCl_2K(THF)]_n$, the structure of which is described below.

Sublimation of $[(C_5Me_5)_2CeCl_2K(THF)]_n$ at $195^\circ C$ forms a hexane- and toluene-insoluble product that dissolves in THF to form $(C_5Me_5)_2CeCl(THF)$. This complex was characterized by spectroscopic and analytical means, and single crystals were found to be isostructural with $(C_5Me_5)_2YCl(THF)$,³⁵ $(C_5Me_5)_2SmCl(THF)$,³⁵ and $(C_5Me_5)_2LuCl(THF)$.³⁶ This sublimation may proceed like that of $(C_5Me_5)_2YCl_2K(THF)_2$ which forms the crystallographically characterized $(C_5Me_5)_2Y(\mu-Cl)YCl(C_5Me_5)_2$.³⁴ The sublimable cerium complex may be $[(C_5Me_5)_2CeCl]_n$ in an oligomerized form that is insoluble in alkane and arene solvents. In contrast, the residue from the $CeCl_3/LiC_5Me_5$ reaction is reported to sublime to form $[(C_5Me_5)_2CeCl]_2$, which gives an NMR spectrum in THF different from the one we observe for $(C_5Me_5)_2CeCl(THF)$.²⁶ Variation in the result of subliming a lithium versus a potassium salt has also been observed in the $(C_5Me_5)_2YCl_2M(THF)_2$ system.^{34,43}

NMR Studies. The measurement of 1H NMR data on $Ce(III)$ complexes is complicated due to the paramagnetic nature of $Ce(III)$ ($4f^1, \mu_J = 2.54 \mu_B$).⁴⁴ This paramagnetism causes the NMR signals to shift and broaden. Too few NMR data have been obtained on crystallographically characterized complexes to make strong correlations. At present the following C_5Me_5 resonances have been reported in the literature for cerium complexes: in $THF-d_3$, $(C_5Me_5)_2Ce(\mu-Cl)_2Li(Et_2O)_2$, δ 3.99 ($\Delta\nu_{1/2} = 19 \text{ Hz}$);²⁷ $[(C_5Me_5)_2CeX_2(THF)_a]_b$ ($X = Cl, I$), no signal observed;²⁷ $[(C_5Me_5)_2Ce(\mu-Cl)]_2$, δ 2.95 (v br);²⁶ in C_6D_6 , $[(C_5Me_5)_2CeH]_2$, δ -1.0 (lw = 35 Hz);²⁸ in toluene- d_8 , $(C_5Me_5)_2CeCH(SiMe_3)_2$, δ 3.64, 3.29 (lw = 9 Hz).²⁸

$[(C_5Me_5)_2CeCl_2K(THF)]_n$ is only slightly soluble in toluene and gives no observable peaks in the 1H NMR when run in C_6D_6 , but in $THF-d_3$ it gives a broad singlet at 4.03 ppm with a half height width of 20 Hz. $(C_5Me_5)_2CeCl(THF)$ is soluble in toluene and hexane, but in C_6D_6 the 1H NMR resonances are approximately 400-Hz wide. In contrast, in $THF-d_3$ a 25-Hz wide signal is ob-

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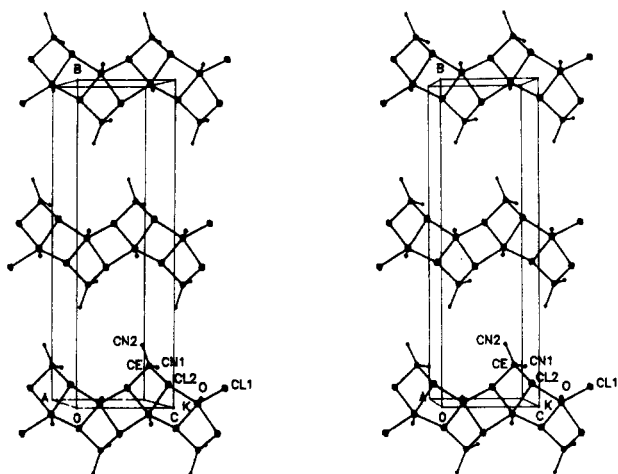


Figure 2. Stereoview of the packing diagram of $[(C_5Me_5)_2CeCl_2K(THF)]_n$. CN1 and CN2 represent the centroids of the C_5Me_5 rings.

served at 4.40 ppm. In C_6D_6 , the spectrum may be complicated by dissociation of the coordinated THF such that the magnetic environment experienced by the C_5Me_5 rings is not constant. In addition, the chemical shift appears to vary with concentration⁴⁵ although the broadness of the absorptions makes it difficult to accurately assign peak maxima.

X-ray Crystal Structure. The oligomeric solid-state structure of $[(C_5Me_5)_2CeCl_2K(THF)]_n$ (1), part of which is shown in Figure 1, can be conveniently described by comparison with the structure of the closely related monomeric $(C_5Me_5)_2Ce(\mu-Cl)_2Li(OEt_2)_2$ (2).²⁶ In 2, the two C_5Me_5 ring centroids and the two chloride atoms form a distorted tetrahedron around cerium. A distorted tetrahedral geometry also exists around lithium due to the two chloride atoms and the two ether molecules. In complex 1, the geometry around cerium is similar to that in 2 except that 2 has eclipsed C_5Me_5 rings (twist angle⁴⁷ of 0°) whereas 1 has rings which are almost completely staggered (twist angle of 32°). The geometry around the alkali-metal cation cannot be the same, however, since only one ether molecule (THF in this case) is available to coordinate to the potassium ion. Rather than crystallize as a monomer with a three-coordinate potassium center, the $(C_5Me_5)_2CeCl_2K(THF)$ units oligomerize via additional chloride bridging to bring the coordination number of potassium to five. Each chloride in 1 is a μ_3 -Cl that coordinates to one cerium and two potassium ions. The packing diagram in Figure 2 shows how the infinite chains in 1 are formed from the basic $(C_5Me_5)_2Ce(\mu_3-Cl)_2K(THF)$ unit. This oligomeric arrangement allows extra coordination to the potassium ion within the steric constraints of the large $(C_5Me_5)_2Ce$ units.

The bond distances and angles in 1 are given in Tables III and IV. The small differences found in the bond angles around cerium in 1 compared to those in 2 may arise due to the larger size of potassium versus lithium. Hence, the $(C_5Me_5 \text{ ring centroid})-Ce-(\text{ring centroid})$ angle in 1, 136° , is comparable to that in 2, 133° , but the $Cl(1)-Ce-Cl(2)$ angle of $86.52(8)^\circ$ is larger than that in 2, $81.7(1)^\circ$. The $Ce-Cl-K$ angles of $98.3(1)^\circ$ are also larger than the $Ce-$

Table III. Bond Distances (Å) in $[(C_5Me_5)_2CeCl_2K(THF)]_n$

Ce-Cl(1)	2.776 (2)	Ce-Cl(2)	2.778 (3)
Ce-Cp(1)	2.83 (1)	Ce-Cp(2)	2.80 (1)
Ce-Cp(3)	2.772 (9)	Ce-Cp(4)	2.79 (1)
Ce-Cp(5)	2.79 (1)	Ce-Cp(6)	2.78 (1)
Ce-Cp(7)	2.77 (1)	Ce-Cp(8)	2.77 (1)
Ce-Cp(9)	2.81 (1)	Ce-Cp(10)	2.82 (1)
K-Cl(1)'	3.157 (3)	K-Cl(1)	3.081 (3)
K-Cl(2)''	3.152 (3)	K-Cl(2)	3.077 (3)
K-O	2.70 (1)	Cp(1)-Cp(2)	1.42 (2)
Cp(1)-Cp(5)	1.39 (2)	Cp(1)-Me(1)	1.54 (2)
Cp(2)-Cp(3)	1.41 (1)	Cp(2)-Me(2)	1.52 (2)
Cp(3)-Cp(4)	1.42 (1)	Cp(3)-Me(3)	1.51 (1)
Cp(4)-Cp(5)	1.42 (2)	Cp(4)-Me(4)	1.53 (2)
Cp(5)-Me(5)	1.55 (2)	Cp(6)-Cp(7)	1.44 (2)
Cp(6)-Cp(10)	1.40 (2)	Cp(6)-Me(6)	1.48 (2)
Cp(7)-Cp(8)	1.37 (2)	Cp(7)-Me(7)	1.52 (2)
Cp(8)-Cp(9)	1.36 (2)	Cp(8)-Me(8)	1.60 (2)
Cp(9)-Cp(10)	1.39 (2)	Cp(9)-Me(9)	1.55 (2)
Cp(10)-Me(10)	1.51 (2)	O-C(1)	1.41 (2)
O-C(4)	1.40 (2)	C(1)-C(2)	1.51 (3)
C(2)-C(3)	1.48 (3)	C(3)-C(4)	1.46 (3)

Table IV. Bond Angles (deg) in $[(C_5Me_5)_2CeCl_2K(THF)]_n$

Cl(1)-Ce-Cl(2)	86.52 (8)	Cl(1)'-K-Cl(1)	128.7 (1)
Cl(1)'-K-Cl(2)''	74.2 (1)	Cl(1)'-K-Cl(2)'	85.2 (1)
Cl(1)-K-Cl(2)''	85.2 (1)	Cl(2)''-K-Cl(2)	156.1 (1)
Cl(1)-K-Cl(2)	117.6 (1)	Cl(1)'-K-O	124.6 (3)
Cl(2)''-K-O	98.4 (2)	Cl(1)-K-O	104.3 (1)
Cl(2)-K-O	83.2 (3)	Ce'-Cl(1)''-K'	98.3 (1)
K-Cl(1)''-K'	90.6 (1)	Ce-Cl(1)-K	156.3 (1)
Ce-Cl(2)-K'	98.3 (1)	K-Cl(2)-K'	90.7 (1)
Ce-Cl(2)-K	141.5 (1)	Cp(2)-Cp(1)-Me(1)	125 (1)
Cp(5)-Cp(1)-Me(1)	128 (1)	Cp(2)-Cp(1)-Cp(5)	107 (1)
Cp(1)-Cp(2)-Cp(3)	109 (1)	Cp(1)-Cp(2)-Me(2)	125 (1)
Cp(3)-Cp(2)-Me(2)	126 (1)	Cp(2)-Cp(3)-Cp(4)	107.1 (9)
Cp(2)-Cp(3)-Me(3)	127 (1)	Cp(4)-Cp(3)-Me(3)	126 (1)
Cp(3)-Cp(4)-Cp(5)	107.4 (9)	Cp(3)-Cp(4)-Me(4)	126 (1)
Cp(5)-Cp(4)-Me(4)	127 (1)	Cp(1)-Cp(5)-Cp(4)	109 (1)
Cp(1)-Cp(5)-Me(5)	125 (1)	Cp(4)-Cp(5)-Me(5)	125 (1)
Cp(7)-Cp(6)-Me(6)	130 (2)	Cp(10)-Cp(6)-Me(6)	123 (2)
Cp(7)-Cp(6)-Cp(10)	106 (1)	Cp(6)-Cp(7)-Cp(8)	108 (1)
Cp(6)-Cp(7)-Me(7)	122 (3)	Cp(8)-Cp(7)-Me(7)	129 (3)
Cp(7)-Cp(8)-Cp(9)	110 (1)	Cp(7)-Cp(8)-Me(8)	126 (2)
Cp(9)-Cp(8)-Me(8)	124 (2)	Cp(8)-Cp(9)-Cp(10)	108 (1)
Cp(8)-Cp(9)-Me(9)	126 (2)	Cp(10)-Cp(9)-Me(9)	126 (2)
Cp(6)-Cp(10)-Cp(9)	109 (1)	Cp(6)-Cp(10)-Me(10)	122 (2)
Cp(9)-Cp(10)-Me(10)	129 (2)	K-O-C(1)	129 (1)
K-O-C(4)	117 (1)	C(1)-O-C(4)	112 (2)
O-C(1)-C(2)	104 (2)	C(1)-C(2)-C(3)	104 (2)
C(2)-C(3)-C(4)	108 (2)	O-C(4)-C(3)	105 (2)

Cl-Li angle of $89(1)^\circ$ in 2. The (ring centroid)-Ce-Cl angles that range from 105.4 to 106.2° in 1 are indistinguishable from those in 2, 107° .

In contrast to the angular data that are similar or slightly larger in 1 compared to 2, the bond distances in 1 are smaller. Hence, Ce-C(ring) distances range from 2.77 (1) to 2.83 (1) Å and average 2.79 (2) Å in 1, whereas in 2 a 2.80 (3)-2.89 (4) Å range with a 2.84 (4) Å average is observed. The Ce-Cl distances of 2.776 (2) and 2.778 (3) Å in 1 are similarly shorter than those in 2, 2.812 (1) Å. This is particularly unusual since the chloride atoms in 1 are triply bridging compared to doubly bridging in 2 and increased bridging tends to give longer bond lengths in complexes of this type.^{34,46,48,49}

It is possible that these bond length differences result because the bond lengths in 2 are unusually long. Comparison of the lengths in 2 versus those in the isostructural $(C_5Me_5)_2Yb(\mu-Cl)_2Li(Et_2O)_2$ (3)⁵⁰ also indicate that the

(45) A situation of this type is observed for the $(C_5Me_5)_2SmCl(THF) = (C_5Me_5)_2SmCl + THF$ system.⁴⁶

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lengths in **2** are abnormally long. Addition of the 0.176 Å difference in radii between Ce(III) and Yb(III) to the Yb-C(ring) and Yb-Cl distances in **3** gives values similar to those found in **1**, not in **2**. Eight-coordinate $(C_5Me_5)_2CeI_2(THF)_3$ ²⁷ also has a Ce-C(ring) average [2.80 (3) Å] closer to that of **1** than **2**.

The five-coordinate geometry around potassium is not regular and displays major distortions from either square-pyramidal or trigonal-bipyramidal idealized geometries. In Figure 1, the geometry around potassium can be viewed as a distorted trigonal bipyramid in which Cl(2) and Cl(2)' are the axial ligands and Cl(1), Cl(1)', and THF are at the equatorial positions. The angles in the plane, Cl(1)-K-Cl(1)', 128.7 (1)°, Cl(1)-K-O, 104.3 (3)°, and O-K-Cl(1)', 124.6 (2)°, are reasonably close to the 120° angles of a trigonal bipyramid. However, the Cl(2)-K-Cl(2)' angle of 156.1 (1)° is not near the theoretical 180° angle for this geometry. The orientation of the ligands around potassium is such that the THF ligand is pointing away from the $(C_5Me_5)_2Ce$ unit. This is sterically optimal.

The K-Cl distances in **1** fall into two ranges. The distances within the $(C_5Me_5)_2CeCl_2K(THF)$ unit, K-Cl(1), 3.081 (3) Å, and K-Cl(2), 3.077 (3) Å, are in the range expected in comparison to Li-Cl distances in **2** and **3** after the difference in alkali-metal radii is taken into account.^{51,52} The K-Cl bonds that connect the $(C_5Me_5)_2CeCl_2K(THF)$ units, K-Cl(1)', 3.157 (3) Å, and K-Cl(2)', 3.152 (3) Å, are longer. The K-O(THF) distance of 2.70 (1) Å is in the range of K-O(THF) values in the literature: Co(*n*-Pr-Salen)K(CO)₂(THF),⁵³ six-coordinate potassium, 2.70 (2) Å, K[(C₆H₅)₂PCHP(C₆H₅)₂CH(NC₅H₄)](THF)₂,⁵⁴ five- to seven-coordinate potassium, 2.620 (7) and 2.745 (9) Å; [C₅Me₅Rh(CO)]₂K₂(THF)₂,⁵⁵ three-coordinate potassium,

2.74 (6)-2.840 (7) Å; Cr(C₂Ph₂)(C₄Ph₄)(CO)₂K(dibenzo-18-crown-6)(THF),⁵⁶ eight-coordinate potassium, 2.680 (7) Å; [K(pinacoloneolate)(THF)]₈,⁵⁷ four-coordinate potassium, 2.731 (9) and 2.747 (4) Å.

Conclusion

The particular product obtained from the synthesis of a " $(C_5Me_5)_2CeCl$ " material is a sensitive function of the alkali metal used and the method in which the sample is handled and recrystallized. Alkali-metal halide adducts as well as the " $(C_5Me_5)_2CeCl$ " unit alone can be obtained, and both systems can exist in various levels of solvation. Clearly, the development of the chemistry of the $(C_5Me_5)_2Ce$ unit will require careful attention to experimental details.

The structure of $[(C_5Me_5)_2CeCl_2K(THF)]_n$ provides one fully characterized example of how desolvation can lead to oligomerization in these systems. This result helps to explain why molecules of this type sometimes become insoluble upon loss of solvent. Complete desolvation could lead to oligomerization in three dimensions giving an insoluble material.

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Supplementary Material Available: A table of thermal parameters (1 page); a listing of structure factor amplitudes (10 pages). Ordering information is given on any current masthead page.

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Preliminary Chemical Study of (2-Oxo-1,2-dihydrophosphete(*P-W*))pentacarbonyltungsten Complexes

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The chemistry of the new four-membered 2-oxo-1,2-dihydrophosphete ring has been investigated in two P-W(CO)₅ complexes. All reactions which have been observed take place at the P-C(O) bond. Hydrolysis gives the corresponding open-chain carboxylic acids. Reduction by $(AlH_3)_n$ at -60 °C in ether gives the corresponding cyclic alcohols as mixtures of two isomers. The 3,4-diphenyl-substituted ring reacts with NaBH₄ at room temperature to yield two isomeric 1,2-oxaphospholenes. The more strained 3,4-diethyl-substituted ring gives the open-chain primary alcohol. It appears that the reactivity of the P-C(O) bond is controlled by the substitution scheme.

In a preliminary note,¹ we recently have described the insertion of carbon monoxide into one of the internal P-C

bonds of phosphirene *P* complexes (1). This led to the previously unknown 2-oxo-1,2-dihydrophosphete ring (2).