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Studies on Organolanthanide Complexes. 53.[1] Effect of Rare Earth Metal Radius on the Molecular Structure: Synthesis and X-ray Crystal Structure of Bis((2-methoxyethyl)cyclopentadienyl) Rare Earth Metal Chlorides

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The bis((2-methoxyethyl)cyclopentadienyl) rare earth metal chlorides $(CH_3OCH_2CH_2C_5H_4)_2LnCl$ [Ln = La (**1**), Pr (**2**), Nd (**3**), Sm (**4**), Gd (**5**), Dy (**6**), Ho (**7**), Er (**8**), Tm (**9**), Yb (**10**), Lu (**11**), Y (**12**)] were synthesized by treating the respective rare earth metal trichlorides with 2 equiv of ((2-methoxyethyl)cyclopentadienyl)sodium in THF. The new compounds have been characterized by elemental analyses, MS, IR and NMR spectra, as well as X-ray diffraction analyses of **1**, **6**, and **10**. **1** crystallizes from toluene in the monoclinic space group $P2_1/n$ (No. 14) with unit cell parameters $a = 8.726(1)$ Å, $b = 12.367(1)$ Å, $c = 14.562(3)$ Å, $\beta = 93.90(9)°$, and $V = 1567.8(2)$ Å^3 with $Z = 4$ for $D_{calcd} = 1.782$ g cm^{-3} and $R = 0.038$ for 6771 independent reflections with $[I > 3\sigma(I)]$. **6** and **10** crystallize from THF in the orthorhombic space group *Pnma* (No. 62) with unit cell parameters $a = 12.242(3)$ Å, $b = 11.723(6)$ Å, $c = 11.293(2)$ Å, and $V = 1620.7(2)$ Å^3 with $z = 4$ for $D_{calcd} = 1.821$ g cm^{-3} (**6**) and $a = 12.207(4)$ Å, $b = 11.705(3)$ Å, $c = 11.176(2)$ Å, and $V = 1596.8(6)$ Å^3 with $z = 4$ for $D_{calcd} = 1.892$ g cm^{-3} (**10**), respectively. Least-squares refinement led to a final R value of 0.027 for 1199 independent reflections $[I > 3\sigma(I)]$ for **6** and for 0.037 for 1118 independent reflections $[I > 3\sigma(I)]$ for **10**. The X-ray structure analyses show that complex **1** is dimer and the formal coordination number of lanthanum is 10, but complexes **6** and **10** are monomeric; the formal coordination number of dysprosium and ytterbium is nine. It indicates that the molecular structure of those chlorides depends on the radius of central metal.

Introduction

Organolanthanide chemistry currently is one of the most rapidly developing areas of organometallic chemistry.[2] In this field, unprecedented structural features and spectacular reactivity have been reported. For example, a number of literature reports have recently emerged concerning C–H activation, alkene and alkyne reduction, alkene polymerization, carbonyl activation, the hydrosilation reaction, and olefin hydroamination.[3]

Since $(C_5H_5)_2LnCl$ complexes are important precursors to lanthanide alkyl and hydride species, their chemistry have been received considerable attention. Many of the early studies of these complexes have mainly involved the smaller elements, in which steric saturation can be more readily achieved. Only recently has the solvated $(C_5H_5)_2NdCl$ been characterized in a higher coordinate form: $[(C_5H_5)_2NdCl(THF)]_2$.[4] Apparently, the earlier, larger lanthanides exhibit greater coordinate spheres than the later ones and require a greater degree of steric coordination. In spite of these limitations, chemists have still pursued early lanthanide chemistry. This is significant since the early lanthanide elements are more abundant in the earth's crust than the later ones.[5] Additionally, the efforts are in part spurred by the observation that the early lanthanides are very active catalysts for polymerization of dienes and highly substituted olefins.[6]

Recently, however, progress has been made in early lanthanide complexes by using sterically bulkier ligands. Generally, the stability of these complexes depends on the coordinate environment of the lanthanide metal. When the size of the cyclopentadienyl ring is increased or when bridged dicyclopentadienyl units are

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used, $(C_5R_5)_2LnX$ derivatives (X = halides) have been obtained for Ln = La–Nd.[3d,e,7–18] Furthermore, our previous studies showed that the complexes having heteroatom-containing bridges, such as $O(CH_2CH_2C_5H_4)_2LnCl$, were more stable, catalytically more active, and solvent-free organolanthanide complexes because an intramolecular coordination from that oxygen atom could satisfy the part of the open coordination sphere of lanthanide metals.[17]

With these effects in mind, we reasoned that a sterically demanding ligand environment and oxophilicity of the metal may greatly enhance the stability of the complexes formed. Therefore, we decided to select $CH_3OCH_2CH_2C_5H_5$ as ligand, by which the formation of an intramolecular coordination bond between oxygen and metal atom can take place, resulting in an increase of the coordination number of the central metal and steric effects so as to satisfy the coordination saturation of early lanthanide metals. We now report on the synthesis of bis((2-methoxyethyl)cyclopentadienyl)lanthanide chlorides containing large and small lanthanide cations (Ln = La, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, Yb, Lu, and Y), as well as the X-ray structure determinations of dimeric $[(CH_3OCH_2CH_2C_5H_4)_2LaCl]_2$ and monomeric $(CH_3OCH_2CH_2C_5H_4)_2LnCl$ (Ln = Dy, Yb). Some of this work has been previously communicated.[18]

Experimental Section

The complexes described in this paper are air and moisture sensitive; therefore, all syntheses and subsequent manipulations were performed under purified, oxygen-free argon by using Schlenk and vacuum line techniques. Solvents were distilled from sodium benzophenone ketyl prior to use. THF-d_8 was transfered under vacuum from sodium–potassium alloy. NMR spectra were recorded on a FX-90Q (90MHz) instrument at room temperature. H chemical shift values are reported in parts permillion and referenced to residual protons in deuteriated solvents THF-d_8 = 1.73 ppm. ^{13}C chemical shift values were referenced to THF-d_8 = 67.39 ppm. Infrared spectra were obtained as previously described.[17] Mass spectra were recorded on a Finnigan 4201 spectrometer at EI, T = 50–200 °C, and EM = 1.3 kV, and the m/z values assigned to Ln containing ions are the most intense peaks of clusters with the correct isotope patterns. Analyses of rare earth metals were accomplished using a direct complexometric titration procedure with Na_2 EDTA.[17] Carbon and hydrogen analyses were performed by the combustion method in an aluminium tube.[17]

$CH_3OCH_2CH_2C_5H_4Na$.[19] A solution of $CH_3OCH_2CH_2OTs$ (104.0 g, 0.45 mmol) in 100 mL of THF was added to a solution of C_5H_5Na (0.46 mmol) in 200 mL of THF with stirring under Ar. After the mixture was stirred for 4 h, H_2O (40 mL) was added and the organic phase was separated. The solvent was evaported and residue was distilled to give the colorless product (24.2 g): yield 44% (bp 40–41 °C (8 mmHg)).

A solution of $CH_3OCH_2CH_2C_5H_5$ (24.2 g) in 20 mL of THF was added to sodium sand (5.0 g, 0.22 mmol) and 40 mL of THF with stirring, which was cooled to 0 °C. After being stirred for 4 h, the mixture was warmed to room temperature, and stirring was continued for 2 h. The solvent was removed under vacuo, the residue was washed with 40 mL of hexane to give a white powder, 22.0 g. ^1H NMR (90 MHz, C_4D_8O): δ 2.50 (t, 2H), 3.05 (s, 3H), 3.28 (t, 2H), 5.18 (t, 2H), 5.31 (t, 2H). ^{13}C NMR (90 MHz, C_4D_8O): δ 32.75, 59.85, 77.46, 103.93, 104.42, 116.17. IR (cm^{-1}): 3060 (m), 2922 (s), 1458 (v), 1095 (s), 1077 (s), 1022 (m), 786 (v), 677 (s), 385 (w), 340 (w), 250 (m), 225 (s).

$(CH_3OCH_2CH_2C_5H_4)_2LaCl$ (1). At room temperature, 16.0 mL (19.6 mmol) of a THF solution of $CH_3OCH_2CH_2C_5H_4Na$ was slowly syringed into a suspension of 2.46 g (10.03 mmol) of anhydrous $LaCl_3$ in 40 mL of THF. The reaction mixture was stirred for 40 h. The solvent was then removed under vacuum, leaving a yellow residue. The dry residue was transfered into a sublimation apparatus. Sublimation at 170–200 °C (4 × 10^{-4} mmHg) gave 3.13 g of white crystals of **1** in 74% yield. ^1H NMR (90 MHz, C_4D_8O): δ 2.60 (t, 2H), 3.40 (s, 3H), 3.60 (t, 2H), 5.63 (s, 4H). ^{13}C NMR (90 MHz, C_4D_8O): δ 32.5, 62.4, 79.3, 112.7, 113.4, 127.0. IR (cm^{-1}): 3100 (m), 3080 (m), 3005 (m), 1445 (s), 1080 (m), 1045 (s), 1002 (w), 719 (vs), 370 (w), 330 (w), 240 (m), 220 (s). Anal. Calcd for $C_{16}H_{22}O_2LaCl$ (**1**): C, 45.67; H, 5.28; La, 33.02. Found: C, 45.32; H, 5.23; La, 32.41. MS (EI, 50–200 °C): m/z: 420 (46.69) M^+, 385 (25.04) $[M - Cl]^+$, 297 (100) $[M - CH_3OCH_2CH_2C_5H_4]^+$, 124 (3.19) $[CH_3OCH_2CH_2C_5H_5]^+$.

$(CH_3OCH_2CH_2C_5H_4)_2PrCl$ (2). This compound was prepared in a manner analogous to the description above, from 1.07 g (4.33 mmol) of $PrCl_3$ and 7.2 mL (8.6 mmol) of $CH_3OCH_2CH_2C_5H_4Na$/THF and stirred for 39 h at room temperature. Sublimation at 170–200 °C (4 × 10^{-4} mmHg) gave 1.3 g of pale-green crystals of **2** in 71% yield. IR (cm^{-1}): 3100 (m), 3010 (m), 2945 (s), 2900 (s), 1440 (s), 1380 (s), 1205 (m), 1060 (s), 1045 (s), 992 (m), 965 (vs), 830 (s), 815 (vs), 775 (vs), 680 (m), 522 (w), 380 (m), 325 (s), 250 (s), 225 (s). Anal. Calcd for $C_{16}H_{22}O_2PrCl$ (**2**): C, 45.45; H, 5.26; Pr, 33.33. Found: C, 45.63; H, 5.16; Pr, 32.77. MS (EI, 50–200 °C): m/z 422 (60.50) M^+, 387 (41.09) $[M - Cl]^+$, 299 (100) $[M - CH_3OCH_2CH_2C_5H_4]^+$, 124 (46.08) $[CH_3OCH_2CH_2C_5H_5]^+$.

$(CH_3OCH_2CH_2C_5H_4)_2NdCl$ (3). This compound was prepared in a manner analogous to the description above, from 2.52 g (10.00 mmol) of $NdCl_3$ and 16.6 mL (19.9 mmol) of $CH_3OCH_2CH_2C_5H_4Na$/THF and stirred for 38 h at room temperature. Sublimation at 170–200 °C (4 × 10^{-4} mmHg) gave 2.98 g of purple crystals of **3** in 70% yield. IR (cm^{-1}): 3100 (m), 3080 (m), 3015 (m), 2945 (s), 2920 (s), 1440 (s), 1380 (s), 1200 (m), 1060 (s), 1045 (s), 992 (m), 965 (vs), 830 (s), 815 (s), 780 (vs), 680 (m), 525 (w), 380 (m), 330 (s), 255 (s), 225 (s). Anal. Calcd for $C_{16}H_{22}O_2NdCl$ (**3**): C, 45.01; H, 5.22; Nd, 33.85. Found: C, 45.62; H, 5.31; Nd, 33.44. MS (EI, 50–200 °C): m/z 425 (56.47) M^+, 390 (40.66) $[M - Cl]^+$, 302 (100) $[M - CH_3OCH_2CH_2C_5H_4]^+$, 124 (6.39) $[CH_3OCH_2CH_2C_5H_5]^+$.

$(CH_3OCH_2CH_2C_5H_4)_2SmCl$ (4). This compound was prepared in a manner analogous to the description above, from 1.33 g (5.20 mmol) of $SmCl_3$ and 8.5 mL (10.2 mmol) of $CH_3OCH_2CH_2C_5H_4Na$/THF and stirred for 38 h at room temperature. Sublimation at 170–200 °C (4 × 10^{-4} mmHg) gave 1.88 g of golden-yellow crystals of **4** in 69% yield. IR (cm^{-1}): 3100 (m), 3080 (m), 3020 (m), 2955 (s), 2920 (s), 1440 (s), 1380 (s), 1200 (m), 1060 (s), 1045 (s), 995 (w), 965 (s), 830 (m), 817 (s), 778 (vs), 680 (m), 525 (w), 380 (m), 330 (s), 255 (s), 230 (s). Anal. Calcd for $C_{16}H_{22}O_2SmCl$ (**4**): C, 44.46; H, 5.14; Sm, 34.79. Found: C, 44.84; H, 5.20; Sm, 35.36. MS (EI, 50–200 °C): m/z: 433 (50.22) M^+, 398 (49.93) $[M - Cl]^+$, 310 (92.16) $[M - CH_3OCH_2CH_2C_5H_4]^+$, 124 (8.51) $[CH_3OCH_2CH_2C_5H_5]^+$.

$(CH_3OCH_2CH_2C_5H_4)_2GdCl$ (5). This compound was prepared in a manner analogous to the description above, from 2.24 g (8.50 mmol) of $GdCl_3$ and 14.1 mL (16.9 mmol) of $CH_3OCH_2CH_2C_5H_4Na$/THF and stirred for 30 h at room temperature. Sublimation at 170–200 °C (4 × 10^{-4} mmHg) gave 2.98 g of colorless crystals of **5** in 80% yield. IR (cm^{-1}): 3100 (m), 3080 (m), 3030 (m), 2945 (s), 2910 (s), 1440 (s), 1380 (s), 1205 (m), 1060 (s), 1045 (s), 995 (w), 970 (s), 840 (m), 820 (s), 780 (vs), 685 (m), 525 (w), 385 (m), 335 (s), 255 (s), 230 (s). Anal. Calcd for $C_{16}H_{22}O_2GdCl$ (**5**): C, 43.76; H, 5.06; Gd, 35.81. Found: C, 43.88; H, 5.11; Gd, 36.52. MS (EI, 50–200 °C): m/z 439 (50.22) M^+, 406 (37.82) $[M - Cl]^+$, 316 (100) $[M - CH_3OCH_2CH_2C_5H_4]^+$, 124 (4.80) $[CH_3OCH_2CH_2C_5H_5]^+$.

$(CH_3OCH_2CH_2C_5H_4)_2DyCl$ (6). This compound was prepared in a manner analogous to the description above, from 1.03 g (3.80 mmol) of $DyCl_3$ and 6.2 mL (7.4 mmol) of $CH_3OCH_2CH_2C_5H_4Na$/THf and stirred for 40 h at room temperature. Sublimation at 170–200 °C (4 × 10^{-4} mmHg) gave 1.7 g of pale-yellow crystals of **6** in 60% yield. IR (cm^{-1}): 3100 (m), 3092 (s), 3018 (s), 2945 (s), 2914 (s), 2830 (s), 1437 (s), 1058 (s), 1044 (s), 781 (vs), 683 (m), 525 (w), 385 (m), 335 (s), 255 (s), 230 (s). Anal. Calcd for $C_{16}H_{22}O_2DyCl$ (**6**): C, 43.25; H, 4.99; Dy, 36.57. Found: C, 43.16; H, 5.04; Gd, 36.70. MS (EI, 50–200 °C): m/z 445

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(18.74) M$^+$, 410 (46.10) [M – Cl]$^+$, 322 (27.22) [M – $CH_3OCH_2CH_2C_5H_4$]$^+$, 124 (19.79) [$CH_3OCH_2CH_2C_5H_5$]$^+$.

($CH_3OCH_2CH_2C_5H_4$)HoCl (7). This compound was prepared in a manner analogous to the description above, from 1.32 g (4.87 mmol) of $HoCl_3$ and 6.2 mL (7.4 mmol) of $CH_3OCH_2CH_2C_5H_4Na$/THF and stirred for 30 h at room temperature. Sublimation at 170–200 °C (4 × 10^{-4} mmHg) gave 1.20 g pale-yellow crystals of **7** in 53% yield. IR (cm^{-1}): 3100 (m), 3080 (m), 3030 (m), 2950 (s), 2920 (s), 1440 (s), 1380 (s), 1205 (m), 1060 (s), 1045 (s), 995 (w), 970 (s), 840 (m), 820 (s), 785 (vs), 685 (m), 530 (w), 388 (m), 335 (w), 250 (s), 230 (s). Anal. Calcd for $C_{16}H_{22}O_2HoCl$ (**7**): C, 43.01; H, 4.97; Ho, 36.92. Found: C, 43.10; H, 4.93; Ho, 37.78. MS (EI, 50–200 °C): *m/z* 446 (58.35) M$^+$, 411 (27.06) [M – Cl]$^+$, 323 (100) [M – $CH_3OCH_2CH_2C_5H_4$]$^+$, 124 (1.00) [$CH_3OCH_2CH_2C_5H_5$]$^+$.

($CH_3OCH_2CH_2C_5H_4$)$_2$ErCl (8). This compound was prepared analogously to the description above, from 1.46 g (5.34 mmol) of $ErCl_3$ and 8.9 mL (10.68 mmol) of $CH_3OCH_2CH_2C_5H_4Na$/THF and stirred for 34 h at room temperature. Sublimation at 170–200 °C (4 × 10^{-4} mmHg) gave 1.43 g of pink crystals of **8** in 60% yield. IR (cm^{-1}): 3100 (m), 3080 (m), 3035 (m), 2955 (s), 2920 (s), 1440 (s), 1380 (s), 1205 (m), 1060 (s), 1048 (s), 995 (w), 970 (s), 835 (m), 820 (s), 785 (vs), 685 (m), 524 (w), 385 (m), 330 (w), 255 (s), 230 (s). Anal. Calcd for $C_{16}H_{22}O_2ErCl$ (**8**): C, 42.79; H, 4.95; Er, 37.25. Found: C, 42.63; H, 4.95; Er, 37.89. MS (EI, 50–200 °C): *m/z* 447 (78.16) M$^+$, 412 (33.13) [M – Cl]$^+$, 324 (85.24) [M – $CH_3OCH_2CH_2C_5H_4$]$^+$, 124 (5.29) [$CH_3OCH_2CH_2C_5H_5$]$^+$.

($CH_3OCH_2CH_2C_5C_4$)$_2$TmCl (9). This compound was prepared in a manner analogous to the description above, from 1.56 g (5.70 mmol) of $TmCl_3$ and 9.1 mL (10.9 mmol) of $CH_3OCH_2CH_2C_5H_4Na$/THF and stirred for 39 h at room temperature. Sublimation at 170–200 °C (4 × 10^{-4} mmHg) gave 1.53 g of yellow crystals of **9** in 60% yield. IR (cm^{-1}): 3100 (m), 3080 (m), 3030 (m), 2955 (s), 2920 (s), 1440 (s), 1380 (s), 1205 (m), 1060 (s), 1045 (s), 995 (w), 970 (s), 838 (s), 820 (s), 785 (vs), 685 (m), 530 (w), 387 (m), 330 (w), 250 (s), 230 (s). Anal. Calcd for $C_{16}H_{22}O_2TmCl$ (**9**): C, 42.63; H, 4.93; Tm, 37.48; Found: C, 42.37; H, 4.97; Tm, 36.63. MS (EI, 50–200 °C): *m/z* 450 (55.23) M$^+$, 415 (25.83) [M – Cl]$^+$, 327 (100) [M – $CH_3OCH_2CH_2C_5H_4$]$^+$, 124 (5.24) [$CH_3OCH_2CH_2C_5H_5$]$^+$.

($CH_3OCH_2CH_2C_5H_4$)$_2$YbCl (10). This compound was prepared in a manner analogous to the description above, from 2.96 g (10.60 mmol) of $YbCl_3$ and 17.2 mL (20.6 mmol) of $CH_3OCH_2CH_2C_5H_4Na$/THF and stirred for 17 h at room temperature. Sublimation at 170–200 °C (4 × 10^{-4} mmHg) gave 3.31 g of orange-red crystals of **10** in 60% yield. IR (cm^{-1}): 3100 (m), 3080 (m), 3030 (m), 2945 (s), 2920 (s), 1440 (s), 1380 (s), 1200 (m), 1060 (s), 1045 (s), 995 (w), 965 (s), 835 (s), 820 (s), 785 (vs), 685 (m), 530 (w), 390 (m), 330 (w), 240 (m), 232 (m). Anal. Calcd for $C_{16}H_{22}O_2YbCl$ (**10**): C, 42.25; H, 4.88; Yb, 38.04; Found: C, 42.07; H, 5.00; Yb, 36.63. MS (EI, 50–200 °C): *m/z* 455 (57.23) M$^+$, 419 (100) [M – Cl]$^+$, 332 (97.11) [M – $CH_3OCH_2CH_2C_5H_4$]$^+$, 124 (11.04) [$CH_3OCH_2CH_2C_5H_5$]$^+$.

($CH_3OCH_2CH_2C_5H_4$)$_2$LuCl (11). This compound was prepared in a manner analogous to the description above, from 1.97 g (7.01 mmol) of $LuCl_3$ and 11.4 mL (13.7 mmol) of $CH_3OCH_2CH_2C_5H_4Na$/THF and stirred for 26 h at room temperature. Sublimation at 170–200 °C (4 × 10^{-4} mmHg) gave 2.2 g of colorless crystals of **11** in 65% yield. IR (cm^{-1}): 3100 (m), 3096 (s), 3025 (s), 2945 (s), 2920 (s), 2830 (m), 1438 (s), 1057 (s), 1045 (s), 785 (vs), 685 (m), 390 (w), 234 (s). ^{1}H NMR (90 MHz, C_4D_8O): δ 2.63 (t, 2H), 3.50 (s, 3H), 3.91 (t, 2H), 5.82 (t, 2H), 5.96 (t, 2H). Anal. Calcd for $C_{16}H_{22}O_2LuCl$ (**11**): C, 42.07; H, 4.85; Lu, 38.31. Found: C, 42.21; H, 4.84; Lu, 38.36. MS (EI, 50–200 °C): *m/z* 456 (67.86) M$^+$, 421 (47.88) [M – Cl]$^+$, 333 (100) [M – $CH_3OCH_2CH_2C_5H_4$]$^+$, 124 (1.38) [$CH_3OCH_2CH_2C_5H_5$]$^+$.

($CH_3OCH_2CH_2C_5H_4$)$_2$YCl (12). This compound was prepared in a manner analogous to the description above, from 2.98 g (15.32 mmol) of YCl_3 and 25.1 mL (30.1 mmol) of $CH_3OCH_2CH_2C_5H_4Na$/THF and stirred for 35 h at room temperature. Sublimation at 170–200 °C (4 × 10^{-4} mmHg) gave 4.35 g of colorless crystals of **12** in 77% yield. IR (cm^{-1}): 3100 (m), 3080 (m), 3030 (m), 2960 (s), 2925 (s), 1440 (s), 1380 (s), 1205 (m), 1060 (s), 1050 (s), 995 (m), 965 (s), 840 (s), 820 (s), 785 (vs), 685 (m), 530 (w), 390 (m), 335 (m), 282 (s), 235 (m). ^{1}H NMR (90 MHz, C_4D_8O): δ 2.54 (t, 2H), 3.42 (s, 3H), 3.80 (t, 2H), 5.80 (t, 2H), 5.88 (t, 2H). ^{13}C NMR: δ 30.8, 64.5, 80.4, 111.5, 111.8, 127.0. Anal. Calcd for $C_{16}H_{22}O_2YCl$ (**12**): C, 51.83; H, 5.99; Y, 23.98. Found: C, 51.86; H, 6.03; Y, 24.76. MS (EI, 50–200 °C): *m/z* 370 (52.17) M$^+$, 335 (26.46) [M – Cl]$^+$, 247 (100) [M – $CH_3OCH_2CH_2C_5H_4$]$^+$, 124 (1.38) [$CH_3OCH_2CH_2C_5H_5$]$^+$.

Table 1. Crystal Data and Summary of Intensity Data Collection and Structure Refinement for [($CH_3OCH_2CH_2C_5H_4$)$_2$LaCl]$_2$ (**1**), ($CH_3OCH_2CH_2C_5H_4$)$_2$DyCl (**6**), and ($CH_3OCH_2CH_2C_5H_4$)$_2$YbCl (**10**)

	1	**6**	**10**
formula	$C_{32}H_{44}Cl_2La_2O_4$	$C_{16}H_{22}ClDyO_2$	$C_{16}H_{22}ClO_2Yb$
fw	420.72 × 2	444.31	454.85
space group	*P*2$_1$/*n* (No.14)	*Pnma* (No.62)	*Pnma* (No.62)
a, Å	8.726(1)	12.242(1)	12.207(4)
b, α	12.367(1)	11.723(2)	11.704(8)
c, Å	14.562(3)	11.293(4)	11.175(7)
β, deg	93.90(9)		
V, Å^3	1567.8(2)	1620.7(2)	1596.8(6)
Z	2 (dimer)	4	4
D_{calcd}, g cm^{-3}	1.782	1.821	1.892
μ(Mo Kα), cm^{-1}	29.06	48.18	60.07
F(000), e	832	868	884
radiatn; λ, Å		Mo Kα; 0.710 73	
temp, K		293	
no. of params	182	136	136
R^a	0.038	0.027	0.037
R_w^{b}	0.048	0.030	0.044
goodness of fit	2.03	1.85	3.27

[a] $R = \sum(\Delta F)/\sum(F_o)$. [b] $R_w = \{\sum[w(\Delta F)^2]/\sum[w(F_o)^2]\}^{1/2}$.

Crystal Structure Determination and Refinement for [($CH_3OCH_2CH_2C_5H_4$)$_2$LaCl]$_2$ (1). Suitable crystals of **1** were obtained by recrystallization of sublimate from toluene. A suitable colorless block-shaped single crystal with dimensions 0.26 × 0.32 × 0.36 mm was sealed under argon in a thin-walled glass capillary and mounted on an Enraf-Nonius CAD-4 diffractometer. A summary of data collection was given in Table 1. Unit cell parameters were determined by least-squares refinement of the setting angles of 25 computer-centered reflections in the range $20.4 < 2\theta \leq 27.8°$. Intensity measurements employed graphite-monochromatized Mo Kα radiation and ω–2θ scan model at room temperature. During date collection, the intensities of three standard reflections monitored at every 3600 s of X-ray exposure time decreased linearly by 4.3%, and the intensities of the data set were corrected for the decay. After taking into account Lorentz and polarization effects, an empirical absorption correction with minimum 86.2% and maximum 99.6% transmission was engaged, which was based on seven Ψ scans. A combination of Patterson and difference Fourier techniques provided the ordinates of all non-hydrogen atoms, which were refined with anisotropic thermal parameters using full-matrix least-squares methods. A final difference Fourier map revealed no significant peaks greater than 0.77 e/Å^3. Scattering factors were taken from ref 42. All computations were performed on a micro VAX-II computer with SDP-plus and ORTEP programs. The final position parameters of non-hydrogen atoms are given in Table 2.

Crystal Structure Determination and Refinement for ($CH_3OCH_2CH_2C_5H_4$)$_2$DyCl (6). Suitable crystals of **6** were obtained by recrystallization of sublimate **6** from THF. A well-formed pale yellow single crystal with dimensions 0.35 × 0.38 × 0.40 mm was sealed under argon in a thin-walled glass capillary, and mounted on an Enraf-Nonius CAD-4 diffractometer. A summary of data collection was given in Table 1. Lattice parameters were derived from the setting angles of 25 reflections with $22.6 < 2\theta < 28.3°$. Raw intensities were corrected for decay, Lorentz, and polarization effects. In addition, an empirical absorption correction was applied. Systematically absent reflections with 0*kl* ($k + l = 2n + 1$), *hk*0 ($h = 2n + 1$) and 0*k*0 ($k = 2n + 1$) reduced the choice of possible space group of *Pn*2$_1$*a* and *Pnma*. Since the statistical data for $|E|$, $|E^2|$, and $|E^2 - 1|$, etc. gave an acentric structure of the crystal, it was supposed that the *Pn*2$_1$*a* was the correct choice. The Dy atom was determined by the Patterson method, and subsequent difference Fourier methods located some non-hydrogen atom. However, during the structural expansion and refinement, it was noticed that there were considerable correlations between the atoms with the same peak height in the subsequent difference map and that it was difficult to improve the model.

Hence, the centrosymmetric space group *Pnma* was employed instead. Although it revealed the metal atom, Cl atom, and Cp′(1) ligand [Cp′(1) denotes the Cp′ group consisting of O(1) and C(*i*) atoms, *i* = 1–6], there were some difficulties in searching for another whole Cp′ group. The ordinates showed that the Dy and some atoms of the first Cp′ [symbolized as Cp′(1)] group resided in the mirror plane, while the remaining atoms found by the difference Fourier methods were observed in the general postions. Thus, it could be deduced that there would be two Cl atoms

Table 2. Positional Parameters and Their Estimated Standard Deviations for $[(CH_3OCH_2CH_2C_5H_4)_2LaCl]_2$ (**1**)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
La	0.05860(3)	0.18162)2)	–0.03119(1)	1.683(3)
Cl	0.1685(1)	–0.00745(8)	0.07272(8)	2.46(2)
O(1)	–0.1245(4)	0.2783(3)	–0.1601(2)	2.95(6)
O(2)	0.1197(4)	0.0734(3)	–0.1916(2)	2.84(6)
C(1)	–0.1779(5)	0.3187(4)	0.0298(3)	2.43(7)
C(2)	–0.0395(6)	0.3624(4)	0.0682(3)	2.53(7)
C(3)	0.0225(6)	0.2896(4)	0.1369(3)	2.85(8)
C(4)	–0.0776(6)	0.2014(4)	0.1394(3)	2.98(8)
C(5)	–0.2028(6)	0.2189(4)	0.0735(3)	2.81(8)
C(6)	–0.2796(6)	0.3653(4)	–0.0488(4)	3.01(8)
C(7)	–0.2799(6)	0.2927(4)	–0.1322(4)	3.12(9)
C(8)	–0.0810(8)	0.3586(5)	–0.2237(4)	4.4(1)
C(9)	0.3552(5)	0.1826(4)	–0.0894(3)	2.60(7)
C(10)	0.2908(5)	0.2759(4)	–0.1330(3)	2.62(7)
C(11)	0.2691(6)	0.3546(4)	–0.0654(4)	2.94(8)
C(12)	0.3232(6)	0.3120(5)	0.0201(4)	3.26(9)
C(13)	0.3764(5)	0.2050(5)	0.0063(4)	3.07(9)
C(14)	0.3848(6)	0.0763(4)	–0.1358(4)	3.5(1)
C(15)	0.2727(6)	0.0584(5)	–0.2187(4)	3.48(9)
C(16)	0.0135(8)	0.0682(5)	–0.2711(4)	4.2(1)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

Table 3. Positional Parameters and Their Estimated Standard Deviations for $(CH_3OCH_2CH_2C_5H_4)_2DyCl$ (**6**)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Dy	0.22921(3)	0.250	0.05736(4)	3.695(7)
Cl	0.3401(3)	0.430(3)	0.0856(4)	7.1(1)
O(1)	0.3606(6)	0.250	–0.1076(6)	8.2(2)
O(2)	0.1473(8)	0.3427(8)	0.2377(9)	6.1(2)
C(1)	0.0262(5)	0.1899(7)	–0.0115(7)	6.6(2)
C(2)	0.0982(6)	0.1525(6)	–0.1021(6)	5.6(2)
C(3)	0.1415(8)	0.250	–0.1583(9)	5.3(2)
C(4)	0.2247(9)	0.250	–0.2581(8)	6.3(3)
C(5)	0.340(1)	0.250	–0.219(1)	10.1(5)
C(6)	0.4781(9)	0.250	–0.087(1)	11.0(5)
C(11)	0.372(1)	0.082(1)	0.108(1)	7.5(4)
C(12)	0.360(1)	0.137(1)	0.208(1)	6.6(4)
C(13)	0.253(1)	0.132(1)	0.258(1)	6.9(4)
C(14)	0.178(2)	0.065(1)	0.196(2)	11.0(6)
C(15)	0.251(2)	0.028(1)	0.097(2)	10.2(5)
C(16)	0.2020(9)	0.1859(9)	0.3562(7)	11.4(4)
C(17)	0.103(1)	0.458(1)	0.234(2)	9.9(5)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as in Table 2.

and two other Cp′ groups except the first Cp′ generated by the mirror operation in the same molecule. But this could not be satisfied with the charge balance, unless the site occupation of Cl and atoms of the second Cp′ group except C(16) and C(16′), which emerged simultaneously as mirror image, was considered to be 50% by assuming their disorders. In addition, the unacceptable Cl··C(ring2) [C(ring2) refers to the carbon atom of the Cp(2) consisting of C(11)–C(12)–C(13)–C(14)–C(15)] contact, 1.124 Å, inferred that Cl and the Cp(2) should be separated from each other by the mirror plane. Then, a reasonable molecule was obtained completely. Unit-weighted anisotropic full-matrix least-squares refinement for all non-hydrogen atoms converged to $R = 0.027$, $R_w = 0.030$ for observed reflections with $I > 3\sigma(I)$ of 1199 unique ones. A final difference Fourier map revealed no significant peaks greater than 0.44 e/Å^3. The conclusive reasonable bond lengths and angles verified *Pnma* to be the correct choice. Scattering factors were taken from ref 42. All computations were performed on a micro VAX-II computer with SDP-plus and ORTEP programs. The final position parameters of non-hydrogen atoms are given in Table 3.

Crystal Structure Determination and Refinement for $(CH_3OCH_2CH_2C_5H_4)_2YbCl$ (10). Suitable crystals of **10** were obtained by recrystallization of sublimate **10** from THF. An adequate orange-red single crystal with dimensions 0.41 × 0.38 × 0.45 mm was used to collect data on an Enraf-Nonius CAD-4 diffractometer by monochromatized Mo Kα radiation, with $\omega/2\theta$ technique. A summary of data collection was given in Table 1.

Table 4. Positional Parameters and Their Estimated Standard Deviations for $(CH_3OCH_2CH_23C_5H_4)_2YbCl$ (**10**)

atom	*x*	*y*	*z*	B_{eq},[a] Å^2
Yb	0.22993(5)	0.250	0.05672(6)	3.15(1)
Cl	0.3390(6)	0.0631(6)	0.0902(7)	6.2(2)
O(1)	0.362(1)	0.250	–0.107(1)	8.2(5)
O(2)	0.145(1)	0.161(1)	0.238(1)	5.2(4)
C(1)	0.0286(9)	0.312(1)	–0.006(1)	5.6(3)
C(2)	0.099(1)	0.348(1)	–0.101(1)	5.2(3)
C(3)	0.146(1)	0.250	–0.159(1)	4.4(4)
C(4)	0.228(1)	0.250	–0.260(1)	4.8(4)
C(5)	0.340(2)	0.250	–0.220(2)	9.8(A9)
C(6)	0.481(2)	0.250	–0.086(2)	12(1)
C(11)	0.133(3)	0.599(3)	0.575(3)	10(1)
C(12)	0.365(2)	0.363(2)	0.203(2)	6.1(6)
C(13)	0.257(2)	0.367(2)	0.258(2)	6.2(6)
C(14)	0.314(3)	0.561(2)	0.688(4)	13(1)
C(15)	0.232(4)	0.531(3)	0.584(3)	10(1)
C(16)	0.205(2)	0.309(2)	0.360(1)	11.0(6)
C(17)	0.100(2)	0.046(2)	0.232(3)	7.5(8)

[a] Values for anisotropically refined atoms are given in the form of the isotropic equivalBent displacement parameter defined as in Table 2.

The cell parameters were defined by 25 reflections in the range of $20.8 < 2\theta < 28.8°$. The corrections were applied to the raw intensities as in the cases of **1** and **6**. Since the unit cell constants of **6** and **10** are actully identical, both the structures of **6** and **10** were assumed to be isomorphous. The ordinates of **6** were utilized in the structural refinement of **10**. A final difference Fourier map exhibited no significant peaks greater than 0.44 e/Å^3. Scattering factors were taken from ref 42. All computations were performed on a micro VAX-II computer with SDP-plus and ORTEP programs. The final position parameters of non-yydrogen atoms are given in Table 4.

Results and Discussion

Synthesis. Reaction of anhydrous lanthanide trichlorides ($LnCl_3$) with 2 equiv of ((2-methoxyethyl)cyclopentadienyl)sodium salt[19] in THF solution at room temperature, followed by removal of solvent and sublimation at 160–210 °C (10^{-4} mmHg) afforded complexes **1**–**12** in good yields (eq 1).

$$LnCl_3 + 2CH_3OCH_2CH_2C_5H_4Na \xrightarrow[\text{room temp}]{\text{THF}} (CH_3OCH_2CH_2C_5H_4)_2LnCl + 2NaCl \quad (1)$$

Ln = La (**1**), Pr (**2**), Nd (**3**), Sm (**4**), Gd (**5**), Dy (**6**),
Ho (**7**), Er (**8**), Tm (**9**), Yb (**10**), Lu (**11**), Y (**12**)

Using this ester-substituted cyclopentadienyl ligand, we have succeeded in synthesizing the early lanthanide chlorides, in which the intramolecular coordination bonds from the oxygen atoms of ligands to lanthanide metal formed and efficiently satisfied the coordination environment of early lanthanide complexes. Unlike most biscyclopentadienyl lanthanide halides, the structures of the new complexes (**1**–**12**), obtained from THF solution, are solvent-free dimers or monomers, because the crystals of compounds **1** and **10** obtained from toluene or THF are the same in unit cell parameters, respectively. Furthermore, the THF fragment was not observed in MS of these crystals. This indicates that an intramolecular coordination bond is more easily formed than an intermolecular one. Although a few structures of solvent-free bis(cyclopentadienyl)lanthanide halides have been obtained, the formation of alkali metal halide adducts or Lewis base adducts is a common feature of organolanthanide chemistry involving the ligands C_5Me_5 and $C_5(SiMe_3)_2H_3$, for example: $C_5R_5LnX_2M$-

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(19) (a) Huang, Q.; Qian, Y.; Xie, W.; Shou, M.; Tang, E. *J. Inorg. Chem. (China)* **1985**, 166. (b) Huang, Q.; Qian, Y.; Li, G.; Tang, Y. *Transition Met. Chem. (Weinheim, Ger.)* **1990**, *15*, 483. (c) Huang, Q.; Qian, Y. *Synthesis* **1987**, 910.

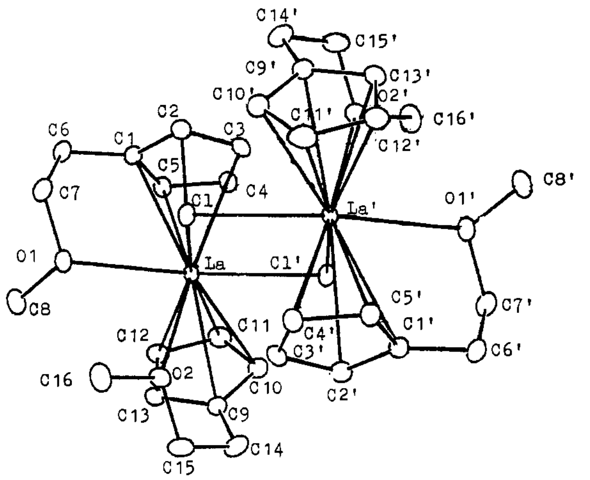

Figure 1. ORTEP drawing of the molecular structure of $[(CH_3OCH_2CH_2C_5H_4)_2LaCl]_2$ (**1**) with the numbering scheme. The halves of the molecular are related by a symmetric center. All hydrogen atoms were omitted for clarity.

(solvent)$_2$M and $(C_5R_5)_2LnX$(solvent) (where R = hydrogen, alkyl, X = halide, and M = alkali metal).[7,8,11,20,21]

The new complexes are so stable to heating that they sublime without decomposition, and a strong parent molecular ion is observed in the EI mass spectrum. The lanthanide chlorides **1**–**12** are slightly soluble in hexane, moderately soluble in toluene, and readily soluble in THF. Elemental analyses, ^1H NMR, mass spectra, and X-ray structure analyses of **1**, **6** and **10** prove the suggested molecular formula and structure.

The IR spectrum analyses imply the presence of intramolecular coordination bond ($O \rightarrow Ln$), because the characteristic absorption peaks of C–O–C asymmetric strenching vibration in these new compounds are shifted to lower frequency and lie between 35 and 40 cm^{-1} compared with that of the ((2-methoxyethyl)cyclopentadienyl)sodium salt.[17–18]

The data of ^1H NMR of the diamagnetic complexes **1**, **11** and **12** together with sodium salt are given in Table 8. All proton resonances were shifted to lower field compared with those of $CH_3OCH_2CH_2C_5H_4Na$. It indicated that the intramolecular coordination bond ($Ln \leftarrow O$) was formed and the charge on cyclopentadienyl ring transfered to metal. Analogue cases are known in complexes $[O(CH_2CH_2C_5H_4)_2LnCl]$ and $[O(CH_2CH_2C_5H_4)_2Ln]_2(\mu\text{-}N_2C_3HMe_2)(\mu\text{-}OH)$ (Ln = Lu, Y).[17] The spectra are consistent with the structures of the compounds. As previously described,[17] the $\Delta\delta$ value implies the torsional ring mobility of the cyclopentadienyl moieties. We found that the $\Delta\delta$ values increased as the ionic radius of the rare earth metal decreased. It demonstrate that the $\Delta\delta$ value depends not only on the angle between the two cyclopentadienyl rings and the crowding arising from the other ligation around the metal but also on the radius of the metal.

Molecular Structure of $[(CH_3OCH_2CH_2C_5H_4)_2LaCl]_2$ (1). The structure of **1** is shown in Figure 1, and selected bond distances and angles are given in Table 5. **1** is made up of a chlorine-bridged dimeric molecule with a symmetric center. Each lanthanum atom is coordinated by two cyclopentadienyl rings, two chlorine atoms, and two oxygen atoms of the ligands. If the η^5-bonded cyclopentadienyl is regarded as occupying a single polyhedral vertex, the structure can be described as a distorted octahedral coordination geometry. The formal coordination number of La is 10 in **1**. It is different from that in previously reported dicyclopentadienyl early lanthanide chlorides, e.g. $\{(Me_3Si)_2C_5H_3\}_2Nd(\mu\text{-}Cl)_2Li(THF)_2$,[11] $[\{(Me_3Si)_2C_5H_3\}_2PrCl]_2$,[10] $[\{(Me_3Si)_2C_5H_3\}_2NdCl_2][AsPh_4]$,[12] $[Cp_2Nd(THF)(\mu\text{-}Cl)]_2$,[4] $Bu^t\text{-}Cp_2PrCl(THF)_2$,[22] $[(C_5Me_5)_2Pr(\mu\text{-}Cl)_2NaDME$,[13] $(C_5Me_5)_2Ce(\mu\text{-}Cl)_2Li(Et_2O)_2$,[14,15] and $[(C_5Me_5)_2CeCl_2K(THF)]_n$,[23] and monomeric dicyclopentadienyl lanthanum iodide, $(CH_3OCH_2CH_2C_5H_4)_2LaI$,[24] in which the coordination number of central metals is eight or nine, respectively. To our knowledge, the largest metal lanthanum dicyclopentadienyl chloride has not been reported. When we used $CH_3OCH_2CH_2C_5H_5$ as a ligand, which can effectively satisfy the need of the largest lanthanum for coordination saturation by forming an intramolecular coordination bond ($O \rightarrow La$), we have succeeded in synthesizing and structurally characterizing the first example of dicyclopentadienyl lanthanum chloride.

Table 5. Selected Bond Distance (Å) and Bond Angles (deg) for $[(CH_3OCH_2CH_2C_5H_4)_2LaCl]_2$ (**1**)

La–Cl	2.9118(7)	La–Cl′	2.9610(7)
La–O(1)	2.665(2)	La–O(2)	2.775(2)
La–C(1)	2.859(3)	La–C(9)	2.778(4)
La–C(2)	2.827(4)	La–C(10)	2.841(4)
La–C(3)	2.825(3)	La–C(11)	2.885(3)
La–C(4)	2.837(3)	La–C(12)	2.873(3)
La–C(5)	2.866(3)	La–C(13)	2.805(3)
La–Cent(1)[a]	2.576	La–Cent(2)	2.569
Cl–La–Cl′	73.39(2)	Cl–La–O(1)	152.50(6)
Cl–La–O(2)	88.56(6)	Cl–La–Cent(1)	100.71
Cl–La–Cent(2)	97.01	Cl′–La–Cent(1)	96.00
Clb–La–Cent(2)	149.86	Cl′–La–O(1)	79.74(6)
Cl′–La–O(2)	69.00(5)	O(1)–La–O(2)	76.34(8)
O(1)–La–Cent(1)	87.59	O(1)–La–Cent(2)	103.50
O(2)–La–Cent(1)	159.54	O(2)–La–Cent(2)	82.51
Cent(1)–La–Cent(2)	113.98		

[a] Cent(1) indicates the centroid of cyclopentadienyl ring C(1–5); cent(2), C(11–15).

The La-C(η^5) distances range from 2.778(4) to 2.885(3) Å; the average La–centroid distance is 2.573 Å, similar to the values reported: 2.548 Å in $(CH_3OCH_2CH_2C_5H_4)_2LaI$,[24] 2.575 Å in $(\eta^5\text{-}C_5H_5)_3La(THF)$,[25] 2.581 Å in $(Me_5C_5)_2La(thf)(\mu\text{-}\eta^1\text{:}\ \eta^3\text{-}C_4H_6)La(C_5Me_5)_2$,[26] and 2.597 Å in $[(C_5H_5)_3La]_\infty$.[27] The average La–Cl bond length is somewhat longer than that in $[(Me_3Si)_2C_5H_3]_2Pr(\mu\text{-}Cl)]_2$,[10] even with the difference in ionic radii of La^{3+} and Pr^{3+} taken into account.[28] The mean distance of La–O (2.720 Å) in **1** is significantly longer than La–O (2.584 Å) in $(CH_3OCH_2CH_2C_5H_4)_2LaI$,[24] La–O(THF) (2.57 Å) in $(C_5H_5)_3La\cdot THF$,[25] the La–O(THF) distance of 2.637 Å in $(Me_5C_5)_2La(thf)(\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_4H_6)La(C_5Me_5)_2$,[26] and the mean La–O(DME) distance of 2.627 Å in $\{[C_5H_3(SiMe_3)_2]_2La(NCMe_3)(DME)\}[BPh_4]\cdot 0.5DME$.[29] The Cl–La–Cl angle [73.39(2)°] is slightly smaller than that of $[(Me_3Si)_2C_5H_3]_2Pr(\mu\text{-}Cl)]_2$(78°),[10] but the Cent(1)–La–Cent(2) angle [113.9(8)°] in **1** is significantly smaller than the angle Cent–La–Cent in all the other cyclopentadienyllanthanum complexes investigated so far by X-ray diffraction, ranging from 114.5° in $(C_5H_5)_2La(\mu\text{-}\eta^5\text{:}\eta^1\text{-}C_5H_5)$[30] to 114.9° in $[(C_5H_5)_2La(\mu\text{-}\eta^5\text{:}\eta^2\text{-}C_5H_5)]$,[27] to 115° in $(C_5H_5)_3La\cdot THF$,[25] to 124.5° in $(MeOCH_2CH_2C_5H_4)_2LaI$,[24] and to

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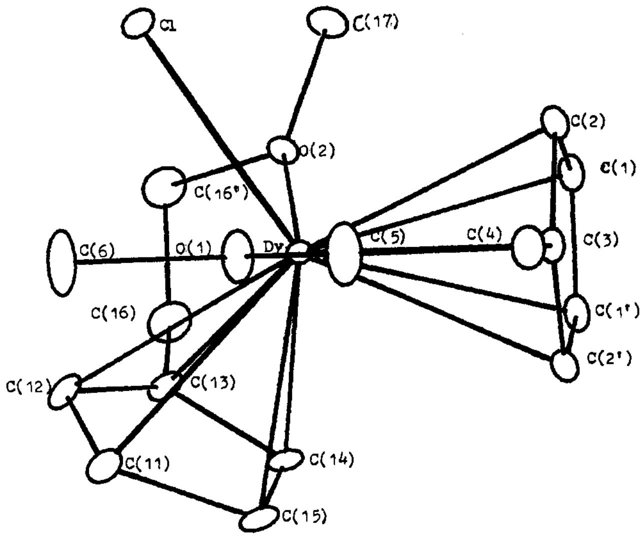

Figure 2. ORTEP drawing of the molecular structure of $(CH_3OCH_2CH_2C_5H_4)_2DyCl$ (**6**) with the numbering scheme. Only one position of each of the disordered atoms C(11), C(12), C(13), C(14), C(15), O(2), C(17), and Cl is shown. All hydrogen atoms were omitted for clarity.

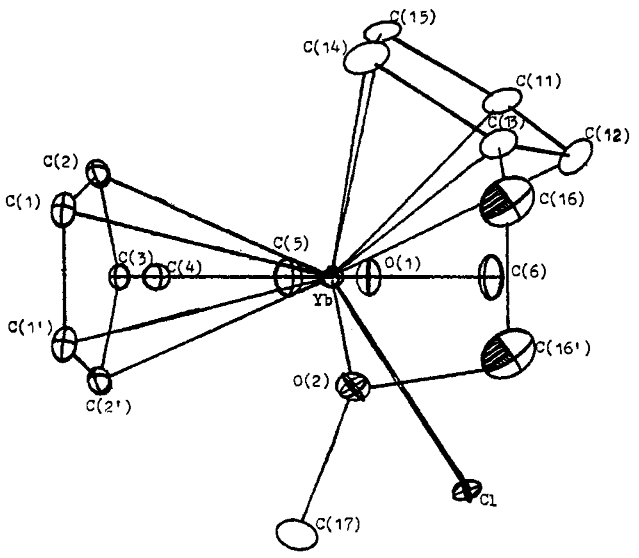

Figure 3. ORTEP drawing of the molecular structure of $(CH_3OCH_2CH_2C_5H_4)_2YbCl$ (10) with the numbering scheme. Only one position of each of the disordered atoms C(11), C(12), C(13), C(14), C(15), O(2), C(17), and Cl is shown. All hydrogen atoms were omitted for clarity.

129.56(5)° in $[(C_5Me_5)_2La(thf)(\mu\text{-}\eta^1\text{:}\eta^3\text{-}C_4H_6)La(C_5Me_5)_2]$.[26] The above difference may reflect that **1** is a coordination-saturated complex and has better stability.

Table 6. Selected Bond Distances (Å) for $(CH_3OCH_2CH_2C_5H_4)_2DyCl$ (**6**) and $(CH_3OCH_2CH_2C_5H_4)_2YbCl$ (**10**)

	Ln = Dy (**6**)	Ln = Yb (**10**)
Ln–Cl	2.63(2)	2.588(6)
Ln–O(1)	2.462(5)	2.437(7)
Ln–O(2)	2.517(8)	2.500(9)
Ln–C(1)	2.698(5)	2.659(6)
Ln–C(2)	2.669(6)	2.640(6)
Ln–C(3)	2.661(7)	2.620(9)
Ln–Cent(1)[a]	2.393	2.344
Ln–C(11)	2.69(5)	2.44(4)
Ln–C(12)	2.69(2)	2.67(1)
Ln–C(13)	2.67(1)	2.66(1)
Ln–C(14)	2.75(2)	2.70(4)
Ln–C(15)	2.65(1)	2.63(3)
Ln–Cent(2)	2.389	2.302
O(1)–C(5)	1.29(1)	1.30(1)
O(1)–C(6)	1.457(9)	1.47(1)
O(2)–C(16′)	1.53(2)	1.59(1)
O(2)–C(17)	1.46(2)	1.45(3)
C(1)–C(1′)	1.41(1)	1.45(2)
C(1)–C(2)	1.420(7)	1.43(1)
C(2)–C(3)	1.412(7)	1.430(9)
C(3)–C(4)	1.52(2)	1.52(1)
C(4)–C(5)	1.48(1)	1.43(2)
C(11)–C(12)	1.31(5)	1.50(4)
C(12)–C(13)	1.43(2)	1.45(3)
C(13)–C(14)	1.40(2)	1.45(4)
C(14)–C(15)	1.49(4)	1.57(4)
C(11)–C(15)	1.60(4)	1.45(5)
C(13)–C(16)	1.43(1)	1.47(2)
C(16)–C(16′)	1.50(2)	1.38(2)

[a] Cent(1) indicates the centroid of cyclopentadienyl ring C(1–3,2′,1′); cent(2), C(11–15).

Table 7. Selected Bond Angle (deg) for $(CH_3OCH_2CH_2C_5H_4)_2DyCl$ (**6**) and $(CH33OCH_2CH_2C_5H_4)_2YbCl$ (**10**)

bond angle	Ln = Dy (**6**)	Ln = Yb (**10**)
Cent(1)[a]–Ln–Cent(2)	124.02	124.10
Cent(1)–Ln–Cl	118.58	119.5
Cent(1)–Ln–O(1)	91.4	92.7
Cent(1)–Ln–O(2)	101.8	100.6
Cent(2)–Ln–Cl	117.4	116.4
Cent(2)–Ln–O(1)	103.6	100.1
Cent(2)–Ln–O(2)	90.4	93.0
Cl–Ln–O(1)	75.7(1)	76.5(2)
Cl–Ln–O(2)	75.1(2)	75.2(4)
O(1)–Ln–O(2)	150.8(2)	151.6(4)
C(5)–O(1)–C(6)	110.7(7)	111(2)
C(16′)–O(2)–C(17)	113(2)	115(2)
C(1)–C(2)–C(3)	107.9(6)	110(1)
C(1′)–C(1)–C(2)	108.0(4)	107(1)
C(2)–C(3)–C(2′)	108.3(7)	107(1)
C(2)–C(3)–C(4)	125.8(4)	127.0(7)
C(2′)–C(3)–C(4)	125.8(4)	126.9(5)
C(3)–C(4)–C(5)	114.6(7)	114(1)
O(1)–C(5)–C(4)	119.2(8)	120(2)
C(11)–C(12)–C(13)	115(2)	114(2)
C(11)–C(15)–C(14)	113(2)	117(3)
C(12)–C(13)–C(14)	114.6(3)	109(3)
C(12)–C(13)–C(16)	134(1)	135(2)
C(12)–C(11)–C(15)	99(4)	94(3)
C(13)–C(14)–C(15)	99(2)	99(3)
C(13)–C(16)–C(16′)	116.2(6)	118(2)
C(14)–C(13)–C(16)	111(2)	116(3)
O(2)–C(16′)–C(16)	102.6(6)	103(1)

[a] Cent(1) indicates the centroid of cyclopentadienyl ring C(1–3,2′,1′); cent(2), C(11–15).

Molecular Structure of $(CH_3OCH_2CH_2C_5H_4)_2DyCl$ (6) and $(CH_3OCH_2CH_2C_5H_4)_2YbCl$ (10). As is evident from the unit cell parameters and atomic coordinates, the structures of **6** and **10** are isomorphous and isostructural. Each complex consists of a Dy or Yb atom surrounded by two cyclopentadienyl rings, one chlorine atom, and two oxygen atoms of the ligands, which is described as a distorted trigonal bipyramid. Their atomic arrangements are shown in Figures 2 and 3. The similarity of their structure can be best seen by examining the compilation of values of selected bond parameters givein Table 6 and 7. These results revealed that they are monomeric structures, which is different from that of the lanthanum chloride. These indicate that the radius of the rare earth metal ion affectes the molecular structure of the chloride; Furthermore, when the smaller chlorine ion replaced iodine ion in the monomeric complex $(CH_3OCH_2CH_2C_5H_4)_2YbI$,[31] which has previously been reported by us, the molecular structure of ytterbium chloride is still monomeric, in other words, in this case, the smaller chlorine ion could satisfy the coordination saturation of late rare earth metals.

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Table 8. ^{1}H NMR Data (ppm) for $[(CH_3OCH_2CH_2C_5H_4)_2LaCl]_2$ (**1**), $(CH_3OCH_2CH_2C_5H_4)_2LuCl$ (**11**), and $(CH_3OCH_2CH_2C_5H_4)_2YCl$ (**12**)

complex	$(C_5H_4)_2$	$\Delta\delta^a$	$-CH_2-$	$-CH_2O-$	$-OCH_3$
$[(CH_3OCH_2CH_2C_5H_4)_2LaCl]_2$	5.63		2.60	3.60	3.40
	5.63	0			
$(CH_3OCH_2CH_2C_5H_4)_2YCl$	5.80		2.54	3.80	3.42
	5.88	0.08			
$(CH_3OCH_2CH_2C_5H_4)_2LuCl$	5.82		2.63	3.91	3.50
	5.96	0.14			
$CH_3OCH_2CH_2C_5H_4Na$	5.18		2.50	3.05	3.28
	5.31	0.13			

[a] $\Delta\delta = \delta(1,4\text{-CH}) - \delta(2,3\text{-CH})$.

The average Yb-C(η^5) distance in **10**, 2.63 Å, is similar to that found in other organoytterbium(III) complexes, such as 2.613(13) Å in $[Cp_2YbMe]_2$,[32] 2.628(11) Å in $Bu^tCp_2YbCl{\cdot}THF$,[22] 2.65 ± 0.03 Å in $(C_5Me_5)_2YbCl(Me_2PCH_2PMe_2)$,[33] 2.60(2) Å in $(C_5H_5)_2Yb(CH_3)(THF)$,[34] 2.611 Å in $(C_5H_5)_2Yb(CH_3COCHCOCH_3)$,[35] 2.65(1) Å in $(C_5Me_5)_2YbCl(THF)$,[36] 2.585 Å in $[(CH_3C_5H_4)_2YbCl]_2$,[37] 2.62 Å in $\{[(Me_3Si)_2C_5H_3]_2YbCl\}_2$,[9] and 2.618 Å in $(CH_3OCH_2CH_2C_5H_4)_2YbI$.[31]

The distance Yb–O(1) is 2.437(7) Å, Yb–O(2) is 2.500(9) Å, and mean Yb–O is 2.468 Å, which is good agreement with the value 2.450 Å in the complex $(CH_3OCH_2CH_2C_5H_4)_2YbI$.[31] The mean Yb–O distance and Yb–Cl distance [2.588(6) Å] are comparable with the mean Pr–O distance [2.618(13) Å] and Pr–Cl distance [2.718(6) Å] in nine-coordinated $Bu^tCp_2PrCl(THF)_2$,[22] respectively, after the differences in rare earth ion radii are taken into account.[28] Moreover, the interesting feature of the structure of **10** is the presence of two intramolecular coordination bonds from the oxygen atom of $CH_3OCH_2CH_2C_5H_4^-$ to ytterbium. The mean Yb–O distance in **10** is significantly longer than those of in eight-coordinated complexes, e.g. containing THF, 2.362 Å in $(C_5Me_5)_2YbCl(THF)$,[36] 2.333(6) Å in $Bu^tCp_2YbCl{\cdot}THF$,[22] and 2.311(6) Å in $Cp_2YbMe{\cdot}THF$.[34] This may well arise from the crowded molecular structure in **10**.

The angles O(1)–C(5)–C(4) [120(2)°], C(3)–C(4)–C(5) [114(1)°], and O(2)–C(16′)–C(16) [103(1)°], C(13)–C(16)–C(16′) [118(2)°] are significantly different from the corresponding angles of the oxygen-atom-free (methoxyethyl)cyclopentadienyl ligand in the complex $(CH_3OCH_2CH_2C_5H_4)_4Pr$.[38] That reveals that the intramolecular coordination bond permits formation of a chelating effect involving the oxygen atom and the centroid of the cyclopentadienyl ring to the metal atom, resulting in an increase in the rigidity of ligand. The formation of a stronger intramolecular coordination bond can provide energy to change the angles in ligands.

The geometry of the dysprosium complex **6** is similar to that of the ytterbium complex **10**, except that the bond distances, involving the metal atom are generally longer for Dy than for Yb. However, the mean Dy–C(η^5) distance in **6**, 2.68 Å, agrees well with that found in other Dy(III) cyclopentadienyl complexes, e.g. (2.59–2.69 Å) in $[(C_5H_5)_2DyCl]_n$[39] and a series of other Dy(III) complexes.[40,41]

Comparing **6** and **10**, the mean Dy–O distance and the Dy–Cl distance are 0.02–0.04 Å longer than that in **10**, but the differences are consistent with a 0.041-Å difference in the radial sizes of Dy and Yb.[28] The angles Cent1–Ln–cent2, and O1–Ln–O2 are about the same in both compounds, [124.02(1) and 150.8(2)° for Dy vs 124.10(1) and 151.6(4)° for Yb].

The special feature of the three structures of **1**, **6**, and **10** is the formation of an intramolecular coordination bond from the oxygen atom of ligand to the central rare earth metal. The average Ln–O distances are 2.720 in **1**, 2.489 in **6**, and 2.468 Å in **10**. When the differences of ionic radii are taken into accounts, they are comparable. A chelating coordination by an oxygen atom and the centroid of cyclopentadienyl to the central metal is a common structural feature of these organolanthanide chlorides. It is very interest that structures of these complexes are different: the larger lanthanum complex contains a Cl-bridged dimer and the coordination number of lanthanum ion is 10; the later dysprosium and ytterbium complexes are monomeric with a formal coordination number of nine, due to the smaller radii of the central metal ions.

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Supplementary Material Available: Complete tables of the data collection, anisotropic thermal parameters, and bond distances and angles for compounds **1**, **6**, and **10** (7 pages). Ordering information is given on any current masthead page. Tables of structure factors are available from the authors.

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