Organometallic Compounds of the Lanthanides. 59.[1] (1,1'-(3-Oxapentamethylene)dicyclopentadienyl)yttrium and -lutetium 3,5-Dimethylpyrazolates. X-ray Crystal Structure of $[O(CH_2CH_2C_5H_4)_2Ln(\mu\text{-}N_2C_3HMe_2)(\mu\text{-}OH)Ln(C_5H_4CH_2CH_2)_2O]$ (Ln = Y, Lu)

Herbert Schumann,* Jörg Loebel, and Joachim Pickardt

Institut für Anorganische und Analytische Chemie der Technischen Universität Berlin, D-1000 Berlin 12, Germany

Changtao Qian* and Zuowei Xie

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai, China

Received April 17, 1990

The reaction of $O(CH_2CH_2C_5H_4)_2LnCl$ (Ln = Y, Lu) with $NaN_2C_3HMe_2$ in tetrahydrofuran at room temperature generates the complexes $O(CH_2CH_2C_5H_4)_2Ln(N_2C_3HMe_2)$ (Ln = Y (**1**), Lu (**2**)). The partial hydrolyses of **1** and **2** form $[O(CH_2CH_2C_5H_4)_2Ln(\mu\text{-}N_2C_3HMe_2)(\mu\text{-}OH)Ln(C_5H_4CH_2CH_2)_2O]$ (Ln = Y (**3**), Lu (**4**)). The new compounds have been characterized by elemental analyses and IR and NMR spectra. The X-ray structural analyses of **3** and **4** show both to be tetragonal, space group $P4_12_12$, $Z = 4$, with $a = 8.980$ (2) Å, $c = 37.403$ (7) Å, and $D(\text{calcd}) = 1.520$ g cm^{-3} for **3** and $a = 8.930$ (5) Å, $c = 36.868$ (9) Å, and $D(\text{calcd}) = 1.95$ g cm^{-3} for **4**. The structure was solved from 2294 observed reflections with $F_o \geq 6\sigma(F_o)$ and refined to a final R factor of 0.0434 for **3** and from 2004 observed reflections with $F_o \geq 4\sigma(F_o)$ to a final R factor of 0.0323 for **4**. The molecular structure shows the pyrazole and the hydroxyl groups both bridging with distances Y-N = 2.445 (5) Å, Y-O = 2.202 (2) Å, Lu-N = 2.392 (8) Å, and Lu-O = 2.154 (3) Å, whereas the oxygen atoms of the oxapentamethylene bridges are separated by 2.662 (4) Å from the Y atoms and 2.667 (7) Å from the Lu atoms.

Introduction

Recently several ring-bridged dicyclopentadienyllanthanide complexes have been synthesized[2-10] and some crystal structures have been reported.[4,5,9,10] Among these, special attention should be given to the compounds having heteroatom-containing bridges such as $[C_5H_4CH_2CH_2OCH_2CH_2C_5H_4]^{2-}$, because an intramolecular coordination from that oxygen should satisfy the part of the open coordination sphere of the lanthanide metals and therefore enhance the possibility for the isolation of more stable, but also catalytically more active, solvent-free organolanthanide complexes.[7,8] However, until now no report had appeared in the literature concerning the crystal structure of a compound containing more than three atoms bridging cyclopentadienyl ligands to prove such an intramolecular stabilization. On the other hand, pyrazolyl ligands have two nitrogen atoms capable of coordination; thus, they can be employed as 1,2-μ-bridging ligands in the formation of η^2-pz complexes (pz = 1,2-pyrazolyl, $C_3H_3N_2$), also providing additional saturation for unsaturated metal centers, as is shown in $[Ni(NO)(pzMe_2)]_2$[11] ($pzMe_2$ = 3,5-dimethylpyrazolyl), $[(C_5H_5)_2Ti(pz)_2Ti(C_5H_5)_2]$,[12] $[(C_5H_5)_3U(pz)]$,[13] and $[(C_5Me_5)_2U(pz)_2]$[14] and in some clusters of the type $[Na(L)_2OLn_3(pzMe_2)_9]$.[15]

We now report on the synthesis of two yttrium and two lutetium compounds containing both ligands, 1,1'-(3-oxapentamethylene)dicyclopentadienyl and 3,5-dimethylpyrazolyl, as well as the first single-crystal structure determinations of cyclopentadienyllanthanide derivatives containing a five-atom bridging chain.

Experimental Section

All procedures were performed by using Schlenk tubes under an atmosphere of dry, oxygen-free argon. The solvents used were dried and freed of oxygen by refluxing and storing over sodium and were distilled under argon prior to use. Anhydrous YCl_3 and $LuCl_3$ were prepared from the pure oxides (Rhone-Poulenc, Frankfurt, Germany) by reaction with NH_4Cl[16] and Soxhlet extraction with THF. The 1,1'-(3-oxapentamethylene)dicyclopentadienyl disodium salt[7] and sodium 3,5-dimethylpyrazolate[15] were prepared as previously described. Elemental analyses were performed on a Perkin-Elmer 240 C CHN analyzer. Reasonably satisfactory analyses could be obtained by using a special Schlenk tube and small aluminum cans for weighing these extremely sensitive compounds. Infrared spectra were recorded on a Perkin-Elmer 560 B spectrometer using KBr pellets. ^1H NMR spectra were obtained in sealed 5-mm tubes on a Bruker WP 80 SY instrument at 30 °C.

(1,1'-(3-Oxapentamethylene)dicyclopentadienyl)yttrium 1,3-Dimethylpyrazolate (1). At room temperature, a solution

---

(1) Part 48: Schumann, H.; Köhn, R. D.; Reier, F. W.; Dietrich, A.; Pickardt, J. *Organometallics* **1989**, *8*, 1388.

(2) John, J. N.; Tsutsui, M. *Inorg. Chem.* **1981**, *20*, 1602.

(3) Qian, C.; Ye, C.; Lu, H.; Li, Y.; Huang, Y. *J. Organomet. Chem.* **1984**, *263*, 333.

(4) Jeske, G.; Schock, L. E.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8103.

(5) Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

(6) Qian, C.; Ye, C.; Li, Y. *J. Organomet. Chem.* **1986**, *302*, 171.

(7) Qian, C.; Xie, Z.; Huang, Y. *J. Organomet. Chem.* **1987**, *323*, 285 and references therein.

(8) Qian, C.; Xie, Z.; Huang, Y. *Inorg. Chim. Acta* **1987**, *139*, 195.

(9) Höck, N.; Oroschin, W.; Paolucci, G.; Fischer, R. D. *Angew. Chem.* **1986**, *98*, 748; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 738.

(10) Swamy, S. J.; Loebel, J.; Schumann, H. *J. Organomet. Chem.* **1989**, *379*, 51.

(11) Chong, K. S.; Rettig, S. J.; Storr, A.; Trotter, J. *Can. J. Chem.* **1979**, *27*, 3090.

(12) Fieselmann, B. F.; Stucky, G. D. *Inorg. Chem.* **1978**, *17*, 2074.

(13) Eigenbrot, C. W.; Raymond, K. N. *Inorg. Chem.* **1981**, *20*, 1553.

(14) Eigenbrot, C. W.; Raymond, K. N. *Inorg. Chem.* **1982**, *21*, 2653.

(15) Schumann, H.; Lee, P. R.; Loebel, J. *Angew. Chem.* **1989**, *101*, 1073; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1033.

(16) Brauer, G. *Handbuch der Präparativen Anorganischen Chemie*; F. Enke Verlag: Stuttgart, Germany, 1962; Vol. 2, p 1002.

0276-7333/91/2310-0215$02.50/0

of 1.10 g (9.32 mmol) of Na(pzMe$_2$) in 20 mL of THF was syringed into a THF solution of O(CH$_2$CH$_2$C$_5$H$_4$)$_2$YCl, resulting from the reaction of 1.85 g (9.46 mmol) of YCl$_3$ with 22.0 mL (9.40 mmol) of a THF solution of [Na]$^+_2$[O(CH$_2$CH$_2$C$_5$H$_4$)$_2$]$^{2-}$ in 58 mL of THF.[7] The reaction mixture was stirred overnight and then filtered. Concentration of the THF solution followed by addition of *n*-pentane afforded a white product, which was washed with 15 mL of pentane and then dried under vacuum to give 1.45 g (40.5%) of **1** as a white solid. It is purified by sublimation at 150–170 °C/10^{-4} mmHg, giving white crystals. IR (cm^{-1}): 3200 (m), 3130 (m), 3080 (m), 3040 (m), 2920 (s), 2870 (s), 1595 (w), 1520 (w), 1485 (w), 1435 (m), 1420 (w), 1305 (w), 1275 (w), 1195 (s), 1065 (s), 1045 (s), 1038 (s), 1028 (s), 975 (s), 890 (m), 815 (s), 780 (s), 760 (vs), 670 (s), 490 (w), 435 (s). Anal. Calcd for C$_{19}$H$_{23}$N$_2$OY: C, 59.38; H, 6.03; N, 7.29. Found: C, 59.02; H, 6.08; N, 7.84.

(1,1′-(3-Oxapentamethylene)dicyclopentadienyl)lutetium 1,3-Dimethylpyrazolate (2). By the procedure for the preparation of **1**, a suspension of 2.84 g (10.09 mmol) of LuCl$_3$ in 70 mL of THF, 8.13 mL (10.08 mmol) of a THF solution of [Na]$^+_2$[O(CH$_2$CH$_2$C$_5$H$_4$)$_2$]$^{2-}$, and 1.18 g (10.00 mmol) of Na(pzMe$_2$) in 20 mL of THF yielded 1.67 g (35.5%) of **2** as a white solid, subliming at 150–170 °C/10^{-4} mmHg to give white crystals. IR (cm^{-1}): 3200 (m), 3130 (m), 3085 (m), 3040 (w), 2920 (s), 2875 (s), 1595 (m), 1522 (m), 1485 (m), 1435 (s), 1420 (m), 1305 (w), 1275 (w), 1195 (s), 1080 (m), 1065 (s), 1045 (s), 1035 (s), 1025 (s), 975 (s), 890 (m), 825 (s), 780 (s), 765 (vs), 730 (s), 670 (m), 485 (m), 440 (s). Anal. Calcd for C$_{19}$H$_{23}$LuN$_2$O: C, 48.51; H, 4.93; N, 5.96. Found: C, 47.98; H, 5.02; N, 6.26.

[O(CH$_2$CH$_2$C$_5$H$_4$)$_2$Ln]$_2$(μ-N$_2$C$_3$HMe$_2$)(μ-OH) (Ln = Y (3), Lu (4)). A toluene solution of **1** or **2** was refluxed for 3 h and then filtered. The transparent solution was put into a –30 °C refrigerator for several days, affording pale yellow crystals that were suitable for X-ray crystallographic analysis. IR for **3** (cm^{-1}): 3350 (w), 3200 (w), 3080 (m), 2920 (s), 2900 (s), 2875 (s), 1520 (s), 1480 (m), 1470 (m), 1440 (m), 1405 (m), 1370 (w), 1315 (w), 1275 (w), 1250 (w), 1205 (m), 1195 (s), 1075 (s), 1065 (s), 1045 (s), 1035 (s), 1025 (s), 975 (s), 895 (m), 815 (s), 780 (s), 765 (vs), 695 (m), 670 (m), 515 (w), 490 (m), 435 (s). Anal. Calcd for C$_{33}$H$_{40}$N$_2$O$_3$Y$_2$ (**3**): C, 57.40; H, 5.84; N, 4.06. Found: C, 56.54; H, 6.06; N, 4.61. Calcd for C$_{33}$H$_{40}$Lu$_2$N$_2$O$_3$ (**4**): C, 45.95; H, 4.67; N, 3.25. Found: C, 46.32; H, 4.82; N, 3.32.

X-ray Data Collection, Structure Determination, and Refinement for 3 and 4. Suitable crystals of **3** and **4** were grown as described above. The crystals were selected with use of a device similar to that reported by Veith and Bärninghausen,[17] glued with grease on top of a glass fiber, and placed in the cold nitrogen stream of the diffractometer. Determination of lattice parameters and intensity measurements were done on an Enraf-Nonius CAD-4 diffractometer for **3** and on a Syntex P2$_1$ instrument for **4**, respectively, both fitted with low-temperature equipment, using Mo Kα radiation (graphite monochromator, λ = 0.71069 Å).

Cell dimensions for **3** were obtained from a least-squares fit of 24 reflections in the range 24° ≤ 2θ ≤ 26° and for **4** from 15 reflections with 2θ ≤ 15°. Both compounds crystallize in a tetragonal crystal system; from the systematic absences (00l, l = 4n; h00, h = 2n) the space group was determined for **3** as well as for **4** to be $P4_12_12$ (No. 92) or $P4_32_12$ (No. 96). For **3** intensities of all reflections in the range 2° ≤ 2θ ≤ 55° (0 ≤ h ≤ 10, 0 ≤ k ≤ 10, 0 ≤ l ≤ 44) were collected; the intensities of three standard reflections, measured every 2 h of X-ray exposure, showed only random fluctuations (≤1.6%). A total of 3029 unique data were obtained, 2294 of which were considered observed ($F_o \geq 6\sigma(F_o)$) and used for subsequent calculations. For **4** the range of data collection was 2° ≤ 2θ ≤ 50° (0 ≤ h ≤ 10, 0 ≤ k ≤ 10, 0 ≤ l ≤ 43). Two standard reflections were measured every 100 reflections, with no significant changes observed; 2462 unique data were collected, of which 2004 with $F_o \geq 4\sigma(F_o)$ were used for the structure determination. The raw data were corrected for Lorentz and polarization effects; empirical absorption corrections were applied (ψ scan for **3**, minimum absorption correction coefficient 0.8059, maximum 0.9983; correction by the method of Walker and Stuart;[18] for **4**, minimum absorption correction coefficient 0.851, maximum 1.255).

Table I. Crystal and Data Collection Parameters for [O(CH$_2$CH$_2$C$_5$H$_4$)$_2$Ln]$_2$(μ-N$_2$C$_3$HMe$_2$)(μ-OH) (Ln = Y (3), Lu (4))

	3	4
formula	C$_{33}$H$_{40}$N$_2$O$_3$Y$_2$	C$_{33}$H$_{40}$Lu$_2$N$_2$O$_3$
fw	690.50	862.62
space group	$P4_12_12$ (No. 92)	$P4_12_12$ (No. 92)
$a = b$, Å	8.980 (2)	8.930 (5)
c, Å	37.403 (7)	36.868 (9)
V, Å^3	3016.2	2940.0
Z	4	4
D_{calcd}, g/cm^3	1.52	1.95
μ, cm^{-1}	38.9	67.2
F(000)	1416	1672
diffractometer	Enraf-Nonius CAD-4	Syntex P2$_1$
radiatn; λ, Å	0.71069	
monochromator	graphite cryst	
temp, K	138 (5)	170 (5)
2θ limits, deg	$2 \leq 2\theta \leq 55$	$2 \leq 2\theta \leq 50$
scan technique	θ–2θ	
no. of unique data	3092	2462
no. of obsd data	2294, $F_o \geq 6\sigma(F_o)$	2004, $F_o \geq 4\sigma(F_o)$
correctns	Lorentz, polarizn, abs, anomalous dispersn	
no. of refined params	185	185
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0434	0.0323
$R_w = [\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o^2]^{1/2}$	0.0457	0.0331
w	$1.2667/[\sigma^2(F_o) + 0.000475F_o^2]$	$1.0146/[\sigma^2(F_o) + 0.000623F_o^2]$

The heavy atoms were found by Patterson methods and all non-hydrogen atoms located by successive difference Fourier syntheses. In order to find the correct absolute configuration and to determine the chirality of the 4-fold screw axes, isotropic refinements for **3** and **4** of the two isomers in $P4_12_12$ (**3**, R = 0.0548, 0.2545; **4**, R = 0.0388, 0.40) and $P4_32_12$ (**3**, R = 0.0768, 0.2456; **4**, R = 0.0445, 0.40) were performed, thus implying $P4_12_12$ to be the correct space group for both compounds. The atoms O2, C16, H1, and H161 lie on 2-fold axes (Wyckoff position 4a). All non-hydrogen atoms were refined anisotropically. The hydrogen atoms H1 and H161 were also refined (isotropically for **3**, only positional parameters for **4**). All other hydrogen atoms were found in the difference Fourier map but added to the structure model on calculated positions ($d_{\text{C-H}}$ = 1.08 Å) with a constant isotropic temperature factor of 0.05 Å^2 for **3** and 0.08 Å^2 for **4**. The maximum ratio of shift to error in the final refinement cycle was 0.012 for **3** and 0.020 for **4**. The final difference Fourier map showed no unusual electron density (maximum 0.93 e/Å^3 for **3** and 0.98 for **4**). Scattering factors for non-hydrogen atoms and the anomalous dispersion terms for Y and Lu were taken from ref 19 and scattering factors for H from ref 20. All calculations were done with SHELX-76.[21] Crystal and data collection details are summarized in Table I. The final atomic parameters are listed in Tables II (**3**) and III (**4**), respectively, and bond distances and angles in Tables IV and V. Further details of the structure investigations are available on request, from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, Germany, on quoting the depository number CSD 55007, the authors, and the full citation of the journal.

Results and Discussion

Yttrium trichloride and lutetium trichloride react with Na$_2$O(CH$_2$CH$_2$C$_5$H$_4$)$_2$ in THF at room temperature to give the corresponding 1,1′-(3-oxapentamethylene)dicyclo-

---

(17) Veith, M.; Bärninghausen, H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1974**, *B30*, 1806.

(18) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1983**, *A39*, 158.

(19) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99, 149.

(20) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(21) Sheldrick, G. M. SHELX-76 System of Programs, 1976.

Table II. Positional Parameters of $[O(CH_2CH_2C_5H_4)_2Y]_2(\mu\text{-}N_2C_3HMe_2)(\mu\text{-}OH)$ (3) with Standard Deviations of the Last Significant Digit in Parentheses and Equivalent Isotropic Thermal Parameters (Å²)[a]

atom	x/a	y/b	z/c	B_{eq}
Y	0.47505 (6)	0.60196 (6)	0.05039 (1)	1.56
C1	0.5945 (7)	0.5846 (7)	0.1155 (1)	2.16
C2	0.4804 (7)	0.4811 (7)	0.1162 (1)	2.41
C3	0.5194 (7)	0.3638 (6)	0.0933 (1)	2.35
C4	0.6563 (7)	0.3967 (7)	0.0778 (1)	2.04
C5	0.7052 (6)	0.5343 (7)	0.0915 (2)	2.06
C6	0.8431 (7)	0.6177 (8)	0.0803 (2)	3.03
C7	0.8165 (7)	0.7839 (7)	0.0759 (2)	2.40
O1	0.6913 (4)	0.8046 (4)	0.0526 (1)	2.26
C8	0.6528 (8)	0.9609 (8)	0.0518 (2)	3.74
C9	0.5119 (8)	0.9837 (8)	0.0318 (2)	3.98
C10	0.3902 (7)	0.8858 (7)	0.0443 (2)	2.79
C11	0.3561 (7)	0.8448 (7)	0.0802 (2)	2.26
C12	0.2388 (7)	0.7394 (8)	0.0791 (2)	2.86
C13	0.2025 (8)	0.7181 (8)	0.0433 (2)	3.02
C14	0.2946 (8)	0.8062 (8)	0.0220 (2)	2.91
N	0.3554 (5)	0.4015 (6)	0.0167 (1)	1.87
C15	0.2407 (7)	0.3119 (7)	0.0266 (2)	2.23
C16	0.2105 (7)	0.2105 (7)	0.0000	2.22
C17	0.1607 (8)	0.3254 (8)	0.0616 (2)	3.23
O2	0.6018 (4)	0.6018 (4)	0.0000	1.82

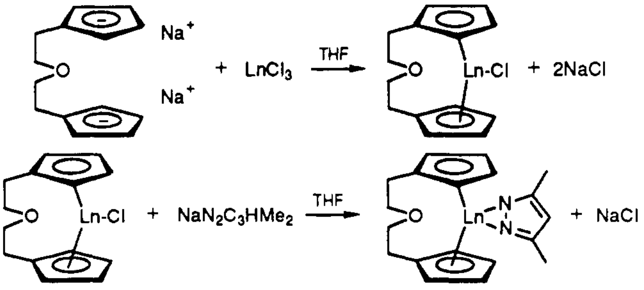
[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*a_ia_j$.

Table III. Positional Parameters of $[O(CH_2CH_2C_5H_4)_2Lu]_2(\mu\text{-}N_2C_3HMe_2)(\mu\text{-}OH)$ (4) with Standard Deviations of the Last Significant Digit in Parentheses and Equivalent Isotropic Thermal Parameters (Å²)[a]

atom	x/a	y/b	z/c	B_{eq}
Lu	0.47525 (4)	0.59906 (4)	0.55033 (1)	1.07
C1	0.5933 (10)	0.5870 (10)	0.6156 (2)	1.37
C2	0.4766 (11)	0.4792 (11)	0.6157 (2)	1.61
C3	0.5154 (12)	0.3618 (12)	0.5923 (2)	2.15
C4	0.6551 (10)	0.3959 (12)	0.5770 (2)	1.77
C5	0.7055 (11)	0.5310 (12)	0.5911 (2)	1.68
C6	0.8437 (11)	0.6149 (14)	0.5798 (3)	2.39
C7	0.8202 (11)	0.7779 (12)	0.5760 (3)	1.67
O1	0.6948 (8)	0.8015 (8)	0.5513 (1)	1.93
C8	0.6573 (14)	0.9617 (13)	0.5513 (4)	3.04
C9	0.5149 (13)	0.9802 (16)	0.5310 (3)	3.35
C10	0.3966 (13)	0.8815 (12)	0.5450 (3)	2.24
C11	0.3609 (11)	0.8395 (11)	0.5806 (3)	1.57
C12	0.2421 (13)	0.7341 (14)	0.5793 (3)	2.67
C13	0.2070 (12)	0.7057 (15)	0.5434 (3)	2.78
C14	0.2956 (13)	0.7989 (14)	0.5227 (3)	2.71
N	0.3560 (9)	0.4023 (9)	0.5171 (2)	1.39
C15	0.2423 (9)	0.3147 (10)	0.5273 (2)	1.28
C16	0.2116 (11)	0.2116 (11)	0.5	1.97
C17	0.1615 (13)	0.3279 (13)	0.5625 (3)	2.25
O2	0.5978 (6)	0.5978 (6)	0.5	0.97

[a] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*a_ia_j$.

pentadienyl rare-earth chlorides.[7] These react with equimolar amounts of (3,5-dimethylpyrazolyl)sodium in THF to yield the dimethylpyrazolyl complexes 1 and 2.



1 (Ln = Y), 2 (Ln = Lu)

Table IV. Selected Bond Distances (Å) for $[O(CH_2CH_2C_5H_4)_2Ln]_2(\mu\text{-}N_2C_3HMe_2)(\mu\text{-}OH)$ (3, 4) with Estimated Standard Deviations of the Last Significant Digit in Parentheses

	Ln = Y (3)	Ln = Lu (4)
M–C1	2.665 (5)	2.629 (8)
M–C2	2.692 (5)	2.639 (8)
M–C3	2.704 (5)	2.647 (9)
N–C4	2.663 (6)	2.615 (9)
M–C5	2.646 (6)	2.618 (9)
M–Cp1	2.39	2.34
M–C10	2.670 (6)	2.626 (9)
M–C11	2.672 (6)	2.626 (9)
M–C12	2.679 (6)	2.632 (9)
M–C13	2.674 (6)	2.591 (9)
M–C14	2.668 (6)	2.608 (9)
M–Cp2	2.39	2.33
M–O1	2.662 (4)	2.667 (7)
M–O2	2.202 (2)	2.154 (3)
M–N	2.445 (5)	2.392 (8)
C1–C2	1.384 (8)	1.42 (1)
C1–C5	1.414 (8)	1.44 (1)
C2–C3	1.402 (8)	1.40 (1)
C3–C4	1.393 (8)	1.40 (1)
C4–C5	1.408 (9)	1.39 (2)
C5–C6	1.506 (9)	1.50 (1)
C6–C7	1.520 (9)	1.48 (2)
C7–O1	1.435 (7)	1.46 (1)
C8–C9	1.48 (1)	1.49 (2)
C8–O1	1.446 (8)	1.47 (2)
C9–C10	1.479 (9)	1.47 (2)
C10–C11	1.424 (9)	1.40 (1)
C10–C14	1.396 (9)	1.43 (2)
C11–C12	1.417 (9)	1.42 (2)
C12–C13	1.392 (9)	1.39 (1)
C13–C14	1.394 (9)	1.38 (2)
C15–C16	1.375 (8)	1.39 (1)
C15–C17	1.498 (8)	1.49 (1)
C15–N	1.358 (7)	1.34 (1)
N–N	1.382 (9)	1.39 (1)
O2–H1	1.00 (12)	0.98 (5)

Table V. Selected Bond Angles (deg) for $[O(CH_2CH_2C_5H_4)_2Ln]_2(\mu\text{-}N_2C_3HMe_2)(\mu\text{-}OH)$ (3, 4) with Estimated Standard Deviations of the Last Significant Digit in Parentheses

	Ln = Y (3)	Ln = Lu (4)
O1–M–N	147.1 (1)	146.3 (2)
C2–C1–C5	108.6 (6)	106.1 (9)
C1–C2–C3	107.9 (6)	108.9 (9)
C2–C3–C4	108.5 (6)	107.8 (9)
C3–C4–C5	108.0 (5)	109.1 (9)
C1–C5–C4	107.0 (5)	108.1 (9)
C1–C5–C6	126.5 (6)	125.0 (9)
C4–C5–C6	126.3 (6)	126.6 (9)
C5–C6–C7	112.9 (5)	113.6 (9)
C6–C7–O1	108.5 (5)	108.0 (8)
Cp1–M–Cp2	127.8	127.3
C7–O1–C8	109.0 (5)	108.2 (8)
M–O1–C7	120.1 (3)	118.3 (5)
M–O1–C8	119.3 (4)	119.7 (6)
C9–C8–O1	110.4 (6)	107.3 (9)
C8–C9–C10	112.8 (6)	112.0 (9)
C9–C10–C11	127.8 (6)	130.9 (9)
C9–C10–C14	124.7 (6)	124.1 (9)
C11–C10–C14	107.4 (6)	105.0 (9)
C10–C11–C12	107.8 (6)	108.5 (9)
C11–C12–C13	107.1 (7)	108.9 (9)
C12–C13–C14	109.4 (7)	106.8 (9)
C10–C14–C13	108.3 (6)	110.8 (9)
C16–C15–C17	126.2 (6)	125.9 (9)
N–C15–C16	110.2 (6)	109.6 (9)
N–C15–C17	123.6 (6)	124.5 (9)
M-N-C15	129.0 (4)	128.7 (6)
M-O2-M′	137.2 (2)	138.3 (3)

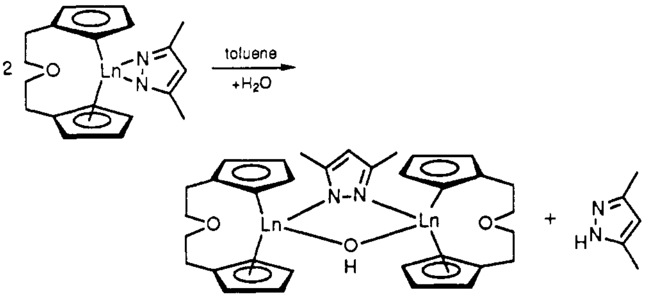
The complexes were isolated after purification via sublimation at 150–170 °C/10^{-4} Torr. Both are soluble in ethers such as THF but less soluble in aromatic hydrocarbons

Table VI. ^1H **NMR Data (ppm) for (1,1'-(3-Oxapentamethylene)dicyclopentadienyl)yttrium and -lutetium Complexes**[a]

complex	$(C_5H_4)_2$	$\Delta\delta$[b]	6,9-CH_2	7,8-CH_2	16-CH	17-CH_3	OH
$[O(CH_2CH_2C_5H_4)_2Y](\eta^2\text{-}N_2C_3HMe_2)$ (1)	6.10 5.85	0.25	2.33	3.40	5.70	2.15	
$[O(CH_2CH_2C_5H_4)_2Lu](\eta^2\text{-}N_2C_3HMe_2)$ (2)	6.05 5.90	0.15	2.32	3.42	5.38	2.18	
$[O(CH_2CH_2C_5H_4)_2Y]_2(\mu\text{-}N_2C_3HMe_2)(\mu\text{-}OH)$ (3)	6.05 5.85	0.20	2.40	3.50	5.70	2.15	9.15
$[O(CH_2CH_2C_5H_4)_2Y]Cl$[c]	5.98 5.84	0.14	2.64	4.18 3.79			
$[O(CH_2CH_2C_5H_4)_2Lu]Cl$[c]	5.87 5.78	0.09	2.63	4.24 3.79			

[a] In toluene-d_8; δ (ppm) referenced to internal toluene. [b] $\Delta\delta = \delta(1,4\text{-CH}) - \delta(2,3\text{-CH})$. [c] In THF-$d_8$.[7]

such as toluene at room temperature. They are highly sensitive toward air and water. Only a very small impurity of water in an inert solvent such as toluene causes partial hydrolysis with formation of 3 and 4, which are isolated after refluxing of 1 or 2, respectively, in toluene followed by cooling down to −30 °C as pale yellow crystals.



3 (Ln = Y), 4 (Ln = Lu)

Partial hydrolytic processes of this type have often been observed during handling of such highly sensitive organometallic compounds, resulting in the formation, isolation, and characterization by single-crystal X-ray structural analyses of new organolanthanide complexes with hydroxyl bridges such as, for example, $[Cp_2Y(\mu\text{-}OH)]_2(PhC{\equiv}CPh)$[22] or organolanthanide clusters containing interstitial oxygen atoms such as, for example, in $[Na_2(^tBuOGd)_4(\mu_3\text{-}O^tBu)_4(\mu_6\text{-}O)]$,[23] $[Ln_3(\mu\text{-}pzMe_2)_6(\eta^2\text{-}pzMe_2)_3(\mu_3\text{-}O)Na_2(THF)_2]$,[15] $[Cp_5Y_5(\mu_3\text{-}OMe)_4(\mu_2\text{-}OMe)_4(\mu_5\text{-}O)]$,[24] or $[Cp_5Gd_5(\mu_3\text{-}OMe)_4(\mu_2\text{-}OMe)_4(\mu_5\text{-}O)]$.[23]

The ^1H NMR data for the diamagnetic complexes 1–3 together with some data for the starting materials are given in Table VI. The spectra are consistent with the structures of the compounds. As previously described,[7,8,25] the $\Delta\delta$ value implies the distribution of charge on the cyclopentadienyl ring and the torsional ring mobility of the cyclopentadienyl moieties. The increased $\Delta\delta$ values of 1–3 compared to those of the corresponding rare-earth chlorides demonstrate that this value depends not only on the angle between the two cyclopentadienyl rings but also on the crowding arising from the other ligation around the metal.

Molecular Structure of $[O(CH_2CH_2C_5H_4)_2Ln(\mu\text{-}N_2C_3HMe_2)(\mu\text{-}OH)Ln(C_5H_4CH_2CH_2)_2O]$ (3, 4). Figure 1 shows the first example of an X-ray structure of a complex with a five-atom chain bridging two cyclopentadienyl rings in the coordination sphere of a rare-earth metal. 3 is a dinuclear complex with both yttriums coordinated each by one 1,1'-(3-oxapentamethylene)dicyclopentadienyl ligand and bridged by a pyrazolate via nitrogen and one hydroxyl group with C_2 symmetry. For this type of highly symmetric structure there is no other example known in dimeric organolanthanide complexes containing two different bridging ligands. The molecule possesses a (noncrystallographic) mirror plane, in which lie the 3,5-dimethylpyrazolyl ligand, the hydroxyl group, both yttriums, and both oxygen atoms of the bridging chains. Both bridging 1,1'-(3-oxapentamethylene) chains are located at the same side of the complex, opposite the 3,5-dimethylpyrazolyl ligand. This is of course caused by the bulk of the ligands, indicating the impossibility of forming a dimeric complex of this type containing two 3,5-dimethylpyrazolyl ligands together with the 1,1'-(3-oxapentamethylene) bridges in the same molecule.

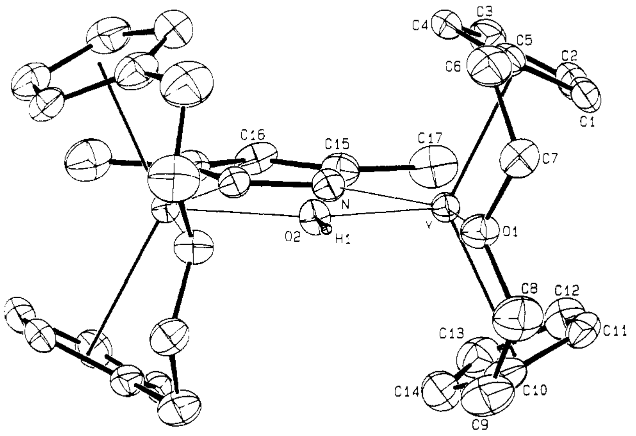


Figure 1. ORTEP drawing[41] of $[O(CH_2CH_2C_5H_4)_2Y]_2(\mu\text{-}N_2C_3HMe_2)(\mu\text{-}OH)$ (3) with the numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

The average yttrium–cyclopentadienyl carbon distance in 3, 2.674 (5) Å, is similar to that found in other organoyttrium(III) complexes, such as 2.66 (2) Å in $[(C_5H_5)_2Y(\mu\text{-}CH_3)]_2$,[26] 2.69 (2) Å in $[(CH_3C_5H_4)_2Y(\mu\text{-}H)(THF)]_2$,[27] 2.68 Å in $[(C_5H_5)_2Y(\mu\text{-}HC{=}N^tC_4H_9)]_2$,[28] 2.64 Å in $[(C_5H_5)_2Y(\mu\text{-}N{=}CH^tC_4H_9)]_2$,[29] 2.651 Å in $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$,[30] and 2.68 (3) Å in $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$.[22] The ring centroid–Y–ring centroid angle (127.8 (3)°) is also in accordance with that in the compounds mentioned above: 128.9°,[26] 127.5°,[27]

---

(22) Evans, W. J.; Hozbor, M. A.; Bott, S. G.; Robinson, G. H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 1990.

(23) Schumann, H.; Kociok, G.; Loebel, J. *Z. Anorg. Allg. Chem.* **1990**, *581*, 69.

(24) Evans, W. J.; Sollberger, M. S. *J. Am. chem. Soc.* **1986**, *108*, 6095.

(25) Chen, Z.; Zhong, X.; Qian, C.; Xie, Z.; Huang, Y. *Youji Huaxue* **1988**, *8*, 235.

(26) Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 54.

(27) Evans, W. J.; Meadows, J. H.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 2008.

(28) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 1552 and references therein.

(29) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291.

(30) Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 1291.

127.2°,[28] 129.7°,[29] 128.1°,[30] and 130°;[22] likewise, the Y–O2 distance (2.202 (2) Å) is similar to the 2.275 (3)- and 2.290 (3)-Å distances in $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$[30] but is slightly shorter than the 2.33 (2) and 2.36 (2) Å found in $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$.[22] The angle Y–O2–Y′ = 137.2 (2)° is significantly larger than that in $[(CH_3C_5H_4)_2Y(\mu\text{-}OCH{=}CH_2)]_2$ (106.9 (1)°)[30] and in $[(C_5H_5)_2Y(\mu\text{-}OH)]_2(C_6H_5C{\equiv}CC_6H_5)$,[22] because of the bulky bridging 3,5-dimethylpyrazolyl ligand. The Y–N distance of 2.445 (5) Å in **3** is between those of an yttrium–nitrogen single bond and a N→Y coordinative bond. Examples of this first type of bonding have been demonstrated in $[(C_5H_5)_2Y(\mu\text{-}N{=}CH^tC_4H_9)]_2$ (2.314 (9) and 2.382 (9) Å),[29] in $[(C_5H_5)_2Y(\mu\text{-}HC{=}N^tC_4H_9)]_2$ (2.325 (4) Å),[28] in $(C_5H_5)_2Lu(NC_4H_2Me_2)(THF)$ (2.289 (4) Å),[31] and in $[Yb_3(\mu\text{-}N_2C_5H_7)_6(\eta^2\text{-}N_2C_5H_7)_3(\mu_3\text{-}O)Na_2(THF)_2]$ (2.275 (5)–2.348 (5) Å).[15] For the second type of bonding a minimum bond length of 2.50 Å is assumed.[28] This larger Y–N distance is due to the crowded molecular structure in **3**.

The most remarkable feature of the structure of **3** is the intramolecular coordinative bond from the oxygen atom of the 1,1′-(3-oxapentamethylene) bridge to yttrium. This Y–O1 distance of 2.662 (4) Å is significantly longer than the distances Y–O in all the other dicyclopentadienylyttrium complexes containing THF coordinated to yttrium investigated so far by X-ray diffraction, ranging from 2.379 (8) Å in $(C_5Me_5)_2Y(CH_3)(THF)$,[32] to 2.410 (7) Å in $(C_5Me_5)_2YCl(THF)$,[33] to 2.451 (4) Å in $(C_5H_5)_3Y(THF)$,[34] to 2.460 (8) Å in $[(CH_3C_5H_4)_2YH(THF)]_2$,[27] to 2.466 (3) Å in $(C_5Me_5)_2Y(C(CH_2C_6H_3Me_2){=}NC_6H_3Me_2)(THF)$,[35] and to 2.491 (5) Å in $[(Me_2C_5H_3)_2YH(THF)]_2$.[36] A shorter Y–O distance would influence the whole geometry around yttrium because of the 3-oxopentamethylene bridge between both cyclopentadienyl rings. Either the ring centroid–yttrium distance or the ring centroid–yttrium–ring centroid angle must be increased, to allow a more close coordination of the oxygen atom to yttrium. The yttrium–ring centroid distances are in agreement with those in other dicyclopentadienylyttrium complexes. The ring centroid–yttrium–ring centroid angle in **3** (127.8 (3)°) is smaller than in other complexes of this type investigated up to now: e.g., 132.0° in $(C_5Me_5)_2Y(C(CH_2C_6H_3Me_2){=}NC_6H_3Me_2)(THF)$,[35] 136.2 (4) and 136.6 (4)° in $(C_5Me_5)_2YCl(THF)$,[34] and 137.0 (3)° in $(C_5Me_5)_2Y(CH_3)(THF)$.[32] Further decrease of this angle is evidently impossible because of the bulky dimethylpyrazolyl ligand bonded to the same yttrium atom. Continuing investigations on other new dicyclopentadienyl ligands with longer bridges between the cyclopentadienyl rings are in progress to prove this statement.

The geometry of the lutetium compound **4** is similar to that of the yttrium complex **3**, except that bond distances involving the metal atom are generally shorter for Lu than for Y. However, the average lutetium–cyclopentadienyl carbon distance in **4**, 2.623 Å, agrees well with that found in other Lu(III) cyclopentadienyl complexes, e.g. $(C_5H_5)_2Lu(NC_4H_2Me_2)(THF)$[31] (2.568–2.657 Å) and a series of other compounds $(C_5H_5)_2Lu(L)(THF)$.[37–39] As in **3**, the metal–nitrogen distance Lu–N, 2.392 (8) Å, is considerably longer than the distances found in complexes with other nitrogen-containing ligands, e.g. $(C_5H_5)_2Lu(NC_4H_2Me_2)(THF)$[31] (2.289 (4) Å) and $[Li(THF)_4][(C_5H_5)_2Lu(NPh_2)_2]$[40] (2.290 (7) and 2.293 (7) Å). The lutetium–oxygen bond distance Lu–O2 is 2.154 (3) Å; it is significantly shorter than the Y–O2 bond. The angle Ln–O2–Ln′ is about the same in both compounds (138.3° for Ln = Lu vs 137.2° for Ln = Y), also a consequence of the bulky 3,4-dimethylpyrazolyl ligand.

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

Supplementary Material Available: Tables of thermal parameters and hydrogen parameters for **3** and **4** (4 pages); listings of observed and calculated structure factors for **3** and **4** (26 pages). Ordering information is given on any current masthead page.

---

(31) Schumann, H.; Lee, P. R.; Dietrich, A. *Chem. Ber.* **1990**, *123*, 1331.

(32) den Haan, K. H.; de Boer, J. L.; Teuben, J. H.; Smeets, W. J. J.; Spek, A. L. *J. Organomet. Chem.* **1987**, *327*, 31.

(33) Evans, W. J.; Grate, J. W.; Levan, K. R.; Bloom, I.; Peterson, T. T.; Doedens, R. J.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1986**, *25*, 3614.

(34) Rogers, R. D.; Atwood, J. L.; Emad, A.; Sikora, D. J.; Rausch, M. D. *J. Organomet. Chem.* **1981**, *216*, 383.

(35) den Haan, K. H.; Luinstra, G. A.; Meetsma, A.; Teuben, J. H. *Organometallics* **1987**, *6*, 1509.

(36) Evans, W. J.; Drummond, D. K.; Hanusa, T. P.; Doedens, R. J. *Organometallics* **1987**, *6*, 2279.

(37) Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 292.

(38) Schumann, H.; Genthe, W.; Bruncks, N.; Pickardt, J. *Organometallics* **1982**, *1*, 1194.

(39) Ni, C.; Zhang, Z.; Deng, D.; Qian, C. *J. Organomet. Chem.* **1986**, *306*, 209.

(40) Schumann, H.; Palamidis, E.; Loebel, J. *J. Organomet. Chem.* **1990**, *390*, 45.

(41) Johnson, C. K. ORTEP; Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.