cis-Methylmanganese tetracarbonyl tributylphosphine: R_f = 0.65; 9:1 hexanes/Et_2O; IR (CCl_4, cm^{-1}) 2962 (m), 2934 (m), 2875 (m), 2053 (s), 1977 (s), 1959 (s), 1930 (s); ^1H NMR ($CDCl_3$) δ 1.69 (br s, 6 H), 1.43 (br s, 12 H), 0.94 (br s, 9 H), −0.47 (br s, 3 H); ^{13}C NMR ($CDCl_3$) δ 26.2 (d, $J_{P,C}$ = 23.0 Hz), 25.2, 24.2 (d, $J_{P,C}$ = 12.5 Hz), 13.5, −17.3 (d, $J_{P,C}$ = 10.0 Hz); mass spectrum, m/z (relative intensity, %) 384 (2), 300 (17), 272 (M^+ − 4CO, 100), 257 (38); high-resolution mass spectrum, m/z 272.1465 (M^+ − 4CO, calcd for $C_{13}H_{30}PMn$, m/z 272.1466). *cis*-Acetylmanganese tetracarbonyl tributylphosphine: R_f = 0.31; 9:1 hexanes/Et_2O; IR (CCl_4, cm^{-1}) 2962 (m), 2933 (m), 2875 (m), 2060 (m), 1986 (s), 1961 (s), 1947 (s), 1634 (m); ^1H NMR ($CDCl_3$) δ 2.53 (br s, 3 H), 1.76 (br s, 6 H), 1.38 (br s, 12 H), 0.92 (br s, 9 H); ^{13}C NMR ($CDCl_3$) δ 52.1, 26.2 (d, $J_{P,C}$ = 24.0 Hz), 25.2, 24.2 (d, $J_{P,C}$ = 12.5 Hz), 13.5; mass spectrum, m/z (relative intensity, %) 384 (3), 369 (1), 300 (19), 272 (M^+ − 5CO, 100), 257 (39); high-resolution mass spectrum, m/z 272.1478 (M^+ − 5CO, calcd for $C_{13}H_{30}PMn$, m/z 272.1466).

Bromination of Manganacycle 7: Formation of Manganacycle 8. Bromination of manganacycle 7 has been described previously.[1f]

Manganacycle 12. The preparation of manganacycle 12 has been previously described.[1f]

Reaction of Manganacycle 13 and Triphenylphosphine. A hexane (4 mL) solution of manganacycle 13 (72 mg, 0.19 mmol) and triphenylphosphine (76 mg, 0.29 mmol) was stirred at room temperature in the dark for 21 h. Evaporation of the solvent and chromatography of the residue on silica gave 94 mg (82%) of manganacycle 14 as a pale yellow gum. The product was a single diastereomer as determined from the ^{31}P NMR spectrum and was assigned the *fac* stereochemistry based upon the CO pattern in the infrared spectrum: R_f = 0.13; 4:1 hexane/EtOAc; IR (CCl_4, cm^{-1}) 2017 (s), 1940 (s), 1906 (s), 1678 (m), 1641 (w), 1436 (m), 1163 (m); ^1H NMR (C_6D_6, very broad signals) δ 7.78, 7.23, 4.02, 3.58, 2.89; ^{13}C NMR (C_6D_6) δ 232.5, 183.8, 134–128, 50.3, 48.5, 47.1, 31.6 (d, $J_{P,C}$ = 10.0 Hz); ^{31}P NMR (C_6D_6, vs H_3PO_4) δ 56.3 (s).

Preparation of Type 2 and Type 3 Manganese Complexes. The preparation of type 2 and type 3 adducts of methyl- and benzylmanganese pentacarbonyl has been described previously.[1f]

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Registry No. 1 (R = Me), 13601-24-6; 3 (R^3 = Me), 25281-94-1; 3 (R^3 = $PhCH_2$), 113749-00-1; 6, 113748-89-3; 7, 113749-01-2; 8, 113749-02-3; 10, 54834-89-8; 11, 88996-56-9; 12, 88996-58-1; 13, 113748-96-2; 14, 120311-01-5; η^1-$H_2C{=}CHCH_2Mn(CO)_5$, 14057-83-1; $PhCH_2Mn(CO)_4(PBu_3)$, 120408-29-9; $PhCH_2Mn(CO)_5$, 14049-86-6; $PhMn(CO)_5$, 13985-77-8; $CH_3C(O)Mn(CO)_4(PBu)_3$, 105180-21-0; $PhCH_2C(O)Mn(CO)_4(PBu_3)$, 120311-00-4; *cis*-methylmanganese tetracarbonyl tributylphosphine, 105180-19-6.

Organometallic Compounds of the Lanthanides. 48.[1] Cyclooctatetraenyl Pentamethylcyclopentadienyl Derivatives of the Rare Earths

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The reaction of $(C_8H_8)LnCl(THF)_n$ compounds (Ln = Pr, Sm, Gd, Tb, Dy, Er, and Lu) with NaC_5Me_5 in tetrahydrofuran leads to cyclooctatetraenyl pentamethylcyclopentadienyl rare earth complexes of the type $(C_8H_8)Ln(C_5Me_5)(THF)_x$ (2). These compounds were characterized by elemental analyses and NMR and mass spectroscopy. The X-ray structural analysis of $(C_8H_8)Lu(C_5Me_5)$ (2i) shows it to be orthorhombic with a = 10.282 (2), b = 11.549 (2), and c = 12.969 (2) Å, space group $Pnam$, Z = 4, and D(calcd) = 1.787 g cm^{-3}. The structure was solved from 1766 observed reflections with $F_o \geqslant 3\sigma(F_o)$ and refined to a final R factor of 0.024. The expected sandwich molecular structure is only slightly bent according to the ring centroid–Lu–ring centroid angle of 173°.

Introduction

Mixed-sandwich compounds of the type $(C_8H_8)M(C_5H_5)$ have been known since 1969 when Oven and Liefde Meijer[2] prepared $(C_8H_8)Ti(C_5H_5)$. The crystal structure of this complex was solved 1 year later by Kroon and Helmholdt.[3] Soon after, analogous compounds of the group 3 elements Sc[4] and Y[5] as well as of the lanthanides Nd, Sm, Ho, and Er[5] were prepared from $(C_8H_8)LnCl$ and NaC_5H_5 or $C_5H_5LnCl_2$ and $K_2C_8H_8$. However, the starting cyclooctatetraenyl rare earth chlorides as well as the mixed sandwiches have not been characterized very well; some of them have been formulated as solvent-free complexes and some as adducts with one or two THF molecules. On the basis of the X-ray structural analyses of $(C_8H_8)CeCl(THF)_2$[7,8] and $(C_8H_8)NdCl(THF)_2$,[9] which show the

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molecules to be built up of two $(C_8H_8)(THF)_2Ln$ units bridged by two chlorine atoms, a dimeric structure was also claimed for the complexes $(C_8H_8)LnCl(THF)_2$ where Ln = Ce and Sm.[6] Ten years later, the original route for the synthesis of cyclooctatetraenyllanthanide chlorides was improved by Wayda in the preparation of the tetrahydrofuran adducts $(C_8H_8)LaCl(THF)_2$, $(C_8H_8)ErCl(THF)$, and $(C_8H_8)LuCl(THF)$.[10]

$(C_8H_8)Ti(C_5Me_5)$ and $(C_8H_8)Zr(C_5Me_5)$, the first cyclooctatetraenyl pentamethylcyclopentadienyl complexes of the early transition metals have been prepared very recently.[11] During the time in which our own investigations have been in progress, the corresponding scandium, yttrium, and lanthanum complexes have been isolated as unsolvated species $(C_8H_8)Ln(C_5Me_5)$, in addition to the solvent-coordinated lanthanum complex $(C_8H_8)La(C_5Me_5)(THF)$. The solid-state IR spectrum of the unsolvated lanthanum derivative indicates a polymeric structure.[12]

We now report on the synthesis and characterization of a larger series of organolanthanide complexes $(C_8H_8)Ln(C_5Me_5)(THF)_x$ (**2**) with Ln = Y, La, Pr, Sm, Gd, Tb, Dy, Er, and Lu as well as on the first X-ray structure determination of one of these mixed lanthanide sandwiches, $(C_8H_8)Lu(C_5Me_5)$ (**2i**).

Experimental Section

All reactions and preparations were performed by using Schlenk tubes in an atmosphere of dry, oxygen-free argon. The solvents used were dried and freed of oxygen by refluxing and keeping over potassium or sodium benzophenone ketyl and were distilled under argon prior to use. Anhydrous rare earth chlorides were prepared from the pure oxides (Rhone-Poulenc, France) by reaction with $SOCl_2$[13] (La, Pr, Gd) or with NH_4Cl[14] (Y, Sm, Tb, Dy, Er, Lu) and Soxhlet extraction with THF. The THF content was determined by C, H analysis. Cyclooctatetraene (Merck) was degassed by vacuum transfer and stored over molecular sieves (4 Å) under argon. C_5Me_5Na was prepared as described previously.[15] Chlorocyclooctatetraenyl(tetrahydrofuran)lanthanide complexes $[(C_8H_8)LnCl(THF)_x]_2$ were obtained in 50–90% yield according to the preparation of $[(C_8H_8)LuCl(THF)]_2$ by Wayda.[10]

Melting points were determined in sealed, argon-filled capillaries and are uncorrected. 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, but only in very few cases because of their especially high sensitivity toward traces of moisture and air of most of the compounds. Mass spectra were obtained on a Varian MAT 311 A. ^1H and ^{13}C NMR spectra were obtained in sealed 5-mm tubes on a Bruker AM-270 instrument at 25 °C or on a Bruker WP 80 SI instrument at 30 °C. Aquisition times were chosen so that no saturation of the sample signals occurred (10 ms to 4 s depending on the metal).

Cyclooctatetraenyl(pentamethylcyclopentadienyl)yttrium(III) (2a). A 0.95 M solution of NaC_5Me_5 (2.7 mL, 2.6 mmol) in THF was added dropwise to a stirred suspension of 0.75 g (2.5 mmol) of **1a** in 50 mL of THF. After 24 h of further stirring, the solvent was removed in vacuo. The residue was extracted with 50 mL of toluene. The clear solution was concentrated in vacuo until the first precipitate appeared. The solution was then decanted and cooled to −20 °C overnight. Colorless crystals could be isolated by decanting of the solution and drying in vacuo yielding 0.30 g (37%) of **2a**; mp >230 °C. Anal. Calcd for $C_{18}H_{23}Y$: C, 65.85; H, 7.06. Found: C, 65.78; H, 7.21.

Cyclooctatetraenyl(pentamethylcyclopentadienyl)(tetrahydrofuran)lanthanum(III) (2b). A 0.7 M solution of NaC_5Me_5 (6.9 mL, 4.8 mmol) in THF was added dropwise to a suspension of 2.7 g (4.8 mmol) of **1b** in 200 mL of THF. After 15 h of stirring, the solvent was removed in vacuo and the residue dried for 1 h at 40 °C (0.1 Torr). The yellowish powder was Soxhlet extracted with 150 mL of benzene for 24 h, yielding 1.33 g (62%) of impure **2b**, which could not be completely purified from Cl^-.

Cyclooctatetraenyl(pentamethylcyclopentadienyl)(tetrahydrofuran)praseodymium(III) (2c). This compound was prepared from 1.6 g (3.8 mmol) of **1c** by using the method described for **2a**. After several extractions only 0.1 g (6%) of yellow **2c** could be isolated because of its low solubility.

Cyclooctatetraenyl(pentamethylcyclopentadienyl)(tetrahydrofuran)samarium(III) (2d). This compound was prepared from 1.35 g (3.7 mmol) of **1d** by using the method described for **2a**: yield 0.92 g (54%) of red-brown crystals of **2d**; mp 145–147 °C.

Cyclooctatetraenyl(pentamethylcyclopentadienyl)(tetrahydrofuran)gadolinium(III) (2e). This compound was prepared from 2.85 g (7.7 mmol) of **1e** by using the method described for **2a**: yield 2.85 g (79%) of yellowish crystals of **2e**; mp 217–218 °C. Anal. Calcd for $C_{18}H_{23}Gd$ (free of THF): C, 54.56; H, 5.85. Calcd for $C_{22}H_{31}GdO$: C, 56.41; H, 6.67. Found: C, 55.93; H, 6.71.

Cyclooctatetraenyl(pentamethylcyclopentadienyl)terbium(III) (2f). This compound was prepared from 0.50 g (1.4 mmol) of **1f** by using the method described for **2a** and recrystallized from hexane: yield 0.24 g (44%) of slightly yellowish crystals of **2f**. Anal. Calcd for $C_{18}H_{23}Tb$: C, 54.28; H, 5.82. Found: C, 54.53; H, 5.62.

Cyclooctatetraenyl(pentamethylcyclopentadienyl)dysprosium(III) (2g). This compound was prepared from 2.0 g (5.3 mmol) of **1g** by using the method described for **2a**: yield 1.66 g (70%) of yellow crystals of **2g**; mp >230 °C. Anal. Calcd for $C_{18}H_{23}Dy$: C, 53.80; H, 5.77. Found: C, 54.12; H, 5.88.

Cyclooctatetraenyl(pentamethylcyclopentadienyl)erbium(III) (2h). This compound was prepared from 2.23 g (5.9 mmol) of **1h** by using the method described for **2a**: yield 1.44 g (60%) of pink crystals of **2h**.

Cyclooctatetraenyl(pentamethylcyclopentadienyl)lutetium(III) (2i). This compound was prepared from 2.30 g (5.9 mmol) of **1i** by using the method described for **2a**: yield 1.2 g (49%) of colorless crystals of **2i**; mp >230 °C. Anal. Calcd for $C_{18}H_{23}Lu$: C, 52.18; H, 5.59; Lu, 42.23. Found: C, 52.24; H, 5.55; Lu, 42.70.

X-ray Data Collection, Structure Determination, and Refinement for 2i. Suitable crystals of **2i** were grown by cooling a concentrated solution in toluene to −20 °C for 1 week. A crystal of size 0.45 × 0.32 × 0.25 mm^3 was selected by using a device similar to that reported by Veith and Bärnighausen,[16] glued with grease on top of a glass fiber, and placed in the cold nitrogen beam (140 (5) K) of the diffractometer.

Initial investigations revealed the crystal system to be orthorhombic. Cell dimensions were obtained from a least-squares fit to the $\pm 2\theta$ values of 48 reflections in the range of $35° \leq 2\theta \leq 54°$. Intensities of all reflections with $1° \leq 2\theta \leq 56°$ ($0 \rightarrow 13$, $-15 \rightarrow 0$, $0 \rightarrow 17$) were measured with Mo Kα radiation (λ = 0.71069 Å) in the θ–2θ scan mode. Reflections were scanned with variable scan time (maximum 80 s), depending on intensities, with two-thirds of the time used for scanning the peak and one-sixth spent on each of the left and right background. The total X-ray exposure time was 54 h. The intensities of three check reflections were monitored every 1.5 h for crystal decay. The maximum fluctuation for these reflections was 2.6%. Corresponding corrections were applied to the raw intensities. The crystal orientation was checked after every 50 intensity measurements by scanning three reflections distributed in reciprocal space. A new orientation matrix was automatically calculated from a list of 25 recentered reflections if the angular change was greater than 0.1°. The raw data were

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Table I. Crystal and Data Collection Parameters for $(C_8H_8)Lu(C_5Me_5)$ (2i)[a]

formula	$C_{18}H_{23}Lu$
fw, g/mol	414.35
space group	*Pnam*
a, Å	10.282 (2)
b, Å	11.549 (2)
c, Å	12.969 (2)
V, Å^3	1540
Z	4
D_{calcd}, g/cm^3	1.787
μ, cm^{-1}	61.1
$F(000)$	808
diffractometer	Enraf-Nonius CAD-4
radiatn; λ, Å	Mo Kα; 0.71069
monochromator	graphite crystal
temp, K	140 (5)
scan technique	θ–2θ
scan angle, deg	$0.95 + 0.30 \tan\theta$
aperture, mm	3.00
2θ limits, deg.	$1 \le 2\theta \le 56$
no. of unique data	1863
no. of obsd data, $F_o \ge 3\sigma(F_o)$	1766
correctns	Lorentz, polarization, absorption, anomalous dispersion
no. of refined parameters	112
$R = \sum\lVert F_o\rvert - \lvert F_c\rVert/\sum\lvert F_o\rvert$	0.024
$R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\sum wF_o^2]^{1/2}$	0.033
weight	$1/[\sigma^2(F_o) + 0.00021F_o^2]$

[a] Estimated standard deviations of the last significant digit are given in parentheses.

Table II. Positional Parameters of $(C_8H_8)Lu(C_5Me_5)$ (2i) with Standard Deviations of the Last Significant Digit in Parentheses and Equivalent Isotropic Thermal Parameters (Å^2)[a]

atom	x/a	y/b	z/c	B_{eq}
Lu	0.13565 (2)	0.51320 (2)	0.2500	1.22
C1	0.3729 (4)	0.4516 (5)	0.2500	1.37
C2	0.3155 (3)	0.4001 (3)	0.1606 (3)	1.35
C3	0.2230 (3)	0.3166 (3)	0.1947 (2)	1.33
C4	0.4774 (5)	0.5432 (5)	0.2500	2.23
C5	0.3485 (4)	0.4276 (3)	0.0505 (3)	1.90
C6	0.1433 (4)	0.2378 (3)	0.1277 (3)	2.08
C7	0.1649 (6)	0.7143 (5)	0.1960 (6)	6.29
C8	0.0897 (9)	0.6620 (7)	0.1226 (5)	6.45
C9	−0.0131 (8)	0.5890 (7)	0.1218 (5)	5.79
C10	−0.0870 (6)	0.5332 (6)	0.1927 (9)	7.44

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

Table III. Selected Bond Distances (Å) for $(C_8H_8)Lu(C_5Me_5)$ (2i) with Estimated Standard Deviations of the Last Significant Digit in Parentheses

Lu–C1	2.533 (4)	C2–C3	1.424 (4)
Lu–C2	2.537 (3)	C2–C5	1.501 (5)
Lu–C3	2.541 (3)	C3–C3′[a]	1.434 (6)
Lu–C7	2.443 (5)	C3–C6	1.501 (5)
Lu–C8	2.432 (5)	C7–C7′[a]	1.401 (15)
Lu–C9	2.429 (5)	C7–C8	1.367 (10)
Lu–C10	2.427 (6)	C8–C9	1.353 (11)
C1–C2	1.431 (4)	C9–C10	1.355 (12)
C1–C4	1.508 (7)	C10–C10′[a]	1.487 (24)
Lu–Cp[b]	2.228 (8)	Lu–Cot[b]	1.634 (7)

[a] Symmetry code: x, y, $^1/_2 - z$. [b] Cp and Cot denote the centroids of the cyclopentadienyl and cyclooctatetraenyl groups.

Table IV. Selected Bond Angles (deg) for $(C_8H_8)Lu(C_5Me_5)$ (2i) with Estimated Standard Deviations of the Last Significant Digit in Parentheses

C2–Lu–C1	32.8 (1)	Lu–C1–C4	119.1 (4)
C3–Lu–C1	54.1 (1)	C2–C1–C4	125.9 (2)
C3–Lu–C2	32.6 (1)	Lu–C2–C1	73.4 (2)
C7–Lu–C1	98.8 (2)	Lu–C2–C3	73.9 (2)
C7–Lu–C2	105.8 (2)	C1–C2–C3	107.8 (3)
C7–Lu–C3	136.6 (2)	Lu–C2–C5	119.3 (2)
C8–Lu–C1	112.9 (2)	C1–C2–C5	126.1 (3)
C8–Lu–C2	101.4 (1)	C3–C2–C5	126.2 (3)
C8–Lu–C3	120.6 (2)	Lu–C3–C2	73.5 (2)
C8–Lu–C7	32.6 (3)	Lu–C3–C6	120.9 (2)
C9–Lu–C1	135.2 (2)	C2–C3–C6	126.5 (3)
C9–Lu–C2	109.4 (2)	C3–Lu–C3′	32.8 (1)
C9–Lu–C3	110.5 (2)	Lu–C7–C8	73.3 (3)
C9–Lu–C7	62.4 (3)	C7–Lu–C7′	33.3 (4)
C9–Lu–C8	32.3 (3)	Lu–C8–C7	74.2 (3)
C1–Lu–C10	159.4 (2)	Lu–C8–C9	73.7 (3)
C2–Lu–C10	126.6 (2)	C7–C8–C9	136.3 (6)
C3–Lu–C10	109.3 (2)	Lu–C9–C8	74.0 (3)
C7–Lu–C10	86.3 (3)	Lu–C9–C10	73.7 (4)
C8–Lu–C10	62.4 (3)	C8–C9–C10	136.8 (6)
C9–Lu–C10	32.4 (3)	C10–Lu–C10′	35.7 (6)
Lu–C1–C2	73.8 (2)	Lu–C10–C9	73.9 (3)
Cp–Lu–Cot	172.9 (3)		

corrected for Lorentz and polarization effects. An empirical absorption correction was applied by using the psi scan method (maximum transition 99.4%, minimum transition 57.7%).

From the systematic absences ($0kl$, $k + l = 2n + 1$; $h0l$, $h = 2n + 1$) the space group was determined to be either the noncentrosymmetric group $Pna2_1$ (No. 33) or the centrosymmetric group *Pnam* (nonstandard setting of *Pnma*, No. 62). Calculation of the density ($\rho_{calcd} = 1.786$ g/cm^3) indicated four molecules in the unit cell. Attempts to refine the structure in $Pna2_1$ failed leaving *Pnam* as the correct choice. The general position in space group *Pnam* is eightfold, so that the center of the molecules have to lie at special positions. This assumption was right and the position of the heavy atom was located from a three-dimensional Patterson map. All non-hydrogen positions were found after successive difference Fourier syntheses and refined anisotropically by full-matrix least squares minimizing the quantity $\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$. The atoms Lu, C1, and C4 lie in the mirror plane. Hydrogen positions were partially located and refined isotropically, partially calculated (d(C–H) = 1.08 Å) and added to the structural model with a constant isotropic temperature factor ($U_{iso,H} = 0.05$ Å^2). At this stage of refinement the agreement values R and R_w were 3.3 and 4.9% for 1807 reflections with $F_o \geqslant 2\sigma(F_o)$. Inspection of the molecule revealed a preferred direction of thermal motion for all atoms. This was most probably caused by an insufficient absorption correction (reflections located for the psi scan method were exclusively of $0kl$ fashion). Therefore an additional empirical absorption correction recommended by Walker and Stuart[17] for cases of insufficient experimental absorption correction was applied by using the program DIFABS ($\mu = 61.1$ cm^{-1}, minimum correction 0.86, maximum correction 1.14). The weighting scheme employed for the least-squares calculation was $1/(\sigma^2(F) + 0.00021F^2)$. The maximum ratio of shift to error (Δ/σ) was 0.002. The final difference Fourier map showed no unusual residual electron density (maximum 0.54 e·Å^{-3}).

All X-ray measurements were done on an Enraf-Nonius CAD-4 automatic diffractometer fitted with low-temperature equipment. Scattering factors and anomalous dispersion terms for C and Lu were taken from ref 18 and scattering factors for H from Stewart, Davidson, and Simpson.[19] All calculations were performed with SHELX-76.[20] Additional data pertinent to the crystal structure determination are summarized in Table I. The final atomic parameters are given in Table II. Bond distances and bond angles are summarized in Tables III and IV, respectively. Further details of the structure investigations are available on request from the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, West-Germany, on quoting the depository number CSD-53799, the authors, and the full citation of the journal.

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Table V. Metal-Containing Fragments in the Mass Spectra of the Complexes $(C_8H_8)Ln(C_5Me_5)(THF)_x$ (2a and 2c–i)[a]

	Ln	temp, °C	M^+	$(M - CH_3)^+$ [M − 15]	$(M - C_8H_8)^+$ [M − 104]	$(LnC_{10}H_{10})^+$ [M − 109]	$(M - C_5Me_5)^+$ [M − 135]	Ln^+ [M − 239]
2c	Pr	135	100			13	215	
2d	Sm	120	100		470	267[b] + 13	32	126
2e	Gd	25	100	3	4	15	124	2
2f	Tb	135	100	7	3	14	203	41
2g	Dy	100	100	9	7	19	135	56
2a	Y	120	100	10	3	8	121	2
2h	Er	100	100	15	7	19	91	24
2i	Lu	120	100	15	12	5	44	10

[a] $M = (C_8H_8)Ln(C_5Me_5)$. [b] Calculated isotope intensity of $(M - C_8H_8)^+$.

Results and Discussion

Rare earth trichlorides react with $K_2C_8H_8$ in THF at room temperature to give the corresponding cyclooctatetraenyl rare earth chlorides. The reactions of $(C_8H_8)LnCl(THF)_n$ with equimolar amounts of NaC_5Me_5 in THF yield the mixed-sandwich complexes $(C_8H_8)Ln(C_5Me_5)(THF)_x$:

$$LnCl_3(THF)_x + K_2C_8H_8 \xrightarrow{THF} \underset{\mathbf{1}}{(C_8H_8)LnCl(THF)_n} + 2\ KCl$$

Ln = Y (**1a**), Sm (**1d**), Gd (**1e**), Tb (**1f**), Dy (**1g**), Er (**1h**), Lu (**1i**), n = 1; Ln = La (**1b**), Pr (**1c**); n = 2

$$\underset{\mathbf{1}}{(C_8H_8)LnCl(THF)_n} + NaC_5Me_5 \xrightarrow{THF} \underset{\mathbf{2}}{(C_8H_8)Ln(C_5Me_5)(THF)_x} + NaCl$$

Ln = Y (**2a**), Tb (**2f**), Dy (**2g**), Er (**2h**), Lu (**2i**), x =0; Ln = La (**2b**), Pr (**2c**), Sm (**2d**), Gd (**2e**), x = 1

The complexes **2a–i** were isolated by extraction of the reaction mixtures with benzene or toluene. However, the solubility in both of these solvents decreases considerably from Lu to La, making the isolation of the early lanthanide derivatives very difficult. All attempts failed to remove the THF from **2b–e** by heating them at 80 °C (0.01 Torr) for several hours. (Recently, it had been reported that sublimation conditions are necessary (200–225 °C (10^{-3} Torr) to remove the THF from $(C_8H_8)Ln(C_5Me_5)(THF)$[11]). However, **2e** loses at least 40–50% of the coordinated solvent as indicated by elemental analysis. Thus, gadolinium seems to be the borderline at which the complexes are stable without or only with THF coordination of the rare-earth metal.

Compound **2i** could also be obtained by a one-pot reaction starting with a mixture of $LuCl_3$ and $K_2C_8H_8$ in THF followed by the addition of NaC_5Me_5 and the final extraction with toluene. However, the yield is only 10% because repeated recrystallization is necessary to obtain the compound in a pure state.

Complexes **2a–i** are all highly sensitive toward air. However, in the absence of oxygen and water, no decomposition is observed up to 230 °C. The THF-free complexes **2a**, **2f**, **2g**, and **2i** are highly soluble in pentane.

The mass spectra of **2a–i**, recorded at 25 °C < T < 135 °C, show for all complexes the THF-free molecular ion peak, whereas there is no peak, attributable to a THF adduct. The rare earth containing fragments are listed in Table V. Additional peaks were observed for $[C_5Me_5H]^+$ (136) and the fragments $[C_5Me_{5-n}H]^+$ (121, 106, 91, 76), $[C_8H_8]^+$ (104), $[C_7H_7]^+$ (91), and $[C_6H_6]^+$ (78). For **2e**, a THF peak (72) was observed at 25 °C. The main fragments can be explained by the loss of the C_5Me_5 ligand, proceeding easier by the small rare earths. In contrast to all other complexes, the Sm compound **2d** shows a base peak for $[Sm(C_5Me_5)]^+$, since it has an accessible oxidation state, Sm(II). All compounds show a peak for $[Ln(C_{10}H_{10})]^+$ of about the same intensity, the origin of which is not clear yet. Takats et al.[4] found in the mass spectra of $(C_8H_8)Ln(C_5H_5)$ peaks of comparable intensity for $[Ln(C_8H_8)]^+$ and $[Ln(C_5H_5)]^+$.

Table VI. ^1H NMR Data (ppm) for $(C_8H_8)Ln(C_5Me_5)(THF)_x$ Complexes (2a–i) (Line Width at Half-Height)

	Ln	solv; υ_0, MHz	C_8H_8	C_5Me_5	THF
2a	Y	C_6D_6; 80	+6.31 s	+1.64 s	
2b	La	C_6D_6; 270	+6.36 s	+1.80 s	+1.17 m, +3.06 m
2c	Pr	THF-d_8; 80	−12 (20 Hz)	+7.5 (10 Hz)	*a*
2d	Sm	C_6D_6, 80	+10.05 (4 Hz)	+0.52 (<2 Hz)	+2.62, +5.30
2e	Gd	toluene-d_8; 80	+116 (2300 Hz)	+4 (1400 Hz)	
2f	Tb	toluene-d_8; 80	+142 (620 Hz)	+4 (325 Hz)	
2g	Dy	toluene-d_8; 80	+95 (1910 Hz)	+2 (1360 Hz)	
		toluene-d_8; 270	+97 (2500 Hz)	+2 (1700 Hz)	
2h	Er	toluene-d_8; 80	−37 (1850 Hz)	−8 (1200 Hz)	
2i	Lu	C_6D_6; 80	+6.25 s	+1.67 s	

[a] Fast exchange of the coordinated THF with the solvent THF.

Table VII. ^{13}C NMR Data (ppm) for $(C_8H_8)Ln(C_5Me_5)(THF)_x$ (2a–d and 2i)

	Ln	solv; υ_0, MHz	C_8H_8	C_5Me_5	C_5Me_5	THF
2a	Y	C_6D_6; 20.15	94.85 d[b]	116.32 d[c]	9.81	
2b	La	C_6D_6; 67.93[a]	97.52	118.50	10.54	69.20, 25.34
2c	Pr	THF-d_8; 67.93[a]	+198	+400	+6.3	
2d	Sm	C_6D_6; 67.93	80.80	109.19	19.20	78.12, 27.23
2h	Lu	C_6D_6; 67.93	93.54	114.99	9.99	

[a] Assignment by DEPT spectrum. [b] ^2J(C–Y) = 3.3 Hz. [c] ^2J(C–Y) = 1.7 Hz.

The detailed NMR spectral data for the complexes $(C_8H_8)Ln(C_5Me_5)(THF)_x$ are given in Tables VI and VII. The signals were assigned by the integral intensity of 8 H (C_8H_8), 15 H (C_5Me_5) and twice 4 H (THF). The presence of one or no THF could be determined by NMR except for **2c** (THF-d_8 as a solvent) and **2e** (very broad and overlapping bands between 0 and 10 ppm). The ^1H NMR data for **2a** and **2b** and the ^{13}C NMR data for **2b** were already reported[12] and agree well with our results. Due to the paramagnetism of most of these compounds the lines are very broad and shifted to unusual frequencies. All compounds reveal the expected signals in the ^1H NMR spectra whereas in the ^{13}C NMR spectra the very paramagnetic derivatives **2e**, **2g**, and **2h** make an exception. Since for the THF-free complex $(C_8H_8)Lu(C_5(CH_2Ph)_5)$[1] the positions of the hydrogen atoms are approximately known from its crystal structure, the series of mixed-sandwich complexes is an ideal system to study the effect of the paramagnetic metals on the NMR behavior of the

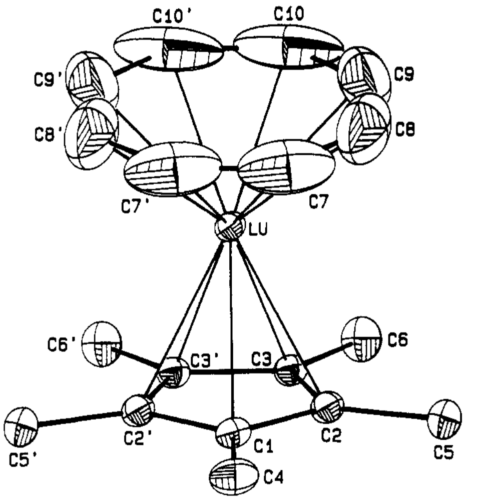

Figure 1. ORTEP drawing[21] of $(C_8H_8)Lu(C_5Me_5)$ (**2i**) with the numbering scheme. Thermal ellipsoids scaled at 50% probability level. Hydrogen atoms omitted for clarity.

neighboring nuclei. This will be the subject of further investigations.

Molecular Structure of $(C_8H_8)Lu(C_5Me_5)$ (2i). The X-ray structure shows the mixed-sandwich compound as discrete monomer with the lutetium atom η^8 bonded to the cyclooctatetraenyl ring and η^5 bonded to the pentamethylcyclopentadienyl unit. The lutetium lies over the center of both rings within the margin of an error. Figure 1 shows an ORTEP plot of the molecule with the atomic numbering scheme. Relevant bond angles and distances are summarized in Tables III and IV. Both the cyclopentadienyl and the cyclooctatetraenyl rings are planar. The maximum deviations from their respective least-squares planes are 0.018 (3) Å for C2′ and 0.075 (8) Å for C9′. The aromaticity of both rings is reflected in their carbon–carbon distances, which average 1.430 Å in the C_5Me_5 ring and 1.394 Å in the C_8H_8 ring.

The Lu–C_8H_8 carbon distance (range 2.427–2.443 Å, average 2.433 Å) is only slightly less than the Lu–C_8H_8 carbon distance (average 2.469 Å) in the previously investigated $(C_8H_8)Lu(C_5(CH_2Ph)_5)$[1] and is more than 0.1 Å less than in the only other $(C_8H_8)Lu$ complex investigated (also eight-coordinate), $(C_8H_8)Lu(C_6H_4CH_2N(Me_2)\text{-}4)(THF)$[22] (average 2.549 Å). The Lu–C_5Me_5 carbon distance (range 2.533–2.541 Å, average 2.536 Å) is also slightly less than in the analogous pentabenzyl compounds (average 2.563 Å)[1] and considerably less than in other eight-coordinate C_5Me_5Lu complexes, e.g. $(C_5Me_5)_2Lu(CH_2)_2PMe_2$[23] (average 2.71 Å), $(C_5Me_5)_2LuCl(THF)$[24] (average 2.63 Å), and $(C_5Me_5)_2Lu(S^tBu)_2Li(THF)_2$[25] (average 2.66 Å). Using the effective ionic radius for eight-coordinate Lu(III) of 0.997 Å,[26] the effective ionic radii of 1.456 Å for the C_8H_8 and 1.559 Å for the C_5Me_5 can be calculated. Those are, in fact, the smallest effective radii we have found for any lanthanoid cyclooctatetraenyl (1.49[1] to 1.57 Å[22]) and lanthanoid pentamethylcyclopentadienyl (1.59–1.84 Å) compound. Therefore, the lutetium–carbon bonds are unusually short.

The sandwich is slightly bent with an angle between the two ring centroids and the Lu atom of 173.0°. This bending is surprisingly less than in the analogous pentabenzylcyclopentadienyl complex (167.7°)[1] but more than in the mixed titanium sandwich $(C_8H_8)Ti(C_5Me_5)$ (178.1°).[11] A bent structure is generally found for ionic sandwich complexes.[27] The angle depends on the size of the ligands (cone angle[28]). Therefore, C_5Me_5 seems to be bigger than $C_5(CH_2Ph)_5$.

The CH_3 groups of the pentamethylcyclopentadienyl unit are only little bent away from the lutetium by 0.7–2.3°. This deviation is small compared to the displacement of up to 13° in $(C_5Me_5)_2LuCl(THF)$.[24]

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Registry No. **1a**, 120034-38-0; **1b**, 120034-39-1; **1c**, 12650-59-8; **1d**, 120034-40-4; **1e**, 120034-41-5; **1f**, 120034-42-6; **1g**, 120034-43-7; **1h**, 96504-51-7; **1i**, 96504-50-6; **2a**, 120034-29-9; **2b**, 120034-30-2; **2c**, 120034-31-3; **2d**, 120034-32-4; **2e**, 120034-33-5; **2f**, 120034-34-6; **2g**, 120034-35-7; **2h**, 120034-36-8; **2i**, 120034-37-9.

Supplementary Material Available: Tables of thermal parameters and hydrogen parameters for **2i** (1 page); a listing of observed and calculated structure factors for **2i** (11 pages). Ordering information is given on any current masthead page.

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