Registry No. 1, 12131-44-1; disodium tetracarbonylferrate, 14878-31-0; PPh_3, 603-35-0; $PhCH{=}CHCH_3$, 637-50-3; [n-$C_5H_{11}COFe(CO)_4]^-Na^+$, 82456-27-7; $[CH_3COFe(CO)_4]^-Li^+$, 71722-65-1; [n-$C_6H_{13}COFe(CO)_3PPh_3]^-Na^+$, 82456-28-8; [$n$-$C_4H_9COFe(CO)_4]^-Li^+$, 31627-07-3; $[\pi\text{-}C_3H_5PdCl]_2$, 12012-95-2; $[\pi\text{-}C_3H_5Pd(\text{diphos})]^+Bf_4^-$, 82456-29-9; $[\pi\text{-}C_3H_5Pd(PPh_3)]^+BF_4^-$, 82456-31-3; $[\pi\text{-}1\text{-}PhC_3H_4Pd(PPh_3)]^+BF_4^-$, 82456-33-5; CO, 630-08-0; $[\pi\text{-}1\text{-}MeC_3H_4Pd(PPh_3)]^+BF_4^-$, 58527-38-1; n-$C_5H_{11}COCH{=}CHCH_3$, 32064-72-5; (E)-$PhCH{=}CHCH_2COCH_3$, 42762-56-1; n-$C_6H_{13}COCH{=}CHCH_3$, 63024-86-2; n-$C_4H_9COCH{=}CHCH_2CH_3$, 82456-34-6; n-$C_5H_{11}COCH_2CH{=}CH_2$, 61168-10-3; $PhCH_2CH{=}CHCOCH_3$, 10521-97-8; n-$C_6H_{13}COCH_2CH{=}CH_2$, 65807-57-0; n-$C_4H_9COCH_2CH{=}CH\text{-}CH_3$, 82456-35-7; $PhCH{=}CHCH_2CH_2CH{=}CHPh$, 4439-45-6; $PhCH{=}CHCH_2COC_4H_9$, 82456-36-8; PhCOCOPh, 134-81-6; $H_2C{=}CH\text{-}CH_2COCH_2Ph$, 82456-37-9; $PhCH{=}CHCH_2OH$, 104-54-1; $H_2C{=}CHCH(Me)COC_4H_9$, 61122-64-3; $NaCo(CO)_4$, 14878-28-5; $Ni(CO)_4$, 13463-39-3; $PhCH_2MgCl$, 6921-34-2; (E)-$Ph\text{-}CH{=}CHCH_3$, 873-66-5; $PhCH{=}CHCH_2OAc$, 103-54-8; $PdCl_2(CH_3CN)_2$, 14592-56-4; $MeOCOCH_2CH{=}CHPh$, 24891-74-5; $[\pi\text{-}C_3H_5Co(CO)_2PPh_3]$, 12149-50-7.

Organometallic Compounds of the Lanthanides. 15.[1] Synthesis and X-ray Crystal Structure of Monomeric Alkyldicyclopentadienyllanthanide Compounds

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Dicyclopentadienyllutetium chloride reacts with organolithium compounds RLi [R = CH_3, C_2H_5, i-C_3H_7, C_4H_9, t-C_4H_9, t-C_5H_{11}, $CH_2Si(CH_3)_3$, $CH_2C_6H_5$, C_6H_4-4-CH_3, $C(C_6H_5)_3$], in tetrahydrofuran at −78 °C, to give monomeric alkyldicyclopentadienyllutetium derivatives, $Cp_2LuR{\cdot}THF$. Dicyclopentadienylsamarium *tert*-butoxide, prepared from $SmCl_3$, NaC_5H_5, and sodium *tert*-butoxide in THF, reacts with $LiCH_2Si(CH_3)_3$ with formation of dicyclopentadienyl(trimethylsilylmethyl)samarium. Analogous THF complexes, $Cp_2LnR{\cdot}THF$, have been prepared from $Cp_2LnCl{\cdot}THF$ and LiR, with Ln = Er and Yb and R = t-C_4H_9 and $CH_2Si(CH_3)_3$ and characterized by elemental analysis and IR spectra. From the reaction of $LuCl_3$, NaC_5H_5, and $NaBH_4$ in THF, dicyclopentadienyllutetium tetrahydroborate has been obtained. The new compounds have been characterized by elemental analyses and IR and NMR (^1H, ^{13}C) spectra. The structures of the complexes $(C_5H_5)_2LuCH_2Si(CH_3)_3{\cdot}THF$ and $(C_5H_5)_2LuC_6H_4\text{-}4\text{-}CH_3{\cdot}THF$ have been elucidated through complete X-ray analyses. The crystals of the first compound are orthorhombic with a = 1738.1 (8) pm, b = 1226.8 (3) pm, c = 917.0 (3) pm, space group $P2_12_12_1$, Z = 4, R = 0.058, and 2735 observed reflections. The crystals of the second compound are orthorhombic with a = 1581.4 (36) pm, b = 1251.1 (11) pm, c = 946.7 (19) pm, space group $Pnma$, Z = 4, R = 0.081, and 798 observed reflections.

Introduction

After the synthesis of the first organometallic compounds of the lanthanides, the tricyclopentadienyl complexes of Sc, Y, La, Ce, Pr, Nd, Sm, and Gd by Wilkinson and Birmingham in 1954,[2] interest in this part of the Periodic Table increased only slowly in the next 15 years but more and more rapidly in the last decade.[3] After the symmetrical tricyclopentadienyl compounds had been studied, attention turned to derivatives of the ionic π-bonded cyclopentadienyl complexes. Dicyclopentadienyllanthanide chlorides[4] and cyclopentadienyllanthanide dichlorides[5] have been used as starting materials for the synthesis of many such derivatives.

The first homoleptic organometallic compounds of the lanthanides with η Ln–C σ bonds were prepared by Hart and co-workers in 1970,[6] and further work on dicyclopentadienyllanthanide alkyls and aryls by Tsutsui and co-workers[7] initiated the extensive search for preparative routes to new organic derivatives of these metals and for an understanding of their structures and their chemistry.

Tsutsui[7] claimed a monomeric structure, $(C_5H_5)_2Ln{-}R$, for these alkyl and aryl derivatives, as well as for some other dicyclopentadienyllanthanide allyl[8] and alkynyl[9] compounds, but without experimental support for such formulations. In 1976, by an X-ray structural investigation of the ytterbium compound,[11] Lappert and co-workers[10] discovered that the methyl derivatives, $(C_5H_5)_2LnCH_3$, are dimeric, with an electron-deficient, three-center bonding involving two lanthanide metals and a methyl bridge. A similar methyl-bridged structure has been demonstrated in complexes of dicyclopentadienyllanthanide alkyls with trimethylaluminum, as shown by the same authors for $(C_5H_5)_2Yb(\mu\text{-}CH_3)_2Al(CH_3)_2$.[12] A monomeric alkyl or aryl derivative of a lanthanide metal of low coordination number and without bulky alkyl groups is known for scandium in the case of the complex $(C_5H_5)_2ScCH_3{\cdot}py$.[13]

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We have now found that dicyclopentadienyllutetium alkyl and aryl complexes are monomeric in tetrahydrofuran.[14] We have undertaken single-crystal X-ray diffraction studies of two of this derivatives.[14,15] ^1H and ^{13}C NMR spectra of the complexes have been recorded, and some interesting features are presented. The synthesis and X-ray structural investigation of the *tert*-butyl derivatives has been published in the meantime.[16,17]

Experimental Section

All reactions and preparations were performed by using Schlenk tubes in an atmosphere of dried, oxygen-free argon. The solvents used were dried and freed of oxygen by refluxing and keeping over NaH or potassium and distillation under argon prior to use. Anhydrous $SmCl_3$, $YbCl_3$, and $LuCl_3$ were prepared from the pure oxides by reaction with NH_4Cl.[18] Dicyclopentadienylsamarium chloride, dicyclopentadienylylterbium chloride, and dicyclopentadienyllutetium chloride were prepared by reaction of the corresponding anhydrous chlorides with NaC_5H_5 in pure tetrahydrofuran.[4] Melting points were determined in sealed, argon-filled capillaries. Elemental analyses were performed by Malissa and Reuter, Microanalytical Laboratory in Elbach, West Germany. Because these compounds are extremely sensitive toward moisture and air, the commercial analyses were mostly unsatisfactory.[19] Metal analyses have been done gravimetrically by precipitating the lanthanides as their oxalates and burning them to the oxides. Molecular weights were determined cryoscopically in benzene.

Infrared spectra were recorded as paraffin or poly(chlorotrifluoroethylene) mulls between CsI plates, using a Perkin-Elmer 580 B (200–4000 cm^{-1}) spectrometer. ^1H NMR spectra were obtained in sealed 5-mm tubes on Varian EM 360, XL 100, and Bruker WP 80, WH 270, and WH 400 instruments and ^{13}C NMR spectra in sealed 10-mm tubes on a Bruker WP 80 instrument. We thank M. Detlaff for recording the spectra.

Methyldicyclopentadienyllutetium (2). Into a Schlenk tube with a connected NMR tube was placed 0.387 g (0.8 mmol) of $(C_5H_5)_2LuCl{\cdot}(THF)_2$ (**1**), and 10 mL of tetrahydrofuran was added. The tube was cooled to –78 °C and 0.5 mL of a freshly prepared, 1.6 M solution of methyllithium in diethyl ether was added slowly. After being stirred for 30 min, the reaction mixture was allowed to warm to 0 °C, and the solvent was distilled away. After addition of 2 mL of benzene-d_6 at 10 °C, the clear solution was decanted into the NMR tube which was sealed off. The NMR spectra then were recorded. The yield of the product and analyses have not been determined because the decomposition point was below 20 °C.

Ethyldicyclopentadienyllutetium (3). This product was prepared from 1.256 g (2.6 mmol) of **1** in 10 mL of tetrahydrofuran and 7.8 mL of a 0.33 M solution of ethyllithium in pentane by using the procedure described above. The compound was not isolated because its decomposition point was below 20 °C, but its NMR spectrum in C_6D_6 was recorded.

Isopropyldicyclopentadienyllutetium (4). A mixture of 0.775 g (1.6 mmol) of **1** in 10 mL of tetrahydrofuran and 3.3 mL of a 0.46 M solution of isopropyllithium in pentane gave the title compound when this procedure was used. The NMR spectra of the clear C_6D_6 solution which resulted were then measured. The decomposition point of the product is below 20 °C.

Butyldicyclopentadienyllutetium (5). A mixture of 0.396 g (0.8 mmol) of **1** in 10 mL of tetrahydrofuran and 1.96 mL of a 0.417 M solution of butyllithium in pentane gave in the same way as above a clear solution of the product in C_6D_6. Decomposition point was <20 °C.

***tert*-Butyldicyclopentadienyllutetium–Tetrahydrofuran (6).** To a slurry of 5.53 g (19.7 mmol) of $LuCl_3$ in 50 mL of tetrahydrofuran at room temperature was added 15.3 mL of a 2.578 M solution of NaC_5H_5 (39.4 mmol) in tetrahydrofuran. The mixture was stirred for 2 h and cooled to –78 °C. After addition of 12.4 mL of a 1.6 M solution of *tert*-butyllithium in pentane and stirring for 6 h at –78 °C, the solution was warmed to room temperature. Volatile materials were removed, and the residue was extracted with toluene (3 × 200 mL). The toluene solution was evaporated at reduced pressure, and the residue was washed with pentane–diethyl ether (20:1). A white crystalline powder remained after filtration and drying: yield 7.3 g (85%) of $(C_5H_5)_2LuC(CH_3)_3{\cdot}(C_4H_8O)$; dec pt 70–80 °C; IR (Nujol–poly(chlortrifluorethylene) oil; cm^{-1}) 3775 (m), 3097 (w), 3080 (w), 2960 (sh), 2940 (s), 2905 (s), 2860 (sh), 2780 (m), 2740 (m), 2680 (m), 1778 (br), 1660 (br), 1550 (br), 1490 (w), 1460 (w), 1440 (m), 1375 (m), 1350 (w), 1300 (w), 1264 (w), 1250 (w), 1175 (m), 1138 (w), 1080 (w), 1070 (w), 1045 (sh), 1015 (vs), 930 (w), 925 (w), 868 (s), 852 (s), 785 (vs), 742 (sh), 675 (m), 630 (w), 580 (w), 512 (m), 498 (m), 445 (br), 398 (br), 240 (br). Anal. Calcd for $C_{18}H_{27}LuO$: C, 49.77; H, 6.27; Lu, 40.28. Found: C, 45.45; H, 5.24; Lu, 40.18.

Neopentyldicyclopentadienyllutetium–Tetrahydrofuran (7). In an analogous manner to that described for **6**, 2.81 g (10 mmol) of $LuCl_3$ in 50 mL of tetrahydrofuran, 7.8 mL of a 2.54 M solution of NaC_5H_5 in tetrahydrofuran, and 21.4 mL of a 0.467 M solution of neopentyllithium in pentane yielded 3.64 g (81%) of $(C_5H_5)_2LuCH_2C(CH_3)_3{\cdot}(C_4H_8O)$ (**7**): dec pt 90–100 °C; IR (Nujol–poly(chlortrifluorethylene) oil; cm^{-1}) 3560 (m), 3094 (w), 3078 (w), 2962 (s), 2938 (s), 2900 (sh), 2870 (sh), 2735 (m) 2420 (w), 1772 (br), 1662 (br), 1558 (br), 1520 (w), 1490 (m), 1432 (w), 1400 (m), 1350 (s), 1300 (w), 1265 (m), 1250 (w), 1230 (m), 1208 (m), 1179 (m), 1140 (w), 1080 (w), 1070 (w), 1040 (w), 1015 (vw), 932 (m), 920 (w), 902 (w), 890 (w), 860 (s), 848 (s), 785 (vs) 745 (sh), 672 (w), 626 (w), 578 (w), 498 (m), 450 (br), 390 (br), 370 (w), 250 (m), 210 (m). Anal. Calcd for $C_{19}H_{29}LuO$: C, 50.89; H, 6.52; Lu, 39.02. Found: C, 43.51; H, 4.86; Lu, 40.17.

((Trimethylsilyl)methyl)dicyclopentadienyllutetium–Tetrahydrofuran (8). In an analogous manner to that described for 6, 3.33 g (11.8 mmol) of $LuCl_3$ in 50 mL of tetrahydrofruan, 9.2 mL of a 2.578 M solution of NaC_5H_5 in tetrahydrofuran, and 16 mL of a 0.756 M solution of $LiCH_2Si(CH_3)_3$ in pentane yielded 4.98 g (91%) of yellowish needles of $(C_5H_5)_2LuCH_2Si(CH_3)_3{\cdot}(C_4H_8O)$ (8): dec pt 100–110 °C; IR (Nujol–poly(chlortrifluorethylene) oil; cm^{-1}) 3570 (m), 3090 (w), 2945 (s), 2900 (sh), 2865 (m), 2815 (m), 2740 (m), 1775 (br), 1662 (br), 1562 (br), 1447 (s), 1370 (m), 1350 (m), 1308 (w), 1253 (m), 1240 (m), 1180 (w), 1040 (sh), 1020 (s), 920 (w), 860 (s), 785 (vs), 728 (m), 672 (m), 578 (w), 510 (m), 450 (w), 408 (m), 390 (m), 250 (w). Anal. Calcd for $C_{18}H_{29}LuOSi$: C, 46.54; H, 6.29; Lu, 37.67. Found: C, 46.27; H, 6.09; Lu, 37.96 (mol. wt., 502 (calcd 465)).

Benzyldicyclopentadienyllutetium–Tetrahydrofuran (9). In an analogous manner to that described for **6**, 2.58 g (9.2 mmol) of $LuCl_3$ in 50 mL of tetrahydrofuran, 7.2 mL of a 2.54 M solution of NaC_5H_5 in tetrahydrofuran, and a solution of 2.24 g (9.2 mmol) of $LiCH_2C_6H_5{\cdot}(THF)_2$ in 50 mL of tetrahydrofuran yield 3.73 g (87%) of crystalline $(C_5H_5)_2LuCH_2C_6H_5{\cdot}(C_4H_8O)$ (**9**): dec pt 100–110 °C; IR (Nujol–poly(chlortrifluorethylene) oil; cm^{-1}) 3560 (m), 3085 (w), 3060 (m), 2978 (s), 2950 (sh), 2880 (st), 2718 (w), 2418 (w), 1763 (br), 1658 (br), 1590 (vs) 1565 (br), 1495 (m), 1475 (s), 1460 (m), 1442 (m), 1348 (m), 1300 (w), 1282 (w), 1252 (m), 1228 (sh), 1215 (vs), 1175 (s), 1142 (m), 1120 (w), 1104 (w), 1069 (w), 1042 (sh), 1012 (vs), 975 (m), 945 (vs), 920 (w), 882 (w), 860 (s), 848 (s), 825 (w), 800 (sh), 780 (vs), 750 (sh), 730 (sh), 702 (s), 680 (sh), 620 (w), 550 (m), 525 (m), 490 (m), 470 (m) 440 (br), 390 (m), 250 (w). Anal. Calcd for $C_{21}H_{25}LuO$: C, 53.85; H, 5.38; Lu, 37.36. Found: C, 52.71; H, 4.78; Lu, 37.80.

***p*-Tolyldicyclopentadienyllutetium–Tetrahydrofuran (10).** In an analogous manner to that described for **6**, 2.94 g (10.44 mmol) of $LuCl_3$ in 50 mL of tetrahydrofuran, 8.2 mL of a 2.54 M solution of NaC_5H_5 in tetrahydrofuran, and 22.7 mL of a 0.46 M solution of *p*-tolyllithiium in diethyl ether yielded 3.62 g (74%)

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of crystalline $(C_5H_5)_2LuC_6H_4$-4-CH_3·(C_4H_8O) (**10**): dec pt 110–120 °C; IR (Nujol–poly(chlortrifluorethylene) oil; cm^{-1}) 3575 (m), 3098 (w), 3080 (w), 3030 (m), 2995 (s), 2950 (s), 2900 (s), 2840 (sh), 2720 (m), 2422 (w), 2278 (w), 2080 (w), 1905 (w), 1770 (br), 1660 (br), 1590 (w), 1554 (br), 1445 (sh), 1432 (sh), 1420 (m), 1350 (m), 1300 w, 1250 (w), 1240 (w), 1228 (m), 1195 (s), 1175 (m), 1140 (w), 1070 (w), 1040 (sh), 1015 (vs), 938 (w), 920 (w), 870 (w), 860 (s), 850 (s), 795 (sh), 785 (vs), 755 (sh), 680 (w), 630 (w), 580 (w), 552 (m), 510 (m), 482 (s), 450 (br), 390 (w), 250 (w). Anal. Calcd for $C_{21}H_{25}LuO$: C, 53.85; H, 5.38; Lu, 37.36. Found: C, 53.80; H, 5.18; Lu, 37.65 (mol wt, 481 (calcd 468)).

Attempted Preparation of Trityldicyclopentadienyllutetium (11). A 1.92-g (6.82-mmol) sample of $LuCl_3$ was suspended in 50 mL of tetrahydrofuran, and 5.4 mL of a 2.54 M solution of NaC_5H_5 in tetrahydrofuran was added at room temperature with stirring for 2 h. After addition of 162 mL of a 0.042 M solution of $NaC(C_6H_5)_3$ in tetrahydrofuran and 12 h of stirring at room temperature, the solvents were removed under reduced pressure and the residue was extracted with tetrahydrofuran and washed with pentane. The red-yellow precipitate could not be freed from impurities and was not characterized.

Dicyclopentadienyl(tetrahydroborato)lutetium–Tetrahydrofuran (12). A 1.42-g (5.04 mmol) sample of $LuCl_3$ was dissolved in 50 mL of tetrahydrofuran, and 8.8 mL of a 1.14 M solution of NaC_5H_5 in tetrahydrofuran was added. After 2 h of stirring at room temperature, 0.28 g (7.4 mmol) of $NaBH_4$ was added quickly to the solution. The reaction mixture was stirred for 3 days at room temperature, after which time it was filtered and the tetrahydrofuran was removed in vacuo. The reaction product was extracted with tetrahydrofuran, dried, and dissolved in ether. After this etheral solution was cooled to −35 °C, colorless crystals precipitated, which were filtered, washed with pentane, and dried in vacuo: yield 1.4 g (72%); IR (Nujol–poly(chlortrifluorethylene) oil; cm^{-1}) 3102 (w), 3080 (w), 2400 (s), 2360 (s), 2180 (m), 2140 (m), 1785 (br), 1680 (br), 1445 (m), 1350 (s), 1265 (br), 1180 (w), 1125 (s), 1045 (w), 1015 (s), 922 (w), 865 (s), 855 (s), 850 (s), 810 (vs), 795 (vs), 785 (vs), 775 (sh), 730 (br), 375 (br), 260 (br). Anal. Calcd for $C_{14}H_{22}BLuO$: C, 44.88; H, 5.65; Lu, 44.62. Found: C, 42.62; H, 5.55; Lu, 44.91.

***tert*-Butoxydicyclopentadienylsamarium (13).** A 11.4-g (30-mmol) sample of $SmCl_3$·$(THF)_{1.6}$ was placed in a 250-mL three-necked flask under argon, and 100 mL of tetrahydrofuran was added. After addition of a solution of 5.62 g (63 mmol) of NaC_5H_5 in 50 mL of tetrahydrofuran in 2 h of stirring at room temperature, 2.96 g (31 mmol) of freshly sublimed sodium *tert*-butoxide was added at 0 °C. The reaction mixture was stirred at 0 °C for 5 h and then warmed to room temperature, and the solvent was removed in vacuo. The resulting solid was extracted three times with 80 mL of toluene, yielding 8.41 g (78%) of a colorless solid, which was washed with pentane and dried in vacuo: IR (Nujol–poly(chlortrifluorethylene) oil; cm^{-1}) 1240 (sh), 1225 (m), 1200 (s), 1115 (s), 990 (s), 930 (s), 895 (m), 860 (w), 835 (w), 775 (s), 765 (s), 755 (s), 525 (m), 500 (m), 475 (m), 390 (m), 355 (w). Anal. Calcd for $C_{14}H_{19}OSm$: Sm, 43.17. Found: Sm, 42.43.

((Trimethylsilyl)methyl)dicyclopentadienylsamarium (8c). A 0.78-g (2.1-mmol) sample of **13** was suspended in 40 mL of toluene and cooled to −78 °C, and 1.4 mL of a 1.6 M solution of $LiCH_2Si(CH_3)_3$ in tetrahydrofuran (2.24 mmol) was added with a dropping funnel. After 1 h of stirring, the mixture was warmed to room temperature. The colorless precipitate was filtered and extracted with toluene, and the collected toluene solutions gave the product after removal of solvent in vacuo. After the mixture was washed twice with pentane and dried, the yield was 0.61 g (78%): IR (Nujol–poly(chlortrifluorethylene) oil; cm^{-1}) 1525 (w), 1250 (m), 1200 (s), 1170 (s), 1010 (m), 960 (br), 900 (m), 860 (m), 840 (sh), 800 (sh), 790 (sh), 780 (sh), 765 (s), 755 (s), 505 (br), 390 (br). Anal. Calcd for $C_{14}H_{21}SiSm$: Sm, 41.53. Found: Sm, 41.45.

((Trimethylsilyl)methyl)dicyclopentadienylerbium–Tetrahydrofuran (8b). A 3.37-g (8.2-mmol) sample of $(C_5H_5)_2ErCl$·(THF) in 50 mL of toluene and 4.7 mL of a 1.75 M solution of $LiCH_2Si(CH_3)_3$ in pentane (8.2 mmol) were allowed to react as described above (3 h of stirring at −78 °C). After being warmed to room temperature, the mixture was filtered and the residue extracted with 150 mL of benzene. The combined extracts were concentrated, yielding a light brown product, which did not contain lithium and chlorine: yield 1.2 g (32%); IR (Nujol–poly(chlortrifluorethylene) oil; cm^{-1}) 1260 (m), 1070 (sh), 1050 (br), 1010 (s), 940 (w), 890 (w), 855 (m), 836 (m), 785 (sh), 770 (s), 695 (w), 665 (s), 520 (s), 380 (br). Anal. Calcd for $C_{18}H_{29}ErOSi$: Er, 36.63. Found: Er, 36.64.

Table I. Crystal Data and Data Collection Details for Compounds $(C_5H_5)_2LuCH_2Si(CH_3)_3$·$(C_4H_8O)$ (8) and $(C_5H_5)_2LuC_6H_4$-4-CH_3·(C_4H_8O) (10)

	8	10
formula	$C_{18}H_{29}LuOSi$	$C_{21}H_{25}LuO$
mol weight, amu	464.51	468.42
space group	$P2_12_12_1$ (No. 19)	*Pnma* (No. 62)
a, pm	1738.1 (8)	1581.4 (36)
b, pm	1226.8 (3)	1251.1 (11)
c, pm	917.0 (3)	946.7 (18)
vol, nm^3	1.955 (4)	1.873 (6)
Z	4	4
ρ(calcd), g/cm^3	1.58	1.66
radiation; λ, pm	Mo Kα; 71.069	Mo Kα; 71.069
abs coeff, cm^{-1}	53.6	55.4
monochromator	graphite	graphite
method	ω–2θ	ω–2θ
scan speed	variable	variable
two stds after each 50 reflctns		
2θ limit, deg	$5 \leqslant 2\theta \leqslant 60$	$5 \leqslant 2\theta \leqslant 40$
no. of reflctns	3345	1145
reflctns obsd	2735, $I \geqslant 3\sigma(I)$	798, $I \geqslant 2\sigma(I)$
data collectn temp, K	293	170
$R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma \lvert F_o\rvert$	0.058	0.081

***tert*-Butyldicyclopentadienylerbium–Tetrahydrofuran (6b).** A 4.02-g (9.93-mmol) sample of $(C_5H_5)_2ErCl$·(THF) and 7.4 mL of a 1.35 M solution of $LiC(CH_3)_3$ in pentane (9.93 mmol) gave as above 0.83 g (20%) of $(C_5H_5)_2ErC(CH_3)_3$·(THF): IR (Nujol–poly(chlortrifluorethylene) oil; cm^{-1}) 1315 (w), 1245 (w), 1195 (w), 1180 (w), 1040 (s), 1010 (s), 975 (sh), 915 (w), 890 (w), 775 (s), 520 (br), 390 (br). Anal. Calcd for $C_{18}H_{27}ErO$: Er, 39.21. Found: Er, 40.1.

((Trimethylsilyl)methyl)dicyclopentadienylytterbium–Tetrahydrofuran (8a). In an analogous manner, 7.71 g (17 mmol) of $(C_5H_5)_2YbCl$·$(THF)_{1.6}$ and 14.17 mL of a 1.2 M solution of $LiCH_2Si(CH_3)_3$ in pentane (17 mmol) yielded 2.43 g (31%) of red-brown $(C_5H_5)_2YbCH_2Si(CH_3)_3$·(THF): IR (Nujol–poly(chlortrifluorethylene) oil; cm^{-1}) 1250 (w), 1170 (w), 1100 (m), 1010 (s), 960 (sh), 900 (sh), 780 (s), 695 (m), 380 (br). Anal. Calcd for $C_{18}H_{29}OSiYb$: Yb, 37.41. Found: Yb, 37.49.

***tert*-Butyldicyclopentadienylytterbium–Tetrahydrofuran (6a).** In an analogous manner, 5.48 g (12.1 mmol) of $(C_5H_5)_2YbCl$·$(THF)_{1.6}$ and 8.0 mL of a 1.45 M solution of $LiC(CH_3)_3$ in pentane (11.6 mmol) yielded 1.3 g (15%) of orange $(C_5H_5)_2YbC(CH_3)_3$·(THF): IR (Nujol–poly(chlortrifluorethylene) oil; cm^{-1}) 1315 (w), 1300 (w), 1245 (w), 1195 (w), 1040 (s), 1010 (s), 975 (sh), 955 (w), 915 (w), 890 (w), 775 (s), 520 (br), 390 (br). Anal. Calcd for $C_{18}H_{27}OYb$: Yb, 40.03. Found: Yb, 39.68.

Quantitative Hydrolysis of 8a. In a Schlenk tube, which was connected to a NMR tube, was placed 0.79 g (1.8 mmol) of **8a** dissolved in 0.2 mL of benzene. The NMR tube contained 0.8 mL of water; this then was distilled into the Schlenk tube. This reaction mixture was then frozen, and 2 g of Na_2SO_4 was added. After the Schlenk tube was warmed and the NMR tube was frozen in liquid nitrogen, the volatile compounds were distilled into the NMR tube. Integration of the signals in the ^1H NMR spectrum gave $Si(CH_3)_4$:C_5H_6:C_4H_8O in a 1:2.13:1.22 ratio.

X-ray Analysis of 8 and 10. A colorless crystal of **8** with the dimensions 0.3 × 0.2 × 0.4 mm was placed in a thin-walled glass capillary and sealed under argon. Final lattice parameters were determined from a least-squares refinement of the angular settings of 15 strong, accurately centered reflections on a Syntex $P2_1$ diffractometer. The same procedure was followed with a 0.1 × 0.4 × 0.4 mm colorless crystal of **10**. The crystal data and some data collection details are given in Table I. The observed reflections were corrected for Lorentz and polarization effects but not for absorption. Atomic scattering factors and anomalous dispersion terms for the lutetium and silicon atoms in **8** were taken from ref 22.

Table II. Positional Parameters for $(C_5H_5)_2LuCH_2Si(CH_3)_3\cdot(C_4H_8O)$ (8)

atom	*x/a*	*y/b*	*z/c*
Lu	0.1480 (1)	0.2413 (1)	0.0771 (1)
Si	0.0053 (3)	0.1484 (4)	−0.2160 (6)
O	0.2374 (5)	0.2403 (8)	−0.1060 (11)
C(1)	0.0388 (9)	0.2456 (12)	−0.0787 (22)
C(2)	−0.0624 (15)	0.0488 (22)	−0.1332 (33)
C(3)	−0.0473 (21)	0.2194 (20)	−0.3638 (32)
C(4)	0.0796 (15)	0.0592 (22)	−0.3023 (29)
C(5)	0.2234 (10)	0.3003 (19)	−0.2438 (20)
C(6)	0.3164 (11)	0.1976 (19)	−0.1066 (23)
C(7)	0.3548 (12)	0.2519 (20)	−0.2344 (24)
C(8)	0.2928 (13)	0.2674 (16)	−0.3367 (26)
C(10)	0.2165 (11)	0.4327 (14)	0.1062 (25)
C(11)	0.1376 (18)	0.4546 (13)	0.0690 (39)
C(12)	0.0890 (21)	0.4189 (19)	0.1841 (44)
C(13)	0.1400 (19)	0.3799 (22)	0.2900 (31)
C(14)	0.2127 (15)	0.3885 (18)	0.2457 (39)
C(20)	0.1127 (21)	0.0397 (17)	0.1187 (43)
C(21)	0.1868 (20)	0.0347 (17)	0.0946 (42)
C(22)	0.2260 (16)	0.0909 (22)	0.2044 (40)
C(23)	0.1690 (18)	0.1153 (22)	0.3012 (24)
C(24)	0.0980 (14)	0.0920 (18)	0.2541 (37)

Table III. Positional Parameters for $(C_5H_5)_2LuC_6H_4\text{-}4\text{-}CH_3\cdot(C_4H_8O)$ (10)

atom	*x/a*	*y/b*	*z/c*
Lu	0.3186 (1)	0.25	0.1004 (2)
O	0.2110 (15)	0.25	0.2574 (27)
C(1)	0.2814 (21)	0.1162 (28)	−0.0960 (40)
C(2)	0.3708 (20)	0.1147 (25)	−0.0887 (35)
C(3)	0.3893 (20)	0.0681 (26)	0.0414 (33)
C(4)	0.3141 (20)	0.0430 (25)	0.1013 (35)
C(5)	0.2489 (23)	0.0725 (27)	0.0213 (36)
C(11)	0.5073 (34)	0.25	0.5499 (49)
C(12)	0.4881 (35)	0.3397 (45)	0.4949 (61)
C(13)	0.4376 (29)	0.3370 (40)	0.3634 (48)
C(14)	0.4158 (23)	0.25	0.2892 (40)
C(15)	0.5579 (34)	0.25	0.6952 (50)
C(20)	0.2165 (33)	0.3260 (43)	0.3745 (55)
C(21)	0.1764 (31)	0.25	0.4978 (51)
C(22)	0.1037 (30)	0.2048 (37)	0.4306 (48)
C(23)	0.1447 (33)	0.1686 (43)	0.2916 (56)

Solution and Refinement of the Structures. A three-dimensional Patterson synthesis yielded the positional parameters of the lutetium and the silicon atom in **8**. Successive Fourier and difference Fourier synthesis showed the positions of all the other non-hydrogen atoms. The structure was refined by the use of the full-matrix least squares using the SHELX program.[23] The minimized function is $\sum w(|F_o| - |F_c|)^2$, where w is the weight assigned to the F_o values according to the expression $w = 1/\sigma(F_o)^2$. The hydrogen atoms of the cyclopentadienyl groups were introduced in calculated positions with an overall temperature factor $U = 600$ pm^2 and were not refined. Their positions were varied in every cycle on the basis of the shift of the carbon atoms (the C–H distance was fixed at 108 pm). Anisotropic temperature factors were used for all non-hydrogen atoms. The final R factor was 0.058. A ΔF Fourier synthesis, calculated at the end of the refinement, showed no anomalies.

The systematical extinctions of the reflections and the existence of four molecules in the unit cell of **10** implied a space group of $Pn2_1a$ (nonstandard for $Pna2_1$, No. 33) or $Pnma$. In the latter case the molecule should have a mirror plane. This seemed to be improbable because of the tetrahydrofuran ligand in the molecule. Therefore $Pna2_1$ was first tried.

The three-dimensional Patterson-synthesis yielded the postions of Lu and O, and successive Fourier and difference Fourier synthesis with the same full-matrix least-squares refinement gave the positions of the carbon atoms. Some peaks of additional electron density were found in proximity of the tetrahydrofuran ligand, which can be assigned to carbon atoms at a distance of 100 pm from the located tetrahydrofuran carbons. Refinement using the space group $Pnma$ gave the final structure. The tetrahydrofuran ligand is located with O and C21 on the crystallographic mirror plane; the other carbons are beyond this plane with a weighting factor of 0.5. The hydrogens were included in calculated positions, using C–H bond distances of 108 pm. The lutetium atom was refined with anisotropic thermal parameters, and C and O atoms were refined with isotropic parameters. The final R factor was 0.081; a final difference Fourier synthesis did not show any remarkable features.

The final values of the parameters for **8** and **10** are reported in Tables II and III. Observed and calculated structure factors are available as supplementary material.

Results and Discussion

Synthesis of Alkyldicyclopentadienyllanthanide Complexes. Lutetium trichloride reacts in tetrahydrofuran with sodium cyclopentadienide in the molar ratio of 1:2 with formation of dicyclopentadienyllutetium chloride (**1**). The reaction of this compound with lithium alkyls at −78 °C gave the appropriate monomeric alkyldicyclopentadienyllutetium derivatives (eq 1 and 2).

$$\mathrm{LuCl_3 + 2NaC_5H_5 \xrightarrow{THF} \underset{\mathbf{1}}{(C_5H_5)_2LuCl\cdot(THF)} + 2NaCl} \tag{1}$$

$$\mathrm{(C_5H_5)_2LuCl\cdot(THF) + LiR \xrightarrow[-78\ ^\circ C]{THF} \underset{\mathbf{2\text{–}10}}{(C_5H_5)_2Lu\text{–}R\cdot(THF)} + LiCl} \tag{2}$$

Dicyclopentadienylyltterbium chloride (**1a**) and dicyclopentadienylerbium chloride (**1b**) react in the same way with lithium *tert*-butyl as well as with $LiCH_2Si(CH_3)_3$ with formation of the corresponding ytterbium complexes **6a** and **8a**, as well as the erbium compounds **6b** and **8b** (eq 3 and 4).

$$\mathrm{\underset{\mathbf{1a}}{(C_5H_5)_2YbCl\cdot(THF)} + LiR \xrightarrow{THF} \underset{\mathbf{6a,\ 8a}}{(C_5H_5)_2Yb\text{–}R\cdot(THF)} + LiCl} \tag{3}$$

$$\mathrm{\underset{\mathbf{1b}}{(C_5H_5)_2ErCl\cdot(THF)} + LiR \xrightarrow{THF} \underset{\mathbf{6b,\ 8b}}{(C_5H_5)_2Er\text{–}R\cdot(THF)} + LiCl} \tag{4}$$

The reaction of **1** with $NaC(C_6H_5)_3$ in tetrahydrofuran did not yield a pure product. The red-yellow precipitate obtained could not be isolated in a pure state.

Interaction of samarium trichloride with sodium cyclopentadienide in tetrahydrofuran, followed by reaction with freshly prepared sodium *tert*-butoxide at 0 °C, gave colorless dicyclopentadienyl-*tert*-butoxysamarium (**13**), which gives in toluene the solvent-free ((trimethylsilyl)methyl)dicyclopentadienylsamarium complex upon reaction with the appropriate lithium alkyl (eq 5 and 6).

$$\mathrm{SmCl_3 + 2NaC_5H_5 + NaOC(CH_3)_3 \xrightarrow{THF} \underset{\mathbf{13}}{(C_5H_5)_2Sm\text{–}OC(CH_3)_3} + 3NaCl} \tag{5}$$

$$\mathrm{\underset{\mathbf{13}}{(C_5H_5)_2Sm\text{–}OC(CH_3)_3} + LiCH_2Si(CH_3)_3 \xrightarrow{toluene} \underset{\mathbf{6c}}{(C_5H_5)_2Sm\text{–}CH_2Si(CH_3)_3} + LiOC(CH_3)_3} \tag{6}$$

The air-sensitive complexes are colored except for the lutetium compounds which are colorless (see Table IV) and were obtained as crystalline powders after extraction with

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(22) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2.A and 2.3.1.

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

Table IV. Yields, Colors, and Decomposition Points for Compounds $(C_5H_5)_2LnR{\cdot}(THF)$

Ln	R		yield, %	color	dec pt, °C
Lu	CH_3	**2**		colorless	<20
Lu	C_2H_5	**3**		colorless	<20
Lu	$CH(CH_3)_2$	**4**		colorless	<20
Lu	$CH_2CH_2CH_2CH_3$	**5**		colorless	<20
Lu	$C(CH_3)_3$	**6**	85	colorless	70–80
Lu	$CH_2C(CH_3)_3$	**7**	81	colorless	90–100
Lu	$CH_2Si(CH_3)_3$	**8**	91	colorless	100–110
Lu	$CH_2C_6H_5$	**9**	87	colorless	100–110
Lu	C_6H_4-4-CH_3	**10**	74	colorless	110–120
Lu	BH_4	**12**	72	colorless	70–80
Yb	$C(CH_3)_3$	**6a**	25	orange	40–50
Yb	$CH_2Si(CH_3)_3$	**8a**	31	red-brown	40–50
Er	$C(CH_3)_3$	**6b**	20	light brown	>40
Er	$CH_2Si(CH_3)_3$	**8b**	32	light brown	>50
Sm	$OC(CH_3)_3$ [a]	**13**	78	colorless	<50
Sm	$CH_2Si(CH_3)_3$ [a]	**8c**	78	colorless	<50

[a] Without coordinated THF.

benzene or toluene and subsequent crystallization from pentane-ether. They are soluble in benzene, toluene, and tetrahydrofuran but insoluble in saturated hydrocarbon solvents. The thermal stability depends upon the particular lanthanide metal as well as on the alkyl ligand. Whereas the ytterbium compounds **6a** and **8a** decompose below 50 °C possibly because of the low redox potential Yb^{3+}/Yb^{2+}, the lutetium and erbium compounds show a much higher thermal stability, depending on the nature of the σ-bonded alkyl ligand. The lower alkyl derivatives with R = methyl, ethyl, isopropyl, and n-butyl are not stable above room temperature. They could be detected only by NMR spectroscopy. An increase of thermal stability is observed with bulky alkyl ligands as well as with alkyl ligands without hydrogen atoms in the β-position of the lanthanide metal, e.g. **7**–**9**.

Interaction of dicyclopentadienyllutetium chloride and sodium borohydride in tetrahydrofuran gave the borohydride **12**, which may be isolated as colorless crystals and which is similar to the corresponding samarium, erbium, and ytterbium derivatives[21] (eq 7).

$$LuCl_3 + 2NaC_5H_5 + NaBH_4 \xrightarrow{THF} \underset{\textbf{12}}{(C_5H_5)_2LuBH_4{\cdot}(THF)} + 3NaCl \quad (7)$$

The compound loses tetrahydrofuran upon heating. It shows the expected bands for the cyclopentadienyl moiety in the IR spectrum,[21] as well as bands at 2360 and 2400 cm^{-1} for $\nu(BH_t)$, 2140 and 2180 cm^{-1} for $\nu(BH_b)$, 1265 cm^{-1} for the bridge stretch, and 1125 cm^{-1} for the BH_2 deformation vibration, consistent with bidentate coordination of the BH_4^- group to the lutetium.

The proton NMR spectrum shows at room temperature a singlet at 6.14 ppm (C_5H_5) and two multiplets at 3.28 and 1.11 ppm (THF) besides a 1:1:1:1 quartet at 1.07 ppm with $J(BH)$ = 84 Hz ($\Delta/2$ = 8 Hz) for the BH_4^- ligand. Such broad signals are representative for organometallic borates of this type with fluxional BH_4^- groups.[24] The ^{13}C NMR spectrum shows three peaks at 110.7 ppm (C_5H_5), 73.6 ppm, and 25.5 ppm (THF) relative to tetramethylsilane.

Spectroscopic Characterization. Organolanthanides with the lanthanide elements in oxidation state +3 are paramagnetic, except those of lanthanum (f^0) and lutetium (f^{14}). ^1H and ^{13}C NMR investigations were carried out on the diamagnetic lutetium derivatives. In addition, Table V gives the ^1H NMR parameters of the broadened spectra of the ytterbium derivatives **6a** and **8a**, measured at room temperature in benzene-d_6 solution.

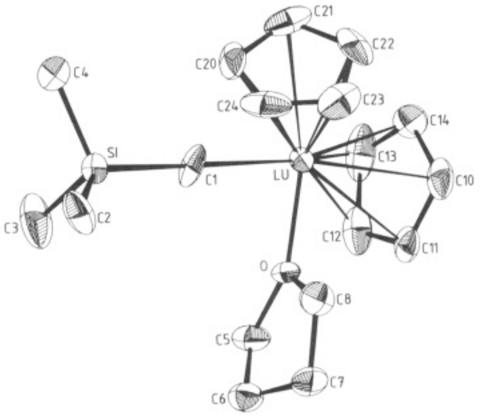

Figure 1. ORTEP drawing of the molecule $(C_5H_5)_2LuCH_2Si(CH_3)_3{\cdot}(THF)$ (**8**; hydrogen atoms omitted). The 50% probability thermal vibration ellipsoids are drawn.

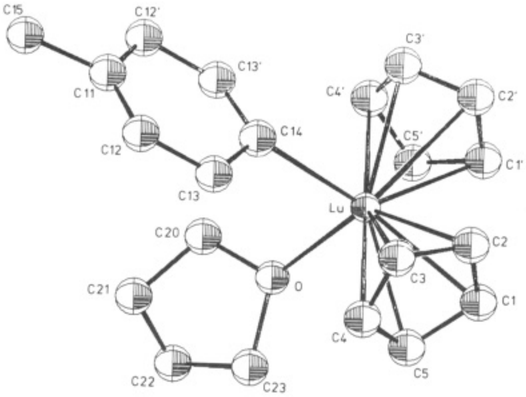

Figure 2. ORTEP drawing of the molecule $(C_5H_5)_2LuC_6H_4$-4-$CH_3{\cdot}(THF)$ (**10**; hydrogen atoms omitted). The 50% probability thermal vibration ellipsoids are drawn.

The ^1H NMR data for solutions of the lutetium complexes in benzene-d_6 or toluene-d_8 (for compound **5**) (Table VI) are consistent with the presence of monomeric complexes with η^5-cyclopentadienyl rings and terminal alkyl ligands as well as a coordinated THF ligand as shown by its shifted signals in comparison to that of free tetrahydrofuran.

Room-temperature ^{13}C NMR spectra give similar structural results (Table VII). A lutetium–hydrogen or lutetium–carbon coupling never could be found. The infrared spectra of the various compounds show the expected vibrations for the cyclopentadienyl, tetrahydrofuran, and alkyl ligands.[25] A reliable assignment of lanthanide–carbon bond stretching vibrations was not possible.

Molecular Structure of $(C_5H_5)_2LuCH_2Si(CH_3)_3{\cdot}(C_4H_8O)$ (8) and $(C_5H_5)_2LuC_6H_4$-4-$CH_3{\cdot}(C_4H_8O)$ (10). The molecular structure and atom numbering schemes of compounds **8** and **10** are shown in Figures 1–3. Some important structural parameters are listed in Table VIII. The structures of both compounds show that lutetium is surrounded by a distorted tetrahedral array of the centers of two cyclopentadienyl ligands, the oxygen atom of tetrahydrofuran, and the σ-bonded carbon atom. This is in agreement with the known structures of $[Li(THF)_4][Lu(C_6H_3Me_2)_4]$,[26] $(C_5H_5)_3Gd{\cdot}(THF)$,[27] and $(C_5H_5)_2LuC(C-$

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Table V. ^1H NMR Spectral Data for $(C_5H_5)_2YbR\cdot(THF)^a$ in C_6D_6

compd	$\delta(C_5H_5)$	$\delta(H_\alpha)$	$\delta(H_\beta)$	$\delta(H_\gamma)$	δ(THF)
$(C_5H_5)_2YbC(CH_3)_3\cdot$(THF) (**6a**)	−30.30 (1300)		0.33 (25)		1.39 (80), 0.97 (48)
$(C_5H_5)_2YbCH_2Si(CH_3)_3\cdot$(THF) (**8a**)	−29.92 (1300)	0.16 (20)		−0.11 (40)	1.44 (120), 1.02 (48)

[a] Chemical shifts are reported in ppm from $Si(CH_3)_4$; in parentheses are the line widths at half-maximum.

Table VI. ^1H NMR Spectral Data for $(C_5H_5)_2LuR\cdot(THF)^a$ in C_6D_6

compd	$\delta(C_5H_5)$	$\delta(H_\alpha)$	$\delta(H_\beta)$	$\delta(H_\gamma)$	$\delta(H_\delta)$	$\delta(H_\epsilon)$	δ(THF)
$(C_5H_5)_2LuCH_3\cdot$(THF) (**2**)	6.27 (s)	−0.62 (s)					3.57 (m), 1.53 (m)
$(C_5H_5)_2LuC_2H_5\cdot$(THF) (**3**)	6.17 (s)	0.16 (q)[b]	1.77 (t)				3.41 (m), 1.41 (m)
$(C_5H_5)_2LuCH(CH_3)_2\cdot$(THF) (**4**)	6.03 (s)	0.22 (sp)[c]	1.65 (t)				3.80 (m), 1.41 (m)
$(C_5H_5)_2LuC_4H_9\cdot$(THF) (**5**)	6.15 (s)		0.15 (m), 1.27 (m)				3.45 (m), 1.45 (m)
$(C_5H_5)_2LuC(CH_3)_3\cdot$(THF) (**6**)	6.16 (s)		1.39 (s)				3.32 (m), 1.13 (m)
$(C_5H_5)_2LuCH_2C(CH_3)_3\cdot$(THF) (**7**)	6.25 (s)	0.27 (s)		1.51 (s)			3.21 (m), 1.17 (m)
$(C_5H_5)_2LuCH_2Si(CH_3)_3\cdot$(THF) (**8**)	6.17 (s)	−0.63 (s)		0.55 (s)			3.16 (m), 1.15 (m)
$(C_5H_5)_2LuCH_2C_6H_5\cdot$(THF) (**9**)	6.17 (s)	1.97 (s)		7.45 (m), 7.37 (m), 7.17 (m)			3.27 (m), 1.24 (m)
$(C_5H_5)_2LuC_6H_4$-4-$CH_3\cdot$(THF) (**10**)	6.25 (s)		7.93 (d)[d]	7.39 (d)[d]		2.78 (s)	3.21 (m), 1.10 (m)
$(C_5H_5)_2LuBH_4\cdot$(THF) (**12**)	6.14 (s)	1.07 (q)[e]					3.28 (m), 1.11 (m)
$(C_5H_5)_3Lu\cdot$(THF)	6.14 (s)						3.54 (m), 1.34 (m)
$(C_5H_5)_2LuCl\cdot$(THF) (**1**)	6.27 (s)						3.55 (m), 1.37 (m)

[a] Chemical shifts are reported in ppm from $Si(CH_3)_4$: s, singlet; d, doublet; t, triplet; q, quartet; sp, septet; m, multiplet. [b] ^3J(HH) = 8 Hz. [c] ^3J(HH) = 7.6 Hz. [d] ^3J(HH) = 7 Hz. [e] 1:1:1:1 quartet, ^1J(BH) = 85 Hz.

Table VII. ^{13}C NMR Spectral Data for $(C_5H_5)_2LuR\cdot(THF)^a$ in C_6D_6

compd	$\delta(C_5H_5)$	$\delta(C_\alpha)$	$\delta(C_\beta)$	$\delta(C_\gamma)$	$\delta(C_\delta)$	$\delta(C_\epsilon)$	δ(THF)
$(C_5H_5)_2LuCH(CH_3)_2\cdot$(THF)[b] (**4**)	109.6	36.4	25.4				69.7,[c] 25.9
$(C_5H_5)_2LuC(CH_3)_3\cdot$(THF) (**6**)	111.3	38.6	36.8				73.8, 25.9
$(C_5H_5)_2LuCH_2C(CH_3)_3\cdot$(THF) (**7**)	110.8	37.7	62.6	38.3			72.9, 25.9
$(C_5H_5)_2LuCH_2Si(CH_3)_3\cdot$(THF) (**8**)	110.8	28.3		5.9			72.6, 26.0
$(C_5H_5)_2LuCH_2C_6H_5\cdot$(THF) (**9**)	111.4	48.6		128.9, 125.7, 118.4			73.4, 26.0
$(C_5H_5)_2LuC_6H_4$-4-$CH_3\cdot$(THF) (**10**)	111.8	184.2	142.2	129.7	134.3	22.6	73.1, 25.9
$(C_5H_5)_2LuBH_4\cdot$(THF) (**12**)	110.7						73.6, 25.5
$(C_5H_5)_3Lu\cdot$(THF)	111.3						74.1, 30.4

[a] Chemical shifts are reported in ppm from $Si(CH_3)_4$. [b] In toluene-d_8. [c] Splits below −32 °C into two peaks at 67.8 and 71.6 ppm.

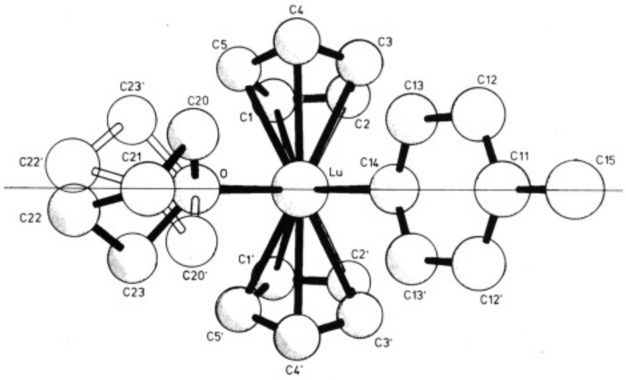

Figure 3. PLUTO drawing and atom numbering of the non-hydrogen atoms of $(C_5H_5)_2LuC_6H_4$-4-$CH_3\cdot$(THF) (**10**), showing the two different possibilities for the tetrahydrofuran ligand in relation to the crystallographic mirror plane.

Table VIII. Selected Bond Lengths (pm) and Angles (Deg) for $(C_5H_5)_2LuCH_2Si(CH_3)_3\cdot(C_4H_8O)$ (8) and $(C_5H_5)_2LuC_6H_4$-4-$CH_3\cdot(C_4H_8O)$ (10)

8		10	
Lu–C(1)	237.6 (17)	Lu–C(14)	234.5 (39)
Lu–O	228.8 (10)	Lu–O	226.5 (28)
Lu–M1[a]	235	Lu–M[c]	232
Lu–M2[b]	234		
Lu–C(10)	264.6 (18)	Lu–C(1)	259.1 (40)
Lu–C(11)	262.3 (17)	Lu–C(2)	259.3 (35)
Lu–C(12)	259.8 (29)	Lu–C(3)	260.7 (35)
Lu–C(13)	259.2 (28)	Lu–C(4)	262.1 (35)
Lu–C(14)	263.0 (28)	Lu–C(5)	256.1 (37)
Lu–C(20)	257.6 (22)		
Lu–C(21)	262.7 (22)		
Lu–C(22)	257.1 (29)		
Lu–C(23)	259.7 (24)		
Lu–C(24)	259.7 (28)		
M1–Lu–M2	130.2	M–Lu–M′	128.8
M1–Lu–O	105.7	M–Lu–O	107.2
M2–Lu–O	104.2		
M1–Lu–C(1)	105.4	M–Lu–C(14)	108.5
M2–Lu–C(1)	110.9		
O–Lu–C(1)	95.8 (9)	O–Lu–C(14)	89.6 (12)
Lu–C(1)–Si	130.7 (8)	Lu–C(14)–C(11)	169.2 (31)

[a] Center of ring 1. [b] Center of ring 2. [c] Center of cyclopentadienyl ring; M′ is symmetry related to M by the mirror plane.

$H_3)_3\cdot$(THF).[16] The recently described compound $(C_5Me_5)_2YbCH_3\cdot$(THF)[28] should have the same arrangement. The cyclopentadienyl rings are η^5 bound to lutetium with distances of lutetium to the centers of the coplanar rings of 234.5 pm in **8** and **10**. The tetrahydrofuran molecule is coordinated in **8** to Lu with a bond distance of 228.8 pm. It appears short in contrast to the known bond lengths La–O = 257 pm,[29] Gd–O = 249.4 pm,[27] and Y–O = 245.1 pm[29] but is in agreement with the distance Lu–O = 231.2 pm in $(C_5H_5)_2LuC(CH_3)_3\cdot$(THF).[16] In **10** there is a crystallographic mirror plane containing the oxygen atom and C21 of the tetrahydrofuran ligand. That

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implies two possibilities for the arrangement of the tetrahydrofuran ring, which are statistically distributed over the crystal. Figure 3 contains both possibilities, marked with the different numbering of the tetrahydrofuran carbon atoms (C20, C22, and C23 for one ring and C20′, C22′, and C23′ for the other one). The lutetium oxygen distance (226.5 pm) is in the same range as in **8**.

The lutetum–carbon σ-bond lengths are 237.6 pm in **8** and 234.5 pm in **10**, about 10 pm shorter than in $[Li(THF)_4][Lu(C_6H_3Me_2)_4]$ with 245 pm[26] and $(C_5H_5)_2LuC(CH_3)_3{\cdot}(THF)$ with 247 pm[16] because of the less crowded situation in **8** and **10** compared with that in the other two complexes. The surprisingly large bond angle of 130.7° at C1 in **8** is determined by the spatial requirement of the trimethylsilyl group bound to the same carbon atom and the cyclopentadienyl and tetrahydrofuran ligands around lutetium. A similar large bond angle at an α-carbon atom was noted for the surrounding of the CH_2 carbon in $[(CH_3)_3CCH_2]_3Ta{\equiv}CC(CH_3)_3{\cdot}Li(dmp)$.[30]

Reactivity. The new compounds are extremely sensitive toward moisture and oxygen. On hydrolysis all the ligands are replaced from the lanthanides with formation of $Ln(OH)_3$, cyclopentadiene, and the appropriate hydrocarbon. In the case of **8**, **8a**, **8b**, and **8c**, tetramethylsilane can be detected in the NMR spectrum of the decomposition products. All compounds decompose above 120 °C first with liberation of tetrahydrofuran. The *tert*-butyllutetium complex **6** then undergoes further decomposition via a β-elimination process, to yield 2-methylpropane and 2-methylpropene, whereas **8** gives tetramethylsilane. Above 200 °C $Lu(C_5H_5)_3$ is formed via intermediate organolutetium hydride formation.[17,31]

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Registry No. 1, 82293-69-4; 2, 76207-05-1; 3, 76207-06-2; 4, 82293-70-7; 5, 76207-07-3; 6, 76207-08-4; 6a, 82293-71-8; 6b, 78683-33-7; 7, 76207-09-5; 8, 76207-10-8; 8a, 82293-72-9; 8b, 82311-89-5; 8c, 82293-73-0; 9, 76207-11-9; 10, 76207-12-0; 11, 82293-74-1; 12, 82293-75-2; 13, 82293-76-3; $LuCl_3$, 10099-66-8; NaC_5H_5, 4984-82-1; $LiCH_2Si(CH_3)_3$, 1822-00-0; $LiCH_2C_6H_5$, 766-04-1; $NaC(C_6H_5)_3$, 4303-71-3; $SnCl_3$, 10361-82-7; $(C_5H_5)_2ErCl$, 53224-35-4; $LiC(CH_3)_3$, 594-19-4; $(C_5H_5)_2YbCl$, 42612-73-7; methyllithium, 917-54-4; ethyllithium, 811-49-4; isopropyllithium, 1888-75-1; butyllithium, 409-72-8; neopentyllithium, 7412-67-1; *p*-tolyllithium, 2417-95-0.

Supplementary Material Available: Tables of thermal parameters, calculated hydrogen atom positions, and additional non-lutetium bond distances and angles for compounds **8** and **10** as well as tables of observed and calculated structure factors (55 pages). Ordering information is given on any current masthead page.

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An X-ray Photoelectron Spectroscopy Study of Transition Metal μ-Methylene Complexes and Related Compounds

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Gas-phase core electron binding energies have been determined for $[Fe(CO)_4]_2CH_2$, $[CpMn(CO)_2]_2CH_2$, $(CpCoCO)_2CH_2$, $(CpRhCO)_2CH_2$, and several structurally related compounds. The binding-energy data indicate that the CH_2 groups in the μ-CH_2 complexes are highly negatively charged, especially in the manganese, cobalt and rhodium compounds. Data for $Fe(CO)_4C_2H_4$ indicate that the CH_2 groups in this compound are negatively charged but less so than in the μ-CH_2 compounds. Data for $Fe_3(CO)_{12}$ suggest the presence of both terminal and bridging carbonyl groups.

Introduction

In recent years several μ-methylene transition metal complexes have been prepared.[2-8] These molecules are of more than usual interest because they are analogs of methylene groups adsorbed on metal surfaces in heterogeneous catalysis and thus they may give information about important but poorly understood processes such as

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