

Organometallic Compounds of the Lanthanides, 57¹⁾

Pyrrolyl Complexes of Yttrium and Lutetium. Molecular Structure of Dicyclopentadienyl(2,5-dimethylpyrrolyl)(tetrahydrofuran)lutetium(III)

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Received January 15, 1990

Key Words: Cyclopentadienyl complexes / Lutetium complexes / Yttrium complexes / Lanthanide amides / Organolanthanides / Pyrrolyl complexes

The reactions of $\text{Na}(\text{NC}_4\text{H}_4)$ with $(\text{C}_5\text{H}_5)_2\text{LuCl}(\text{THF})$ and $(\text{C}_5\text{Me}_5)_2\text{YCl}(\text{THF})$ result in the formation of the pyrrolyl complexes $(\text{C}_5\text{H}_5)_2\text{Lu}(\text{NC}_4\text{H}_4)$ (**1**) and $(\text{C}_5\text{Me}_5)_2\text{Y}(\text{NC}_4\text{H}_4)(\text{THF})$ (**2**), respectively. $\text{Na}(\text{NC}_4\text{H}_2\text{Me}_2)$ reacts with $(\text{C}_5\text{H}_5)_2\text{LuCl}(\text{THF})$ to

form $(\text{C}_5\text{H}_5)_2\text{Lu}(\text{NC}_4\text{H}_2\text{Me}_2)(\text{THF})$ (**3**). The ^1H - and ^{13}C -NMR spectra of the new compounds as well as the X-ray single-crystal structure analysis of **3** are reported and discussed.

Organometallic compounds containing the pyrrolyl anion $(\text{NC}_4\text{H}_4)^{\ominus}$ have been known since the early 1960s²⁻¹⁴). However, only a few of these have been investigated in comparison to the cyclopentadienyl complexes studied in the same period. The pyrrolyl ligand, isoelectronic with the cyclopentadienyl group, is able to coordinate to transition metals in either an η^1 fashion with the lone pair at nitrogen or in an η^5 fashion as a π complex. It can be shown that the pyrrolyl anion is a weaker π -bonding but a stronger σ -bonding ligand than the cyclopentadienyl ligand. In $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-NC}_4\text{H}_4)^3$, $\text{Fe}(\eta^5\text{-C}_5\text{Me}_4\text{NBH}_3)_2^{13}$, and $(\eta^5\text{-NC}_4\text{H}_4)\text{Mn}(\text{CO})_3^{2-4}$ the pyrrolyl ligands are π -bonded to the metal. In contrast, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^1\text{-NC}_4\text{H}_4)(\text{CO})_2^4$ and the complexes $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\eta^1\text{-NC}_4\text{H}_4)_2$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\eta^1\text{-NC}_4\text{H}_4)_2^8$ contain pyrrolyl ligands σ -bonded to the metals. ^1H -NMR investigations on the actinide complex $\text{U}(\text{NC}_4\text{H}_2\text{Me}_2)_4$ have revealed that the pyrrolyl system also acts both as a σ -bonding amido ligand and as a π -bonding multihapto ligand¹⁵).

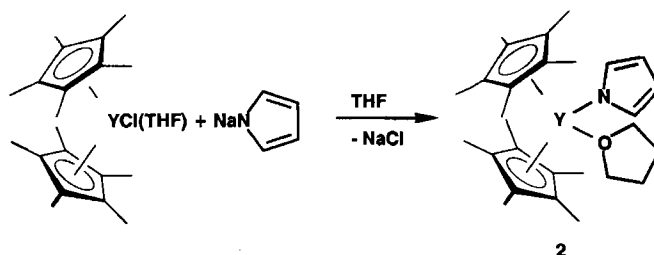
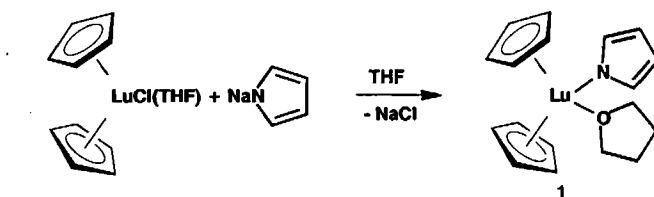
As part of our work in the field of organolanthanide amides, we have introduced the pyrrolyl ligand in organolanthanide chemistry; since no lanthanide derivative of this ligand system has been reported until today. We now report on the synthesis and characterization of the first pyrrolyl complexes of yttrium and lutetium as well as on the first X-ray structure determination of a lanthanide pyrrolyl complex.

Synthesis and Properties

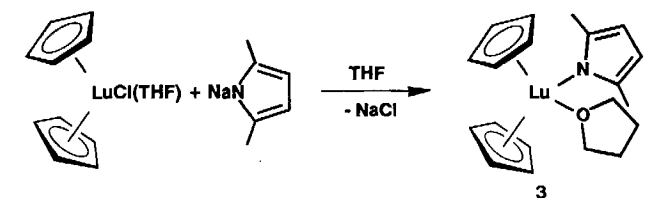
Pyrrolylsodium, prepared by the reaction of pyrrole with sodium in tetrahydrofuran⁸), reacts in the same solvent with dicyclopentadienyllutetium chloride to give dicyclopentadienyl(pyrrolyl)(tetrahydrofuran)lutetium(III) (**1**). The similar reaction using bis(pentamethylcyclopentadienyl)yttrium chloride results in the formation of the corresponding (pentamethylcyclopentadienyl)yttrium derivative **2**.

1 is isolated as yellowish crystals in moderate yield. It is highly soluble in tetrahydrofuran, but only slightly in aromatic hydrocarbons like toluene. The colorless **2** crystallizes from a 1:1 mixture of diethyl ether and tetrahydrofuran. Both complexes show ^1H - and ^{13}C -NMR spectra which are in agreement with two η^5 -cyclopentadienyl ligands and the pyrrolyl anion η^1 -coordinated with the nitrogen to lutetium and yttrium, respectively. The ^1H -NMR spec-

trum shows in both cases two signals at $\delta = 6.82$ and 7.27 (**1**) and $\delta = 6.42$ and 7.30 (**2**) for the protons of the pyrrolyl ligand. The splitting between the α and the β protons is much more complicated than in neutral pyrrole, which indicates a σ -bonded pyrrolyl lutetium or yttrium system⁹). The ^{13}C -NMR spectrum of **2** shows no coupling of the carbon atoms with ^{89}Y . This expected coupling is also absent in the NMR spectra of some other $(\text{C}_5\text{Me}_5)\text{Y}$ derivatives¹⁶).



$(\text{C}_5\text{H}_5)_2\text{Lu}(\text{NC}_4\text{H}_2\text{Me}_2)(\text{THF})$ (**3**) is prepared by the reaction of $(\text{C}_5\text{H}_5)_2\text{LuCl}(\text{THF})$ with 2,5-dimethylpyrrolylsodium in tetrahydrofuran. It is isolated as a yellowish crystalline solid in 38% yield after cooling the concentrated tetrahydrofuran solution down to



4°C. **3** is insoluble in inert aromatic hydrocarbons. NMR spectra can be measured only in DMSO which causes decomposition of the compound.

Molecular Structure

The molecular structure of **3** has been determined by X-ray diffraction. The data-collection details and the crystallographic details are given in Table 1, the atomic coordinates are listed in Table 2, and selected bond lengths and angles are compiled in Table 3. Figure 1 shows an ORTEP¹⁷ plot with the atom numbering scheme.

Table 1. Crystallographic data and data-collection details of **3**^{a)}

Formula: C₂₀H₂₆LuNO; mol. mass: 471.40; crystal size: 0.32 × 0.07 × 0.14 mm; space group: P2₁/c; Z = 4; a = 811.6(2), b = 1400.1(2), c = 1604.4(4) pm; β = 100.41(2)°; V = 1793.1 × 10⁻³⁰ m³; ρ_{calc.} = 1.746 g/cm³; μ = 52.6 cm⁻¹; radiation: Mo K_α, λ = 71.069 pm; temperature: 140(5) K; 2θ_{max} = 53°; total no. of unique reflections: 3998; observed reflections [F_o ≥ 4σ(F_o)]: 2662; R = 0.025; R_w = 0.029 [w⁻¹ = σ²(F_o) + 0.0003(F_o)²]; residual electron density: -0.87 (min.), 0.94 (max.) e/Å³.

^{a)} Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-54450, the names of the authors, and the journal citation.

Table 2. Final atomic coordinates for **3** with estimated standard deviations in parentheses and equivalent isotropic thermal parameters [Å²]^{a)}

Atom	x/a	y/b	z/c	B _{eq} ^{a)}
LU	0.46262(3)	0.20519(1)	0.21078(1)	1.38
C1	0.1852(8)	0.3003(5)	0.1696(4)	3.07
C2	0.3123(9)	0.3653(5)	0.1609(4)	3.28
C3	0.4065(8)	0.3832(4)	0.2397(4)	2.99
C4	0.3342(8)	0.3315(5)	0.2996(4)	2.88
C5	0.1985(8)	0.2814(4)	0.2557(5)	3.21
C6	0.6839(8)	0.1120(5)	0.1378(4)	3.10
C7	0.5264(8)	0.0998(5)	0.0862(4)	2.88
C8	0.4704(8)	0.1875(5)	0.0522(4)	3.06
C9	0.5928(8)	0.2569(5)	0.0826(4)	3.15
C10	0.7236(7)	0.2101(5)	0.1348(4)	3.14
N	0.3138(5)	0.0775(3)	0.2466(3)	1.71
C11	0.3062(7)	0.0494(4)	0.3293(3)	1.86
C12	0.1745(8)	-0.0112(4)	0.3292(4)	2.52
C13	0.0931(7)	-0.0230(4)	0.2445(4)	2.67
C14	0.1779(7)	0.0317(4)	0.1952(4)	2.05
C15	0.4232(9)	0.0856(5)	0.4038(4)	2.76
C16	0.1316(9)	0.0444(5)	0.1018(4)	2.77
O	0.6848(4)	0.2101(3)	0.3224(2)	2.02
C17	0.7375(7)	0.2911(4)	0.3795(4)	2.67
C18	0.9055(8)	0.2635(5)	0.4320(4)	3.28
C19	0.8993(9)	0.1546(6)	0.4301(5)	3.45
C20	0.8127(7)	0.1343(5)	0.3407(4)	2.73

^{a)} B_{eq} = 8π²/3 × Σ_iU_{ii}a_i^{*}a_i.

The X-ray structure shows **3** as a discrete monomer with the lutetium atom η⁵-bonded to two cyclopentadienyl rings and coordinated by one tetrahydrofuran and the dimethylpyrrolyl ligand η¹-bonded with the nitrogen atom. The Lu–C(η⁵) distances [256.8(6)–265.7(7) pm] as well as the ring centroid–lutetium–ring centroid angle [127.8(4)°] and Lu–O bond distance [230.2(3) pm] are in the range of values found in other (C₅H₅)₂Lu(L)(THF) complexes^{18–20}. The pyrrole ligand is planar within 5 pm. The lutetium–nitrogen bond length, 228.9(4) pm, agrees well (after correction for ionic radii and coordination numbers²¹) with corresponding values observed in [Li(THF)][(C₅H₅)₂Lu(NPh₂)₂] [229.0(7) and 229.3(7) pm]²², (C₅Me₅)₂YN(SiMe₃)₂ [227.4(5) or 225.3(5) pm]¹⁶,

and C₅Me₅Ce[N(SiMe₃)₂]₂ [235.7(7) and 234.9(5) pm]²³. However, it is significantly shorter than in [Li(Ho(NMeCH₂CH₂NMe₂)₄)] [227.9(3) and 229.0(3) pm, corrected value 236 pm]²⁴ and [Yb₃(pzMe₂)₉(μ-O)Na₂(THF)₂] (pzMe₂ = 2,4-dimethylpyrrolyl) [227.5(5)–234.8(5) pm, corrected values 232.5–239.8 pm]²⁵. The L–N–pyrrole centroid angle is 166.4(5)°. A π stabilization of the metal ion through the pyrrole ring can therefore be ruled out which also applies to the cyclopentadienyltitanium and -zirconium pyrrole complexes⁸.

Table 3. Selected bond distances [pm] and angles [°] in **3** with estimated standard deviations in parentheses [Cp denotes the centroids of the cyclopentadienyl groups (Cp1: C1–C5; Cp2: C6–C10)]

Lu–C1	259.6(6)	Lu–Cp1	231.6(8)	Cp1–Lu–Cp2	127.8(4)
Lu–C2	260.9(6)	Lu–Cp2	232(1)	Cp1–Lu–N	102.4(2)
Lu–C3	259.1(6)	Lu–N	228.9(4)	Cp1–Lu–O	108.0(3)
Lu–C4	260.4(7)	C11–C12	136.4(8)	N–Lu–O	101.7(1)
Lu–C5	261.0(7)	C11–C15	147.5(8)	Cp2–Lu–N	113.1(2)
Lu–C6	265.7(7)	C11–N	139.6(7)	Cp2–Lu–O	101.0(2)
Lu–C7	261.0(7)	C12–C13	141.0(9)	Lu–N–C11	125.1(3)
Lu–C8	256.8(6)	C13–C14	137.1(9)	Lu–N–C14	127.1(3)
Lu–C9	258.0(7)	C14–C16	148.8(9)	C11–N–C14	105.3(4)
Lu–C10	262.9(7)	C14–N	140.6(6)		
		Lu–O	230.2(3)		

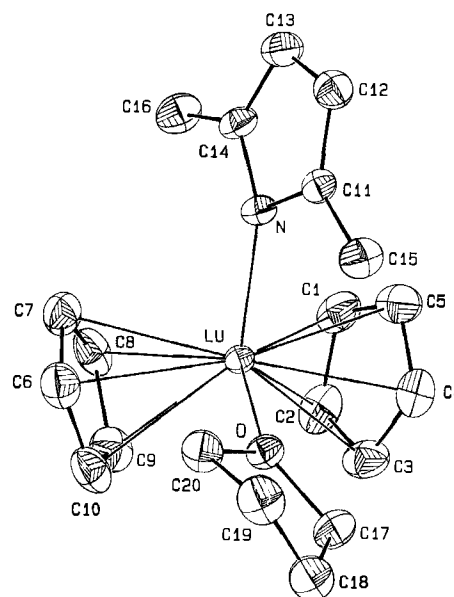


Figure 1. Molecular structure of **3**

Financial support by the *Deutsche Forschungsgemeinschaft*, the *Bundesminister für Bildung und Wissenschaft* (Graduiertenkolleg „Synthese und Strukturaufklärung niedermolekularer Verbindungen“), and the *Fonds der Chemischen Industrie* is gratefully acknowledged.

Experimental

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 heating at reflux over sodium and were distilled under argon prior to use. Melting points were determined in sealed, argon-filled capillaries. Elemental analyses were performed with a Perkin-Elmer 240C CHN-Analyzer. Rea-

sonably satisfactory analyses could be obtained by using a special Schlenk tube and small aluminum cans for weighing these extremely sensitive compounds. Mass spectra were obtained with a Varian MAT 311 A. ^1H - and ^{13}C -NMR spectra were obtained in sealed 5-mm tubes with a Bruker WP 80 SY and a Bruker WH 270 instrument.

Dicyclopentadienyl(pyrryl)(tetrahydrofuran)lutetium(III) (**1**): 3.6 ml of a 0.71 M solution of NaNc_4H_4 ⁸⁾ (2.6 mmol) in THF was added dropwise to a stirred suspension of 1.0 g (2.4 mmol) of $(\text{C}_5\text{H}_5)_2\text{LuCl}(\text{THF})$ in 50 ml of THF. After 24 h of further stirring, the solution was decanted from the NaCl formed. The solution was concentrated in vacuo to 30 ml and cooled to -30°C . Yellowish crystals of **1** could be isolated by decanting off the solution and drying in vacuo; yield 0.39 g (36%), m.p. 270°C (dec.). — ^1H NMR (80 MHz, C_6D_6): $\delta = 1.21$ [m, 4H, CH_2 (THF)], 3.33 [m, 4H, CH_2 (THF)], 6.18 (s, 10H, C_5H_5), 6.82 [m, 2H, β -CH (pyrrolyl)], 7.27 [m, 2H, α -CH (pyrrolyl)]. — ^{13}C NMR (20.15 MHz, C_6D_6): $\delta = 25.37, 71.39, 108.34, 110.80, 129.68$.

$\text{C}_{18}\text{H}_{22}\text{LuNO}$ (443.35) Calcd. C 48.76 H 5.00 N 3.16
Found C 48.78 H 5.16 N 3.50

Bis(pentamethylcyclopentadienyl)(pyrryl)(tetrahydrofuran)yttrium(III) (**2**): 3.3 ml of a 0.79 M solution of NaC_5Me_5 ²⁹⁾ in THF was added dropwise to a stirred suspension of YCl_3 (0.4 g, 2.1 mmol) in 40 ml of THF. The solution was stirred for 24 h, and 2.9 ml of a 0.71 M solution of NaNc_4H_4 (2.1 mmol) in THF was added slowly. After 24 h of further stirring, the solution was decanted from the NaCl formed, and the clear solution was concentrated in vacuo to ca. 10 ml. 10 ml of diethyl ether was added and the solution cooled to -30°C . Colorless crystals of **2** could be isolated by decanting off the solution and drying in vacuo; yield 0.22 g (22%), m.p. 165°C (dec.). — ^1H NMR (80 MHz, C_6D_6): $\delta = 1.45$ [m, 4H, CH_2 (THF)], 2.06 (s, 30H, C_5Me_5), 3.55 [m, 4H, CH_2 (THF)], 6.42 [m, 2H, β -CH (pyrrolyl)], 7.30 [m, 2H, α -CH (pyrrolyl)]. — ^{13}C NMR (67.89 MHz, C_6D_6): $\delta = 11.31, 25.60, 67.92, 105.83, 117.39, 129.37$. — MS (70 eV): m/z (%) = 425 (15.2) [$\text{M}^+ - \text{THF}$], 359 (17.8) [$\text{M}^+ - \text{THF} - \text{NC}_4\text{H}_4$], 290 (100) [$\text{M}^+ - \text{THF} - \text{C}_5\text{Me}_5$].

$\text{C}_{28}\text{H}_{42}\text{NOY}$ (497.56) Calcd. C 67.59 H 8.51 N 2.82
Found C 66.88 H 9.09 N 3.14

Dicyclopentadienyl(2,5-dimethylpyrryl)(tetrahydrofuran)lutetium(III) (**3**): This compound was prepared from 0.29 g (2.5 mmol) of $\text{NaNc}_4\text{H}_2\text{Me}_2$ in 20 ml of THF and a suspension of 1.00 g (2.4 mmol) of $(\text{C}_5\text{H}_5)_2\text{LuCl}(\text{THF})$ in 50 ml of THF by using the method described for **1**. Yellowish crystals of **3** could be isolated; yield 0.45 g (39%), m.p. 260°C (dec.). — ^1H NMR (80 MHz, $(\text{CD}_3)_2\text{SO}$): $\delta = 1.75$ [m, 4H, CH_2 (THF)], 2.09 (s, 6H, Me), 2.59 [m, 4H, CH_2 (THF)], 5.34 (s, C_5H_5), 5.49 (s, C_5H_5), 5.91 [m, 2H, CH (pyrrolyl)].

$\text{C}_{20}\text{H}_{26}\text{LuNO}$ (471.40) Calcd. C 50.96 H 5.56 N 2.97
Found C 50.46 H 5.40 N 2.71

X-ray Single-Crystal Structure Determination of 3: Data collection and calculations were carried out with an Enraf-Nonius CAD-4 automatic diffractometer controlled by a Microwax II and fitted with a low-temperature equipment. Cell dimensions were obtained from the angles of 25 automatically centered reflections in the range of $22^\circ \leq 2\theta \leq 28^\circ$. Reflections were scanned with variable scan time (maximum 60s), depending on intensities, with 2/3 of the time used for scanning the peak and 1/6 spent on each of the left and right background. The intensities of three check reflections were monitored every hour for crystal decay. The maximum fluctuation for these reflections was 3.3%. Corresponding corrections were ap-

plied to the raw intensities. The crystal orientation was checked after every 150 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 0.08° . The raw data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using the program DIFABS²⁷⁾ (min./max. absorption corrections were 0.84/1.29).

The space group, $P2_1/c$, was confirmed by successful refinement of the structure. The heavy-atom position was located from a three-dimensional Patterson map, using the program SHELX 76²⁸⁾. All non-hydrogen atoms were refined anisotropically. Hydrogen positions located from the difference Fourier map were refined isotropically, others were placed on calculated [$d[\text{C}-\text{H}] = 1.08 \text{ \AA}$] positions and added to the structural model. Scattering factors and anomalous dispersion terms for Lu, O, N, and C were taken from ref.²⁹⁾, for H from ref.³⁰⁾. All further details are given in Table 1.

CAS Registry Numbers

1: 125995-98-4 / **2**: 125995-99-5 / **3**: 125996-00-1 / NaNc_4H_4 : 7697-45-2 / $(\text{C}_5\text{H}_5)_2\text{LuCl}(\text{THF})$: 82293-69-4 / NaC_5Me_5 : 40585-51-1 / YCl_3 : 10361-92-9 / $\text{NaNc}_4\text{H}_2\text{Me}_2$: 89532-36-5

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