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## Synthesis and Properties of Lanthanum – Pyrene Complexes—Structure of $[(Cp^*La)_3(\mu\text{-}Cl)_3(thf)(\mu\text{-}\eta^2\text{:}\eta^6\text{:}\eta^6\text{-}C_{16}H_{10})]$, the First Complex with a Pyrene Trianion**

Karl-Heinz Thiele,* Sergio Bambirra, Joachim Sieler, and Svea Yelonek

The reduction of polyarenes with alkali metals in ethers leads to compounds in which ether-stabilized contact-ion pairs,[1] triples,[2] or even quintuples[3] occur. The known magnesium anthracene[4] and probably also some naphthalene complexes of europium, samarium, and ytterbium[5] are similarly built. Complexes of trivalent lanthanoids with naphthalene and anthracene have also been described in the last few years.[6] In this context, the reduction of benzanthracene, pyrene, and acenaphthylene with decamethylsamarocene to form dinuclear complexes is of particular interest.[7] In these compounds, $\eta^2$, $\eta^3$, $\eta^4$, and $\eta^5$ bonds are found between the metal atom and the arene.

Most organolanthanoid compounds examined so far contain $\{(C_5H_5)_2Ln\}$ and $\{(C_5Me_5)_2Ln\}$ units. Reactions of $[CpLnX_2]$ derivatives, for which diverse conversions with condensed aromatic hydrocarbons in the presence of alkali metals can be expected, have been far less extensively investigated. We report here on the synthesis, structure, and bonding of lanthanum – pyrene complexes with partly novel and completely unexpected coordination modes.

In the reaction of $[Cp^*LaCl](\mu\text{-}Cl)_2Li(thf)_2]$ (**1**) in toluene with pyrene and potassium under the strictest exclusion of air and moisture, a red-violet solution is obtained from which the pyrene complex $[(Cp^*LaCl)_3(C_{16}H_{10})]\cdot thf$ (**2**) was isolated in the form of red-violet, extremely air-sensitive crystals ($Cp^* = C_5Me_5$). Unusual bonding modes prevail in **2**, in which La atoms are coordinated in two different ways. According to the crystal-structure analysis,[8] La1 and La2 are positioned above opposite rings of the pyrene molecule in a $\eta^6$ coordination hitherto unknown in polyarene complexes of the lanthanoids, and the La – C bond lengths lie between 2.76 and 3.07 Å (Figure 1). La3 is $\eta^2$-bound to one of the middle rings of the pyrene molecule. The La3 – C4 and La3 – C5 distances of 2.82 and 2.84 Å, respectively, are almost identical. Thus, La3 is coordinatively unsaturated and sterically less shielded, which is compensated at least in part by the addition of a THF molecule. Therefore, La1 and La2 form the centers of distorted tetrahedrons and both have a coordination number (CN) of eight, whereas La3 with CN = 7 is arranged in a distorted trigonal bypramid. Pyrene, which is planar when uncoordinated, is slightly twisted in **2**. The atoms C9 and C14 lie 0.115(9) and 0.095(9) Å, respectively, above the plane determined for the $C_{16}H_{10}$ system, with C11 and C12 both lying 0.095(10) Å below it. As with the $\{La_3(pyrene)\}$system, the pyrene unit thus adopts trianionic character.[9] Compound **2** can also be understood as a trinuclear complex with a phenanthrene bridge to which a noncoordinated double bond is attached; this view is supported by the strongly differing bond lengths C4 – C5 and C11 – C12 of 1.41 and 1.35 Å, respectively. The angles of the perpendiculars of the Cp*La and $LaC_6$ fragments are 128.13° and 128.56°, respectively, for La1 and La2, and thus lie between those values for $[\{Cp_3La\}_n]$[10] and $\{Cp^*_2La\}$ systems.[11]

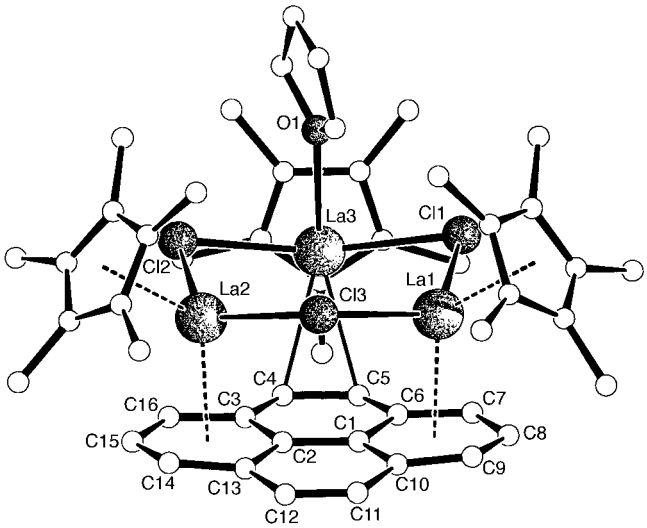


Figure 1. Structure of **2** in the crystal. Selected bond lengths [Å] and angles [°]: La1 – C1 3.047(9), La1 – C6 3.072(8), La1 – C7 2.951(8), La1 – C8 2.843(8), La1 – C9 2.766(8), La1 – C10 2.936(9), La2 – C2 3.014(8), La2 – C3 3.061(8), La2 – C16 2.951(9), La2 – C15 2.872(11), La2 – C14 2.903(10), La2 – C13 2.959(9), La3 – C4 2.823(9), La3 – C5 2.841(8), La – Cl 2.810(3) – 2.894(2), La3 – O1 2.694(7), C11 – C12 1.35(2), C4 – C5 1.417(13); La3-Cl1-La1 93.96(8), La3-Cl2-La2 94.04(6), La1-Cl3-La2 102.10(6)

These results indicate that the formation of **2**, a compound with different coordination modes for La atoms bound in the complex, can be described by Equation (1). The reaction of

$$3\,\mathbf{1} + 3\,K + C_{16}H_{10} \xrightarrow[-5\,THF]{\text{toluene}} \mathbf{2} + 3\,LiCl + 3\,KCl \qquad (1)$$

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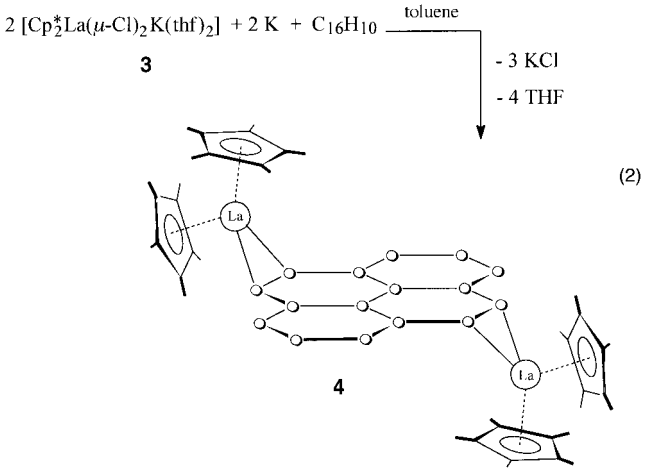
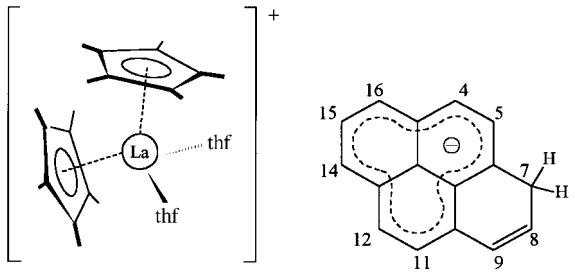
$[Cp^*_2La(\mu\text{-}Cl)_2Li(thf)_2]$ (**3**) with potassium and pyrene in a molar ratio of 2:2:1 in toluene [Eq. (2)] yields the dinuclear lanthanum–pyrene complex **4**, which was isolated from a




(2)

dark green solution in the form of green-black crystals. The $^1$H NMR spectrum displays one signal for the H atoms H4, H5, H11, and H12, and a broad singlet at $\delta = 4.39$ (numbering of the atoms according to Figure 1). The atoms H7, H9, H14, and H16 give a doublet at $\delta = 4.25$, H8 and H9 a triplet at $\delta = 5.51$. The signals of the Cp* groups are included as two singlets of equal intensity at $\delta = 2.18$ and 1.87. The $^{13}$C NMR spectrum also displays only one signal for the atoms C4, C5, C11, and C12 ($\delta = 101.9$). Therefore **4** is highly symmetrical, and free rotation of the $Cp^*_2La$ units can be ruled out. Thus, **4** can be regarded as $[(Cp^*_2La)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-}C_{16}H_{10})]$, in accord with the formula given in Equation (2).

The reaction of **3** with dipotassium pyrenediide in THF does not lead to **4**. Instead the deep red reaction solutions gave red crystals of the mononuclear lanthanum–pyrene complex $[Cp_2Ln(thf)_2][C_{16}H_{11}]$ (**5**) in modest yields. The




**5**

$^1$H NMR spectrum displays ten split signals for the pyrene moiety (see Experimental Section). Of these, one doublet at $\delta = 4.12$ (H7) is twice as intense as the other signals. According to the results of single-beam experiments and the coupling constants, the pyrene unit is significantly less symmetrical, which can be explained with a protonation of C7. The formation of **5** is probably accompanied by ether cleavage, after which an H atom is transferred to the C7 atom of the pyrene framework, thereby forming a substituted phenalene anion. Due to the homogeneous distribution of the negative charge throughout this anion, a solvent-separated ion pair of the composition $[Cp^*_2La(thf)_2]^+[C_{16}H_{11}]^-$ (**5**) is evidently obtained instead of the concentration of a partial charge in one position. The course of the reaction and the properties of **5**, for example the strikingly low solubility in aromatic hydrocarbons, resemble those described by Müllen et al. for the alkali metal–hydropyrene salts also built from ion pairs.[12]

*Experimental Section*

**2**: Potassium (0.38 g, 10.0 mmol) and pyrene (0.40 g, 2.0 mmol) were added to a suspension of **1**[13] (1.8 g, 4.00 mmol) and toluene (150 mL). The reaction mixture was sonicated at 65 °C for about 20 h, after which the red-violet solution was filtered, the filtrate was evaporated to dryness and the residue extracted with *n*-pentane (100 mL). After the mixture was cooled to about −10 °C, red-violet crystals of **2** were isolated from the extract (yield: 1.11 g, 28 %). Recrystallization from *n*-pentane afforded red-violet, cuboid single crystals. Correct C,H,La analysis; $^1$H NMR (300 MHz, $C_6D_6$, 20 °C): $\delta = 3.81$ (m; THF), 2.22 (br. s; $C_5Me_5$), 1.63 (m; THF).

**4**: Potassium (0.62 g, 16.00 mmol) and pyrene (1.61 g, 8.00 mmol) were added to a suspension of $[Cp^*_2La(\mu\text{-}Cl)_2K(thf)_2]$ (11.9 g, 16 mmol) and toluene (150 mL) at room temperature. The mixture was sonicated for 5–8 h at 55–60 °C, in the course of which the color changed from pale yellow to dark green. After filtration the solvent was drawn off and the black-green residue extracted from a circulation frit with *n*-pentane until the discharged solvent remained colorless. After the mixture had been cooled to −10 °C, black-green crystals of **4** were obtained from the dark green extract (yield 4.28 g, 26 %). $^1$H NMR (300 MHz, $C_6D_6$, 25 °C): $\delta = 5.51$ (t, $J = 7.3$ Hz, 2H; $C_{16}H_{10}$), 4.39 (s, 4H; $C_{16}H_{10}$), 4.25 (d, $J = 7.0$ Hz, 4H; $C_{16}H_{10}$), 2.18 (s, 30H; Cp*), 1.87 (s, 30H; Cp*); $^{13}$C NMR (300 MHz, $C_6D_6$, 25 °C): $\delta = 140.7$, 139.6, 126.0, 125.2 ($C_{16}H_{10}$), 120.2, 119.3 (Cp*), 101.9 ($C_{16}H_{10}$).

**5**: A solution of dipotassium pyrenediide $[K_2(C_{16}H_{10})]$ (5 mmol), prepared from pyrene ($C_{16}H_{10}$) (1.01 g, 5 mmol) and potassium (0.39 g, 10 mmol) in THF (100 mL), was added dropwise to a stirred and cooled (−50 °C) suspension of $[Cp^*_2La(\mu\text{-}Cl)_2K(dme)]$ (7.22 g, 10 mmol) and THF (100 mL), with concomitant color change to bright red (dme = 1,2-dimethoxyethane). After warming the mixture to room temperature and stirring for 12 h, the solvent was removed in vacuo, the residue was transferred to a circulation frit, then washed with *n*-pentane and finally extracted with diethyl ether (60 mL). Red crystals of **5**, which were obtained after the extract had been concentrated and cooled to −5 °C, were filtered off and dried in vacuo (yield 0.98 g, 13 %). $^1$H NMR (300 MHz, [D$_8$]THF, 25 °C): $\delta = [5.87$ (t, $J = 7.4$ Hz), 5.69 (d, $J = 7.5$ Hz), 5.52 (d, $J = 7.8$ Hz), 5.50 (d, $J = 7.8$ Hz), 5.45 (d, $J = 9.7$ Hz), 5.25 (d, $J = 7.7$ Hz), 5.15 (d, $J = 7.4$ Hz), 4.90 (d, $J = 7.5$ Hz) 4.33 (dt, $J = 3.7$, 9.4 Hz), 4.12 (d, $J = 9.4$ Hz) ($C_{16}H_{11}$)], 1.97 (s, 30H; Cp*).

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[8] Crystal structure determination: $C_{50}H_{63}Cl_3La_3O$ ($M_r = 1203.08$), $a = 12.299(3)$, $b = 18.734(3)$, $c = 23.954(5)$ Å, $\beta = 101.11(2)^\circ$, $V = 5416(2)$ Å$^3$ ($T = 220$ K), $\rho_{calcd} = 1.476$ g cm$^{-1}$, $F(000) = 2372$, $\lambda = 0.71073$ Å, monoclinic, $P2_1/n$, $Z = 4$, diffractometer: STOE-STADI 4, crystal dimensions: $0.30 \times 0.28 \times 0.22$ mm$^3$, $\omega$-$\theta$ scans, 7409 measured reflections in the range $\theta = 1.69 - 25.02^\circ$, of which 7409 were independent and used for refinement. All C, O, Cl, and La layers were refined anisotropically, the H centers in calculated positions isotropically, *R* values: for [$F > 2\sigma(F)$] $R1 = 0.0397$, $wR2 = 0.1413$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100445. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: int. code + (44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).
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## Coupling of a Nucleoside with DNA by a Methyltransferase**

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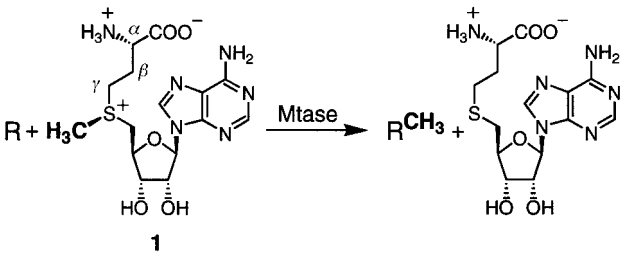
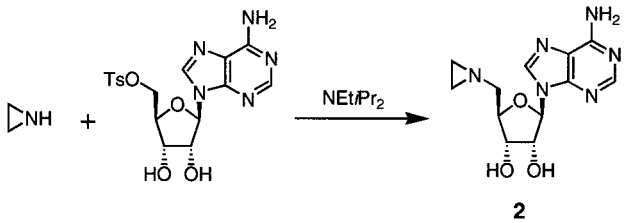
*S*-Adenosyl-L-methionine-dependent methyltransferases (Mtases) catalyse the transfer of the activated methyl group from the cofactor *S*-adenosyl-L-methionine (**1**) to sulfur, nitrogen, oxygen, and carbon acceptors (Scheme 1) of small molecules, phospholipids, proteins, RNA, and DNA with high specificty.[1] The transfer of larger chemical entities in a Mtase-catalyzed reaction has not been reported and thus represents an interesting challenge for bioorganic chemists. In principal, covalent linking of the activated methyl group with the $\gamma$C atom of **1** would yield a three-membered thiiranium compound, which could lead to a coupling of the whole cofactor to the target substrate. Since thiiranium compounds are known to be unstable in nucleophilic solvents,[2] we concentrated on the more stable aziridine analogues, which can be activated as alkylating reagents upon protonation of their ring nitrogen atom.[3] *N*-Adenosylaziridine (**2**) was synthesized by nucleophilic substitution of the tosylate group of 5′-deoxy-5′-tosyladenosine (tosyl = Ts = toluene-4-sulfonyl) with aziridine (Scheme 2).




Scheme 1. Reaction catalyzed by *S*-adenosyl-L-methionine-dependent methyltransferases (Mtases). R = an acceptor with sulfur, nitrogen, oxygen, or carbon atoms to which the methyl groups become attached.




Scheme 2. Synthesis of *N*-adenosylaziridine (**2**).

To test whether the cofactor analogue **2** serves as a cofactor for a Mtase we used the DNA Mtase from *Thermus aquaticus* (M · *Taq*I). Naturally, M · *Taq*I catalyzes the transfer of the methyl group from the cofactor **1** to the exocyclic amino group of 2′-deoxyadenosine within the double-stranded 5′-TCGA-3′ DNA sequence (Scheme 3, top).[4] For our studies we used the short duplex oligodeoxynucleotide **3** · **4** (Scheme 3), in which strand **4** contains N$^6$-methyl-2′-deoxyadenosine (A$^{Me}$) at the target position, so that it cannot be further methylated by M · *Taq*I. The reaction of the cofactor analogue **2** with the duplex **3** · **4** was performed in the presence of a stoichiometric amount of M · *Taq*I and monitored by anion exchange chromatography. A new compound with a shorter retention time relative to **3** · **4** was formed during the reaction (Figure 1), and after 240 min the duplex **3** · **4** had reacted quantitatively. The shorter retention time of the product is consistent with the proposed structure **5** · **4** (Scheme 3, bottom), since **5** · **4** contains an additional aliphatic amino group that ought to be protonated under the conditions used to elute the reaction mixture (pH 7.6).

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