

Synthesis, properties and X-ray crystal structure of bis(decamethylanthanocene)-anthracene

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Abstract

Reaction of $[\text{Cp}_2^* \text{La}(\mu\text{-Cl})_2 \text{K}(\text{dme})_2]$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$) **1** with disodium anthracenide $[\text{Na}_2(\text{C}_{14}\text{H}_{10})]$ **2** in toluene in the molar ratio 2:1 results in the formation of $[\text{Cp}_2^* \text{La}]_2[\mu\text{-}\eta^3:\eta^3\text{-(C}_{14}\text{H}_{10})] \cdot 2\text{C}_6\text{H}_5\text{CH}_3$ **3**, which was characterized by elemental analyses, ¹H and ¹³C NMR spectroscopy as well as X-ray crystal structure determination. The title compound crystallizes in the triclinic space group $P\bar{1}$ with $Z = 1$, $a = 10.471(2)$, $b = 11.234(2)$, $c = 11.382(3)$ Å, and $\alpha = 81.22(2)$, $\beta = 86.36(2)$, $\gamma = 77.62(2)^\circ$, $V = 1291.8(5)$ Å³. The molecule contains two $\text{Cp}_2^* \text{La}$ moieties which are η^3 -coordinated to two of the aromatic rings from opposite sides of the anthracene ligand.

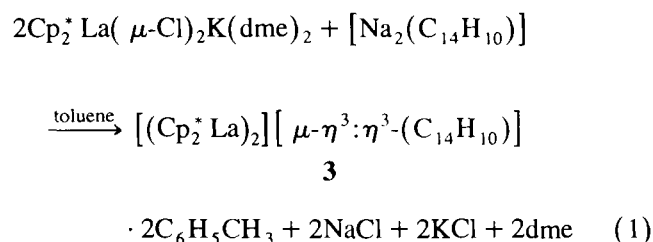
Keywords: Lanthanocene; Anthracene; X-ray structure; Metallocene; π -Bonding

1. Introduction

Compounds of early d-elements with anions of polyaromatic hydrocarbons are of much current interest. Recently, the complexes $[\text{K}(15\text{-C-5})_2[\text{Ti}(\eta^4\text{-C}_{10}\text{H}_8)_2(\text{SnMe}_3)_2]$ [1] and $[\text{K}(15\text{-C-5})_2[\text{Zr}(\eta^4\text{-C}_{10}\text{H}_8)_3]$ [2] have been described. Other related examples, such as $[(\eta^5\text{-C}_5\text{H}_5)\text{Lu}(\eta^4\text{-C}_{10}\text{H}_8)(\text{dme})]$ [3] and the La(III) and Eu(II) complexes $[\mu^2\text{-}\eta^4:\eta^4\text{-C}_{10}\text{H}_8][\text{Ln}_n(\text{L})_x]_2$ ($\text{Ln} = \text{La}$, $n = 2$, $\text{L} = \text{thf}$, $x = 3$; $\text{Ln} = \text{Eu}$, $n = 1$, $\text{L} = \text{dme}$, $x = 2$) which contain bridging naphthalene dianions [4], are also known. With respect to their molecular structure, anthracene complexes of Group IV [5] and rare earth elements [6,7] are also of interest, because either one or two metal centers can be attached to the aromatic system. An example of a binuclear complex is $[\text{Cp}_2^* \text{Sm}]_2[\mu^2\text{-}\eta^3:\eta^3\text{-(C}_{14}\text{H}_{10})]$ [8], which was obtained by the oxidative addition of decamethylsamarocene to anthracene. We have found that similar complexes can also be synthesized by nucleophilic substitution reactions of decamethylanthanocene chloride with the anthracene dianion.

2. Results and discussion

$[\text{Cp}_2^* \text{La}(\mu\text{-Cl})_2 \text{K}(\text{dme})_2]$ **1** reacts with one equivalent of $[\text{Na}_2(\text{C}_{14}\text{H}_{10})]$ **2** in toluene according to Eq. (1) under formation of a dark-green solution from which $[\text{Cp}_2^* \text{La}]_2[\mu\text{-}\eta^3:\eta^3\text{-(C}_{14}\text{H}_{10})]$ **3**, with two molecules toluene incorporated in the crystal lattice, can be isolated as black-green crystals.



The isolated compound was found to be well soluble in common organic solvents. Upon exposure to air, **3** undergoes rapid oxidation accompanied by liberation of anthracene. Hydrolysis of **3** led to the formation of dihydroanthracene. In the ¹H NMR spectrum only one signal was observed for the 60 protons of the Cp^* rings (1.90 ppm). The signals of the two protons of the central anthracene ring appeared at 3.84 ppm, with the expected high field shift in comparison with the corre-

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sponding signal of free anthracene (8.41 ppm). The high field shifts of the eight protons of the side rings (7.20 dd; 7.01 dd; ppm) are quite small in comparison with the shifts for these protons in free anthracene (8.11 dd; 7.83 dd; ppm). This situation indicates that the distribution of electron density towards two $\text{Cp}_2^* \text{La}$ moieties significantly reduces the anionic character of the anthracene dianion. Examples of molecules with considerably ionic character include $[\text{Li}_2(\text{C}_{14}\text{H}_{10})]$ and $[\text{Mg}(\text{C}_{14}\text{H}_{10})]$ [9,10]. The molecular structure of **3** was established by X-ray crystallography (Fig. 1). Crystallographic data are presented in Table 1, and important geometric parameters in Table 2.

The two crystallographically equivalent $\text{Cp}_2^* \text{La}$ units are located on opposite sides of the nearly planar bridging anthracene moiety. On closer inspection the external rings of the anthracene ligand were found to deviate from planarity by 0.098(13) Å.

The distance between the La atom and the anthracene system (centroid) in **3** is 2.215 Å. The metal atom is nine-fold coordinated to the anthracene ligand (in an η^3 -fashion) as well as to the two Cp^* rings. The binding mode corresponds to that found in $[\text{Cp}_2^* \text{Sm}]_2[\mu\text{-}\eta^3\text{:}\eta^3\text{-(C}_{14}\text{H}_{10})]$, in which the metal–anthracene plane distance is 2.037 Å [8]. The angle Cn–La–Cn of 134.82(5)° (Cn = centroid of the Cp^* ring) and the distance Cn–La of 2.5252(15) Å are comparable with those found in related complexes [11,12].

3. Experimental details

All manipulations of the complex described below were conducted under rigorous exclusion of air and water using Schlenk techniques. THF and toluene were distilled from sodium benzophenone ketyl before use. **1** was prepared according to the literature [13]. **2** was obtained by stirring two equivalents of Na with an-

Table 1

Crystal data and structure refinement for $[\text{Cp}_2^* \text{La}]_2[\mu\text{-}\eta^3\text{:}\eta^3\text{-(C}_{14}\text{H}_{10})]$

Empirical formula	$\text{C}_{54}\text{H}_{70}\text{La}_2 \cdot 2\text{C}_6\text{H}_5\text{CH}_3$
Formula weight	996
Temperature	165(2) K
Wavelength	0.71069 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 10.471(2)$ Å, $\alpha = 81.22(2)^\circ$, $b = 11.234(2)$ Å, $\beta = 86.36(2)^\circ$, $c = 11.382(3)$ Å, $\gamma = 77.62(2)^\circ$.
Volume	$1291.8(5)$ Å ³
Z	1
Density (calculated)	1.2213 g cm ⁻³
Absorption coefficient	1.668 mm ⁻¹
$F(000)$	501
Crystal size	$0.1 \times 0.1 \times 0.15$ mm ³
θ range for data collection	1.81° to 24.97°
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 13$, $0 \leq l \leq 13$
Reflections collected	4789
Independent reflections	4518 [$R_{\text{int}} = 0.0120$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4468/0/309
Goodness-of-fit on F^2	1.009
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0202$, $wR_2 = 0.0565$
R indices (all data)	$R_1 = 0.0212$, $wR_2 = 0.0621$
Largest difference peak and hole	0.720 and -0.489 e Å ⁻³

thracene in THF for about 48 h. NMR spectra were recorded on a Varian Gemini 300 MHz.

4. Synthesis of $[\text{Cp}_2^* \text{La}]_2[\mu\text{-}\eta^3\text{:}\eta^3\text{-(C}_{14}\text{H}_{10})] \cdot 2\text{C}_6\text{H}_5\text{CH}_3$ (**3**)

Into a suspension of 5.8 g (8.29 mmol) of **1** in 150 ml toluene was dropped 1.8 g (8.30 mmol) of **2** dis-

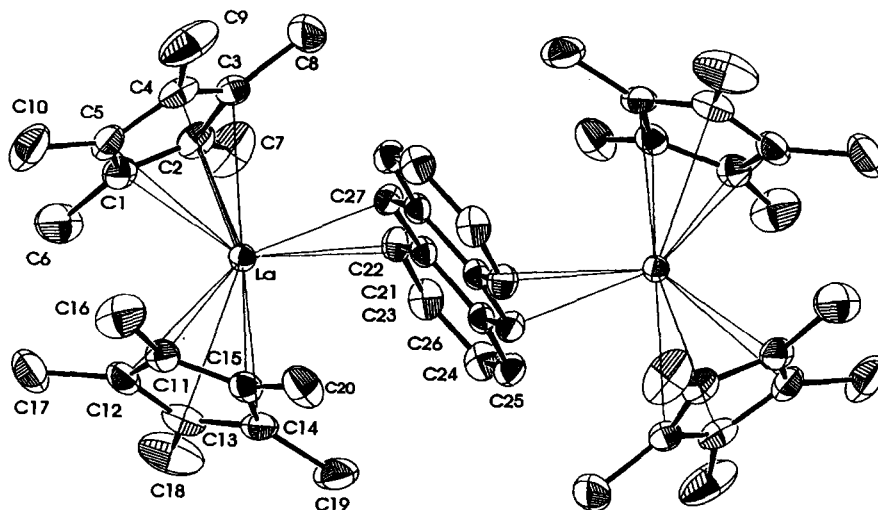


Fig. 1. ORTEP drawing [16] of $[\text{Cp}_2^* \text{La}]_2[\mu\text{-}\eta^3\text{:}\eta^3\text{-(C}_{14}\text{H}_{10})]$ **3** with the numbering scheme. Terminal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2
Selected bond distances (Å) and bond angles (°) in $[\text{Cp}_2^* \text{La}]_2[\mu\text{-}\eta^3\text{-}\eta^3\text{-(C}_{14}\text{H}_{10})_2]_3$

Bond distance (Å)		Bond angle (°)	
La–C(27)	2.689(2)	Cn ^a –La–Cn ^b	134.82(5)
La–C(22)	2.850(2)	C(27)–La–Cn ^a	104.61(6)
La–C(21)	2.882(2)	C(27)–La–Cn ^b	114.00(6)
La–Cn ^a	2.5535(14)	C(22)–La–C(27)	53.50(8)
La–Cn ^b	2.5252(15)	La–C(21)–C(26)	127.41(15)
C(26)–C(25)	1.385(4)		
C(25)–C(24)	1.405(4)		
C(24)–C(23)	1.368(4)		
C(23)–C(22)	1.416(4)		
C(22)–C(21)	1.405(3)		
C(21)–C(27)	1.446(3)		
C(21)–C(26)	1.438(3)		

^a Cn defines the centroid of the ring formed by C(1), C(2), C(3), C(4), C(5).

^b Cn defines the centroid of the ring formed by C(11), C(12), C(13), C(14), C(15).

solved in 50 ml THF. After 24 h of stirring, the mixture was filtered, the toluene and THF were removed, and the resulting solid was washed twice with n-pentane, yielding 1.89 g (48%) of a black–green microcrystalline solid.

Anal. Found: C, 68.82; H, 7.10; La, 23.26. $\text{C}_{54}\text{H}_{70}\text{La}_2 \cdot 2\text{C}_6\text{H}_8\text{CH}_3$. Calc.: C 69.12; H, 7.34; La, 23.52%.

¹H NMR (300 MHz, THF-*d*₈, 20°C): δ = 7.18 (dd, 4H; C₁₄H₁₀), 7.08 (dd, 4H; C₁₄H₁₀), 3.84 (s, 2H; C₁₄H₁₀), 1.90 (s, 60H; C₅Me₅).

¹³C NMR (300 MHz, THF-*d*₈, 20°C): δ = 11.2; 106.8 (C₅Me₅); 36.5; 116.2; 118.4; 137.5 (C₁₄H₁₀).

5. X-ray crystal structure determination of 3

A black-green crystal of dimensions 0.1 × 0.1 × 0.15 mm³ was mounted on a glass fiber and transferred to an Enraf-Nonius CAD-4 diffractometer equipped with a low temperature device which was controlled by a Micro VAX II computer. Unit cell parameters were obtained from 25 reflections in the range 18° < 2θ < 30°. As a check on crystal and electronic stability three representative reflections were measured every 2 h. The net intensities were corrected for decay, Lorentz and polarization effects. A Patterson map revealed the location of the La atoms. The positions of all non-hydrogen atoms were obtained from difference Fourier maps. An

empirical absorption correction (DIFABS [14], min 0.900, max 1.116) was applied to the structure factors. Data reduction and all other calculations were performed using SHELX 93 [15]. Further details of the structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, upon quoting the depository number CSD-404595, author names, and full citation of the journal.

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References

- [1] J.E. Ellis, D.W. Blackburn, Pong Yuen and Meehae Jang, *J. Am. Chem. Soc.*, **115** (1993) 11616.
- [2] Meehae Jang and John E. Ellis, *Angew. Chem.*, **106** (1994) 2036.
- [3] A.V. Protchenko, L.N. Zakharov, M.N. Bochkarev and Yu.T. Struchkov, *J. Organomet. Chem.*, **447** (1993) 209.
- [4] I.L. Fedushkin, M.N. Bochkarev, H. Schumann, L. Esser and G. Kociok-Köhn, *J. Organomet. Chem.*, **489** (1995) 145.
- [5] J. Scholz and K.-H. Thiele, *J. Organomet. Chem.*, **314** (1986) 7.
- [6] D.M. Roitershtein, A.M. Ellem, M.Yu. Antipin, L.F. Rybakova, Yu.T. Struchkov and E.S. Petrov, *Mendeleev Commun.*, (1992) 118.
- [7] D.M. Roitershtein, L.F. Rybakova, E.S. Petrov, A.M. Ellem, M.Yu. Antipin and Yu.T. Struchkov, *J. Organomet. Chem.*, **460** (1993) 39.
- [8] W.J. Evans, S.L. Gonzales and J.W. Ziller, *J. Am. Chem. Soc.*, **116** (1994) 2600.
- [9] R.G. Lawler and C.V. Ristagno, *J. Am. Chem. Soc.*, **91** (1969) 1534.
- [10] B. Bogdanovic, S. Liao, R. Mynott, K. Schlichte and U. Westeppe, *Chem. Ber.*, **117** (1984) 1378.
- [11] J. Scholz, A. Scholz, R. Weimann, C. Janiak and H. Schumann, *Angew. Chem.*, **106** (1994) 1220.
- [12] A. Scholz, A. Smola, J. Scholz, J. Loebel, H. Schumann and K.-H. Thiele, *Angew. Chem.*, **103** (1991) 444.
- [13] H. Schumann, I. Albrecht, J. Loebel, E. Hahn, M. Bilayet Hossain and D. van der Helm, *Organometallics*, **5** (1986) 1296.
- [14] D. Walker and D. Sewart, *Acta Crystallogr.*, **A39** (1983) 159.
- [15] G. Sheldrick, *SHELX 93, Program for Crystal Structure Determination*, Universität Göttingen, Germany, 1993.
- [16] C. Johnson, *ORTEP, Rep. ORNL-3794*, Oak Ridge National Laboratory, Oakridge, TN, 1965.