Synthesis and Molecular Structure of Calcium Difluoranthenide, $[Ca(THF)_6][C_{16}H_{10}]_2 \cdot 2C_{16}H_{10}$

Igor L. Fedushkin,*[a] Anton N. Lukoyanov,[a] Sebastian Dechert,[b] and Herbert Schumann*[b]

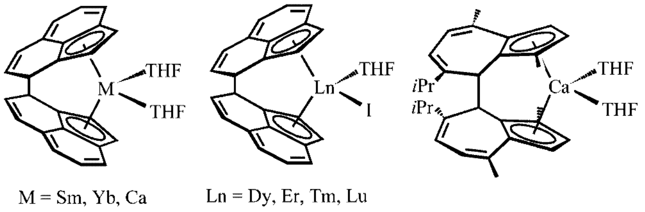
Dedicated to Prof. Mikhail N. Bochkarev on the occasion of his 65th birthday

Keywords: Calcium / Fluoranthene / Radical-anion / Structure elucidation

The treatment of $CaI_2(THF)_2$ with potassium and fluoranthene (mole ratio 1:2:2) in THF affords $[Ca(THF)_6][C_{16}H_{10}]_2 \cdot 2C_{16}H_{10}$ (**1**). The X-ray structure analysis of **1** shows that the compound consists of separate $[Ca(THF)_6]^{2+}$ cations, $[C_{16}H_{10}]^{\cdot -}$ radical anions and neutral fluoranthene molecules. The neutral and radical-anionic fluoranthene species can be distinguished by the differences in the skeleton C–C bond lengths. The presence of fluoranthene radical anions in THF solutions of **1** is proved by ESR spectroscopy and is further supported by the ^1H NMR spectrum of **1**, which does not give any indication of radical coupling.

Introduction

ansa-Metallocenes are an important class of organometallic compounds, which serve as versatile reagents for a number of organic-substrate transformations, especially for the polymerization of α-olefins.[1] In 2001, we reported on *ansa*-metallocenes of the type $(\eta^5{:}\eta^5\text{-}C_{24}H_{16})M(THF)_2$ (where M = Yb,[2] Sm,[2] Ca[3]), formed by reduction of acenaphthylene with the respective metals or their naphthalenides, $[C_{10}H_8]M(THF)_2$. The calcium derivative can also be prepared by treating $CaI_2(THF)_2$ with potassium and acenaphthylene,[4] and, quite recently, we succeeded in the preparation of the *ansa*-calcocene $(\eta^5{:}\eta^5\text{-}C_{15}H_{18})_2Ca(THF)_2$ from $CaI_2(THF)_2$, potassium, and guaiazulene.[5] (Acenaphthylene)lanthanide(III) complexes $(\eta^5{:}\eta^5\text{-}C_{24}H_{16})LnI(THF)$ (where Ln = Dy, Er, Tm, Lu) were prepared by treating $LnI_3(THF)_3$ with 2 equiv. of potassium and 2 equiv. of acenaphthylene in THF.[4] These results show that the radical anions of the nonalternating hydrocarbons (acenaphthylene and guaiazulene), initially formed in these reactions, combine diastereoselectively to give C_2-symmetric *ansa*-ligands (see Scheme 1).



Scheme 1

Since the first and the second reduction potentials of fluoranthene (−1.77 and −2.18 V), a nonalternating hydrocarbon, compare well with those of acenaphthylene (−1.63 and −1.85 V) and guaiazulene (−1.65 and −2.45 V),[6] we investigated the reaction of $CaI_2(THF)_2$ with potassium and fluoranthene, in order to find out whether the hydrocarbons would be reduced to mono-valent radical anions and whether the latter would combine to form a two-valent *ansa*-ligand, coordinating the calcium ion.

Results and Discussion

Synthesis

The one-pot reaction of calcium diiodide with potassium and fluoranthene in a mole ratio of 1:2:2 in THF proceeds smoothly and within two hours produces a dark red-brown suspension. The compound $[Ca(THF)_6][C_{16}H_{10}]_2 \cdot 2C_{16}H_{10}$ (**1**) was isolated in 87 % yield [calculated for Ca on the basis

---

[a] G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences
Tropinina 49, 603950 Nizhny Novgorod GSP-445, Russia
Fax: (internat) +7-8312-127497
E-mail: igorfed@imoc.sinn.ru
[b] Institut für Chemie der Technischen Universität Berlin
Straße des 17. Juni 135, 10623 Berlin, Germany
Fax: (internat.) +49-30-31422168
E-mail: schumann@chem.tu-berlin.de

DOI: 10.1002/ejic.200300924

of the stoichiometry of Equation (1)] from the solution obtained after separation of the potassium iodide and of a dark coloured solid formed in the reaction. The deep red, almost black crystals of **1** melt with decomposition at 148 °C. The formulation of **1** as calcium difluoranthenide containing separate, THF-coordinated calcium cations and fluoranthene radical anions is justified by the spectroscopic and structural properties of **1**, described below. Considering the composition of **1** on the one hand and the stoichiometry of the reagents used for its synthesis on the other hand, one is lead to suggest that, in the course of the reaction, a partial disproportionation of the fluoranthene radical anions into neutral fluoranthene and fluoranthene dianions also take place and we assume that the dark coloured solid precipitating from the reaction mixture, along with the potassium iodide, is probably the calcium fluoranthenide $[Ca(THF)_x][C_{16}H_{10}]$ [see Equation (1)]. Similar observations have been made in the reactions of radical anions of naphthalene with calcium diiodide or lanthanide halides.[4,7] However, in these reactions the disproportionation to naphthalene and naphthalene dianions was almost complete and no calcium or lanthanide compounds containing naphthalene radical anions were isolated.

$$3\,CaI_2(THF)_2 + 6\,K + 6\,C_{16}H_{10} \xrightarrow[-\,6\,KI]{THF} \underset{\mathbf{1}}{[Ca(THF)_6][C_{16}H_{10}]_2 \cdot 2\,C_{16}H_{10}} + 2\,[Ca(THF)_x][C_{16}H_{10}] \qquad (1)$$

The IR spectrum of **1** shows absorptions at 1015 and 865 cm^{-1}, indicating the presence of coordinated THF molecules. The most intense absorptions appear at 785 and 730 cm^{-1} and can be assigned to the aromatic C−H stretching vibrations of the fluoranthene radical anions. The corresponding vibrations of neutral fluoranthene appear at 775 and 735 cm^{-1}.

The ^1H NMR spectrum of **1** shows only the broadened signals of THF. However, the ^1H NMR spectrum of the *ansa*-acenaphthylene complex, $(\eta^5{:}\eta^5\text{-}C_{24}H_{16})Ca(THF)_2$,[4] shows along with the THF signals, the expected eight signals for the ring protons of the *ansa*-ligand.

The assumption that compound **1** is paramagnetic, due to the presence of uni-negative fluoranthene radical anions is confirmed by the ESR spectrum. The spectrum of a solution of **1** in THF shows an ESR signal [$g = 2.0029$; $A_H =$ 0.008 (2H), 0.017 (2H), 0.121 (2H), 0.390 (2H) and 0.520 (2H) mT], which corresponds to the signal reported by Gerson et al.[8] for the fluoranthene radical anion. Solutions of the above-mentioned *ansa*-acenaphthylene complex $(\eta^5{:}\eta^5\text{-}C_{24}H_{16})Ca(THF)_2$ in THF also show an ESR signal, although a very weak one, due to partial dissociation of the *ansa*-ligand into radical anions. However, the presence of such small amounts of paramagnetic radical anions does not seem to affect the ^1H NMR spectroscopy behaviour of this complex.

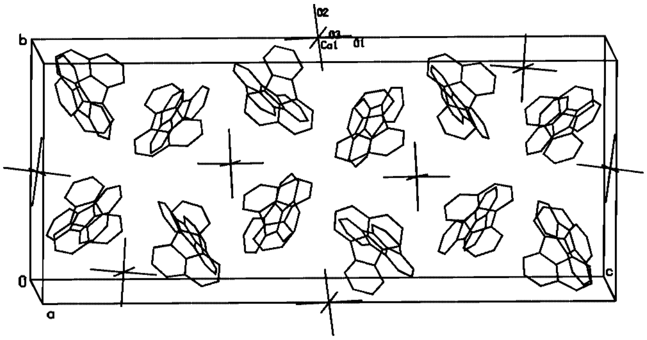


Figure 1. Crystal packing in **1**

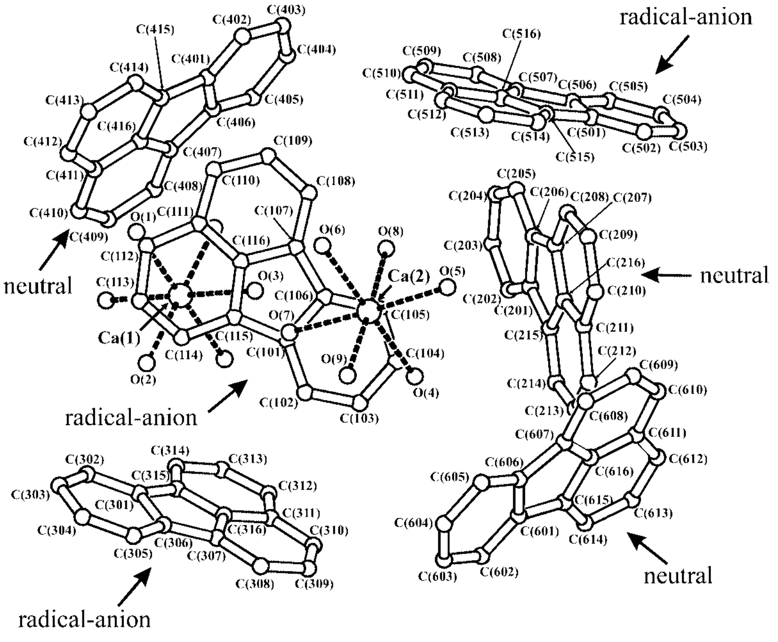


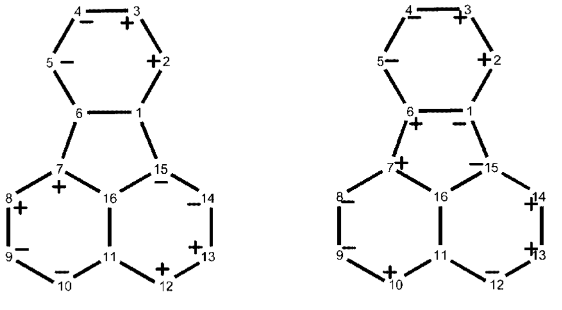
Figure 2. Molecular structure of **1**; the hydrogen atoms as well as the carbon atoms of THF are omitted for clarity

Thus, the spectroscopic data of **1** clearly demonstrate that, in contrast to our initial expectation, the radical anions of fluoranthene formed in the reduction reaction do not couple to give the corresponding *ansa*-ligand.

Molecular Structure

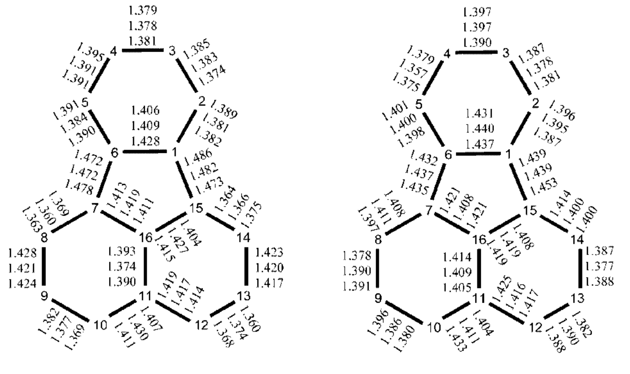
To determine the "non-metallocene" structure of **1**, the X-ray structure analysis of a crystal grown from THF was carried out. Compound **1** crystallizes in the monoclinic space group $P2_1/n$. Figure 1 shows the crystal packing. The asymmetric unit of **1** (see Figure 2) consists of 1.5 solvated $[Ca(THF)_6]^{2+}$ cations, three radical-anionic, and three neutral fluoranthene species. One cation occupies only general positions, whereas the metal atom of the second cation resides on a centre of inversion. Each calcium atom is surrounded by six coordinating THF molecules in an almost regular, octahedral fashion with virtually identical $Ca-O_{THF}$ distances, which range from 2.325(3) to 2.341(3) Å.

To decide which of the six fluoranthene molecules in the asymmetric unit are the radical anions, an accurate analysis of their skeleton C−C bond lengths, with respect to the symmetry of the ligand boundary molecular orbitals, was carried out (see Figure 3). The C(6)−C(7) and C(1)−C(15) bonds of three molecules show the most significant differences. Since the HOMO of the radical anion is of bonding character, it seems reasonable to assign the fluoranthene molecules with the shortest C(6)−C(7) and C(1)−C(15) bonds as the radical anions. The shorter C(1)−C(6) bond lengths of the other three molecules thus declared the neutral fluoranthene molecules [1.406(7), 1.409(7) and 1.428(7) Å], agree quite well with the length of the corresponding bond in the free ligand (1.40 Å) and in the silver complex $[Ag_3(C_{16}H_{10})(ClO_4)_3]$ (1.40 Å).[9]



fluoranthene HOMO fluoranthene radical-anion HOMO

a



neutral fluoranthene fluoranthene radical-anion

b

Figure 3. Molecular symmetry of the HOMO of fluoranthene and of its radical anion (a); C−C bond lengths of the fluoranthene moieties in the asymmetric unit of **1** (b)

Conclusion

In contrast to the radical anions of acenaphthylene and guaiazulene, the radical anions of fluoranthene do not dimerize to form twofold negatively charged *ansa*-ligands, under the same reaction conditions. This behaviour can be attributed to the fact that the negative charge is not strongly localized on the five-membered ring unit of the fluoranthene radical anion, thus preventing the formation of a metal-coordinating cyclopentadienyl-like π-system. On the contrary, the negative charge is delocalized over the whole ring system of the radical anion. Furthermore, in contrast to the dimerizing radical anions of acenaphthylene and guaiazulene, the radical anions of fluoranthene tend to disproportionate into neutral ligands and dianionic species.

Experimental Section

General Remarks: All manipulations were carried out under vacuum using Schlenk ampoules. The solvent THF was distilled from sodium benzophenone prior to use. Fluoranthene was purchased from Aldrich and used without further purification. The melting point of **1** was measured in a sealed capillary. IR spectra were recorded on a Specord M80 spectrometer, ESR spectra on a Bruker ER 200D-SRC spectrometer equipped with the low-temperature controller ER 4111 VT. The ESR signal was referenced to the signal of diphenylpycrylhydrazil (DPPH, $g = 2.0037$).

$[Ca(THF)_6][C_{16}H_{10}]_2{\cdot}2C_{16}H_{10}$ (1): A mixture of $CaI_2(THF)_2$ (3.65 g, 8.3 mmol), potassium (0.65 g, 16.6 mmol), and fluoranthene (3.36 g, 16.6 mmol) in THF (40 mL) was stirred for 2 hours. Within this time frame, the potassium had dissolved completely and the mixture had turned dark red-brown with the precipitation of potassium iodide and of a dark coloured solid. After separation of the solids by filtration, the THF was removed in vacuo and the residue was dried in vacuo at ambient temperature for 30 min. Then THF (40 mL) was added to the dried solid and the insoluble parts were filtered off. Reduction of the solution volume, by partial evaporation of the solvent in vacuo, caused precipitation of crystals, which were redissolved by heating the mixture to 60 °C. After standing the solution at room temperature for 24 hours, large black crystals of **1** separated. Yield 3.1 g (87 %). M.p. 148 °C(dec). IR (Nujol): 1505 m, 1430 s, 1380 m, 1445 w, 1290 s, 1215 m, 1165 s, 1130 m, 1080 m, 1115 vs, 1015 vs, 915 w, 865 vs, 830 m, 785 vs, 730 vs, 670 w, 615 m cm^{-1}. The extremely high air sensitivity of **1** prevented its analytical characterization.

Single-Crystal X-ray Structure Determination of 1: The crystal data and details of data collection are given in Table 1. The data were collected on a SMART CCD diffractometer (graphite-monochromated Mo-K_α radiation, ω-scan technique, $\lambda = 0.71073$ Å) at −100 °C. The structure was solved by direct methods using SHELXS-

Table 1. Crystal data and structure refinement for **1**

Empirical formula	$C_{88}H_{88}CaO_6$
Molecular mass	1281.66
Temperature [K]	173(2)
Wavelength [Å]	0.71073
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a [Å]	15.7291(2)
b [Å]	16.5059(3)
c [Å]	39.4418(6)
α [°]	90
β [°]	92.567(1)
γ [°]	90
V [Å^3]	10229.7(3)
Z	6
Density (calcd.) [Mg/m^3]	1.248
Absorption coefficient [mm^{-1}]	0.150
F(000)	4104
Crystal size [mm^3]	0.42 × 0.42 × 0.18
θ range for data collection [°]	1.03 to 25.00
Index ranges	$-18 \leq h \leq 17$, $-15 \leq k \leq 19$, $-46 \leq l \leq 39$
Reflections collected	49363
Independent reflections	17925 [R(int) = 0.1191]
Completeness to θ = 25.00°	99.4 %
Absorption correction	Empirical
Max. and min. transmission	0.955248 and 0.546909
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	17925/0/1417
Goodness-of-fit on F^2	0.903
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0717$, $wR_2 = 0.1120$
R indices (all data)	$R_1 = 0.1823$, $wR_2 = 0.1451$
Largest diff. peak and hole [e × Å^{-3}]	0.260 and −0.402

97[10] and was refined on F^2 with SHELXL-97[11] using all reflections. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. SADABS[12] was used to perform area-detector scaling and absorption corrections. The geometrical aspects of the structure were analyzed by using the PLATON program.[13] CCDC-223839 contains the supplementary crystallographic data, which can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Grant No. 03-03-32246a), the Grant of President of Russian Federation (No. 58.2003.03), the Alexander von Humboldt Stiftung (ILF), the Fonds der Chemischen Industrie, and the Deutsche Forschungsgemeinschaft (Graduiertenkolleg "Synthetische, mechanistische und reaktionstechnische Aspekte von Metallkatalysatoren").

---

[1] [1a] H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem.* **1995**, *107*, 1255−1283; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143−1170. [1b] K. Angermund, G. Fink, V. R. Jensen, R. Kleinschmidt, *Chem. Rev.* **2000**, *100*, 1457−1470. [1c] G. G. Hlatky, *Coord. Chem. Rev.* **2000**, *199*, 235−329.

[2] I. L. Fedushkin, S. Dechert, H. Schumann, *Angew. Chem.* **2001**, *113*, 584−586; *Angew. Chem. Int. Ed.* **2001**, *40*, 561−563.

[3] I. L. Fedushkin, T. V. Petrovskaya, M. N. Bochkarev, S. Dechert, H. Schumann, *Angew. Chem.* **2001**, *113*, 2540−2543; *Angew. Chem. Int. Ed.* **2001**, *40*, 2474−2477.

[4] I. L. Fedushkin, Y. A. Kurskii, V. I. Nevodchikov, M. N. Bochkarev, S. Muehle, H. Schumann, *Russ. Chem. Bull., Int. Ed.* **2002**, *51*, 160−169.

[5] I. L. Fedushkin, Y. A. Kurskii, T. V. Balashova, M. N. Bochkarev, S. Dechert, S. Mühle, H. Schumann, *Russ. Chem. Bull., Int. Ed.* **2003**, *52*, 1363−1371.

[6] E. de Boer, *Adv. Organomet. Chem.* **1964**, *2*, 115−155.

[7] [7a] A. V. Protchenko, L. N. Zakharov, M. N. Bochkarev, Yu. T. Struchkov, *J. Organomet. Chem.* **1993**, *447*, 209−212. [7b] I. L. Fedushkin, M. N. Bochkarev, H. Schumann, L. Esser, G. Kociok-Kohn, *J. Organomet. Chem.* **1995**, *489*, 145−151. [7c] M. N. Bochkarev, I. L. Fedushkin, R. B. Larichev, *Russ. Chem. Bull. Int. Ed.* **1996**, *45*, 2443−2444. [7d] M. N. Bochkarev, I. L. Fedushkin, A. A. Fagin, H. Schumann, J. Demtschuk, *Chem. Commun.* **1997**, 1783−1784.

[8] F. Gerson, *High Resolution ESR spectroscopy*, John Wiley & Sons, Verlag Chemie, **1970**.

[9] M. Munakata, L. P. Wu, G. L. Ning, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, N. Maeno, *J. Am. Chem. Soc.* **1999**, *121*, 4968−4976.

[10] G. M. Sheldrick, *SHELXS-97 Program for the Solution of Crystal Structures*; University of Göttingen, **1990**.

[11] G. M. Sheldrick, *SHELXL-97 Program for the Refinement of Crystal Structures*; University of Göttingen, **1997**.

[12] G. M. Sheldrick, *SADABS Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen, **1996**.

[13] A. L. Spek, *PLATON A Multipurpose Crystallographic Tool*, University of Utrecht, **2000**.

Received December 11, 2003
Early View Article
Published Online April 20, 2004