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# Synthesis and structural determination of a neodymium(III) complex derived from 9-(cyclopentadienyl-1-methylethyl)-9,10-dihydroanthracene

Yves Chauvin <sup>a</sup>, Susan Heyworth <sup>a,1</sup>, H  l  ne Olivier <sup>a</sup>, Francis Robert <sup>b</sup> and Lucien Saussine <sup>a</sup><sup>a</sup> Institut Fran  ais du P  trole, B.P. 311, 92506 Rueil-Malmaison (France)<sup>b</sup> Laboratoire de Chimie des M  taux de Transition, Universit   Pierre et Marie Curie, 75257 Paris (France)

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## Abstract

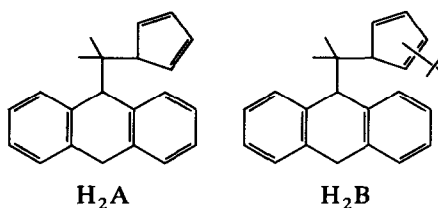
Neodymium trichloride reacts with 2 equiv. of the lithium salt of 9-(cyclopentadienyl-1-methylethyl)-9,10-dihydroanthracene in THF to give the "ate" complex  $[\text{Li}(\text{THF})_4][\text{Nd}(\{\text{C}_5\text{H}_4\text{CMe}_2(\text{C}_{14}\text{H}_{10})\}_2)]$  which has been characterized by its crystal structure and elemental analysis. The neodymium atom is situated in tetrahedral environment. It is  $\eta^5$ -bonded to the two cyclopentadienyl rings and  $\sigma$ -bonded to the C(10) atoms of the two dihydroanthracene moieties.

## 1. Introduction

The chemistry of cyclopentadienyl and substituted cyclopentadienyl derivatives of lanthanides is particularly rich [1]. This can be ascribed to their interesting reactivity which can be adjusted by varying the substituents in the cyclopentadienyl ring [2]. A few years ago, we tried to develop a new family of lanthanide compounds by direct reaction of aromatic hydrocarbons such as anthracene in ether with the more electropositive rare-earth metals [3]. The complexes obtained in this way are not soluble in ethers and have the characteristics of charge-transfer complexes. However, their chemical characterization indicates that lanthanide can be considered from a chemical point of view as being bonded to the C(9) and C(10) carbon atoms of the anthracene moiety. It is well known that, in a similar way, magnesium forms a 1:1 adduct with anthracene, with magnesium bridging the C(9) and C(10) atoms of anthracene [4]. In order to obtain more soluble compounds, we undertook the synthesis of donors containing both a cyclopentadienyl ring and a 9,10-dihydroanthracene moiety.

## 2. Results and discussion

Two donors ( $\text{H}_2\text{A}$  and  $\text{H}_2\text{B}$ ) containing a cyclopentadienyl ring bridged to a dihydroanthracene moiety by an isopropylidene group were synthesized.  $\text{H}_2\text{B}$  differs from  $\text{H}_2\text{A}$  only in the presence of a tertiary butyl group on the cyclopentadienyl ring, which enhances the solubility.



The reaction of  $\text{H}_2\text{A}$  or  $\text{H}_2\text{B}$  with 2 or 3 equiv. of  $\text{Li}^n\text{Bu}$  in THF yields a bright yellow suspension ( $\text{H}_2\text{A}$ ) and a solution ( $\text{H}_2\text{B}$ ). The  $^1\text{H}$  NMR spectrum of the lithium derivative of B in  $\text{THF-}d_8$  shows the disappearance of the allylic protons in the cyclopentadienyl ring present in the original compound. On the other hand, two benzylic protons are still present on the anthracene moiety. This suggests that lithiation was achieved on the cyclopentadienyl ring and on one position of anthracene.

The tetrahydrofuran adduct of neodymium trichloride,  $\text{NdCl}_3 \cdot x\text{THF}$  ( $1.5 < x < 2$ ) reacts in THF with  $\text{Li}_2\text{A}$  or  $\text{Li}_2\text{B}$  dilithium derivatives in a 1:2 ratio to

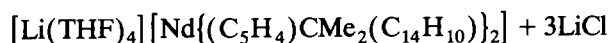
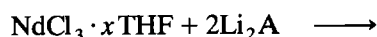
Correspondence to: Dr. Y. Chauvin.

<sup>1</sup> Present address: Johnson-Matthey, Royston, Herts SG8 5HE, UK.

TABLE 1. Selected intramolecular distances (Å) and angles (°) of complex I

Nd–C(2)	2.60(2)	Nd–C(39)	2.62(2)
Nd–C(16)	2.87(2)	Nd–C(17)	2.77(2)
Nd–C(18)	2.72(2)	Nd–C(19)	2.68(2)
Nd–C(20)	2.81(2)	Nd–C(24)	2.76(2)
Nd–C(25)	2.68(2)	Nd–C(26)	2.75(2)
Nd–C(27)	2.83(2)	Nd–C(28)	2.78(2)
C(16)–C(20)	1.44(3)	C(16)–C(17)	1.40(3)
C(17)–C(18)	1.49(3)	C(18)–C(19)	1.44(2)
C(19)–C(20)	1.45(3)	C(14)–C(15)	1.42(3)
C(2)–C(3)	1.44(2)	C(2)–C(11)	1.47(2)
C(3)–C(4)	1.46(3)	C(3)–C(8)	1.42(2)
C(4)–C(5)	1.43(3)	C(5)–C(6)	1.37(3)
C(6)–C(7)	1.46(3)	C(7)–C(8)	1.36(2)
C(8)–C(9)	1.57(2)	C(9)–C(10)	1.51(3)
C(9)–C(21)	1.60(3)	C(10)–C(11)	1.41(2)
C(10)–C(15)	1.48(3)	C(11)–C(12)	1.47(3)
C(12)–C(13)	1.40(3)	C(13)–C(14)	1.37(3)
C(16)–C(21)	1.51(3)	C(27)–C(29)	1.52(2)
C(16)–Nd–C(2)	80.4(6)	C(17)–Nd–C(2)	83.5(2)
C(19)–Nd–C(2)	129.1(6)	C(18)–Nd–C(2)	114.2(5)
C(20)–Nd–C(2)	104.7(5)	C(39)–Nd–C(2)	120.5(2)
C(20)–Nd–C(17)	49.9(6)	C(28)–Nd–C(39)	87.9(6)

give, respectively, a red (complex I) or a clear yellow solution (complex II).



Complex I was isolated as yellow-brown crystals. Its solid-state structure has been solved and is shown in Fig. 1 with relevant data in Table 1.

The molecule is composed of a well separated anion  $[\text{Nd}(\text{A})_2]^-$  and cation  $[\text{Li}(\text{THF})_4]^+$  (not represented). The structure indicates that the ligand is bidentate. In the anion, the Nd<sup>III</sup> is in a tetrahedral environment. It is bonded to the five carbon atoms of each cyclopentadienyl ring and to the C(10) carbon centre of each anthracene moiety. The two last Nd–C  $\sigma$ -bond distances are almost equal (2.60(2) and 2.62(2) Å) and are longer than those described for the Nd–C  $\sigma$ -bond distances of 2.506(7) and 2.517(7) Å in  $[\text{Me}_2\text{SiCp}_2^*\text{Nd}-\text{CH}(\text{SiMe}_3)_2]$  [2a] and  $[\text{Cp}_2^*\text{NdCH}(\text{SiMe}_3)_2]$  [5], respectively. The five carbon atoms from each C<sub>5</sub>H<sub>5</sub> ring are coplanar and form a regular pentagon. The ten Nd–C (from Cp) bond distances are reasonably constant, ranging from 2.68(2) to 2.87(2) Å (mean = 2.77 Å). This average value agrees well with the Nd–C (Cp) bond distances described in the literature [2a,5].

### 3. Experimental details

All manipulations were performed using a glove box, or Schlenk techniques, under argon. THF was distilled from benzophenone-sodium. Anhydrous NdCl<sub>3</sub> was prepared from the commercial hydrated salt as described [6]. 6,6-Dimethylfulvene [7] and t-

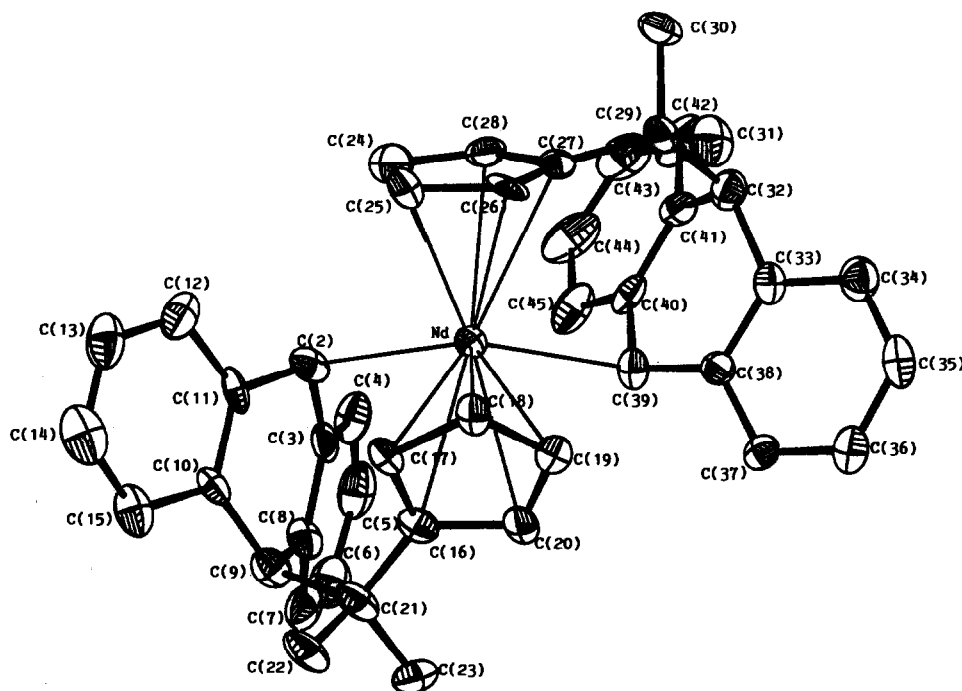


Fig. 1. Molecular structure of complex I  $[\text{Nd}\{(\text{C}_5\text{H}_4)\text{CMe}_2(\text{C}_{14}\text{H}_{10})\}_2]^-$ .

TABLE 2. Atomic and thermal parameters

Atom	x	y	z	U <sub>eq</sub>
Nd	-0.37475(9)	-0.24985(7)	-0.10186(4)	0.0514
C(2)	-0.444(2)	-0.3503(7)	-0.0942(8)	0.0555
C(3)	-0.561(2)	-0.3584(7)	-0.143(1)	0.0563
C(4)	-0.695(2)	-0.3525(9)	-0.125(1)	0.0804
C(5)	-0.813(2)	-0.367(1)	-0.171(2)	0.0872
C(6)	-0.806(2)	-0.389(1)	-0.229(1)	0.0941
C(7)	-0.673(2)	-0.3938(8)	-0.248(1)	0.0767
C(8)	-0.562(2)	-0.3777(7)	-0.206(1)	0.0589
C(9)	-0.419(2)	-0.3864(8)	-0.227(1)	0.0710
C(10)	-0.323(2)	-0.4040(7)	-0.168(1)	0.0586
C(11)	-0.331(2)	-0.3846(6)	-0.106(1)	0.0451
C(12)	-0.224(2)	-0.4007(9)	-0.053(1)	0.0863
C(11)	-0.122(3)	-0.436(1)	-0.065(2)	0.1007
C(14)	-0.116(3)	-0.456(1)	-0.124(2)	0.1057
C(15)	-0.216(2)	-0.4423(9)	-0.178(1)	0.0807
C(16)	-0.309(2)	-0.2887(9)	-0.220(1)	0.0634
C(17)	-0.191(2)	-0.2911(7)	-0.174(1)	0.0497
C(18)	-0.153(2)	-0.2342(7)	-0.158(1)	0.0547
C(19)	-0.259(2)	-0.2008(9)	-0.192(1)	0.0559
C(20)	-0.357(3)	-0.2341(7)	-0.232(1)	0.0610
C(21)	-0.369(2)	-0.3352(8)	-0.262(1)	0.0701
C(22)	-0.246(2)	-0.3573(9)	-0.294(1)	0.0762
C(23)	-0.485(2)	-0.3186(9)	-0.3157(9)	0.0744
C(24)	-0.304(2)	-0.274(1)	0.026(1)	0.0814
C(25)	-0.188(2)	-0.258(1)	0.004(1)	0.0830
C(26)	-0.194(2)	-0.1997(9)	-0.0086(8)	0.0458
C(27)	-0.318(2)	-0.1805(8)	0.0053(8)	0.0505
C(28)	-0.386(2)	-0.2268(9)	0.0253(9)	0.0674
C(29)	-0.358(2)	-0.1222(8)	0.014(1)	0.0729
C(30)	-0.373(2)	-0.1158(9)	0.084(1)	0.0859
C(31)	-0.242(2)	-0.08337(9)	-0.001(1)	0.0964
C(32)	-0.496(2)	-0.1004(8)	-0.027(1)	0.0732
C(33)	-0.492(2)	-0.0841(8)	-0.096(1)	0.0626
C(34)	-0.463(2)	-0.0298(9)	-0.105(1)	0.0844
C(35)	-0.454(2)	-0.0129(8)	-0.166(1)	0.0841
C(36)	-0.474(2)	-0.0493(9)	-0.218(1)	0.0802
C(37)	-0.504(2)	-0.1035(8)	-0.2075(9)	0.0560
C(38)	-0.515(2)	-0.1228(8)	-0.1455(8)	0.0551
C(39)	-0.560(2)	-0.1755(7)	-0.1335(9)	0.0546
C(40)	-0.635(2)	-0.1786(8)	-0.0804(9)	0.0551
C(41)	-0.610(2)	-0.1411(9)	-0.0297(9)	0.0577
C(42)	-0.692(3)	-0.142(1)	0.019(1)	0.0947
C(43)	-0.789(3)	-0.184(1)	0.019(1)	0.1015
C(44)	-0.805(3)	-0.223(1)	-0.029(1)	0.1053
C(45)	-0.730(2)	-0.2207(9)	-0.079(1)	0.0827

butylcyclopentadiene [8] were prepared as described. The concentration of NdCl<sub>3</sub> in THF solutions was determined by complexometry. Elemental analyses were obtained from Mikroanalytisches Labor Pascher, Remagen, Germany. <sup>1</sup>H NMR spectra were recorded by using a Bruker AC200 F spectrometer.

### 3.1. Synthesis of the donors

H<sub>2</sub>A: 9,10-Dihydroanthracene (9 g, 50 mmol) was dissolved in THF (50 ml) to give a colourless solution.

This was cooled to -30°C and Li<sup>n</sup>Bu (55 mmol, 34 ml) was added slowly (10–15 min) to give a brick-red solution. This was stirred for 30 min at -15°C, then cooled down to -78°C, and 6,6-dimethylfulvene (6.72 g, 63 mmol) dissolved in THF (20 ml) was added dropwise. The mixture was stirred, increasing the temperature from -78°C to room temperature overnight. This was treated with water (20 ml), extracted with ether, washed with hexane and recrystallized in hot methanol to give white crystals (7.50 g, yield 52%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 200 MHz): δ 1.14 and 1.21 (s, 6H, CH<sub>3</sub>); 2.5 and 2.85 (s, 2H, allylic H); 3.5–4 (m, 3H, benzylic H); 5.6, 5.72 and 6.4 (m, 3H, vinylic H); 7.1 (m, broad, 8H, aromatic H) ppm.

H<sub>2</sub>B: This was prepared in a similar way starting from 25 mmol of 9,10-dihydroanthracene and using 6,6-dimethyl-*t*-butylfulvene. Melting point 115.3°C; yield 5.46 g (64%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 200 MHz): δ 1.19–1.35 (m, 15H, CH<sub>3</sub>); 2.44, 2.57 and 2.9 (s, 2H, allylic H); 3.4–4 (m, 3H, benzylic H); 5.5, 5.68, 5.92 and 6.1 (s, 2H, vinylic H); 7.25 (s, 8H, aromatic H) ppm.

### 3.2. Lithiation of H<sub>2</sub>A

H<sub>2</sub>A (0.3159 g, 1.10 mmol) was dissolved in THF (10 ml) to give a pale yellow solution. This was cooled

TABLE 3. Crystal data

Formula	[Li(THF) <sub>4</sub> ][Nd{(C <sub>5</sub> H <sub>4</sub> )CMe <sub>2</sub> -(C <sub>14</sub> H <sub>10</sub> ) <sub>2</sub> }
FW	1008.41
Crystal system	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	9.988 (6)
<i>b</i> (Å)	24.832 (2)
<i>c</i> (Å)	21.228 (2)
$\beta$	99.51 (1)
<i>V</i> (Å <sup>3</sup> )	5193 (53)
<i>Z</i>	4
$\rho$ (calcd) (g cm <sup>-3</sup> )	1.29
Crystal dimensions (mm)	0.22 × 0.30 × 0.38
Systematic absences	<i>h</i> 0 <i>l</i> <i>h</i> + <i>l</i> = 2 <i>n</i> + 1, 0 <i>k</i> 0 <i>k</i> = 2 <i>n</i> + 1
Diffractometer	Enraf-Nonius CAD-4
Radiation (graphite monochromator)	Mo K $\alpha$ ( $\lambda$ = 0.71069 Å)
Linear absolute coefficient (cm <sup>-1</sup> )	10.46
Scan type	$\omega$ -2 $\theta$
Scan range (°)	0.8 + 0.345 tg $\theta$
$\theta$ limits (°)	1–23
Octants collected	-10,10; 0,27; 0,23
No. of data collected	7916
No. of unique data collected	7145
No of unique data used	2876 ( $F_o^2 > 3\sigma(F_o^2)$ )
Decay of the standards (%)	30
$R = \Sigma( F_o  -  F_c ) / \Sigma  F_o $	0.058
$R_w = [\Sigma w( F_o  -  F_c )^2 / \Sigma w F_o^2]^{1/2}$	0.065

to  $-78^{\circ}\text{C}$ , and  $\text{Li}^n\text{Bu}$  (3.36 mmol, 2.1 ml) was added dropwise. The mixture was stirred as the temperature increased from  $-78^{\circ}\text{C}$  to ambient temperature over a period of 4 h, yielding a bright yellow precipitate. Repetition of the reaction with the  $\text{Li}/\text{H}_2\text{A}$  ratio of 2:1 gave identical results.

### 3.3. Synthesis of complex I

The above suspension was transferred to  $\text{NdCl}_3$  (0.254 g, 1.01 mmol) dissolved in THF (40 ml), and the resulting solution was stirred at ambient temperature for 24 h. The solvent was removed *in vacuo*, giving an oily solid. This was recrystallized as brown-yellow crystals, at room temperature, by slow diffusion of 10 ml of ether into a 5 ml THF solution of the complex (0.220 g, yield 40%).

Anal. Found: C, 70.7; H, 7.19; O, 6.30; Nd, 14.6.  $\text{C}_{60}\text{H}_{72}\text{LiNdO}_4$  calc.: C, 71.5; H, 7.2; O, 6.3; Nd, 14.3%.

### 3.4. Lithiation of $\text{H}_2\text{B}$

The experimental procedure was the same as for  $\text{H}_2\text{A}$ , but an orange solution was obtained. THF was removed *in vacuo*, giving a yellow oil. This was washed with pentane ( $2 \times 5$  ml), and the yellow solid was dried *in vacuo*. The  $^1\text{H}$  NMR spectrum in  $\text{THF-}d_8$  was recorded.  $^1\text{H}$  NMR (200 MHz):  $\delta$  0.95 and 1.1 (s, 15H,  $\text{CH}_3$ ); 3.15, 3.42 and 3.5 (d, s and s, 2H, benzylic H); 4.7, 4.81 and 5.08 (t, 3H, vinylic H), 6–6.9 (m, 9H, aromatic H) ppm.

### 3.5. Synthesis of complex II

The identical reaction with  $\text{Li}_2\text{B}$  gave an analogous complex, isolated as yellow crystals from toluene (0.210 g, yield 34%).

Anal. Found: C, 72.20; H, 7.75; O, 6.11; Nd, 13.2.  $\text{C}_{68}\text{H}_{88}\text{LiNdO}_4$  calc.: C, 72.9; H, 7.9; O, 5.7; Li, 0.6; Nd, 12.9%.

### 3.6. Crystal structure determination

The structure was solved by direct methods using SHELXS 86 [9]. Data reduction and structure refinement were performed using the CRYSTALS package [10]. The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined by full matrix least-squares. The hydrogen atoms were located on difference Fourier maps but not introduced in the last least-square cycles. The intensities were corrected for absorption using DIFABS [11] and for secondary extinction. The real and imaginary parts of the scattering factors for neutral atoms were taken from the International Tables for X-ray Crystallography.

Full lists of atomic coordinates and thermodynamic parameters are available from the Cambridge Crystallographic Data Centre.

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