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Preparation and molecular structure of methylbis(t-butylcyclopentadienyl)neodymium and -gadolinium

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Abstract

Bis(t-butylcyclopentadienyl)lanthanide chloride (Ln = Nd or Gd) reacts with one equivalent of methyllithium in ether/tetrahydrofuran to give the complex $[(C_5H_4{}^tBu)_2LnCH_3]_2$ (Ln = Nd or Gd). The structure of $[(C_5H_4{}^tBu)_2NdCH_3]_2$ has been determined by X-ray analysis. The crystals are monoclinic of space group *Cm* with $a = 9.538(2)$, $b = 23.298(4)$, $c = 9.505(3)$ Å, $\beta = 119.53(2)°$, $V = 1828.0(7)$ Å^3, $D_{calc.} = 1.458$ g/cm^3 and $Z = 2$ for the dimer. The two $(C_5H_4{}^tBu)_2Nd$ units in the dimer are connected by asymmetrical methyl bridges with independent Nd–C bond lengths of 2.70(2) and 2.53(2) Å and Nd–C–Nd angles of 94.7(9) and 87.3(6)°.

Introduction

The cyclopentadienyl and substituted cyclopentadienyl methyl derivatives of lanthanides are of importance in the synthetic chemistry of organolanthanides [1–4]. Many of the studies on the syntheses and structures of these complexes have involved the smaller and later elements in the series, Er–Lu [1,2,4–10].

The first methyl derivatives of early lanthanides are the permethylated complexes of the type $[Li(tmed)]_3[Ln(CH_3)_6]$ [11]. Later, Schumann reported the synthesis of $(C_5Me_5)_2La(\mu\text{-}CH_3)_2$ Li(tmed) through the reaction of $(C_5Me_5)_2La$-ClLi(tmed) and $LiCH_3$ [12]. However, no X-ray molecular structure has been reported up to now. This led us to study the synthesis and structure of substituted cyclopentadienylmethyl complexes of lanthanides for Ln = La–Gd. We now describe the synthesis of $[(C_5H_4{}^tBu)_2LnCH_3]_2$ (Ln = Nd and Gd) and the X-ray molecular structure of $[(C_5H_4{}^tBu)_2NdCH_3]_2$.

Experimental

All manipulations were performed using Schlenk tubes under argon. The solvents were dried and freed of oxygen by refluxing over Na or sodium benzophenone ketyl and distilling under argon prior to use. Anhydrous $LnCl_3$ was made according to the literature [13].

Metal analysis was carried out by complexometric titration. IR spectra were recorded on a Perkin–Elmer spectrometer as KBr pellets.

$[(C_5H_4{}^tBu)_2NdCH_3]_2$

A 20.10 mmol sample of $NaC_5H_4{}^tBu$ in 77 ml of THF was added to a slurry of 2.52 g (10.0 mmol) of $NdCl_3$ in 10 ml THF. The mixture was stirred at 60 ° C for 72 h. After centrifugation the solution was cooled to −78 ° C. A 12.0 ml of a 0.81 *M* solution of $LiCH_3$ in diethyl ether was added. The solution was stirred for 1 h at −78 ° C and then warmed to room temperature. After the mixture was stirred at room temperature for 10 h, the solvent was removed and the oily residue was extracted with toluene. After filtration the clear solution was concentrated to dryness and the residue was diluted in toluene again. After centrifugation, the resulting solution was crystallized at −5 ° C. Purple crystals were collected: yield 1.744 g (51.1%). Anal. $C_{19}H_{29}Nd$ calc.: Nd, 35.95; Cl, 0. Found: Nd, 35.74; Cl, 0%. IR: 3110(m), 3080(w), 2940(s), 2880(m), 2840(m), 1650(w), 1470(m), 1450(m), 1370(w), 1360(m), 1272(m), 1196(m), 1150(m), 1042(m), 1010(m), 910(m), 815(m), 760(s) cm^{-1}.

$[(C_5H_4{}^tBu)_2GdCH_3]_2$

This compound was prepared from 0.74 g of $GdCl_3$ (2.8 mmol), 5.6 mmol of $NaC_5H_4{}^tBu$, 3 ml of 1.2 *M* solution of $LiCH_3$ in diethyl ether using the procedure described above. Colorless crystals of $[(C_5H_4{}^tBu)_2GdCH_3]_2$ were obtained: yield 0.46 g (37.4%). Anal. $C_{19}H_{29}Gd$ calc.: Gd, 37.96; Cl, 0. Found: Gd, 37.44; Cl, 0%. IR: 3110(m), 3080(w), 2942(s), 2880(m), 2850(m), 1450(m), 1385(w), 1270(m), 1190(m), 1150(m), 1010(m), 945(w), 820(m), 762(s) cm^{-1}.

X-Ray crystallography of $[(C_5H_4{}^tBu)_2NdCH_3]_2$

A suitable crystal was sealed in a glass capillary. Intensity data were collected on a Nicolt R3M/E diffractometer with Mo-K_α radiation in the ω-scan mode. Experimental details are given in Table 1. The intensities were corrected for Lorentz, polarization and absorption effects (transmission factors min 0.211, max 0.381). The range for h was 0 to 14, for k 0 to 33, and for l −14 to 14.

The structure was solved by Patterson techniques and refined by full-matrix least-squares techniques with anisotropic thermal parameters. H atoms were placed in calculated positions and were assigned isotropic thermal parameters ($U = 0.05$ Å^2). Final $R = 0.054$, $R_w = 0.048$).

Calculations were carried out with the SHELXTL system of computer programs. The atomic coordinates for $[(C_5H_4{}^tBu)_2NdCH_3]_2$ are given in Table 2.

Supplementary material available. Tables of bond lengths and angles, temperature factors and least-squares plane (13), a listing of calculated and observed structure factors (9) are available from the authors.

Results and discussion

The reaction of $(C_5H_4{}^tBu)_2LnClTHF$ with one equiv of $LiCH_3$ gave straightforwardly $[(C_5H_4{}^tBu)_2LnCH_3]_2$ (eq. 1)

$$(C_5H_4{}^tBu)_2LnClTHF + LiCH_3 = \left[(C_5H_4{}^tBu)_2LnCH_3\right]_2, \quad Ln = Nd, Gd \qquad (1)$$

Table 1

Crystal data and details of the structure analysis of $[(C_5H_4{}^tBu)_2NdCH_3]_2$

Formula	$C_{38}H_{58}Nd_2$
Mol. wt.	802.48
Crystal size (mm)	0.24×0.16×0.30
Crystal system	Monoclinic
Space group	*Cm*
a (Å)	9.538(2)
b (Å)	23.298(4)
c (Å)	9.505(3)
β (°)	119.53(2)
V (Å^3)	1828.0(7)
Z	2
$D_{calc.}$ (g cm^{-1})	1.458
2θ range (°)	3.0–60
Scan technique	ω
Reflections	2912
Reflections for $I \geqslant 3\sigma(I)$	1449
F(000)	1624
$R = \Sigma \lvert \lvert F_o \rvert - \lvert F_c \rvert \rvert / \Sigma \lvert F_o \rvert$	0.054
$R_w = (\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \Sigma w F_o^2)^{1/2}$	0.048

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for $[(C_5H_4{}^tBu)_2NdCH_3]_2$ (Å$^2 \times 10^3$) with esd's in parentheses

Atom	*x*	*y*	*z*	U_{eq}
Nd	1478(7)	799(1)	4476(8)	34(1)
C(11)	−192(18)	1781(9)	4512(21)	51(9)
C(12)	−1137(21)	1475(13)	2761(20)	66(11)
C(13)	−1815(20)	926(11)	2817(22)	65(10)
C(14)	−1446(40)	848(11)	4410(34)	44(10)
C(15)	−603(21)	1317(10)	5393(22)	46(9)
C(16)	−263(22)	1425(11)	7084(20)	51(9)
C(17)	−494(31)	834(13)	−2122(26)	95(15)
C(18)	1416(27)	1686(13)	8038(26)	79(13)
C(19)	−1537(31)	1863(12)	6969(27)	85(15)
C(21)	4483(43)	873(15)	4410(39)	85(12)
C(22)	3073(22)	993(11)	2740(22)	67(11)
C(23)	2386(22)	1508(12)	2712(21)	60(11)
C(24)	3456(16)	1671(7)	4528(16)	26(6)
C(25)	4540(17)	1304(10)	5398(19)	37(8)
C(26)	5852(19)	1408(10)	7071(18)	47(8)
C(27)	6925(23)	891(10)	7919(24)	65(10)
C(28)	5072(35)	1652(16)	8013(30)	136(20)
C(29)	−3639(46)	1914(19)	7126(34)	579(70)
C(1)	2983(26)	0	6815(28)	41(9)
C(2)	729(34)	0	2416(30)	136(22)

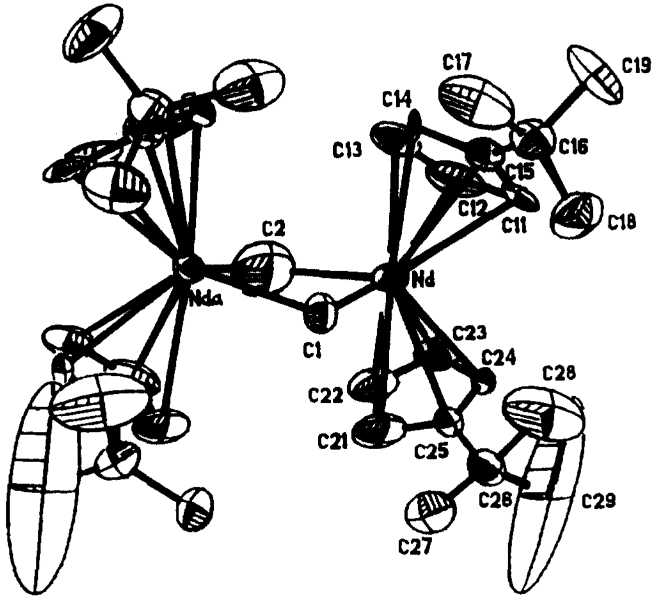

Fig. 1. The molecular structure of $[(C_5H_4{}^tBu)_2NdCH_3]_2$.

Although a variety of methyl complexes of lanthanides have been crystallographically characterized, including $[(C_5H_5)_2Ln(\mu\text{-}CH_3)]_2$ (Ln = Yb, Y) [6], $[(C_5H_5)_2Er(CH_3)_2Li(tmed)]$ [8], $[(C_5Me_5)_2Lu(CH_3)_2Li(tmed)]$ [12], $(C_5H_5)_2Yb(CH_3)_2Al(CH_3)_2$ [10], $(C_5Me_5)_2LnCH_3THF$ (Ln = Yb [1], Lu [15], Y [9]) and $(C_5Me_5)_2ScCH_3$ [2], no X-ray studies of methyl complexes of lanthanides for Ln = La–Gd have been reported. Therefore, full characterization of this early lanthanide complex was desirable.

The crystal structure of $[(C_5H_4{}^tBu)_2NdCH_3]_2$ demonstrates that the complex is a dimer in which the two $(C_5H_4{}^tBu)_2Nd$ units are connected together by asymmetric methyl bridges. It was not possible to locate the hydrogen atoms of the CH_3 groups in the difference Fourier calculation, mainly because of high thermal vibrations. Therefore, we could not confirm if the CH_3 group has an agostic interaction with the Nd or not. The molecular structure and atom-numbering scheme for the neodymium complex is shown in Fig. 1 and its stereoscopic view of the unit-cell packing is presented in Fig. 2. Important bond lengths and angles are given in Table 3.

Nd–C (ring) distances range from 2.70(2) to 2.90(5) Å with the longest distances being those involving carbon atoms bonded to tert-butyl groups. The average Nd–C (ring) distance of 2.78(6) Å is comparable to 2.629(10) Å in $(C_5H_4{}^tBu)_2YbCl(THF)$ and 2.81(2) Å in $(C_5H_4{}^tBu)_2PrCl(THF)_2$ [14], when corrections are made for differences in ionic radii.

The Nd–C methyl distances of 2.53(2) and 2.70(2) Å are somewhat longer than the Nd–C bond lengths of 2.517(7) Å in $(C_5Me_5)_2NdCH[Si(CH_3)_3]_2$ [16] and 2.506(7) Å in $Me_2Si(C_5Me_4)_2$ $NdCH[Si(CH_3)_3]_2$ [17]. Normally, the bridging alkyls are longer than terminal alkyls in organolanthanide complexes. For example, the

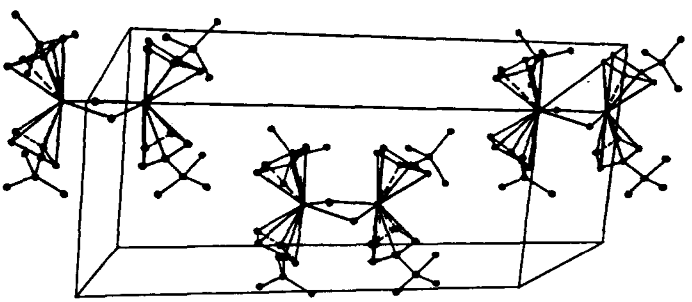

Fig. 2. The unit cell packing of $[(C_5H_4{}^tBu)_2NdCH_3]_2$.

Yb–CH_3 bonds in $[(C_5H_5)_2Yb(CH_3)]_2$, 2.49(2) and 2.54(2) Å [6], are 0.13–0.18 Å longer than the Yb–CH_3 bond in $(C_5H_5)_2Yb(CH_3)(THF)$, 2.36(1) Å [1], and Lu–C (bridging methyl) bonds, 2.440(9) and 2.756(9) Å, are also 0.10–0.42 Å longer than the Lu–C (terminal methyl) bond, 2.34(1) Å, in $(C_5Me_5)_2Lu(\mu\text{-}CH_3)Lu(C_5Me_5)_2CH_3$ [15]. Thus the present Nd–CH_3 distances are not unusual.

Comparison of the Nd–CH_3 distances, 2.53(2) and 2.70(2) Å, can also be made with the other isostructural lanthanide methyl complexes. The Ln–CH_3 distances in $[(C_5H_5)_2LnCH_3]_2$ are 2.49(2) and 2.54(2) Å for Ln = Yb, and 2.553(10) and 2.537(9) Å for Ln = Y [6]. The Nd–CH_3 bond lengths observed are therefore reasonable in comparison with the Yb–CH_3 bonds and the Y–CH_3 bonds when differences in ionic radii (0.124 Å) for Yb^{III} and Nd^{III}, (0.104 Å) for Y^{III} and Nd^{III} are considered.

The Nd metal is surrounded in a distorted tetrahedral fashion. The angle involving the metal and the two bridged methyl groups, C(1)–Nd–C(2) 87.5(5)°, is much smaller than the angle Cen–Nd–Cen 124.1° (Cen is the centroid of the tert-butylcyclopentadienyl ring) and shows the large deviation from the ideal tetrahedral geometry. This behavior is normal for other such complexes $[(C_5H_5)_2Ln(CH_3)]_2$ Ln = Y, C–Ln–C 92.3(3)°, Cen–Ln–Cen 128.9°; Ln = Yb, C–Ln–C 93.4(5)°, Cen–Ln–Cen 128.2° [6]. The angles Nd–C(1)–Nda and Nd–

Table 3

Important bond lengths (Å) angles (°) with esd's in parentheses

Nd–C(1)	2.70(2)	Nd–C(2)	2.53(2)
Nd–C(11)	2.80(2)	Nd–C(12)	2.70(2)
Nd–C(13)	2.73(2)	Nd–C(14)	2.76(4)
Nd–C(15)	2.81(3)	Nd–C(21)	2.90(5)
Nd–C(22)	2.70(3)	Nd–C(23)	2.78(3)
Nd–C(24)	2.76(2)	Nd–C(25)	2.85(2)
Nd–Cen(1) [a]	2.46	Nd–Cen(2)	2.55
Nd–C(1)–Nda	87.3(6)	Nd–C(2)–Nda	94.7(9)
C(1)–Nd–C(2)	87.5(5)	C(1)–Nd–Cen(1)	122
C(1)–Nd–Cen(2)	108	C(2)–Nd–Cen(1)	108
C(2)–Nd–Cen(2)	96	Cen(1)–Nd–Cen(2)	124

[a] Cen is the centroid of the tert-butylcyclopentadienyl ring.

C(2)–Nda are 87.3(6) and 94.7(9)° respectively, showing that the four atoms C(1), Nd, Nda, and C(2) are not in a plane.

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