Journal of Organometallic Chemistry, 427 (1992) 141–149
Elsevier Sequoia S.A., Lausanne
JOM22403

Synthesis and crystal structure of the tris(cyclopentadienyl)phenyl complex of neodymium, $(Li \cdot 3DME)[(\eta^5\text{-}C_5H_5)_3NdC_6H_5]$

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(Received May 12, 1991)

Abstract

$(Li \cdot 3DME)[(\eta^5\text{-}C_5H_5)_3NdC_6H_5]$, **1** was synthesized by the reaction of $NdCl_3 \cdot 2LiCl$, 2 equivalents of cyclopentadienylsodium and one equivalent of phenyllithium in THF at −78°C, and crystallized from THF and DME. The crystal structure of **1** was determined by X-ray diffraction method at −80°C. The crystal of **1** is triclinic, space group $P\bar{1}$ with $a = 15.752(6)$, $b = 16.232(3)$, $c = 23.038(7)$ Å, $\alpha = 108.81(2)$, $\beta = 93.31(3)$, $\gamma = 108.38(2)°$, $Z = 6$ and $D = 1.33$ g/cm^3. Least-squares refinement (5732 observed reflections) led to a final R of 0.053. The complex consists of disconnected ion pairs of $(Li \cdot 3DME)^+$ and $[(\eta^5\text{-}C_5H_5)_3NdC_6H_5]^-$. The neodymium atom was connected to three η^5-bonded cyclopentadienyls and one σ-bonded phenyl in a distorted tetrahedral arrangement with Nd–C(σ-) 2.593(17), 2.613(13) and 2.601(13) Å.

Introduction

Phenyl derivatives of lanthanoids $Sc(C_6H_5)_3$, $Y(C_6H_5)_3$, $LiLa(C_6H_5)_4$ and $LiPr(C_6H_5)_4$ were prepared by Hart *et al.*, [1,2] and phenyl complexes of lanthanoids stabilized by cyclopentadienyl ligands have been reported recently [3–5], but the only molecular structures of such complexes to have been described in detail are those of $(C_5Me_5)_2SmC_6H_5(THF)$ [6] and $(C_5H_5)_2LuC_6H_4\text{-}p\text{-}CH_3(THF)$ [5]. We reported here the synthesis and X-ray crystal structure of a new type of anionic phenyl complex of neodymium $(Li \cdot 3DME)[(\eta^5\text{-}C_5H_5)_3NdC_6H_5]$. To our knowledge, this is the first report of the structure of a cyclopentadienyl phenyl complex of an early lanthanoid.

Experimental

All manipulations were performed in Schlenk tubes in an argon atomsphere. THF, DME and toluene were distilled over sodium benzophenone. Anhydrous

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LiCl was obtained under vacuum at high temperature. Anhydrous $NdCl_3$ was prepared according to the literature [7]. Elemental analyses were performed by direct combustion. Metal analyses of Nd and Li were carried out by complexometric titration of EDTA and atomic absorption spectra respectively. Infrared spectra were recorded on a FTS-20E spectrometer as KBr pellets.

(Li·3DME)[(η^5-C_5H_5)$_3$NdC_6H_5], 1

A THF solution of NaC_5H_5 (1.51 g, 17.2 mmol) was added at room temperature to 20 ml of a THF solution of $NaCl_3 \cdot 2LiCl$ (2.887 g, 8.6 mmol) which was obtained from reaction of $NdCl_3$ and LiCl in molar ratio of 1:2 [8]. The mixture was stirred overnight, then centrifugated and cooled to −78°C. 10 ml of a diethyl ether solution of phenyllithium (0.722 g, 8.6 mmol) was added dropwise. The solution was stirred for 1 h at −78°C, then for another 24 h at room temperature. The solvent was removed under vacuum and the red oily residue extracted with toluene. After filtration a two-layer mixture of toluene and a red oily solution was obtained. After removing the toluene layer, the red oily solution was extracted with THF–DME (1:1). The resulting red THF–DME solution was concentrated and cooled to −10°C for crystallization. Analytically pure purple crystals of **1** were collected in 25% yield (1.5 g). Anal. Found: C, 56.30; H, 6.34; Li, 1.21; Nd, 20.34. $C_{33}H_{50}LiNdO_6$ calc.: C, 57.12; H, 7.21; Li, 1.10; Nd, 20.78%. IR (KBr): 3075(m), 2990(w), 2920(s), 2810(w), 1620(w), 1580(w), 1440(s), 1479(s), 1360(m), 1238(m), 1185(m), 1075(s), 1005(w), 860(m), 760(s), 745(s), 690(w) cm^{-1}.

Reaction of (C_5H_5)$_3$Nd with LiC_6H_5

A diethyl ether solution of LiC_6H_5 (0.63 g, 7.5 mmol) was added to 40 ml of a THF solution of $(C_5H_5)_3Nd$ (2.544 g, 7.5 mmol), and the mixture was stirred for 1 h at −78°C, then for another 24 h at room temperature. The solvent was removed under vacuum and the residue was extracted with THF–DME. After filtration, the resulting THF–DME solution was concentrated and cooled to −10°C. 0.52 g of white crystals LiC_6H_5 (Anal. Li, 4.2; Nd, 0%) and 1.5 g of violet crystals $(C_5H_5)_3NdTHF$ (Anal. Li, 0; Nd, 32.24%) were obtained.

X-ray crystallography of 1

A block-shaped crystal (0.2 × 0.3 × 0.2 mm) of **1** was selected in an argon atmosphere and mounted on a glass fibre. The unit cell parameters were refined from the setting angles of reflections. Data were collected on a Nicolet four circle diffractometer with an LT–1 low temperature device at about −80°C using graphite monochromated Mo-K_α radiation. The ω scan mode, scan speeds variable from 4.88–29.3°/min and scan range of 1.10 were used. The intensity of one check reflection was monitored for every 68 reflections. A total of 8920 reflections was collected within the range of $3° \leqslant 2\theta \leqslant 44°$, of which 5732 reflections with $I \geqslant 3\sigma(I)$ were considered observable. There was no obvious change in check reflection intensity indicating that the crystal remained stable during data collection. The intensities were corrected for Lorentz and polarization factors, but not for absorption. A summary of data collection parameters is given in Table 1.

The crystal structure was solved by the heavy-atom method. The coordinates of Nd and Li atoms derived from Patterson analysis were used to calculate the Fourier map. Successive Fourier syntheses gave the coordinates of all non-hydro-

Table 1

Crystal and refinement data for $(Li \cdot 3DME)[(C_5H_5)_3NdC_6H_5]$

Molecular weight	693.2
Crystal size (mm)	$0.20 \times 0.30 \times 0.20$
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	15.752(6)
b (Å)	16.232(3)
c (Å)	23.083(8)
α (deg)	108.81(2)
β (deg)	93.31(3)
γ (deg)	108.38(2)
V (Å^3)	5202.74
D_c (g/cm^3)	1.33
Z	6
Temperature (°C)	−80
Scan type	ω
2θ range (deg)	3–44
Reflections	8920
Reflections for $I \geqslant 3\sigma(I)$	5732
$F(000)$	1556
$R = \Sigma \| \|F_o\| - \|F_c\| \| / \Sigma \|F_o\|$	0.053
$R_w = \{\Sigma w(\|F_o\| - \|F_c\|)^2 / \Sigma w F_o^2\}^{1/2}$	0.043

gen atoms refined by the block-diagonal least-squares method. H atoms were placed in calculated positions and assigned isotropic thermal parameters ($U = 0.08$ Å^2), Table 2. Further refinement led to final convergence at $R = 0.053$. All calculations were performed on an Eclipse S/140 computer using SHELXTL programs.

Results and discussion

Synthesis of complex 1

Yi *et al.* [8] reported that the $NdCl_3 \cdot 2LiCl$ complex reacts in THF solution with 2 equivalents of NaC_5H_5 to form $(C_5H_5)_2NdCl \cdot 2LiCl$. In order to see if the THF solution of $(C_5H_5)_2NdCl \cdot 2LiCl$ would be a valuable precusor for synthesis of an organoneodymium complex containing Nd–C σ-bond, the reaction of phenyllithium with the above mentioned $(C_5H_5)_2NdCl \cdot 2LiCl$ in THf solution was studied. It is interesting that a new phenyl complex of neodymium, **1** should be formed from the above reaction instead of the expected complex $(C_5H_5)_2NdC_6H_5$.

Tris(cyclopentadienyl)praseodymium was reported to react with n-butyllithium in THF to form $[(C_5H_5)_3PrC_4H_9]^-$ [9]. In order to see if complex **1** might be formed through the reaction of phenyllithium with the $(C_5H_5)_3Nd$ which comes from the $(C_5H_5)_2NdCl \cdot 2LiCl$ THF solution by disproportion *in situ*, the reaction of $(C_5H_5)_3Nd$ and phenyllithium in THF was studied. However, when $(C_5H_5)_3Nd \cdot THF$ reacts with phenyllithium in THF, after work up, only the reactants phenyllithium and $(C_5H_5)_3Nd$ have been isolated. So until now the detailed reaction paths by which the complex **1** is formed have not been clarified.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\times 10^3$) (e.s.d.s of last significant figure in parentheses)

Atom	*x*	*y*	*z*	*U*
Nd(1)	2313(1)	2387(1)	370(1)	33(1)
C(1)	1377(11)	514(10)	212(8)	50(9)
C(2)	2231(12)	758(9)	563(7)	46(8)
C(3)	2915(11)	887(10)	195(7)	45(8)
C(4)	2480(11)	698(10)	−426(7)	44(8)
C(5)	1529(11)	489(10)	−422(8)	53(9)
C(6)	4092(11)	3476(11)	1081(7)	47(8)
C(7)	3736(11)	2819(11)	1374(7)	47(8)
C(8)	3017(11)	3021(11)	1648(7)	52(8)
C(9)	2927(11)	3829(10)	1551(7)	49(8)
C(10)	3607(10)	4096(10)	1183(7)	41(8)
C(11)	3119(10)	2840(10)	−490(7)	41(8)
C(12)	2709(13)	2271(12)	−1119(7)	69(10)
C(13)	3062(15)	2470(14)	−1626(8)	88(12)
C(14)	3863(14)	3248(12)	−1513(9)	74(11)
C(15)	4286(13)	3795(12)	−904(9)	67(11)
C(16)	3909(11)	3589(11)	−405(8)	51(9)
C(17)	1364(12)	3621(13)	429(9)	70(11)
C(18)	1305(13)	3164(12)	−210(10)	70(11)
C(19)	733(13)	2191(14)	−372(9)	79(11)
C(20)	460(10)	2105(11)	189(11)	90(10)
C(21)	850(12)	2973(13)	700(9)	71(11)
C(22)	9252(11)	4394(10)	10 667(8)	57(8)
C(23)	9088(10)	3354(11)	9611(7)	46(8)
O(1)	8742(7)	3496(7)	10 197(5)	46(5)
C(24)	8625(9)	2312(10)	9208(7)	39(8)
O(2)	7650(7)	2104(6)	9146(4)	36(5)
C(25)	7156(11)	1169(10)	8735(7)	54(8)
C(26)	6898(11)	3648(11)	8948(7)	53(9)
O(3)	7132(7)	3850(7)	9622(5)	47(5)
C(27)	6766(14)	4498(11)	10 001(7)	85(10)
C(28)	7052(13)	4684(11)	10 673(7)	58(9)
O(4)	6987(8)	3841(7)	10 760(5)	59(6)
C(29)	7119(13)	3938(12)	11 406(6)	62(10)
C(30)	8042(11)	1738(12)	10 662(8)	54(10)
O(5)	7274(7)	1962(7)	10 470(5)	46(5)
C(31)	6445(11)	1161(10)	10 285(7)	47(8)
C(32)	5573(11)	1501(10)	10 177(7)	46(8)
O(6)	5833(7)	1889(6)	9687(4)	41(5)
C(33)	5069(11)	2177(11)	9537(8)	57(9)
Nd(2)	9662(1)	3213(1)	6947(1)	46(1)
C(34)	9896(13)	3450(11)	8224(7)	61(10)
C(35)	9814(11)	2495(11)	7895(7)	49(9)
C(36)	8941(11)	1974(13)	7561(7)	58(10)
C(37)	8430(11)	2592(13)	7690(8)	63(10)
C(38)	9030(13)	3508(14)	8094(8)	73(11)
C(39)	8843(14)	4541(13)	7152(9)	80(12)
C(40)	8823(15)	4254(13)	6502(10)	76(12)
C(41)	9741(20)	4577(16)	6405(13)	94(16)
C(42)	10 299(18)	5064(17)	6980(15)	110(18)
C(43)	9786(14)	5047(12)	7471(10)	97(12)
C(44)	8354(11)	1940(11)	6055(7)	48(8)
C(45)	7727(12)	1143(11)	6113(8)	65(9)

Table 2 (continued)

Atom	*x*	*y*	*z*	*U*
C(46)	7082(12)	445(12)	5613(8)	67(10)
C(47)	7078(14)	503(14)	5024(10)	77(12)
C(48)	7639(15)	1256(15)	4926(8)	75(12)
C(49)	8309(12)	1979(13)	5468(7)	59(10)
C(50)	10880(12)	3085(15)	6107(9)	82(13)
C(51)	10492(12)	2147(13)	6089(8)	70(11)
C(52)	10765(12)	2103(12)	6662(8)	62(10)
C(53)	11365(12)	2976(14)	7057(8)	72(12)
C(54)	11454(12)	3612(13)	6713(10)	83(13)
C(55)	6569(14)	4634(12)	5839(9)	82(11)
C(56)	6096(14)	5379(11)	6758(8)	72(10)
O(7)	5820(7)	4671(7)	6155(5)	53(6)
C(57)	5255(11)	5450(11)	7036(8)	60(9)
O(8)	4724(7)	4540(7)	6989(5)	52(5)
C(58)	4014(11)	4570(12)	7358(8)	60(9)
C(59)	3990(15)	4135(15)	5279(10)	93(13)
O(9)	3842(8)	3369(8)	5509(5)	62(7)
C(60)	2956(13)	3083(14)	5676(9)	76(12)
C(61)	2881(13)	2243(13)	5862(10)	74(11)
O(10)	3630(8)	2499(7)	6341(5)	61(8)
C(62)	3543(14)	1821(12)	6609(9)	76(11)
C(63)	4938(14)	2007(13)	4985(7)	80(11)
O(11)	5306(8)	2473(7)	5629(5)	60(6)
C(64)	5912(16)	2192(16)	5867(9)	107(14)
C(65)	6228(14)	2610(13)	6534(7)	74(11)
O(12)	5823(9)	3232(8)	6849(5)	71(7)
C(66)	6007(11)	3582(13)	7514(7)	61(10)
C(67)	5386(12)	10501(12)	6921(11)	61(11)
Nd(3)	4809(1)	8981(1)	7321(1)	32(1)
C(68)	5140(15)	10864(11)	7494(9)	69(11)
C(69)	4194(12)	10478(11)	7425(8)	54(10)
C(70)	3841(13)	9853(11)	6817(8)	61(10)
C(71)	4557(13)	9876(11)	6482(8)	57(10)
C(72)	3743(11)	9221(11)	8282(7)	50(9)
C(73)	4699(10)	9689(10)	8576(6)	41(8)
C(74)	5104(11)	9016(11)	8544(7)	49(9)
C(75)	4419(10)	8104(10)	8198(7)	39(8)
C(76)	3609(10)	8232(11)	8042(7)	42(8)
C(77)	3554(11)	7501(11)	6530(8)	49(9)
C(78)	3190(11)	7454(13)	5944(7)	61(9)
C(79)	2569(13)	6638(14)	5498(8)	74(10)
C(80)	2326(11)	5810(11)	5614(9)	66(10)
C(81)	2707(13)	5816(13)	6180(9)	72(11)
C(82)	3305(12)	6669(11)	6628(8)	54(9)
C(83)	6096(10)	8685(11)	6556(7)	38(8)
C(84)	6619(10)	9318(11)	7125(7)	44(8)
C(85)	6537(10)	8821(10)	7558(7)	42(8)
C(86)	5949(10)	7912(10)	7244(7)	42(8)
C(87)	5664(10)	7809(10)	6622(8)	50(8)
C(88)	−1642(21)	290(35)	2260(17)	307(34)
O(13)	−1083(12)	1273(20)	2802(9)	259(20)
C(89)	−1443(15)	1949(20)	2967(11)	125(18)
C(90)	−1038(15)	2652(19)	3616(12)	135(18)
O(14)	−132(11)	2645(10)	3814(8)	127(10)
C(91)	366(21)	3290(19)	4406(14)	204(21)

Table 2 (continued)

Atom	x	y	z	U
C(92)	929(24)	3302(16)	2729(19)	234(29)
O(15)	862(15)	2408(12)	2673(13)	257(20)
C(93)	613(20)	1740(18)	1941(15)	161(22)
C(94)	846(14)	838(16)	1888(10)	99(15)
O(16)	321(9)	560(8)	2325(6)	81(7)
C(95)	387(24)	−335(15)	2310(12)	166(21)
C(96)	2204(13)	2385(18)	3574(11)	130(15)
O(17)	1429(9)	1849(11)	3759(6)	117(9)
C(97)	1531(20)	1065(22)	3892(15)	165(23)
C(98)	792(18)	874(24)	4183(12)	176(22)
O(18)	−138(13)	555(10)	3672(9)	164(13)
C(99)	−1050(19)	251(18)	3846(15)	167(21)
Li(1)	7311(18)	2842(19)	9987(12)	53(14)
Li(2)	4860(19)	3440(17)	6268(13)	47(13)
Li(3)	235(19)	1578(21)	3228(13)	60(15)

X-ray crystal structure

Complex **1** consists of disconnected ion pairs $(\mathrm{Li \cdot 3DME})^+$ and $[(\eta^5\text{-}C_5H_5)_3\mathrm{Nd}\text{-}C_6H_5]^-$ and the crystal structure of **1** is composed of three crystallographically independent molecules. Figure 1 shows the molecular structure of one of them, the structures of the other two are essentially the same (see supplementary material). Each neodymium atom lies at the centre of a distorted tetrahedron formed by the centroids of the three cyclopentadienyl rings and one of the C atoms of the phenyl, and the coordination polyhedron is similar to that of complex $[(C_5H_5)_3\mathrm{U}\text{-n-}C_4H_9](\mathrm{LiC_{14}H_{28}N_2O_4})$, **2** [10].

Important bond lengths and angles are given in Tables 3 and 4. Nd–C(ring) distances range from 2.765(19) to 2.869(17) Å, and the average distances Nd1–C(ring) = 2.825 Å, Nd2–C(ring) = 2.820 Å and Nd3–C(ring) = 2.824 Å are a little longer than the distances found in other neodymocene organometallics: $(C_5H_5)_3$ Nd · THF, **3**, 2.79 Å [11], $(\mathrm{Na \cdot 6THF})(C_5H_5)_3\mathrm{Nd}(\mu\text{-H})\mathrm{Nd}(C_5H_5)_3 \cdot \mathrm{2THF}$, **4**, 2.793

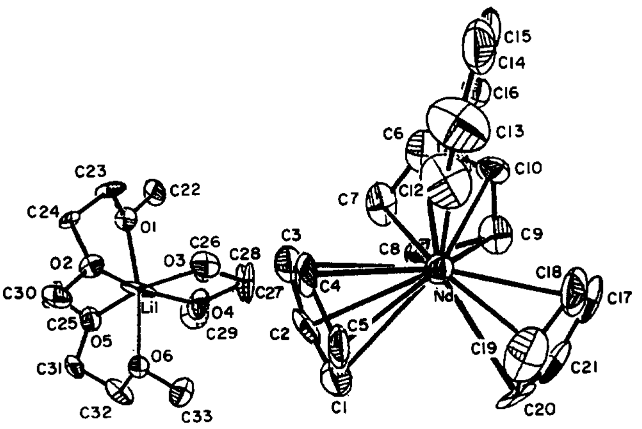

Fig. 1. The molecular structure of $(\mathrm{Li \cdot 3DME})[(C_5H_5)_3\mathrm{NdC_6H_5}]$, **1**.

Table 3

Important bond lengths (Å) (e.s.d.s of last significant figure in parentheses)

Cyclopentadienyl					
Ring 1		*Ring 2*		*Ring 3*	
Nd(1)–C(1)	2.819(16)	Nd(1)–C(6)	2.853(13)	Nd(1)–C(17)	2.829(23)
Nd(1)–C(2)	2.785(17)	Nd(1)–C(7)	2.869(17)	Nd(1)–C(18)	2.830(25)
Nd(1)–C(3)	2.804(19)	Nd(1)–C(8)	2.813(15)	Nd(1)–C(19)	2.807(22)
Nd(1)–C(4)	2.866(15)	Nd(1)–C(9)	2.825(13)	Nd(1)–C(20)	2.793(16)
Nd(1)–C(5)	2.839(13)	Nd(1)–C(10)	2.828(12)	Nd(1)–C(21)	2.814(21)
Nd(1)–C(ring) 2.829(17) (average)					
Nd(2)–C(34)	2.827(17)	Nd(2)–C(39)	2.776(24)	Nd(2)–C(50)	2.809(20)
Nd(2)–C(35)	2.818(19)	Nd(2)–C(40)	2.833(26)	Nd(2)–C(51)	2.851(20)
Nd(2)–C(36)	2.813(20)	Nd(2)–C(41)	2.847(31)	Nd(2)–C(52)	2.835(21)
Nd(2)–C(37)	2.824(19)	Nd(2)–C(42)	2.825(28)	Nd(2)–C(53)	2.837(21)
Nd(2)–C(38)	2.827(19)	Nd(2)–C(43)	2.765(19)	Nd(2)–C(54)	2.816(20)
Nd(2)–C(ring) 2.820(22) (average)					
Nd(3)–C(67)	2.814(24)	Nd(3)–C(72)	2.855(17)	Nd(3)–C(83)	2.816(20)
Nd(3)–C(68)	2.822(18)	Nd(3)–C(73)	2.783(13)	Nd(3)–C(84)	2.822(16)
Nd(3)–C(69)	2.835(21)	Nd(3)–C(74)	2.807(17)	Nd(3)–C(85)	2.853(17)
Nd(3)–C(70)	2.809(23)	Nd(3)–C(75)	2.815(18)	Nd(3)–C(86)	2.841(19)
Nd(3)–C(71)	2.844(22)	Nd(3)–C(76)	2.832(17)	Nd(3)–C(87)	2.815(17)
Nd(3)–C(ring) 2.829(18) (average)					
Nd(1)–Cent(1)	2.544(2)	Nd(1)–Cent(2)	2.564(2)		
Nd(1)–Cent(3)	2.608(2)	Nd(2)–Cent(4)	2.548(2)		
Nd(2)–Cent(5)	2.534(3)	Nd(2)–Cent(6)	2.554(2)		
Nd(3)–Cent(7)	2.557(1)	Nd(3)–Cent(8)	2.539(1)		
Nd(3)–Cent(9)	2.554(1)				
Phenyl					
Nd(1)–C(11)	2.593(17)	Nd(2)–C(44)	2.613(13)	Nd(3)–C(77)	2.601(13)
Dimethoxyethane					
Li(1)–O(1)	2.116(28)	Li(2)–O(7)	2.196(29)	Li(3)–O(13)	2.080(37)
Li(1)–O(2)	2.122(28)	Li(2)–O(8)	2.089(28)	Li(3)–O(14)	2.091(36)
Li(1)–O(3)	2.148(37)	Li(2)–O(9)	2.251(34)	Li(3)–O(15)	2.201(45)
Li(1)–O(4)	2.196(30)	Li(2)–O(10)	2.110(29)	Li(3)–O(16)	2.244(31)
Li(1)–O(5)	2.065(36)	Li(2)–O(11)	2.111(31)	Li(3)–O(17)	2.022(34)
Li(1)–O(6)	2.267(26)	Li(2)–O(12)	2.141(36)	Li(3)–O(18)	2.166(42)

Å [12]. The average metal–ring centroid (cent) distances are Nd1–cent = 2.572 Å, Nd2–cent = 2.545 Å and Nd3–cent = 2.550 Å. The angles, ring centroid 1 (cent1)–Nd–ring centroid 2 (cent2), cent2–Nd–ring centroid 3 (cent3) and cent1–Nd–cent3 are 115.5, 119.9, 116.7° (Nd1 molecule); 116.3, 115.8, 117.9° (Nd2 molecule) and 116.9, 116.9, 117.0° (Nd3 molecule), respectively, which are similar to 118.0, 114.9, 118.0° in **3** and 117, 117, 118° in **4**.

The Nd–C(phenyl) σ-bond lengths are 2.593(17) Å (Nd1 molecule), 2.613(13) Å (Nd2 molecule) and 2.601(13) Å (Nd3 molecule). The Nd–C (phenyl) distances are,

Table 4

Selected bond angles (deg) (e.s.d.s of last significant figure in parentheses)

cent1-Nd(1)-cent2	115.5	O(1)-Li(1)-O(2)	80.3(11)
cent1-Nd(1)-cent3	119.9	O(1)-Li(1)-O(3)	92.8(12)
cent2-Nd(1)-cent3	116.7	O(2)-Li(1)-O(5)	100.0(14)
C(11)-Nd(1)-cent1	101.3(8)	O(3)-Li(1)-O(4)	75.1(11)
C(11)-Nd(1)-cent2	100.9(7)	O(4)-Li(1)-O(6)	91.6(12)
C(11)-Nd(1)-cent3	96.1(10)	O(5)-Li(1)-O(6)	79.1(10)
cent4-Nd(2)-cent5	116.3	O(7)-Li(2)-O(8)	77.1(9)
cent4-Nd(2)-cent6	115.8	O(7)-Li(2)-O(12)	96.2(11)
cent5-Nd(2)-cent6	117.9	O(8)-Li(2)-O(9)	98.2(14)
C(44)-Nd(2)-cent4	101.9	O(9)-Li(2)-O(10)	76.5(10)
C(44)-Nd(2)-cent5	101.7	O(10)-Li(2)-O(11)	98.3(10)
C(44)-Nd(2)-cent6	98.2	O(11)-Li(2)-O(12)	76.6(12)
cent7-Nd(3)-cent8	116.9	O(13)-Li(3)-O(14)	77.3(15)
cent7-Nd(3)-cent9	116.9	O(13)-Li(3)-O(18)	95.2(15)
cent8-Nd(3)-cent9	117.0	O(14)-Li(3)-O(15)	93.1(16)
C(77)-Nd(3)-cent7	104.1	O(15)-LI(3)-O(17)	94.3(14)
C(77)-Nd(3)-cent8	99.2	O(16)-Li(3)-O(17)	101.3(15)
C(77)-Nd(3)-cent9	97.1	O(16)-Li(3)-O(18)	94.1(14)

to our knowledge, the third non-cyclopentadienyl terminal Nd–C distances reported. Comparison of these distances can be made with the two Nd–C(alkyl) bond lengths of 2.517(7) Å in $(C_5Me_5)_2NdCH(SiMe_3)_2$ [13] and 2.506(7) Å in $Me_2Si(C_5Me_5)_2NdCH(SiMe_3)_2$ [14]. The larger Nd–C distances in **1** might be caused by the greater steric congestion.

Complex **1** is the first cyclopentadienyl phenyl neodymate to be reported, so comparison of Nd–C(phenyl) distances 2.593(17), 2.613(13) and 2.601(13) Å can only be made with other lanthanide aryl complexes if metal size is taken into account. Two other cyclopentadienyl and substituted cyclopentadienyl aryl lanthanide complexes, $(C_5H_5)_2LuC_6H_4$-*p*-CH_3(THF) **5** [5] and $(C_5Me_5)_2SmC_6H_5$ (THF) **6** [6], have been studied by crystallography. Complexes **4** and **5** have Ln–C(phenyl) distances of 2.345(39) and 2.511(8) Å, respectively. Since Lu^{3+} and Sm^{3+} are respectively approximately 0.187 Å and 0.084 Å smaller than Nd^{3+} [15], the Lu–C(phenyl) and Sm–C(phenyl) distances are shorter than the Nd–C(phenyl) distances in **1**. This may be due both to the greater steric congestion caused by the three cyclopentadienyls and to electronic reasons. Here **1** is an anionic complex while **5** and **6** are neutral.

The cation consists of one lithium atom and three DME molecules. Each lithium atom is coordinated by six oxygen atoms offered from three DME molecules forming a six-coordinated octahedron structure with average Li–O = 2.152 (Nd1 molecule), 2.150 (Nd2 molecule) and 2.134 (Nd3 molecule) Å.

Supplementary material available. Tables of thermal parameters, bond distances and angles, and observed and calculated structure factors (43 pages), are obtainable from the authors.

Acknowledgment

The authors thank the Chinese National Foundation of Natural Science for financial support.

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