Tris(4-methylbenzyl)(1,4,7-trimethyl-1,4,7-triazacyclononane)lanthanum(III)

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Received 17 October 2007; accepted 26 October 2007

Key indicators: single-crystal X-ray study; T = 100 K; mean |C27–C27| = 0.012 Å; R factor = 0.048; wR factor = 0.109; data-to-parameter ratio = 18.4.

The title compound, [La(C8H9)3(C9H21N3)], incorporating a fac-κ3N ligand and formed by reaction of La(CH2C6H4-4-Me)3(THF)3 (THF is tetrahydrofuran) and 1,4,7-trimethyl-1,4,7-triazacyclononane (Me3-TACN), was synthesized in THF solution. In the crystal structure, the La atom is seven-coordinated by three N atoms from a TACN ligand and four C atoms from three benzyl ligands, one of which is bound in a cis-fashion.

Related literature

For related literature, see: Hitchcock et al. (1988); Harder (2005); Bambirra et al. (2006)

Experimental

Crystal data

[La(C8H9)3(C9H21N3)]

M_r = 625.67

Orthorhombic, Pna2_1

a = 16.094 (2) Å

b = 13.472 (1) Å

c = 14.488 (1) Å

V = 3141.3 (5) Å³

Z = 4

Mo Kα radiation

µ = 1.38 mm⁻¹

T = 100 (1) K

0.22 × 0.15 × 0.06 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer

Absorption correction: multi-scan (SADABS; Bruker, 2006)

T_min = 0.758, T_max = 0.920

23512 measured reflections

6249 independent reflections

4265 reflections with I > 2σ(I)

R(int) = 0.093

Refinement

R[F² > 2σ(F²)] = 0.048

wR(F²) = 0.109

S = 0.97

6249 reflections

340 parameters

1 restraint

H-atom parameters constrained

Δρ_max = 1.47 e Å⁻³

Δρ_min = −0.60 e Å⁻³

Absolute structure: Flack (1983), 3077 Friedel pairs

Flack parameter: 0.05 (2)

Table 1

Selected geometric parameters (Å, °).

La—N1 2.717 (7)

La—N2 2.806 (7)

La—N3 2.761 (6)

La—C10 2.641 (7)

La—C11 2.959 (7)

La—C12 3.111 (7)

La—C18 2.605 (9)

La—C19 3.165 (7)

La—C26 2.662 (7)

La—C27 3.744 (7)

N1—La—N2 63.4 (2)

N1—La—N3 64.94 (19)

N2—La—N3 63.6 (2)

C10—La—C18 105.1 (2)

C10—La—C26 115.9 (2)

C18—La—C26 117.6 (3)

La—C10—C11 87.9 (4)

La—C18—C19 98.8 (5)

La—C26—C27 127.7 (5)

Data collection: SMART (Bruker, 2006); cell refinement: SAINT-Plus (Bruker, 2006); data reduction: SAINT-Plus; program(s) used to solve structure: DIRDIF99 (Beurskens et al., 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: PLATON (Spek, 2003).

This project was supported by NRSC-C.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BV2078).

References


supplementary materials
Tris(4-methylbenzyl)(1,4,7-trimethyl-1,4,7-triazacyclononane)lanthanum(III)

S. Bambirra, A. Meetsma and B. Bart Hessen

Comment

Homoleptic trialkyl complexes of the type $M(CH_2SiMe_3)_3(THF)_n$ ($n = 2, 3$) of the group 3 metals and lanthanides are valuable starting materials for organo-rare-earth-metal chemistry. These, however, are only available for the small to medium sized metals ($M = Sc—Sm$). For the larger metals such as neodymium and lanthanum they can not be isolated. Nevertheless, trialkyl complexes of lanthanum have been reported. Examples are La[$CH(SiMe_3)_2]$ with relatively large alkyls and La($CH_2C_6H_4$-2-NMe$_2$)$_3$ with an internal Lewis base. Recently we have described the synthesis, structures and reactivity studies of La($CH_2C_6H_4$-4-$R$)$_3$($THF)_3$ ($R = H, Me$). Here we report the molecular structure of (Me$_3$—TACN)La($CH_2C_6H_4$-4-Me)$_3$($THF)_3$ (I) that has been generated by addition of Me$_3$—TACN to a solution of La($CH_2C_6H_4$-4-Me)$_3$($THF)_3$ in THF. Compound I could be isolated as yellow-orange crystals that are thermally much more stable than its precursor. The asymmetric unit of I contains one formula unit of the title compound shown in Figure 1. As expected the TACN ligand is facially coordinated to the metal center as opposed to the structure of La($CH_2C_6H_4$-2-NMe$_2$)$_3$ (Harder, 2005) where the coordination of one of the aminobenzyl ligands is "upside-down". It appears that the fac-$\kappa^3$ coordination of the TACN ligand increases steric congestion around the metal center compared to La($CH_2C_6H_4$-4-Me)$_3$($THF)_3$. This is evidenced by the bonding mode of the benzyl ligands, of which two are clearly $\eta^1$ bound to La and one that is bound in a $\eta^2$-fashion. The former have rather large La—C—C bond angles of 98.8 (5)$^\circ$ and 127.7 (5)$^\circ$, while the latter has a acute angle of 87.9 (4)$^\circ$.

Experimental

All preparations were performed under an inert nitrogen atmosphere, using standard Schlenk and glovebox techniques. Solid La($CH_2Ph$-4-Me)$_3$($THF)_3$ (134.0 mg, 200.0 µmol) was reacted with a solution of [Me$_3$—TACN] (34.0 mg, 200 µmol) in THF (2 ml). The formed red solution was left to stand over night at $-30$ °C, after which time yellow-orange crystals of the title compound deposit (90 mg, 72%)·$\text{H NMR}$ (500 MHz, THF-$d_8$, 20°C): $\delta$ 6.66 (t, $^3J_{HH} = 8.1$ Hz, 6 H, o-Ar), 6.14 (d, $^3J_{HH} = 8.1$ Hz, 6 H, o-Ar), 2.70 (m, 6 H, NCH$_2$), 2.60 (m, 6 H, NCH$_2$), 2.37 (s, 9 H, NMe), 2.10 (s, 9 H, Me), 1.29 (s, 6 H, LaCH$_2$), $^{13}$C $\text{NMR}$ (125.7 MHz, THF-$d_8$, 20°C): $\delta$ 150.7 (Ar C$_{ipso}$), 131.8 (d, $^1J_{CH} = 153.3$ Hz, Ar CH), 125.9 (Ar CMe), 123.6 (d, $^1J_{CH} = 152.0$ Hz, Ar CH), 68.7 (t, $^1J_{CH} = 125.0$ Hz, LaCH$_2$), 56.6 (t, $^1J_{CH} = 134.8$ Hz, NCH$_2$), 48.2 (q, $^1J_{CH} = 134.8$ Hz, NMe), 21.8 (q, $^1J_{CH} = 125.2$ Hz, ArMe). Anal. Calcd for C$_{33}$H$_{48}$N$_3$La: C 63.35; H 7.73; N 6.72. Found: C, 63.20; H, 7.68; N, 6.45.

Refinement

The structure was solved by Patterson methods and extension of the model was accomplished by direct methods applied to difference structure factors using the program DIRDIF. The positional and anisotropic displacement parameters for the
non-hydrogen atoms were refined. The hydrogen atoms were generated by geometrical considerations, constrained to idealized geometries, and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. The methyl-groups were refined as rigid groups, which were allowed to rotate freely.

Figures

![Fig. 1. Perspective ORTEP drawing of I. Displacement ellipsoids for non-H are represented at the 50% probability level. The H-atoms have been omitted to improve clarity.](image)

tris(4-methylbenzyl)(1,4,7-trimethyl-1,4,7-triazacyclononane)lanthanum(III)

Crystal data

$$[\text{La}((\text{C}_8\text{H}_{10})_3\text{C}_9\text{H}_{21}\text{N}_3)]$$


$$M_r = 625.67$$

$$D_x = 1.323 \text{ Mg m}^{-3}$$

Orthorhombic, $Pna_2_1$

Hall symbol: P 2c -2n

Cell parameters from 5692 reflections

$$a = 16.094 (2) \text{ Å}$$

$$b = 13.472 (1) \text{ Å}$$

$$c = 14.488 (1) \text{ Å}$$

$$\theta = 2.4–27.2^\circ$$

$$\lambda = 0.71073 \text{ Å}$$

$$\mu = 1.38 \text{ mm}^{-1}$$

$$T = 100 (1) \text{ K}$$

$$V = 3141.3 (5) \text{ Å}^3$$

Platelet, orange

$$Z = 4$$

$$F_{000} = 1296$$

$$F_{\text{int}} = 0.093$$

Data collection

Bruker SMART APEX CCD area-detector diffractometer

$$6249 \text{ independent reflections}$$

Radiation source: fine focus sealed Siemens Mo tube

$$4265 \text{ reflections with } I > 2\sigma(I)$$

Monochromator: parallel mounted graphite
Detector resolution: 66.06 pixels mm\(^{-1}\)  
\(T = 100(1)\) K  
\(\theta_{\text{max}} = 26.4^\circ\)  
\(\theta_{\text{min}} = 2.5^\circ\)  
Absorption correction: multi-scan  
(SADABS; Bruker, 2006)  
\(h = -20\rightarrow20\)  
\(k = -16\rightarrow16\)  
\(l = -18\rightarrow17\)  
23512 measured reflections

Reifnement  
Hydrogen site location: inferred from neighbouring sites  
Least-squares matrix: full  
H-atom parameters constrained  

\[ \frac{\sum w(\sigma(F_2)^2)}{\sum w(\sigma(F_2)^2)} = 0.048 \]  
\[ wR(F^2) = 0.109 \]  
\[ S = 0.97 \]  
6249 reflections  
340 parameters  
1 restraint  
Primary atom site location: heavy-atom method  
Secondary atom site location: structure-invariant direct methods  

Special details  
Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of \(F^2\) against ALL reflections. The weighted \(R\)-factor \(wR\) and goodness of fit \(S\) are based on \(F^2\), conventional \(R\)-factors \(R\) are based on \(F\), with \(F\) set to zero for negative \(F^2\). The threshold expression of \(F^2 > 2\sigma(F^2)\) is used only for calculating \(R\)-factors(gt) etc. and is not relevant to the choice of reflections for refinement. \(R\)-factors based on \(F^2\) are statistically about twice as large as those based on \(F\), and \(R\)- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\(\text{Å}^2\))

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<th>(y)</th>
<th>(z)</th>
<th>(U_{iso}^{*}/U_{eq})</th>
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Geometric parameters (Å, °)

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<td>H5···H18&lt;sup&gt;i&lt;/sup&gt;</td>
<td>2.3400</td>
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<td>C10···C12</td>
<td>2.486 (9)</td>
<td>H5···C26&lt;sup&gt;iii&lt;/sup&gt;</td>
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<td>C10···C4</td>
<td>3.497 (10)</td>
<td>H5···C27&lt;sup&gt;iii&lt;/sup&gt;</td>
<td>2.9200</td>
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<td>C10···C16</td>
<td>2.531 (10)</td>
<td>H5···H26&lt;sup&gt;iii&lt;/sup&gt;</td>
<td>2.4200</td>
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<td>C11···C3&lt;sup&gt;iv&lt;/sup&gt;</td>
<td>3.575 (9)</td>
<td>H5···H3</td>
<td>2.3900</td>
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<td>C12···C24</td>
<td>3.561 (10)</td>
<td>H5···H4&lt;sup&gt;ii&lt;/sup&gt;</td>
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<td>C12···C3&lt;sup&gt;iv&lt;/sup&gt;</td>
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<td>H6···C3</td>
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<td>C16···C9&lt;sup&gt;iv&lt;/sup&gt;</td>
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<td>2.6200</td>
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supplementary materials

C17···C4\textsuperscript{v}
\quad 3.383 (12)  
\quad H6···H3  
\quad 2.0500

C18···C5  
\quad 3.437 (11)  
\quad H6···H8\textsuperscript{i}  
\quad 2.3800

C24···C32  
\quad 3.565 (11)  
\quad H6···H9  
\quad 2.1200

C24···C12  
\quad 3.561 (10)  
\quad H6···C10\textsuperscript{i}  
\quad 3.0700

C26···C1  
\quad 3.600 (10)  
\quad H6···H10\textsuperscript{i}  
\quad 2.3400

C26···C8  
\quad 3.585 (10)  
\quad H6'···H7'  
\quad 2.3600

C27···C5\textsuperscript{vi}  
\quad 3.523 (11)  
\quad H6'···H7''  
\quad 2.3200

C32···C24  
\quad 3.565 (11)  
\quad H7···C27  
\quad 3.0600

C1···H18\textsuperscript{vi}  
\quad 2.8300  
\quad H7···C28  
\quad 2.7200

C1···H7\textsuperscript{vii}  
\quad 3.0800  
\quad H7···H8  
\quad 2.3300

C2···H33\textsuperscript{vii}  
\quad 2.9400  
\quad H7'···C18  
\quad 3.0300

C3···H6  
\quad 2.7600  
\quad H7'···H6'  
\quad 2.3600

C4···H17\textsuperscript{vii}  
\quad 2.9400  
\quad H7'···H18  
\quad 2.2700

C4···H18'  
\quad 3.0300  
\quad H7'···C1\textsuperscript{iii}  
\quad 3.0800

C6···H3  
\quad 2.5700  
\quad H7'···H1\textsuperscript{iii}  
\quad 2.4300

C6···H9  
\quad 2.7900  
\quad H7''···H6'  
\quad 2.3200

C7···H18  
\quad 3.0300  
\quad H7''···H8'  
\quad 2.3800

C8···H26\textsuperscript{v}  
\quad 3.0400  
\quad H8···C26  
\quad 2.8400

C9···H6  
\quad 2.6200  
\quad H8···H7  
\quad 2.3300

C9···H3  
\quad 2.7000  
\quad H8···H26'  
\quad 2.1900

C10···H4\textsuperscript{vii}  
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\quad H8···H6  
\quad 2.3800

C10···H2  
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\quad H8···H7''  
\quad 2.3800

C10···H3\textsuperscript{v}  
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\quad H9···C3  
\quad 2.5600

C10···H9\textsuperscript{v}  
\quad 2.9700  
\quad H9···C6  
\quad 2.7900

C10···H6\textsuperscript{v}  
\quad 3.0700  
\quad H9···H2'  
\quad 2.4200

C11···H10\textsuperscript{v}  
\quad 2.0500  
\quad H9···H3  
\quad 2.0200

C11···H10  
\quad 2.0500  
\quad H9···H6  
\quad 2.1200

C11···H9\textsuperscript{v}  
\quad 2.7200  
\quad H9···C10\textsuperscript{i}  
\quad 2.9700

C11···H3\textsuperscript{v}  
\quad 2.8100  
\quad H9···C11\textsuperscript{i}  
\quad 2.7200

C12···H3\textsuperscript{v}  
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\quad H9···C16\textsuperscript{i}  
\quad 2.3900

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C12···H3\textsuperscript{v}  
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\quad H9'···H1''  
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C13···H26  
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\quad H9'···C19\textsuperscript{vi}  
\quad 2.8400

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\quad H10···H3\textsuperscript{iv}  
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\quad 3.0000  
\quad H10···H6\textsuperscript{iv}  
\quad 2.3400

C14···H26  
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\quad H10'···H2  
\quad 2.3000

C16···H1\textsuperscript{v}  
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\quad H10'···H16  
\quad 2.4800

C16···H9\textsuperscript{v}  
\quad 2.8900  
\quad H12···C19  
\quad 2.8000

C17···H4\textsuperscript{v}  
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\quad H12···C20  
\quad 2.8600

C18··H26\textsuperscript{iii}  
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\quad H12···C21  
\quad 2.9600

C18···H1\textsuperscript{iii}  
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C30···H21\textsuperscript{v} 3.0600 H18'···H20 2.4100
C32···H24 2.9400 H20···H18' 2.4100
C33···H2\textsuperscript{iiii} 3.0900 H21···H25\textsuperscript{v} 2.5400
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H2···H10\textsuperscript{a} 2.3000 H26'···H28 2.3800
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N3—C6—C5 113.3 (6) C13—C12—H12 119.00
supplementary materials

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C22—C23—C24 121.6 (8)  C22—C25—H25 109.00
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La—C26—C27 127.7 (5)  C22—C25—H25"" 109.00
C26—C27—C28 122.4 (6)  H25—C25—H25" 109.00
C26—C27—C32 122.9 (6)  H25—C25—H25"" 109.00
C28—C27—C32 114.6 (6)  H25—C25—H25""" 110.00
C27—C28—C29 122.3 (7)  La—C26—H26 105.00
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C29—C30—C31 117.1 (8)  C27—C26—H26 105.00
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<tr>
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<td>C7—N3—C6—C5</td>
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<tr>
<td>C11—La—N2—C3</td>
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<td>C6—N3—C8—C9</td>
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<td>N2—C5—C6—N3</td>
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<td>N3—C8—C9—N1</td>
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<td>La—C18—C19—C24</td>
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C26—La—N3—C6  173.2 (5)  C18—C19—C20—C21  176.7 (8)
C26—La—N3—C7  −64.5 (4)  C24—C19—C20—C21  0.2 (12)
C26—La—N3—C8  50.9 (5)  C18—C19—C24—C23  −176.1 (8)
N1—La—C10—C11  104.1 (4)  C20—C19—C24—C23  0.5 (11)
N2—La—C10—C11  167.4 (4)  C24—C19—C20—C21  −0.8 (14)
N3—La—C10—C11  143.6 (4)  C20—C21—C22—C23  0.7 (14)
C18—La—C10—C11  −113.8 (4)  C20—C21—C22—C25  −179.2 (9)
C26—La—C10—C11  17.8 (5)  C21—C22—C23—C24  0.0 (13)
N1—La—C11—C10  −77.4 (4)  C25—C22—C23—C24  179.9 (9)
N1—La—C11—C12  152.4 (4)  C22—C23—C24—C19  −0.6 (13)
N1—La—C11—C16  37.9 (6)  La—C26—C27—C28  −96.6 (8)
N2—La—C11—C10  −13.7 (5)  La—C26—C27—C32  81.4 (8)
N2—La—C11—C12  −143.9 (4)  C26—C27—C28—C29  176.9 (7)
N2—La—C11—C16  101.6 (6)  C32—C27—C28—C29  −1.2 (11)
C10—La—C11—C12  −130.2 (6)  C26—C27—C32—C31  −177.5 (7)
C10—La—C11—C16  115.3 (8)  C28—C27—C32—C31  0.6 (11)
C18—La—C11—C10  76.4 (5)  C27—C28—C29—C30  1.1 (12)
C18—La—C11—C12  −53.8 (5)  C28—C29—C30—C31  −0.3 (12)
C18—La—C11—C16  −168.4 (6)  C28—C29—C30—C33  178.6 (8)
C26—La—C11—C10  −164.0 (4)  C29—C30—C31—C32  −0.3 (12)
C26—La—C11—C12  65.8 (4)  C33—C30—C31—C32  −179.3 (8)
C26—La—C11—C16  −48.8 (6)  C30—C31—C32—C27  0.2 (12)
N1—La—C18—C19  172.5 (4)

Symmetry codes: (i) x+1/2, −y+3/2, z; (ii) −x+1/2, y+1/2, z+1/2; (iii) −x+1, −y+1, z+1/2; (iv) x−1/2, −y+3/2, z; (v) −x+1/2, y−1/2, z−1/2; (vi) −x+1, −y+1, z−1/2; (vii) x, y+1, z; (viii) x, y−1, z; (ix) −x+1/2, y+1/2, z−1/2; (x) −x+1/2, y−1/2, z+1/2.