METAL-ORGANIC COMPOUNDS

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Tris(*tert*-butylcyclopentadienyl)praseodymium-μ-bromo-tris(tetrahydrofuran)lithium†

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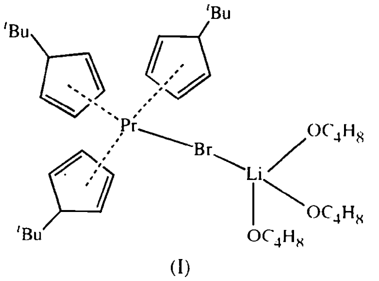
Abstract

The title complex $[\{Li(C_4H_8O)_3\}Br\{Pr(C_9H_{13})_3\}]$ has a distorted pseudo-tetrahedral geometry around the ten-coordinate Pr atom. The $(^tBuCp)_3Pr$ unit and $Li(thf)_3^+$ cation (where thf is tetrahydrofuran) are connected by a μ-Br atom. The Pr—Br and Li—Br distances are 2.995 (1) and 2.495 (15) Å, respectively, and the Pr—Br—Li angle is 137.3 (3)°.

Comment

Anionic complexes containing a $(C_5H_5)_3Ln$ unit, such as $[(C_5H_5)_3PrC_4H_9]^-$ (Jahn *et al.*, 1984), $[(C_5H_5)_3Nd\text{-}C_6H_5]^-$ (Gao *et al.*, 1992) and $[(C_5H_5)_3Ln(C_5H_5)]^-$ (Ln = La, Ce, Pr, Nd) (Jacob *et al.*, 1989), have been reported. Recently, we described the syntheses and molecular structures of $[(^tBuCp)_3Nd(\mu\text{-}Br)Li(thf)_3]$ (Song *et al.*, 1992) and $[(^tBuCp)_3Ln(\mu\text{-}Cl)Li(thf)_3]$, with Ln = Nd (Guan *et al.*, 1994) and La (Ren *et al.*, 1994). We now report the structure of the analogous complex $[(^tBuCp)_3Pr(\mu\text{-}Br)Li(thf)_3]$, (I), which was isolated from the reaction between equimolar amounts of $(^tBuCp)_2PrCl$ and LiPh in a solution of LiBr in THF–Et_2O. It was supposed that disproportionation occurred during the metathesis reaction.



(I)

The crystal structure determination confirms that the title complex, (I), is a heteronuclear bimetal complex, similar to those of analogous formula quoted above (Fig. 1). The central metal Pr^{3+} ion is coordinated by three ^tBuCp groups in a η^5 manner and by one Br^- ion to give a coordination number of 10. The Li^+ ion is coordinated by three O atoms from three thf molecules and one Br^- anion. The coordination polyhedra of the Pr^{3+} and Li^+ ions both have distorted pseudo-tetrahedral geometries.

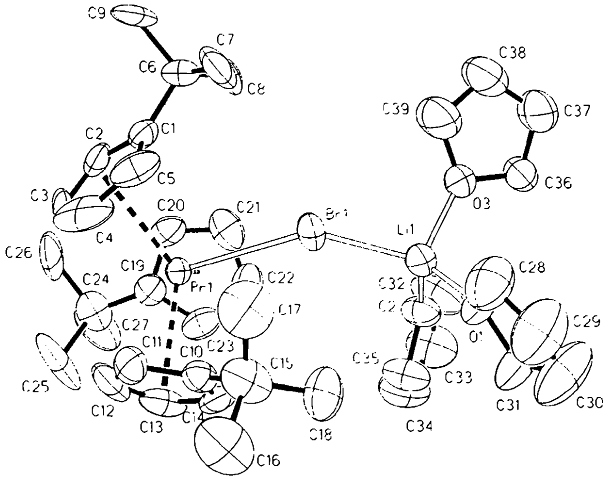


Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and disorder has not been represented.

The Pr—Br [2.995(1) Å] and Li—Br [2.495 (15) Å] distances, and the bond angle Pr—Br—Li [137.3 (3)°] in the title complex are similar to those of Nd—Br [2.978 (2) Å], Li—Br [2.502 (3) Å] and Nd—Br—Li [136.4 (6)°], respectively, found in $[(^tBuCp)_3Nd(\mu\text{-}Br)Li(thf)_3]$ (Song *et al.*, 1992). The average Pr—C distance is 2.8 (2) Å. In Table 1, Cp denotes the centroid of a cyclopentadienyl ring.

The methyl groups C7–C9 and C25–C27, atoms C36–C39 of one tetrahydrofuran ligand and atoms C3 and C4 of a cyclopentadienyl ring were found to be disordered.

Experimental

The title complex was isolated from the reaction between equimolar amounts of $(^tBuCp)_2PrCl$ and LiPh in a solution of LiBr in THF–Et_2O, followed by crystallization from a toluene solution at 243 K. The compound is very sensitive to air and moisture. Consequently, all manipulations were carried out under argon using Schlenk techniques. A suitable crystal was

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† Alternative name: μ-bromo-tris[2,2,2(η^5)-*tert*-butylcyclopentadienyl]tris(tetrahydrofuran-1κ*O*)lithiumpraseodymium.

sealed in a thin-walled glass capillary for the crystal structure determination.

Crystal data

[LiPrBr(C$_9$H$_{13}$)$_3$(C$_4$H$_8$O)$_3$]
M_r = 807.68
Triclinic
$P\bar{1}$
a = 11.905 (4) Å
b = 12.337 (3) Å
c = 14.218 (4) Å
α = 88.17 (2)°
β = 80.50 (3)°
γ = 84.52 (2)°
V = 2049.9 (3) Å^3
Z = 2
D_x = 1.308 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 20 reflections
θ = 18.52–21.67°
μ = 2.194 mm^{-1}
T = 293 (2) K
Prismatic
0.30 × 0.20 × 0.20 mm
Yellow

Data collection

Rigaku AFC-7R diffractometer
ω–2θ scans
Absorption correction: empirical ΔF (Walker & Stuart, 1983)
$T_{\min}$ = 0.569, $T_{\max}$ = 0.645
4993 measured reflections
4717 independent reflections

3252 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.027
$\theta_{\max}$ = 21.5°
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 0$
$l = -14 \rightarrow 14$
3 standard reflections every 200 reflections intensity decay: 1.73%

Refinement

Refinement on F^2
$R(F)$ = 0.039
$wR(F^2)$ = 0.086
S = 1.067
4706 reflections
496 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 4.6185P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.009
$\Delta\rho_{\max}$ = 0.603 e Å^{-3}
$\Delta\rho_{\min}$ = −0.388 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Pr1—Br1	2.995 (1)	Br1—Li1	2.495 (15)
Pr1—Cp1	2.602 (7)	Li1—O2	1.918 (13)
Pr1—Cp2	2.585 (8)	Li1—O3	1.924 (13)
Pr1—Cp3	2.589 (7)	Li1—O1	1.929 (14)
Br1—Pr1—Cp1	102.4 (3)	Cp1—Pr1—Cp3	117.5 (3)
Br1—Pr1—Cp2	102.1 (4)	Cp2—Pr1—Cp3	116.9 (4)
Br1—Pr1—Cp3	97.8 (4)	Li1—Br1—Pr1	137.3 (3)
Cp1—Pr1—Cp2	115.3 (3)		

The structure was solved by the heavy-atom Patterson method and refined by least-squares calculations. H atoms were included but not refined. The quality of the crystals and disorder prevented collection of intensity data to greater than θ = 21.5°.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992*a*). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1291). Services for accessing these data are described at the back of the journal.

References

Gao, H., Shen, Q., Hu, J., Jin, S. & Lin, Y. (1992). *J. Organomet. Chem.* **427**, 141–149.
Guan, J., Shen, Q., Jin, S. & Lin, Y. (1994). *Acta Cryst.* C**50**, 891–893.
Jacob, K., Glanz, M., Tittes, K., Thiele, K. H., Pavlik, I. & Lycka, A. Z. (1989). *Z. Anorg. Allg. Chem.* **577**, 145–154.
Jahn, W., Yunlu, K., Oroschin, W., Amberger, H. D. & Fischer, R. D. (1984). *Inorg. Chim. Acta*, **95**, 84–104.
Molecular Structure Corporation (1992*a*). *MSC/AFC Diffractometer Control Software*. Version 4.3.0. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Molecular Structure Corporation (1992*b*). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Ren, J., Guan, J., Jin, S. & Shen, Q. (1994). *Polyhedron*, **13**, 2979–2982.
Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990*b*). *SHELXTL/PC Users Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
Song, S., Shen, Q. & Jin, S. (1992). *Polyhedron*, **11**, 2863–2865.
Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158–166.

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Chloro(1,4,8,12-tetraazacyclopentadecane-κ^4N)zinc(II) Perchlorate

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Abstract

The Zn$^{\rm II}$ ion in [ZnCl(C$_{11}$H$_{26}$N$_4$)]ClO$_4$ has a distorted trigonal-bipyramidal geometry, with the tetradentate macrocyclic ligand and the Cl$^-$ ion constituting the