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A Holmium(III) 'Carbons Adjacent' Carborane Cluster, $[Li(C_6H_{16}N_2)_2][Li_2(C_6H_{16}N_2)_2\{HoCl_2(C_8H_{22}B_4Si_2)_2\}].0.5C_6H_6$

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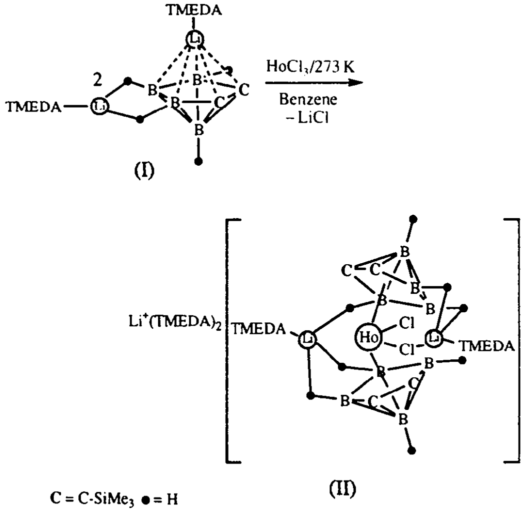
Abstract

The title compound, bis(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)lithium μ-{1,1'-*commo*-1,1'-dichlorobis[2,3-bis(trimethylsilyl)-2,3-dicarba-1-holma-*closo*-heptaborato]}-$1\kappa^3H^{4',5',6}$:$2\kappa^2H^{4,5}$,$2\kappa Cl$-bis[(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine)lithium] benzene hemisolvate, $[Li(TMEDA)_2][\{1\text{-}Cl\text{-}1\text{-}(\mu\text{-}Cl)\text{-}2,2',3,3'\text{-}(SiMe_3)_4\text{-}5,6\text{-}[(\mu\text{-}H)_2Li(TMEDA)]\text{-}4,4',5'\text{-}[(\mu\text{-}H)_3Li(TMEDA)]\}\text{-}1,1'\text{-}commo\text{-}Ho(2,3\text{-}C_2B_4H_4)_2].0.5C_6H_6$ (TMEDA = tetramethylethylenediamine), crystallized in a monoclinic space group, $P2_1/n$. The structure of this cluster consists of an Ho^{III} 'carbons adjacent' carborane bent-sandwich complex in which two Cl^- ions are present, in different bonding environments, in the primary coordination sphere of the Ho atom, giving a very distorted tetrahedral arrangement about the metal with the Ho—Cnt(1,2) = 2.378, 2.350 Å, Cnt(1)—Ho—Cnt(2) = 128.5°, Cnt(1)—Ho—Cl(1,2) = 107.9, 103.2°, Cnt(2)—Ho—Cl(1,2) = 110.6, 104.4°, and Cl(1)—Ho—Cl(2) = 97.17 (6)° (Cnt = C_2B_3 centroid). One of the *exo*-polyhedral Li(TMEDA) units is linked to both opposing C_2B_3 faces *via* three $B—H_{(terminal)}$ bonds and the other interacts with only one of the C_2B_3 faces *via* two $B—H_{(terminal)}$ groups with an additional linkage to the central Ho atom *via* an Ho—Cl—Li bridge.

Comment

It has been established that the reactivity of the dianionic $C_2B_4^{-}$ carborane ligands toward the lanthanide trihalides in anhydrous thf solvent results in the formation of unusual trinuclear lanthanacarborane clusters, in which an O atom triply bridges the three Ln atoms and a methoxy moiety binds to the apical Li atoms of the three *closo*-lithiacarboranes (Oki, Zhang & Hosmane, 1992; Zhang, Oki, Wang, Maguire & Hosmane, 1995; Hosmane *et al.*, 1994). Since all of the lanthanacarborane clusters are isostructural and their yields are reproduced even when the solvent, thf, was freshly distilled and extremely dehydrated, it is believed that a systematic reactivity pattern exists in this system. Nevertheless, it was speculated that the methoxide and O^{2-} ions might be the decomposition products of a side-reaction between the solvent and the reactant species. This speculation is not entirely inconceivable when one considers the high reactivity and great oxophilicity of the lanthanide compounds in general (Evans, 1985). In order to verify whether thf is the actual source for both the O^{2-} and the OMe^- units, we carried out a reaction between $HoCl_3$ and the TMEDA-solvated dilithiacarborane (I) (Hosmane, Saxena *et al.*, 1993) in a 1:2 ratio in an exclusively non-oxygen-containing solvent, benzene, at 273 K. We obtained the title compound, (II), as an air-sensitive orange crystalline solid in over 90% yield (Hosmane *et al.*, unpublished results).



(I)

(II)

The exclusive formation of (II) from (I) clearly indicates that the formation of the trinuclear Ho^{III} cluster is not possible in the absence of thf in the solvent mixture. Therefore, it is most likely that the thf is the source of both the O^{2-} and the OMe^- anions which, subsequently, induces the formation of trinuclear Ln^{III} carborane clusters.

Determination of the molecular structure (Fig. 1) revealed that (II) is a novel mononuclear holmacarborane bent-sandwich complex in which the Ho metal is η^5-bonded to each of the C_2B_3 faces with Ho—Cnt (Cnt = centroid) distances of 2.378 (3) and 2.350 (3) Å, which are slightly longer than those of a dinuclear 'carbons apart' holmacarborane sandwich (Zhang, Wang, Maguire & Hosmane, 1996) but are comparable to the Ho—Cp centroid distances of 2.366 Å in $Me_2Ge(C_5Me_4)_2HoCH(SiMe_3)_2$ (Schumann *et al.*, 1991) and are within the range of Ln—C_2B_3(Cnt) distances of 2.358 (3)–2.399 (3) Å in the half-sandwich (*closo*) trinuclear Gd^{III}– and Tb^{III}–C_2B_4 carborane clusters (Oki, Zhang & Hosmane, 1992; Zhang, Oki, Wang, Maguire & Hosmane, 1995), the bent-sandwich erbacarborane monomer and the mixed 2,3-C_2B_4– and 2,4-C_2B_4–Er^{III} carborane bent-sandwich dimer (Hosmane *et al.*, 1995). The linkages of the B—$H_{(terminal)}$ groups of the C_2B_3 bonding faces to two *exo*-polyhedral Li(TMEDA) units falls in the range from 2.34 (2) [B(24)···Li(1)] to 2.62 (2) Å [B(14)···Li(2)], which is almost identical to that found in the analogous Er^{III} carborane complexes (Hosmane *et al.*, 1995). The distorted tetrahedral geometry about the Ho atom [Ho—Cnt(1,2) = 2.378, 2.350 Å, Cnt(1)—Ho—Cnt(2) = 128.5°, Cnt(1)—Ho—Cl(1,2) = 107.9, 103.2°, Cnt(2)—Ho—Cl(1,2) = 110.6, 104.4°, and Cl(1)—Ho—Cl(2) = 97.17 (6)°] is essentially the same as that in the analogous mononuclear erbacarborane complex (Hosmane *et al.*, 1995) and in the dinuclear Ho^{III} 'carbons apart' carborane cluster (Zhang, Wang, Maguire & Hosmane, 1995), and similar to those of the d^0 Group 4 metallocene, lanthanocene and actinocene derivatives (Rogers & Rogers, 1991; Evans, 1985, 1987; Wilkinson, Stone & Abel, 1982; Wilkinson, Gillard & McCleverty, 1987; Cotton & Wilkinson, 1988) as well as their carborane analogues (Hosmane & Maguire, 1993; Saxena & Hosmane, 1993).

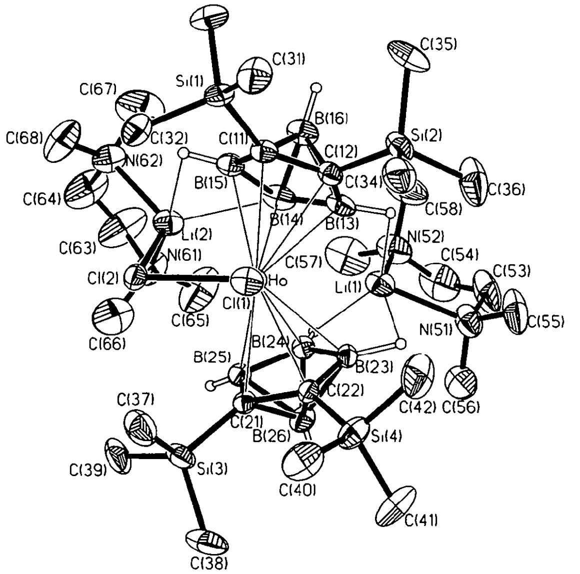


Fig. 1. Displacement ellipsoid (*SHELXTL-Plus*; Sheldrick, 1990) drawing of the title compound plotted at the 40% probability level. H atoms, except for those of the C_2B_4-cage atoms, and the *exo*-polyhedral $Li(TMEDA)_2$ unit are omitted for clarity.

This work, together with our recent results on the analogous Er^{III} carborane complex and the Ho^{III} 'carbons apart' carborane sandwich complex, indicates that the reactivity of the lanthanide reagents with the carborane ligand systems is dependent upon the solvents in which the reactions are being carried out. Consequently, the trinuclear half-sandwich lanthanacarborane clusters are produced in thf or in the solvent mixture containing thf, while the mononuclear bent-sandwich lanthanacarborane is the only product of the reaction in thf-free solvent. Thus, the significant role of the solvents in the organometallics of the lanthanides has been demonstrated.

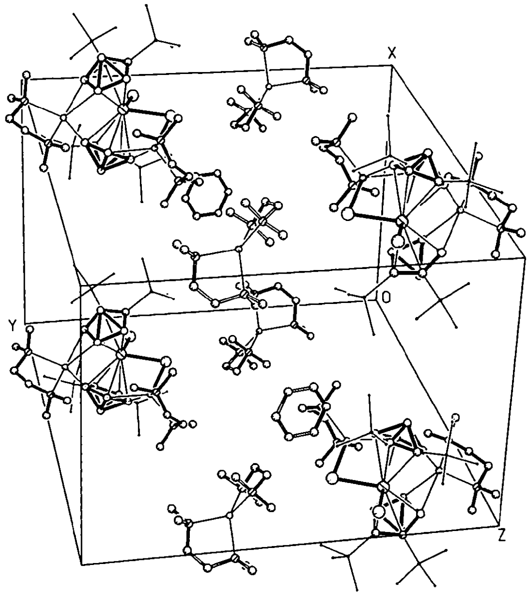


Fig. 2. Packing diagram of (II) showing both the cationic and the anionic units along with the co-crystallized benzene molecule in the unit cell.

Experimental

Compound (II) was prepared (see *Comment*) and recrystallized from anhydrous TMEDA.

Crystal data

$[Li(C_6H_{16}N_2)_2][Li_2(C_6H_{16}N_2)_2\{HoCl_2(C_8H_{22}B_4Si_2)_2\}].0.5C_6H_6$
M_r = 1195.89

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 24 reflections

Monoclinic
*P*2₁/*n*
$a = 14.708(2)$ Å
$b = 21.098(4)$ Å
$c = 23.127(3)$ Å
$\beta = 93.29(1)°$
$V = 7165(2)$ Å^3
$Z = 4$
$D_x = 1.109$ Mg m^{-3}

$\theta = 11–15°$
$\mu = 1.277$ mm^{-1}
$T = 230(2)$ K
Plates
0.30 × 0.15 × 0.05 mm
Pale yellow

Data collection

*R*3*m*/*V* diffractometer
$\omega/2\theta$ scans
Absorption correction:
  ψ scan (*SHELXTL-Plus*; Sheldrick, 1990)
  $T_{\min} = 0.796$, $T_{\max} = 0.935$
10428 measured reflections
9977 independent reflections
6428 observed reflections
  $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0329$
$\theta_{\max} = 23°$
$h = 0 \rightarrow 16$
$k = 0 \rightarrow 23$
$l = -25 \rightarrow 25$
3 standard reflections
  monitored every 200 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0496$
$wR(F^2) = 0.1148$
$S = 0.992$
8681 reflections
623 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.002$

$\Delta\rho_{\max} = 0.581$ e Å^{-3}
$\Delta\rho_{\min} = -0.299$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
  from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ho	0.02952 (2)	0.241539 (13)	0.850762 (13)	0.03651 (11)
Cl1	0.04919 (13)	0.28578 (9)	0.95626 (8)	0.0563 (5)
Cl2	0.02419 (13)	0.35310 (8)	0.79623 (8)	0.0545 (5)
Si1	0.29582 (14)	0.29591 (10)	0.89669 (9)	0.0537 (6)
Si2	0.2299 (2)	0.12479 (10)	0.94137 (11)	0.0650 (7)
Si3	−0.22011 (15)	0.32435 (10)	0.86488 (11)	0.0631 (7)
Si4	−0.1636 (2)	0.17855 (12)	0.96194 (10)	0.0691 (7)
C11	0.2147 (4)	0.2376 (3)	0.8619 (3)	0.046 (2)
C12	0.1849 (5)	0.1724 (3)	0.8776 (3)	0.047 (2)
B13	0.1330 (6)	0.1396 (4)	0.8248 (4)	0.056 (3)
B14	0.1367 (6)	0.1889 (5)	0.7697 (4)	0.064 (3)
B15	0.1884 (5)	0.2526 (4)	0.7975 (3)	0.049 (2)
B16	0.2387 (7)	0.1793 (4)	0.8149 (4)	0.064 (3)
C21	−0.1514 (4)	0.2525 (3)	0.8498 (3)	0.043 (2)
C22	−0.1270 (4)	0.1977 (3)	0.8881 (3)	0.043 (2)
B23	−0.0867 (6)	0.1430 (4)	0.8542 (3)	0.044 (2)
B24	−0.0908 (6)	0.1658 (4)	0.7855 (4)	0.046 (2)
B25	−0.1301 (5)	0.2376 (4)	0.7859 (3)	0.044 (2)
B26	−0.1882 (6)	0.1809 (4)	0.8255 (4)	0.053 (2)
C31	0.3260 (6)	0.2862 (4)	0.9760 (3)	0.083 (3)
C32	0.2452 (5)	0.3760 (3)	0.8899 (3)	0.070 (2)
C33	0.4039 (5)	0.2946 (4)	0.8578 (4)	0.084 (3)
C34	0.1985 (6)	0.1560 (4)	1.0131 (3)	0.082 (3)
C35	0.3571 (6)	0.1162 (5)	0.9406 (4)	0.103 (4)
C36	0.1808 (8)	0.0432 (4)	0.9370 (4)	0.123 (4)
C37	−0.1593 (6)	0.3790 (4)	0.9172 (4)	0.088 (3)
C38	−0.3358 (5)	0.3043 (5)	0.8897 (4)	0.101 (3)
C39	−0.2399 (6)	0.3722 (4)	0.7980 (4)	0.095 (3)
C40	−0.1809 (6)	0.2478 (4)	1.0096 (3)	0.094 (3)
C41	−0.2718 (7)	0.1308 (5)	0.9545 (4)	0.112 (4)
C42	−0.0756 (7)	0.1296 (4)	1.0012 (4)	0.103 (3)
Li1	0.0056 (9)	0.0779 (6)	0.7848 (6)	0.064 (4)
Li2	0.0918 (9)	0.2976 (7)	0.7212 (6)	0.065 (4)
Li3	0.0479 (8)	0.3836 (5)	1.1667 (6)	0.055 (3)
N51	−0.0495 (5)	−0.0160 (3)	0.8083 (3)	0.082 (2)
N52	0.0452 (6)	0.0292 (4)	0.7084 (4)	0.095 (3)
C53	−0.0148 (9)	−0.0588 (4)	0.7647 (6)	0.128 (5)
C54	−0.0100 (9)	−0.0284 (6)	0.7067 (6)	0.141 (5)
C55	−0.0229 (8)	−0.0416 (4)	0.8658 (5)	0.125 (5)
C56	−0.1491 (6)	−0.0108 (4)	0.8023 (4)	0.101 (4)
C57	0.0244 (9)	0.0636 (6)	0.6529 (5)	0.145 (5)
C58	0.1424 (7)	0.0180 (5)	0.7146 (5)	0.130 (5)
N61	0.0059 (6)	0.2966 (5)	0.6425 (3)	0.100 (3)
N62	0.1834 (5)	0.3506 (4)	0.6697 (3)	0.078 (2)
C63	0.0650 (9)	0.3177 (7)	0.5978 (4)	0.152 (6)
C64	0.1297 (9)	0.3646 (7)	0.6171 (5)	0.146 (5)
C65	−0.0329 (9)	0.2361 (6)	0.6303 (4)	0.152 (6)
C66	−0.0688 (8)	0.3411 (6)	0.6481 (5)	0.138 (5)
C67	0.2621 (8)	0.3128 (7)	0.6590 (5)	0.153 (5)
C68	0.2130 (8)	0.4085 (5)	0.6982 (5)	0.136 (5)
N71	−0.0720 (5)	0.4280 (4)	1.1327 (4)	0.102 (3)
N72	0.0309 (6)	0.4317 (4)	1.2467 (3)	0.082 (2)
C73	−0.0886 (9)	0.4741 (7)	1.1761 (9)	0.192 (9)
C74	−0.0604 (11)	0.4592 (7)	1.2330 (6)	0.164 (7)
C75	−0.1453 (8)	0.3846 (6)	1.1242 (6)	0.154 (6)
C76	−0.0659 (10)	0.4610 (8)	1.0774 (7)	0.232 (10)
C77	0.0227 (7)	0.3941 (6)	1.2983 (4)	0.134 (5)
C78	0.1012 (10)	0.4795 (6)	1.2551 (6)	0.216 (9)
N81	0.1689 (5)	0.3894 (4)	1.1212 (3)	0.081 (2)
N82	0.0677 (6)	0.2854 (3)	1.1695 (4)	0.083 (2)
C83	0.1901 (10)	0.3209 (7)	1.1150 (6)	0.146 (6)
C84	0.1582 (12)	0.2801 (7)	1.1546 (9)	0.185 (9)
C85	0.1585 (8)	0.4169 (5)	1.0640 (4)	0.119 (4)
C86	0.2400 (7)	0.4242 (7)	1.1541 (5)	0.166 (6)
C87	0.0075 (8)	0.2516 (4)	1.1294 (5)	0.130 (4)
C88	0.0663 (12)	0.2554 (5)	1.2266 (5)	0.189 (8)
C91	0.5790 (6)	0.5328 (7)	−0.0006 (6)	0.184 (8)
C92	0.5019 (11)	0.5622 (3)	0.0142 (6)	0.219 (10)
C93	0.4221 (7)	0.5300 (7)	0.0124 (6)	0.199 (8)

Table 2. *Selected geometric parameters (Å, °)*

Cnt(1) and Cnt(2) are the centroids are the carborane rings C11–B15 and C21–B25, respectively.

Ho—Cnt(1)	2.378 (3)	C12—B13	1.564 (10)
Ho—Cnt(2)	2.350 (3)	C12—B16	1.698 (12)
Ho—Cl1	2.613 (2)	B13—B14	1.647 (13)
Ho—Cl2	2.669 (2)	B13—B16	1.793 (13)
Ho—C11	2.723 (6)	B14—B15	1.656 (12)
Ho—C12	2.752 (7)	B14—B16	1.789 (12)
Ho—B13	2.722 (8)	B15—B16	1.751 (12)
Ho—B14	2.751 (9)	C21—C22	1.489 (8)
Ho—B15	2.714 (8)	C21—B25	1.559 (10)
Ho—C21	2.670 (6)	C21—B26	1.690 (10)
Ho—C22	2.670 (7)	C22—B23	1.534 (10)
Ho—B23	2.695 (8)	C22—B26	1.698 (10)
Ho—B24	2.767 (8)	B23—B24	1.658 (11)
Ho—B25	2.713 (7)	B23—B26	1.787 (11)
C11—C12	1.495 (9)	B24—B25	1.620 (11)
C11—B15	1.552 (10)	B24—B26	1.777 (12)
C11—B16	1.693 (10)	B25—B26	1.756 (11)
Cnt(1)—Ho—Cnt(2)	128.5	Cnt(2)—Ho—Cl2	104.4
Cnt(1)—Ho—Cl1	107.9	Cl1—Ho—Cl2	97.17 (6)
Cnt(1)—Ho—Cl2	103.2	Li2—Cl2—Ho	84.7 (3)
Cnt(2)—Ho—Cl1	110.6		

Data were corrected for Lorentz, polarization and absorption effects. The structure was solved by heavy-atom methods and subsequent difference Fourier syntheses. Refinement and relevant calculations were based on F^2. Full-matrix least-squares refinement was performed. The structure consists of a carborane–holmium anion, TMEDA–lithium cation and a solvated benzene molecule. The disordered benzene molecule was elastically restrained during final cycles of refinement.

Methyl, methylene and aromatic H atoms were positioned using a riding model, while the carborane-cage H atoms were located in ΔF maps.

Data collection: *R*3*m*/*V* diffractometer system. Cell refinement: *R*3*m*/*V* diffractometer system. Data reduction: *R*3*m*/*V* diffractometer system. Program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CR1207). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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