

TEN-VERTEX MONOCARBABORANE CHEMISTRY.* A CONVENIENT NEW PREPARATION OF THE $[closo-1-CB_9H_{10}]^-$ ANION AND THE CRYSTAL AND MOLECULAR STRUCTURE OF $[(\eta^5-C_5Me_5)_2Ir_2Cl_3]^+ [closo-1-CB_9H_{10}]^-$

Karl NESTOR^a, Bohumil ŠTÍBR^b, John D. KENNEDY^a, Mark THORNTON-PETT^a and Tomáš JELÍNEK^b

^a School of Chemistry of the University of Leeds, Leeds LS2 9JT, England

^b Institute of Inorganic Chemistry,

Czechoslovak Academy of Sciences, 25068 Řež near Prague, Czechoslovakia

Received July 8, 1991

Accepted October 7, 1991

A more convenient synthesis of the $[closo-1-CB_9H_{10}]^-$ anion, from the reaction of $[6-(NMe_3)-nido-6-CB_9H_{11}]$ with piperidine in THF, is reported. Reaction of $[NMe_4]^+ [1-CB_9H_{10}]^-$ and $[(\eta^5-C_5Me_5)_2Ir_2Cl_3]^+ [closo-1-CB_9H_{10}]^-$ as a yellow crystalline compound. Crystals are orthorhombic, space group *Pnma*, with $a = 2505.9(6)$, $b = 1223.6(3)$, $c = 1029.8(3)$ pm, and $Z = 4$. The structure was refined for 2329 reflections $F > 4.0\sigma(F)$ to $R = 0.0439$. Both cation and anion possess crystallographic mirror-plane symmetry. Comparison of the structure of the anion with other formally *closo* ten-vertex structures reveals a previously unrecognised general opening.

A survey of the literature shows that there is often a partial opening of formally *closo* ten-vertex boron-containing clusters species that appears to be induced by the heteroatom constituents of the clusters. This phenomenon appears generally to have been overlooked. In this context we here report the crystal and molecular structure of $[(\eta^5-C_5Me_5)_2Ir_2Cl_3]^+ [CB_9H_{10}]^-$, which contains the *closo* ten vertex $[1-CB_9H_{10}]^-$ anion. Associated with this work we report a new convenient synthesis of the $[closo-1-CB_9H_{10}]^-$ anion, using a method that makes use of piperidine, rather than sodium metal¹, to effect the conversion from $[6-(NMe_3)-nido-6-CB_9H_{11}]$.

EXPERIMENTAL

Preparation of $[NMe_4]^+ [closo-1-CB_9H_{10}]^-$. A mixture of $[6-(NMe_3)-nido-6-CB_9H_{11}]$ (1.5 g, 8.29 mmol; prepared as in ref.²) and piperidine (20 cm³) was heated at 70°C for three days under dinitrogen. The excess piperidine was removed in vacuo (50°C, oil pump) and the semi-solid residue treated with H₂O (50 cm³) followed by concentrated hydrochloric acid (ca

* Contribution no. 17 from the Řež-Leeds Anglo-Czech Polyhedral Collaboration (A.C.P.C.).

12 mol dm⁻³; 5 cm³). The resulting insoluble precipitate was filtered, washed with water (ca 20 cm³), dried in vacuo at 50°C, and then digested with 5% aqueous NaOH (ca 50 cm³). The piperidine thus liberated was removed under reduced pressure (rotary evaporator, water pump), the remaining aqueous solution filtered with charcoal (ca 1 g), and the clear filtrate treated with an aqueous solution of [NMe₄]⁺Cl⁻ (1 mol dm⁻³; 10 cm³) to precipitate [NMe₄]⁺[CB₉H₁₀]⁻, which was filtered, washed with water (ca 20 cm³), and dried in vacuo (50°C, oil pump) to give the final product (1.1 g, 5.68 mmol; 69% based on [6-(NMe₃)-*nido*-6-CB₉H₁₁]) [$\delta(^{11}\text{B})$ (ref. F₃B.OEt₂) { (CD₃)₂CO, 294 K (relative intensities in parentheses)}: +29.9 (1), -19.5 (4), and -25.0 ppm (4)] [TLC *R_F* 0.20 (Silufol silica gel sheets, CHCl₃-CH₃CN 2 : 1 v/v)].

Preparation of [(η -C₅Me₅)₂Ir₂Cl₃]⁺[CB₉H₁₀]⁻. Reaction between [(η ⁵-C₅Me₅)IrCl₂]₂ (105 mg, 130 μ mol; prepared as in ref.³) and [NMe₄]⁺[CB₉H₁₀]⁻ (87 mg, 450 μ mol) in CH₂Cl₂ solution (ca 10 cm³) for 24 h at room temperature, followed by chromatographic separation (TLC; silica gel; CH₂Cl₂ solvent; *R_F* 0.31) yielded [(η ⁵-C₅Me₅)₂Ir₂Cl₃]⁺[CB₉H₁₀]⁻ (20 mg; 17%). A crystal of suitable size for X-ray crystallography (ca 0.2 \times 0.3 \times 0.6 mm) was obtained by the diffusion of pentane into a solution of the complex in dichloromethane.

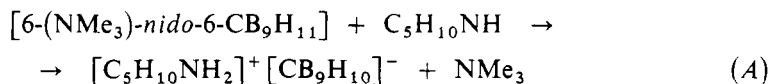
Crystallography

All crystallographic measurements were made on a Nicolet P3/F diffractometer: 25 reflections were centered (35.0 < 2 θ < 40°); graphite-monochromated Mo-K α radiation; $\omega/2\theta$ scans, scan widths = (1.8° + α -doublet splitting), scan speeds 2.0–29.3° min⁻¹ subject to a fast pre-scan. The complete data set (*h*0–29, *k*0–14, *l*0–12) was measured over 105.17 exposure hours with no significant decay of a standard reflection (measured every 50 reflections). 2 826 unique data were collected, with 2 329 that had *F* > 4.0 σ (*F*) used in structure solution and refinement. Solution was by Patterson synthesis (for Ir) and difference Fourier methods. Hydrogen atoms were not located. A post-refinement empirical absorption correction was applied⁴, and full-matrix least-squares refinement was carried out with anisotropic thermal parameters for all located (total number of parameters = 175). Scattering factors and anomalous dispersion factors were obtained from *International Tables for X-Ray Crystallography* (1974). Refinement converged to *R* = 0.0439, *R_w* = 0.0437, using the weighting scheme $\omega^{-1} = \sigma^2(F_0) + 0.0004(F_0)^2$, and the final difference synthesis showed its maximum density of +1.05 eÅ⁻³ at 96 pm from the heavy atom (min. -1.00 eÅ⁻³), with $\Delta/\sigma(\text{max}) = 0.505$ in *U*₂₂ of C(18). All calculations were performed on an Acorn Archimedes 440 microcomputer, programs used were SHELX76⁵, ORTEPII⁶, and PARST⁷.

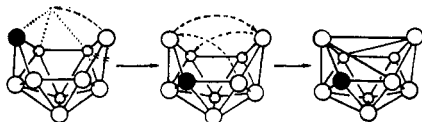
RESULTS AND DISCUSSION

Synthesis of [NMe₄]⁺[*closo*-1-CB₉H₁₀]⁻

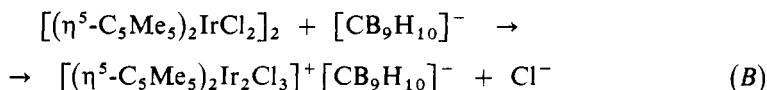
We report first a new high-yield (68%) modification of the synthesis of the [*closo*-1-CB₉H₁₀]⁻ anion, based on the reaction between [6-(NMe₃)-*nido*-6-CB₉H₁₁] and piperidine at 70°C, as in Eq. (A). This represents a simpler and more convenient procedure in comparison with the original method of Knoth¹, who used sodium metal as reducing agent to give the [*closo*-1-CB₉H₁₀]⁻ product in yields of 15–40% depending on the cation.



The gross mechanism of this conversion is of interest because a straightforward closure from the {*nido*-6-CB₉} skeleton would yield a {*closo*-2-CB₉} species which would then have to rearrange to give the observed product. On the other hand, if the closure were preceded or accompanied by a base-induced vertex-flip, for which there is good precedent in the *nido* ten-vertex system⁸, then the closure would yield the {*closo*-1-CB₉} cluster type directly, as indicated in the Scheme 1. We would favour this second mechanism.



Reaction of a sample of $[\text{NMe}_4]^+ [\text{closo-1-CB}_9\text{H}_{10}]^-$ with $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{IrCl}_2]_2$ in dichloromethane solution readily yielded the salt $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ir}_2\text{Cl}_3]^+ \cdot [\text{CB}_9\text{H}_{10}]^-$ as a yellow air-stable crystalline solid, purified by chromatography and isolated in a yield of 17% (Eq. (B)). This compound was examined by single-crystal X-ray diffraction analysis (see following section), suitable crystals being grown by the diffusion of pentane into a solution of the complex in dichloromethane.



Structure of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ir}_2\text{Cl}_3]^+ [\text{CB}_9\text{H}_{10}]^-$

The final fractional coordinates are listed in Table I and the molecular structure and its numbering scheme are shown in Fig. 1. Selected interatomic distances and angles are in Table II. The structure of the binuclear cation $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ir}_2\text{Cl}_3]^+$ has been determined previously in its $[\text{ClO}_4]^-$ salt⁹, and the dimensions are similar to those found here. More interest derives from the $[\text{closo-1-CB}_9\text{H}_{10}]^-$ anion, which is previously unexamined by crystallography, although its synthesis¹ and NMR properties^{1,10} have been reported. The bicapped square Archimedean antiprismatic structure, with the carbon atom in a lower-connectivity polar position, is in accord with the Williams–Wade cluster geometry and electron-counting formalisms,^{11,12} and the shorter polar-tropical boron–carbon and interboron distances compared with the intra- and intertropical distances, are as observed^{13,14} in the analogous binary borane anion $[\text{closo-B}_{10}\text{H}_{10}]^{2-}$.

The intratropical distances among B(2)—B(5) bound to C(1) appear to be on average shorter than those in the B(6)—B(10) belt. In this context the longest intratropical distance of 191.7(37) pm observed for B(7)—B(7') may represent a statistical-

TABLE I

Atom co-ordinates ($\times 10^4$) for $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ir}_2\text{Cl}_3]^+ [\text{closo-1-CB}_9\text{H}_{10}]^-$ with estimated standard deviations (e.s.d.'s) in parentheses

Atom	x	y	z	U_{eq}^a
Ir(1)	5444.8(2)	2500 ^b	3625.6(6)	45.9(2)
Ir(2)	4363.3(2)	2500 ^b	1792.5(6)	44.8(2)
Cl(1)	4490(2)	2500 ^b	4148(4)	77.8(14)
Cl(2)	5103(1)	1230(3)	2015(4)	88.7(12)
C(11)	5788(4)	1937(9)	5386(9)	61(2)
C(12)	6090(5)	1552(11)	4346(11)	76(2)
C(13)	6303(7)	2500 ^b	3677(15)	73(2)
C(16)	5496(5)	1177(13)	6372(13)	90(2)
C(17)	6206(7)	367(14)	4033(15)	125(3)
C(18)	6665(9)	2500 ^b	2525(21)	116(3)
C(21)	3563(4)	1924(8)	1611(9)	52(2)
C(22)	3867(4)	1543(10)	561(11)	63(2)
C(23)	4059(7)	2500 ^b	-113(15)	78(3)
C(26)	3274(5)	1204(10)	2597(12)	79(2)
C(27)	3949(6)	336(12)	208(14)	104(2)
C(28)	4390(10)	2500 ^b	-1336(21)	113(2)
C(1)	2421(8)	2500 ^b	5607(21)	103(3)
B(2)	1932(11)	2500 ^b	6484(22)	98(3)
B(3)	2448(6)	1438(15)	6498(15)	87(2)
B(4)	2947(9)	2500 ^b	6400(19)	76(3)
B(6)	2086(6)	1758(11)	7966(14)	67(3)
B(7)	2822(7)	1716(15)	7876(16)	92(3)
B(10)	2493(9)	2500 ^b	8891(21)	82(3)

^a U_{eq} is defined as one third of the trace of the orthogonalised U_{ij} tensor. ^b Parameter fixed on special position.

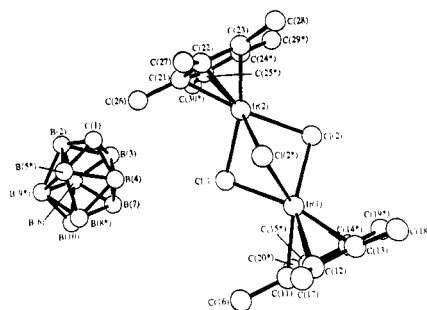


FIG. 1

ORTEP-type diagram of the crystallographically determined molecular structure of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ir}_2\text{Cl}_3]^+ [\text{closo-1-CB}_9\text{H}_{10}]^-$

TABLE II

Selected bond lengths (pm) and angles ($^{\circ}$) for $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ir}_2\text{Cl}_3]^+[\text{closo-1-CB}_9\text{H}_{10}]^-$ with e.s.d.'s in parentheses^a

bond lengths			
Ir(2)—Ir(1)	330.3(4)	Cl(1)—Ir(1)	245.3(6)
Cl(2)—Ir(1)	242.8(5)	C(11)—Ir(1)	212.2(11)
C(12)—Ir(1)	212.4(12)	C(13)—Ir(1)	215.0(18)
Cl(1)—Ir(2)	244.6(6)	Cl(2)—Ir(2)	243.0(5)
C(21)—Ir(2)	213.5(12)	C(22)—Ir(2)	212.7(12)
C(23)—Ir(2)	210.5(17)	C(12)—C(11)	139.3(15)
C(16)—C(11)	156.0(17)	C(11)—C(15*)	137.8(22)
C(13)—C(12)	145.0(16)	C(16)—C(12)	151.4(21)
C(18)—C(13)	149.4(25)	C(22)—C(21)	140.2(14)
C(26)—C(21)	152.6(16)	C(21)—C(25*)	141.1(20)
C(23)—C(22)	144.3(15)	C(27)—C(22)	153.5(18)
C(28)—C(23)	150.9(28)		
B(2)—C(1)	152.1(32)	B(3)—C(1)	159.3(23)
B(4)—C(1)	155.2(31)	B(3)—B(2)	183.3(28)
B(6)—B(2)	181.7(25)	B(4)—B(3)	180.7(24)
B(6)—B(3)	180.5(20)	B(7)—B(3)	173.4(24)
B(7)—B(4)	182.5(24)	B(7)—B(6)	184.6(24)
B(10)—B(6)	166.4(24)	B(6)—B(9*)	181.5(28)
B(10)—B(7)	164.0(26)	B(7)—B(8*)	191.7(37)
bond angles			
Cl(1)—Ir(1)—Ir(2)	47.5(1)	Cl(2)—Ir(1)—Ir(2)	47.2(1)
Cl(2)—Ir(1)—Cl(1)	78.8(2)	Cl(2)—Ir(1)—Cl(2*)	79.6(3)
Cl(1)—Ir(2)—Ir(1)	47.7(1)	Cl(2)—Ir(2)—Ir(1)	47.1(1)
Cl(2)—Ir(2)—Cl(1)	78.9(2)	Cl(2)—Ir(2)—Cl(2*)	79.5(3)
Ir(2)—Cl(1)—Ir(1)	84.8(2)	Ir(2)—Cl(2)—Ir(1)	85.7(2)
B(3)—C(1)—B(2)	72.1(12)	B(4)—C(1)—B(2)	111.8(18)
B(4)—C(1)—B(3)	70.1(11)	B(3)—C(1)—B(5*)	109.4(17)
B(3)—B(2)—C(1)	55.8(11)	B(3)—B(2)—B(5*)	90.4(17)
B(6)—B(2)—C(1)	109.1(17)	B(6)—B(2)—B(3)	59.3(9)
B(6)—B(2)—B(9*)	59.9(12)	B(2)—B(3)—C(1)	52.2(12)
B(4)—B(3)—C(1)	53.9(11)	B(4)—B(3)—B(2)	88.7(13)
B(6)—B(3)—C(1)	106.5(14)	B(6)—B(3)—B(2)	59.9(10)
B(6)—B(3)—B(4)	103.8(11)	B(7)—B(3)—C(1)	109.5(14)
B(7)—B(3)—B(2)	104.3(13)	B(7)—B(3)—B(4)	62.0(11)
B(7)—B(3)—B(6)	62.8(10)	B(3)—B(4)—C(1)	56.0(10)
B(3)—B(4)—B(5*)	92.0(16)	B(3)—B(4)—B(8*)	102.2(10)
B(7)—B(4)—C(1)	107.0(14)	B(7)—B(4)B(3)	57.0(9)
B(3)—B(6)—B(2)	60.8(11)	B(3)—B(6)—B(9*)	102.6(13)
B(7)—B(4)—B(8*)	63.4(14)	B(2)—B(6)—B(9*)	60.0(11)
B(7)—B(6)—B(2)	100.6(12)	B(7)—B(6)—B(3)	56.7(9)

TABLE II
(Continued)

B(7)—B(6)—B(9*)	91.6(12)	B(10)—B(6)—B(2)	109.8(11)
B(10)—B(6)—B(3)	106.9(13)	B(10)—B(6)—B(7)	55.4(11)
B(10)—B(6)—B(9*)	56.9(12)	B(3)—B(7)—B(8*)	101.4(13)
B(4)—B(7)—B(3)	61.0(10)	B(4)—B(7)—B(8*)	58.3(11)
B(6)—B(7)—B(3)	60.5(9)	B(6)—B(7)—B(4)	101.5(12)
B(6)—B(7)—B(8*)	88.4(12)	B(10)—B(7)—B(3)	111.4(15)
B(10)—B(7)—B(4)	108.1(12)	B(10)—B(7)—B(6)	56.7(11)
B(10)—B(7)—B(8*)	54.2(12)	B(6)—B(10)—B(9*)	66.1(10)
B(7)—B(10)—B(6)	67.9(11)	B(7)—B(10)—B(8*)	71.5(12)

^a The following pairs of atoms are related by the symmetry operator ($x, 0.5 - y, z$):

Cl(2) and Cl(2*)	B(7) and B(8*)	C(16) and C(20*)	C(22) and C(24*)
B(3) and B(5*)	C(11) and C(15*)	C(17) and C(19*)	C(26) and C(30*)
B(6) and B(9*)	C(12) and C(14*)	C(21) and C(25*)	C(27) and C(29*)

ly significant anomalous lengthening, because a "stretched" distance for the equivalent linkage in a variety of other formally *closo* ten-vertex heteroborane species is also apparent (see Table III), though not previously remarked upon. In a more marked form this type of distortion results in a so-called *isonido* structure^{15,16} with an interboron distance of ca 230 pm, which would represent an intermediate in fluxional processes such as that observed for $[2-(\eta^5\text{-C}_5\text{Me}_5)\text{-closo-2,1,6-RhC}_2\text{B}_7\text{H}_9]$, a *closo* ten-vertex compound that is in dynamic equilibrium with its enantiomer in solution at slightly elevated temperatures (ΔG^\ddagger 58 kJ mol⁻¹ at 345 K)¹⁷. In its

TABLE III
Intratropical interboron stretching in closed ten-vertex clusters

Compound	Interboron distance pm	Reference
$[\text{B}_{10}\text{H}_{10}]^{2-}$	180.9(6)–183.9(5)	14
$[(\text{PPh}_3)(\text{CH}_3\text{COO})\text{HfCB}_8\text{H}_7(\text{PPh}_3)]$	188.9(32)	19
$[\text{CB}_9\text{H}_{10}]^-$	191.7(37)	this work
$[(\text{PPh}_3)_2\text{HfCB}_8\text{H}_8(\text{PPh}_3)]$	198.5 ^a	20
$[(\text{C}_5\text{Me}_5)\text{RhB}_9\text{H}_8(\text{PMe}_2\text{Ph})_2]$	199.9(8)	21
$[\{(\text{C}_5\text{Me}_5)\text{RhB}_9\text{H}_{10}(\text{SMe}_2)\}\text{Rh}\{\text{B}_9\text{H}_7(\text{SMe}_2)\}]$	202.8(12)	22
$[(\text{PH}_3)_2(\text{Ph}_2\text{PC}_6\text{H}_4)\text{HfB}_9\text{H}_7(\text{PPh}_3)]$	205.0(10)	23

^a No e.s.d.'s available for this structure.

extreme form the distortion results in a complete diamond-square-diamond re-arrangement of the two faces in question to result in the so-called *isocloso* cluster shape^{17,18} in which the interboron distance in question becomes ca 300 pm.

The authors wish to thank Dr J. Bould for stimulating discussions, Dr T. S. Griffin and Dr D. M. Wagnerová for helpful cooperation. We thank the British Council, the S.E.R.C., the Royal Society, the Czechoslovak Academy of Sciences (Grant No. 43204) and Borax Research Ltd for support.

REFERENCES

1. Knoth W. H.: *Inorg. Chem.* **10**, 598 (1971).
2. Baše K., Štíbr B., Dolanský J., Duben J.: *Collect. Czech. Chem. Commun.* **46**, 2345 (1981).
3. Kang J. W., Mosely K., Maitlis P. M.: *J. Am. Chem. Soc.* **91**, 5970 (1969).
4. Walker N., Stuart D.: *Acta Crystallogr.*, **A 39**, 158 (1983).
5. Sheldrick G. M.: *SHELX76, Program for X-ray Structure Determination*. University of Cambridge, Cambridge 1976.
6. Johnson C. K.: *ORTEP II, Report ORNL-5138*. Oak Ridge National Laboratory, Oak Ridge 1976.
7. Nardelli M.: *Comput. Chem.* **7**, 95 (1983).
8. Štíbr B., Plešek J., Zobáčová A.: *Polyhedron* **1**, 824 (1982).
9. Valderrama M., Scotti S., Campos P., Sariego R., Peters K., von Schnering H. G., Werner H.: *New J. Chem.* **12**, 633 (1988).
10. Nestor K., Štíbr B., Jelínek T., Baše K., Fontaine X. L. R., Kennedy J. D., Thornton-Pett M.: *J. Chem. Soc., Dalton Trans.* **1990**, 2887.
11. Williams R. E.: *Inorg. Chem.* **10**, 210 (1971); *Adv. Inorg. Chem. Radiochem.* **18**, 67 (1976).
12. Wade K.: *J. Chem. Soc., Chem. Commun.* **1971**, 792; *Adv. Inorg. Chem. Radiochem.* **18**, 1 (1976).
13. Dobrott R. D., Lipscomb W. N.: *J. Chem. Phys.* **37**, 1779 (1962).
14. Fuller D. J., Kepert B. L., Skelton B. W., White A. H.: *Austr. J. Chem.* **40**, 2097 (1987).
15. Bould J.: *Thesis*. University of Leeds, Leeds 1983.
16. Bould J., Kennedy J. D., Thornton-Pett M.: *J. Chem. Soc., Dalton Trans.* **1992**, 563.
17. Bown M., Jelínek T., Štíbr B., Heřmánek S., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Thornton-Pett M.: *J. Chem. Soc., Chem. Commun.* **1988**, 974.
18. Bould J., Greenwood N. N., Kennedy J. D.: *J. Chem. Soc., Dalton Trans.* **1990**, 1451.
19. Crook J. E., Greenwood N. N., Kennedy J. D., McDonald W. S.: *J. Chem. Soc., Chem. Commun.* **1983**, 83.
20. Alcock N. W., Taylor J. G., Wallbridge M. G. H.: *J. Chem. Soc., Chem. Commun.* **1983**, 1168.
21. Fontaine X. L. R., Fowkes H., Greenwood N. N., Kennedy J. D., Thornton-Pett M.: *J. Chem. Soc., Dalton Trans.* **1987**, 143.
22. Ditzel E. K., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Thornton-Pett M.: *J. Chem. Soc., Chem. Commun.* **1989**, 1262.
23. Bould J., Brint P., Fontaine X. L. R., Kennedy J. D., Thornton-Pett M.: *J. Chem. Soc., Chem. Commun.* **1989**, 1763.

Translated by the author (B.Š.).