

Preliminary communication

# Synthesis and characterization of the first charge-compensated monocarbollide(octacarbonyl) triosmium complex<sup>1</sup>

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## Abstract

The trinuclear osmium complex  $[\text{Os}_3(\text{CO})_8(\eta^5\text{-}7\text{-NMe}_3\text{-}7\text{-CB}_{10}\text{H}_{10})]$  (**1**) has been synthesized by heating  $[\text{Os}_3(\text{CO})_{12}]$  with *nido*-7-NMe<sub>3</sub>-7-CB<sub>10</sub>H<sub>12</sub> in bromobenzene. The structure has been established by X-ray diffraction. © 1997 Elsevier Science S.A.

**Keywords:** Osmium; Boron; Carbonyl; Carborane; Group VIII

## 1. Introduction

Dicarbollide ligands were introduced into transition metal chemistry in the 1960s [1] and many novel complex compounds containing these groups are known [2]. However, although complexes of the transition metals with monocarbollide ligands were discovered soon after [3] this type of compound has been much less studied [2]. Recently, we have shown that the zwitterionic *nido*-carboranes 7-NR<sub>3</sub>-7-CB<sub>10</sub>H<sub>12</sub> are useful precursors to monocarbollide transition metal complexes with *closo*-MCB<sub>10</sub> cage structures [4,5]. In extending these studies, we have prepared, as far as we are aware, the first such 12-vertex osmacarborane complex. A few dicarbon 12-vertex osmacarboranes with *closo*-OsC<sub>2</sub>B<sub>9</sub> cage structures are known, see Ref. [6]; a monocarbon 10-vertex *closo*-OsCB<sub>8</sub> species has also been described [7].

## 2. Results and discussion

If bromobenzene solutions containing  $[\text{Os}_3(\text{CO})_{12}]$  and *nido*-7-NMe<sub>3</sub>-7-CB<sub>10</sub>H<sub>12</sub> in a 1:1 mole ratio are heated at reflux temperatures for a few hours the cluster compound  $[\text{Os}_3(\text{CO})_8(\eta^5\text{-}7\text{-NMe}_3\text{-}7\text{-CB}_{10}\text{H}_{10})]$  (**1**) is obtained after purification of the mixture by column chromatography. An X-ray diffraction analysis revealed the structure shown in Fig. 1.

Crystal data for compound **1**. C<sub>12</sub>H<sub>19</sub>B<sub>10</sub>NO<sub>8</sub>Os<sub>3</sub> · 0.5C<sub>7</sub>H<sub>8</sub>;  $M_r = 1030.0$ ; crystal size  $0.26 \times 0.39 \times 0.56 \text{ mm}^3$ ; unit cell dimensions:  $a = 10.088(2) \text{ \AA}$ ,  $b = 11.501(3) \text{ \AA}$ ,  $c = 12.316(2) \text{ \AA}$ ,  $\alpha = 105.68(2)^\circ$ ,  $\beta = 96.20(2)^\circ$ ,  $\gamma = 97.09(2)^\circ$ ; cell volume  $1350.2(5) \text{ \AA}^3$ ; crystal system triclinic; space group  $P\bar{1}$  (no. 2) with  $Z = 2$ ;  $\rho_{\text{calcd}} = 2.534 \text{ g cm}^{-3}$ ; absorption coefficient  $14.14 \text{ mm}^{-1}$ ;  $F(000) 930$ ; diffractometer Enraf–Nonius CAD4-F, Mo K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ , graphite monochromator; temperature 292 K; reflections collected 2696; independent reflections 2505 ( $R(\text{int}) = 0.0370$ ); corrections: Lorentz, polarization, absorption effects (min., max.: 0.96715, 0.99997) and decay. Solution: Patterson, difference Fourier methods (SHELXL-PC [8]). Refinement: full-matrix least squares on  $F$ , all non-hydrogen atoms except solvent (toluene) anisotropic, hydrogen atoms calculated in idealized positions (B–H groups by BHGEN [9] program, B–H → Os by XHYDEX [10] program:  $d(\text{C–H}) = 0.96 \text{ \AA}$ ,  $U_{\text{iso}} = 0.08 \text{ \AA}^2$ ,  $d(\text{B–H}) = 1.10 \text{ \AA}$ ,  $U_{\text{iso}} = 0.06 \text{ \AA}^2$ ); goodness-of-fit on  $F$ : 2.17, 2432 observed reflections for 324

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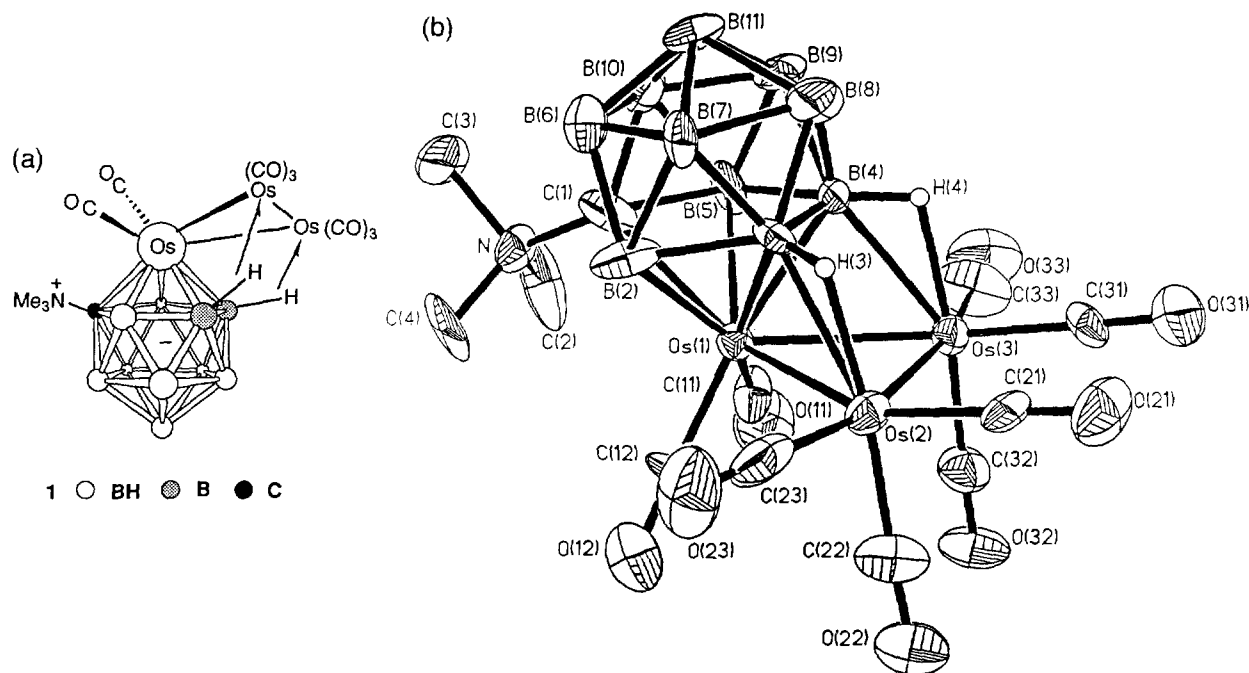


Fig. 1. ORTEP diagram of **1** with the probability ellipsoids at 50%. Selected distances (Å) and angles (deg): Os(1)–Os(2) 2.785(1), Os(1)–Os(3) 2.772(1), Os(2)–Os(3) 2.814(1), Os(1)–C(1) 2.33(2), Os(1)–B(2) 2.29(2), Os(1)–B(3) 2.22(1), Os(1)–B(4) 2.25(2), Os(1)–B(5) 2.25(2), C(1)–N(1) 1.57(2), C(1)–B(2) 1.80(2), B(2)–B(3) 1.82(3), B(3)–B(4) 1.72(3), B(4)–B(5) 1.86(2), C(1)–B(5) 1.80(3), B(3)–Os(2) 2.42(2), H(3)–Os(2) 1.87, B(3)–H(3) 1.12, B(4)–Os(3) 2.39(2), H(4)–Os(3) 1.84, B(4)–H(4) 1.11; Os(2)–Os(1)–Os(3) 60.8(1), Os(1)–Os(2)–Os(3) 59.3(1), Os(1)–Os(3)–Os(2) 59.8(1), Os(1)–C(1)–N 111.3(7), Os(1)–B(3)–H(3) 121.5, Os(1)–B(3)–Os(2) 73.7(4), B(3)–H(3)–Os(2) 105.6, Os(1)–B(4)–H(4) 120.6, Os(1)–B(4)–Os(3) 73.2(4), B(4)–H(4)–Os(3) 105.7, Os–C–O av. 177.5.

refined parameters;  $R = 0.0466$ ,  $R_w = 0.0551$  ( $F > 4\sigma(F)$ ) with a residual electron density of max.  $2.29 \text{ e } \text{Å}^{-3}$ , min.  $-2.08 \text{ e } \text{Å}^{-3}$ . Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

The molecule is similar in structure to the previously reported species  $[\text{Ru}_3(\text{CO})_8(\eta^5\text{-7-NMe}_3\text{-7-CB}_{10}\text{H}_{10})]$  [4]. A triangular core of metal atoms (Os(1)–Os(2) = 2.785(1), Os(1)–Os(3) = 2.772(1), and Os(2)–Os(3) = 2.814(1) Å) is bridged by the *nido*-7-NMe<sub>3</sub>-7-CB<sub>10</sub>H<sub>10</sub> group. The bonding of the carborane cage to the metal atoms involves pentahapto coordination to Os(1) and formation of two three-center two-electron B–H → Os interactions, one between atoms B(3) and Os(2), and the other between atoms B(4) and Os(3). The positions of atoms H(3) and H(4) were determined using the steric-potential-energy-minimization technique [10], and their presence was confirmed by the <sup>1</sup>H NMR spectrum discussed below.

Although the 7-NMe<sub>3</sub>-7-CB<sub>10</sub>H<sub>10</sub> ligand is neutral it is charge-compensated, with a cationic nitrogen atom attached to the carbon vertex of the monoanionic CB<sub>10</sub>H<sub>10</sub> group. The C(1)–N bond length (1.57(2) Å) is virtually the same as in  $[\text{Ru}_3(\text{CO})_8(\eta^5\text{-7-NMe}_3\text{-7-CB}_{10}\text{H}_{10})]$  and little different from that in 7-NH<sub>2</sub>Bu-7-CB<sub>10</sub>H<sub>12</sub> (1.508(2) Å) [11]. Atom Os(1) is ligated by

two CO groups, and the other osmium atoms by three such groups. The ligand  $\eta^5\text{-7-NMe}_3\text{-7-CB}_{10}\text{H}_{10}$  formally contributes eight electrons to the cluster, so the overall the valence electron count is 48, and the species is thus electronically saturated.

The <sup>1</sup>H and <sup>11</sup>B{<sup>1</sup>H} NMR spectra are in accord with the structure established for the solid state. In the <sup>1</sup>H NMR spectrum there is a quartet resonance at  $\delta -13.1$  ( $J(\text{BH}) = 76 \text{ Hz}$ ) for the B–H → Os bonds, this signal being diagnostic for B–H → M systems [12]. The appearance of only one such signal is as expected, being in accord with the symmetrical structure. The B–H → Os groups are chemically equivalent, since both involve B<sub>β</sub>–H bonds of the CB<sub>4</sub>BBB ring ligating Os(1), and lie on either side of a mirror plane in the molecule through C(1), and the mid-points of the B(3)–B(4) and of the Os(2)–Os(3) connectivities. The presence of the B–H → Os linkages is also revealed by the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum, which showed a resonance at  $\delta 12.9$  corresponding in intensity to two boron nuclei; this peak becomes a doublet in a fully coupled <sup>11</sup>B spectrum ( $J(\text{HB}) = 76 \text{ Hz}$ ). The pattern of peaks of relative intensity 2:1:1:2:2:2 seen in the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum is in accord with the symmetry of the molecule. Owing to the relative insolubility of the complex the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum was weak and the generally broad resonance for the cage-carbon atom was not observed.

However, four peaks for the CO groups were seen as anticipated [4]. Other resonances in the  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra are as expected.

Compound  $[\text{Os}_3(\text{CO})_8(\eta^5\text{-7-NMe}_3\text{-7-CB}_{10}\text{H}_{10})]$  (**1**) having a closo-icosahedral  $\text{OsCB}_{10}$  fragment and forming exopolyhedral linkages from the cage framework to the  $\text{Os}_2(\text{CO})_6$  group provides a link between metal-carborane clusters and the many cluster complexes with osmium carbonyl fragments [13,14]. Conversion of complexes of type **1** into species of higher nuclearity in osmium with incorporation of the carborane cage may be a fruitful area for study.

### 3. Experimental section

#### 3.1. General considerations

All experiments were conducted under an atmosphere of dry nitrogen using Schlenk tube techniques. Solvents were freshly distilled under nitrogen from appropriate drying agents before use. NMR measurements were recorded at the following frequencies:  $^1\text{H}$  at 360.1 MHz,  $^{13}\text{C}$  at 90.6 MHz, and  $^{11}\text{B}$  at 115.6 MHz. The reagent  $[\text{7-NMe}_3\text{-nido-7-CB}_{10}\text{H}_{12}]$  was made by a procedure previously described [15].

#### 3.2. Preparation of $[\text{Os}_3(\text{CO})_8(\eta^5\text{-7-NMe}_3\text{-7-CB}_{10}\text{H}_{10})]$

A mixture of the compounds  $[\text{Os}_3(\text{CO})_{12}]$  (0.90 g, 1.0 mmol) and *nido-7-NMe}\_3\text{-7-CB}\_{10}\text{H}\_{12} (0.19 g, 1.0 mmol) was refluxed in bromobenzene (30 ml) for 7 h, during which period the color of the solution changed slowly from yellow to brown. Solvent was removed in vacuo and the residue dissolved in  $\text{CH}_2\text{Cl}_2$  (10 ml) and chromatographed on silica gel (Aldrich, 70–230 mesh). Elution with  $\text{CH}_2\text{Cl}_2$ –light petroleum (2:1) removed a yellow fraction. Solvent was removed in vacuo and the residue crystallized from toluene (15 ml) to give yellow microcrystals of  $[\text{Os}_3(\text{CO})_8(\eta^5\text{-7-NMe}_3\text{-7-CB}_{10}\text{H}_{10})]$  (**1**) (0.23 g, 23%). Anal. Found: C, 17.8; H, 2.1; N, 1.3.  $\text{C}_{12}\text{H}_{19}\text{B}_{10}\text{NO}_8\text{Os}_3 \cdot 0.5\text{C}_6\text{H}_5\text{Me}$ : Calc.: C, 18.0; H, 2.3; N, 1.4%. IR:  $\nu_{\text{max}}(\text{BH})$  2558 m br  $\text{cm}^{-1}$ ;  $\nu_{\text{max}}(\text{CO})$  2086s, 2043s, 2010s, 1978w, 1892vw  $\text{cm}^{-1}$ . NMR ( $\text{CD}_2\text{Cl}_2$ ):  $^1\text{H}$ ,  $\delta$  –13.1 (q br, 2 H, B–H  $\rightarrow$  Os,  $J(\text{BH}) = 76$  Hz), 3.24 (s, 9 H,  $\text{NMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$ ,  $\delta$  181.5, 181.0, 177.0, 174.0 (CO), 59.8 (Me).  $^{11}\text{B}\{^1\text{H}\}$ ,  $\delta$  (positive to high frequency of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (external))*

12.9 (2 B, B–H  $\rightarrow$  Os,  $J(\text{HB}) = 76$  Hz), –3.3 (1 B), –7.4 (1 B), –8.6 (2 B), –13.0 (2 B), –16.9 (2 B).

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