SYNTHESIS AND STRUCTURE OF μ-6,9-METALLA-BIS(LIGAND)-6,9-DICARBA-*nido*-DECABORANES(10) FROM THE $[6,9\text{-}C_2B_8H_{10}]^{2-}$ ANION

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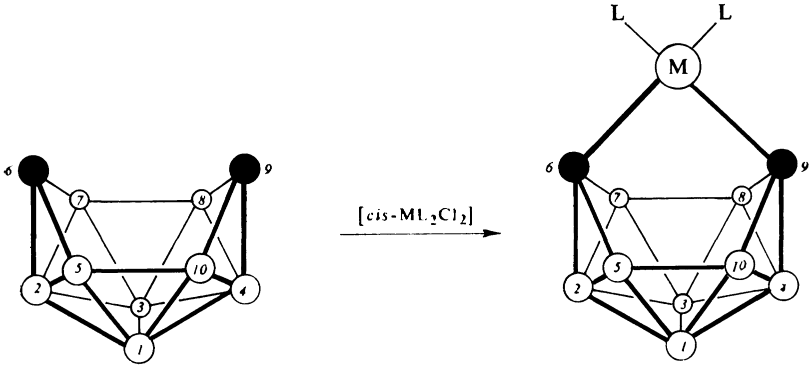
A revised structure for the $[6,9\text{-}C_2B_8H_{10}]^{2-}$ anion is suggested on the basis of its NMR spectra. The anion reacts with the [*cis*-PtL_2CL_2] (L = $P(C_6H_5)_3$, $S(C_2H_5)_2$) and [Ni(*cis*-1,2-DACH).Cl_2] (DACH = diaminocyclohexane) complexes to produce a family of suare-planar [μ-6,9-ML_2-6,9-$C_2B_8H_{10}$] (M = Pt, Ni) *nido*-metalladicarbaboranes containing an unusual metallic bridge linking both skeletal carbon atoms of the carborane ligand. The structure of the complexes is proposed on the basis of their NMR spectra and an X-ray diffraction study.

We have recently[1] reported the synthesis of 10-vertex platinaheteroboranes of the general formula $[9,9'\text{-}(P(C_6H_5)_3)_2\text{-}6,9\text{-}EPtB_8H_{10}]$ ($E = CH_2, NH, S$), containing a pseudo-square planar environment of ligands around the central platinum atom. We wish to report the preparation and properties of other square planar metallacarboranes with the $[C_2B_8H_{10}]^{2-}$ anion as one of the ligands.

In 1973 we have described the pyrolysis of the $[5,6\text{-}C_2B_8H_{11}]^-$ anion affording the readily available $[C_2B_8H_{10}]^{2-}$ dianion (*I*) in high yield[2]. Its newly remeasured high resolution ^1H NMR spectrum (hexadeuterioacetone), consisting of one skeletal CH singlet (δ 4·43), and the ^{11}B NMR spectrum (hexadeuterioacetone), displaying three doublets δ_B −5·6 (4 B), −8·6 (2 B), −33·5 (2 B, 140), are most simply related to the $[6,9\text{-}C_2B_8H_{10}]^{2-}$ structure for *I* than to the originally proposed 5,7-configuration[2]. The former alternative should be also favoured due to the location of both carbons in a preferred low coordinate cage position[3].

The dianion *I* is known to form *closo* complexes of the general formula $[M^{III}.(2,3\text{-}C_2B_8H_{10})]^-$ with cobalt[2] and iron[4] in almost quantitative yields. In contrast, the [*cis*-PtL_2Cl_2] /L = $P(C_6H_5)_3$, $S(C_2H_5)_2$/ and [Ni(*cis*-1,2-DACH)Cl_2] complexes react smoothly with anion *I* to obtain a family of *nido*-[μ-6,9-ML_2-6,9-C_2B_8.H_{10}] metallaboranes (*II*–*IV*) [M = Pt, L = $P(C_6H_5)_3$, *II*; M = Pt, L = $S(C_2H_5)_2$, *III*; M = Ni, L_2 = *cis*-1,2-DACH, *IV*] (see Scheme) that exhibit new structural features in having the central metal atom located at the site bridging the 6,9-carbons in the open cage of the anion *I*.



I

II, M = Pt, L = $P(C_6H_5)_3$
III, M = Pt, L = $S(C_2H_5)_2$
IV, M = Ni, L_2 = *cis*-1,2-DACH

Ⓜ Pt or Ni
● CH
○ BH

The above discussed structure was unambiguously determined by an X-ray diffraction study[5] on the complex *II*, showing a square planar environment around the central Pt^{2+} ion. The found $Pt–B_{(5,7,8,10)}$ distances were too long (2·60 – 2·66 Å) to be considered as bonding ones. Consistent with the 6,9-bridge metal structure are also the ^1H and ^{11}B NMR spectra of all *II*–*IV* compounds. The relevant ^{11}B NMR spectra display the anticipated 2 : 4 : 2 patterns of doublets and the ^1H NMR spectra consist of one cage CH singlet and signals assigned to the organic ligand, which is in agreement with the propsed C_{2v} geometry of the molecules.

Taking into account the electronic structure of complexes *II*–*IV*, the metal-$C_{(6 \text{ or } 9)}$ bonds should be normal two-electron bonds. Accordingly, the $[6,9\text{-}C_2B_8.H_{10}]^{2-}$ moiety contributes two axial 6,9-electron pairs capable of interacting with metal hybrid orbitals of suitable symmetry.

EXPERIMENTAL

The ^1H (200 MHz) and ^{11}B (64·18 MHz) NMR spectra were obtained on a Varian XL-200 spectrometer; chemical shifts are given in δ/ppm, relative to tetramethylsilane and $BF_3.O(C_2H_5)_2$, negative values upfield). The UV spectra were recorded using a Beckman Acta M IV equipment and the IR spectra were measured on a Beckman IR-20A device. TLC was performed on Silufol sheets (silica gel on aluminium foil, producer Kavalier, Votice, Cezchoslovakia; detection by I_2 followed by $AgNO_3$ spray). Melting points were determined in sealed capillaries and are uncorrected. Unless otherwise stated, all reactions were performed under dry nitrogen. The [6,9-$C_2B_8H_{10}$]Na_2 salt and the starting metallic complexes were prepared according to the literature[2,6-8]. Tetrahydrofuran was distilled with $NaAlH_2(OC_2H_4OCH_3)_2$ and dichloromethane with P_2O_5 prior to use. Other chemicals were reagent grade and were used as received.

μ-6,9-Platina bis(triphenylphosphine)-6,9-dicarba-*nido*-decaborane(10) (*II*)

A solution of [6,9-$C_2B_8H_{10}$]Na_2 (0·69 g; 4·14 mmol) in tetrahydrofuran (50 ml) was slowly added to a suspension of [*cis*-$Pt(P(C_6H_5)_3)_2Cl_2$] (3·27 g; 4·14 mmol) in tetrahydrofuran (30 ml). The mixture was stirred at ambient temperature for 10 h and the solid separated from the brown solution was filtered, washed with water (50 ml) and crystallized from dichloromethane–hexane to obtain 1·5 g (43%) of pale yellow crystals of compound *II*; m.p. 278°C (decomp.); R_F (benzene) 0·20. For $Pt(P(C_6H_5)_3)_2C_2B_8H_{10}$ (840·3) calc.: 23·22% Pt, 7·31% P, 10·30% B; found: 23·93% Pt, 7·34% P, 9·69% B; ^1H NMR spectrum (deuteriochloroform): δ 7·42—7·14 [30 H, m, $P(C_6H_5)_3$], 3·93 (2 H, s, CH skel.); ^{11}B NMR spectrum (dichloromethane): δ_B —5·46 (4 B, d, vbr, $B_{(5,7,8,10)}$, —8·96 (2 B, d, vbr), —12·80 (2 B, d, vbr); UV spectrum (dichloromethane): $\lambda_{max}(\varepsilon)$ 232 (49 900), 249 (35 445), 275 (sh), 411 (1 016) nm; IR spectrum (Nujol mull): ν_{BH} 2 490 (sh), 2 510 (sh), 2 510, 2 570 (sh) cm^{-1}.

μ-6,9-Platina bis(diethylsulphide)-6,9-dicarba-*nido*-decaborane(10) (*III*)

To a suspension of [6,9-$C_2B_8H_{10}$]Na_2(0·65 g; 3·9 mmol) in tetrahydrofuran (30 ml) cooled down to —30°C was slowly added solid [*cis*-$Pt(S(C_2H_5)_2)_2Cl_2$] (1·5 g; 3·36 mmol) under intensive stirring for 30 min. After spontaneous warming up to 0°C, the mixture was stirred for additional 2 h, left to stand overnight at room temperature and then filtered. The solid residue obtained on evaporating the tetrahydrofuran *in vacuo* was dissolved in benzene (10 ml) and placed on a column (2·5 . 10 cm) of silica gel. Benzene developed a yellow band of the product and the combined fractions of R_F 0·16 (TLC in benzene) were concentrated to a volume of *c*. 20 ml. Careful addition of hexane (*c*. 20 ml) caused spontaneous crystallization of compound *III* as orange-yellow platelets, 0·3 g (18%, based on the Pt complex used;) m.p. below 280°C (decomp.) without any noticeable change in the crystal shape. For $Pt(S(C_2H_5)_2)_2C_2B_8H_{10}$ (496·1) calcd.: 39·32% Pt, 12·93% S, 17·45% B; found: 38·95% Pt, 12·98% S, 17·40% B; ^1H NMR spectrum (deuteriochloroform): δ 3·99 (2 H, t, br, J_{H-Pt} 13 Hz, CH skel.), 1·29 (12 H, t, CH_3), 2·86 (8 H, q, CH_2S); ^{11}B NMR spectrum (dichloromethane): δ_B —6·73 (4 B, d, 152), —11·62 (2 B, d, 180), —14·52 (2 B, d, 142); UV spectrum (dichloromethane); $\lambda_{max}(\varepsilon)$ 231 (17 106), 278 (8 274), 324 (4 470) nm; IR spectrum (dichloromethane): ν_{BH} 2 510 cm^{-1}.

μ-6,9-Nickela (*cis*-1,2-diaminocyclohexane)-6,9-dicarba-*nido*-decaborane(10) (*IV*)

A mixture of [6,9-$C_2B_8H_{10}$]Na_2 (0·5 g; 3·0 mmol) and [Ni(*cis*-1,2-DACH)Cl_2] (0·75 g; 3·1 mmol) was stirred in tetrahydrofuran (50 ml) for 6 h and then left to stand overnight. The dark green mixture was filtered and the filtrate was evaporated with silica gel (10 g) and placed atop a column (2·5 × 25 cm) of silica gel. Ethyl acetate developed an intensive green band of the complex *IV* which was isolated after removing the solvent *in vacuo* and washing the residue with hexane. Analytical product, 0·15 g (17%, based on compound *I* used), was obtained by crystallization from acetone–hexane as dark green crystals; m.p. 235—245°C (decomp.). For $Ni(C_6H_{14}N_2)C_2.B_8H_{10}$ (293·6) calc.: 20·00% Ni, 9·54% N, 29·48% B; found: 19·62% Ni, 9·48% N, 29·35% B. ^1H NMR spectrum (hexadeuterioacetone) consisted of one singlet of the skeletal CH group (δ 4·95, 2 H) and the signals assigned to the *cis*-1,2-DACH ligand at δ 3·46 (2 H, sbr, NH_2), 3·11 (2 H, sbr, CH—N), 2·713 (2 H, sbr, NH_2), 2·00 (2 H, m, CH_2) and 1·75 (2 H, m, CH_2).

^{11}B NMR spectrum (hexadeuterioacetone): δ_B −1·49 (2 B, d, 155), −11·76 (4 B, d, 140), −18·46 (2 B, d, 155); UV spectrum (acetonitrile): $\lambda_{max}(\varepsilon)$ 340 (4 949), 239·6 (14 537), 225 (13 410) nm; IR spctrum (KBr disc): ν_{BH} 2 480, 2 515, 2 540 (sh) cm^{-1}.

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