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Macropolyhedral boron-containing cluster chemistry. Assessment of the possibilities of thermolytic mixed-cluster fusion, and of the use of synchrotron X-radiation for the examination of small single crystals of metallaboranes. Isolation and structure of eighteen-vertex [7-(CO)-7,7-(PMe$_3$)$_2$-*syn*-7-IrB$_{17}$H$_{20}$]*

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Thermolysis of [(CO)(PMe$_3$)$_2$HIrB$_8$H$_{12}$] with molten B$_{10}$H$_{14}$ resulted in small yields of eighteen-vertex [7-(CO)-7,7-(PMe$_3$)$_2$-*syn*-7-IrB$_{17}$H$_{20}$] for which a small crystal was examined by single-crystal diffraction analysis, using synchrotron X-radiation, in order to determine the molecular structure.

Macropolyhedral boron-containing cluster compounds in which the multicentre bonding characteristic of boranes extends contiguously over two or more subclusters that are fused together is currently an expanding area of new chemistry. In any novel area of chemistry exploratory work is necessary to reveal the extent of structure and reactivity available. Reaction types are unknown, and in initial exploratory work yields are often small. Nevertheless it is essential that the chemistry be pursued in order to establish the structural parameters available in a new area so that focused rational and targeted chemistry may thence be developed to define the new field. In this context there are often severe difficulties in structural characterisation if only very small quantities of new products are available, and suitable techniques have to be developed. Here we report a new eighteen-vertex metallaborane [7-(CO)-7,7-(PMe$_3$)$_2$-*syn*-7-IrB$_{17}$H$_{20}$], obtained in very small yield from a mixed-cluster fusion reaction between [(CO)(PMe$_3$)$_2$HIrB$_8$H$_{12}$] and B$_{10}$H$_{14}$. Only one very small single crystal was ultimately obtained, and so synchrotron radiation in a new experimental facility was used to obtain sufficiently intense diffraction data for the precise determination of the molecular structure.

Macropolyhedral borane clusters derive from the fusion of smaller single-cluster species. Previously they have been generally synthesised from thermolytic auto-fusion of single compounds. Mixed fusions should provide a larger variety. Here we report results from a mixed cluster fusion between *arachno* nine-vertex [4-(CO)-4,4-(PMe$_3$)$_2$-4-H-4-IrB$_8$H$_{12}$] and *nido* ten-vertex B$_{10}$H$_{14}$. A set of *arachno* nine-vertex compounds[1–5] constitutes the system so far known to be most prone to macropolyhedral generation by auto-fusion. Of these compounds, we have noted that auto-fusion and other reactions of [(PMe$_2$Ph)$_2$-PtB$_8$H$_{12}$] and [(CO)(PMe$_3$)$_2$HIrB$_8$H$_{12}$] show indications of reaction with their solvent media.[3,6] Hence we are investigating the thermolysis of [(CO)(PMe$_3$)$_2$HIrB$_8$H$_{12}$] in molten B$_{10}$H$_{14}$ as solvent, and report a preliminary result here.

The cluster compounds [(CO)(PMe$_3$)$_2$HIrB$_8$H$_{12}$] (134 mg, 280 μmol)[7] and B$_{10}$H$_{14}$ (500 mg, 4.1 mmol) were finely ground together and heated under dry dinitrogen at 134 °C (oil bath). Excess B$_{10}$H$_{14}$ was removed by vacuum sublimation (water bath at 80 °C), and preparative TLC (silica gel G, CH$_2$Cl$_2$–hexane mixtures) showed many orange and yellow bands. Repeated TLC separations ultimately gave an orange band (R_F 0.7 using 50 : 50 CH$_2$Cl$_2$–hexane), which upon further separation by HPLC (silica, Lichrosorb Si60 7 μm; 260 × 16 mm column; rapid initial gradient 25% CH$_2$Cl$_2$ in hexane to 100% CH$_2$Cl$_2$, flow rate 4 cm^3 min^{-1}) gave one major component R_T 32 min (*ca.* 500 μg), a compound that we currently formulate as a {B$_{26}$Ir$_2$} cluster species, and which we hope to be able to report on when we complete work upon it. The several minor HPLC components were each systematically screened for microcrystal formation by hexane diffusion into concentrated CDCl$_3$ solutions at +4 °C and one of these, with R_T 30 min, gave a crop of six very small orange crystals of [7-(CO)-7,7-(PMe$_3$)$_2$-*syn*-7-IrB$_{17}$H$_{20}$] [<*ca.* 20 μg (estimate)]. One of these was isolated at room temperature for single-crystal diffraction work, but in doing so redissolution of the others occurred, so far irreversibly, into the solvent mixture thus precluding NMR assessment of the pure product.

The crystal was of size 0.25 × 0.10 × 0.08 mm. In our experience, crystals of metallaboranes of this type with dimensions *ca.* 0.1–0.5 mm often give relatively weak diffracted intensities with conventional equipment and require extended exposure times even with a CCD area detector. The crystal was therefore examined on a newly constructed single-crystal diffraction station at CCLRC Daresbury Laboratory, with wiggler-generated synchrotron radiation of wavelength 0.6956 Å (calibrated against samples of known cell parameters, monochromated and focused by a bent silicon crystal)[8] and a specially adapted Siemens SMART CCD diffractometer.† Individual

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* 7-Carbonyl-7,7-bis(trimethylphosphine)-*nido*-decaborano-(5′,6′ : 5,6)-*nido*-7-iridadecaborane.

† All measurements were made on a Siemens SMART CCD area-detector diffractometer at 160 K with narrow ω-rotation frames using synchroton radiation ($\lambda = 0.6956$ Å; SRS station 9.8, Daresbury Laboratory). The structure was solved by heavy-atom methods using SHELXS 86[9] and refined by full-matrix least squares (against all the unique F^2 data) using SHELXL 93.[10] Non-hydrogen atoms were refined with anisotropic displacement parameters. Methyl hydrogen atoms were constrained to idealised positions (C–H 0.98 Å) whereas hydrogen atoms associated with the cluster were located in Fourier-difference syntheses and freely refined. The complex crystallised as a racemic twin; the twin component parameter[11] refined to 0.493(5). Crystal data for [7-(CO)-7,7-(PMe$_3$)$_2$-*syn*-7-IrB$_{17}$H$_{20}$], C$_7$H$_{38}$B$_{17}$IrOP$_2$, $M = 576.28$, crystal dimensions 0.25 × 0.10 × 0.08 mm, orthorhombic, space group $P2_12_12_1$, $a = 10.5204(11)$, $b = 14.6809(15)$, $c = 15.863(2)$ Å, $Z = 4$, $U = 2450.0(4)$ Å^3, $D_c = 1.56$ g cm^{-3}; 21 372 reflections were collected to $\theta = 26.00$; 4704 unique reflections ($R_{\text{int}} = 0.0395$) were used in calculations after Lorentz, polarisation and absorption corrections (based on repeated and symmetry-equivalent reflections; $\mu = 5.579$ mm^{-1}, transmission factors 0.374–0.491). Final $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]\}^{\frac{1}{2}} = 0.040$, conventional $R = 0.018$ for F values of 4591 reflections with $F_o^2 > 2\sigma(F_o^2)$. Weighting scheme $w = 1/[\sigma^2(F_o^2) + 0.0201P^2]$

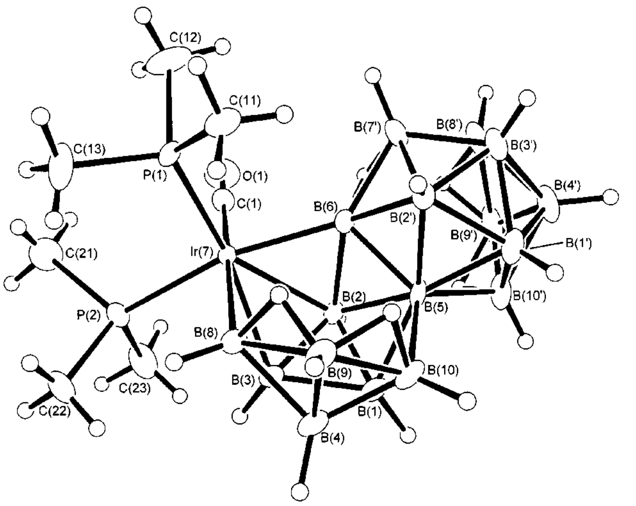
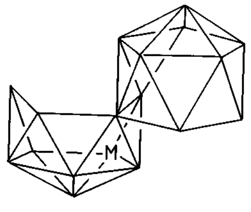


Fig. 1 An ORTEP-type drawing[12] of the molecular structure of [7-(CO)-7,7-$(PMe_3)_2$-*syn*-7-$IrB_{17}H_{20}$]. Some salient interatomic distances (Å) are: B(5)–B(6) 1.779(6), B(5)–B(10) 2.032(6), B(9)–B(10) 1.776(6), B(8)–B(9) 1.818(6), B(5)–B(10′) 1.981(6), B(8′)–B(9′) 1.782(9), B(9′)–B(10′) 1.770(8), B(7′)–B(8′) 1.979(7) and B(7′)–B(6) 1.805(5) [the other interboron distances being in the range 1.712(6)–1.846(6)], and from Ir(7) to B(2) 2.253(4), B(3) 2.235(4), B(6) 2.133(4), B(8) 2.295(4), C(1) 1.891(4), P(1) 2.3329(10) and to P(2) 2.3791(9). Angles (°) at Ir(7) between vectors are as follows: to C(1) and P(1) 95.33(12), C(1) and P(2) 85.27(11), P(1) and P(2) 100.53(4), B(6) and P(1) 97.47(11), and B(8) and P(1) 89.02(11). The longer interboron distances B(5)–B(10), B(5)–B(10′) and B(7′)–B(8′) characterise *nido* ten-vertex structures. The short iridium–boron distance Ir(7)–B(6) has precedent in short interatomic distances in other ten-vertex *nido* (6,7)-type positions that lack hydrogen bridges[13]

exposures of 3 s gave strong diffraction effects, so that a complete set of data was collected in 1.25 h of X-ray exposure time (3 h elapsed time); further symmetry-equivalent sets of data were also measured. The crystal was cooled to 160 K and there was no evidence of significant decomposition, the observed steady decay in intensities being accounted for by the monitored synchrotron beam current decay. The final residual indices of $R = 0.018$ and $wR2 = 0.040$ from the structure refinement are the lowest achieved so far from this experimental station and are excellent by the standards of conventional equipment. Even a much smaller crystal would probably have yielded perfectly satisfactory results.

The basic cluster structure of [7-(CO)-7,7-$(PMe_3)_2$-*syn*-7-$IrB_{17}H_{20}$] (Fig. 1) consists of *nido* $\{B_{10}\}$ plus *nido* $\{IrB_9\}$ ten-vertex subclusters fused with a common two-boron edge. The position of fusion generates a new eighteen-vertex metallaoctadecaborane of *syn-nido*:*nido* ten-vertex:ten-vertex macropolyhedral configuration (schematic **I**). The $\{Ir(CO)(PMe_3)_2\}$ unit, formally octahedral iridium(III), contributes three electrons to the cluster bonding scheme, and thus generates a cluster analogous to the [*syn*-$B_{18}H_{21}]^-$ monoanion. The *syn*-$\{7\text{-}IrB_{17}\}$ configuration contrasts to the only other reported $\{MB_{17}\}$ type, the $\{$*syn*-10-$MB_{17}\}$ configuration (schematic **II**) seen in $\{RhB_{17}\}$ and in $\{CoB_{17}\}$ cluster formation from *anti*-$B_{18}H_{22}$ systems.[14] These latter 10-metallaoctadecaborane structures **II** can be visualised as forming relatively simply *via* a boron-vertex pseudo-replacement from *anti*-$B_{18}H_{22}$-based residues (schematic **III**). However, a mechanism to generate the 7-hetero configuration **I** is not feasible by this or related pathways from either *syn* or *anti* $B_{18}H_{22}$-type residues without much fundamental cluster rearrangement. Rather, in the mixed-fusion reaction system, it may well occur *via* a loss of a boron vertex during the course of the reaction to generate an *arachno*-type of $\{MB_7\}$ species which then adds to the *nido*-$B_{10}H_{14}$ substrate (schematic **IV**). There is precedent for the generation of seven-boron systems from eight-boron and nine-vertex systems.[15] That the iridium atom is next to the *nido*-decaboranyl subcluster in the product suggests fusion *via* electrophilic attack by the metal centre in the 5,6 region of the $B_{10}H_{14}$ substrate.



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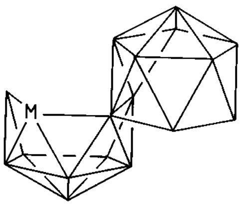

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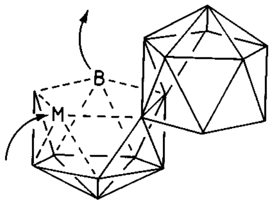

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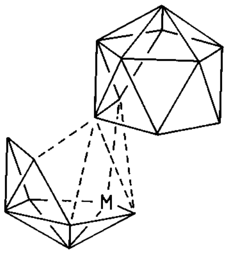

IV

In any event, it is clear that this mixed-fusion method can viably generate new macropolyhedral species not otherwise obtainable, albeit in very small yields so far. We currently explore for other mixed fusions, and also hope to report soon on other low-yield macropolyhedral products from this preliminary siting experimentation in the $[(CO)(PMe_3)_2HIrB_8H_{12}]$–$B_{10}H_{14}$ system, such as the $\{Ir_2B_{26}\}$ species mentioned above. The excellent structural results show that the application of new synchrotron single-crystal diffraction facilities provides an effective means of characterising materials obtainable only as very small crystals, a situation by no means uncommon in metallaborane chemistry. We are currently exploring the practical limits of the technique.

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where $P = (F_o^2 + 2F_c^2)/3$, goodness of fit = 1.035 for all F^2 values and 341 parameters. Maximum and minimum residual electron density +0.90 and −0.68 e Å^3 respectively. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/544.

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