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ARTICLE

A simple and high-yield route to iridium, rhodium, osmium and ruthenium *nido*-6-metalladecaborane compoundsJonathan Bould,^{a,b} Michael G.S. Londesborough,^a Vincenzo Passarelli,^b William Clegg,^c Paul G. Waddell,^c Josef Cvačka,^d and Ramón Macías,^{*b}Received 00th January 20xx,
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We report a high-yield heterogeneous solid/liquid phase synthetic method to a series of *nido*-6-metalladecaboranes. The hydrido- and hydrido- and hydrido- decaboranes, [6,6,6-H(PPh₃)₂-*nido*-6-MB₉H₁₃] [M = Ir (**1**), Rh (**2**)] are isolatable in 98 % yields from the reaction of the square-planar M(II) complexes, [MCl(PPh₃)₃] (M = Rh, Ir), with K[B₉H₁₄]. The same synthetic procedure but using [MCl(CO)H(PPh₃)₃] (M = Ru, Os) as metal starting reagents produces the CO-ligated clusters, [6,6,6-(CO)(PPh₃)₂-*nido*-6-MB₉H₁₃] [M = Ru (**3**), Os (**4**)], in yields of 83% and 95%, respectively. These highly convenient syntheses permit the investigation of the reaction chemistry of the new *nido*-6-metalladecaboranes. Thus, the CO-ligated compounds, **3** and **4**, react with the square-planar platinum(II) complex, [PtCl₂(PMe₂Ph)₂], in the presence of potassium triethylborohydride, to give the bimetallic clusters, [1,1,1-(CO)H(PPh₃)-*isocloso*-1-RuB₉H₈-μ-(1,2)-(Pt(PMe₂Ph)₂)] (**5**) and [7,7-(PMe₂Ph)₂-9,9,9-(CO)(PPh₃)₂-*nido*-7,9-PtOsB₉H₁₁].CH₂Cl₂ (**6**), and the monometallic *nido*-5-osamadecaborane, [5,5,5-(PPh₃)₂(CO)-*nido*-5-OsB₉H₁₃] (**7**). This reactivity illustrates the potential of polyhedral boron-based clusters as molecular scaffolds ("B-frames") for the construction of multimetallic species. Single-crystal X-ray diffraction analyses have revealed the molecular structures of **3**, **5**, **6** and **7**; the compounds are also studied by multielement NMR spectroscopy, mass spectrometry, IR spectroscopy, and in some cases computationally. Furthermore, the rotation of the {M(X)(PR₃)₂} moiety (X = H, CO), as PH₃-ligated models, is studied by means of DFT-calculated relaxed potential energy surface scans, giving some insight into the lability of the metal-to-borane fragment interaction and of the *exo*-polyhedral ligands.

Introduction

For some time we have been investigating the chemistry of *nido*-metalladecaboranes, and in particular how the redox flexibility of these compounds can be used to unlock uncommon reaction pathways involving unsaturated hydrocarbons. For example, the reaction of the iridadecaborane [6,6-(H)(PPh₃)₂-6^p,5^c-μ-(Ph₂P-o-C₆H₄)₂-*nido*-6-IrB₉H₁₂] (Chart 1a) with acetylene affords [2,2-(PH₃)₂-1^c,2^p-μ-(Ph₂P-o-C₆H₄)₂-10-(PPh₃)-*closo*-2-IrB₉H₇] (Chart 1b) together with [1,1-(C₄H₄)₂-1^p,2^c-μ-(Ph₂P-o-C₆H₄)₂-5-(PPh₃)-*isocloso*-1-IrB₉H₇] (Chart 1c).^{1, 2} In the first of these products, the PPh₃ ligands have been converted to PH₃ groups, and the

metallaborane cluster oxidized from *nido* to *closo* geometry, which implies the formal elimination of a skeletal electron pair (*vide infra*). In the second product, two acetylene groups have coupled to form an iridacyclopenta-2,4-dienyl moiety, and the geometry of the metallaborane cluster transformed from *nido* to *isocloso* (another two-electron formal oxidation process).

This type of reactivity is possible in large part due to the capacity of the iridadecaborane cluster to undergo internal oxidative closure concomitant to a structural *nido-closo/isocloso* structural transformation with the loss of dihydrogen. This dehydrogenative process entails an intimate cooperation between the metal fragment and the nonaborane ligand, which can offer further chemical flexibility in the form of its *exo*-polyhedral substitution and/or ligation.

In recent years, it has been shown that 11-vertex metallathiaboranes can catalyse the heterolytic cleavage of H₂.³ It has also been demonstrated that the rhodadecaborane [6-(η⁶-C₆Me₆)-*nido*-6-RhB₉H₁₃] catalyses the cyclotrimerization of alkynes,⁴ and that the dirhodaboranes [2,3-(η⁶-C₆Me₆Rh)₂B₃H₇] and [(η⁶-C₆Me₆Rh)₂B₆H₁₀] catalyse the cycloadditions of alkynes.^{5, 6}

These metallaboranes and metallaheteroboranes often feature M–B–H and B–H–B bonds and it has been suggested that these type of interactions may play a key role in the catalytic activity of, for example, forced *exo-nido* rhoda- and ruthena-dicarbaboranes.^{7, 8}

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Chart 1. Schematics for ten-vertex iridaboranes illustrating their metallaborane skeletons

These examples demonstrate a unique synergy between metal centres and borane fragments in useful catalytic processes, suggesting that such “B-frame” species have great potential for novel chemistry, particularly that involving the activation and modification of small molecules, encouraging, therefore, the further investigation of this type of compound.

Key to progress in this area is the development of synthetic methods to such metallaboranes in high yield, in high purity and with a minimum of effort. The work reported herein focuses on the simple high-yield syntheses of 10-vertex $\{MB_9H_{13}\}$ *nido*-metallaboranes of ruthenium, osmium, rhodium and iridium. In these clusters, the borane fragments act as *polyhapto* non-innocent ligands featuring different reactive centres such as B–H vertices, B–H–B acidic “bridging” hydrogen atoms, and *exo*-polyhedral ligands. The potential for reactivity at these sites provides opportunity for molecular tuning of the metalladecaboranes and the assembly of a range of complexes from a common precursor (*vide infra*). One possibility, that we also report on herein, is the incorporation of further metal centres into the metallaborane framework of the $\{MB_9H_{13}\}$ clusters to form novel bimetallic species. In previous work,^{9, 10} other platinum and palladium bimetallic clusters, prepared from neutral decaborane, demonstrate reversible interactions with small gaseous molecules. We anticipate that the new synthetic methods presented here will ultimately enable progress in this area too.

The new metallaboranes reported herein are characterized by single-crystal X-ray diffraction analysis, mass spectrometry and NMR spectroscopy. We also provide the DFT optimization of the structures of some of the clusters, and include a theoretical analysis of the metal-to-ligand rotational lability in the metalladecaboranes.

Results and discussion

High-yield synthesis of 10-vertex $\{MB_9\}$ *nido*-metallaboranes

The synthesis and characterization of the iridadecaborane compound $[6,6,6-(PPh_3)_2H-nido-6-IrB_9H_{13}]$ (**1**) was first reported some time ago, from the reaction between “Vaska’s compound”, $[IrCl(CO)(PPh_3)_2]$, and $[NMe_4][B_9H_{14}]$ in dichloromethane solution, but the reported yield was low, being around 1%.¹¹ Later, the yield of this product was increased to *ca.* 80% through the reaction of $[IrCl(PPh_3)_3]$ with $[NEt_4][B_9H_{14}]$.¹² In addition, a number of minor components were formed, which required separation by preparative thin-

layer chromatography (TLC). In contrast, when $[RhCl(CO)(PPh_3)_2]$ or $[RhCl(PPh_3)_3]$ was used it was not possible to isolate any rhodaborane products; alternatively, small yields, *ca.* 5%, of $[Cl(cod)-nido-MB_9H_{13}]$ were formed from the reaction of $\{MCl(cod)\}_2$ (*cod* = cyclooctadiene) with $[B_9H_{14}]^-$ (*M* = Ir, Rh).¹¹

Here, we report that the addition of the metal complexes $[IrCl(PPh_3)_3]$, $[RhCl(PPh_3)_3]$, $[RuCl(CO)H(PPh_3)_3]$ and $[OsCl(CO)H(PPh_3)_3]$ to stirred diethyl ether solutions of excess $K[B_9H_{14}]$ give the *nido*-metalladecaborane cluster compounds $[6,6,6-H(PPh_3)_2-nido-6-MB_9H_{13}]$ (*M* = Ir (**1**), Rh (**2**)), and $[6,6,6-(CO)(PPh_3)_2-nido-6-MB_9H_{13}]$ (*M* = Ru (**3**), Os (**4**)). Compounds **1**, **2**, **3** and **4** precipitate from the diethyl ether in their pure form, and are readily isolated by simple filtration in yields of 99%, 98%, 83% and 95%, respectively (Scheme 1).

The convenience of this procedure is, in good measure, derived from the choice of diethyl ether as solvent, in which the starting metal complexes are essentially insoluble, whereas the freshly prepared potassium salt of the nonaborane, $K[B_9H_{14}]$, is completely soluble (as opposed to the previously used alkylammonium salts of $[B_9H_{14}]^-$, which are insoluble in diethyl ether). Under these heterogeneous reaction conditions, the resulting 10-vertex product metallaboranes precipitate upon formation. Thus, the target compounds are immediately isolated in the reaction medium, minimizing potential side reactions with the solvent or reactants, and eliminating the requirement for laborious and material-consuming silica gel preparative TLC purification. A further utility of this new synthetic method is its potential for the preparation of novel species, such as $[6,6,6-H(PPh_3)_2-nido-6-RhB_9H_{13}]$ (**2**) and the *bis*- PPh_3 -ligated ruthenadecaborane (**3**), that are otherwise highly unstable in solution at room temperature and therefore cannot be prepared by previously reported synthetic methods. Here, orange-coloured **2**, which precipitates immediately on its formation, can be stored in a freezer for months without change.

The *nido*-osmadecaboranyl compound **4**, isolated by our method in 95% yield, was originally obtained as a very minor side-product isolated from the reaction between $Na[B_5H_8]$ and $[OsCl(CO)H(PPh_3)_3]$, its molecular structure revealed by a single-crystal X-ray diffraction analysis.¹³ Here, the high-yield synthesis of **4**, from the readily available $B_{10}H_{14}$ (via the $K[B_9H_{14}]$ anion) rather than from the rare and difficult-to-handle $Na[B_5H_8]$,¹⁴ enables access to its further chemistry.

Scheme 1 Synthesis of $\{MB_9\}$ *nido*-metallaboranes **1**, **2**, **3** and **4**.

NMR studies of compounds 1 to 4. As mentioned above, compound **1** was characterized previously by multielement NMR spectroscopy and by single-crystal X-ray diffraction.⁹ A detailed assignment of the resonances for the rhodaborane **2** is complicated by the fact that it is unstable in solution, and it appears to react with those solvents in which it is soluble, *viz.* CD_2Cl_2 , $CDCl_3$ and tetrahydrofuran- d^8 . Its proton NMR characterization is possible at ≤ 253 K. However, the reduced rate of molecular tumbling due to the lower temperature causes a considerable broadening in the already broad boron resonances, thereby precluding the application of 2D NMR techniques in their assignments.

The similarity of the proton spectra of compounds **1** and **2** (Figure S1) in the high-field region indicate that the two clusters are isostructural. Similarly, the boron spectra are directly comparable with only the resonance due to the B2 vertex adjacent to the rhodium atom showing a shift to lower field. Relevant NMR data for **1**, **2**, **3** and **4** are gathered in Table 1, and Figure 1 shows a graphical comparison between the ^{11}B NMR spectra of the *nido*-6-metalladecaboranes and the nonaborane anion precursor. In addition, Figures S1 to S6, Figure S8, and Figures S10 to S13 illustrate some MNR spectra for these 10-vertex metalladecaboranes.

All the metalladecaboranes exhibit similar patterns in their ^{11}B NMR spectra, with resonances spanning $\delta_B +17.4$ to -30.0 ppm. The signals corresponding to the cluster B1, B3, B5, B7 and B9 atoms, are found between $+17.4$ and $+5.6$ ppm. At lower frequencies, between 0.0 and -5.0 ppm, we find the signals of the B8 and B10 vertices with the lowest ^{11}B frequency resonances corresponding to the B2 and B4 atoms.

The highly delocalized three-dimensional bonding in these types of polyhedral boron-containing compounds, transfers the electronic effects of the asymmetric metal-borane conformation throughout the cage, such that all the cluster vertices are influenced by the bonding to the metal centres.

Consequently, we should note that the resonances of the B(5,7) vertices, which are equivalent in the symmetric conformer (schematics I in Chart 2), split into two signals (the highest frequency corresponds to B5) with chemical shift differences spanning 3.7 to 7.4 ppm.

Figure 1. From bottom to top, representation of the ^{11}B NMR spectra of $[B_9H_{14}]^-$, **2**, **1**, **3** and **4**. Dashed lines connect equivalent positions.

Chart 2. Symmetric, I, and asymmetric, II, conformers for **1** and **2**

The B(1,3) and B(8,10) pairs are similarly split, collectively affording four ^{11}B peaks, confirming an asymmetric molecular structure in solution (schematics II in Chart 2), although the chemical shift differences are smaller than those found for the B5 and B7 ^{11}B signals.

The lower-frequency resonances of B2 and B4 are consistent with boron atoms that lie *trans* to B–H–B bridging hydrogen atoms on the open faces of the polyhedral boron-containing cluster.¹⁵ It may be noted that the compounds containing 2nd row elements Rh **2** and Ru **3** show a relative deshielding of the B2 resonance compared to B4 of 8.3 and 5.6 ppm, respectively, whereas this is not evident in the 3rd row iridium and osmium compounds **1** and **4**.

The 1H NMR spectra of **1**, **2**, **3** and **4** also reflect the asymmetric structure of the clusters in solution. Thus, the metalladecaboranes exhibit nine *exo*-terminal proton resonances ranging $+5.50$ to -1.23 ppm. Of these terminal hydrogen peaks the lowest frequency resonances between -0.22 and -1.23 ppm found for **1**, **2**, **3** and **4**, are due to the B2–H_t proton. The X-ray crystallographic molecular structure, described in the next section for **3**, reveals that the H(2) atom occupies a region where the local magnetic field of the aromatic phenyl rings opposes the main magnetic field, H_0 , leading to a shielding of the nucleus and a shift to lower frequency, compared to the rest of the B–H_t proton resonances.

The resonances due to the bridging hydrogen atoms on the boat-type hexagonal faces of the metalladecaboranes are well resolved in the negative region of the 1H - $\{^{11}B\}$ spectra. The 1H signals assigned to the hydrogen atoms along the M6–B5 and M6–B7 edges are found between -4.91 and -11.14 ppm, whereas those proton resonances corresponding to the B8–μH–B9 and B9–μH–B10 bridging hydrogen atoms appear at significantly higher frequencies, in the -3.08 to -4.67 ppm range.

In Table 1, it may be seen that the proton signals, assigned to the M6–H–B7 bridging hydrogen atoms, which lie *trans* either to the hydride or to CO ligands in **1** and **2**, in **3** and **4**, respectively, shift to higher frequencies with respect to the M6–H–B5 bridging hydrogen atoms that are *trans* to a PPh_3 ligand. This chemical shift difference is *ca.* 4.5 ppm for the hydride-ligated clusters, and around 1.6 ppm for the carbonyl-ligated compounds. Similar to the ^{11}B spectra, the chemical shift differences of hydrogen atoms that are equivalent in the symmetric conformation, Schematic structure I, reflect the

electronic asymmetry induced by the metal-to-nonaborane linkage (Schematic II).

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Table 1 ^{11}B - $\{^1\text{H}\}$, ^1H - $\{^{11}\text{B}\}$, and ^{31}P - $\{^1\text{H}\}$ NMR data for $[(\text{PPh}_3)_2\text{HMB}_9\text{H}_{13}]$ (M = Ir **1**, Rh **2**) and $[(\text{CO})(\text{PPh}_3)_2\text{MB}_9\text{H}_{13}]$ (M = Ru **3**, Os **4**) in CD_2Cl_2 solution together with DFT/GIAO-Calculated ^{11}B -Nuclear Shielding, given in brackets.

Assignment ^a	Ir(1)		Rh(2)		Ru(3)		Os(4)	
	$\delta(^{11}\text{B})$	$\delta(^1\text{H})$	$\delta(^{11}\text{B})$	$\delta(^1\text{H})$	$\delta(^{11}\text{B})$	$\delta(^1\text{H})$	$\delta(^{11}\text{B})$	$\delta(^1\text{H})$
5	+14.3 [+12.1]	+4.81	+15.2 [+17.3]	+4.43	+17.4 [+19.1]	+4.22	+13.0 [+10.7]	+4.83
1	+11.2 [+9.4]	+4.19	+13.1 [+16.1]	+3.84	+12.7 [+16.4]	+3.65	+11.1 [+10.1]	+4.34
7	+9.1 [+11.5]	+5.50	+11.5 [+16.9]	+3.46	+10.0 [+12.4]	+4.47	+7.4 [+11.5]	+5.19
3	+8.1 [+5.2]	+4.07	+8.3 [+9.6]	+3.14	+9.2 [+10.6]	+3.31	+7.4 [+8.1]	+3.96
9	+6.8 [+2.1]	+3.05	+6.7 [+6.9]	+2.99	+5.6 [+5.9]	+2.41	+6.0 [+11.5]	+2.44
8	-0.4 [+4.7]	+2.24	+1.3 [+0.2]	+2.08	-0.2 [+0.3]	+2.70	-0.5 [+4.6, +1.0]	+2.59
10	-4.9 [+8.6]	+2.24	-4.9 [+4.4]	+1.11	-4.0 [+4.2]	+2.45	-3.9 [+4.3, -7.4]	+2.49
2	-27.4 [+21.8]	-1.23	-18.7 [+9.3]	-1.14	-23.6 [+16.7]	-0.22	-29.7 [+26.3]	-0.33
4	-27.4 [+29.9]	+2.14	-27.0 [+23.3]	+1.06	-28.0 [+25.3]	+1.44	-30.0 [+32.3]	+1.94
$\mu\text{H}(8,9)^a$		-3.85		-3.08		-3.98		-4.52
$\mu\text{H}(9,10)^a$		-4.67		-4.17		-4.14		-4.67
$\mu\text{H}(6,7)$		-6.65		-4.91 ^b		-8.61		-8.88
$\mu\text{H}(5,6)$		-11.14		-9.65 ^c		-10.23 ^d		-10.47 ^e
H(6)		-12.31		-10.17 ^f				
$\delta(^{31}\text{P})^g$								
1	+19.2		+50.4 ^h		+45.3 ⁱ		+15.0	
2	+14.6[21]		+35.8 ^j		+43.4[56]		+8.8[17]	

^a Assignments supported by ^1H - $\{^{11}\text{B}_{\text{selective}}\}$ experiments and DFT calculations. ^b Phosphorus decoupling does not affect the half-height peak width 57 Hz (compared to the H(8,9) H(9,10) resonances of 36 Hz and 49 Hz for the broad H(5,6)), thus the broadness of the peak is not due to unresolved ^{31}P coupling. ^c Broad doublet $^2J(^{31}\text{P}-^1\text{H})_{\text{trans}}$ 72.5 Hz with probable unresolved coupling to ^{103}Rh and possibly $^2J(^1\text{H}-^1\text{H})_{\text{trans}}$. ^d Doublet, $^2J(^{31}\text{P}-^1\text{H})$ 36.5 Hz. ^e Broad doublet $^2J(^{31}\text{P}-^1\text{H})$ 40 Hz. ^f Complex multiplet; apparent overlapping triplets: $^2J(^{31}\text{P}_{\text{cis}}-^1\text{H}_{\text{cis}})$ ca. 15.5 Hz, $^2J(^{31}\text{P}_{\text{trans}}-^1\text{H}_{\text{trans}})$ ca. 15.5 Hz, $^1J(^{103}\text{Rh}-^1\text{H})$ ca. 16 Hz. The ^{31}P decoupled spectrum shows an apparent triplet, meaning that the rhodium and *trans* hydride couplings are approximately equal. ^g Doublets, couplings, $^2J(^{31}\text{P}-^{31}\text{P})$ in square brackets. ^h Doublet of doublets, $^2J(^{31}\text{P}-^{31}\text{P})$ 26 Hz, $^1J(^{103}\text{Rh}-^{31}\text{P})$ 133 Hz. ⁱ 292 K, CD_2Cl_2 . ^j Doublet of doublets, $^2J(^{31}\text{P}-^{31}\text{P})$ 26 Hz, $^1J(^{103}\text{Rh}-^{31}\text{P})$ 99 Hz.

X-ray analysis of 3. The molecular structures of compounds **1**¹¹ and **4**,¹³ as determined by single-crystal X-ray diffraction analyses, have been previously reported. Compound **2** proved too unstable in solution to produce suitable crystals for X-ray diffraction. The molecular structure of the ruthenadecaborane **3** was, however, elucidated by single-crystal X-ray diffraction analysis. Figure 2 is a displacement ellipsoid drawing of the molecular structure of **3** together with some selected interatomic distances and angles (for additional structural data see Table S1 in the Supporting Information, SI).

Compound **3** has a basic cluster geometry that can be formally derived from the replacement of the $\{\text{B}_6\text{H}\}$ vertex in the ten-vertex *nido*-decaborane, $\text{B}_{10}\text{H}_{14}$, by a $\{\text{Ru}(\text{CO})(\text{PPh}_3)_2\}$ fragment, making **3** structurally analogous to eight other *nido*-6-monometalladecaboranes catalogued in the Cambridge Structural Database (CSD)¹⁶ that incorporate the metal fragments $\{\text{W}(\text{H})_2(\text{PMe}_2\text{Ph})_3\}$,¹⁷ $\{\text{ReH}(\text{PMe}_2\text{Ph})_3\}$,¹⁸ $\{\text{Ru}(\eta^6-$

$\text{C}_6\text{Me}_6\}$,¹⁹ $\{\text{Os}(\text{CO})(\text{PPh}_3)_2\}$,¹³ $\{\text{Os}(\text{PMe}_2\text{Ph})_3\}$,¹⁷ $\{\text{Co}(\eta^5-\text{Cp}^*)\}$,²⁰ $\{\text{Rh}(\eta^5-\text{Cp}^*)\}$ ²¹ and $\{\text{IrH}(\text{PPh}_3)_2\}$ (**1**)¹¹.

Interatomic distances and angles within the CO-ligated ruthenadecaborane (**3**) are unexceptional, but include the noteworthy structural feature found in all the crystallographically determined 10-vertex metalladecaboranes of elongated B5–B10 and B7–B8 distances of around 2 Å. In **3**, the Ru–P2 bond distance is 0.0075 Å longer than the Ru–P1 bond. The P2Ph₃ ligand is *trans* to the Ru6–H–B5 bridging hydrogen atom, whereas P1Ph₃ is *trans* to the {B2–H} vertex; therefore, the Ru–P bond distance difference may be understood as the result of a slightly stronger *trans* influence of the bridging hydride *versus* the BH vertex.

Figure 2. Drawing of the molecular structure of $[6,6-(\text{CO})(\text{PPh}_3)_2\text{-nido-6-RuB}_9\text{H}_{13}]$ **3** with 50 % probability ellipsoids for non-hydrogen atoms. Selected interatomic distances (Å) from Ru6 to: C1 1.873(3); B2 2.298(3); B5 2.305(3); B7 2.325(3); P1 2.3731(8); P2 2.3806(8); also: B5-B10 2.003(4); B7-B8 2.031(4); B9-B10 1.792(4); B8-B9 1.782(4). Angles (°): P1-Ru-P2 100.77(3); P1-Ru-C1 93.37(7); P2-Ru-C1 89.65(7).

With regard to the Ru6–B distances found in the molecular structure of **3**, it may be noted that the values are slightly greater than the mean value of 2.227 Å, and that they are in the upper quartile, which is defined by the distance of 2.287 Å (CSD search for the Ru–B bond). The distance between the carbonyl ligand and the ruthenium atom at 1.873(3) Å is slightly shorter than the mean value of 1.894 Å, found in the CSD.¹⁶

If we assume that these metal ligand moieties contribute three atomic orbitals and two electrons to the cluster-bonding scheme, then the metal fragments and the {BH} vertex are both isolobal and isoelectronic and, therefore, the *nido*-metalladecaboranes, discussed here all exhibit 12 skeletal-electron pairs ($n+2$, n being the number of vertices): a count that agrees with their 10-vertex *nido*-structures.^{22–25}

Scheme 2. Reactions of **3** and **4** with $\text{cis-}[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$ to afford the bimetallic clusters **5** and **6**

Reactions of **3** and **4** with the *cis*-dichlorobis-(dimethylphenylphosphine)platinum(II) complex

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The high-yield syntheses of the CO-ligated metalladecaboranes, **3** and **4**, enabled the study of their reactivity with $\text{cis-}[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$. We have demonstrated that icosahedral bimetalloboranes that feature adjacent $\{\text{Pt}(\text{PMe}_2\text{Ph})_2\}$ fragments can take up O_2 , CO and SO_2 across the Pt–Pt cluster edge in a process that is reversible thermally or by UV irradiation, opening new opportunities for the activation of small molecules.^{9, 10} The presence of the CO group in the precursors **3** and **4** could, with the addition of $\text{cis-}[\text{PtCl}_2(\text{PMe}_2\text{Ph})_2]$, potentially allow the formation of a bimetallic $\text{M}_1\text{-CO-M}_2$ bridging CO group which might then be expelled thermally to form new structures with possible analogous properties to those in the group 10 bimetalloboranes.

Thus, deprotonation of the metalladecaboranes with lithium triethylborohydride in toluene, and the subsequent addition of the platinum(II) complex (Scheme 2), gave new compounds **5–7**. The products were isolated by column chromatography, and characterized by multielement NMR spectroscopy, MS and X-ray diffraction analysis. The reaction with the ruthenadecaborane afforded $[1,1,1\text{-}(\text{CO})\text{H}(\text{PPh}_3)\text{-isocloso-1-RuB}_9\text{H}_8\text{-}\mu\text{-(1,2)-}\{\text{Pt}(\text{PMe}_2\text{Ph})_2\}]$ (**5**), whereas the osmadecaborane gave $[7,7\text{-(PMe}_2\text{Ph)}_2\text{-9,9,9-(CO)(PPh}_3)_2\text{-nido-7,9-PtOsB}_9\text{H}_{11}\text{].CH}_2\text{Cl}_2$ (**6**) as the major product and $[5,5,5\text{-(CO)(PPh}_3)_2\text{-nido-5-OsB}_9\text{H}_{13}]$ (**7**), obtained as a trace product, for which, however, a single crystal suitable for X-ray diffraction analysis was isolated.

Single-crystal X-ray diffraction analysis of 5 and 6. The molecular structures of compounds **5** and **6** were determined by single-crystal X-ray diffraction analysis. Figure 3 depicts a displacement ellipsoid drawing for **5** together with selected interatomic distances and angles (Tables S2 lists additional distances and angles). The core cluster is of 10-vertex $\{\text{RuB}_9\}$ metallaborane *isocloso* geometry that conforms to an idealized C_{3v} point group. The $\{\text{B}_9\}$ unit binds to the $\{\text{Ru}(\text{H})(\text{PPh}_3)_2\}$ moiety in a *hexahapto* chair configuration. Thus, there are three shorter and three longer Ru–B distances, averaging 2.155(4) and 2.425 Å, respectively.

The molecular geometry of **5** is similar to the previously crystallographically characterized 10-vertex metallaboranes: *ortho*-cycloboronated $[1,1,1\text{-(PPh}_3)\text{H-1}^p,2^c\text{-}\mu\text{-(Ph}_2\text{P-o-C}_6\text{H}_4\text{)Ir-B}_9\text{H}_8]$,¹² butadiene-ligated $[1,1,1\text{-(CH=CH-CH=CH)-1}^p,2^c\text{-}\mu\text{-(Ph}_2\text{PC}_6\text{H}_4\text{)IrB}_9\text{H}_7\text{-5-(PPh}_3)]$,²⁶ *exo*-polyhedrally bound $[1,1,1\text{-(PPh}_3)\text{HClRuB}_9\text{H}_7\text{-5,6-(PPh}_3)_2]$,²⁷ trimetallic $[(\text{PPh}_3)\text{RuB}_9\text{H}_9\text{-}\{\text{RuCl}_2(\text{PPh}_3)_2\}_2]$,²⁸ the hydridoosmaborane $[1,1,1\text{-H(PMe}_2\text{Ph)}_2\text{OsB}_9\text{H}_7\text{-5-(PMe}_2\text{Ph)}]$,²⁹ dianionic $[1,1,1\text{-(CO)}_3\text{WB}_9\text{H}_9]^{2-}$,²⁹ glycol-substituted $[1,1,1\text{-(PPh}_3)\text{HClRuB}_9\text{H}_7\text{-2,3-(OCH}_2\text{CH}_2\text{OH)-5,6-(PPh}_3)_2]$,³⁰ *p*-cymene-ligated $[1\text{-(}\eta^6\text{-pcym)RuB}_9\text{H}_9]$, (where pcym = 1-CH₃-4-CH(CH₃)₂-C₆H₄),³¹ and anilino-substituted $[1\text{-(}\eta^6\text{-C}_6\text{Me}_6\text{)RuB}_9\text{H}_8\text{-2-(NHPh)}]$.³²

Figure 3. Structure of $[1,1,1-(\text{CO})\text{H}(\text{PPh}_3)\text{-isocloso-1-RuB}_9\text{H}_8\text{-}\mu\text{-(1,2)-}\{\text{Pt}(\text{PMe}_2\text{Ph})_2\}]$ **5** with 50 % probability ellipsoids for non-hydrogen atoms. Selected interatomic distances (Å) from Ru1 to: Pt1 2.9152(3); H1 1.93(6); B2 2.091(4); B3 2.183(5); B4 2.191(4); B5 2.412(5); B6 2.424(4); B7 2.438(4); P2 2.2426(10); C1 1.950(4). To Pt1: H1 1.65(6); B2 2.032(4); P1 2.3397(9); P2 2.2426(10). Angles (°): C1–Ru1–P3 88.17(13); P1–Pt1–P2 105.36(3); B2–t1–P1 165.80(12); B2–Pt1–P2 87.36(12); Pt1–Ru1–C1 8.57(12); Pt1–Ru1–P3 106.43(2).

Amongst these metallaboranes, only two compounds exhibit unsubstituted cages, suggesting that the formation of 10-vertex *isocloso* metallaborane clusters is facilitated by the activation of B–H vertices adjacent to the metal, leading to a diversity of boron-substituted derivatives such as *ortho*-cycloboronated, Lewis-base ligated, or metal-fragment coordinated species. Compound **5** exhibits this latter feature, since the central *isocloso* cluster holds an *exo*-polyhedral $\{\text{Pt}(\text{PMe}_2\text{Ph})_2\}$ fragment *via* a Ru–H–Pt bridge and a direct B2–Pt bond. The geometry around the platinum centre is clearly planar, with a dihedral angle of 7° between the $\{\text{Pt1-B2-Ru1}\}$ and $\{\text{P1-Pt1-P2}\}$ planes; and the $\{\text{P1-P2-Pt1-B2-Ru1}\}$ plane is virtually parallel to the $\{\text{Ru1-B2-B8-B6}\}$ plane, which, if we disregard the ligands at the Ru centre, bisects the cluster into two equal parts.

The type of $\{\text{Pt-}\mu\text{-H-Ru}\}$ linkage found in compound **5** has been previously characterized by X-ray diffraction only in the 12-vertex metalladiboraborane, $[(\text{CO})_2\text{-closo-Ru}_2\text{B}_9\text{H}_{11}\text{-}\mu\text{-}\{\text{H}(\text{Pt}(\text{PET}_3))\}]$ (Scheme 3a), and provides a “snapshot” of how some polyhedral boron-based clusters can act as “molecular scaffolds” to the formation of polymetallic assemblies. For example, the palladaborane, $[(\text{PPh}_3)_3(\text{PPh}_2)_2\text{Pd}_4\text{B}_{20}\text{H}_{16}]$, illustrates this concept well; its 21-vertex macropolyhedral $\{\text{PdB}_{20}\}$ -cluster core supporting a tri-metallic $\{(\text{Ph}_3\text{P})\text{Pd}(\text{PPh}_2)\text{Pd}(\text{PPh}_2)\text{Pd}(\text{PPh}_3)\}$ string³⁴ (Scheme 3b). Other interesting examples of this phenomenon are the rhenacarborane, $[(\text{CO})_2\text{-closo-ReCB}_9\text{H}_8\text{-Ph-}\mu\text{-}\{\text{Au}_2(\text{PPh}_3)_2\text{Ir}(\text{CO})_3\}]$, that exhibits a $\{\text{ReIrAu}_2\}$ butterfly cluster bound to a 11-vertex rhenacarborane³⁵ (Scheme 3c), and the hexaruthenium carbonyl, $[(\text{CO})_{15}\text{Ru}_6\text{CB}_8\text{H}_9]$, that features a planar $\{\text{Ru}_6\}$ triangular “raft” formally ligated by a $\{\text{CB}_8\text{H}_9\}$ ⁷⁻ monocarborane (Scheme 3d).³⁶

We can also appreciate the potential of polyhedral “B-frames” for the construction of multimetallic species, in more

recently reported complexes such as $\text{Os}_3(\text{CO})_9[(\text{C}_2\text{B}_{10}\text{H}_8\text{S}(\text{CH}_3))\text{Os}_3(\text{CO})_9(\text{H})]$ and $\text{Os}_3(\text{CO})_9(\text{H})[(\text{C}_2\text{B}_{10}\text{H}_8\text{S}(\text{CH}_3))\text{Os}_3(\text{CO})_9(\text{H})]$, which feature one and two triangular Os_3 clusters, supported on the surface of a twelve-vertex *closo*-carborane, $\{\text{C}_2\text{B}_{10}\text{H}_8\}$ and on an eleven-vertex *nido*-carborane, $\{\text{C}_2\text{B}_{10}\text{H}_8\text{S}(\text{CH}_3)\}$, respectively.^{37, 38}

Compound **6** exhibits an 11-vertex *nido* structure, which is shown in Figure 4 together with selected distances and angles (Table S3, in the SI, lists additional data). Two metal fragments, $\{\text{Os}(\text{CO})(\text{PPh}_3)\}$ and $\{\text{Pt}(\text{PMe}_2\text{Ph})_2\}$, and three $\{\text{BH}\}$ units form an open pentagonal face. The metal moieties occupy non-adjacent positions, and there are two bridging hydrogen atoms along the B10–B11 and Os8–B8 edges. It is a direct analogue of the crystallographically determined heterobimetallic counterparts: *ortho*-cycloboronated $[(\text{Me}_3\text{P})_2\text{Pt}(\text{Ph}_3\text{P})(\text{Ph}_2\text{PC}_6\text{H}_4)\text{H}(\text{IrB}_9\text{H}_{10})]$ ^{26, 39} and the platinaruthena-borane $[(\text{Me}_3\text{P})_2\text{Pt}(\text{isoPrC}_6\text{H}_4\text{Me})\text{Ru-B}_9\text{H}_{11}]$.³¹

This 11-vertex *nido*-structure of **6** can be notionally derived from a 12-vertex icosahedral *closo*-cluster by the removal of one vertex.⁴⁰ However, a formal contribution of two electrons from the $\{\text{Os}(\text{CO})(\text{PPh}_3)_2\}$ and $\{\text{Pt}(\text{PMe}_2\text{Ph})_2\}$ vertices would afford 12 skeletal electron pairs (sep’s) ($\{\text{Os}(\text{CO})(\text{PPh}_3)_2\} = \{\text{Pt}(\text{PMe}_2\text{Ph})_2\} = \{\text{BH}\} = 2\text{e}^-$: 11 units $\times 2\text{e}^-/\text{unit} + 2\text{e}^-/\mu\text{-H} \times 1\text{e}^-/\mu\text{-H} = 24\text{e}^-$), but Wade’s rules predict $(n+2)$ sep’s for a *nido*-metallaborane with n vertices.²⁰⁻²³

We may conclude, therefore, that compound **6** deviates by one skeletal electron pair from the dictates of the structure-electron counting formalism. In this regard, the $\{\text{Pt}(\text{PMe}_2\text{Ph})_2\}$ fragment in **6** is a two-electron donor, isoelectronic with a neutral $\{\text{BH}\}$ unit; however, if we consider that the platinum centre is a *pseudo*-square-planar centre that features a two-orbital interaction with the cluster, then these two fragments are not isolobal and we have discrepancies between the cluster geometry and the electron counting rules.^{41, 42}

Scheme 3. Metallic assemblies supported by boron-based clusters

Figure 4. Structure of [7,7-(PMe₂Ph)₂-9,9,9-(CO)(PPh₃)₂-nido7,9-PtOsB₉H₁₁] **6** with 50 % probability ellipsoids for non-hydrogen atoms (only the *ipso* carbon atoms of the phenyl rings are shown). Selected interatomic distances (Å) from Os9: P3 2.3663(7); P4 2.4115(6); C9 1.860(3); B4 2.266(3); B5 2.314(3); B8 2.379(3); B10 2.356(3). From Pt7: P1 2.3367(7); P2 2.3328(7); B8 2.392(3); B2 2.209(3); B5 2.287(3); B6 2.230(3). Also: C9–O9 1.158(4). Angles (°): P1–Pt7–P2 97.01(3); P3–Os9–P4 102.06(2); C9–Os9–P4 92.50(8); C9–Os9–P3 90.16(9).

Alternatively, the {Os(CO)(PPh₃)₂} fragment is isolobal and isoelectronic with a {BH} vertex, adhering to the 18-electron rules.

NMR analysis of compounds 5 and 6. Relevant NMR data for the platinaruthenaborane **5** are listed in Table 2. The ten-vertex *isocloso*-cluster that forms the core of this compound exhibits three groups of three inequivalent resonances: (i) signals in the range +128 to +87 ppm that correspond to the upper layer of three boron atoms, B2, B3 and B4; (ii) resonances between +25 and +16 ppm, assigned to the lowest layer of boron vertices, B8, B9 and B10; (iii) and three peaks between –6 and –19 ppm that are assigned to the middle layer of boron vertices, B5, B6 and B7 (Figure S16 illustrates the ¹¹B-{¹H} spectrum).

It is interesting to note that the proton resonances on the upper ring B3 and B4 vertices are shifted towards the high-frequency region of the ¹H-{¹¹B} NMR spectrum, in the aromatic region. This high-frequency ¹¹B-to-¹H correlation, found in the inequivalent upper stack of boron vertices, is a spectroscopic signature of 10-vertices *isocloso*-metalladecaboranes, which serve, therefore, as a diagnostic.⁴³

We should expect that the assignments within each closely spaced set of measured resonances are somewhat uncertain. However, DFT-GIAO calculations are helpful here in that, whereas the error in the calculated value of the absolute chemical shift may be as large as the difference between the measured chemical shifts, the relative ordering of the calculated values often follows the pattern seen in the observed chemical shifts.⁴³ Thus, the B4 and B3 resonances at δ_B +89.5 and +86.7 ppm, which have calculated values of δ_B +94.1 and +92.4 ppm, respectively, are a good example. The lower-field boron resonance of δ_B +89.5 ppm has an attached terminal hydrogen atom that exhibits a *higher* field proton resonance at δ_H +8.58 ppm (H4); whereas the relatively higher-field boron, δ_B +86.7 ppm, is bound to the terminal hydrogen atom that gives a lower-field proton signal at +9.36 ppm. The calculated proton resonances mirror this reversal. The assignment is additionally supported by the coupling observed

between the ³¹P nucleus on ruthenium H4, improving the confidence in the calculated data and the assignments (Table 2).

We also note that the B2 vertex does not exhibit ¹J(¹¹B–¹H) coupling, which is indicative of the substitution of the terminal hydrogen atom, in this case by a {Pt(PMe₂Ph)} fragment, as is visible in the molecular structure of **5** as determined by a single-crystal X-ray diffraction analysis.

The ¹H-{¹¹B} spectrum exhibits a doublet of doublets of doublets, with platinum satellites of 450 Hz, at –9.36 ppm. This low-frequency proton multiplet can be assigned with confidence to the bridging Pt–H–Ru hydrogen atom. The ³¹P-{¹H} NMR spectrum shows three singlets at +40.3, –5.3 and –9.1 ppm. The two latter resonances, at low frequencies, exhibit ¹⁹⁵Pt satellites and they are assigned to the {Pt(PMe₂Ph)} fragment, whereas the high-frequency ³¹P resonance corresponds to the {Ru(PPh₃)} moiety (Figure S17 shows the ³¹P-{¹H} spectrum; and Figure S18 ¹H-{¹¹B_{selective}} experiments). The PMe₂Ph ligands are clearly characterized by the four inequivalent doublets, with platinum satellites, that we find at +0.86, +0.93, +2.06 and +2.09 ppm: the first low-frequency doublets are assigned to the methyl groups of the PMe₂Ph ligand that lies *cis* to PPh₃, bound to the Ru centre, and the high-frequency pair to the methyl groups of the other phosphine, *trans* to PPh₃. We make this assignment based on the stereochemistry found in the X-ray diffraction analysis and on DFT calculations. Figure 3 illustrates that the methyl groups on P1 lie within the magnetic shielding cones of phenyl rings on P2 and P3. This is consistent with the methyl resonances on P1 that appear at *ca.* +0.9 ppm compared to the CH₃ resonances on the P2Me₂Ph ligand of *ca.* +2.1 ppm. Calculated Gauge Independent Atomic Orbitals (GIAO) ¹H nuclear shieldings are not as accurate compared to ¹¹B shieldings, but trends can be useful. In the case of compound **5**, the DFT/GIAO-calculated proton data show that the proton resonances of the methyl groups corresponding to P1Me₂Ph are shielded by *ca.* 1.7 ppm with respect to those on P2Me₂Ph, thus supporting the proposed effect of the phenyl ring shielding cone.

For the 11-vertex platinaosmaundecaborane **6**, we were unable to collect complete NMR data on a pure sample. Nevertheless, we can report that the ¹¹B NMR spectrum exhibits six signals in the region between +30 and –35 ppm; some of the peaks are the result of overlapping resonances, giving an uncertain relative intensity ratio (see Figure S19).

Collectively, the NMR data obtained for both **5** and **6** suggest that their molecular structures in solution are consistent with their solid-state structures.

Single-crystal X-ray diffraction analysis of 7. Figure 5 depicts the molecular structure of **7**, together with some selected distances and angles (Figure S4 gathers additional data). Compound **7** is a 10-vertex *nido*-5-osmadecaborane, which can be notionally formed by the substitution of the {B5–H} vertex in the *nido*-B₁₀H₁₄ cluster with the {Os(CO)(PPh₃)₂} fragment.

Table 2. ^{11}B , ^1H (^{11}B), and ^{31}P (203 K) NMR data for $[1,1,1\text{-(CO)H(PPh}_3\text{)}_2\text{-isocloso-1-RuB}_9\text{H}_8\text{-}\mu\text{-(1,2)-(Pt(PMe}_2\text{Ph)}_2\text{)}_2]$ (**6**) in CD_2Cl_2 solution, 292 K, together with DFT/GIAO-calculated Nuclear Shielding, given in brackets.

Assignment	$\delta(^{11}\text{B})/\text{ppm}$	$\delta(^1\text{H})/\text{ppm}$
2	+128.3 [+121.1]	--- (Pt)
4	+89.5 [+94.1]	+8.58 ^a [+9.18]
3	+86.7 [+92.4]	+9.36 [+9.86]
10	+25.9 [+29.6]	+4.43
9	+25.0 [+28.3]	+3.45
8	+16.5 [+17.4]	+3.43
6	-6.1 [-0.4]	+1.73
7	-16.7 [-14.8]	+1.52
5	-18.5 [-15.1]	+1.57
μH		-9.05 ^b
P1Me ₂ Ph ^c		+0.86, +0.93
P2Me ₂ Ph ^d		+2.06, +2.09
	$\delta(^{31}\text{P})$	
P3 ^e	+40.3	
P2 ^f	-5.3	
P1 ^g	-9.1	

^a Doublet; probably $^3J(^{31}\text{P}_3\text{-}^{11}\text{H})_{\text{cis}} = 31\text{ Hz}$. ^b Doublet of doublet of apparent triplets, $^2J(^{31}\text{P}_2\text{-}^{11}\text{H}) = 16\text{ Hz}$, $^2J(^{31}\text{P}_1\text{-}^{11}\text{H})_{\text{trans}} = 64.5\text{ Hz}$, $^2J(^{195}\text{Pt-}^{11}\text{H}) = 458$. ^c Doublets $^2J(^{31}\text{P-}^{11}\text{H}) = 7.5\text{ Hz}$, $^3J(^{195}\text{Pt-}^{11}\text{H}) = 48\text{ Hz}$. ^d Doublets $^2J(^{31}\text{P-}^{11}\text{H}) = 10.2\text{ Hz}$, $^3J(^{195}\text{Pt-}^{11}\text{H}) = 50\text{ Hz}$. ^e Sharp singlet. ^f Sharp singlet, $J(^{195}\text{Pt-}^{31}\text{P}) = 4057\text{ Hz}$. ^g Broad singlet, probably P1, $J(^{195}\text{Pt-}^{31}\text{P}) = 2049\text{ Hz}$.

In its molecular structure, we observe a slightly larger difference in the M–P distances than in **3**, being longer for the PPh_3 ligand that lies *trans* to the {B2–H} vertex, in comparison to that *trans* to the {B10–H} vertex. This difference suggests a somewhat stronger *trans* influence for the B2 vertex than for B10. The OC–Os distance at 1.878(3) Å is below the mean value of 1.902 Å found in the CSD for OC–Os distances.

Figure 5. Molecular structure of $[5,5,5\text{-(CO)(PPh}_3\text{)}_2\text{-nido-5-OsB}_9\text{H}_{13}]$ (**7**) (only the *ipso* carbon atoms of the phenyl rings are only shown). Selected interatomic distances (Å) from Os5: P1 2.3862(8); P2; 2.4043(9); C1 1.878(3); B6 2.247(4); B10 2.385(4); B2 2.334(4); B1 2.294(4); also: B7–B8 1.964(7). Angles (°): P1–Os5–P2 94.94(3); C1–Os5–P1 87.59(11); C1–Os5–P2 99.29(11); B1–Os5–C1 76.10(15); B6–Os5–C1 134.25(16); B10–Os5–P1 173.55(11); B2–Os5–P2 158.94(12).

The *nido*-5-metallaborane cluster geometry evident in **7** is known for the following metal fragments: $\{\text{Fe}(1,3,5\text{-Me}_3\text{-}\eta^6\text{-C}_6\text{H}_3)\}$,⁴⁴ $\{\text{Co}(\eta^5\text{-Cp})\}$,⁴⁵ $\{\text{Rh}(\eta^5\text{-Cp}^*)\}$ and $\{\text{Ir}(\eta^5\text{-Cp}^*)\}$.^{46, 47} According to some electron-counting procedures,^{22–25} these transition-element moieties (and others described above that include $\{\text{Ru}(\text{CO})(\text{PPh}_3)_2\}$ in **3** and $\{\text{Os}(\text{CO})(\text{PPh}_3)_2\}$ in **6**) provide two electrons (Number of valence shell electrons on the metal + No. of electrons from ligands – 12) to the skeletal bonding of the metalladecaboranes.

Some mechanistic considerations

Theoretical calculations. The 10-vertex *nido*-metalladecaboranes, **1**, **2**, **3**, and **4** reported here uniformly exhibit asymmetric metal-to-nonaborane configurations in solution and in the solid state (for those clusters studied by X-ray diffraction). This indicates that the asymmetric ligand distribution about the metal centres is more stable than the symmetric configuration. This is supported by DFT calculations, which show that the energy for the asymmetric conformer of the hydridoiridadecaborane, **1**, is 6.2 kcal/mol lower than the symmetric configuration. For the rhodadecaborane counterpart, **2**, this difference rises to 8.4 kcal/mol, whereas the asymmetric conformer of the CO-ligated ruthenadecaborane **3** is 5.0 kcal/mol more stable than the symmetric.

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Figure 6. Variation of energy and the PH_3 -Rh6 distances in the relaxed PES scan upon the rotation of the $\{\text{M}(\text{H})(\text{PH}_3)_2\}$ ligand sphere, where $\text{M} = \text{Rh}$, in the PH_3 -ligated hydridorhodadecaborane model, $[6,6,6-(\text{H})(\text{PH}_3)_2\text{-nido-RhB}_9\text{H}_{13}]$, using as a reference the torsion angle defined by $\text{B}_9\text{-B}_4\text{-Rh6-P1}$. (n.b. to reduce the computational load, H atoms were used instead of phenyl rings on the PPh_3 ligand)

The metal-to-borane linkage is often non-rigid in metallaboranes and metallaheteroboranes, giving rise to diverse fluxional and/or isomerization processes.⁴⁸⁻⁵⁵ In particular, the rotation of a metal moiety around a face-bound borane/heteroborane fragment is a mechanism that can explain the fluxional behaviour of some polyhedral metallaborane clusters.⁵⁶⁻⁶³ We have recently reported that metal-to-borane rotation can have an effect on the lability of the metal-bound *exo*-polyhedral ligands, and hence the opening of coordination sites for ligand substitutions.⁶⁴ The isomerization of the metal *exo*-ligand symmetric conformer in *ortho*-cyclometallated $[6\text{-H-6-(PPh}_3\text{)}-\mu\text{-6}^p, 5^c\text{-(PPh}_2\text{-ortho-C}_6\text{H}_4\text{)}\text{-nido-6-IrB}_9\text{H}_{12}]$ to its asymmetric isomer,⁶⁵ suggests that rotation of the metal vertex with respect to the $\{\eta^3\text{-B}_9\text{H}_{13}\}$ fragment in **1**, **2**, **3** and **4** is a feature worthy of study. We therefore modelled the rotation of the *exo*-polyhedral ligand sphere by performing a DFT-calculated relaxed Potential Energy Surface (PES) scan of the system, in which the PPh_3 ligands are replaced by PH_3 in order to save computational time.

As depicted in Figure 6, we varied the torsion angle defined by $\text{B}_9\text{-B}_4\text{-Rh6-P1}$ from -7.4° (first point in Figure 6) to 242.6° (final point in Figure 6) in 50 increments of 5° (51 points); the result is an anticlockwise rotation of the *exo*-polyhedral metal ligands with respect to the $\eta^3\text{-B}_9\text{H}_{13}$ fragment. The energy profile of this dynamic process is essentially symmetric between the two enantiomeric asymmetric conformers that exhibit the lowest energy values (0 kcal/mol) along the rotational coordinate.

As the angle increases, from the first low-energy asymmetric conformer, the energy rises to reach a maximum of +14.1 kcal/mol. In the structure of the resulting high-energy conformer, the P2H_3 ligand lies *pseudo-trans* to the Rh6-H-B7 edge, the hydride ligand *pseudo-trans* to the B2 vertex and the P1H_3 ligand *pseudo-trans* to the B5 unit.

In view of this profile, it is reasonable that the energy increase corresponds to the approach of the Rh-PH_3 vectors of the $\{\text{RhH}(\text{PH}_3)_2\}$ unit to the B7-H-Rh6 edge and the B2 vertex.

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Scheme 4. Reactions pathways proposed for the formation of **1** and **2** (path A); for **5** (path B); and for **6** (path C).

In this regard, the M–H (M = Rh or Ir) and Ru–CO bond distances increase significantly when the rotation approaches the high-energy asymmetric conformer. This elongation is concomitant with the occupation of the *endo*-space *pseudo-trans* to the B2 vertex (see Figures S21 and S22).

In addition, the M–B distances are longer in the high-energy conformers compared to the low-energy rotamers, with the M–B2 linkage being always the shortest on the metal-to- η^3 -B₉H₁₃ allyl-type interaction.

In summary, the strengthening of the metal-ligated *exopolyhedral* ligands appears to compensate for the concomitant weakening of the metal-to-nonaborane interaction, which the PES demonstrates for the high-energy conformers.

Reaction types and pathways. The formation of the hydridometalladecaboranes, **1** and **2**, implies the addition of the metal center to the {B₆B₇B₈} allyl-type side of the hexagonal open face of the *nido*-[B₉H₁₄][−] anion. The reaction most likely involves the nucleophilic displacement of the chloride ligand, in the square-planar M(II) complexes, [MCl(PPh₃)₃], where M = Rh or Ir, affording a three-centre B–

M–B link, which could open the route for the oxidative addition of one of the *endo/bridging* hydrogen atoms to the metal.

This oxidative process is likely to proceed in a concerted fashion with hydrogen migration on the open face of the borane anion accompanied by the substitution of one PPh₃ ligand. The fluxional nature of the five *endo/bridging* hydrogen atoms, on the hexagonal chair-type open face, should facilitate the approach and “accommodation” of the metal centres on the η^3 -boron face, leading to the formation of the final 10-vertex clusters (Scheme 4, A). It is noteworthy that in the case of [MCl(CO)H(PPh₃)₃], where M = Ru or Os, the reactions proceed with the formal substitution of the chlorine and hydride ligands. The former affords KCl, whereas H[−] can abstract a proton from the boron cage to give H₂(g).

The deprotonation of **3** and **4** with two equivalents of KBHET₃ potentially leads to [6,6,6-(CO)(PPh₃)₂-*nido*-6-MB₉H₁₁]^{2−} dianions. Subsequent addition of the platinum(II) complex would then result in nucleophilic displacement of halide ligands by the metalladecaborane anions. However, the

structures of the final products **5**, **6** and **7**, indicate that the initial metalladecaborane anions and/or reaction intermediates undergo cluster transformations, the nature of which depend on the starting *nido*-6-metalladecaboranes, **3** and **4**. Thus, for the formation of **5**, loss of H₂ and PPh₃ is a possible route toward a [(CO)(H)(PPh₃)RuB₉H₉][−] species.

Assuming its transient formation, this *isocloso*-anion could react with the platinum(II) complex, substituting the chlorine ligands and undergoing boron metalation to form the final {Pt1–B2–Ru1} linkage (Scheme 4 B). This reaction implies the substitution of the terminal B2–H hydrogen atom and its formal migration to the Pt1–Ru1 edge.

The electrophilic attack of the platinum complex on the hexagonal open face of the presumed *nido*-6-osmadecaborane anion would afford an 11-vertex osmaplatinaborane featuring adjacent metal centres. Therefore, the formation of **6** implies a rearrangement of the initial 10-vertex anion or some other intermediate. Given the fact that we have characterized **7** as a *nido*-5-osmadecaborane, it is reasonable to propose that the *nido*-6-osmadecaborane anion may undergo a vertex-swing,^{47, 66–69} as illustrated in Scheme 4 C, which transforms the metal centre from a vertex coordinated to three boron units into an osmium centre linked to four boron vertices. This hypothetical *nido*-5-anion could substitute the chlorine ligands of the platinum complex and liberate a proton to finally form **6**, which exhibits the metal centres apart, forming the pentagonal face of the 11-vertex cluster.

Experimental

General procedures

Reactions were carried out under an argon atmosphere. Metal starting materials were prepared according to literature methods [IrCl(PPh₃)₃], [RhCl(PPh₃)₃],⁷⁰ [OsCl(CO)H(PPh₃)₃],⁷¹ [RuCl(CO)H(PPh₃)₃].⁷¹ Dry and oxygen-free solvents were obtained using an Innovative Technology Inc. Solvent Purification System. Et₂O was stored over 3 Å molecular sieve in a glass bulb with a Young's tap. Preparative thin-layer chromatography (TLC) was carried out using 1 mm layers of silica gel G (Macherey-Nagel Silica Gel G/UV254) made from water slurries on glass plates of dimensions 20 × 20 cm and dried in air at 80 °C. Infrared spectra were on a Nicolet Nexus 670 FTIR spectrometer using KBr discs or a Perkin-Elmer Spectrum 100 spectrometer, using a Universal ATR Sampling Accessory. NMR spectra were recorded on JEOL 600 MHz and Bruker Avance 300-MHz and AV 400 and 500 MHz spectrometers, using ¹¹B, ¹¹B-{¹H}, ³¹P-{¹H}, ¹H, ¹H-{¹¹B} and ¹H-{¹¹B(selective)} techniques. ¹H NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported in ppm relative to tetramethylsilane. ¹¹B chemical shifts are quoted relative to [F₃B(OEt₂)] and ³¹P chemical shifts are quoted relative to 85% aqueous H₃PO₄. Mass spectrometric data were recorded on an LTQ Orbitrap XL hybrid mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with an electrospray ion source. The mobile phase was acetonitrile flowing at 100 µL/min. The

sample was dissolved in chloroform/acetonitrile and injected using a 5-µL loop into the mobile phase. Spray voltage, capillary voltage, tube lens voltage, and capillary temperature were 4.9 kV, 35 V, 145 V, and 275 °C, respectively. The spectra were recorded at the resolution of 100,000.

X-ray diffraction. Single crystals of the compounds were obtained by diffusion of hexane into 1,2-dichloroethane, dichloromethane, or chloroform solutions of the compounds. Intensities were collected following standard procedures. For compound **3** intensities were integrated and corrected for absorption effects using the SAINT-PLUS and SADABS programs,^{72, 73} included in the APEX2 package. The structure was solved by the Patterson method with SHELXS-97 and refined by full-matrix least-squares on *F*² with SHELXL-2014,⁷⁴ under WinGX.⁷⁵ The selected crystal was a twin, which was analysed with Cell_Now,⁷⁶ assigning the collected reflections to three domains. The twin analysis, resolution and refinement details of compound **3** are gathered in the SI.

Most C–H hydrogen atoms were placed in calculated positions with fixed isotropic displacement parameters 1.2U_{eq}(C). Collection and refinement data are listed in Table 3. For compounds **5**, **6** and **7** data collection, integration and analytical absorption corrections were performed with CrysAlisPro software.⁷⁷ The structures were solved by the dual-space SHELXT method⁷⁸ and refined as for compound **3**, using SHELXL-2018.⁷⁴

DFT calculations. Calculations were performed using the *Gaussian 09* package.⁷⁹ Some structures were modelled using H atoms rather than phenyl groups on the PPh₃ ligands in order to reduce the computation time. The structures were initially optimized using standard methods with the STO-3G basis set for B, P and H, and the LANL2DZ basis set for the Rh, Ir, Ru, Os and Pt atoms. The final optimizations, including frequency analyses to confirm the true minima, together with GIAO NMR nuclear-shielding predictions, were performed by the B3LYP methodology with the 6-31G* and LANL2DZ basis sets. Calculated ¹¹B shielding values were related to chemical shifts by comparison with the computed value for B₂H₆ which was taken to be δ(¹¹B) + 16.6 ppm relative to the [F₃B(OEt₂)] = 0.0 ppm standard. Tables S5 to S22 list the coordinates of optimized geometries.

[6,6,6-H(PPh₃)₂-*nido*-6-IrB₉H₁₃] (1). B₁₀H₁₄ (0.600g, 4.9 mmol), KOH (90%, 0.31 g, 5.5 mmol), and MeOH (12 ml) were stirred overnight in a two-neck 100ml round-bottom flask. Next morning, the solvent was removed (rotary evaporator, water bath at ambient temperature) and then dried further on a Schlenk line for 1 h (2 × 10^{−2} mm Hg). The contents were then dissolved in deionised water and K₂CO₃ added for salting out purposes and then extracted three times with Et₂O. The combined extracts were dried with anhydrous K₂CO₃, filtered and dried on the rotary evaporator and then on the Schlenk line. The round-bottom flask was refilled with argon and [IrCl(PPh₃)₃] (1.0034 g, 0.9890 mmol) added and the system evacuated. Et₂O (ca. 75 ml) was condensed into the flask and stirred after thawing. A weak orange ether solution together with solid was formed. Within a few minutes of stirring a small amount of the yellow solid product was evident. After stirring

overnight, the resultant yellow mixture was filtered through a glass frit and washed well with ether. After drying on the Schlenk, 0.8106 g of **1** (yellow, 0.983 mmol, 99.4%) was obtained. The NMR data demonstrated that the isolated product was **1**.

[6,6,6-H(PPh₃)₂-nido-6-RhB₉H₁₃] (2). The rhodadecaborane was prepared following the same procedure described for **1** (81 mg, KOH, 0.187 g, 3.3 mmol and B₁₀H₁₄ 0.187 g, 1.53 mmol, and 15 ml MeOH). However, after obtaining the Et₂O (75 ml) solution of K[B₉H₁₄] as above, it was then cooled to –25 °C before adding [RhCl(PPh₃)₃] (0.706 g, 0.763 mmol). After stirring overnight and washing with Et₂O, H₂O and then a small

amount of MeCN to remove the water, **2** (orange, 0.5528 g, 0.748 mmol, 98%) was obtained as an orange powder after drying on the Schlenk. FTIR (ATR) (s, strong, sh, shoulder, w, weak)/cm⁻¹: ν(BH) 2510s, 2542sh, 2579sh, ν(RhH) 2084w. (Figure S7). LRMS (ESI⁺): m/z 762 [M + H + Na]⁺ (isotope envelope corresponding to the parent ion [C₃₆H₄₄B₉NaP₂Rh]⁺); HR-MS (ESI⁺): m/z 763.27030 [M + H + Na]⁺, calcd for [C₃₆H₄₄B₉NaP₂Rh]⁺; measd m/z 763.27143.

Table 3. X-ray crystallographic collection^a and refinement data.

Compound No.	3	5	6	7
CCDC deposition no.	2097079	2103311	2103312	2103313
Empirical formula	C ₃₇ H ₄₃ B ₉ OP ₂ Ru	C ₅₃ H ₆₃ B ₉ OOSp ₄ Pt·0.85C ₂ H ₄ Cl ₂	C ₃₅ H ₄₆ B ₉ OP ₃ PtRu	C ₃₇ H ₄₃ B ₉ OOSp ₂ ·0.76CHCl ₃
M (g mol ⁻¹)	764.01	1421.44	969.08	944.85
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$	P2 ₁	P $\bar{1}$
Crystal size /mm	0.32×0.30×0.20	0.24×0.16×0.06	0.21×0.10×0.04	0.18×0.09×0.04
a /Å	10.562(3)	9.7993(2)	11.49283(13)	11.9431(3)
b /Å	15.544(5)	13.3272(2)	16.98921(13)	12.4326(3)
c /Å	22.521(8)	22.1505(4)	11.52564(15)	15.0763(3)
α /°	89.307(7)	82.1298(14)	90	84.5650(17)
β /°	88.185(4)	81.7826(15)	116.8368(15)	78.068(2)
γ /°	89.273(5)	87.9309(15)	90	71.413(2)
V / Å ³	3695(2)	2835.72(9)	2008.05(4)	2074.98(9)
Z	4	2	2	2
μ /mm ⁻¹	0.542	10.807	10.796	8.119
Measured reflns	98919	78764	28920	57342
R _{int}	0.0484	0.0361	0.0256	0.0512
Data/restraint/parameters	18360 / 64 / 911	10033 / 410 / 799	6668 / 1 / 484	7334 / 363 / 613
R (on F; F ² > 2σ)	0.0383	0.0182	0.0151	0.0244
R _w (on F ² ; all data)	0.0925	0.0430	0.0341	0.0586
GoF on F ²	1.037	1.079	1.051	1.037
Max, min Δρ / e Å ⁻³	0.880 and –0.896	0.93 and –0.57	0.34 and –0.31	1.77 and –0.83
Flack parameter	---	---	–0.042(4)	---

^a Diffractometer, radiation wavelength and collection temperature for **3**: Bruker APEX-DUO, MoKα 0.71073 Å, 100(2) K; for **5**, **6**, **7**: Oxford Diffraction Gemini A Ultra, CuKα, 1.54184 Å, 150(2) K.

[6,6,6-(CO)(PPh₃)₂-nido-6-MB₉H₁₃] [M = Ru (3**), Os (**4**)].** The CO-ligated metalladecaboranes, **3** and **4**, were obtained similarly from [RuCl(CO)H(PPh₃)₃] and [OsHCl(CO)(PPh₃)₃], in yields of 83% and 95% respectively of red and orange solids. FTIR (KBr disc) /cm⁻¹: **3**: ν(BH) 2539s, ν(CO) 1980s; **4**: ν(BH) 2530s, 2560sh, 2468sh, and ν(CO) 1975 cm⁻¹ (Figures S9 and S14). LRMS (ESI⁺): **3**: m/z 787 [M + Na]⁺ (isotope envelope corresponding to the parent ion [C₃₇H₄₃B₉ORuP₂Na]⁺); HR-MS (ESI⁺): **3**: m/z 789.26309 [M + Na]⁺, calcd for [C₃₇H₄₃B₉ORuP₂Na]⁺; measd m/z 789.26244. LRMS (ESI⁺): **4**: m/z 872 [M + NH₄]⁺ (isotope envelope corresponding to the parent ion [C₃₇H₄₇B₉OOSp₂N]⁺); HR-MS (ESI⁺): **4**: m/z 879.31336 [M + Na]⁺, calcd for [C₃₇H₄₃B₉OOSp₂Na]⁺; measd m/z 879.31497.

[1,1,1-(CO)H(PPh₃)-isocloso-1-RuB₉H₈-μ-(1,2)-{Pt(PMe₂Ph)₂}] (5**).** Dry deoxygenated toluene (60 ml) was added to a two-neck round-bottom flask containing the ruthenadecaborane **3** (0.237 g, 0.310 mmol) under an argon atmosphere. KBHET₃ (THF solution, 0.62 ml, 0.62 mmol) was injected and the yellow

mixture stirred overnight during which time it became a clear yellow solution. Against a flow of argon, [PtCl₂(PMe₂Ph)₂] (0.167 g, 0.31 mmol) was dropped in and the stirring continued for ca. 24 h. A clear reddish mixture formed and this was filtered and washed with toluene and then pentane and filtered through a frit. The isolated solid, 52 mg, was predominantly unreacted **3**. Pentane was added to the filtrate affording, after air drying, 0.244 g of tan solid. A 25 mg portion of the solid was run on a preparative TLC plate with dichloromethane affording a number of faint yellow or orange bands and one principal yellow band, which, with further plating in 75% dichloromethane/hexane, afforded [1,1,1-(CO)H(PPh₃)-isocloso-1-RuB₉H₈-μ-(1,2)-{Pt(PMe₂Ph)₂}] (**5**, 2 mg, 2.6 μg or an estimated ca. 8% yield based on the overall 0.244 g of tan solid). Single crystals were obtained from hexane diffusion into a CDCl₃ solution of the compound. Unfortunately, in this case, we were unable to obtain a mass spectrum for the compound.

[7,7-(PMe₂Ph)₂-9,9,9-(CO)(PPh₃)₂-nido-7,9-PtOsB₉H₁₁] (6) and [5,5,5-(CO)(PPh₃)₂-nido-5-OsB₉H₁₃] (7). A procedure similar to the above was carried out. In a dry ice/isopropanol bath, **4** (0.204 g, 0.24 mmol) was stirred in 80 ml toluene at -36 °C and KHBET₃ (0.55 ml, 0.55 mmol) injected with the stirring continued until the temperature rose to -3 °C, at which point, the temperature was reduced to ca. -23 °C and [PtCl₂(PMe₂Ph)₂] (0.129 g, 0.24 mmol) was dropped in. After slow warming and stirring overnight, the dirty red solution was washed through a column of silica gel with CH₂Cl₂ giving a reddish solution. The red band was replated until one orange band was obtained, R_F 0.40, 50/50 CH₂Cl₂/hexane, and identified as **6** (yellow/orange, 47.5 mg, 36 μmol, 15%). FTIR(ATR)/cm⁻¹: **6**: ν(BH) 2517s, ν(CO) 2027s. LRMS (ESI⁺): m/z 1346 [M + Na]⁺ (isotope envelope corresponding to the parent ion [C₅₃H₆₃B₉OP₄OsPtNa]⁺); HR-MS (ESI⁺): m/z 1348.38216 [M + Na]⁺, calcd for [C₅₃H₆₃B₉OP₄OsPtNa]⁺; measd m/z 1348.38535. In this case only boron NMR data were obtainable for **6**: ¹¹B{¹H} (128 MHz, CD₂Cl₂, 298 K) δ: +32.1(2), +19.8, +7.0, -1.9, -3.1, -4.5, -9.4, -27.9. In one experiment an amount of [5,5,5-(CO)(PPh₃)₂-nido-5-OsB₉H₁₃] (**7**) was serendipitously isolated in amounts only sufficient for characterization by single-crystal X-ray diffraction analysis.

Conclusions

The use of diethyl ether as solvent in the reactions between the K[B₉H₁₄] and transition element complexes is a crucial factor in the high-yield synthesis of 10-vertex *nido*-6-metalladecaboranes and their easy isolation. This method is thus an important improvement on the previous synthesis of the iridadecaborane, [6,6,6-H(PPh₃)₂-*nido*-6-IrB₉H₁₃] (**1**) and is the first route to the preparation of the rhodadecaborane counterpart, [6,6,6-H(PPh₃)₂-*nido*-6-RhB₉H₁₃] (**2**). Likewise, the hitherto unreported CO-ligated cluster [6,6,6-(CO)(PPh₃)₂-*nido*-6-RuB₉H₁₃] (**3**) and its osmaborane analogue, [6,6,6-(CO)(PPh₃)₂-*nido*-6-OsB₉H₁₃] (**4**), isolated previously as very minor side-products, can be now also synthesized in high yields and convenience using this method. The multielement NMR data reveal the structural similarities between compounds **1–4**, that all feature four bridging hydrogen atoms on their cluster hexagonal open faces. The most significant deviations from the NMR spectroscopic patterns are assigned to the rhodadecaborane **2** that exhibits the largest B2/B4 split in the ¹¹B resonances and the lowest chemical shifts for the Rh6-*H*-B7 and Rh6-*H*-B5 proton resonances. The high-yield syntheses of these metalladecaboranes opens the possibility for study of their reaction chemistry. Thus, the reactions of the CO-ligated clusters, **3** and **4**, with the *cis*-dichlorobis-(dimethylphenyl-phosphine)platinum(II) complex afford the new bimetallic clusters, [1,1,1-(CO)H(PPh₃)₃-*isocloso*-1-RuB₉H₈-μ-(1,2)-{Pt(PMe₂Ph)₂}] (**5**) and [7,7-(PMe₂Ph)₂-9,9,9-(CO)(PPh₃)₂-*nido*-7,9-PtOsB₉H₁₁].CH₂Cl₂ (**6**), together with the *nido*-5-osmadecaborane, [5,5,5-(CO)(PPh₃)₂-*nido*-5-OsB₉H₁₃] (**7**). The platinarutheborane **6** is the first example of a metallaborane featuring a {Pr-μ-H-Ru} linkage, whereas the platinaosma-borane is another example of a cluster that

deviates from the predictions of Wade's rules. Both bimetallic clusters **6** and **7** illustrate the potential of B-frames as molecular scaffolds onto which multimetallic assemblies can form.

DFT modelling of the metal fragment rotation about the allylic-type {η³-B5B2B7} face in the metalladecaboranes indicates that the *exo*-polyhedral ligand bond strength weakens upon approaching rotational positions *pseudo-trans* to the B2 vertex. Additionally, the labilization of the metal-to-boron linkage found in the high-energy conformers is concomitant with a strengthening of the *exo*-polyhedral ligand sphere. These DFT-modelled structural changes suggest that the energy of the metalladecaboranes is largely directed by the strong *trans* influences of the boron vertices that changes upon rotation. The instability, in solution, of the rhodadecaborane **2** may be rationalized as the result of a large energy penalty upon the rotation of the {Rh(H)(PPh₃)₂} moiety that leads to the detachment from the {η³-B₉H₁₃} fragment.

The metal-to-borane fragment rotational *exo*-polyhedral ligand lability and the presence of M-H-B and B-H-B bonds in **1–4** suggest that these metalladecaboranes may find application in catalysis.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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