

Polyhedral metallathiaborane chemistry: Synthesis and characterisation of metallathiaboranes based on the twelve-vertex icosahedral *closo*-{MSB₁₀H₁₀} unit, where M is Rh or Ir

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Abstract

The reaction of [*nido*-7-SB₁₀H₁₂] with [RhCl(PPh₃)₃] in the presence of *N,N,N',N'*-tetramethylnaphthalene-1,8-diamine (tmnd) in CH₂Cl₂ gives twelve-vertex [2,2-(PPh₃)₂-2-H-*closo*-2,1-RhSB₁₀H₁₀] (**1**) and eleven-vertex [8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀] (**2**), as major products, plus the dimeric species [(PPh₃)-*closo*-RhSB₁₀H₁₀]₂ (**3**) as a minor product. Reaction of **1** with PMe₂Ph in CH₂Cl₂ results in phosphine exchange and hydride substitution, affording the chloro analogue of **1**, [2,2-(PMe₂Ph)₂-2-Cl-*closo*-2,1-RhSB₁₀H₁₀] (**4**). By contrast, reaction between [IrCl(PPh₃)₃] and [*nido*-7-SB₁₀H₁₂] in CH₂Cl₂ with tmnd affords only one product, twelve-vertex [2,2-(PPh₃)₂-2-H-*closo*-2,1-IrSB₁₀H₁₀] (**5**). [RhCl₂(η⁵-C₅Me₅)₂] with [*nido*-7-SB₁₀H₁₂] under the same conditions gives twelve-vertex [2-(η⁵-C₅Me₅)-*closo*-2,1-RhSB₁₀H₁₀] (**6**). All the compounds are characterised by NMR spectroscopy, and by mass spectrometry, and the molecular structure of [2,2-(PMe₂Ph)₂-2-Cl-*closo*-2,1-RhSB₁₀H₁₀] (**4**) was established by single-crystal X-ray diffraction analysis. This last rhodathiaborane **4** is fluxional in solution through a process that involves a reversible partial rotation of the {RhCl(PMe₂Ph)₂} unit above the {SB₄} pentagonal face of the {SB₁₀H₁₀} fragment.

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Keywords: Metallathiaborane; Polyhedral chemistry

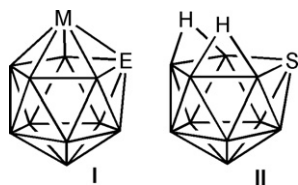
1. Introduction

Contiguous metallaheteroborane cluster compounds based on the icosahedral twelve-vertex {2,1-MEB₁₀H₁₀} unit (schematic cluster structure **I**) have been reported for a variety of transition-elements M, where M is Cr, Mo, W, Fe, Co, Ni, Pd, or Pt, and for a variety of heteroatoms E, where E is C, Si, N, P, As, S, Se or Te [1–18]. The synthetic procedures developed for the preparation of these species are numerous. The first twelve-vertex icosahedral

metallaheteroborane compounds prepared were ‘mixed-sandwich’ compounds [(η⁵-C₅H₅)MC₂B₉H₁₀], obtained from three-component reactions between simple transition-element chlorides with Group 1 salts of the [η⁵-C₅H₅][−] hydrocarbon anion and the *nido* eleven-vertex [C₂B₉H₁₂][−] or [C₂B₉H₁₁]^{2−} carbaborane anions [1–3]. Routes to {MEB₁₀} species extend from this type of process by the reactions of *nido* eleven-vertex anions based on {EB₁₀} units with transition-element complexes that contain metal halide bonds, and this route has been the one predominantly used for the synthesis of a wide range of twelve-vertex metallaheteroborane species [13–16]. Here we report the synthesis of some {MSB₁₀} species starting from the *nido* eleven-vertex {SB₁₀} system.

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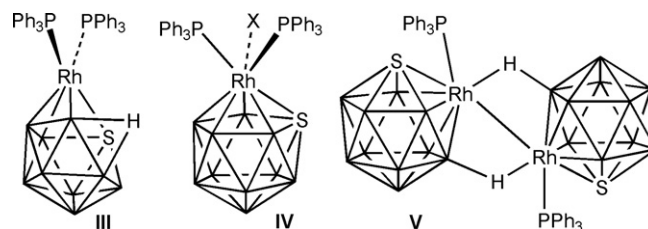


Eleven-vertex [*nido*-7-SB₁₀H₁₂] (schematic cluster structure **II**) was originally reported by Muetterties and co-workers [19], and successively improved preparations have subsequently been reported by Sneddon and co-workers [20]. Although its metallathiaborane derivatives [2,2-(PEt₃)₂-*closo*-2,1-PtSB₁₀H₁₀] [12] and [2,2-(PPh₃)₂-2-H-*closo*-2,1-RhSB₁₀H₁₀] [15] were among the earliest examples of reported twelve-vertex metallaheteroboranes, the chemistry of {MSB₁₀} cluster species has not been very well developed compared with their isoelectronic metalladiborane analogues. For example, there are only two crystallographic studies of such *closo* twelve-vertex metallathiaboranes: one is the ferrathiaborane [2-(η⁶-C₆H₅Me)-*closo*-2,1-FeSB₁₀H₁₀] [18] and the other is the platinum derivative [2,2-(PMe₂Ph)₂-*closo*-2,1-PtSB₁₀H₁₀] (referred to below as compound **7**) [21]. In the crystallographic analysis of [2-(η⁶-C₆H₅Me)-*closo*-2,1-FeSB₁₀H₁₀] the sulfur atom was found to be disordered, precluding accurate structural comparisons with analogous species. Moreover, available NMR data on previous metallathiaboranes are largely based on low-dispersion spectroscopy with little assignment work. Therefore, as part of our general interest in heteroboranes [22,23] and their metal derivatives [11,13,14,16,21,24–29], herein we report synthetic, structural and NMR studies on some new twelve-vertex rhodium and iridium metallathiaboranes incorporating the {SB₁₀H₁₀} ligand fragment.

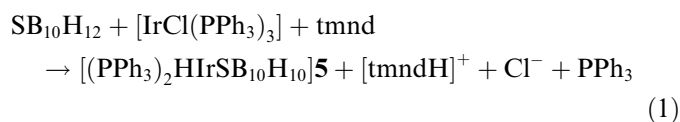
2. Results and discussion

The rhodium(I) complex [RhCl(PPh₃)₃] was added to [*nido*-7-SB₁₀H₁₂] in the presence of the non-nucleophilic base *N,N,N',N'*-tetramethylnaphthalene-1,8-diamine (tmnd) in CH₂Cl₂ solution at room temperature. The resulting reaction gave several products. After repeated preparative-scale thin-layer chromatography (TLC), we were able to isolate and characterise three major components: yellow [2,2-(PPh₃)₂-2-H-*closo*-2,1-RhSB₁₀H₁₀] (**1**) (26% yield), orange [8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀] (**2**) (17% yield) and purple [(PPh₃)₂-*closo*-RhSB₁₀H₁₀]₂ (**3**) (5% yield). The *nido* eleven-vertex compound **2** (schematic cluster structure **III**) was previously well characterised [25], and is of a recognised structural type [28,29], but the characterisation of the twelve-vertex *closo* compound **1** (schematic cluster structure **IV**, where X = H), though previously mentioned in the literature [15], was incomplete. To better characterise compound **1**, as part of this present work NMR data for **1** have been gathered at higher field, and are now assigned, and compared with reported data for the other *closo* twelve-vertex

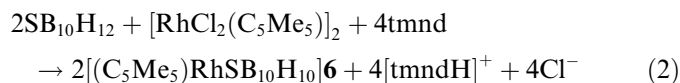
ter compound **3** (schematic cluster structure **V**) was characterised as such by comparison of its NMR properties with those of the previously reported and crystallographically determined [27] direct tellurium analogue [(PPh₃)₂-*closo*-RhTeB₁₀H₁₀]₂ (**8**) as well as by mass spectrometry. In addition to this first-order synthesis work, and in an attempt to effect phosphine–ligand replacement, we treated the rhodathiaborane **1** with PMe₂Ph in CH₂Cl₂, resulting in the synthesis of the chloro species [2,2-(PMe₂Ph)₂-2-Cl-*closo*-2,1-RhSB₁₀H₁₀] (**4**) (schematic cluster structure **IV**, where X = Cl), isolated in 20% yield.



The 100-mg-scale reaction of the iridium(I) complex [IrCl(PPh₃)₃] under the same conditions as those used in the preparation of the rhodium compound **1** above gave only one predominant metallaheteroborane product, readily identified by NMR spectroscopy and mass spectrometry as the iridium analogue of the rhodium compound **1**, *i.e.* as [2,2-(PPh₃)₂-2-H-*closo*-2,1-IrSB₁₀H₁₀] (**5**), isolated in 12% yield (Eq. (1)).



The pentamethylcyclopentadienyl rhodium analogue of **1**, *i.e.* [2-(η⁵-C₅Me₅)-*closo*-2,1-RhSB₁₀H₁₀] (**6**), was similarly obtained in 25% yield from the reaction between [RhCl₂(η⁵-C₅Me₅)₂] and [*nido*-7-SB₁₀H₁₂] in the presence of tmnd in CH₂Cl₂ solution at ambient temperature (Eq. (2)). This colourless rhodathiaborane was also purified by preparative TLC and characterised by NMR spectroscopy and mass spectrometry.



The molecular structures of the metallathiaboranes in solution were readily established by means of ¹¹B, ³¹P and ¹H multinuclear and multiple resonance NMR spectroscopy. The data are summarised in Tables 1–3. For the four monomeric *closo* species [2,2-(PPh₃)₂-2-H-*closo*-2,1-RhSB₁₀H₁₀] (**1**), [2,2-(PMe₂Ph)₂-2-Cl-*closo*-2,1-RhSB₁₀H₁₀] (**4**), [2,2-(PPh₃)₂-2-H-*closo*-2,1-IrSB₁₀H₁₀] (**5**) and [2-(η⁵-C₅Me₅)-*closo*-2,1-RhSB₁₀H₁₀] (**6**), the ¹¹B and ¹H resonances were assigned on the reasoned basis of relative intensities and ¹H–{¹¹B(selective)} experiments, and thence by comparison with other previously assigned *closo* twelve-vertex

Table 1

¹¹B and ¹H NMR data for [2,2-(PPh₃)₂-2-H-*closo*-2,1-RhSB₁₀H₁₀] (**1**), [2,2-(PMe₂Ph)₂-2-Cl-*closo*-2,1-RhSB₁₀H₁₀] (**4**), [2,2-(PPh₃)₂-H-*closo*-2,1-IrSB₁₀H₁₀] (**5**) and [2-(η⁵-C₅Me₅)-*closo*-2,1-RhSB₁₀H₁₀] (**6**) at 284–297 K, together with those of [2,2-(PMe₂Ph)₂-2,1-PtSB₁₀H₁₀] (**7**) for comparison

Assignment ^a		1 ^{b,d}		4 ^b		5 ^c		6 ^{b,c,f}		7 ^b	
		δ(¹¹ B)	δ(¹ H)	δ(¹¹ B)	δ(¹ H)	δ(¹¹ B)	δ(¹ H)	δ(¹¹ B)	δ(¹ H)	δ(¹¹ B)	δ(¹ H)
12	(1B)	+14.2	+4.29	+14.9	+4.35	+12.0	+4.03	+9.1	+3.32	+15.6	+3.70 ^g
9	(1B)	+13.8	+3.55	+13.4	+3.00	+13.2	+6.04	+5.3 ^h	+4.18	+1.6	+5.07
3,6	(2B)	+7.7	+2.10	+13.0	+2.88	+4.6	+2.28	+5.3 ^h	+2.23	−9.1	+1.18
7,11	(2B)	+7.4	+3.51	+9.3	+3.59	+1.6	+3.57	+14.1	+2.99	+3.3	+3.14
4,5	(2B)	−13.3	+1.85	−10.3	+2.08	−16.0	+2.02	−18.1	+1.86	−13.6	+2.42
8,10	(2B)	−13.0	+1.79	−14.2	+1.75	−19.4	+2.00	−10.5	+2.14	−22.5	+1.59
2	(MH)		−7.13 ⁱ				−8.93 ^j				

^a See text.

^b CD₂Cl₂ solution, data from O'Connell et al. (Ref. [21]).

^c CDCl₃ solution.

^d Mass spec.: *m/z*_{max}: 780; ¹²C₃₆¹H₄₁³¹P₂¹¹B₁₀³²S¹⁰³Rh requires 780.

^e Mass spec.: *m/z*_{max}: 388; ¹²C₁₀¹H₂₅¹¹B₁₀³²S¹⁰³Rh requires 390.

^f δ(¹H)(η⁵-C₅Me₅) +2.03.

^g ⁴J(¹⁹⁵Pt–¹H) 62 Hz.

^h Accidental coincidence of resonances.

ⁱ Triplet [²J(³¹P–¹H) *ca.* 22 Hz] of doublets [¹J(¹⁰³Rh–¹H) *ca.* 19 Hz].

^j Triplet [²J(³¹P–¹H) *ca.* 23.5 Hz].

Table 2

³¹P and additional ¹H NMR data for [2,2-(PPh₃)₂-2-H-*closo*-2,1-RhSB₁₀H₁₀] (**1**), [2,2-(PMe₂Ph)₂-2-Cl-*closo*-2,1-RhSB₁₀H₁₀] (**4**) and [2,2-(PPh₃)₂-H-*closo*-2,1-IrSB₁₀H₁₀] (**5**)

	1 ^a	4 ^b	5 ^c
δ(³¹ P)/ppm	+31.5	A +12.9 ^d B −0.8	+9.2
¹ J(¹⁰³ Rh– ³¹ P)/Hz	+106.2		
¹ J(¹⁰³ Rh– ³¹ P _A)/Hz		121	
¹ J(¹⁰³ Rh– ³¹ P _B)/Hz		95	
² J(³¹ P _A – ³¹ P _B)/Hz		37.5	

^a CDCl₃ solution, 220 K.

^b CD₂Cl₂ solution, 176 K; additional ¹H NMR data: (CDCl₃, 293 K) δ(¹H)(CH₃)_A +1.90, [AX₃]₂ system, *N* = ²J(³¹P–¹H) + ⁴J(³¹P–¹H) = 10.4 Hz; δ(¹H)(CH₃)_B +1.52, [AX₃]₂ system, *N* = ²J(³¹P–¹H) + ⁴J(³¹P–¹H) = 11.3 Hz.

^c CDCl₃ solution, 223 K.

^d At higher temperatures these signals coalesce into one resonance [δ(³¹P) +5.0, ¹J(¹⁰³Rh–³¹P) 110 Hz at 291 K]; coalescence temperature 213 K at 100 MHz.

{MEB₁₀H₁₀} species [13,14,17]. For each species, the cluster atoms show 1:1:1:2:2:2 relative-intensity patterns in both their ¹¹B and ¹H NMR spectra, and the absence of bridging hydrogen atoms on the borane cage, which is consistent with twelve-vertex *closo* clusters that have C_s symmetry in solution at room temperature. In addition, the ¹H NMR spectrum of **1** exhibits a triplet of doublets at δ(¹H) −7.13 and that of **5** exhibits a triplet at δ(¹H) −8.93, these resonances corresponding to the *exo*-polyhedral hydride ligands on the rhodium and iridium metal centres, respectively. The ¹H spectrum of **4** at room temperature contains two *N*(³¹P–¹H) doublets centred at δ +1.90 and +1.52, which are assigned to the methyl protons of the PMe₂Ph groups. The ¹H NMR spectrum of **6** exhibits a resonance of relative intensity 15 at δ +2.03 ppm, demonstrating the presence of

Table 3

NMR data for [{(PPh₃)₂-*closo*-RhSB₁₀H₁₀]₂] (**3**) and [{(PPh₃)₂RhTeB₁₀H₁₀]₂] (**8**)

Assignments	Compound 3 ^{c,g}		Compound 8 ^d	
	δ(¹¹ B) ^a	δ(¹ H)	δ(¹¹ B) ^b	δ(¹ H)
11 (1B)	+23.5 +11.7	−6.39 ^e +2.19	+26.5 +17.0	−7.28 ^f +3.8
7,9,12 (3B)	+8.3 +3.2 <i>ca.</i> +10.0	+3.91 +2.95 +2.68	+9.0 +6.0 <i>ca.</i> +11.1	+4.66 +4.47 +3.02
3,6 (2B)	<i>ca.</i> +1.0 −8.5	+1.52 +1.97	+0.8 −9.7	+2.02 +2.75
8,10 (2B)	−15.4 <i>ca.</i> −13.5	+1.53 +1.76	−16.0 <i>ca.</i> −14.5	+2.41 +1.92
4,5 (2B)	−19.3	+1.97	<i>ca.</i> −17.7	+1.88

^a CDCl₃ at 294–303 K.

^b CD₂Cl₂ at 294–303 K.

^c δ(³¹P) +24.8 ppm, ¹J(¹⁰³Rh–³¹P) 134 Hz, CDCl₃ at 222 K.

^d Data from Ferguson, Lough et al. (Ref. [26]); additionally δ(³¹P) +29.1 ppm, ¹J(¹⁰³Rh–³¹P) 97 Hz, CD₂Cl₂ at 213 K.

^e Apparent 1:2:1 triplet [¹J(¹⁰³Rh–¹H) + ²J(³¹P–¹H)]/2 *ca.* 17 Hz (mean value).

^f Apparent 1:2:1 triplet [¹J(¹⁰³Rh–¹H) + ²J(³¹P–¹H)]/2 *ca.* 17 Hz (mean value).

^g Mass spec.: *m/z*_{max}: 1032; ¹²C₃₆¹H₅₀¹¹B₂₀³¹P₂³²S₂¹⁰³Rh₂ requires 1034.

a {η⁵-C₅Me₅} fragment bound to the rhodium atom. The corresponding datum for [2-(η⁵-C₅Me₅)-*closo*-2,1-RhTeB₁₀H₁₀] (**9**), the tellurium analogue of **6**, for which an X-ray diffraction study has been reported, is δ(¹H) +2.01 ppm [13].

The NMR data of the dimer [{2-(PPh₃)₂-*closo*-2,1-RhSB₁₀H₁₀]₂] (**3**) are likewise analogous to those for its previously reported and crystallographically determined

group-16 tellurium congener $[\{2-(\text{PPh}_3)\text{-}closo\text{-}2,1\text{-RhTeB}_{10}\text{H}_{10}\}_2]$ (**8**) [26]. Each of **3** and **8** shows a triplet in the high-field region between $\delta(^1\text{H})$ -6 and -8 in its ^1H NMR spectra (Table 3), which in each case is readily assigned to the B–H–Rh bridging hydrogen atom position (schematic cluster **V** above). The formulation of **3** is additionally supported by mass spectrometry that shows a molecular envelope that is centred at m/e 1032 and that matches the isotope pattern of an ion of formulation $[\text{C}_{36}\text{H}_{50}\text{B}_{20}\text{P}_2\text{S}_2\text{Rh}_2]^+$.

The ^{11}B shielding pattern of the new twelve-vertex compounds can be traced as in Fig. 1 to those of the thiaborane starting material, [*nido*-7-SB₁₀H₁₂], and the previously reported [21] *closo* twelve-vertex platinathiaborane, [2,2-(PMe₂Ph)₂-2,1-PtSB₁₀H₁₀] (**7**). In all these *closo* metallathiaboranes, the groupings of the $^{11}\text{B}(9)$, $^{11}\text{B}(12)$, $^{11}\text{B}(3,6)$ and $^{11}\text{B}(7,11)$ resonances tend to be less shielded than the groupings of the $^{11}\text{B}(4,5)$ and $^{11}\text{B}(8,10)$ resonances. The

gap between these higher-field and lower-field groupings is markedly larger for the rhodium and iridium compounds **1**, **4** and **6** (Fig. 1), with an average gap of *ca.* 20 ppm. By contrast, the resonances of the {Pt(PMe₂Ph)} species **7** are much more closely grouped, and more evenly distributed throughout the spectrum, although maintaining a similar sequence of relative shielding. This difference, between **7** on one hand, and **1**, **4** and **6** on the other hand, is probably a consequence of differences in the nature of the metal-to-cluster bonding as discussed below (compare also schematic cluster structure **IV** with **VII**). The $^{11}\text{B}(12)$ resonance that is antipodal to the sulfur atom appears at lowest shielding in all compounds, except for the {Rh($\eta^5\text{-C}_5\text{Me}_5$)} derivative **6**. The ^1H and ^{11}B nuclear shielding of the {BH(*exo*)} units follow a line of approximate slope $\delta(^{11}\text{B}):\delta(^1\text{H})$ 11:1, which is in accord with previously reported *closo* twelve-vertex {MEB₁₀} relative shielding patterns [16,26]. Noteworthy in this context is the exceptional

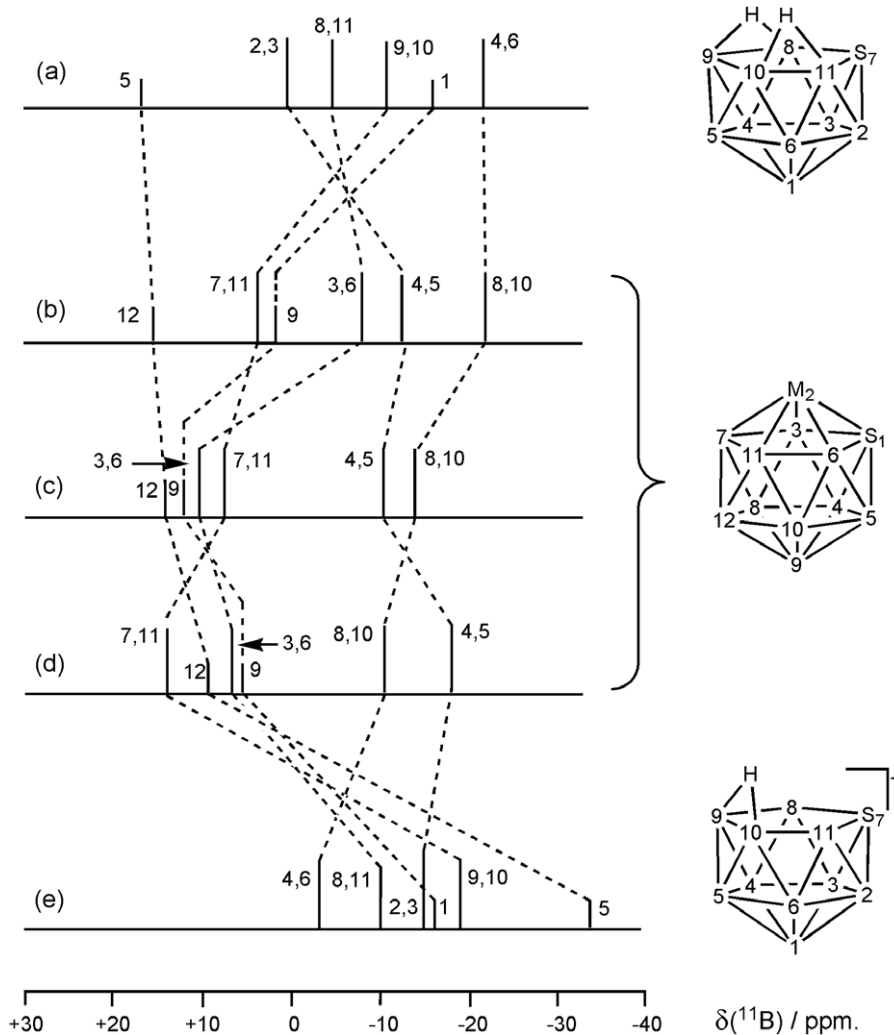


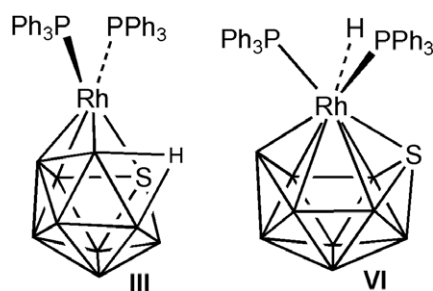
Fig. 1. Stick representations of the resonance positions and relative intensities in the $^{11}\text{B}\text{-}\{^1\text{H}\}$ NMR spectra of (a) [*nido*-7-SB₁₀H₁₂], (b) [2,2-(PMe₂Ph)₂-2,1-PtSB₁₀H₁₀] (**7**) (data from O'Connell et al. [21]), (c) [2,2-(PMe₂Ph)₂-2-Cl-*closo*-2,1-RhSB₁₀H₁₀] (**4**), (d) [2-($\eta^5\text{-C}_5\text{Me}_5$)-*closo*-2,1-RhSB₁₀H₁₀] (**6**) and (e) the [*nido*-7-SB₁₀H₁₂]⁻ anion. Hatched lines join equivalent positions. (Note that the numbering conventions for the eleven-vertex *nido* and *closo* twelve-vertex *closo* clusters differ.)

lower ^1H shielding for the BH(9) position when the antipodal atom is iridium or platinum. This effect is previously noted as an antipodal ^1H shielding characteristic of *closo* twelve-vertex compounds [13,14,16], and indeed other cluster types [30], that contain third-row transition-element centres as cluster constituents.

The reactions that produce compounds [2,2-(PPh₃)₂-2-H-*closo*-2,1-RhSB₁₀H₁₀] (**1**), [2,2-(PPh₃)₂-2-H-*closo*-2,1-IrSB₁₀H₁₀] (**5**) and [2-(η^5 -C₅Me₅)-*closo*-2,1-RhSB₁₀H₁₀] (**6**) are presumably initiated by a deprotonation of [*nido*-7-SB₁₀H₁₂] by the non-nucleophilic strong proton-abstracting base tmnd, affording the [*nido*-7-SB₁₀H₁₁][−] anion in solution. Subsequent addition of the metal halide complexes would then result in displacement of halide by the *nido*-7-thiaborane anion to form intermediate metallathiaborane species. In the synthesis of the {Rh(C₅Me₅)} species **6**, the intermediate, of presumed formulation {(C₅Me₅)ClRh(SB₁₀H₁₁)} with a low thiaborane-to-metal coordination number, would then further eliminate HCl, of which the H⁺ would become sequestered by tmnd in a simple salt elimination, resulting in the final intimate *pentahapto* coordination of the thiaborane ligand to the metal centre to give the final [(C₅Me₅)RhSB₁₀H₁₀] formulation for **6**; overall the rhodium atom would maintain its initial rhodium(III) oxidation state. In the formation of **1** and **5**, by contrast, the intermediate would now be of presumed formulation {(PPh₃)₂M(SB₁₀H₁₁)}, and the metal centre would then add a hydrogen atom from the {SB₁₀H₁₁} unit into its coordination sphere, resulting in a formal overall oxidative addition of the metal centre into the cluster to give the final [(PPh₃)₂HRhSB₁₀H₁₀] formulation. Thus, in the formation of **1** and **5**, the formal oxidation states of the metal-atoms change from rhodium(I) and iridium(I) in the starting [MCl(PPh₃)₂] complexes to rhodium(III) and iridium(III) in the metallathiaborane products.

The formation of [8,8-(PPh₃)₂-*nido*-8,7-RhSB₉H₁₀] (**2**) would appear to be more complicated. It may be possible that the tmnd base causes the abstraction of a {BH} unit from either [*nido*-7-SB₁₀H₁₂] or its [*nido*-7-SB₁₀H₁₁][−] monoanion and the resulting species, *i.e.* either neutral [*nido*-7-SB₉H₁₁] or the [*nido*-7-SB₉H₁₀][−] anion, reacts with [RhCl(PPh₃)₃] to give a [(PPh₃)₂RhSB₉H₁₀] formulation for **2** directly. Certainly the ready formation of *nido* ten-vertex species from real or incipient eleven-vertex species is a well-recognised phenomenon in metal-atom-containing borane cluster chemistry [31,32]. However, it is not clear why the reaction of the corresponding iridium complex [IrCl(PPh₃)₃] does not give an analogous [8,8-(PPh₃)₂-*nido*-8,7-IrSB₉H₁₀] by-product under otherwise identical conditions. Also, in view of the closed structures of the twelve-vertex [2,2-(PPh₃)₂-2-X-*closo*-2,1-RhSB₁₀H₁₀] species **1** and **4**, it is of interest that this *nido* eleven-vertex species **2** (schematic cluster structure **III**), a formal rhodium(I) species [25], does not adopt the isomeric closed configuration [1,1-(PPh₃)₂-1-H-*closo*-1,2-RhSB₉H₉] that would have a rhodium(III) formulation (schematic cluster structure **VI**). As recently published [29b], this arises from an inher-

ently greater stability of the *nido* eleven-vertex {RhSB₁₀H₁₁} unit that has one bridging hydrogen atom as opposed to less stable *closo* eleven-vertex configuration **VI**. This preferential stability is also found in the eleven-vertex rhodaazaborane [8,8-(PPh₃)₂-*nido*-8,7-RhNB₉H₁₁] [29b], and in related manner in [8-(η^4 -HC₅Me₅)-*nido*-8,7-RhSB₉H₉- μ -9,10-(SMe)] which also adopts the *nido* configuration with a rhodium(I) centre (incidentally forcing the unusual *tetrahapto* η^4 -HC₅Me₅ cyclopentadiene ligand) rather than an alternative closed structure with a formal rhodium(III) oxidation state and a more usual *pentahapto* η^5 -C₅Me₅ cyclopentadienyl ligand [29a].



The mechanism of formation of the purple dimeric species [(2-(PPh₃)-*closo*-2,1-RhSB₁₀H₁₀)₂] (**3**) is also not clear. A spontaneous intermolecular reaction of the rhodathiaborane [2,2-(PPh₃)₂-2-H-*closo*-2,1-RhSB₁₀H₁₀] (**1**) is a possible route, although no double-cluster products were observed when a sample of **1** was stirred in a CH₂Cl₂ solution at room temperature. In this context, it may be noted that the group-16 tellurium congener [2,2-(PPh₃)₂-2-H-*closo*-2,1-RhTeB₁₀H₁₀] (**10**) also did not give any bimetallic rhodatelluraborane products when it was stirred in CH₂Cl₂, C₆H₆ or thf solutions at room temperature, but that very low yields of two purple compounds were isolatable from solutions of **10** that had undergone the more forcing conditions of heating at reflux temperature in toluene or xylene for two days. An initial characterisation of one of these two purple rhodatelluraborane products by ¹¹B and ¹H NMR spectroscopy has suggested the presence of twenty {BH} units including two that exhibited ¹H resonances at $\delta(^1\text{H})$ *ca.* −8.0 and −7.0 ppm, respectively [33], which correspond to Rh–H–B bridges and which compare to the ¹H resonance at $\delta(^1\text{H})$ −6.39 observed for **3**. Here it can be noted that the molecular structures of two other purple tellurium analogues, specifically the direct analogue of **3**, *viz.* [(2-(PPh₃)-*closo*-2,1-RhTeB₁₀H₁₀)₂] (**8**), and the closely related mixed-ligand species [(2-(PPh₃)-*closo*-2,1-RhTeB₁₀H₁₀){2-(CO)-*closo*-2,1-RhTeB₁₀H₁₀}] (**11**), have been established by single-crystal X-ray diffraction methods [26]. These compounds were obtained from the reactions of [2,2-(PPh₃)₂-2-H-*closo*-2,1-RhTeB₁₀H₁₀] (**10**) with metal carbonyl complexes, *i.e.* either with [Mo(CO)₆] to give **8** (reaction in thf at ambient temperature for eighteen hours) or with [Os₃H₂(CO)₁₀] to give **11** (reaction in CH₂Cl₂ heated at reflux for three days) [26]. Both compounds **8** and **11** contained Rh–H–B bridges, exhibiting

^1H resonances at $\delta(^1\text{H}) -7.28$ for the symmetrical $\{\text{Rh}_2(\text{PPh}_3)_2\}$ species **8**, and at $\delta(^1\text{H}) -7.65$ and -6.39 for the asymmetric $\{\text{Rh}_2(\text{CO})(\text{PPh}_3)\}$ species **11**, again comparable to the $\delta(^1\text{H}) -6.39$ value observed for **3**. Hence, a likely mechanism for the formation of **3** may involve the thermolytic cleavage of a PPh_3 ligand from **1** and the dimerisation of the “unsaturated” $\{(\text{PPh}_3)\text{H-closo-RhSB}_{10}\text{H}_{10}\}$ intermediate species so formed, concomitant with a further elimination of dihydrogen to give the stoichiometry of the observed product. The reaction conditions used in the present study that here gave $[\{2-(\text{PPh}_3)\text{-closo-2,1-RhSB}_{10}\text{H}_{10}\}_2]$ (**3**) in 5% yield were not as forcing as those used to prepare the $\{(\text{RhTeB}_{10}\text{H}_{10})_2\}$ cluster compounds **8** and **11**, which were isolated in yields of 46% and 33%, respectively.

The molecular structure of **4** was confirmed by a single-crystal X-ray diffraction analysis (Fig. 2 and Tables 4 and 5). The crystals were monoclinic, space group $P2_1/c$, with

Table 4

Selected interatomic distances (Å) for $[2,2-(\text{PMe}_2\text{Ph})_2\text{-2-Cl-closo-2,1-RhSB}_{10}\text{H}_{10}]$ (**4**) together with those for $[2,2-(\text{PMe}_2\text{Ph})_2\text{-closo-2,1-PtSB}_{10}\text{H}_{10}]$ (**7**) (data from O’Connell et al. [21]) for comparison, with estimated standard deviations (e.s.d.s) in parentheses

(a) From the metal-atom			
Compound 4		Compound 7	
Rh(2)–B(3)	2.269(2)	Pt(2)–B(3)	2.318(3)
Rh(2)–B(6)	2.244(2)	Pt(2)–B(6)	2.296(3)
Rh(2)–B(7)	2.258(2)	Pt(2)–B(7)	2.230(3)
Rh(2)–B(11)	2.232(2)	Pt(2)–B(11)	2.248(3)
Rh(2)–S(1)	2.3629(5)	Pt(2)–S(1)	2.6633(7)
Rh(2)–P(1)	2.3992(5)	Pt(2)–P(1)	2.2870(7)
Rh(2)–P(2)	2.3286(5)	Pt(2)–P(2)	2.3021(7)
Rh(2)–Cl(1)	2.4179(5)		
(b) Sulfur–boron			
Compound 4		Compound 7	
S(1)–B(3)	2.101(2)	S(1)–B(3)	2.034(3)
S(1)–B(4)	1.993(2)	S(1)–B(4)	1.979(3)
S(1)–B(5)	1.993(2)	S(1)–B(5)	1.973(4)
S(1)–B(6)	2.098(2)	S(1)–B(6)	2.060(3)
(c) Boron–boron			
Compound 4		Compound 7	
B(3)–B(4) (longest)	1.920(3)	B(3)–B(4)	1.919(5)
B(3)–B(7)	1.787(3)	B(3)–B(7)	1.848(4)
B(4)–B(5)	1.851(3)	B(4)–B(5)	1.840(5)
B(5)–B(6)	1.913(3)	B(5)–B(6) (longest)	1.938(5)
B(5)–B(9)	1.764(3)	B(5)–B(9) (shortest)	1.750(5)
B(6)–B(11)	1.787(3)	B(6)–B(11)	1.836(4)
B(7)–B(11)	1.837(3)	B(7)–B(11)	1.821(4)
B(6)–B(10) (shortest)	1.747(3)	B(6)–B(1)	1.821(4)

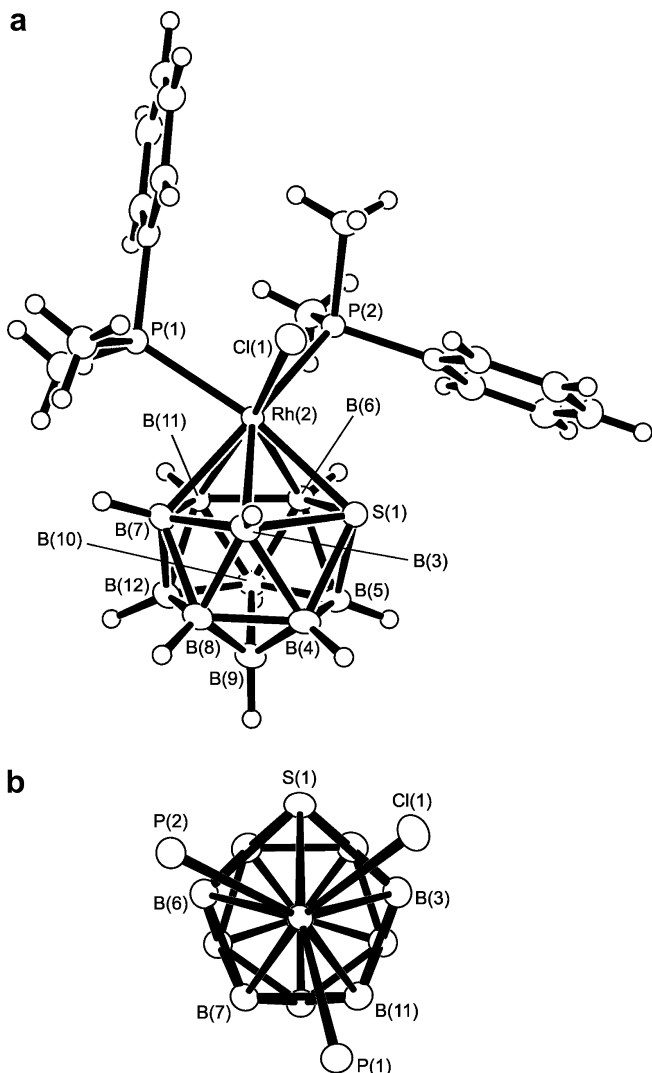


Fig. 2. ORTEP-3 type drawings [51] for $[2,2-(\text{PMe}_2\text{Ph})_2\text{-2-Cl-closo-2,1-RhSB}_{10}\text{H}_{10}]$ (**4**) showing (a) the numbering scheme, and (b) the conformation of the metal centre.

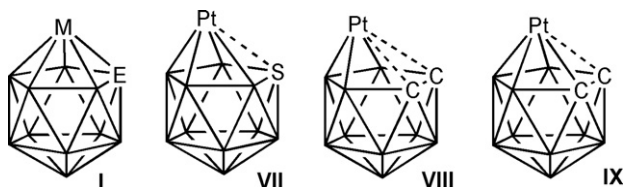
four molecules per unit cell. The compound is based on a closed icosahedral $\{\text{RhSB}_{10}\text{H}_{10}\}$ cluster unit. There is a *pentahapto* interaction of the $\{\text{SB}_4\}$ face of the $\{\text{SB}_{10}\text{H}_{10}\}$ cluster fragment with the rhodium centre, and interboron distances are within normal metallathaborane ranges [13,14,16]. The interatomic distances and angles within the coordination sphere of the rhodium centre of **4** are of interest when compared to those for platinum [21] in the $[2,2-(\text{PMe}_2\text{Ph})_2\text{-2,1-PtSB}_{10}\text{H}_{10}]$ species **7**. Thus, whereas the rhodium–sulfur distance of 2.3629(5) Å in **4** is within the bonding range found in other polyhedral rhodathiaborane species [27–29], it is markedly shorter than the corresponding platinum–sulfur distance of 2.6633(7) Å in **7**. Thus, in the platinum compound **7**, there is a significant displacement of the platinum centre away from the sulfur atom, which generates a distortion (schematic **VII**) from closed icosahedral geometry as in schematic **I**. This distortion is towards a more open ‘*isonido*’ type of geometry [34,35] that would have a four-membered $\{\text{PtBSB}\}$ open face: the metal centre thereby exhibits more of a *tetrahapto* η^4 interaction with the $\{\text{SB}_{10}\text{H}_{10}\}$ unit, rather than η^5 *pentahapto*. In twelve-vertex *closo*-type 3,2,1-platinadiboranes a related phenomenon generates a ‘*slipped-closo*’ configuration as in schematic **VIII** [21,30,36,37]. Here, the ‘*slipped-closo*’ configuration **VIII** describes a distortion towards *trihapto* η^3 and a *nido*-type twelve-vertex configuration with a five-membered $\{\text{PtBCCB}\}$ open face,

Table 5

Selected angles (°) between interatomic vectors for [2,2-(PMe₂Ph)₂-2-Cl-*closo*-2,1-RhSB₁₀H₁₀] (**4**), together with those for [2,2-(PMe₂Ph)₂-2-*closo*-2,1-PtSB₁₀H₁₀] (**7**) for comparison, with e.s.d.s in parentheses

(a) About the metal-atom			
Compound 4		Compound 7	
B(11)–Rh(2)–P(2)	89.90(6)	B(11)–Pt(2)–P(2)	106.70(8)
B(6)–Rh(2)–P(2)	131.56(6)	B(6)–Pt(2)–P(2)	88.45(8)
B(7)–Rh(2)–P(2)	80.82(6)	B(7)–Pt(2)–P(2)	151.82(8)
B(3)–Rh(2)–P(2)	112.29(6)	B(3)–Pt(2)–P(2)	154.77(8)
B(11)–Rh(2)–S(1)	88.82(6)	B(11)–Pt(2)–S(1)	84.26(8)
B(6)–Rh(2)–S(1)	54.11(6)	B(6)–Pt(2)–S(1)	48.39(8)
B(7)–Rh(2)–S(1)	88.10(6)	B(7)–Pt(2)–S(1)	83.81(8)
B(3)–Rh(2)–S(1)	53.91(6)	B(3)–Pt(2)–S(1)	47.58(8)
P(2)–Rh(2)–S(1)	166.20(2)	P(2)–Pt(2)–S(1)	108.50(3)
B(11)–Rh(2)–P(1)	109.75(6)	B(11)–Pt(2)–P(1)	137.76(8)
B(6)–Rh(2)–P(1)	81.87(6)	B(6)–Pt(2)–P(1)	170.87(8)
B(7)–Rh(2)–P(1)	157.71(6)	B(7)–Pt(2)–P(1)	98.90(8)
B(3)–Rh(2)–P(1)	147.92(6)	B(3)–Pt(2)–P(1)	93.54(8)
P(2)–Rh(2)–P(1)	97.37(2)	P(2)–Pt(2)–P(1)	95.46(3)
S(1)–Rh(2)–P(1)	96.00(2)	S(1)–Pt(2)–P(1)	122.48(2)
P(2)–Rh(2)–Cl(1)	84.83(2)		
S(1)–Rh(2)–Cl(1)	93.01(2)		
P(1)–Rh(2)–Cl(1)	84.67(2)		
(b) About the sulfur atom			
Compound 4		Compound 7	
B(5)–S(1)–Rh(2)	108.48(7)	B(5)–S(1)–Pt(2)	106.01(10)
B(4)–S(1)–Rh(2)	108.90(7)	B(4)–S(1)–Pt(2)	106.24(10)
B(6)–S(1)–Rh(2)	60.07(6)	B(6)–S(1)–Pt(2)	56.44(9)
B(3)–S(1)–Rh(2)	60.76(6)	B(3)–S(1)–Pt(2)	57.28(9)
B(5)–S(1)–B(4)	55.36(9)	B(5)–S(1)–B(4)	55.5(2)
B(5)–S(1)–B(6)	55.71(9)	B(5)–S(1)–B(6)	57.39(13)
B(4)–S(1)–B(6)	97.09(9)	B(4)–S(1)–B(6)	97.53(14)
B(5)–S(1)–B(3)	97.32(9)	B(5)–S(1)–B(3)	97.53(14)
B(4)–S(1)–B(3)	55.86(9)	B(4)–S(1)–B(3)	57.11(14)
B(6)–S(1)–B(3)	95.51(8)	B(6)–S(1)–B(3)	92.39(13)

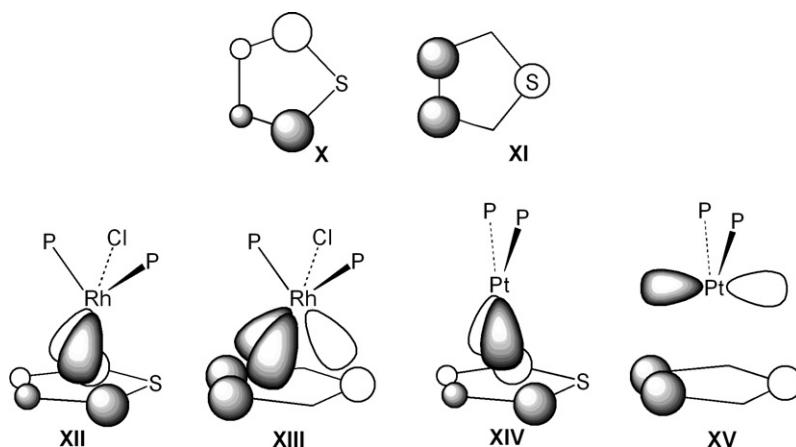
although it has been shown that the *isonido*-type *tetrahapto* η^4 configurations such as **IX** are energetically very similar [21,30].



According to a simplistic application of cluster-geometry/electron-counting formalisms [38], [2,2-(PMe₂Ph)₂-2-Cl-*closo*-2,1-RhSB₁₀H₁₀] (**4**) and [2,2-(PMe₂Ph)₂-2,1-PtSB₁₀H₁₀] (**7**) could both be regarded as 26-electron systems for which an icosahedral *closo* twelve-vertex structure would be predicted. However, the geometrical considerations discussed above suggest that the bonding interactions between the metal units and the thiaborane residues in **4** and **7** are somewhat different from each other. Thus, the twelve-vertex cluster unit of the rhodium compound **4** is clearly icosahedral, whereas the platinum compound **7** exhibits a marked and significant distortion from

this ideal. As also mentioned above, there are significant differences in the ¹¹B nuclear shielding patterns when the two compounds are compared (Fig. 1). A treatment of these compounds from a metal-orientated viewpoint is perhaps helpful to describe and rationalize the bonding differences implied by these geometrical and NMR differences.

In accord with such an approach, the rhodathiaborane **4** could thence be regarded as an eighteen-electron rhodium(III) complex between a formal {RhCl(PMe₂Ph)₂}²⁺ unit and a formal {SB₁₀H₁₀}²⁻ fragment, the latter acting as a tridentate *pentahapto* η^5 ligand by means of its {SB₄} open face. By contrast, compound **7** could be described as a sixteen-electron platinum(II) complex in which a formal {Pt(PMe₂Ph)₂}²⁺ fragment is bound to a {SB₁₀H₁₀}²⁻ fragment that acts as a bidentate *tetrahapto* η^4 ligand by means of the {B₄} unit of its {SB₄} open face. To examine these differences further, a simplistic frontier orbital approach to the orbital interactions of a metal unit with a thiaborane ligand unit can be adopted. Schematics **X** and **XI**, respectively, represent the HOMO and SHOMO orbitals of the formal {SB₁₀H₁₀}²⁻ ligand, the size of the circles approximating to the percentage components of AO's on those atomic positions. The metal-based molecular orbitals are LUMOs, thus the symmetry-determined overlaps of these HOMO and SHOMO frontier orbitals with the relevant LUMOs of the {RhCl(PMe₂Ph)₂}²⁺ and {Pt(PMe₂Ph)₂}²⁺ units would be expected to lead to stronger overall interactions between the {RhCl(PMe₂Ph)₂}²⁺ unit and the {SB₄} face of the {SB₁₀H₁₀}²⁻ ligand (schematics **XII** and **XIII**) than between the {Pt(PMe₂Ph)₂}²⁺ unit and the {SB₁₀H₁₀}²⁻ ligand (schematics **XIV** and **XV**). This treatment of course ignores any change in the energies of interacting orbitals as the units bond. However, bearing in mind that the angles made by the non-cluster ligands about the rhodium atom are close to 90°, it may be considered that three of the atomic orbitals on the rhodium-based unit are involved in bonding to the phosphine and chlorine ligands and three others are symmetry-arranged to be directed towards the {SB₁₀H₁₀}²⁻ cluster ligand HOMO and SHOMO: this interaction would give the rhodium centre a pseudo-octahedral configuration, and result in increased electron density along the Rh–S vector on cluster bonding. The resulting configuration of the {RhCl(PMe₂Ph)₂} unit would thence be as that observed in the solid-state structure. On the other hand, the {Pt(PMe₂Ph)₂}²⁺ fragment does not have any suitably directed unfilled molecular orbital for overlap with the SHOMO of the {SB₁₀H₁₀}²⁻ fragment, and so the most efficient cluster bonding does not involve a major interaction with the sulfur atom. Thus, the platinum fragment in **7** is observed to engender a ‘slipped structure’ in which the platinum centre has a pseudo-square-planar configuration. Such bonding requirements of the {Pt(PMe₂Ph)₂}²⁺ and related fragments, and how they may produce ostensibly anomalous cluster structures and cluster electron counts, have been discussed in adequate detail elsewhere [35,39].



As mentioned above, the metal-to-thiaborane bonding differences between the rhodium and platinum metallathiorborane species are additionally manifested in their ^{11}B NMR shielding patterns (Fig. 1), which show that the resonances for the boron atoms flanking the metal–sulfur linkage, *i.e.* for B(3) and B(6), shift about 17 ppm towards higher field on changing the metal-containing fragment from octahedral rhodium(III) or iridium(III) to square-planar platinum(II). The general ^{11}B shielding pattern of [2,2-(PMe₂Ph)₂-2,1-PtSB₁₀H₁₀] (7) [Fig. 1, diagram (b)] traces readily to that of neutral [nido-7-SB₁₀H₁₂] [Fig. 1, diagram (a)], implying intra-cluster bonding parallel between the *nido*-shaped {SB₁₀H₁₀} fragments in each case. In this regard a straightforward replacement of the two-electron three-centre BHB bonds in [nido-7-SB₁₀H₁₂] by two-electron three-centre BPTb bonds in 7 can be envisaged. This would be consistent with the frontier orbital approach and an essentially square-planar platinum(II) centre as discussed above. On the other hand, the shielding pattern for the rhodium species [2,2-(PMe₂Ph)₂-2-Cl-*closo*-2,1-RhSB₁₀H₁₀] (4) [Fig. 1, diagram (c)], which also parallels those for compounds 1 and 5, is markedly different from that of [nido-7-SB₁₀H₁₂] [diagram (a)], consistent with a much greater perturbation of the bonding within the {SB₁₀H₁₀} unit, as expected from the permitted interactions of the thiaborane ligand HOMO and SHOMO with the octahedral rhodium(III) metal centre. Similar considerations apply to the octahedral rhodium(III) species [2-(η^5 -C₅Me₅)-*closo*-2,1-RhSB₁₀H₁₀] (6) [Fig. 1, diagram (d)]. The ^{11}B shielding pattern for the [nido-7-SB₁₀H₁₁][−] monoanion [Fig. 1, diagram (e)] is much more fundamentally different, with an essentially inverted shielding sequence compared to the metal species, indicating few intra-cluster bonding similarities with the metal complexes.

The crystallographically determined molecular structure of [2,2-(PMe₂Ph)₂-2-Cl-*closo*-2,1-RhSB₁₀H₁₀] (4) (Fig. 2) also reveals an asymmetric conformation of the {RhCl(PMe₂Ph)₂} vertex above the {SB₄} pentagonal face of the thiaborane ligand. This configuration is fully in accord with the ^{31}P NMR spectrum at 176 K (Table 2),

which exhibits two doublets of doublets. However, these two ^{31}P signals coalesce into one resonance at 213 K (36.4 MHz spectrum), demonstrating that the metal-atom environment of 4 is stereochemically non-rigid. We attribute this fluxional behaviour to a reversible metal-to-heteroborane partial rotation that equilibrates the two enantiomeric conformations of the metal centre above the {SB₄} face (schematics XVI and XVII). Variable-temperature NMR experiments give an activation energy ΔG^\ddagger for this fluxional process of 41 kJ mol^{−1} at 213 K.

This ‘rocking’ mechanism contrasts to the fluxional behaviour of a number of metallaheteroboranes containing the {Pd(PMe₂Ph)₂} or {Pd(PMe₂Ph)₂} groups that exhibit complete 360° contrarotational fluxionality associated with the metal-to-heteroborane bonding [1,11,16,21]. The reported activation energies ΔG^\ddagger for these complete rotational processes range from less than 30 up to *ca.* 65 kJ mol^{−1} [21]. In compound 4, however, the complete rotation of the {RhCl(PMe₂Ph)₂} unit above the pentagonal {SB₄} face is not achieved, even at higher temperatures (100 °C in C₆D₆CD₃ solution), implying a lower limit for ΔG^\ddagger of *ca.* 80 kJ mol^{−1} for any such complete contrarotation. This is demonstrated by the higher temperature ^1H NMR spectra that show two distinct sets of *P*-methyl resonances, which in a complete rotation would coalesce into one resonance set. Related hindered rotational fluxionalities in metal-to-heteroborane coordination are common, and, for example, have been previously reported for a large series of *closo* twelve-vertex rhodium and iridium dicarbaboranes of general formulation [L₂HM{carb}], where M is Rh or Ir, L is PPh₃, PEt₃, or PMe₂Ph and {carb} is {1,2-C₂B₉H₁₀R}, {1,7-C₂B₉H₁₀R}, or {1,12-C₂B₉H₁₀R}, with R being H, Me, Ph, or *n*-Bu [40]. Conversely, fluxionality involving a complete contrarotation of the heteroborane and non-heteroborane and ligand spheres about the metal centre is a general behaviour for *closo* twelve-vertex metallaheteroboranes of palladium and platinum (*e.g.* compound 7). The intimate mechanism of the complete rotation of {Pt(PR₃)₂} or {Pd(PR₃)₂} units versus the heteroborane ligand faces has been reported to involve the

shifting of these fragments via various η^4 - and η^3 -bonded coordinations (e.g. schematics **VIII** and **IX** above) with a concomitant twisting of the $\{M(PR_3)_2\}$ units about an axis passing approximately through the metal-atom and its antipodal boron atom [21]. Here it is of interest that the less intimate two-orbital metal-to-cluster bonding of the pseudo-square-planar palladium and platinum species gives a freer fluxionality than the more intimate, and more symmetric, three-orbital involvement in the cluster bonding shown by the octahedral $\{RhX(PR_3)_2\}$ and $\{IrX(PR_3)_2\}$ species. Finally, in terms of ligand-sphere fluxionality, it should be mentioned that the less localised rhodium-to-hydrocarbon bonding in $[2-(\eta^5-C_5Me_5)\text{-}closo\text{-}2,1\text{-}RhSB_{10}H_{10}]$ (**6**) will also of course enable fluxionality, specifically a very ready rotation of the symmetrically bound $\{C_5Me_5\}$ unit relative to a cluster axis approximately defined by the Rh(2)–B(9) vector, so that all five $\{CMe\}$ units of the $\{C_5Me_5\}$ moiety are rendered on time-average chemically equivalent in solution.

2.1. Experimental

2.1.1. General

The reactants $[cis\text{-}RhCl(PPh_3)_3]$ [41], $[cis\text{-}IrCl(PPh_3)_3]$ [42], $[\{RhCl_2(\eta^5-C_5Me_5)\}_2]$ [43] and $[nido\text{-}7\text{-}SB_{10}H_{12}]$ [19,20] were prepared by standard literature methods. The *N,N,N',N'*-tetramethylnaphthalene-1,8-diamine (tmnd), PPh_3 and PMe_2Ph were obtained from commercial sources. The reactions were carried out under an inert atmosphere of dry dinitrogen, although subsequent manipulations were carried out in air. Dried and degassed solvents were used throughout. Preparative thin-layer chromatography (TLC) was carried out using 1 mm layers of Silica Gel G (Fluka, type GF254) made from water slurries on glass plates of dimensions 20×20 cm followed by drying in air at 80 °C. NMR spectroscopy was performed at 2.4 and/or 9.4 T on commercially available instrumentation, with the general techniques being essentially as detailed in other paper from our laboratories [16c,44,45], and using the general approach as summarised, for example, by Reed [46]. Chemical shifts δ are given in ppm, relative to $\varepsilon = 100$ MHz for $\delta(^1H)$ (quoted ± 0.05 ppm) (nominally $SiMe_4$), $\varepsilon = 40.480$ 730 MHz for $\delta(^{31}P)$ (quoted ± 0.5 ppm) (nominally 85% H_3PO_4), and $\varepsilon = 32.083$ 971 MHz for $\delta(^{11}B)$ [47] (quoted ± 0.5 ppm) (nominally F_3BOEt_2 in $CDCl_3$); ε is as defined by McFarlane [48]. Mass spectrometry was carried out on a VG AUTO-SPEC instrument using either 70 eV EI (electron-impact) ionization and the solid-sample introduction probe, or using FAB ionisation (fast-atom bombardment; Cs^+ -ion bombardment of a target solution in 3-nitrobenzyl alcohol; gas-phase pressure 10^{-6} mm Hg), according to the characteristics of the sample. Compounds were characterised with multinuclear NMR spectra and mass spectrometry. Mass-spectrometric parent ions consistent with the proposed molecular formulations were observed in all cases, except for dimeric compound **3**, which showed an $\{M-2\}^+$

isotopomer envelope indicating ready dihydrogen loss. The relatively hydrogen-rich *nido* compound **2** also showed significant fragmentation with dihydrogen loss. All NMR spectra clearly showed that pure single compounds were present. Compound identification was assisted by comparison with established NMR data [13,14,17] for selenium- and tellurium-containing analogues of compounds **1**, **3**, **4**, **5**, and **6**. In the case of compound **4** the structure was confirmed in the solid-state by a single-crystal-X-ray diffraction analysis.

2.2. Synthesis of $[2,2-(PPh_3)_2\text{-}2\text{-}H\text{-}closo\text{-}2,1\text{-}RhSB_{10}H_{10}]$ (compound **1**) and $[\{(PPh_3)\text{-}closo\text{-}RhSB_{10}H_{10}\}_2]$ (compound **3**)

$[RhCl(PPh_3)_3]$ (100 mg; 120 μ mol) was added to a solution of $[nido\text{-}7\text{-}SB_{10}H_{12}]$ (20 mg; 130 μ mol) and tmnd (26 mg; 120 μ mol) in dry CH_2Cl_2 (ca. 20 ml) at room temperature. The reaction mixture was stirred under dinitrogen for 2 h. The resulting yellow solution was filtered off through silica. The filtrate was concentrated (rotary evaporator, 30 °C, water-pump pressure) and applied to preparative TLC plates. Elution with 3:2 CH_2Cl_2 /hexane gave three different bands: (a) purple, $R_F = 0.9$, (b) yellow, $R_F = 0.8$, and (c) orange, $R_F = 0.7$. These were removed from the plates and the compounds extracted with CH_2Cl_2 . After recrystallisation from CH_2Cl_2 /hexane, the components of these bands were thence, respectively, characterised as the purple dimer $[\{(PPh_3)\text{-}closo\text{-}RhSB_{10}H_{10}\}_2]$ (**3**) (6 mg; 3 μ mol; 5%), yellow $[2,2-(PPh_3)_2\text{-}2\text{-}H\text{-}closo\text{-}2,1\text{-}RhSB_{10}H_{10}]$ (**1**) (24 mg; 35 μ mol; 26%) and orange $[8,8-(PPh_3)_2\text{-}nido\text{-}8,7\text{-}RhSB_9H_{11}]$ (**2**) (16 mg; 21 μ mol; 17%).

2.3. Synthesis of $[2,2-(PMe_2Ph)_2\text{-}2\text{-}Cl\text{-}closo\text{-}2,1\text{-}RhSB_{10}H_{10}]$ (compound **4**)

PMe_2Ph (0.4 ml of a 0.1 M solution in CH_2Cl_2) was added to a yellow solution of $[2,2-(PPh_3)_2\text{-}2\text{-}H\text{-}closo\text{-}RhSB_{10}H_{10}]$ (**1**) (prepared as above; 20 mg; 26 μ mol) in CH_2Cl_2 (30 ml) at room temperature. The reaction mixture was stirred for 4 h under dinitrogen, then filtered through silica, reduced in volume as above, and applied to a preparative TLC plate. The chromatogram was developed with 1:1 CH_2Cl_2 /hexane, leading to the isolation of a yellow component of $R_F = 0.43$ that was characterised as $[2,2-(PMe_2Ph)_2\text{-}2\text{-}Cl\text{-}closo\text{-}2,1\text{-}RhSB_{10}H_{10}]$ (**4**) (3 mg; 5 μ mol; 20%). Crystals suitable for X-ray diffraction analysis were grown by diffusion of hexane into a solution of **4** in CH_2Cl_2 using the overlaying technique.

2.4. Synthesis of $[2,2-(PPh_3)_2\text{-}2\text{-}H\text{-}closo\text{-}2,1\text{-}IrSB_{10}H_{10}]$ (compound **5**)

Using the same procedure as in the synthesis of compound **3** above, the reaction between $[IrCl(PPh_3)_3]$ (100 mg; 100 μ mol) and *nido*-7- $SB_{10}H_{12}$ (17 mg; 108 μ mol) in the presence of tmnd afforded a pale-yellow product of

$R_F = 0.43$ (eluent mixture 3:2 $\text{CH}_2\text{Cl}_2/\text{hexane}$), which was recrystallised from $\text{CH}_2\text{Cl}_2/\text{hexane}$ and identified as [2,2-(PPh_3)₂-H-closo-2,1-IrSB₁₀H₁₀] (**5**; 10 mg; 12 μmol ; 12%).

2.5. Synthesis of [2-(η^5 -C₅Me₅)-closo-2,1-RhSB₁₀H₁₀] (compound **6**)

Dimeric [$\{\text{RhCl}_2(\eta^5\text{-C}_5\text{Me}_5)\}_2$] (50 mg; 83 μmol) was added to a colourless solution of [*nido*-7-SB₁₀H₁₂] (28 mg; 180 μmol) and tmnd (71 mg; 330 μmol) in CH_2Cl_2 (50 ml) at room temperature. The resulting red solution was stirred for 15 h, and monitored periodically by analytical TLC. The final reaction mixture was filtered through silica gel, concentrated (rotary evaporator) and subjected to preparative TLC on silica gel with $\text{CH}_2\text{Cl}_2/\text{hexane}$ (1:1) as eluting medium. The major band ($R_F = 0.5$) was located under UV irradiation, extracted into CH_2Cl_2 , recrystallised from $\text{CH}_2\text{Cl}_2/\text{hexane}$, and characterised by mass spectrometry and NMR spectroscopy as colourless [2-(η^5 -C₅Me₅)-closo-2,1-RhSB₁₀H₁₀] (**6**) (16 mg; 41 μmol ; 25%).

2.6. Single-crystal X-ray diffraction analysis

Crystals of [2,2-(PMe₂Ph)₂-2-Cl-closo-2,1-RhSB₁₀H₁₀] (**4**) suitable for the X-ray analysis were grown from concentrated CH_2Cl_2 solution by liquid–liquid diffusion from an overlayer of hexane. The collection of data was carried out using a Stoe STADI4 diffractometer operating in the ω – θ scan mode using Mo K α radiation. The structure was solved by direct methods using SHELXS 86 [49] and was refined by full-matrix least squares using SHELXL 93 [50]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The cluster-associated hydrogen atoms were located on Fourier-difference syntheses and were freely refined isotropically.

Crystal data are as follows. [2,2-(PMe₂Ph)₂-2-Cl-closo-2,1-RhSB₁₀H₁₀] (**4**): C₁₆H₃₂B₁₀P₂SClRh; $M = 564.88$, yellow prism, $0.46 \times 0.42 \times 0.38$ mm, from $\text{CH}_2\text{Cl}_2/\text{hexane}$, monoclinic, $a = 11.8132(7)$, $b = 13.1857(12)$, $c = 16.4234(13)$ Å, $\beta = 98.582(6)^\circ$, $U = 2529.6(6)$ Å³, $D_{\text{calc}} = 1.483$ Mg m⁻³; $\lambda = 0.71073$ Å (Mo K α), $T = 173$ K, space group $P2_1/c$, $Z = 4$, $\mu(\text{Mo K}\alpha) = 0.995$ mm⁻¹, $R_1 = 0.0181$ for 4058 reflections with $I > 2\sigma(I)$, and $wR_2 = 0.0473$ for all 4444 unique reflections.

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Appendix A. Supplementary material

CCDC 280332 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.11.014.

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