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Polyhedral metallathiaborane chemistry: Synthesis and characterisation of metallathiaboranes based on the twelve-vertex icosahedral *closo*-$\{MSB_{10}H_{10}\}$ unit, where M is Rh or Ir

Ramón Macías [a,b,*], Mark Thornton-Pett [a], Josef Holub [c], Trevor R. Spalding [d], Yousafzai Faridoon [d], Bohumil Štíbr [c], John D. Kennedy [a]

[a] *School of Chemistry, University of Leeds, Leeds, West Yorkshire UK LS2 9JT, United Kingdom*
[b] *Instituto Universitario de Catálisis Homogénea, Facultad de Ciencias, Edificio D (4ª planta), Pedro Cerbuna 12, 50009 Zaragoza, Spain*
[c] *Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic, 25068 Řež u Prahy, Czech Republic*
[d] *Department of Chemistry, University College Cork, National University of Ireland, Cork, Ireland*

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Abstract

The reaction of [*nido*-7-$SB_{10}H_{12}$] with [$RhCl(PPh_3)_3$] in the presence of *N*,*N*,*N′N′*-tetramethylnaphthalene-1,8-diamine (tmnd) in CH_2Cl_2 gives twelve-vertex [2,2-$(PPh_3)_2$-2-H-*closo*-2,1-$RhSB_{10}H_{10}$] (**1**) and eleven-vertex [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (**2**), as major products, plus the dimeric species [{(PPh_3)-*closo*-$RhSB_{10}H_{10}\}_2$] (**3**) as a minor product. Reaction of **1** with PMe_2Ph in CH_2Cl_2 results in phosphine exchange and hydride substitution, affording the chloro analogue of **1**, [2,2-$(PMe_2Ph)_2$-2-Cl-*closo*-2,1-$RhSB_{10}H_{10}$] (**4**). By contrast, reaction between [$IrCl(PPh_3)_3$] and [*nido*-7-$SB_{10}H_{12}$] in CH_2Cl_2 with tmnd affords only one product, twelve-vertex [2,2-$(PPh_3)_2$-2-H-*closo*-2,1-$IrSB_{10}H_{10}$] (**5**). [$RhCl_2(\eta^5$-$C_5Me_5)]_2$ with [*nido*-7-$SB_{10}H_{12}$] under the same conditions gives twelve-vertex [2-(η^5-C_5Me_5)-*closo*-2,1-$RhSB_{10}H_{10}$] (**6**). All the compounds are characterised by NMR spectroscopy, and by mass spectrometry, and the molecular structure of [2,2-$(PMe_2Ph)_2$-2-Cl-*closo*-2,1-$RhSB_{10}H_{10}$] (**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 $\{RhCl(PMe_2Ph)_2\}$ unit above the $\{SB_4\}$ pentagonal face of the $\{SB_{10}H_{10}\}$ fragment.

Keywords: Metallathiaborane; Polyhedral chemistry

1. Introduction

Contiguous metallaheteroborane cluster compounds based on the icosahedral twelve-vertex $\{2,1\text{-}MEB_{10}H_{10}\}$ 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 [$(\eta^5$-$C_5H_5)MC_2B_9H_{10}$], obtained from three-component reactions between simple transition-element chlorides with Group 1 salts of the $[\eta^5$-$C_5H_5]^-$ hydrocarbon anion and the *nido* eleven-vertex $[C_2B_9H_{12}]^-$ or $[C_2B_9H_{11}]^{2-}$ carbaborane anions [1–3]. Routes to $\{MEB_{10}\}$ species extend from this type of process by the reactions of *nido* eleven-vertex anions based on $\{EB_{10}\}$ 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 $\{MSB_{10}\}$ species starting from the *nido* eleven-vertex $\{SB_{10}\}$ system.

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[*] Corresponding author.
E-mail address: rmacia@unizar.es (R. Macías).

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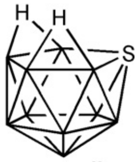
I

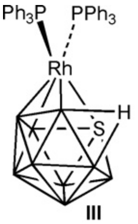


II

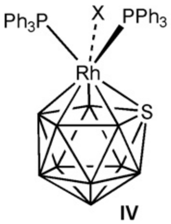
Eleven-vertex [*nido*-7-$SB_{10}H_{12}$] (schematic cluster structure **II**) was originally reported by Muetterties and co-workers [19], and successively improved preparations have subsequently been reported by Sneddon and co-workers [20]. Although its metallathiaborane derivatives [2,2-$(PEt_3)_2$-*closo*-2,1-$PtSB_{10}H_{10}$] [12] and [2,2-$(PPh_3)_2$-2-H-*closo*-2,1-$RhSB_{10}H_{10}$] [15] were among the earliest examples of reported twelve-vertex metallaheteroboranes, the chemistry of {MSB_{10}} cluster species has not been very well developed compared with their isoelectronic metalladicarbaborane analogues. For example, there are only two crystallographic studies of such *closo* twelve-vertex metallathiaboranes: one is the ferrathiaborane [2-(η^6-C_6H_5Me)-*closo*-2,1-$FeSB_{10}H_{10}$] [18] and the other is the platinum derivative [2,2-$(PMe_2Ph)_2$-*closo*-2,1-$PtSB_{10}H_{10}$] (referred to below as compound **7**) [21]. In the crystallographic analysis of [2-(η^6-C_6H_5Me)-*closo*-2,1-$FeSB_{10}H_{10}$] 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 {$SB_{10}H_{10}$} ligand fragment.

2. Results and discussion

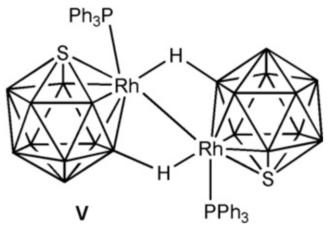
The rhodium(I) complex [$RhCl(PPh_3)_3$] was added to [*nido*-7-$SB_{10}H_{12}$] in the presence of the non-nucleophilic base *N*,*N*,*N*′,*N*′-tetramethylnaphthalene-1,8-diamine (tmnd) in CH_2Cl_2 solution at room temperature. The resulting reaction gave several products. After repeated preparative-scale thin-layer chromatography (TLC), we were able to isolate and characterise three major components: yellow [2,2-$(PPh_3)_2$-2-H-*closo*-2,1-$RhSB_{10}H_{10}$] (**1**) (26% yield), orange [8,8-$(PPh_3)_2$-*nido*-8,7-$RhSB_9H_{10}$] (**2**) (17% yield) and purple [{(PPh_3)-*closo*-$RhSB_{10}H_{10}$}$_2$] (**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 species. The new double-cluster 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 [{(PPh_3)-*closo*-$RhTeB_{10}H_{10}$}$_2$] (**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 PMe_2Ph in CH_2Cl_2, resulting in the synthesis of the chloro species [2,2-$(PMe_2Ph)_2$-2-Cl-*closo*-2,1-$RhSB_{10}H_{10}$] (**4**) (schematic cluster structure **IV**, where X = Cl), isolated in 20% yield.



III



IV



The 100-mg-scale reaction of the iridium(I) complex [$IrCl(PPh_3)_3$] 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-$(PPh_3)_2$-2-H-*closo*-2,1-$IrSB_{10}H_{10}$] (**5**), isolated in 12% yield (Eq. (1)).

$$\begin{aligned}&SB_{10}H_{12} + [IrCl(PPh_3)_3] + \text{tmnd}\\&\quad\rightarrow [(PPh_3)_2HIrSB_{10}H_{10}]\mathbf{5} + [\text{tmndH}]^+ + Cl^- + PPh_3\end{aligned} \tag{1}$$

The pentamethylcyclopentadienyl rhodium analogue of **1**, *i.e.* [2-(η^5-C_5Me_5)-*closo*-2,1-$RhSB_{10}H_{10}$] (**6**), was similarly obtained in 25% yield from the reaction between [$RhCl_2(\eta^5$-$C_5Me_5)]_2$ and [*nido*-7-$SB_{10}H_{12}$] in the presence of tmnd in CH_2Cl_2 solution at ambient temperature (Eq. (2)). This colourless rhodathiaborane was also purified by preparative TLC and characterised by NMR spectroscopy and mass spectrometry.

$$\begin{aligned}&2SB_{10}H_{12} + [RhCl_2(C_5Me_5)]_2 + 4\text{tmnd}\\&\quad\rightarrow 2[(C_5Me_5)RhSB_{10}H_{10}]\mathbf{6} + 4[\text{tmndH}]^+ + 4Cl^-\end{aligned} \tag{2}$$

The molecular structures of the metallathiaboranes in solution were readily established by means of ^{11}B, ^{31}P and ^1H multinuclear and multiple resonance NMR spectroscopy. The data are summarised in Tables 1–3. For the four monomeric *closo* species [2,2-$(PPh_3)_2$-2-H-*closo*-2,1-$RhSB_{10}H_{10}$] (**1**), [2,2-$(PMe_2Ph)_2$-2-Cl-*closo*-2,1-$RhSB_{10}H_{10}$] (**4**), [2,2-$(PPh_3)_2$-2-H-*closo*-2,1-$IrSB_{10}H_{10}$] (**5**) and [2-(η^5-C_5Me_5)-*closo*-2,1-$RhSB_{10}H_{10}$] (**6**), the ^{11}B and ^1H resonances were assigned on the reasoned basis of relative intensities and ^1H–{^{11}B(selective)} experiments, and thence by comparison with other previously assigned *closo* twelve-vertex