

METALLABORANE REACTION CHEMISTRY. PART 4. POLYHEDRAL THIAMETALLABORANE SYNTHESIS *via* DIRECT INCORPORATION OF SULFUR INTO METALLABORANES*Young-hee KIM, Robert GREATREX¹ and John D. KENNEDY²*School of Chemistry, University of Leeds, Leeds LS2 9JT, England;**e-mail: ¹ robertg@chem.leeds.ac.uk, ² johnk@chem.leeds.ac.uk*

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It is a pleasure to dedicate this paper to Professor Jaromir Plesek on the occasion of his 70th birthday, in recognition both of his stimulating presence in the world community of boron chemists, and of his outstanding personal contributions to the pioneering, and the subsequent development, of polyhedral boron-containing cluster chemistry.

A preliminary investigation of the direct reaction of elemental sulfur with the representative metallaboranes [6-(η^5 -C₅Me₅)-*nido*-6-RhB₉H₁₃] and [6-(η^6 -MeC₆Me₄i-Pr)-*nido*-6-RuB₉H₁₃] in the presence of base gives products that result from (i) the addition of one sulfur vertex and (ii) the addition of two sulfur vertices into the metallaborane cluster, as well as (iii) boron-vertex elimination accompanied by sulfur-vertex addition. Products characterised include [7-(η^5 -C₅Me₅)-*nido*-7,11,12-RhS₂B₉H₉], [7-(η^6 -MeC₆H₄i-Pr)-*nido*-7,11,12-RuS₂B₉H₉], [8-(η^6 -MeC₆H₄i-Pr)-*nido*-8,7-RuSB₉H₁₁], and a species tentatively identified as [9-(η^6 -MeC₆H₄i-Pr)-*nido*-9,7,8-RuS₂B₈H₈].

Key words: Metallaborane; Thiametallaborane; Cluster; NMR; Metallaboranes, reactions of; Elemental sulfur.

There is current increasing interest in polyhedral thiametallaborane chemistry, with results in {MSB₈} (ref.¹), {MSB₉} (refs¹⁻⁷), {MS₂B₆} (refs⁸⁻¹¹), {MS₂B₉} (refs^{11,12}), {MS₂B₈} (ref.⁶), {MS₂B₉} (ref.⁶), {MS₂B₁₅} (ref.¹³), {MS₂B₁₆} (ref.¹⁴), {M₂SB₉} (refs^{1,2}), {M₂S₂B₆} (ref.¹¹), {M₂S₂B₇} (ref.¹¹) and {M₂S₂B₁₅} (ref.¹⁵) cluster systems being recently reported. All these cluster types have been synthesized from the reactions of metal centres with pre-formed polyhedral thaborane substrates. Surprisingly, the converse synthetic approach, the reaction of sulfur with pre-formed polyhedral metallaborane substrates, is not previously reported, although reaction of sulfur (either

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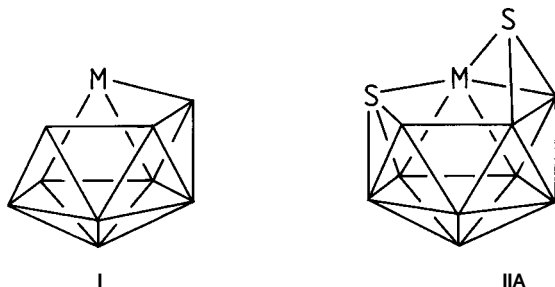
elemental or as anionic polysulfide) with boranes or borane anions is a well recognised route to thiaborane cluster compounds that do not contain metal atoms (ref.¹⁶) (see, for example, ref.¹⁷, together with other references cited therein). We have now tested this converse approach, working at small scale (*ca* 100 μmol) in these initial siting experiments, and using the ten-vertex metallaborane species [6-($\eta^5\text{-C}_5\text{Me}_5$)-*nido*-6-RhB₉H₁₃] (**1a**)¹⁸ and [6-($\eta^6\text{-MeC}_6\text{Me}_4\text{i-Pr}$)-*nido*-6-RuB₉H₁₃] (**1b**)¹⁹ (both of schematic cluster structure **I** as representative metallaborane examples. We conclude that direct reaction with sulfur is in fact a convenient and viable route for interesting thiametallaborane syntheses. We present preliminary results from these siting experiments here.

RESULTS AND DISCUSSION

Reaction between [6-($\eta^5\text{-C}_5\text{Me}_5$)-*nido*-6-RhB₉H₁₃] (**1a**)¹⁸ or [6-($\eta^6\text{-MeC}_6\text{Me}_4\text{i-Pr}$)-*nido*-6-RuB₉H₁₃] (**1b**)¹⁹ and an excess of elemental sulfur (S₈) in the presence of *N,N,N',N'*-tetramethylnaphthalene-1,8-diamine (tmnd) as non-nucleophilic base is complete in each case in one-to-two hours in CHCl₃ solution at *ca* +65 °C. Under the same conditions, but with no tmnd present, no significant reaction occurs.

Chromatography of the products of the reaction with the rhodaborane **1a** results in the isolation of only one predominant product, a red solid identified as the known^{6,20} species [7-($\eta^5\text{-C}_5\text{Me}_5$)-*nido*-7,11,12-RhS₂B₉H₉] (**2a**), of twelve-vertex *nido*-type architecture as in schematic cluster structure **IIA**. It was isolatable in the excellent yield of *ca* 80%. It was readily identified by mass spectrometry and NMR spectroscopic comparison with reported^{6,20} data (Table I), and has close spectroscopic analogies with the diselenacobaltaborane analogue [7-(C₅H₅)-*nido*-7,11,12-CoSe₂B₉H₉] (ref.²¹) and the more recently reported^{6,20} phosphine iridium analogue [7,7,7-(PPh₃)₃H-*nido*-7,11,12-IrS₂B₉H₉]. It has previously been prepared *via* the more conventional reaction between the [*arachno*-S₂B₉H₁₀]⁻ anion¹⁷ and [($\eta^5\text{-C}_5\text{Me}_5$)RhCl₂]₂ but the isolated yield was an order of magnitude lower^{6,20}, at 8%.

The ruthenium congener [7-($\eta^6\text{-MeC}_6\text{Me}_4\text{i-Pr}$)-*nido*-7,11,12-RuS₂B₉H₉] (**2b**) is isolated and identified similarly from the reaction of the ruthenaborane **1b**, but now the yield is somewhat smaller than for **2a**, at *ca* 30%, and several other metallathaborane products are present in yields sufficient for further characterisation (see below).



It can be seen (schematic cluster structure **IIA**) that the cluster architecture of compounds **2a** and **2b** derives geometrically from compounds **1a** and **1b** (schematic cluster structure **I**) by the addition of two sulfur atoms at cluster sites adjacent to the metal centre. Note that compounds **2a** and **2b**, together with the {CoSe₂} analogue [7-(C₅H₅)-*nido*-7,11,12-CoSe₂B₉H₉] (ref.²¹) are all fluxional (schematics **IIB** and **IIC**)^{6,20}, and at room temperature give ¹B and ¹H 2 : 2 : 2 : 1 : 1 : 1 NMR relative intensity patterns for their {B₉H₉} units rather than nine separate resonance positions in each case. Δ*G*[‡] for the fluxional process is estimated at *ca* 30 kJ mol⁻¹ for compound **2a** (ref.²⁰).

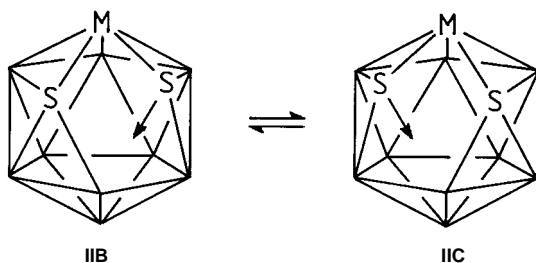


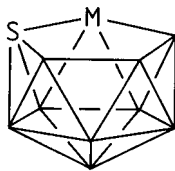
TABLE I

Observed ¹H and ¹B NMR data (CDCl₃ solutions) for [7-(MeC₆H₄i-Pr)-*nido*-7,11,12-RuS₂B₉H₉] (**2b**) and the proposed anion [Ru(*nido*-S₂B₉H₉)₂]²⁻ (**6**), together with data for [7-(C₅Me₅)-*nido*-7,11,12-RhS₂B₉H₉] (**2a**) for comparison

Assignment	2a ^{a,b}		2b ^{b,c}		6 ^{d,e}	
	δ(¹ B)	δ(¹ H)	δ(¹ B)	δ(¹ H)	δ(¹ B)	δ(¹ H)
BH(10)	+17.6	+4.17	+13.4	+3.93	+10.3	+3.69
BH(2,8)	+8.2	+2.98	+3.0	+3.06	+7.0	+3.66 ^f
BH(3)	+0.3	+2.71	-2.4	+3.45	+1.2	+3.45
BH(5)	-4.3	+3.06	-3.0	+3.14	-2.3	+3.87
BH(1,4)	-6.6	+3.20	-9.0	+3.04	-13.3	+2.70 ^g
BH(6,9)	-23.8	+1.35	-24.1	+1.28	-23.0 ^h	<i>ca</i> +1.60 ⁱ

^a Data from ref.²⁰; δ(¹H)(C₅Me₅) +1.92 ppm. ^b 294–297 K. ^c δ(¹H) (MeC₆H₄i-Pr) at +2.18 (Me), +1.35 (Me₂; doublet), +2.85 (CH; septet) and +5.6 to +5.9 (C₆H₄; multiplet). ^d 313 K. ^e No ¹H resonances attributable to [MeC₆H₄i-Pr] exhibited. ^f At <295 K, separates into two resonances at δ(¹H) +4.53 and +2.95. ^g At <295 K, separates into two resonances at δ(¹H) +2.61 and +2.25. ^h At <295 K, separates into two resonances at δ(¹B) *ca* -32 and *ca* -14; coalescence temperature *ca* 300 K at 128 MHz, implying Δ*G*[‡] *ca* 46 kJ mol⁻¹. ⁱ At <295 K, separates into two resonances at δ(¹H) +2.45 and +0.76.

Chromatography also isolates additional thimetallaboranes in viable yields from the reaction of the ruthenaborane **1b** with elemental sulfur. The principal one of these is the yellow solid monothiaruthenaborane [8-(η^6 -MeC₆Me₄i-Pr)-*nido*-8,7-RuSB₉H₁₁] (**3**) of eleven-vertex *nido* architecture as in schematic structure **III**, obtained in *ca* 30% yield.



III

Although it is previously unreported, it is a straightforward analogue of the known³ $\{(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}\}$ species, and its 11-chloro derivative has also been tentatively identified¹. It is also therefore readily formulated by mass spectrometry and NMR spectro-

TABLE II
Observed ¹H and ¹¹B NMR data for [8-(MeC₆H₄i-Pr)-*nido*-8,7-RuSB₉H₁₁] (**3**) and its iridium analogue [8-(C₅Me₅)-*nido*-8,7-IrSB₉H₁₁] for comparison; CDCl₃ solutions at 291–297 K

Assignment	3 ^a		(C ₅ Me ₅)Ir analogue ^b	
	$\delta(^{11}\text{B})$	$\delta(^1\text{H})$	$\delta(^{11}\text{B})$	$\delta(^1\text{H})$
BH(5)	+10.1	+3.75	+7.7	+4.80
BH(3)	+1.3	+2.67	+1.1	+2.52
BH(9)	-2.2	+2.70	-2.6	+2.90
BH(11)	-8.7	+2.06	-12.9	+2.57
BH(4)	-12.3	+2.32	-13.8	+1.20
BH(2)	-14.3	+2.23	-17.0	+2.61
BH(6)	-16.0	+2.47	-18.2	+3.91
BH(1)	-20.0	+1.77	-22.1	+1.46
BH(10)	-21.2	+1.40	-23.0	+1.64
$\mu\text{H}(8,9)$	-	-11.35	-	-11.40
$\mu\text{H}(10,11)$	-	-4.35	-	-4.52

^a Assignment by comparison with the (C₅Me₅)Ir compound; there may be some uncertainty among BH(11), BH(4) and BH(2). $\delta(^1\text{H})$ (MeC₆H₄i-Pr) at +2.25 (Me), +1.40 (Me₂; doublet), +2.97 (CH; septet) and +5.6 to +5.9 (C₆H₄; multiplet). ^b Data from ref.³; $\delta(^1\text{H})(\text{C}_5\text{Me}_5)$ +2.11 ppm.

scopy in comparison with these previously reported species (Table II). It can be seen that its cluster architecture is derived from compound **1b** *via* a second synthetic principle, *viz.* the addition of one rather than two sulfur atoms to the basic metallaborane substrate (compare structures **I** and **III**). The yield of compound **3** of *ca* 30% is an order of magnitude higher than the yield (*ca* 2%) of its 11-chloro analogue which is the only {RuSB₉} product isolated from the more conventional metallathiaborane synthetic approach using [(η⁶-MeC₆H₄i-Pr)RuCl₂]₂ and the [*arachno*-SB₉H₁₂]⁻ anion¹.

An interesting, third, product from the ruthenaborane reaction, but in smaller yield (*ca* 7%), is a yellow solid which we tentatively propose, from mass spectrometry and NMR spectroscopy (Table III), to be the eleven-vertex dithiaruthenaborane [9-(η⁶-MeC₆H₄i-Pr)-*nido*-9,7,8-RuS₂B₈H₈] (compound **4**, schematic structure **IVA**). For compound **4**, the mass spectrum as well as the NMR data are entirely consistent with the molecular formulation [(MeC₆H₄i-Pr)RuS₂B₈H₈]. A cluster electron-count thence gives 26 cluster electrons as required for an eleven-vertex *nido* geometry. The compound is therefore a close relative of the known⁶ dithiarhodaborane [8,8,8-(PPh₃)₂H-*nido*-8,7,9-RhS₂B₈H₈] (compound **5**, schematic cluster structure **V**). However, NMR spectroscopy distinguishes eight different BH(*exo*) units, demonstrating asymmetry, whereas a direct analogue of compound **5**, *viz.* [8-(η⁶-MeC₆H₄i-Pr)-*nido*-8,7,9-RuS₂B₈H₈], would have mirror-plane symmetry and exhibit a 2 : 2 : 2 : 1 : 1 : 1 relative intensity pattern in each of

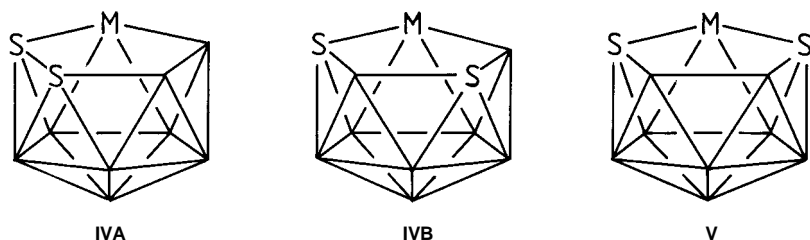
TABLE III

Observed ¹H and ¹¹B NMR data (CDCl₃ at 294–297 K) for compound **4**, tentatively proposed to be [9-(η⁶-MeC₆H₄i-Pr)-*nido*-9,7,8-RuS₂B₈H₈]

BH designation	δ(¹¹ B)	δ(¹ H) ^a	[¹¹ B- ¹¹ B]COSY correlations ^b	[¹ H- ¹ H]COSY correlations ^c
A	+10.2	+3.87	E	D
B	+7.5	+2.51	E H	G H?
C	+4.5	+4.28	–	F
D	–1.0	+3.00	H	A E?
E	–3.8	+2.03	A B	D H
F	–10.3	+2.50	–	C G
G	–18.9	+2.35	H	B F H?
H	–32.6	+1.55	B D G	B E

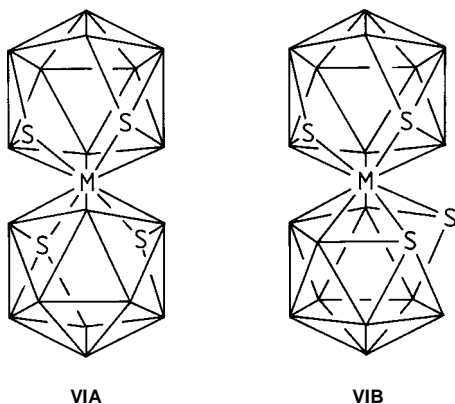
^a Additionally δ(¹H) (MeC₆H₄i-Pr) at +2.28 (Me), +1.42 (Me₂; doublet), +2.79 (CH; septet) and +5.7 to +6.0 (C₆H₄; multiplet). ^b Recorded under conditions of complete {¹H(broad band)} decoupling; correlations are generally not observed for ⁿJ(¹¹B-¹¹B) when *n* > 1. ^c Recorded under conditions of complete {¹¹B(broad band)} decoupling; correlations are most generally observed for ⁿJ(¹H-¹H) when *n* = 2 or 3; sometimes 4.

its solution ^{11}B and ^1H NMR spectra. Compounds **4** and **5** therefore differ in the disposition of the one ruthenium and two sulfur centres. On the presumption¹¹ of the retention of open-face positions for the three heteroatoms, either of two structural types, a $\{9,7,8\text{-RuS}_2\text{B}_8\}$ structure **IVA**, or a $\{10,7,9\text{-RuS}_2\text{B}_8\}$ structure **IVB**, can be entertained. Of these, we tentatively propose the former $\{9,7,8\text{-RuS}_2\text{B}_8\}$ structure **IVA** on the basis of the tendency of metal and sulfur atoms to group together on the open face of B-frame clusters¹¹. However, although sufficient [$^{11}\text{B}\text{-}^{11}\text{B}$] and [$^1\text{H}\text{-}^1\text{H}$] COSY NMR correlations are present to establish a contiguous $\{(\text{BH})_8\}$ system, there are insufficient correlations precisely to define a specific eight-boron framework, and so the possibility of the alternative $\{10,7,9\text{-RuS}_2\text{B}_8\}$ structure **IVB** cannot be excluded on present evidence.



Both reactions yield other boron-containing by-products, in smaller yields, that we have not been able thoroughly to characterise so far. One of the most interesting of these is an unstable, intensely coloured, blue species **6**, obtained from the ruthenium system. It is also obtained, in somewhat higher yield, when the reaction starting from compound **1b** and elemental sulfur is carried out using KH as base in THF solution, rather than using tmnd as base in CH_2Cl_2 solution. Its ^{11}B and ^1H cluster NMR properties at temperatures higher than ambient (Table I) show a 2 : 2 : 2 : 1 : 1 : 1 relative intensity pattern and analogous shielding characteristics to those of compounds **2a** and **2b**, suggesting the same $\{\text{MS}_2\text{B}_9\}$ structural type **IIA**, and suggesting, in addition, the same fluxionality **IIB/IIIC** at higher temperatures. There are now no ^1H resonances corresponding to the $\{\text{MeC}_6\text{H}_4\text{-i-Pr}\}$ residue, showing that this is lost, which may imply that the ruthenium coordination sites in compound **6** are taken up by two $\{\text{S}_2\text{B}_9\text{H}_9\}$ residues. This in turn implies a dianionic formulation $[\text{Ru}(\text{S}_2\text{B}_9\text{H}_9)_2]^{2-}$ (e.g. schematic structures **VIA** and **VIB**). An ionic formulation would be consistent with the observed lower chromatographic mobility. The countercation cannot be assessed on present evidence. As just mentioned, like compounds **2a** and **2b**, the species is also fluxional. As the temperature is lowered through room temperature, there is an incipient splitting of the ^{11}B resonances of relative intensity 2. This splitting is most apparent for the (6,9) resonance at $\delta(^{11}\text{B})$ ca -23 ppm, which at 223 K is clearly split into two resonances at $\delta(^{11}\text{B})$ ca -14 and ca -32 ppm. The coalescence temperature for these last two resonances is observed to be ca 300 K in the 128 MHz spectrum, implying ΔG^\ddagger ca 46 kJ mol $^{-1}$ for

the fluxional process at this temperature. This value is much higher than the value of *ca* 30 kJ mol⁻¹ determined^{6,20} for **2a**, but much lower than for the phosphine iridium analogue [7,7,7-(PPh₃)₂H-*nido*-7,11,12-IrS₂B₉H₉], which exhibits no evidence of fluxionality^{6,20}. Interestingly, at 223 K there appears to be additional incipient broadening and thence splitting of the ¹¹B resonances of relative intensity 1, which may imply equilibration among fluxamer-rotamers such **VIA** and **VIB**. We currently plan to investigate these phenomena, as well as the other minor products revealed in this preliminary survey, in more detail.



CONCLUSIONS

A principal conclusion from these siting experiments that are presented in this preliminary communication is that the direct reaction of elemental sulfur with pre-formed metallaborane substrates is indeed a viable and potentially useful alternative synthetic entry into thiametallaborane chemistry. It thereby complements the hitherto predominant route^{1-14,20} that involves the converse approach, *viz.* the reactions of metal centres with pre-formed thiaborane substrates. Within the general approach, several different reaction processes are observable. In terms of the sulfur incorporation itself, three fundamental modes are readily discernable: (i) the addition of one sulfur vertex to a cluster (as in the generation of compound **3**), (ii) the addition of two sulfur vertices to a cluster (as in the generation of compounds **2a** and **2b**), and (iii) sulfur-vertex addition accompanied by boron-vertex elimination (as in the generation of compound **4**). Some features of these reactions are currently a challenge to explain. For example, the formation of species **6**, in which the loss of the ruthenium-bound MeC₆H₄i-Pr residue is very unusual, and also the different behaviour of the closely related ruthenaborane and the rhodaborane compounds **1a** and **1b**, which give non-equivalent products under the same reaction conditions. An interesting chemistry is thereby presaged. In future work we hope to be able to apply the approach to the use of other main-group elements, and

to metallaborane systems other than the ten-vertex *nido* one. The route, *viz.* the direct reaction of metallaboranes with main-group elements themselves, constitutes an interesting adjunct to a second new entry into heterometallaborane contemporaneously reported elsewhere²², *viz.* the direct reaction of metallaboranes with the hydrides of main-group elements, such as H_4N_2 , H_2S , and H_2C_2 , which has been examined in siting experiments using the versatile²³ nine-vertex *arachno* iridaborane $[(CO)(PMe_3)_2HIrB_8H_{12}]$ as a representative metallaborane model.

EXPERIMENTAL

General

The starting materials $[6-(\eta^6-MeC_6H_4i-Pr)-nido-6-RuB_9H_{13}]$ and $[6-(\eta^5-C_5Me_5)-nido-6-RhB_9H_{13}]$ were prepared as described^{18,19}. Elemental sulfur, *N,N,N',N'*-tetramethylnaphthalene-1,8-diamine (tmnd) and potassium hydride were obtained commercially. Potassium hydride was freed of mineral oil by washing with hexane. 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. Tetrahydrofuran was distilled from sodium in the presence of sodium benzophenone. Thin-layer chromatography (TLC) was performed using 1 mm layers of silica gel G (Fluka type GF254) on 20 × 20 cm glass plates, made from aqueous slurries followed by drying in air at 80 °C.

Nuclear Magnetic Resonance Spectroscopy and Mass Spectrometry

NMR spectroscopy was performed at *ca* 5.9 T and 9.4 T (fields corresponding to 250 and 400 MHz ¹H frequencies, respectively) using commercially available instrumentation and using techniques and procedures as described and enunciated elsewhere²⁴. Chemical shifts δ are given in ppm to high frequency (low field) of $\Xi = 100$ MHz for $\delta(^1H)$ (± 0.05 ppm) (nominally TMS) and $\Xi = 32.083972$ MHz for $\delta(^{11}B)$ (± 0.5 ppm) (nominally F_3B-OEt_2 in $CDCl_3$). Ξ is as defined by McFarlane²⁵. Mass spectrometry was performed on a VG Autospec instrument with EI ionisation at 70 eV: the neutral molecular compounds **2a**, **2b**, **3** and **4** all had high-mass cut-offs corresponding to their highest molecular isotopomers.

Reaction of $[6-(\eta^5-C_5Me_5)-nido-6-RhB_9H_{13}]$ **1a** with Elemental Sulfur and tmnd

To an orange solution of $[6-(\eta^5-C_5Me_5)-nido-6-RhB_9H_{13}]$ (**1a**; 26 mg, 86 μ mol) in chloroform (25 ml) was added tmnd (18 mg, 86 μ mol) and yellow elemental sulfur, S_8 (8 mg, 255 μ mol). The solution was heated at reflux (oil bath at 70 °C) for one hour whereupon it turned to a red-brown. It was filtered through TLC-grade silica using CH_2Cl_2 , and the filtrate then evaporated to dryness (rotary evaporator, <45 °C, water-pump pressure). The resulting solid was dissolved in minimum CH_2Cl_2 and applied to preparative TLC plates, which were then developed using CH_2Cl_2 as liquid phase to give one major compound and several minor products. The major product was a red compound (R_F 0.6), identified by NMR spectroscopy and mass spectrometry (Table I) as known^{6,20} $[7-(\eta^5-C_5Me_5)-nido-7,11,12-RhS_2B_9H_9]$ (**2a**; 25 mg, 80%). The minor products were present in insufficient amounts for satisfactory identification on the reaction scale used.

Reaction of [6-(η^6 -MeC₆H₄i-Pr)-*nido*-6-RuB₉H₁₃] **1b** with Elemental Sulfur and tmnd

To a suspension of [6-(η^6 -MeC₆H₄i-Pr)-*nido*-6-RuB₉H₁₃] (**1b**; 60 mg, 170 μ mol) in chloroform (20 ml) was added tmnd (36 mg, 170 μ mol) and S₈ (16 mg, 510 μ mol). The reaction mixture was heated at reflux (oil bath at 70 °C) for two hours, during which time the starting yellow solution turned to dark-brown. The resulting mixture was filtered through TLC-grade silica with CH₂Cl₂, and the filtrate then evaporated to dryness (rotary evaporator, <45 °C, water-pump pressure). The resulting solid was taken up in minimum CH₂Cl₂, and applied to preparative TLC plates. Development with CH₂Cl₂ as mobile phase revealed four main coloured components: (i) a yellow compound (R_F 0.95) proposed to be [9-(η^6 -MeC₆H₄i-Pr)-*nido*-9,7,8-RuS₂B₈H₈] (**4**; 5 mg, 7%), (ii) a yellow compound (R_F 0.65) characterised as [8-(η^6 -MeC₆H₄i-Pr)-*nido*-8,7-RuSB₉H₁₁] (**3**; 20 mg, 31%), (iii) an orange component (R_F 0.6) characterised as twelve-vertex [7-(η^6 -MeC₆H₄i-Pr)-*nido*-7,11,12-RuS₂B₉H₉] (**2b**; 20 mg, 29%) and (iv) an unstable blue species (R_F 0.1) that was further purified by preparative TLC using CH₂Cl₂-CH₃CN 1 : 9 as mobile phase, and is tentatively proposed to be a salt of an unstable [Ru(*nido*-S₂B₉H₉)₂]²⁻ anion **6** (R_F 0.5; 5 mg, *ca* 8%). Other products were also present, but in insufficient amounts for satisfactory investigation on the reaction scale used.

Reaction of [6-(η^6 -MeC₆H₄i-Pr)-*nido*-6-RuB₉H₁₃] (**1b**) with Elemental Sulfur in the Presence of Potassium Hydride

Potassium hydride (8 mg, 340 μ mol) was added to a stirred solution of [6-(η^6 -MeC₆H₄i-Pr)-*nido*-6-RuB₉H₁₃] (60 mg, 170 μ mol) and yellow sulfur, S₈ (27 mg, 850 μ mol) in THF (10 ml). After two hours the colour had changed from yellow to dark-blue. The solution was filtered through TLC-grade silica, the solvent removed as above, the solid residue taken up in minimum CH₂Cl₂, and applied to preparative TLC plates. Elution with CH₂Cl₂-CH₃CN 1 : 1 as liquid phase thence gave one principal product, an unstable blue species with R_F 0.5. This product (16 mg) was tentatively characterised by NMR spectroscopy as a salt of the anionic [Ru(S₂B₉H₈)₂]²⁻ species **6**.

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REFERENCES

1. Bown M., Fontaine X. L. R., Greenwood N. N., Kennedy J. D.: *Z. Anorg. Allg. Chem.* **602**, 17 (1991).
2. Ferguson G., Jennings M. C., Lough A. J., Coughlan S., Spalding T. R., Kennedy J. D., Fontaine X. L. R., Stibr B.: *J. Chem. Soc., Chem. Commun.* **1990**, 891.
3. Nestor K., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Thornton-Pett M.: *J. Chem. Soc., Dalton Trans.* **1991**, 2657.
4. Coughlan S., Spalding T. R., Ferguson G., Gallagher J. F., Lough A. J., Stibr B., Fontaine X. L. R., Kennedy J. D.: *J. Chem. Soc., Dalton Trans.* **1992**, 2865.
5. Ferguson G., Lough A. J., Coughlan S., Spalding T. R.: *Acta Crystallogr.*, **C 48**, 440 (1992); Murphy M., Spalding T. R., Ferguson G., Gallagher J. F.: *Acta Crystallogr.*, **C 48**, 638 (1992).
6. Macias R., Holub J., Kennedy J. D., Stibr B., Thornton-Pett M.: *J. Chem. Soc., Chem. Commun.* **1994**, 2265.
7. Adams K. J., McGrath T. D., Welch A. J.: *Acta Crystallogr.*, **C 51**, 401 (1995).
8. Mazighi K., Carroll P. J., Sneddon L. G.: *Inorg. Chem.* **31**, 3197 (1992).
9. Kang C-H., Kun S-J., Ko J-J., Lee K-B., Kang S-O.: *Bull. Korean Chem. Soc.* **14**, 537 (1993).

10. Murphy M., Spalding T. R., Kennedy J. D., Thornton-Pett M., Malik K. L. M., Hursthouse M. B., Holub J.: *J. Chem. Soc., Chem. Commun.* 1994, 2403.
11. Murphy M. P., McCarthy D., Spalding T. R., Macias R., Holub J., Kennedy J. D., Thornton-Pett M.: Unpublished results; Murphy M. P., Spalding T. R., Cowey C., Kennedy J. D., Thornton-Pett M., Holub J.: *J. Organomet. Chem.*, in press.
12. Jones J. H., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Thornton-Pett M., Stibr B., Langhoff H.: *J. Organomet. Chem.* 445, C15 (1993).
13. Kaur P., Brownless A., Perera S. D., Cooke P. A., Jelinek T., Kennedy J. D., Thornton-Pett M., Stibr B.: *J. Organomet. Chem.*, in press.
14. Kaur P., Thornton-Pett M., Clegg W., Kennedy J. D.: *J. Chem. Soc., Dalton Trans.* 1996, 4155.
15. Kaur P., Kennedy J. D., Thornton-Pett M., Jelinek T., Stibr B.: *J. Chem. Soc., Dalton Trans.* 1996, 1775.
16. Holub J., Wille A. E., Stibr B., Carol P. J., Sneddon L. G.: *Inorg. Chem.* 33, 4920 (1994).
17. Herter W. R., Klanberg F., Muettterties E. L.: *Inorg. Chem.* 6, 1696 (1967); Rudolph R. W., Pretzer W. R.: *Inorg. Synth.* 22, 226 (1983); Binder H., Wolfer K., Ehemann W., Pfeffer W-P., Peters K., Horn H., Ahlrichs R.: *Chem. Ber.* 125, 651 (1992); Holub J., Jelinek T., Plešek J., Stibr B., Hermanek S., Kennedy J. D.: *J. Chem. Soc., Chem. Commun.* 1991, 1389; Holub J., Kennedy J. D., Jelinek T., Stibr B.: *J. Chem. Soc., Dalton Trans.* 1994, 1317; Jelinek T., Kennedy J. D., Stibr B., Thornton-Pett M.: *Angew. Chem., Int. Ed. Engl.* 33, 1599 (1994).
18. Fowkes H., Fontaine X. L. R., Greenwood N. N., Kennedy J. D., Thornton-Pett M.: *J. Chem. Soc., Dalton Trans.* 1986, 547.
19. Bown M., Fontaine X. L. R., Greenwood N. N., Kennedy J. D.: *Z. Anorg. Allg. Chem.* 598/599, 45 (1991).
20. Macias R.: *Ph.D. Thesis.* University of Leeds, Leeds 1996; Macias R., Holub J., Stibr B., Kennedy J. D., Thornton-Pett M.: Unpublished results.
21. Friesen G. D., Barriola A., Daluga P., Ragatz P., Huffman J. C., Todd L. J.: *Inorg. Chem.* 19, 458 (1980).
22. Bould J., Rath N. P., Barton L.: *Organometallics* 15, 4916 (1996).
23. Bould J., Crook J. E., Greenwood N. N., Kennedy J. D., McDonald W. S.: *J. Chem. Soc., Chem. Commun.* 1982, 346; Bould J., Greenwood N. N., Kennedy J. D.: *J. Chem. Soc., Dalton Trans.* 1984, 2477; Barton L., Bould J., Kennedy J. D., Rath N. P.: *J. Chem. Soc., Dalton Trans.* 1996, 3145; Bould J., Clegg W., Kennedy J. D., Teat S. J., Thornton-Pett M.: *J. Chem. Soc., Dalton Trans.* 1997, 2005.
24. MacKinnon P., Fontaine X. L. R., Kennedy J. D., Salter P. A.: *Collect. Czech. Chem. Commun.* 61, 1773 (1996); Ferguson G., Kennedy J. D., Fontaine X. L. R., Faridooon, Spalding T. R.: *J. Chem. Soc., Dalton Trans.* 1988, 2555; Reed D.: *Chem. Soc. Rev.* 22, 109 (1993).
25. McFarlane W.: *Proc. R. Soc. London, A* 306, 185 (1968).