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Mixed-metal chalcogenide tetrahedral clusters with an *exo*-polyhedral metal fragment†

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The reaction of metal carbonyl compounds with group 6 and 8 metallaboranes led us to report the synthesis and structural characterization of several novel mixed-metal chalcogenide tetrahedral clusters. Thermolysis of *arachno*-[(Cp*RuCO)₂B₂H₆], **1**, and [Os₃(CO)₁₂] in the presence of 2-methylthiophene yielded [Cp*Ru(CO)₂(μ-H){Os₃(CO)₉}S], **3**, and [Cp*Ru(μ-H){Os₃(CO)₁₁}], **4**. In a similar fashion, the reaction of [(Cp*Mo)₂B₅H₉], **2**, with [Ru₃(CO)₁₂] and 2-methylthiophene yielded [Cp*Ru(CO)₂(μ-H){Ru₃(CO)₉}S], **5**, and *conjuncto*-[(Cp*Mo)₂B₅H₉(μ-H){Ru₃(CO)₉}S], **6**. Both compounds **3** and **5** can be described as 50-cve (cluster valence electron) mixed-metal chalcogenide clusters, in which a sulfur atom replaces one of the vertices of the tetrahedral core. Compounds **3** and **5** possess a [M₃S] tetrahedral core, in which the sulfur is attached to an *exo*-metal fragment, unique in the [M₃S] metal chalcogenide tetrahedral arrangements. All the compounds have been characterized by mass spectrometry, IR, and ¹H, ¹¹B and ¹³C NMR spectroscopy in solution, and the solid state structures were unequivocally established by crystallographic analysis of compounds **3**, **5** and **6**.

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Introduction

Over the years the development of heterometallic clusters, in particular the transition metal hydrido/carbonyl clusters,¹ has been noteworthy. Due to their significant role in understanding relevant catalytic processes, and the interesting structures exhibited by various coordination modes, these clusters are of significant interest.² However, transition metal hydrido/carbonyl clusters with encapsulation of a chalcogen atom have been explored less.³ In the past several decades, great advances have been made for chalcogenido carbonyl species both in terms of fundamental research and practical fields.^{4,5} For example, the replacement of framework anions (*i.e.*, O²⁻) of microporous oxides with chalcogens (*e.g.*, S²⁻) or organic ligands⁴ (*e.g.*, nitriles, carboxylates, amines) represents a recent approach for generating microporous materials.⁵ These compounds hold good potential for applications in solid electrolytes, semiconductor electrodes, sensors⁶ and photocatalysis.⁷ On the other hand, regardless of finding intimate links to organometallic systems,⁸ metallaborane chemistry has experienced obstacles

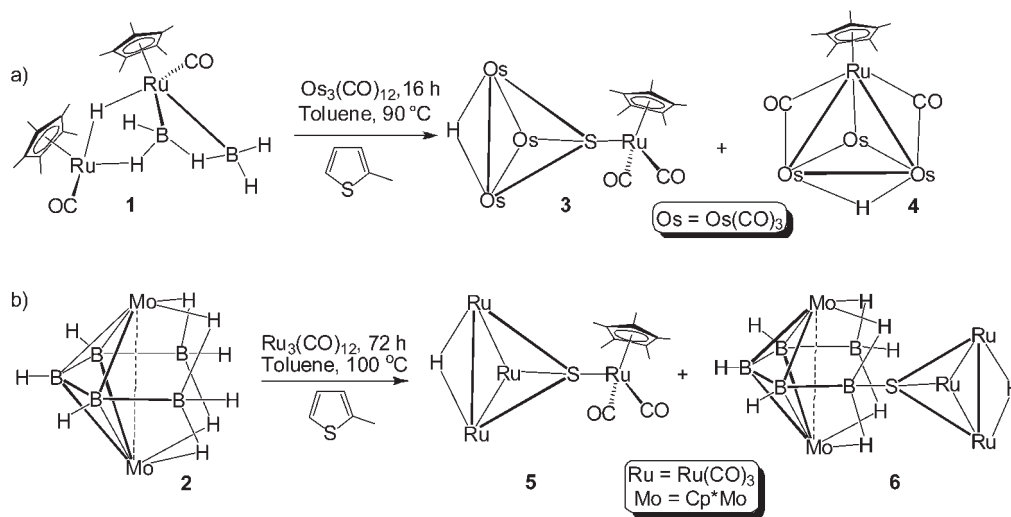
in exploring the systematic reaction chemistry due to limited synthetic routes to high-yield metallaborane compounds. As a result, their reactivity has remained underdeveloped relative to that of organometallic compounds.⁹ In contrast to organometallic chemistry, the study of the role of transition metals in polyhedral borane chemistry is limited.^{8b} However, in this area, Suzuki coupling,¹⁰ functionalization of hydrocarbyl groups^{11,12} and boranes,¹³ oxidative coupling of carboranes,¹⁴ alkyne cyclotrimerisation^{15,16} and alkene hydrogenation¹⁷ are significant.

We recently described the synthesis and structure of diruthenatetaborane *arachno*-[(Cp*RuCO)₂B₂H₆], **1**, from the reaction of [1,2-(Cp*RuH)₂B₃H₇] and the mono-metal carbonyl fragment [Mo(CO)₃(CH₃CN)₃],^{18a} in good yield. Subsequently, the availability of *arachno*-**1** led us to study the systematic reaction chemistry, including the synthesis of novel homo and heterometallic bridged-borylene complexes^{18,19} from metal carbonyl compounds, such as [Fe₂(CO)₉], [Mn₂(CO)₁₀] and [Ru₃(CO)₁₂]. Further, the reaction of *arachno*-**1** with HBcat (cat = 1,2-O₂C₆H₄) yielded a bridged-boryl complex, [(Cp*Ru)₂(μ-H)(μ-CO)(μ-Bcat)].²⁰ As part of a recently initiated study into the reactivity of *arachno*-**1** and other early and late transition metallaboranes, we report the synthesis of various unusual mixed-metal chalcogenide tetrahedral clusters [M₃S (3: M = Os, 5: M = Ru)], fastened to (Cp*Ru(CO)₂) metal fragments. Structural characterization of these species allows direct experimental comparison of the bonding to different *exo*-polyhedral clusters.

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Scheme 1 (a) Synthesis of mixed-metal clusters **3** and **4**; (b) synthesis of mixed-metal clusters **5** and **6**.

Results and discussion

Synthesis and structure of mixed-metal tetrahedral clusters

The development of both electron counting rules²¹ and the isolobal principle²² offered a solid foundation for understanding the interrelationships between the structure and composition of cluster compounds. Keeping in mind the authenticity of the isolobal analogy, we have started with the reaction of *arachno*-1 with $[\text{Os}_3(\text{CO})_{12}]$ in search of osmium bridged-borylene complexes. Although the objective of generating bridged-borylene complexes was not achieved, we have isolated an interesting mixed-metal chalcogenide cluster $[\text{Cp}^*\text{Ru}(\text{CO})_2(\mu\text{-H})\{\text{Os}_3(\text{CO})_9\}\text{S}]$, **3**, and a hybrid tetrahedral cluster $[\text{Cp}^*\text{Ru}(\text{CO})_2(\mu\text{-H})\{\text{Os}_3(\text{CO})_{11}\}\text{S}]$, **4** (see ESI† for characterization).‡

The mass spectrum of compound **3** shows a molecular ion peak at m/z 1148 along with the envelopes that correspond to the successive loss of eleven CO ligands. The IR spectrum indicates the presence of terminal carbonyl absorption bands at 2048, 2015 and 1990 cm^{-1} . In addition to the Cp^* protons, the ^1H NMR spectrum reveals one sharp singlet at $\delta = -20.81$ ppm which can be assigned as an Os–H–Os bridging hydrogen. In a similar fashion, reaction of molybdaborane $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9]$, **2**, with $[\text{Ru}_3(\text{CO})_{12}]$, as described in Scheme 1, led to the formation of a tetrahedral mixed-metal chalcogenide cluster $[\text{Cp}^*\text{Ru}(\text{CO})_2(\mu\text{-H})\{\text{Ru}_3(\text{CO})_9\}\text{S}]$, **5**, along with a *conjuncto*- $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_8(\mu\text{-H})\{\text{Ru}_3(\text{CO})_9\}\text{S}]$ cluster, **6**. The IR spectrum of

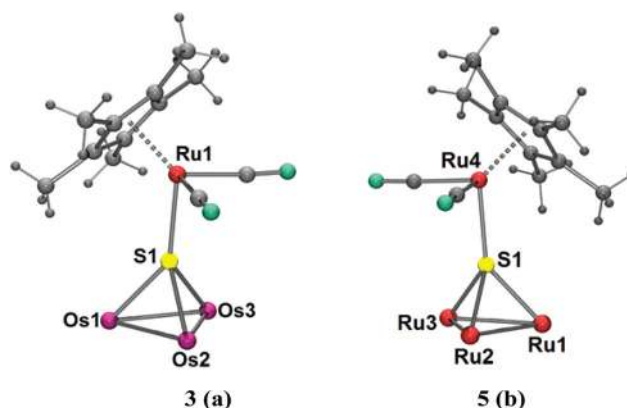


Fig. 1 Molecular structure and labeling diagram of compounds **3** (a) and **5** (b). The carbonyl ligands on the $\text{M}(\text{CO})_3$ ($\text{M} = \text{Os}, \text{Ru}$) fragments are not shown for clarity. Relevant bond lengths (Å) and angles ($^\circ$): **3** (a) Os1–Os3 2.7666(10), Os1–Os2 2.7733(10), Os2–Os3 2.8968(10), S1–Ru1 2.418(4), S1–Os3 2.374(4); Os1–S1–Os2 71.82(11), Os1–Os3–Os2 58.59(2), Os1–S1–Ru1 142.66(19), Os2–S1–Ru1 129.91(19); **5** (b) Ru1–Ru2 2.7477(5), Ru2–Ru3 2.8650(5), Ru1–Ru3 2.7434(5), Ru4–S1 2.4122(11), S1–Ru1 2.3418(11); Ru3–Ru1–Ru2 62.896(14), S1–Ru1–Ru3 54.41(3), S1–Ru3–Ru1 54.06(3).

5 features terminal carbonyl absorption bands at 2040, 2008 and 1982 cm^{-1} . The molecular structure, shown in Fig. 1, can be seen as a tetrahedral arrangement of one sulfur and three $\text{M}(\text{CO})_3$ (**3**: $\text{M} = \text{Os}$, **5**: $\text{M} = \text{Ru}$) moieties which form a triangular plane. Further, the *exo*-polyhedral $\text{Cp}^*\text{Ru}(\text{CO})_2$ units are bound to the sulfur atom of the tetrahedral core. Ignoring the $\text{Cp}^*\text{Ru}(\text{CO})_2$ *exo*-polyhedral fragment, molecules **3** and **5** have near-perfect C_{3v} symmetry.

The average Os–Os bond distance of 2.8122 Å in **3** is normal as compared to other tetrahedral clusters, for example, $[\text{Cp}^*\text{RhOs}_3(\text{CO})_{11}]^{23a}$ (2.778(2)–2.8297(8) Å), $[\text{12S}_3\text{Os}_4(\text{CO})_{11}(\mu\text{-H})_4]^{24c}$ (2.821(1)–2.978(1) Å) and $[(\mu\text{-H})\text{Os}_3(\text{CO})_{11}(\text{OC})_3\text{-RePh}_3\text{P}]^{25b}$ (2.793–3.004 Å). Similarly, the average Ru–Ru bond

‡The choice of 2-methylthiophene ligand as the sulfur source originated from the fact that when the thermolysis of *arachno*- $[(\text{Cp}^*\text{RuCO})_2\text{B}_2\text{H}_6]$, **1** and $[\text{Os}_3(\text{CO})_{12}]$ was carried out in toluene, compound **3** was isolated in moderate yield. Therefore, we checked the purity of the starting materials as well as the solvent (toluene). It was observed that among the common impurities existing in toluene, 2-methylthiophene resides as a major component.³⁸ Consequently, we performed all the reactions again in the presence of 2-methylthiophene that yielded compounds **3**, **5** and **6**, albeit in better yields. Note that compound **4** has been identified based on spectroscopic data and combustion analysis. All our attempts to have a suitable X-ray crystallographic data set failed.

Table 1 Structural parameters and spectroscopic data (¹H NMR and IR) of various metal clusters^a

Compound	Exo-type	Avg. <i>d</i> [M–M] ^j [Å]	<i>d</i> [M–exo atom] [Å]	¹ H _(M–H–M) NMR [ppm]	IR (CO) ν bar [cm ⁻¹]	Ref.
[Cp*Ru(CO) ₂ (μ-H)Td ₁] ^b		2.647	2.504 (M–Ru)	–23.03	2015, 1968	24a
[Cp*Ru(CO) ₂ Td ₂] ^c 3		2.812	2.418 (M–S)	–18.34	2080, 1929	This work
[Cp*Ru(CO) ₂ Td ₃] ^d 5		2.786	2.412 (M–S)	–18.60	2040, 1982	This work
[(Cp*Mo) ₂ B ₅ H ₈ Td ₄] ^e 6		2.789	—	–18.5	2018, 1985	This work
[Ph ₃ PTd ₅] ^f		2.733 (M = Mo) 2.717 (M = W)	2.208 (M–P) 2.219 (M–P)	— —	2040, 1986 (Mo) 2041, 1983 (W)	24b
[12S ₃ Td ₆] ^g		2.927	2.419 (M–S)	–18.83, –20.47	2097, 1956	24c
[Cp ₂ (μ-k ¹ :k ¹ , η ⁶ -PMes*)(CO) _{9–n} Td ₇] ^h		3.039 (M = W) 2.732 (M = Fe)	2.284 (M–P) 2.087 (M–P)	— —	2031, 1949 (M = W) 2020, 1941 (M =)	25a
[Ph ₃ PM _B] ⁱ		2.955	2.386 (M–P)	–12.14	2070, 1969	25b

^a[Td] = Tetrahedral moiety. [M_B] = Butterfly moiety. ^bTd₁ = [[RuFe₃(CO)₉]. ^cTd₂ = [[(μ₃-S)Os₃(CO)₉H]. ^dTd₃ = [[(μ₃-S)Ru₃(CO)₉H]. ^eTd₄ = [[(μ₃-S)Ru₃(CO)₉H]. ^fTd₅ = [M(η⁵-MeCOC₅H₄)FeCo(μ₃-S)(CO)₇] (M = Mo, W). ^gTd₆ = [OS₄(CO)₁₁(μ-H)₄]. ^hTd₇ = [Mo₂M₂(μ₃-S)] (M = W, n = 0; M = Fe, n = –2); (Cp = η⁵-C₅H₅; Mes* = 2,4,6-C₆H₂Bu₃). ⁱM_B = [(μ-H)Os₃(CO)₁₁(OC)₃Re]. ^jAvg. M–M distance of the tetrahedral core.

distances of **5** are also comparable with [(μ₃-S)Ru₃(CO)₈(CSN-MePh)] (2.7452(11)–2.882(2) Å).^{23b} A range of tetrahedral metal clusters with the *exo*-fragment are listed in Table 1, and their structural parameters and chemical shift values are compared. The average Ru–S bond distance (2.3477 Å) for **5** is similar as related to the analogous tetrahedral cluster, (μ₃-S)CoMoRu(CO)₈[(η⁵-C₄H₄)C(O)O-CH₂(OH)CH₃] (2.322(15) Å).^{24d} All the terminal carbonyl groups are almost linear, with M–C–O angles ranging from 176° to 179°. The spatial arrangements of the Cp* and CO ligands around the *exo*-metal centre are similar for both compounds **3** and **5**, and the dihedral angle between the Cp* plane and the mean plane of osmium (**3**) or ruthenium (**5**) are 132.9° and 133.3° respectively. If we examine the bond distances of the M₃ core of both compounds **3** and **5**, it is revealed that one of the M–M bonds is longer than the others (for **3**: Ru2–Ru3 (2.8649(5)); for **5**: Os2–Os3 (2.8968(10))). This indicates that the hydride ligand is bridged between the longer M–M bond.

The structure of any stable molecule or molecular ion is strongly related to its number of valence electrons,^{21,22} and thus, one can comment that to a particular structure relates a given valence electron count²¹ and *vice versa*. Housecraft *et al.*, has shown that an *exo*-{Cp*Ru(CO)₂} of boride cluster [H₂Ru₅(CO)₁₃Cp*BH₂] contributes one electron towards the Ru₄B core.^{26b} Considering the same fact that the {Cp*Ru(CO)₂} moiety is a one-electron fragment,^{26a} the *exo*-units {Cp*Ru(CO)₂} for **3** and **5** donate one electron to the tetrahedral core to achieve 50 cluster valence electrons. Both clusters **3** and **5** possess six skeletal electron pairs and can be classified as the *nido* geometry based on a *closo*-trigonal bipyramidal arrangement.

Pairs of molecules in both compounds **3** and **5** are related through two types of short contacts: (i) C–H...O interactions and (ii) O...O short interactions of the carbonyl oxygen. In the case of **3**, two C–H...O interactions, (a) C7–H7B...O3 (symm: $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$) and (b) C10–H10C...O4 (symm: $\frac{1}{2} + x, \frac{1}{2} - y,$

$\frac{1}{2} + z$) with lengths and angles of 2.41 Å, 145.99° and 2.43 Å, 137.43° respectively, form a 1D chain parallel to the *ac* diagonal (Fig. S1a†). The O...O interaction is between the carbonyl oxygen atoms O9 and O10 (symm: 1 - x, -y, 1 - z). The distance between the atoms is 2.899 Å, which is 0.14 Å shorter than the sum of the oxygen van der Waals radii (3.04 Å). On the other hand, for compound **5**, two prominent C-H...O interactions, (a) C17-H17C...O5 (2.555 Å, 142.75°; symm: x - 1, y, z) and (b) C18-H18B...O7 (2.681 Å, 172.74°; symm: x, y, z - 1), make the 2D network parallel to the *ac* plane. Molecules in these layers are bound to their inversion (layer) through van der Waal and O...O short interactions through the carbonyl oxygens, and these bi-layers thus formed are only weakly linked among themselves (Fig. S1b†).

In order to investigate the redox properties of these mixed-metal chalcogenide clusters, the electrochemistry of compounds **3** and **5** was examined using cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The cyclic voltammetry was carried out using a sample solution containing 10^{-4} M [*n*-Bu₄NPF₆] in CH₃CN as a supporting electrolyte, and a standard three-electrode system (glassy carbon working electrode, platinum wire counter electrode and SCE as the reference electrode) was employed for the measurements. The results of the voltammetric experiments are summarized in Fig. 2. Both compounds **3** and **5** exhibit similar types of irreversible anodic peaks (*E*_p), except they differ in the shifting of the signals. The highest peak for **5** at 1.31 V was shifted to 1.57 V for **3**, which may correspond to one electron oxidation process for the Ru-centre as evident by the lack of a return wave. This irreversible behavior has similarly been observed for compound [Cp*₂FeRu(C₈H₈)]²⁷ which decomposes upon electrochemical oxidation, meaning it is electrochemically inactive.

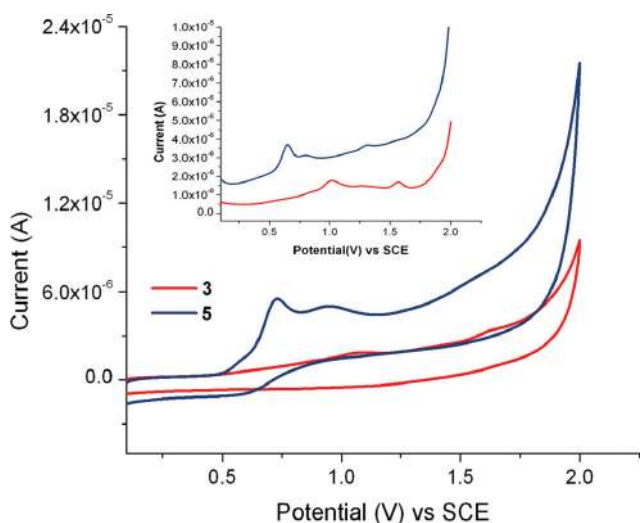


Fig. 2 Cyclic voltammograms and differential pulse voltammograms (inset) for **3** and **5** in CH₃CN containing 10^{-4} M [*n*-Bu₄NPF₆]. The cyclic voltammograms and the differential pulse voltammograms were scanned from 0 to 2 V at a scan rate of 0.10 V s⁻¹.

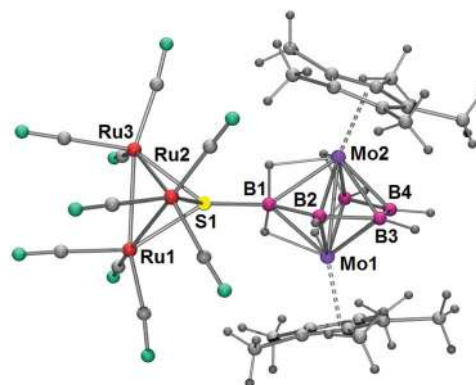


Fig. 3 Molecular structure and labeling diagram of **6**. The terminal CO ligands on the Ru atom have been omitted for clarity. Selected bond lengths (Å) and angles (°): B3–B4 1.720(18), Ru1–S1 2.344(3), Mo1–B4 2.195(12), S1–B1 1.914(11); B3–Mo2–Mo1 50.0(3), S1–Ru3–Ru1 53.97(7), B1–S1–Ru1 141.4(4), Ru3–Ru1–Ru2 63.26(4).

Compound **6** was isolated in modest yield. The ¹¹B NMR spectrum displays five resonances of equal intensity at $\delta = 73.4, 65.2, 56.1, 33.7$ and 29.2 ppm. The ¹H NMR spectrum confirms the presence of a single resonance for two equivalents of Cp* protons at $\delta = 2.05$ ppm. The IR spectrum shows intense bands at 2018 and 1985 cm⁻¹, characteristic of terminal carbonyl groups, and a band at 2403 cm⁻¹ due to B–H_t stretches. In agreement with the spectroscopic data, the solid-state structure, as shown in Fig. 3, reveals that compound **6** holds the [Mo₂B₅] core with an *exo*-moiety {Ru₃S} attached to one of the boron atoms (B1). The two fragments are united through a direct 2-centre B–S σ bond.

Generally, the cluster compounds can be composed into a larger entity through two different modes; either *via* (i) 2c–2e or 3c–2e bonds^{28–30} (*conjuncto*-clusters) or (ii) *via* sharing vertices between individual units (fused clusters).^{31–33} Cluster **6** may be considered as a fused cluster, composed of a bicapped trigonal bipyramidal and a tetrahedral cage, linked by a 2c–2e boron–sulfur bond. Thus, **6** can be considered as a *conjuncto* cluster. The B–S bond distance in **6** (1.914(11) Å) is comparable to [(Cp*Co)₂B₄H₅SFe₃(CO)₉] (1.901(7) Å), whereas it is on the long side if compared with the B–S distances in [(Cp*Mo)₂B₅H₈(SPh)]^{34a} (1.887(4) Å) and in [(Cp*Mo)₂(μ_3 -S)-(μ - η^1 -SPh)₂(H₂BSPH)]^{34b} (1.874(5) Å). The average Mo–Mo (2.825 Å), Mo–B (2.252 Å) and B–B (1.718 Å) distances in **6** are similar to those observed in **2**. This suggests that the formation of the *exo*-polyhedral boron–sulfur linkage did not perturb the cluster bonding pattern significantly.

Conclusions

With the goal of obtaining hybrid bridged-borylene compounds, we intended to carry out the cluster growth reaction of *arachno*-**1** and **2** with [Os₃(CO)₁₂] and [Ru₃(CO)₁₂]. However, the reaction yielded, serendipitously, unusual tetrahedral chalcogenide clusters anchored to the *exo*-polyhedral Cp*Ru(CO)₂

moiety. Based on the structural parameters of the compound $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_8(\mu\text{-H})\{\text{Ru}_3(\text{CO})_9\}\text{S}]$, it is evident that the *exo*-fragment does not disturb the core geometry of $[(\text{Cp}^*\text{Mo})_2\text{B}_5\text{H}_9]$. Although many parallels exist between the metal carbonyl and boron hydride or metallaborane clusters, examples of mixed-metal tetrahedral chalcogenide clusters with an *exo*-polyhedral metal fragment attached to the chalcogen are rare. In most cases the discovery of new compounds is serendipitous; however, the synthesis of new materials has been recognized as the essential building block in advancing new chemistry, and we expect that the unanticipated method will continue to yield interesting compounds with novel geometries.

Experimental section

General procedures and instrumentation

All syntheses were carried out under an argon atmosphere with standard Schlenk and glove box techniques. Solvents were dried by common methods and distilled under N_2 before use. Compounds *arachno-1*^{18a} and **2**³⁵ were prepared according to literature methods, while other chemicals were obtained commercially and used as received. The external reference for the ^{11}B NMR, $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$, was synthesized by the literature method.³⁶ Thin layer chromatography was carried out on 250 mm dia aluminum supported silica gel TLC plates (MERCK TLC Plates). NMR spectra were recorded on a 400 and 500 MHz Bruker FT-NMR spectrometer. Residual solvent protons were used as the reference (δ , ppm, $[\text{D}_6]$ -benzene, 7.16), while a sealed tube containing $[\text{Bu}_4\text{N}(\text{B}_3\text{H}_8)]$ in $[\text{D}_6]$ -benzene (δ_{B} , ppm, -30.07) was used as an external reference for the ^{11}B NMR. Infrared spectra were recorded on a Nicolet iS10 spectrometer. The mass spectra were recorded on a Bruker MicroTOF-II mass spectrometer. The CV measurements were performed on a CH Potentiostat model CHI630D.

Synthesis of 3 and 4. In a flame-dried Schlenk tube, compound *arachno-1* (0.24 g, 0.43 mmol) was added. $[\text{Os}_3(\text{CO})_{12}]$ (0.391 g, 0.43 mmol) was added to this, and the resulting mixture was dissolved in toluene and thermolysed in the presence of an excess of 2-methylthiophene for 16 h at 90 °C. The volatile components were removed under vacuum and the remaining residue was extracted into hexane and passed through Celite. After removal of the solvent, the residue was subjected to a chromatographic work up using silica gel TLC plates. Elution with a hexane- CH_2Cl_2 (90:10 v/v) mixture yielded yellow **3** (0.02 g, 4%) and orange **4**† (0.16 g, 32%).

3: MS (MALDI): m/z 1148 $[\text{M}]^+$; isotope envelope $\text{C}_{21}\text{H}_{16}\text{O}_{11}\text{Os}_3\text{RuS}$: requires 1148; m/z 840 $[\text{M} + \text{H} - 11\text{CO}]^+$; isotope envelope $\text{C}_{10}\text{H}_{16}\text{Os}_3\text{RuS}$: requires 840. ^1H NMR (22 °C, 400 MHz, $[\text{D}_6]$ -benzene): δ = 1.84 (s, 15H, 1Cp*), -20.81 (s, 1H, Os-H-Os). ^{13}C NMR (22 °C, 100 MHz, $[\text{D}_6]$ -benzene): δ = 198.7, 195.1 (CO), 98.8 (C_5Me_5), 10.1 (C_5Me_5). IR $\nu_{\text{bar}}/\text{cm}^{-1}$: 2048, 2015, 1990 (CO).

Synthesis of 5 and 6. Compound **2** (0.25 g, 0.475 mmol) was added to a flame-dried Schlenk tube. To this $[\text{Ru}_3(\text{CO})_{12}]$ (0.30 g, 0.475 mmol) was added, and the mixture was dissolved

in toluene and thermolysed for 72 h at 100 °C in the presence of an excess of 2-methylthiophene. The volatile components were removed under vacuum and the remaining residue was extracted into hexane and passed through Celite. After removal of the solvent, the residue was subjected to a chromatographic work up using silica gel TLC plates. Elution with a hexane- CH_2Cl_2 (70:30 v/v) mixture yielded yellow **5** (0.075 g, 18%) and orange **6** (0.20 g, 36%).

5: ^1H NMR (22 °C, 400 MHz, $[\text{D}_6]$ -benzene): δ = 1.89 (s, 15H, 1Cp*), -18.60 (s, 1H, Ru-H-Ru). ^{13}C NMR (22 °C, 100 MHz, $[\text{D}_6]$ -benzene): δ = 188.3, 183.1 (CO), 98.2 (C_5Me_5), 10.7 (C_5Me_5). IR $\nu_{\text{bar}}/\text{cm}^{-1}$: 2040, 2008, 1982 (CO). Elemental analysis (%) calcd for $\text{C}_{21}\text{H}_{16}\text{O}_{11}\text{SRu}_4$: C, 28.64; H, 1.83. Found: C, 29.69; H, 1.99.

6: MS (MALDI): m/z 1113 $[\text{M} + \text{H}]^+$; isotope envelope $\text{C}_{29}\text{H}_{39}\text{B}_5\text{O}_9\text{SMo}_2\text{Ru}_3$: requires 1113. ^{11}B NMR (22 °C, 128 MHz, $[\text{D}_6]$ -benzene): δ = 73.4 (br, 1B), 65.2 (br, 1B), 56.1 (br, 1B), 33.7 (br, 1B), 29.2 (br, 1B). ^1H NMR (22 °C, 400 MHz, $[\text{D}_6]$ -benzene): δ = 7.81 (B-H_t), 2.05 (s, 30H, 2Cp*), -4.9 (br, 2H, Mo-H-B), -6.8 (br, 2H, Mo-H-B), -18.5 (s, 1H, Ru-H-Ru). ^{13}C NMR (22 °C, 100 MHz, $[\text{D}_6]$ -benzene): δ = 188.3, 183.1 (CO), 97.0 (C_5Me_5), 12.6 (C_5Me_5). IR $\nu_{\text{bar}}/\text{cm}^{-1}$: 2403 (B-H_t), 2018, 1985 (CO). Elemental analysis (%) calcd for $\text{C}_{29}\text{H}_{39}\text{B}_5\text{O}_9\text{SMo}_2\text{Ru}_3$: C, 31.28; H, 3.53. Found: C, 32.51; H, 3.42.

X-ray structure determination

The crystal data for compounds **3** and **6** were collected and integrated using a Bruker Axs kappa apex2 CCD diffractometer, with graphite monochromated Mo-K α (λ = 0.71073 Å) radiation at 296 K. Crystal data for **5** was collected and integrated using an Oxford Diffraction Super Nova CCD system equipped with graphite-monochromated Cu K α radiation (λ = 1.5418 Å) at 296 K. The structures were solved by heavy atom methods using SHELXS-97 or SIR92 and refined using SHELXL-97.³⁷ The crystals suitable for X-ray diffraction studies were grown by cooling a concentrated hexane solution of **3**, **5** and **6** to -10 °C.

Crystal data for **3**: CCDC 1017199, $\text{C}_{21}\text{H}_{16}\text{O}_{11}\text{Os}_3\text{RuS}$, M_r = 1148.06, monoclinic, space group $P2_1/n$, a = 8.6735(3) Å, b = 28.0865(9) Å, c = 11.7927(4) Å, β = 102.006(2)°, V = 2809.96(16) Å³, Z = 4, ρ_{calcd} = 2.713 g cm⁻³, μ = 14.175 mm⁻¹, $F(000)$ = 2072, R_1 = 0.0465, wR_2 = 0.1094, 4124 independent reflections [$2\theta \leq 47.14^\circ$] and 334 parameters.

Crystal data for **5**: CCDC 1017200, $\text{C}_{21}\text{H}_{16}\text{O}_{11}\text{Ru}_4\text{S}$, M_r = 880.68, monoclinic, space group $P2_1/n$, a = 8.7820(2) Å, b = 28.1031(5) Å, c = 11.6956(2) Å, β = 101.670(2)°, V = 2826.82(9) Å³, Z = 4, ρ_{calcd} = 2.069 g cm⁻³, μ = 18.142 mm⁻¹, $F(000)$ = 1688, R_1 = 0.0318, wR_2 = 0.0832, 5519 independent reflections [$\theta \leq 72.40^\circ$] and 339 parameters.

Crystal data for **6**: CCDC 1017201, $\text{C}_{29}\text{H}_{38}\text{B}_5\text{Mo}_2\text{O}_9\text{Ru}_3\text{S}$, M_r = 1111.79, monoclinic, space group C_2/c , a = 25.7689(9) Å, b = 25.0277(9) Å, c = 14.7792(5) Å, β = 122.069(2)°, V = 8077.3(5) Å³, Z = 8, ρ_{calcd} = 1.829 g cm⁻³, μ = 1.796 mm⁻¹, $F(000)$ = 4328, R_1 = 0.0284, wR_2 = 0.0555, 4232 independent reflections [$2\theta \leq 41.68^\circ$] and 674 parameters.

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