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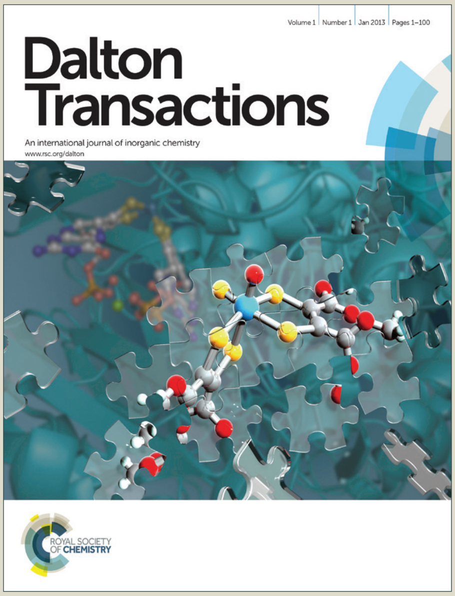

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ARTICLE

Mixed-Metal Chalcogenide Tetrahedral Clusters with an *Exo*-polyhedral Metal Fragment

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Reaction of metal carbonyl compounds with group 6 and 8 metallaboranes led us to report the syntheses and structural characterization of several novel mixed-metal chalcogenide tetrahedral clusters. Thermolysis of *arachno*-$[(Cp^*RuCO)_2B_2H_6]$, **1** and $[Os_3(CO)_{12}]$ in presence of 2-methylthiophene yielded $[Cp^*Ru(CO)_2(\mu\text{-}H)\{Os_3(CO)_9\}S]$, **3** and $[Cp^*Ru(\mu\text{-}H)\{Os_3(CO)_{11}\}]$, **4**. In a similar fashion, the reaction of $[(Cp^*Mo)_2B_5H_9]$, **2** with $[Ru_3(CO)_{12}]$ and 2-methylthiophene yielded $[Cp^*Ru(CO)_2(\mu\text{-}H)\{Ru_3(CO)_9\}S]$, **5** and *conjuncto*-$[(Cp^*Mo)_2B_5H_8\{Ru_3(CO)_9\}S]$, **6**. Both compounds **3** and **5** can be described as 50-cve (cluster valence electron) mixed-metal chalcogenide clusters, in which sulphur atom replaces one of the vertices of tetrahedral core. Compounds **3** and **5** possess $[M_3S]$ tetrahedral core, in which the sulphur is attached to an *exo*-metal fragment, unique in the $[M_3S]$ metal chalcogenide tetrahedral arrangements. All the compounds have been characterized by mass spectrometry, IR, ^1H, ^{11}B, ^{13}C NMR spectroscopy in solution and the solid state structures were unequivocally established by crystallographic analysis of compounds **3**, **5** and **6**.

Introduction

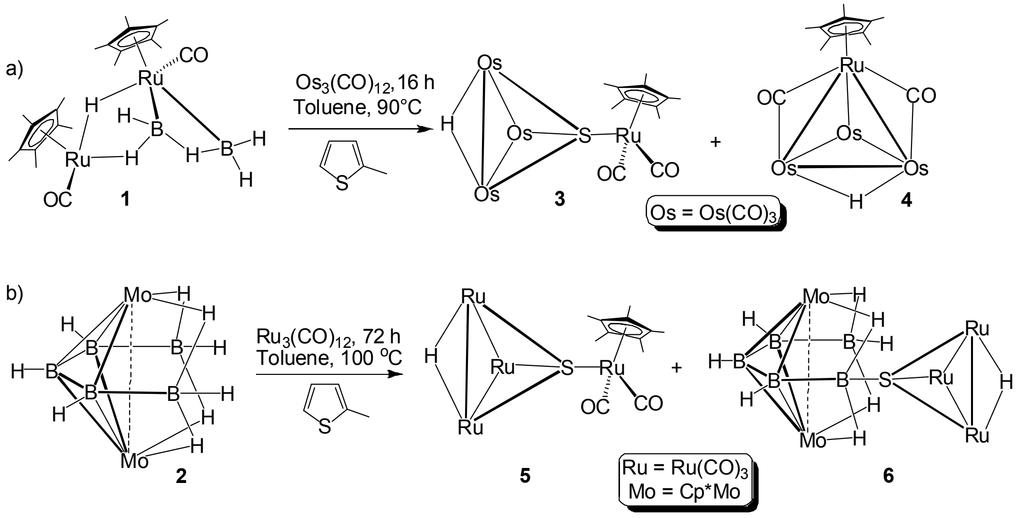
Over the years the development of heterometallic clusters in particular, the transition-metal hydrido/carbonyl clusters[1] is noteworthy. Due to their significant role in understanding relevant catalytic processes, interesting structures exhibited by various coordination modes, these clusters are of significant interest.[2] However, transition-metal hydrido/carbonyl clusters with encapsulation of a chalcogen atom are less explored.[3] During the past several decades chalcogenido carbonyl species possess great advancement both for fundamental research and practical fields.[4,5] For example, the replacement of framework anions (i.e., O^{2-}) of microporous oxides with chalcogens (e.g., S^{2-}) or organic ligands[4] (e.g., nitriles, carboxylates, amines) represents a recent approach for generating microporous materials.[5] These compounds hold good potentials for applications in solid electrolytes, semiconductor electrodes, sensors,[6] and photo catalysis.[7] On the other hand, regardless of finding intimate link to organometallic systems,[8] metallaborane chemistry have 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 contrary to the organometallic chemistry, the role of transition metals in polyhedral borane chemistry is a limited area.[8b] However, among them Suzuki coupling,[8] functionalization of hydrocarbyl groups[11,12] and boranes,[13] oxidative coupling of carboranes,[14] alkyne cyclotrimerisation[15,16] and alkene hydrogenation[17] are significant.

We have recently described the synthesis and structure of diruthenatetraborane *arachno*-$[(Cp^*RuCO)_2B_2H_6]$, **1**, from the reaction of $[1,2\text{-}(Cp^*RuH)_2B_3H_7]$ and mono-metal carbonyl fragment $[Mo(CO)_3(CH_3CN)_3]$[18a] in good yield. Subsequently, the availability of *arachno*-**1** led us to study the systematic reaction chemistry that includes the synthesis of novel homo and heterometallic bridged-borylene complexes[18,19] from metal carbonyl compounds, such as $[Fe_2(CO)_9]$, $[Mn_2(CO)_{10}]$, and $[Ru_3(CO)_{12}]$. Further, the reaction of *arachno*-**1** with HBcat (cat = $1,2\text{-}O_2C_6H_4$), yielded a bridged-boryl complex, $[(Cp^*Ru)_2(\mu\text{-}H)(\mu\text{-}CO)(\mu\text{-}Bcat)]$.[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 $[M_3S$ (**3**: M = Os, **5**: M = Ru)], fastened to $(Cp^*Ru(CO)_2)$ metal fragments. Structural characterization of these species allows direct experimental comparison of bonding to different *exo*-polyhedral clusters.

Results and discussion

Synthesis and structure of mixed-metal tetrahedral clusters:

The development of both electron counting rules[21] and isolobal principle[22] offered a solid foundation for understanding the interrelationships between structure and composition of cluster compounds. Keeping in mind the authenticity of isolobal analogy, we have started the reaction of *arachno*-**1** with $[Os_3(CO)_{12}]$ in search

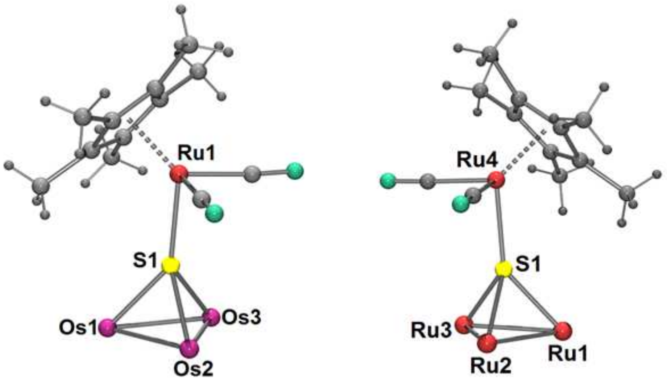


Scheme 1. a) Synthesis of mixed metal clusters **3** and **4**; b) Synthesis of mixed-metal clusters **5** and **6**.

of osmium bridged-borylene complexes. Although the objective of generating bridged-borylene complexes was not achieved, we have isolated interesting mixed-metal chalcogenide cluster $[Cp^*Ru(CO)_2(\mu\text{-}H)\{\{Os_3(CO)_9\}S]$, **3** and a hybrid tetrahedral cluster $[Cp^*Ru(\mu\text{-}H)\{Os_3(CO)_{11}\}]$, **4** (see supporting information 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 δ = -20.81 ppm which can be assigned as Os-H-Os bridging hydrogen. In a similar fashion, reaction of molybdaborane $[(Cp^*Mo)_2B_5H_9]$, **2** with $[Ru_3(CO)_{12}]$, as described in Scheme 1, led to the formation of a tetrahedral mixed-metal chalcognide cluster $[Cp^*Ru(CO)_2(\mu\text{-}H)\{Ru_3(CO)_9\}S]$, **5** along with a *conjuncto*-$[(Cp^*Mo)_2B_5H_8\{Ru_3(CO)_9\}S]$, **6**. The IR spectrum of **5** concludes the presence of 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 $M(CO)_3$ (**3**: M = Os, **5**: M = Ru) moieties which form a triangular plane. Further, the *exo*-polyhedral units $Cp^*Ru(CO)_2$ are bound to the sulfur atom of the tetrahedral core. Ignoring the $Cp^*Ru(CO)_2$ *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** are normal as compared to other tetrahedral clusters, for example, $[Cp^*RhOs_3(CO)_{11}]$[23a] (2.778(2)-2.8297(8) Å), $[12S_3Os_4(CO)_{11}(\mu\text{-}H)_4]$[24c] (2.821(1)-2.978(1) Å) and $[(\mu\text{-}H)Os_3(CO)_{11}(OC)_3\text{-}RePh_3P]$[25b] (2.793-3.004 Å). Similarly, the average Ru-Ru bond distances of **5** are also comparable with $[(\mu_3\text{-}S)Ru_3(CO)_8(CSNMePh)]$ (2.7452(11)-2.882(2) Å).[23b] A range of tetrahedral metal clusters having *exo*-fragment have been 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, $(\mu_3\text{-}S)CoMoRu(CO)_8[(\eta^5\text{-}C_4H_4)C(O)O\text{-}CH_2(OH)CH_3]$ (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, both for compounds **3** and **5**, are similar and the dihedral angle between the Cp* plane with the mean plane of osmium (**3**) or ruthenium (**5**) are respectively 132.9° and 133.3°. If we examine the bond distances of the M_3 core of both compounds **3** and **5**, it reveals 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 the hydride ligand is bridged between the longer M-M bond.



3 (a) **5 (b)**

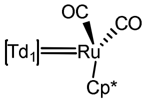
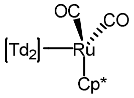
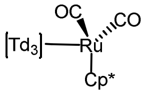
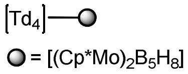
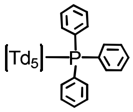
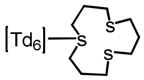
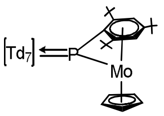
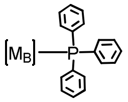
Fig. 1. Molecular structure and labeling diagram of compounds **3 (a)** and **5 (b)**. Carbonyl ligands on $M(CO)_3$ (M = Os, Ru) fragments are not shown for clarity. Relevant bond lengths (A°) and angles (deg) a) **3**: Os1-Os3 2.7666(10), Os1-Os2 2.7733(10), Os2-Os3 2.8968(10), S1-Ru1 2.418(4), S1-Os3 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).

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 count[21] and vise versa. Housecraft et. al., has shown earlier that an *exo*-$\{Cp^*Ru(CO)_2\}$ of boride cluster $[H_2Ru_5(CO)_{13}Cp^*BH_2]$ contributes one electron toward the Ru_4B core.[26b] Considering the same fact that {Cp*Ru(CO)$_2$} moiety is an one-electron fragment,[26a] the *exo*-units {Cp*Ru(CO)$_2$} [M$_3$(CO)$_9$ (**3**: M = Os, **5**: M = Ru)] 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 pair and can be classified as *nido* geometry based on a *closo*-trigonal bipyramidal arrangement.

Pairs of molecules both in compounds **3** and **5** are related through two types of short contacts i) C-H···O interaction and ii) O…O short interactions of the carbonyl's oxygen. In case of **3**, two C-H···O interactions such as (a) C7-H7B···O3 (symm: ½+x, ½-y, ½+z), and (b) C10-H10C···O4 (symm: ½+x, ½-y, ½+z) having length and angles 2.41 Å; 145.99° and 2.43 Å; 137.43° respectively form 1D chain parallel to ac diagonal (Fig. S1a)†. The O···O interaction is in between the carbonyl oxygen atoms O9 and O10 (symm: 1-x, -y, 1-z). Distance between the atoms is 2.899 Å, which is 0.14 Å shorter than 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 ac plane. Molecules in these layers are bound to their inversion (layer) through van der Waal and O···O short interactions through carbonyl oxygen's and these bi-layers thus formed are only weakly linked among themselves (Fig. S1b)†.

In order to investigate the redox property of these mixed-metal chalcogenide clusters, the electrochemistry of compounds **3** and **5** was examined using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. The cyclic voltammetry was carried out using a sample solution containing 10^{-4} M [n-Bu$_4$NPF$_6$] in CH$_3$CN as a supporting electrolyte and a standard three-electrode system (glassy carbon working electrode, platinum wire counter electrode and SCE as reference electrode) was employed for the measurements. The results of the voltametric experiments are summarized in Fig. 2. Both compound **3** and **5** exhibit similar types of irreversible anodic peaks (Ep$_a$), except they differ in shifting of the signals. The highest peak for **5** at 1.31 V has been shifted to 1.57 V for **3** that may correspond to one electron oxidation process for Ru-centre as evident by the lack of return wave. This irreversible behavior has similarly been observed for compound [Cp*$_2$FeRu(C$_8$H$_8$)][27] that decomposes upon electrochemical oxidation which is electrochemically inactive.

Table 1. Structural Parameters and Spectroscopic data (^{1}H NMR and IR) of Various Metal Clusters

Compounds	*Exo*-type	Avg. *d* [M-M][Å][i]	*d* [M-exo atom][Å]	^{1}H$_{(M\text{-}H\text{-}M)}$ NMR [ppm]	IR (CO) νbar/cm^{-1}	Ref.
[Cp*Ru(CO)$_2$(μ-H)Td$_1$][a]		2.647	2.504 (M-Ru)	-23.03	2015, 1968	24a
[Cp*Ru(CO)$_2$Td$_2$][b] **3**		2.812	2.418 (M-S)	-18.34	2080, 1929	This work
[Cp*Ru(CO)$_2$Td$_3$][c] **5**		2.786	2.412 (M-S)	-18.60	2040, 1982	This work
[(Cp*Mo)$_2$B$_5$H$_8$Td$_4$][d] **6**		2.789	--	-18.5	2018, 1985	This work
[Ph$_3$PTd$_5$][e]		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$_6$][f]		2.927	2.419 (M – S)	-18.83, -20.47	2097, 1956	24c
[Cp$_2$(μ-k^1:k^1,η^6-PMes*)(CO)$_{9\text{-}n}$Td$_7$][g]		3.039 (M = W) 2.732 (M = Fe)	2.284 (M -P) 2.087 (M - P)	-- --	2031, 1949 (M = W) 2020, 1941 (M = Fe)	25a
[Ph$_3$PM$_B$][h]		2.955	2.386 (M-P)	-12.14	2070, 1969	25b

[Td] = Tetrahedral moiety. [M$_B$] = Butterfly moiety.

[a] Td$_1$ = {RuFe$_3$(CO)$_9$}]. [b] Td$_2$ = [(μ$_3$-S)Os$_3$(CO)$_9$H]. [c] Td$_3$ = [(μ$_3$-S)Ru$_3$(CO)$_9$H]. [d] Td$_4$ = [(μ$_3$-S)Ru$_3$(CO)$_9$H]. [e] Td$_5$ = [M(η^5-MeCOC$_5$H$_4$)FeCo(μ$_3$-S)(CO)$_7$] (M = Mo, W). [f] Td$_6$ = [OS$_4$(CO)$_{11}$(μ-H)$_4$]. [g] Td$_7$ = [Mo$_2$M$_2$(μ$_3$-S)] (M = W, n = 0; M = Fe, n = -2); (Cp = η^5-C$_5$H$_5$; Mes* = 2,4,6-C$_6$H$_2{}^t$Bu$_3$). [h] M$_B$ = [(μ-H)Os$_3$(CO)$_{11}$(OC)$_3$Re]. [i] Avg. M-M distance of the tetrahedral core.

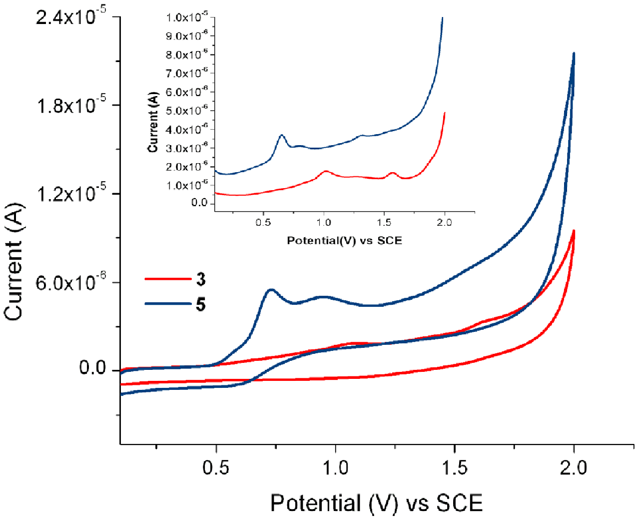


Fig. 2. Cyclic voltammograms and Differential Pulse Voltammograms (inset) for **3** and **5** in CH_3CN containing 10^{-4} M [*n*-Bu_4NPF_6. The cyclic voltammograms and the Differential Pulse Voltammograms are scanned from 0 to 2 V at a scan rate of 0.10 V/s.

Compound **6** has been isolated in modest yield. The ^{11}B NMR displays five resonances in equal intensity at δ = 73.4, 65.2, 56.1, 33.7 and 29.2 ppm. The ^{1}H NMR spectrum confirms the presence of a single resonance for two equivalents of Cp* protons at δ = 2.05 ppm. The IR spectrum shows intense band at 2018, 1985 cm^{-1} characteristic of terminal carbonyl groups and a band at 2403 cm^{-1} due to B–H_t stretches. With an agreement to the spectroscopic data, the solid-state structure, as shown in Fig. 3, revealed that compound **6** holds the [Mo_2B_5] core with an *exo*-moiety {Ru_3S} attached to one of the boron atom (B1). The two fragments are united through a direct 2-centre B-S σ bond.

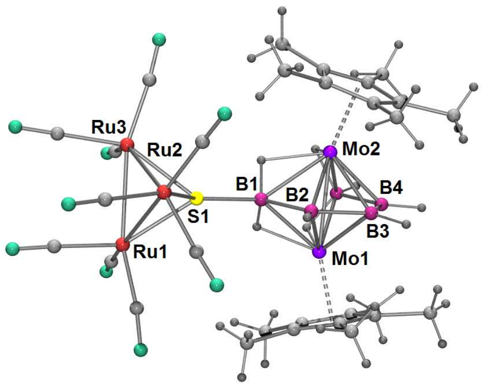


Fig. 3. Molecular structure and labeling diagram of **6**. Terminal CO ligands on Ru atom are omitted for clarity. Selected bond lengths (Å) and angles (°): B3-B4 1.720(18), Ru1-S1 2.344(3), Mo1-B4 2.195(12), S1-B1 1.914(11); B3-Mo2-Mo1 50.0(3), S1-Ru3-Ru1 53.97(7), B1-S1-Ru1 141.4(4), Ru3-Ru1-Ru2 63.26(4).

Generally, the cluster compounds can be composed into a larger entity through two different modes; either via (i) 2c-2e or 3c-2e bond[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-sulphur bond. Thus, **6** can be considered as a *conjuncto* cluster. The B-S bond distance in **6** (1.914(11) Å) can be comparable with [$(Cp^*Co)_2B_4H_5SFe_3(CO)_9$] (1.901(7) Å), whereas it is in the longer side if compared with the B-S distance in [$(Cp^*Mo)_2B_5H_8(SPh)$][34a] of (1.887(4) Å) and in [$(Cp^*Mo)_2(\mu_3$-S)(μ-η^1-SPh$)_2(H_2BSPh)$][34b] of 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-sulphur linkage did not perturb the cluster bonding pattern significantly.

Conclusions

With the goal of obtaining hybrid bridged-borylene compounds, we set out for the cluster growth reaction of *arachno*-**1** and **2** with [$Os_3(CO)_{12}$] and [$Ru_3(CO)_{12}$]. However, the reaction yielded, serendipitously, unusual tetrahedral chalcogenide clusters anchored to *exo*-polyhedral moiety $Cp^*Ru(CO)_2$. Based on the structural parameters of compound [$(Cp^*Mo)_2B_5H_8\{Ru_3(CO)_{12}\}S$] it is evident that the *exo*-fragment does not disturb the core geometry of [$(Cp^*Mo)_2B_5H_9$]. Although many parallels exist between 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 of the cases discovery of new compounds are 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, [$Bu_4N(B_3H_8)$], was synthesized with the literature method.[36] Thin layer chromatography was carried 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 reference (δ, ppm, [D_6]-benzene, 7.16), while a sealed tube containing [$Bu_4N(B_3H_8)$] in [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 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** (0.24g, 0.43 mmol) was taken. To this [$Os_3(CO)_{12}$] (0.391 g, 0.43 mmol) was added and the resulting mixture was dissolved in toluene and thermolysed in presence of excess of 2-methylthiophene for 16h 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 solvent, the residue was subjected to 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 $[M]^+$; isotope envelope $C_{21}H_{16}O_{11}Os_3RuS$: requires 1148; m/z 840 $[M+H-11CO]^+$; isotope envelope $C_{10}H_{16}Os_3RuS$: requires 840. ^1H NMR (22 °C, 400 MHz, $[D_6]$-benzene): δ = 1.84 (s, 15H, 1Cp*), -20.81 (s, 1H, Os-H-Os). ^{13}C NMR (22 °C, 100 MHz, $[D_6]$-benzene): δ = 198.7, 195.1 (*C*O), 98.8 (C_5Me_5), 10.1 ($C_5\mathit{Me}_5$). IR νbar/cm^{-1}: 2048, 2015, 1990 (CO).

Synthesis of 5 and 6: Compound **2** (0.25 g, 0.475 mmol) was taken in a flame-dried Schlenk tube. To this $[Ru_3(CO)_{12}]$ (0.30 g, 0.475 mmol) was added and the mixture was dissolved in toluene and thermolyzed for 72 h at 100°C in presence of 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 solvent, the residue was subjected to 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, $[D_6]$-benzene): δ = 1.89 (s, 15H, 1Cp*), -18.60 (s, 1H, Ru-H-Ru). ^{13}C NMR (22 °C, 100 MHz, $[D_6]$-benzene): δ = 188.3, 183.1 (*C*O), 98.2 (C_5Me_5), 10.7 ($C_5\mathit{Me}_5$). IR νbar/cm^{-1}: 2040, 2008, 1982 (CO). Elemental analysis (%) calcd for $C_{21}H_{16}O_{11}SRu_4$: C, 28.64; H, 1.83. Found: C, 29.69; H, 1.99.

6: MS (MALDI): m/z 1113 $[M+H]^+$; isotope envelope $C_{29}H_{39}B_5O_9SMo_2Ru_3$: requires 1113. ^{11}B NMR (22 °C, 128 MHz, $[D_6]$-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, $[D_6]$-benzene): δ = 7.81 (B-H_t), 2.05 (s, 30H, 2Cp*), -4.7 (s, 1H, B-H-B), -4.9 (s, 1H, B-H-B), -6.8 (s, 1H, B-H-B), -18.5 (s, 1H, Ru-H-Ru). ^{13}C NMR (22 °C, 100 MHz, $[D_6]$-benzene): δ = 188.3, 183.1 (*C*O), 97.0 (C_5Me_5), 12.6 ($C_5\mathit{Me}_5$). IR νbar/cm^{-1}: 2403 (B-H_t), 2018, 1985, (CO). Elemental analysis (%) calcd for $C_{29}H_{39}B_5O_9SMo_2Ru_3$: 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-Kα (λ = 0.71073 Å) radiation at 296 K. Crystal data for **5** was collected and integrated using OXFORD DIFFRACTION SUPER NOVA CCD system equipped with graphite-monochromated Cu Kα radiation (λ = 1.5418 Å) radiation 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, $C_{21}H_{16}O_{11}Os_3RuS$, M_r = 1148.06, Monoclinic, space group *P2₁/n*, a = 8.6735(3) Å, b = 28.0865(9) Å, c = 11.7927(4) Å, β = 102.006(2)°, V = 2809.96(16) Å^3, 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 [2θ≤47.14°] and 334 parameters.

Crystal data for **5**: CCDC 1017200, $C_{21}H_{16}O_{11}Ru_4S$, 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) Å^3, 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 [θ≤72.40°] and 339 parameters.

Crystal data for **6**: CCDC 1017201, Crystal data for **6**: $C_{29}H_{38}B_5Mo_2O_9Ru_3S$, M_r = 1111.79, Monoclinic space group *C2/c*, a = 25.7689(9) Å, b = 25.0277(9) Å, c = 14.7792(5) Å, β = 122.069(2)°, V = 8077.3(5) Å^3, 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 [2θ≤41.68°] and 674 parameters.

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Notes and references

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† The choice of 2-methylthiophene ligand as sulfur source originated from the fact that when the thermolysis of *arachno*-$[(Cp^*RuCO)_2B_2H_6]$, **1** and $[Os_3(CO)_{12}]$ was carried out in toluene compounds **3** was isolated in moderate yields. Therefore, we checked the purity of 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 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 suitable X-ray crystallographic data set failed.

Electronic Supplementary Information (ESI) available: For crystal packing diagram for **3** and **5**; CCDC reference numbers 1017199-1017201 or other electronic format see DOI: 10.1039/b000000x/

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Table of Content Entry Only

Mixed-Metal Chalcogenide Tetrahedral Clusters with an *Exo*-polyhedral Metal Fragment

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Mixed-metal chalcogenide tetrahedral clusters, [Cp*Ru(CO)$_2$(μ-H){Os$_3$(CO)$_9$}S] and [Cp*Ru(CO)$_2$(μ-H){Ru$_3$(CO)$_9$}S] have been isolated from *arachno*-[(Cp*RuCO)$_2$B$_2$H$_6$] and [(Cp*Mo)$_2$B$_5$H$_9$], in which [Cp*Ru(CO)$_2$] fragment is attached in an *exo*-polyhedral manner.