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Introduction

Over the years the development of heterometallic clusters in particular, the transition-metal hydrido/carbonyl clusters 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. However, transition-metal hydrido/carbonyl clusters with encapsulation of a chalcogen atom are less explored. During the past several decades chalcogenido carbonyl species possess great advancement both for fundamental research and practical fields. For example, the replacement of framework anions (i.e., $O^2$) of microporous oxides with chalcogens (e.g., S$^2$) or organic ligands (e.g., nitriles, carboxylates, amines) represents a recent approach for generating microporous materials. These compounds hold great potentials for applications in solid electrolytes, semiconductor electrodes, sensors, and photo catalysis. On the other hand, regardless of finding intimate link to organometallic systems, 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. In contrast to the organometallic chemistry, the role of transition metals in polyhedral borane chemistry is a limited area. However, among them Suzuki coupling, functionalization of hydrocarbyl groups and boranes, oxidative coupling of carboranes, alkene cyclotrimerisation and alkene hydrogenation are significant.

We have recently described the synthesis and structure of diruthenatetraphosphorane arachno-$[\text{[Cp}^*\text{Ru(CO)}_3\text{B}_2\text{H}_3]$, 1, from the reaction of $[\text{1,2-}\text{(Cp}^*\text{RuH)}_2\text{B}_3\text{H}_3]$ and mono-metal carbonyl fragment $[\text{Mo(CO)}_3\text{CHCN}]$ 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 from metal carbonyl compounds, such as $[\text{Fe}_2\text{(CO)}_9]$, $[\text{Mn}_2\text{(CO)}_9]$, and $[\text{Ru}_3\text{(CO)}_{12}]$. Further, the reaction of arachno-1 with HBCat (cat = 1,2-O$_2$C$\text{CH}_2$), yielded a bridged-boryl complex, $[(\text{Cp}^*\text{Ru})(\mu-H)(\mu-Co)(\mu-Bcat)]$. 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 $[\text{M}_3\text{S} \ (3: M = \text{Os}, 5: M = \text{Ru})]$, 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 and isolobal principle 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 $[\text{Os}_6\text{(CO)}_{12}]$ 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)]_{3}((µ-H){[Os_{4}(CO)]_{5}S}], 3 and a hybrid tetrahedral cluster [Cp*Ru((µ-H){[Os_{6}(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 \(^1\)H NMR spectrum reveals one sharp singlet at \(\delta = -20.81\) ppm which can be assigned as Os-H-Os bridging hydrogen. In a similar fashion, reaction of molybdaborane [(Cp*Mo)]_{3}B\(_{3}\)H\(_{8}\), as described in Scheme 1, led to the formation of a tetrahedral mixed-metal chalcogenide cluster [Cp*Ru(CO)]_{3}((µ-H){[Ru_{3}(CO)]_{5}S}], 5 along with a \textit{conjectur-}
([Cp*Mo])_{3}B\(_{3}\)H\(_{8}\)Ru_{3}(CO)\(_{5}\)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)\(_{5}\) (3: M = Os; 5: M = Ru) moieties which form a triangular plane. Further, the \(\textit{exo}\)-polyhedral units Cp*Ru(CO)\(_{3}\) are bound to the sulfur atom of the tetrahedral core. Ignoring the Cp*Ru(CO)\(_{2}\) \(\textit{exo}\)-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_{5}(CO)]_{12}\(^{13a}\), (2.7787(2)Å), [Cp*RhOs_{7}(CO)]_{12}(µ-H)\(_{4}\)\(^{24c}\), (2.8211-2.9781(1)Å) and [μ-HOs_{5}(CO)]_{9}(OC)\(_{3}\)Re_{3}Ph\(_{12}\)^{15b}, (2.793-3.004 Å). Similarly, the average Ru-Ru bond distances of 5 are also comparable with [(µ-I)Ru_{4}(CO)\(_{3}\)+(CSNMePh)]\(^{23b}\), (2.7452(11)-2.8822(2) Å). A range of tetrahedral metal clusters having \textit{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, (µ-S)CoMoRu(CO)\(_{3}\)\(\{[η^{2}-C_{5}H_{4}]C(O)OC_{7}(OH)CH_{3}\}\) (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 \(\textit{exo}\)-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.
same fact that \{Cp*Ru(CO)_3\} moiety is an one-electron fragment,\textsuperscript{26a} the exo-units \{Cp*Ru(CO)_2\} \[M(CO)_3(3: M = Os, 5: M = Ru)\] 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 closo 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^{-3} M [n-Bu_4NPF_6] in CH_2CN 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 voltammetric experiments are summarized in Fig. 2. Both compound 3 and 5 exhibit similar types of irreversible anodic peaks (E_{pa}), 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 \[Cp^*_{2}FeRu(C_6H_5)_2\]\textsuperscript{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

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Exo-type</th>
<th>(\text{Avg. } d) [M-M][Å]</th>
<th>(\text{d[M-exo atom][Å]})</th>
<th>(\text{(^1)H(M-M)}) NMR [ppm]</th>
<th>IR (CO) (^{-1})vbar/cm(^{-1})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cp*Ru(CO),(μ-H)Td]\textsuperscript{a}</td>
<td></td>
<td>2.647</td>
<td>2.504 (M-Ru)</td>
<td>-23.03</td>
<td>2015, 1968</td>
<td>24a</td>
</tr>
<tr>
<td>[Cp*Ru(CO),Td]\textsuperscript{b}</td>
<td></td>
<td>2.812</td>
<td>2.418 (M-S)</td>
<td>-18.34</td>
<td>2080, 1929</td>
<td>This work</td>
</tr>
<tr>
<td>[Cp*Ru(CO),Td]\textsuperscript{c}</td>
<td></td>
<td>2.786</td>
<td>2.412 (M-S)</td>
<td>-18.60</td>
<td>2040, 1982</td>
<td>This work</td>
</tr>
<tr>
<td>[Cp*Mn,B,H,Td]\textsuperscript{d}</td>
<td></td>
<td>2.798</td>
<td>--</td>
<td>-18.5</td>
<td>2018, 1985</td>
<td>This work</td>
</tr>
<tr>
<td><a href="C_6H_5">Cp,μ-k:(\eta^5)-PMes\textsuperscript{e}</a>\textsubscript{p}(μ-Td)\textsuperscript{f}</td>
<td></td>
<td>3.039 (M = W)</td>
<td>2.284 (M -P)</td>
<td>--</td>
<td>2031, 1949 (M = W)</td>
<td>25a</td>
</tr>
<tr>
<td>[Ph,PMn]\textsuperscript{g}</td>
<td></td>
<td>2.955</td>
<td>2.386 (M-P)</td>
<td>-12.14</td>
<td>2070, 1969</td>
<td>25b</td>
</tr>
</tbody>
</table>

\(\text{Td} = \text{Tetrahedral moiety, } [M_{\text{ex}}] = \text{Butterfly moiety.}\)

\(\text{a Td}_1 = [\text{RuFe}_{(C_6H_5)}]^{2+}, \text{b Td}_2 = [(\mu_5-S)OS_{(C_6H_5)}H], \text{c Td}_3 = [(\mu_3-S)Ru_{(C_6H_5)}H], \text{d Td}_4 = [(\mu_3-S)Ru_{(C_6H_5)}OH], \text{e Td}_5 = [M(\eta^5-MeCO}_3C_5H_5)FeCo(\mu_5-S)(C_6H_5)] (M = Mo, W), \text{f Td}_6 = [OS_{(C_6H_5)}(\mu-H)_2], \text{g Td}_7 = [Mo_{2}M_{2}(\mu-5)] (M = W, n = 0; M = Fe, n = -2); (Cp = \eta^5-C_5H_5; \text{Mes} = 2,4,6-C_6H_3(Bu)_3).\)

\(\text{Avg. M-M distance of the tetrahedral core.}\)
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)₂B₄H₁₄SFe₂(CO)₅] (1.901(7) Å), whereas it is in the longer side if compared with the B-S distance in [(Cp*Mo)₂B₄H₁₄(SPh)] of 1.874(5) Å and in [(Cp*Mo)₂(S₂C(SPh)₂)(H₂B₃SPh)] 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 [Os₂(CO)₁₂] and [Ru₂(CO)₁₂]. However, the reaction yielded, serendipitously, unusual tetrahedral chalcogenide clusters anchored to exo-polyhedral moiety CpRu(CO)₂. Based on the structural parameters of compound [(Cp*Mo)₂B₄H₁₄(Ru₃(CO)₁₂)S] it is evident that the exo-fragment does not disturb the core geometry of [(Cp*Mo)₂B₄H₄]. 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 N₂ before use. Compounds arachno-1 and 2 were prepared according to literature methods, while other chemicals were obtained commercially and used as received. The external reference for the ¹¹B NMR, [Bu₄N(B₄H₄)], was synthesized with the literature method. 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, [D₆]-benzene, 7.16), while a sealed tube containing [Bu₄N(B₄H₄)] in [D₆]benzene (δ, ppm, –30.07) was used as an external reference for the ¹¹B 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 (0.24 g, 0.43 mmol) was taken. To this [Os₂(CO)₁₂] (0.391 g, 0.43 mmol) was added and the resulting mixture was dissolved in toluene and thermostated 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/CH₂Cl₂ (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 C₅H₁₀O₃S₃RuS: requires 1148; m/z 840 [M-H-11CO]⁻; isotope envelope C₁₉H₁₆O₅S₃RuS: requires 840. ¹H NMR (22 °C, 400 MHz, [D₆]benzene): δ = 1.84 (s, 15H, 1CP*), -0.81 (s, 1H, Os-H-Os). ¹³C NMR (22 °C, 100 MHz, [D₆]benzene): δ = 198.7, 195.1 (CO), 98.8 (C₅Me₅), 10.1 (C₅Me₅). IR vbar/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 [Ru₂(CO)₅]₂ (0.30 g, 0.475 mmol) was added and the mixture was dissolved in toluene and thermolysed 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/CH₂Cl₂ (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, [D₆]benzene): δ = 1.89 (s, 15H, 1CP*), -18.60 (s, 1H, Ru-H-Ru). ¹³C NMR (22 °C, 100 MHz, [D₆]benzene): δ = 188.3, 183.1 (CO), 98.2 (C₅Me₅), 10.7 (C₅Me₅). IR vbar/cm⁻¹: 2040, 2008, 1982 (CO). Elemental analysis (%) calced for C₇₂H₉₀O₁₁Ru₄: C, 28.64; H, 1.83. Found: C, 29.69; H, 1.99.

6: MS (MALDI): m/z 1113 [M+H]⁺; isotope envelope C₉₀H₇₂O₂₇S₃Ru₂: requires 1113. ¹³B NMR (22 °C, 128 MHz, [D₆]benzene): δ = 73.4 (br, 1B), 65.2 (br, 1B), 56.1 (br, 1B), 33.7 (br, 1B), 29.2 (br, 1H). ¹H NMR (22 °C, 400 MHz, [D₆]benzene): δ = 7.81 (B-H), 2.05 (s, 3OH, 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). ¹³C NMR (22 °C, 100 MHz, [D₆]benzene): δ = 188.3, 183.1 (CO), 97.0 (C₅Me₅), 12.6 (C₅Me₅). IR vbar/cm⁻¹: 2403 (B-H₂), 2018, 1985, 1950 (CO). Elemental analysis (%) calced for C₁₁₀H₈₀O₂₇S₃Ru₂: 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 Bruker X-AREA 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 DIFRACTION 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 SHELXL-97 or SIR92 and refined using SHELXL-97. 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 1017799, C₁₂H₁₀O₃S₃Ru₄S₄, Mᵣ = 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) Å³, Z = 4, ρcalcd = 2.713 g cm⁻³, μ = 14.175 mm⁻¹, F(000) = 2072, R₁ = 0.0345, wR₂ = 0.0392, 339 independent reflections [2θ≤24.1°] and 339 parameters.

Crystal data for 6: CCDC 1017201, Crystal data for 6: C₅₂H₈₀B₃O₇Ru₄S₄, Mᵣ = 1111.79, Monoclinic space group P2₁/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, ρcalcd = 1.829 g cm⁻³, μ = 1.796 mm⁻¹, F(000) = 4328, R₁ = 0.0284, wR₂ = 0.0555, 4232 independent reflections [2θ≤41.68°] and 674 parameters.

Acknowledgements

Generous support of the Department of Science and Technology, DST (Project No. SR/S1/IC–13/2011), New Delhi, India, and Institute Research and Development Award Fellowship, Indian Institute of Technology Madras are gratefully acknowledged. KY and DKR thank CSIR, India, for research fellowship.

Notes and references

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2. Sophisticated Analytical Instruments Facility, Indian Institute of Technology Madras, Chennai 600 036, India.
3. The choice of 2-methylthiophene ligand as sulfur source originated from the fact that when the thermolysis of arachno-[Ru(CO)₂B₁₂H₁₁], 1 and [Os(CO)₂Cl] was carried out in toluene compounds 3, 5 and 6 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. 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/


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)3Os3(CO)9]S and [Cp*Ru(CO)2(µ-H)3Ru3(CO)9]S have been isolated from arachno-[(Cp*RuCO)2B2H6] and [(Cp*Mo)2B2H6], in which [Cp*Ru(CO)2] fragment is attached in an exo-polyhedral manner.