

## Cycloosmathioborane Compounds: Other Manifestation of the Hückel Aromaticity

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**ABSTRACT:** The discovery of cycloosmathioborane compounds is reported. These species, which are prepared by simultaneous dehydrogenation of a trihydride-hydrogensulfide-osmium(IV) complex and a  $\text{BH}_3\text{NHR}_2$  amine-borane, bear an Os, S, B three-membered ring, being a manifestation of  $4n + 2$  Hückel aromaticity in which  $n = 0$  and where the two  $\pi$ -electrons of the ring are provided by the S atom.

Aromaticity is a classical concept in chemistry which is continually evolving.<sup>1</sup> It was initially introduced to account for the special properties of some unsaturated hydrocarbons and conjugated heterocycles. In 1979, Thorn and Hoffmann proposed to extend it to organic aromatic compounds where a CH unit is replaced by an isolobal transition metal fragment<sup>2</sup> and, three years later, Roper's group reported the first metallabenzene.<sup>3</sup> Since then, a significant number of aromatic derivatives based on both carbon and transition elements have been isolated and characterized,<sup>4</sup> most of them, as Hückel aromatic species.<sup>4c</sup>

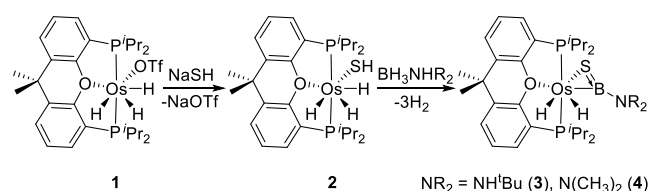
Frogly and Wright have recently defined metallaromatic compounds as those bearing at least a transition metal in the ring<sup>4d</sup> whereas, in 1979, Bursten and Fenske used the term “*metalloaromaticity*” to describe the aromatic behavior appeared to have been induced into cyclobutadiene as a result of its coordination to the Fe(CO)<sub>3</sub> metal fragment.<sup>5</sup> Nevertheless, metalloaromaticity has been employed by some authors without distinction for both situations.<sup>6</sup> In addition, the term all-metal aromaticity has been invoked to address different aspects of the behavior of clusters of both main-groups elements and transition metals.<sup>7</sup>

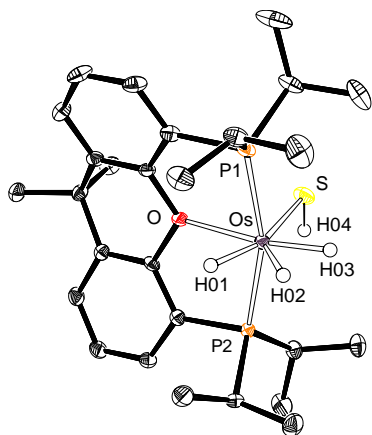
Cyclo-gallene dianion  $[\text{Ga}_3\text{L}_3]^{2-}$  ( $\text{L} = \text{Mes}_2\text{C}_6\text{H}_3$ ) was the first compound of this class.<sup>8</sup> Today, homoleptic aromatic 3-10 membered rings with elements of group 2 as well as of groups 13-16 are known,<sup>9</sup> besides tripalladium<sup>10</sup> and trigold cations.<sup>11</sup> Three-membered ring compounds are certainly the most challenging due to the strain imposed by the small size of the ring. Computational methods have revealed that the aromaticity of group 14 cyclopropenyl cation analogues ( $\text{E}_3\text{H}_3^+$ ) decreases in the sequence  $\text{C} > \text{Si} > \text{Ge} > \text{Sn} > \text{Pb}$ .<sup>12</sup> In addition to homoleptic species, a few heteroleptic ones with two different main-group elements are also known. Cummins and coworkers have reported  $\text{EP}_2$  triangles ( $\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$ ), which are stabilized within the coordination sphere of a sterically protected diniobium unit<sup>13</sup> whereas the Guha's group has computationally predicted that the substitution of a boron atom in the triangle  $[\text{B}_3\text{H}_3]^{2-}$  by a group 15 element should afford neutral aromatic  $\text{H}_2\text{B}_2\text{XH}$  rings ( $\text{X} = \text{N}, \text{P}$ ).<sup>14</sup> Herein, we take one

step forward in this fascinating field by reporting the preparation and full characterization of the first aromatic triangles having three different vertexes, namely two main-group elements, S and B, and a transition metal with its associated ligands.

Scheme 1 summarizes the preparation of the new compounds, which starts from the 9,9-dimethyl-4,5-bis(diisopropylphosphine)xanthene complex  $\text{OsH}_3(\text{OTf})\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$  (**1**) and takes place through the hydrogensulfide derivative  $\text{OsH}_3(\text{SH})\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$  (**2**). The synthesis of the latter was inspired by the recent preparation of its hydroxo counterpart  $\text{OsH}_3(\text{OH})\{\kappa^3\text{-P,O,P-}[\text{xant}(\text{P}^i\text{Pr}_2)_2]\}$ ,<sup>15</sup> which is stable towards the reductive elimination of water in spite of that this process is generally favored from a thermodynamic point of view.<sup>16</sup> Similarly to the  $\text{OH}^-$  group,  $\text{SH}^-$  replaces the trifluoromethanesulfonate anion ( $[\text{OTf}]^-$ ) from **1** to give **2**, which was isolated as red crystals in 47 % yield. The coordination of the  $\text{SH}^-$  group to the osmium atom is demonstrated by the X-ray diffraction analysis structure (Figure 1). The osmium(IV) center shows the expected pentagonal bipyramidal arrangement with axial  $\text{P}^i\text{Pr}_2$  groups and the oxygen atom of the diphosphine and the SH anion in the perpendicular plane, along with the *cisoid* inequivalent hydrides which display three resonances at -8.07, -13.01, and -13.78 ppm in the  $^1\text{H}$  NMR spectrum, in toluene- $d_8$ , at 193 K. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows a singlet at 48.1 ppm for the equivalent  $\text{P}^i\text{Pr}_2$  groups. Complexes of platinum group metals bearing terminal hydrogensulfide ligands are rare due to the high tendency of this group to act as a bridging ligand.<sup>17</sup> The five-coordinate catecholboryl derivative  $\text{Os}(\text{Bcat})(\text{SH})(\text{CO})(\text{P}^i\text{Pr}_3)_2$  was the first mononuclear SH-complex of these metals characterized by X-ray diffraction analysis. It was prepared by reaction of the monohydride  $\text{OsH}(\text{SH})(\text{CO})(\text{P}^i\text{Pr}_3)_2$ <sup>18</sup> with  $\text{HBcat}$  via the dihydrogen intermediate  $\text{OsH}(\text{SBcat})(\eta^2\text{-H}_2)(\text{CO})(\text{P}^i\text{Pr}_3)_2$ .<sup>19</sup> Braun and co-workers have recently reported the rhodium(I) derivative  $\text{Rh}(\text{SH})\{\kappa^3\text{-P,O,P-xant}(\text{Bu}_2)_2\}$ , which has been also characterized by X-ray diffraction analysis.<sup>20</sup>

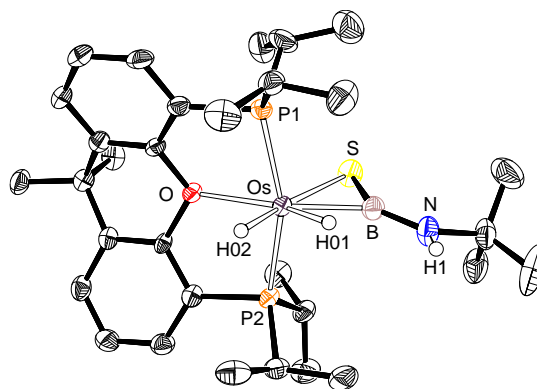
### Scheme 1. Synthetic Strategy for the Preparation of Cycloosmathioborane Complexes





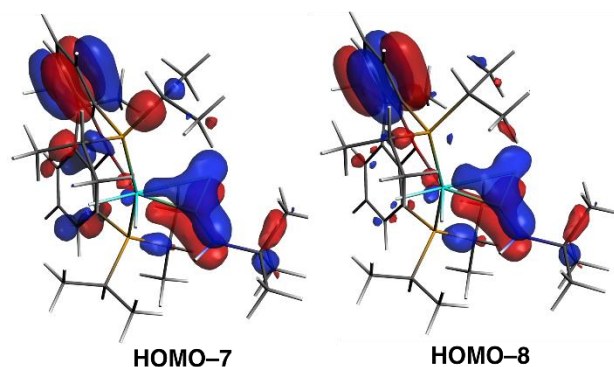
**Figure 1.** Molecular drawing of complex **2**. Hydrogen atoms (except hydrides and H04) are omitted for clarity. Selected distances and angles: Os-S = 2.4483(6) Å, S-H04 = 1.16(3) Å, Os-S-H = 105.8(13)°, O1-Os-S = 80.92(4)°, P1-Os-P2 = 162.26(2)°.

Complex **2** reacts with  $\text{BH}_3\text{NHR}_2$  amine-boranes to give the unprecedented cycloosmathioborane derivatives  $\text{OsH}_2\{\kappa^2\text{-S,B-[SBNR}_2\}\{\kappa^3\text{-P,O,P-[xant(P'Pr}_2)_2\}\}$  ( $\text{NR}_2 = \text{NH}^t\text{Bu}$  (**3**),  $\text{NMe}_2$  (**4**)), as a result of the releasing of  $\text{H}_2$  from both the metal center and the amine-boranes. The dehydrogenation is favored by the polyhydride character of **2**<sup>21</sup> and by the presence of the hydrogensulfide ligand, which traps the resulting amino-borane monomer.<sup>22</sup> The capture facilitates the complete extraction of the hydrogen atoms attached to the boron atom. Complex **3** and **4** were isolated as yellow solids in about 60 % yield. The X-ray diffraction analysis structure of **3** (Figure 2) proves the triangular shape of the ring determined by the Os, S, and B atoms. The most noticeable feature of the triangle is the B-S distance of 1.782(6) Å, which suggests a significant double bond character. It is only about 0.03 Å longer than the B-S bond length reported in the manganese complex  $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)\{\text{S=B}^t\text{(Bu)IME}\}(\text{CO})_2$  (IME = 1,3-dimethylimidazolyliene; 1.747(3) Å)<sup>23</sup> and in the thioxoboranes  $\text{S=B}\{\kappa^2\text{-N,N-[N(2,6-Me}_2\text{C}_6\text{H}_3)\text{C(Me)CHC(Me)N(2,6-Me}_2\text{C}_6\text{H}_3)]\}$  (1.741(2) Å)<sup>24</sup> and  $\text{S=B}\{\kappa^2\text{-N,N-[N(2,4,6-Me}_3\text{C}_6\text{H}_2)\text{P(Ph)}_2\text{NP(Ph)}_2\text{N(2,4,6-Me}_3\text{C}_6\text{H}_2)]\}$  (1.752(5) Å),<sup>25</sup> and about 0.07 Å longer than that found in the cation  $\text{S=B}\{\kappa^2\text{-N,N-[N(L}^{\text{Mes}}\text{)CH}_2\text{CH}_2\text{N(L}^{\text{Mes}}\text{)]}\}^+$  ( $\text{L}^{\text{Mes}} = 1,3\text{-dimesitylimidazolinyliene}$ ; 1.710(5) Å),<sup>26</sup> species reported as the first ones featuring a B-S double bond. The three-membered rings of **3** and **4** resemble that of the intermediate recently proposed by Braunschweig and co-workers for the reaction of the alkylborylene complex  $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(=\text{B}^t\text{Bu})(\text{CO})_2$ , with  $\text{SPPH}_3$ , which yields the metathesis product  $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\text{PPh}_3)$ . This intermediate has been suggested to be a  $\kappa^2\text{-S,B-[SB}^t\text{Bu]}$  derivative.<sup>27</sup> The Os-S distance of 2.5572(14) Å is scarcely 0.08 Å longer than that of **2**, whereas the Os-B bond length of 2.073(6) Å is consistent with an Os(IV)-B single bond.<sup>28</sup> In fact, the  $\text{OsH}_2(\text{POP})$  moiety can be described as a 16-electron valence *cis*-dihydride  $\text{L}_5\text{Os(IV)}$  fragment, which gives rise to the typical pentagonal bipyramidal arrangement around the metal center, with a *mer*-coordination of the POP-pincer. This arrangement generates two high field signals at about -9 and -18 ppm in the  $^1\text{H}$  NMR spectra and a singlet at about 47 ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra. A broad resonance at 56.3 ppm for **3** and at 62.0 ppm for **4** in the  $^{11}\text{B}$  NMR spectra are also characteristic features of these compounds.



**Figure 2.** Molecular drawing of complex **3**. Hydrogen atoms (except hydrides and H1) are omitted for clarity. Selected distances and angles: B-N = 1.391(7) Å, Os-S-B = 53.5(2)°, S-B-Os = 82.8(2)°, B-Os-S = 43.7(2)°.

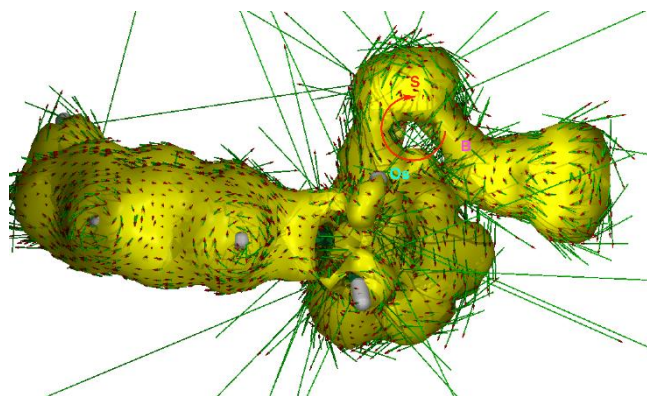
Density Functional Theory (DFT) calculations at the dispersion corrected BP86-D3/def2-TZVPP level were carried out on **3** to gain more insight into the bonding situation in the three-membered ring. Theoretical support for a significant double character of the B-S bond is given by the corresponding computed Wiberg Bond Index (WBI) of 1.40 and by the shape of HOMO-7 and HOMO-8. They can be viewed as  $\pi$ -molecular orbitals delocalized within the ring, also involving the lone pair of the attached nitrogen atom (Figure 3). According to the Natural Bond Order (NBO) method, the multiple bond character of the B-S bond derives from the delocalization of the lone pair of the sulfur atom into the vacant  $p_z$  atomic orbital of the boron (associated second-order perturbation energy of -55.7 kcal/mol). In addition, the NBO method also locates a significant delocalization of a doubly-occupied  $d_{\pi}(\text{Os})$  atomic orbital to this vacant  $p_z(\text{B})$  (associated energy of -21.3 kcal/mol), which is also fully consistent with the delocalized  $\pi$ -orbitals depicted in Figure 3.



**Figure 3.** Computed  $\pi$ -molecular orbitals delocalized into the Os-B-S metallacycle of **3** (isosurface value of 0.04 a.u.).

The previous mentioned findings are consistent with a formally  $4n + 2$  Hückel aromatic system in which  $n = 0$  and where the two  $\pi$ -electrons of the ring are provided by the sulfur atom. To confirm the aromaticity of the novel Os, S, B three-membered ring, we first computed the Nuclear Independent Chemical Shift (NICS) values at the center of the ring. A highly negative value of NICS (0) = -32.1 ppm was found, which would at first glance support the aromatic nature of the metallacycle. Nevertheless, it is well-known that isotropic NICS values, particularly in small rings, are usually contaminated by local shielding effects of the nearby bonds and therefore are not always reliable.<sup>12a</sup> The situation is even more dramatic if a transition metal is present in the ring.<sup>4c</sup> For this reason, we also computed the out-of-plane tensor

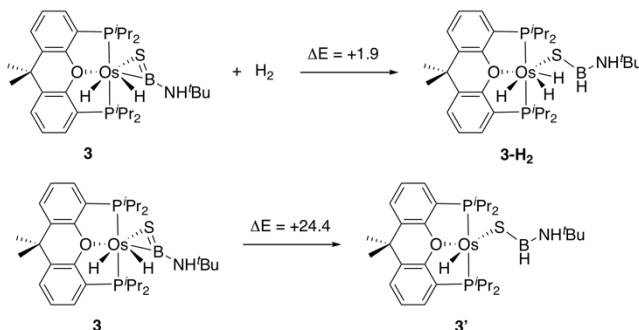
contribution to the NICS value at 1 Å above and below the ring center, which has been recommended as a reliable measure of the magnetic aromaticity.<sup>29</sup> The highly negative computed values, NICS(1)<sub>zz</sub> = -17.9 and -18.4 ppm are overwhelming evidence of the aromatic nature of the Os-S-B metallacycle. In addition, the Anisotropy of the Induced Current Density (ACID)<sup>30</sup> method was applied to visualize the aromatic ring current in the metallacycle. As depicted in Figure 4, the ACID method, computed for a model system where the bulky isopropyl and *tert*-butyl groups were replaced by hydrogen atoms (NICS(1)<sub>zz</sub> = -15.9 ppm), clearly shows the occurrence of a diatropic (clockwise vectors) ring current within the three-membered ring, therefore confirming the aromatic nature of this novel metallacycle.



**Figure 4.** ACID plot for the model compound  $\text{OsH}_2\{\kappa^2\text{-S,B-[SBNH}_2\}]\{\kappa^3\text{-P,O,P-[xant(PH}_2)_2]\}$  with a 0.04 a.u. isosurface value.

We have obtained additional support for the aromatic character of complexes **3** and **4** by means of energetic descriptors. However, the application of the energetic methods (ASE or ISE methods)<sup>4c</sup> typically used in other aromatic compounds, including those having transition-metals in their structures, is not possible for these particular species. We have carried out two alternative isodesmic reactions, namely the hydrogenation and the reductive elimination depicted in Scheme 2. For both reactions, the cleavage of the three-membered ring is computed to be endothermic, which is fully consistent with the thermodynamic stability (due to aromaticity) of the metallacycle.

**Scheme 2. Computed Isodesmic Reactions Involving Complex 3. Energies (in kcal/mol) Were Computed at the BP86-D3/def2-TZVPP Level**



In conclusion, the assembly of a 16-electron valence  $\text{L}_5\text{Os(IV)}$  metal fragment, a sulfur atom, and a  $\text{B-NR}_2$  moiety gives rise to three-membered  $\pi$ -aromatic rings, which are formed by different vertexes, representing a novel manifestation of  $4n + 2$  Hückel aromaticity in which  $n = 0$ . These cycloosmathioborane compounds are prepared by simultaneous dehydrogenation of a trihy-

dride-hydrogensulfide-osmium(IV) complex and a  $\text{BH}_3\text{NHR}_2$  amine-borane.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. General information, instrumental methods, preparation and characterization of **2**, **3** and **4**, NMR spectra, structural analysis of **2** and **3**, and computational details (PDF) Crystallographic information for **2** (CCDC 1878692) (CIF) Crystallographic information for **3** (CCDC 1878693) (CIF) Cartesian coordinates (xyz)

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### Notes

The authors declare no competing financial interests.

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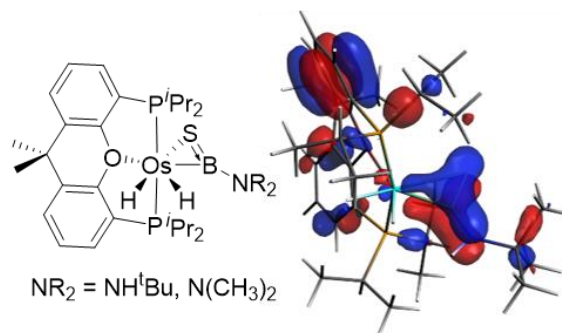
## DEDICATION

Dedicated to Professor Pablo Espinet by his outstanding contribution to the field of the organometallic compounds, on the occasion of his 70th birthday.

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Cycloosmathioboranes bearing an Os, S, B three-membered ring are a manifestation of  $4n + 2$  Hückel aromaticity in which  $n = 0$  and where the two  $\pi$ -electrons of the ring are provided by the S atom.

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