

Cycloosmathioborane Compounds: Other Manifestations of the Hückel Aromaticity

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Supporting Information

ABSTRACT: The discovery of cycloosmathioborane compounds is reported. These species, which are prepared by the simultaneous dehydrogenation of a trihydride hydrogensulfide osmium(IV) complex and a BH₃NHR₂ amine–borane, bear an Os–S–B three-membered ring, being a manifestation of the 4*n* + 2 Hückel aromaticity in which *n* = 0 and where the two π electrons of the ring are provided by the S atom.

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

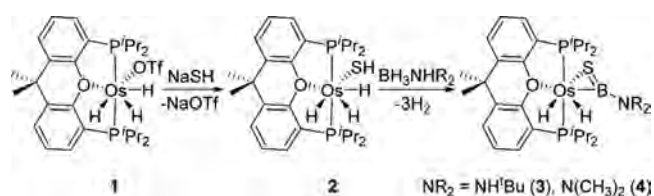
Frogley and Wright recently defined metallaaromatic compounds as those bearing at least a transition metal in the ring,^{4d} whereas in 1979, Bursten and Fenske used the term “metalloaromaticity” to describe the aromatic behavior that appeared to have been induced in cyclobutadiene as a result of its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

The cyclogallene dianion [Ga₃L₃]^{2−} (L = Mes₂C₆H₃) was the first compound of this class.⁸ Today, homoleptic aromatic 3–10-membered rings with elements of group 2 as well as of groups 13–16 are known,⁹ besides tripalladium¹⁰ and trigold cations.¹¹ Three-membered ring compounds are certainly the most challenging because of the strain imposed by the small size of the ring. Computational methods have revealed that the aromaticity of group 14 cyclopropenyl cation analogues (E₃H₃⁺) decreases in the sequence C > Si > Ge > Sn > Pb.¹² In addition to homoleptic species, a few heteroleptic species with two different main-group elements are also known. Cummins and co-workers

have reported EP₂ triangles (E = Ge, Sn, Pb), which are stabilized within the coordination sphere of a sterically protected dinobium unit,¹³ whereas Guha's group has computationally predicted that the substitution of a B atom in the triangle [B₃H₃]^{2−} by a group 15 element should afford neutral aromatic H₂B₂XH rings (X = N, P).¹⁴ 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 new compounds, which starts from the 9,9-dimethyl-4,5-bis-

Scheme 1. Synthetic Strategy for the Preparation of Cycloosmathioborane Complexes



(diisopropylphosphine)xanthene complex OsH₃(OTf){κ³-P,O,P-[xant(PⁱPr₂)₂]} (1) and takes place through the hydrogensulfide derivative OsH₃(SH){κ³-P,O,P-[xant(PⁱPr₂)₂]} (2; CCDC 1878692). Synthesis of the latter was inspired by the recent preparation of its hydroxo counterpart OsH₃(OH){κ³-P,O,P-[xant(PⁱPr₂)₂]},¹⁵ which is stable toward the reductive elimination of water despite this process is generally favored from a thermodynamic point of view.¹⁶ Similar to the OH[−] group, SH[−] replaces the trifluoromethanesulfonate anion ([OTf][−]) from 1 to give 2, which was isolated as red crystals in 47% yield. Coordination of the SH[−] group to the Os atom is demonstrated by the X-ray diffraction analysis structure (Figure 1). The Os^{IV} center shows the expected pentagonal-bipyramidal arrangement with axial PⁱPr₂ groups and the O atom of the diposphine 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 ¹H NMR

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Figure 1. Molecular drawing of complex 2. H atoms (except hydrides and H04) are omitted for clarity.

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 P^iPr_2 groups. Complexes of platinum group metals bearing terminal hydrogensulfide ligands are rare because of the high tendency of this group to act as a bridging ligand.¹⁷ The five-coordinate catecholboranyl 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 $\text{OsH}(\text{SH})(\text{CO})(\text{P}^i\text{Pr}_3)_2$ with HBcat via the dihydrogen intermediate $\text{OsH}(\text{SBcat})(\eta^2\text{-H}_2)(\text{CO})(\text{P}^i\text{Pr}_3)_2$.¹⁹ Braun and co-workers have recently reported the rhodium(I) derivative $\text{Rh}(\text{SH})\{\kappa^3\text{-P,O,P-[xant}(\text{tBu})_2]\}$, which has also been characterized by X-ray diffraction analysis.²⁰

Complex 2 reacts with BH_3NHR_2 amine-boranes to give the unprecedented cycloosmathioborane derivatives $\text{OsH}_2\{\kappa^2\text{-S,B-[SBNR}_2\}\{\kappa^3\text{-P,O,P-[xant}(\text{P}^i\text{Pr}_2)_2]\}$ [$\text{NR}_2 = \text{NH}^t\text{Bu}$ (3; CCDC 1878693), NMe_2 (4)], as a result of the release of H_2 from both the metal center and amine-boranes. Dehydrogenation is favored by the polyhydride character of 2²¹ and by the presence of the hydrogensulfide ligand, which traps the resulting amino-borane monomer.²² The capture facilitates the complete extraction of the H atoms attached to the B atom. Complexes 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 $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)\{\text{S}=\text{B}(\text{tBu})\text{Ime}\}(\text{CO})_2$ [$\text{Ime} = 1,3\text{-dimethylimidazolyldiene}$;

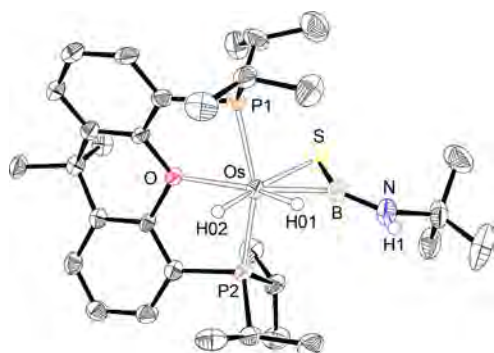


Figure 2. Molecular drawing of complex 3. H atoms (except hydrides and H1) are omitted for clarity.

1.747(3) Å²³ and in the thioxoboranes $\text{S}=\text{B}\{\kappa^2\text{-N,N-[N(2,6-Me}_2\text{C}_6\text{H}_3)\text{C(Me)CHC(Me)N(2,6-Me}_2\text{C}_6\text{H}_3)]}\}$ [1.741(2) Å²⁴ and $\text{S}=\text{B}\{\kappa^2\text{-N,N-[N(2,4,6-Me}_3\text{C}_6\text{H}_2)\text{P(Ph)}_2\text{NP(Ph)}_2\text{N-(2,4,6-Me}_3\text{C}_6\text{H}_2)]}\}$ [1.752(5) Å²⁵ and about 0.07 Å longer than that found in the cation $\text{S}=\text{B}\{\kappa^2\text{-N,N-[N(L}^{\text{Mes}}\text{)-CH}_2\text{CH}_2\text{N(L}^{\text{Mes}}\text{)]}\}^+$ [$\text{L}^{\text{Mes}} = 1,3\text{-dimesitylimidazolynilidene}$; 1.710(5) Å],²⁶ 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 reaction of the alkylborylene complex $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(=\text{B}^t\text{Bu})(\text{CO})_2$ with 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.²⁷ 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 $\text{Os}^{\text{IV}}\text{-B}$ single bond.²⁸ In fact, the $\text{OsH}_2(\text{POP})$ moiety can be described as a 16-electron valence *cis*-dihydride $\text{L}_5\text{Os}^{\text{IV}}$ 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 ^1H NMR spectra and a singlet at about 47 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. Broad resonances at 56.3 ppm for 3 and at 62.0 ppm for 4 in the ^{11}B NMR spectra are also characteristic features of these compounds.

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 of 1.40 and by the shapes of HOMO-7 and HOMO-8. They can be viewed as π molecular orbitals delocalized within the ring, also involving the lone pair of the attached N atom (Figure 3). According of the natural

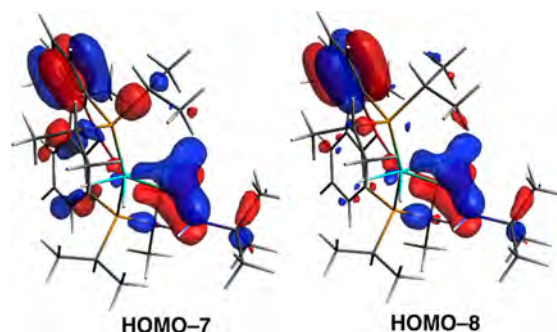


Figure 3. Computed π molecular orbitals delocalized in the Os-B-S metallacycle of 3 (isosurface value of 0.04 au).

bond order (NBO) method, the multiple bond character of the B-S bond derives from delocalization of the lone pair of the S atom into the vacant p_z atomic orbital of the B atom (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 π orbitals depicted in Figure 3.

The previously mentioned findings are consistent with a formally $4n + 2$ Hückel aromatic system in which $n = 0$ and where the two π electrons of the ring are provided by the S 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 $\text{NICS}(0) = -32.1$ ppm was found that 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.^{12a} The situation is even more dramatic if a transition metal is present in the ring.^{4c} 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.²⁹ The highly negative computed values, $\text{NICS}(1)_{zz} = -17.9$ 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)³⁰ method was applied to visualize the aromatic ring current in the metallacycle. As depicted in Figure 4, the ACID method,

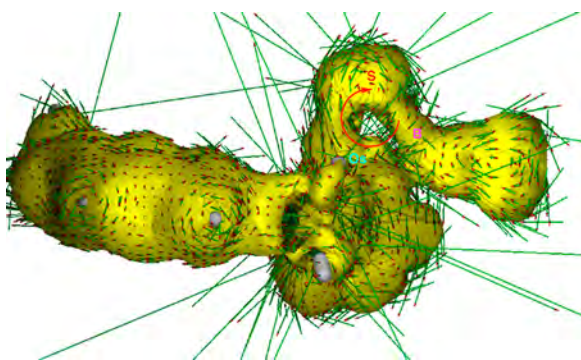


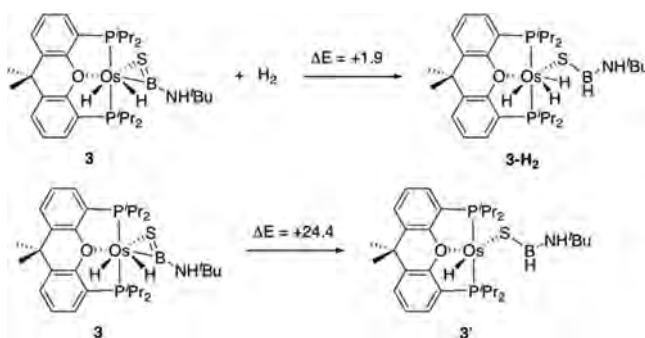
Figure 4. ACID plot for the model compound $\text{OsH}_2\{\kappa^2\text{-S,B-[SBNH}_2\}]\{\kappa^3\text{-P,O,P-[xant(PH}_2)_2\}]\}$ with a 0.04 au isosurface value.

computed for a model system where the bulky isopropyl and *tert*-butyl groups were replaced by H atoms [$\text{NICS}(1)_{zz} = -15.9$ 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.

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)^{4c} 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 reductive elimination depicted in Scheme 2. For both reactions, 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.

In conclusion, the assembly of a 16-electron valence $\text{L}_5\text{Os}^{\text{IV}}$ metal fragment, a S atom, and a B–NR₂ moiety gives rise to three-membered π -aromatic rings, which are formed by different vertexes, representing a novel manifestation of the $4n + 2$ Hückel aromaticity in which $n = 0$. These cycloosmathioborane compounds are prepared by the simultaneous dehydrogenation of a trihydride hydrogensulfide osmium(IV) complex and a BH_3NHR_2 amine–borane.

Scheme 2. Computed Isodesmic Reactions Involving Complex **3**^a



^aEnergies (in kcal/mol) were computed at the BP86-D3/def2-TZVPP level.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.8b03366.

General information, instrumental methods, preparation and characterization of **2**–**4**, NMR spectra, structural analysis of **2** and **3**, computational details, and ACID plot (PDF)

Cartesian coordinates (XYZ)

Accession Codes

CCDC 1878692–1878693 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

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

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