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# Synthesis, Characterization, and Reactivity of Metalla-chalcogenirenium Compounds

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edicated to the 10th anniversary of Southern University of Science and Technology

#### Keywords

Metalla-chalcogenirenium |DFT calculations | Metallacycles | P-block cations | Aromaticity

#### Main observation and conclusion

Chalcogenirenium cations, featuring an unsaturated three-membered organic ring, are limited but known to be synthesizable from alkynes with bulky electron-donating groups. Metalla-chalcogenirenium compounds have been synthesized as stable compounds through the reactions of a cyclic metal-carbyne complex-metallapentalyne with PhSCI, PhSeCI or PhTeCI. As a result of the high strain in the three-membered metallacycles, the metalla-chalcogenirenium cations react readily with the base or chloride ions. These reactions furnish a series of unprecedented chalcogenirenium cations with intact M=C bonds. The intrinsic stabilization effect of aromaticity is further elucidated by DFT calculations.

#### **Comprehensive Graphic Content**

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Aromaticity-driven strategy for the construction of unusual chalcogenirenium cations

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#### **Background and Originality Content**

Reactive p-block cations with weakly coordinating anions have been the focus of considerable research investigating their structure, bonding, and reactivity, especially in view of the utility of such species in catalysis.<sup>[1,2]</sup> In the case of Group VIA, most of the isolable examples, such as [S<sub>8</sub>]<sup>+</sup>,<sup>[3]</sup> [Nap(SPh)(SePh)]<sup>+</sup>,<sup>[4]</sup>  $Ph_5Te^{+}$ ,<sup>[5]</sup> and [MesTe(EPh<sub>3</sub>)]<sup>+</sup> (E = P, As, Sb)<sup>[6]</sup> depend on delocalization and other electronic or steric effects for their relatively high ionization potentials and electronegativities. Thus, t' e obviously heavier cation species, especially selenirenium and cellurirenium ions, i.e. unsaturated three-membered cationic halcogen (Ch)-containing ring, have been unstable transient intermediates. In 2008, Poleschner et al. treated disubstituted a'kynes with (MeSe)<sub>3</sub>\*SbCl<sub>6</sub><sup>-</sup> or PhTe\*SbF<sub>6</sub><sup>-</sup> to give the first lenirenium and tellurirenium cations (Scheme 1a).<sup>[7]</sup> In a similar fashion, they recently reported oxidative generation of [RS]<sup>+</sup> and e synthesis of thiirenium salts.<sup>[8,9]</sup> To date, however, synthetic studies of such chalcogenirenium cations or etalla-chalcogenirenium cations are scarce, perhaps due to the lack of suitable precursors and efficient synthetic routes. The only known examples of three-membered metalla-chalcogenirenium tions are metallathiirenium species, which were prepared by the reaction of thiocarbyne with acid or addition of [RS]<sup>+</sup> to rbyne complexes.<sup>[10]</sup> However, metallaselenirenium and metallatellurirenium ions have never been reported.

The unsaturated three-membered cationic Ch-containing ring have been assumed as important intermediates in addition reactions of chalcogenium-containing electrophiles to alkynes<sup>[11]</sup> or carbon-heteroatom coupling reactions of metal-carbynes<sup>[12]</sup>. olation of these reactive chalcogenirenium cations would help better understand the mechanism of electrophilic additions of iganochalcogen cation ([RCh]<sup>+</sup>) to alkynes or metal-carbynes, however, this seems very challenging. Our interest in new building b ocks for metallacycles<sup>[13]</sup> prompted us to examine the previously are family of metalla-chalcogenirenium cations. Inspired by metalla-aromatic chemistry,<sup>[14,15]</sup> we speculated that the nbiphilic nature of the metal-carbyne units in metallapentalynes should be susceptible to [RCh]<sup>+</sup>, and could be utilized as excellent uilding blocks that, with an electrophilic addition reaction, could produce the desired metalla-chalcogenirenium cations.

**S heme 1** Synthesis of chalcogenirenium or metalla-chalcogenirenium cations by electrophilic addition of organochalcogen cations [RCh]<sup>+</sup> to alkynes or cyclic metal-carbynes.

) Cyclic chalcogenirenium lons by reactions of alkynes



[M] =Transition metal fragments

#### **Results and Discussion**

We reacted the osmapentalyne compound  $(1)^{[16]}$  with PhChCl (Ch = S, Se, Te) at room temperature (RT). As indicated by NMR spectra, stirring a mixture of 1, PhChCl and two equivalents of NaBF<sub>4</sub> in dichloromethane for 1 h resulted in almost quantitative conversion of 1 to the complexes 2 (Scheme 2). The results

demonstrated good compatibility and efficiency of this reaction in which different chalcogen reagents can readily participate to afford the corresponding products (2a-2c). The compounds (2a-2c) were characterized by nuclear magnetic resonance (NMR) spectra and elemental analysis (EA). For 2a, the three proton signals at 14.41, 10.16, and 9.57 ppm are assigned to H1, H3, and H5, respectively. With the aid of DEPT-135 and <sup>1</sup>H-<sup>13</sup>C HSQC (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>), the <sup>13</sup>C NMR signals of 2a were assigned to 235.9 ppm (C1), 218.6 ppm (C7), 192.5 ppm (C4), 167.4 ppm (C5), 163.5 ppm (C3), 154.4 ppm (C6), and 141.8 ppm (C2). The signals of C7 and C1 are downfield from that of C4, suggesting the carbene characters of these two atoms. The <sup>31</sup>P NMR spectrum of OsPPh<sub>3</sub> displays two doublets at  $\delta$  = -8.22 ppm (d,  $J_{P-P}$  = 270.5 Hz) and -18.37 ppm (d,  $J_{P-P}$  = 270.5 Hz) because the phenyl group is bent out of the plane of the 3-membered ring. Analogous phenomena were observed in the NMR data of complexes 2b and 2c. The <sup>13</sup>C NMR signals for C7 in the newly formed three-membered ring are shifted significantly downfield due to the influence of different chalcogen cations (218.6 ppm (2a), 233.4 ppm (2b), and 239.9 ppm (2c)). The <sup>77</sup>Se NMR spectrum of 2b and <sup>125</sup>Te NMR spectrum of 2c show resonances at 39.8 ppm ( $J_{P-Se}$  = 39.5 Hz) and 1238.3 ppm (br), respectively, which are more upfield than the reported selenirenium (between –79 and –185 ppm) and tellurirenium ions (between -380 and -426 ppm).<sup>[7]</sup> This might be attributed to the interaction between selenium or tellurium atom with osmium.

**Scheme 2** Synthesis of osma-chalcogenirenium cations (2) by reactions of PhChCl with the osmapentalyne (1).



Adding ether to a concentrated solution of 2a or 2b in dichloromethane allowed for the formation of single crystals suitable for an X-ray diffraction study. As shown in Figure 1, complexes 2a and 2b are tricyclic systems with a metalla-chalcogenirenium ring fused to metallapentalene rings. The mean deviation from the least-squares plane through the nine atoms is 0.0803 Å (Os1, C1-C7, S1) for 2a, indicating that the tricyclic metallacycle units are essentially planar. The C-C bond distances of the osmapentalene rings are in the range of 1.370–1.412 Å (2a), which are comparable to those of reported metallapentalenes with electron delocalized metallacyles.<sup>[13]</sup> In the case of 2a, the C7-S1 (1.709 Å) and Os1–S1 bonds (2.631 Å) are slightly longer than those of osmathiirene (1.643 Å and 2.563 Å),<sup>[16]</sup> while the Os1-C7 bond length (1.957 Å) is shorter (2.000 Å in osmathiirene).<sup>[16]</sup> On the other hand, the C7–S1 (1.709 Å) in 2a is much shorter than the corresponding bonds in thiireniums  $([^{t}Bu_{2}C_{2}SMe]^{+}BF_{4}^{-}:$ 1.820 Å•[8b]  $[^{t}Bu_{2}C_{2}SMe]^{+}CH-B_{11}Cl_{11}^{-}$ : 1.832 Å). <sup>[7]</sup> The angle subtended at the chalcogen atom of 2a (48.1°) is obviously larger than those in the reported chalcogenirenium ions (37.6°-41.3°). [7-9] Although the systematic disorder of **2b** in the solid state does not permit a detailed discussion of bond lengths and angles, the connectivity of metalla-selenirenium is unambiguously confirmed. As a supplement to metal-carbyne chemistry,<sup>[17]</sup> the reactions of cyclic metal-carbynes 1 with PhChCl (Ch = Se, Te) expand the understanding of electrophilicity of metal-carbynes and led to the first examples of three-membered metalla-selenirenium cation and metalla-tellurirenium cation.



gure 1 X-ray molecular structures for the cations of 2a (a) and 2b (b) with 50% probability ellipsoids. Hydrogen atoms in the phenyl moieties are nitted for clarity. Selected bond lengths [Å] and angles [deg] for 2a: Os(1)-C(1) 2.016(3), Os(1)-C(4) 2.125(3), Os(1)-C(7) 1.957(3), Os(1)-S(1) 2 6306(9), C(7)-S(1) 1.709(3); Os(1)-C(1)-C(2) 123.5(2), C(7)-Os(1)-S(1) J.50(9), C(7)-S(1)-Os(1) 48.06(12), S(1)-C(7)-Os(1) 91.44(15).

Compounds 2 can be stored in the solid state at ambient temperature under air for over a week without noticeable ecomposition. The solid samples of 2a and 2b can even survive 3 hours at 60 °C in air. Its aromaticity may account for of the the stability three-membered etalla-chalcogenirenium cation (2). Nucleus-independent chemical shifts (NICS) were calculated,<sup>[18]</sup> based on the substituted model compounds 2' in which PH<sub>3</sub> groups were used to replace the PPh<sub>3</sub> ligands in **2**. In general, negative NICS values indicate aromaticity, and positive NICS values ir dicate anti-aromaticity. As shown in Figure 2a, the calculated NICS(1)<sub>zz</sub> value for the three fused metallacycles (rings A, B, and C) of 2' are all negative, revealing the omatic nature of these rings. Together with the bending of the phenyl substituents out of the planes of the nree-membered rings, we think the aromaticity of the three-membered metalla-chalcogenirenium cations 2 are cosely related to the reported metallacyclopropenes with -aromaticity.<sup>[19]</sup> The aromaticity of **2** was further confirmed by the anisotropy of the induced current density (ACID) halysis.<sup>[20]</sup> The electron delocalization within the metallacycles can be visualized by the clockwise current ensity vectors plotted on the ACID isosurface employing all  $\pi$ -molecular orbitals of model **2a'** (Figure 2b). Further calculations show that the natural bond orbital (NBO) charge at the chalcogen atom increases from S (0.510) through Se (737) to Te (1.023). These values are comparable to those ound for typical chalcogenirenium<sup>[7]</sup> and chalcogeniranium cations<sup>[21]</sup>.



**Figure 2** Aromaticity evaluation. (a) NICS(1)<sub>27</sub> values (in ppm) for the model **2'** calculated at the B3LYP/6-311++G(d,p) level. [Os]' = OsCl(PH<sub>3</sub>)<sub>2</sub>. (b) ACID isosurface of model **2a'** from all  $\pi$ -MOs contribution. Current density vectors are plotted onto the ACID isosurface of 0.030 to indicate diatropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic). (c) The isodesmic reactions resulting from breaking the Ch–Os bonds in different types of three membered fused rings. The energies, including the zero-point energy corrections, are given in kcal mol<sup>-1</sup>.

It is noteworthy that the fused metallapentalene rings in 2 play a crucial role in the remarkable stabilization of the metalla-chalcogenirenium skeleton. The stability of the three-membered metalla-chalcogenirenium cation 2 has also been studied by means of isodesmic reactions,<sup>[22]</sup> in which the types and numbers of chemical bonds in the reactants are the same as those in the products (Figure 2c). As expected, a positive value of the computed reaction energies is shown for model compound 2'. The difference between the reaction energies in two equations can be attributed to the aromaticity of the three membered ring in 2'. The loss of the support of fused metallapentalene is the origin of the endothermicity of the two equations in Figure 2c. This raises an intriguing possibility of the future synthesis of chalcogenirenium cations through aromaticity-driven strategy, which would provide promising expansion of this reactive p-block cation family.

The rich chemistry of unsaturated three-membered rings<sup>[23]</sup> promoted us to explore the reactivity of metalla-chalcogenirenium cations. The reaction at 80 °C in dichloroethane of 2a or 2b with Bu4NCl provided complexes 3a or 3b, respectively (Scheme 3). Complex 3b was determined to be a substitution product of 2b, in which one of the PPh<sub>3</sub> ligands at the osmium center was replaced by a Cl ligand (Figure 3a). Nevertheless, complex 2c rapidly underwent a decomposition reaction with Bu<sub>4</sub>NCl reverting to 1 in a stoichiometric fashion. The different outcomes of reactions of 2a/2b or 2c with chloride ion are in good agreement with the more electropositive chalcogen atoms supported by the calculated NBO charges. Moreover, 2 proved to be extremely sensitive to base. Thanks to the positive charge in these aromatic systems, the addition of 5 equivalents of pyridine to 2a or 2b at room temperature quantitatively converted each compound into a new cyclic

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carbyne species (4a or 4b) (Scheme 4) with the elimination of HBF<sub>4</sub>. In the presence of excess pyridine, 2c was converted to **1**, similar to the reaction with chloride ion. Single crystal X-ray structural analysis reveals 4 to result from the uptake of one H atom of the metallapentalene ring by base, producing a metallapentalyne ring (Figure 3b). The distance between Os and Se in 4b (3.380 Å) is much greater than those in 2b (2.752 Å) and 3b (2.705 Å), which indicates a ring-opening of the three-membered metalla-chalcogenirenium ring. The <sup>77</sup>Se NMR spectroscopy of 4b (666.7 ppm) is more downfield than t at of **3b** (461.7 ppm) due to the absence of any interactions Jetween selenium and osmium, however, both <sup>77</sup>Se resonances are more downfield than that of **2b** (39.8 ppm). milar reactions of chalcogenirenium ring with nucleophiles have been demonstated in literature.<sup>[24]</sup> Interestingly, rapid covery of the three-membered metalla-chalcogenirenium ring can be achieved by the addition of an acid, such as cess tetrafluoroboric acid, to the solution of **4a** or **4b**.

**C:heme 3** Reactions of osma-chalcogenirenium cations **2**.



Figure 3 X-ray molecular structures for the cations of **3b** (a) and **4b** (b) with % probability ellipsoids. Hydrogen atoms in the phenyl moieties are omitted for clarity. Selected bond distances (Å) and angles (deg): for **3b**: Os(1)-C(1) 2.017(6), Os(1)-C(4) 2.112(6), Os(1)-C(7) 1.936(6), Os(1)-Se(1) 2.7055(6), C(7)-Se(1) 1.875(6); Os(1)-C(1)-C(2) 122.7(4), C(7)-Os(1)-Se(1) 43.86(18), C(7)-Se(1)-Os(1) 45.68(17), Se(1)-C(7)-Os(1) 90.5(3). For **4b**: Os(1)-C(1) 1.841(5), Os(1)-C(4) 2.074(5), Os(1)-C(7) 2.082(5), C(7)-Se(1) 1.888(5); Os(1)-C(1)-C(2) 130.1(4), C(7)-Os(1)-Se(1) 116.7(3).

Above experimental and computational results indicate that the metalla-chalcogenirenium cation (2) can be represented by the resonance structures **2A-2D** (Figure 4).





Figure 4 Resonance structures for the cationic moiety of 2.

#### Conclusions

In summary, the synthesis, reactivity studies and DFT calculations of the metalla-chalcogenirenium species have been achieved. Similar to typical chalcogenirenium or chalcogeniranium cations, chalcogen atoms in these metalla-chalcogenirenium compounds are Lewis acidic and susceptible to interaction with Lewis bases. Notably, computational studies suggest the aromaticity of the three-membered metalla-chalcogenirenium rings and indicate that the fused metallapentalene rings play a substantial role in the stabilization of three-membered p-block cation frameworks, which are otherwise difficult to prepare.

#### Experimental

All reactions were carried out under an inert atmosphere (N<sub>2</sub>) using standard Schlenk techniques. Solvents were distilled from calcium hydride (dichloromethane and dichloroethane) or sodium/benzophenone (hexane and diethyl ether) under N<sub>2</sub>. The osmapentalyne 1 was synthesized as reported by the published procedure<sup>[16]</sup> and benzenetellurenyl chloride<sup>[25]</sup> was prepared in situ by the reaction of Ph2Te2 and SO2Cl2 and used immediately. Other reagents were used as purchased from commercial sources without further purification. NMR data were obtained on a Bruker AVII-400 (1H 400.1 MHz; 31P 162.0 MHz; 13C 100.6 MHz) spectrometer at room temperature. In <sup>1</sup>H and <sup>13</sup>C NMR, tetramethylsilane is used as the reference, and <sup>31</sup>P NMR chemical shifts are relative to 85% H<sub>3</sub>PO<sub>4</sub>. One-dimensional and two-dimensional NMR are abbreviated as distortionless enhancement by polarization transfer (DEPT), heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond correlation (HMBC). The coupling constants are expressed in Hertz (Hz). The abbreviations for multiplicities are singlet (s), doublet (d) and broad (br). EAs were collected on a Vario EL III elemental analyzer.

Synthesis and characterization of complex 2a: The mixture of complex 1 (286 mg, 0.24 mmol),  $NaBF_4$  (53 mg, 0.48 mmol), and PhSCI (35 mg, 0.24 mmol) in dichloromethane (10 mL) were stirred for one hour at room temperature. The reddish-yellow solution was filtered and evaporated under vacuum to a small volume. The precipitate was produced by adding diethyl ether and collected by filtration and dried under vacuum to give 2a (295 mg, 92%) as an orange solid. <sup>1</sup>H NMR plus <sup>1</sup>H-<sup>13</sup>C HSQC (400.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 14.43 (br, 1H, H1), 10.41 (s, 1H, H3), 9.71 (s, 1H, H5), 3.66 (s, 3H, COOCH<sub>3</sub>), 7.96–6.94 ppm (m, 50H, Ph). <sup>31</sup>P NMR (162.0 MHz,  $CD_2Cl_2$ ):  $\delta$  = 13.61 (s,  $CPPh_3$ ), -8.22 (d,  $J_{P-P}$  = 270.5 Hz, OsPPh<sub>3</sub>), -18.37 ppm (d, J<sub>P-P</sub> = 270.5 Hz, OsPPh<sub>3</sub>). <sup>13</sup>C NMR plus DEPT-135 and  ${}^{1}\text{H}{}^{-13}\text{C}$  HSQC (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 235.9 (br, C1), 218.6 (br, C7), 192.5 (d, J<sub>P-C</sub> = 20.1 Hz, C4), 167.4 (s, C5), 163.5 (br, C3), 158.4 (s, COOCH<sub>3</sub>, confirmed by <sup>1</sup>H-<sup>13</sup>C HMBC), 154.4 (s, C6), 141.8 (d, J<sub>P-C</sub> = 81.6 Hz, C2), 52.6 (s, COOCH<sub>3</sub>), 137.3–127.6 ppm (m, Ph). Anal. Calcd (%) for C<sub>69</sub>H<sub>56</sub>B<sub>2</sub>ClF<sub>8</sub>O<sub>2</sub>OsP<sub>3</sub>S<sup>:</sup> C 57.49, H 3.92;

Found: C 57.67, H 4.28.

Synthesis and characterization of complex 2b: The mixture of complex 1 (286 mg, 0.24 mmol), NaBF<sub>4</sub> (53 mg, 0.48 mmol), and PhSeCl (46 mg, 0.24 mmol) in dichloromethane (10 mL) were stirred for one hour at room temperature. The reddish-yellow solution was filtered and evaporated under vacuum to a small volume. The orange precipitate was produced by adding diethyl ether and collected by filtration and dried under vacuum to give 2b (298 mg, 90%) as an orange solid. <sup>1</sup>H NMR plus <sup>1</sup>H-<sup>13</sup>C HSQC  $(400.1 \text{ MHz}, \text{CD}_2\text{Cl}_2)$ :  $\delta = 14.51$  (br, 1H, H1), 10.22 (s, 1H, H3), 9.68 ( 1H, H5), 3.75 (s, 3H, COOCH<sub>3</sub>), 8.00–7.02 ppm (m, 50H, Ph). <sup>31</sup>P NMR (162.0 MHz, CDCl<sub>3</sub>):  $\delta$  = 13.26 (s, CPPh<sub>3</sub>), -10.05 (d, J<sub>P-P</sub> = 213.8 Hz, OsPPh<sub>3</sub>), -21.09 ppm (d, J<sub>P-P</sub> = 213.8 Hz, OsPPh<sub>3</sub>). <sup>13</sup>C wMR plus DEPT-135 and  $^{1}H^{-13}C$  HSQC (100.6 MHz, CDCl<sub>3</sub>):  $\delta$  = 236.6 (br, C1), 233.4 (br, C7), 191.2 (d, *J*<sub>P-C</sub> = 20.1 Hz, C4), 168.6 (s, (), 165.0 (br, C3), 159.1 (s, COOCH<sub>3</sub>, confirmed by <sup>1</sup>H-<sup>13</sup>C HMBC), 156.8 (s, C6), 142.3 (d, J<sub>P-C</sub> = 79.2 Hz, C2), 53.2 (s, COOCH<sub>3</sub>), 136.8-127.6 ppm (m, Ph). <sup>77</sup>Se NMR (76.3 MHz, (CD<sub>2</sub>Cl<sub>2</sub>)) δ = 39.8 (d, J<sub>PSe</sub> = 39.5 Hz). Anal. Calcd (%) for C<sub>69</sub>H<sub>56</sub>B<sub>2</sub>ClF<sub>8</sub>O<sub>2</sub>OsP<sub>3</sub>Se: C 55.68, H <sup>2</sup> 79; Found: C 55.93, H 4.12.

Synthesis and characterization of complex 2c: To a stirred solution of bisphenyl ditelluride (49.1 mg, 0.12 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (<sup>r</sup>.0 mL) was added SO<sub>2</sub>Cl<sub>2</sub> (18.9 mg, 0.14 mmol) at r.t. to prepare benzenetellurenyl chloride in situ. After the color of the reaction rixture turned orange to dark red (ca. 1 h), the solution was added into complex 1 (286 mg, 0.24 mmol) and NaBF<sub>4</sub> (53 mg, 0.48 mmol) in dichloromethane (10 mL) and the mixture was stirred for one hour at room temperature. The solution was filtered and evaporated under vacuum dried under vacuum to give 2c (326 mg, 95%) as an orange solid. <sup>1</sup>H NMR plus <sup>1</sup>H-<sup>13</sup>C  $^{\text{L}}$ SQC (400.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 14.51 (br, 1H, H1), 9.83 (s, 1H, H3), 9 55 (s, 1H, H5), 3.73 (s, 3H, COOCH<sub>3</sub>), 8.43–6.91 ppm (m, 50H, Ph). <sup>2</sup> P NMR (162.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 13.57 (s, CPPh<sub>3</sub>), -14.00 (d, J<sub>P-P</sub> = 260.8 Hz, OsPPh<sub>3</sub>), –25.59 ppm (d, J<sub>P-P</sub> = 260.8 Hz, OsPPh<sub>3</sub>). <sup>13</sup>C NMR plus DEPT-135 and  $^{1}H^{-13}C$  HSQC (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = +6.9 (br, C1), 239.9 (br, C7), 189.0 (d, J<sub>P-C</sub> = 20.1 Hz, C4), 168.0 (s, C5), 162.1 (d, J<sub>P-C</sub> = 16.9 Hz, C3), 159.8 (s, COOCH<sub>3</sub>, confirmed by <sup>11</sup>I-<sup>13</sup>C HMBC), 151.7 (s, C6), 114.6 (d, J<sub>P-C</sub> = 79.2 Hz, C2), 53.9 (s, COOCH3), 138.3-116.5 ppm (m, Ph). 125Te NMR (126.2 MHz,  $(CD_2Cl_2))$   $\delta$  = 1238.3 (br). Anal. Calcd (%) for C<sub>19</sub>H<sub>56</sub>B<sub>2</sub>ClF<sub>8</sub>O<sub>2</sub>OsP<sub>3</sub>Te: C 53.92, H 3.67; Found: C 53.67 H 3.53.

nthesis and characterization of complex 3a: The complex 2a (268 mg, 0.20 mmol) and Bu<sub>4</sub>NCl (55.6 mg, 0.20 mmol) in d chloroethane was stirred for 4 hours at 80 °C. The solution was itered and evaporated under vacuum to a small volume. The brown precipitate was produced by adding diethyl ether and c llected by filtration, washed with diethyl ether and dried under acuum to give **3a** (150 mg, 70%) as a brown solid. <sup>1</sup>H NMR plus <sup>1</sup>H-<sup>13</sup>C HSQC (400.1 MHz, CDCl<sub>3</sub>): δ = 14.18 (br, 1H, H1), 9.88 (s, 1H, H3), 9.77 (s, 1H, H5), 3.82 (s, 3H, COOCH<sub>3</sub>), 8.26–6.98 ppm (m, 50H, Ph).<sup>31</sup>P NMR (162.0 MHz, CDCl<sub>3</sub>):  $\delta$  = 15.28 (s, CPPh<sub>3</sub>), -14.52 (s, OsPPh<sub>3</sub>) <sup>13</sup>C NMR plus DEPT-135 and <sup>1</sup>H-<sup>13</sup>C HSQC (100.6 MHz,  $Cl_3$ :  $\delta = 236.7$  (br, C1), 217.2 (d,  $J_{P-C} = 9.5$  Hz C7), 193.3 (d,  $J_{P-C} =$ 20.8 Hz, C4), 165.6 (s, C5), 163.7 (d, J<sub>P-C</sub> = 18.8 Hz, C3), 159.9 (s, COOCH<sub>3</sub>, confirmed by <sup>1</sup>H-<sup>13</sup>C HMBC), 155.4 (s, C6), 142.3 (d,  $J_{P-C}$  = 82.8 Hz, C2), 53.0 (s, COOCH<sub>3</sub>), 135.7–126.4 ppm (m, Ph). Anal. Calcd (%) for C<sub>51</sub>H<sub>41</sub>BCl<sub>2</sub>F<sub>4</sub>O<sub>2</sub>OsP<sub>2</sub>S<sub>:</sub> C 54.31, H 3.66; Found: C 54.54, H 4.04.

Synthesis and characterization of complex 3b: The complex 2b (277 mg, 0.20 mmol) and Bu<sub>4</sub>NCl (55.6 mg, 0.20 mmol) in dichloroethane was stirred for 4 hours at 80 °C to give solution. The solution was filtered and evaporated under vacuum to a small volume. The brown precipitate was produced by adding diethyl ether and collected by filtration, washed with diethyl ether and dried under vacuum to give 3b (191 mg, 85%) as a brown solid. <sup>1</sup>H NMR plus <sup>1</sup>H-<sup>13</sup>C HSQC (400.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 14.09 (d, *J*<sub>P-H</sub> = 12.3 Hz, 1H, H1), 9.72 (s, 1H, H5), 9.51 (s,1H, H3), 3.88 (s, 3H, COOCH<sub>3</sub>), 7.80–7.22 ppm (m, 35H, Ph). <sup>31</sup>P NMR (162.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 13.28 (s, CPPh<sub>3</sub>), -17.44 ppm (s, OsPPh<sub>3</sub>). <sup>13</sup>C NMR plus DEPT-135 and <sup>1</sup>H-<sup>13</sup>C HSQC (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 237.1 (br, C1), 232.2 (d,  $J_{P,C}$  = 8.63 Hz, C7), 191.4 (d,  $J_{P,C}$  = 20.3 Hz, C4), 162.6 (s, C5), 160.0 (s, COOCH<sub>3</sub>, confirmed by <sup>1</sup>H-<sup>13</sup>C HMBC), 157.2 (d,  $J_{P,C}$  = 19.6 Hz, C3), 156.2 (s, C6), 141.0 (d,  $J_{P,C}$  = 79.5 Hz, C2), 53.9 (s, COOCH<sub>3</sub>), 136.1–128.6 ppm (m, Ph). <sup>77</sup>Se NMR (76.3 MHz, (CD<sub>2</sub>Cl<sub>2</sub>)) δ = 461.7 (s). Anal. Calcd (%) for C<sub>51</sub>H<sub>41</sub>BCl<sub>2</sub>F<sub>4</sub>O<sub>2</sub>OSP<sub>2</sub>Se: C 52.14, H 3.52; Found: C 52.38, H 3.95.

Synthesis and characterization of complex 4a: Pyridine (16 µL, 1.00 mmol) was added to dichloromethane solution complex 2a (268 mg, 0.20 mmol). The mixture was stirred for 5 min at room temperature. The reddish solution was evaporated under vacuum to a small volume. The red precipitate was produced by adding diethyl ether and collected by filtration, washed with diethyl ether and dried under vacuum to give 4a (247 mg, 95%) as a red solid. <sup>1</sup>H NMR plus <sup>1</sup>H-<sup>13</sup>C HSQC (400.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 8.65 (s, 1H, H5), 7.44 (m, included in Phenyl groups, 1H, H3), 2.92 (s, 3H, COOCH<sub>3</sub>), 7.77–6.29 ppm (m, 50H, Ph). <sup>31</sup>P NMR (162.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 5.01 (t,  $J_{P-P} = 5.0 \text{ Hz}$ , CPPh<sub>3</sub>), -0.77 ppm (d,  $J_{P-P} = 3.9 \text{ Hz}$ , OsPPh<sub>3</sub>). <sup>13</sup>C NMR plus DEPT-135 and <sup>1</sup>H-<sup>13</sup>C HSQC (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 322.4 (br, C1), 231.7 (t, J<sub>P-C</sub> = 8.17 Hz, C7), 176.8 (d, J<sub>P-C</sub> = 22.9 Hz, C4), 165.5 (s, COOCH<sub>3</sub>, confirmed by <sup>1</sup>H-<sup>13</sup>C HMBC), 156.7 (s, C5), 152.9 (s, C6), 151.3 (d, J<sub>P-C</sub> = 14.9 Hz, C3), 120.5 (d, J<sub>P-C</sub> = 91.1 Hz, C2), 51.5 (s, COOCH<sub>3</sub>), 135.5-127.9 ppm (m, Ph). Anal. Calcd (%) for C<sub>69</sub>H<sub>55</sub>BClF<sub>4</sub>O<sub>2</sub>OsP<sub>3</sub>S<sub>2</sub> C 61.22, H 4.10; Found: C 60.77, H 4.07.

Synthesis and characterization of complex 4b: Pyridine (16 µL, 1.00 mmol) was added to dichloromethane solution complex 2b (277 mg, 0.20 mmol) (268 mg, 0.20 mmol). The mixture was stirred for 5 min at room temperature to give a reddish solution. The solution was evaporated under vacuum to a small volume. The red precipitate was produced by adding diethyl ether and collected by filtration, washed with diethyl ether and dried under vacuum to give 4b (256 mg, 95%) as a red solid. <sup>1</sup>H NMR plus <sup>1</sup>H-<sup>13</sup>C HSQC (400.1 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 8.62 (s, 1H, H5), 7.33 (m, included in Phenyl groups, 1H, H3), 2.97 (s, 3H, COOCH<sub>3</sub>), 7.79-6.54 ppm (m, 50H, Ph). <sup>31</sup>P NMR (162.0 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = 5.06 (t, J<sub>P-P</sub> = 5.4 Hz, CPPh<sub>3</sub>), -2.53 ppm (d, J<sub>P-P</sub> = 4.8 Hz, OsPPh<sub>3</sub>). <sup>13</sup>C NMR plus DEPT-135 and  $^{1}H^{-13}C$  HSQC (100.6 MHz, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 322.1 (br, C1), 236.4 (t, J<sub>P-C</sub> = 9.1 Hz, C7), 179.1 (d, J<sub>P-C</sub> = 22.8 Hz, C4), 165.7 (s, COOCH<sub>3</sub>, confirmed by <sup>1</sup>H-<sup>13</sup>C HMBC), 157.0 (s, C6), 154.5 (s, C5), 152.1 (d, J<sub>P-C</sub> = 16.3 Hz, C3), 120.2 (d, J<sub>P-C</sub> = 89.6 Hz, C2), 51.6 (s, COOCH<sub>3</sub>), 135.6–127.9 ppm (m, Ph). <sup>77</sup>Se NMR (76.3 MHz, (CD<sub>2</sub>Cl<sub>2</sub>))  $\delta$  = 666.7 (s). Anal. Calcd (%) for C<sub>69</sub>H<sub>55</sub>BClF<sub>4</sub>O<sub>2</sub>OsP<sub>3</sub>Se: C 59.17, H 3.96; Found: C 59.12, H 4.08.

**Conversion of complex 4a to complex 2a:** Complex **4a** (13.1 mg, 0.01 mmol) reacted with HBF<sub>4</sub>·Et<sub>2</sub>O (6  $\mu$ L, 0.012 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) for 5 min at room temperature in an NMR tube, complex **4a** transformed into complex **2a** in 100% NMR yield.

Conversion of complex 4b to complex 2b: Complex 4b (13.5 mg, 0.01 mmol) reacted with HBF<sub>4</sub>·Et<sub>2</sub>O (6 ul, 0.012 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) for 5 min at room temperature in an NMR tube, complex 4b transformed into complex 2b in 100% NMR yield.

**Conversion of complex 2c to complex 1:** To solution of complex **2c** (286 mg, 0.20 mmol) in dichloromethane (0.2 mL), a solution of pyridine (16  $\mu$ L, 1.00 mmol) was added. The reaction mixture was stirred for 5 min at room temperature The solution was evaporated under vacuum to a volume of approximately 2 mL, then diethyl ether (20 mL) was added to the solution. The red precipitate was collected by filtration, washed with diethyl ether (2 × 5 mL) and dried under vacuum to give **1** (230 mg, 96%).

**Crystallographic Analysis**. Crystals suitable for x-ray diffraction were grown from dichloromethane solution layered with hexane. Single crystal X-ray diffraction data were collected on an Oxford Gemini S Ultra CCD Area Detector with graphite-monochromated Mo<sub>Ka</sub> radiation ( $\lambda = 0.71073$  Å). All of the data were corrected for absorption effects by using the multiscan technique. With

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Olex2,<sup>[26]</sup> the structure was solved using the ShelXT<sup>[27]</sup> structure solution program and refined with the ShelXL<sup>[28]</sup> refinement package using least-squares minimisation. All of the non-hydrogen atoms were refined anisotropically unless otherwise stated. The hydrogen atoms were placed at their idealized positions and assumed the riding model unless otherwise stated. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at idealized positions and assumed the riding model. X-ray crystal structures have been deposited in the Cambridge Crystallographic Database under the deposition n imbers CCDC 1916574 (2a), CCDC 1983245 (2b), CCDC 1916575 (**3b**), and CCDC 1916576 (**4b**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

**Computational details.** All the calculations were performed the Gaussian 09 software package.<sup>[29]</sup> The structures **2a-2c** were optimized by M06L/6-31G\*, and then the natural bond ortical (NBO) analysis were performed at the M06L/6-311G\*\* level. The structures **2a', 2b', 2c'** were optimized by B3LYP/6-31G\*, and then the NICS and ACID calculations were performed at the B3LYP/6-311++G\*\* level.<sup>[30]</sup> The structures of **1-Ch, 2-Ch, 3-Ch, 4-Ch, 5-Ch** were optimized by wB97XD/6-31+G\*\*. The effective core potentials (ECPs) of Hay and Wadt with a double- $\zeta$  valence basis set (SDD for M06L, and LanL2DZ for B3LYP) were used to d scribe Os, P, Cl, S, Se, and Te atom, whereas the standard o-31G\*, 6-311G\*\* or 6-311++G\*\* basis set was used for C, O, and H.<sup>[31]</sup> Polarization functions were added for Os ( $\zeta$ (f) = 0.886), P( $\zeta$ (d) = 0.340), Cl ( $\zeta$ (d) = 0.514), S ( $\zeta$ (d) = 0.421), Se ( $\zeta$ (d) = 0.0.338) and Te ( $\zeta$ (d) = 0.237).<sup>[32]</sup>

#### Supporting Information

The supporting information for this article is available on the V WW under https://doi.org/10.1002/cjoc.2021xxxxx.

#### A cknowledgement

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