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σ-Aromaticity

Rational Design and Synthesis of Unsaturated Se-Containing Osmacycles with σ-Aromaticity

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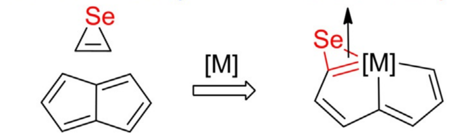
Abstract: Isolation of the simplest 4π three-membered heterocycles (1H-azirine, oxirene, thiirene, and selenirene) remains a big challenge due to their π-antiaromaticity and significant ring strain. Here we demonstrate that the incorporation of a transition-metal fragment could stabilize the antiaromatic selenirene and pentalene frameworks simultaneously by density functional theory (DFT) calculations. Experimental verification leads to the Se-containing metallapolycycles, osmapentaloselenirenes, with remarkable thermal stability. The osmaselenirene unit in the metallapolycycle is determined to be the first example of σ-aromaticity dominating in an unsaturated Se-containing ring. Our results not only highlight a remarkable stabilization by the transition-metal but also widen the scope of σ-aromaticity in unsaturated rings, which is traditionally reserved for the domain of π-aromaticity.

Introduction

Synthesis and characterization of the simplest 4π three-membered heterocycles (1H-azirine, oxirene, thiirene, and selenirene) has attracted much attention from both experimental and theoretical scientists[1] because of large ring strain and low thermodynamic stability. Only a few derivatives of them have been observed by infrared spectroscopy under matrix isolation[1b,e,2] or ultrafast time-resolved laser spectroscopy techniques at room temperature.[3] Meanwhile, numerous theoretical investigations[1a,c,f,h,4] have been carried out to examine their equilibrium structures and prove high reactivity arising from $4n$ π-antiaromaticity.[1d,5] Therefore, finding ways to reduce inherent antiaromatic property and obtain stable heterocyclic derivatives becomes a great challenge.

The introduction of a metal fragment is an efficient strategy to stabilize antiaromatics. Two recent outstanding examples are metallapentalene[6] and metallapentalyne,[7] switching the antiaromatic frameworks (pentalene and pentalyne) to the stable aromatic ones. However, the simultaneous stabilization of two antiaromatic systems by one metal fragment has been rarely reported.[8] The only example was the stabilization of cyclobutadiene (CBD) and pentalene at the same time by introducing an osmium fragment.[8a] Different from the 4-center 4-electron π-conjugation of CBD, selenirene is a heteroatom-containing 4π antiaromatic with a three-membered ring framework. It is interesting to test whether selenirene and pentalene could be stabilized by the osmium fragment simultaneously, thus leading to the related stable osmapentaloselenirenes, a fairly new type of heteroatom-containing metallapolycycle (Scheme 1).

Metallapolycycles containing main group heteroatoms are essential to the understanding of aromaticity.[9] Traditionally, mobile π-electrons in closed circuits of unsaturated compounds result in π-aromaticity,[10] whereas σ-electron delocalization in saturated rings leads to σ-aromaticity.[11] σ-Aromaticity has attracted wide interests since it was initially proposed in 1979, intending to explain the small strain of cyclopropane.[12]



Scheme 1. Stabilization of two π-antiaromatic frameworks (selenirene and pentalene) with one metal fragment ([M] = metal and its ligands) leads to a complex with σ-aromaticity dominating in an unsaturated Se-containing ring.

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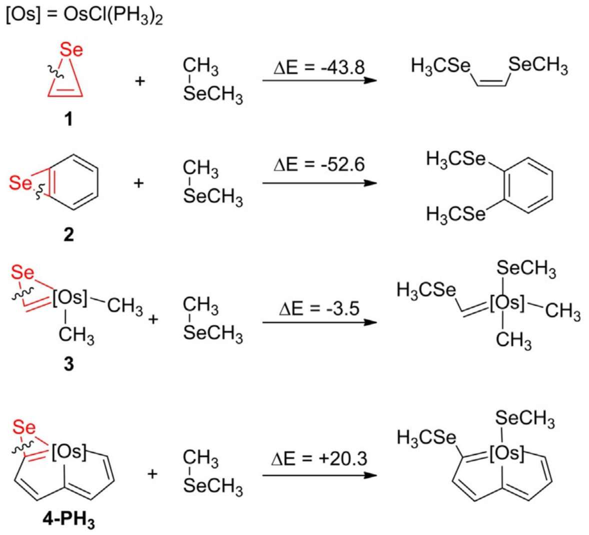
Although this concept is controversial in cyclopropane,[12c] it has been extended to many other σ-electron delocalization systems, including hydrogen[13] or main group atom clusters,[14] metal-hydride clusters,[15] metal-carbonyl clusters,[16] all-metal molecules,[17] and so on. Recently, σ-aromaticity has been determined to be dominant in unsaturated rings.[18] However, such examples were very rare and all of the reported examples were limited to the osmacyclopropene units.[18a,c,d] Here, we report a combined theoretical and experimental study on the design and synthesis of osmapentaloselenirenes, demonstrating the first example of σ-aromaticity dominating in an unsaturated Se-containing ring.

Results and Discussion

Density functional theory (DFT) calculations

To probe a possible stabilization of the metal fragment, we performed DFT calculations on the osmapentaloselenirene **4-PH$_3$**. Specially, the optimized bond length of Os–Se is 2.699 Å, which is within the range of Os–Se single bond (2.266–2.726 Å).[19] Further calculations show that its Wiberg bond index and Mayer bond order are 0.49 and 0.57, respectively, which are within the range of W–X (X = F, Cl, Br, O) single bond orders (0.48–0.97) in tungsten carbene and carbyne complexes,[20] and are comparable to those found for typical Os–C single bonds (0.55–0.62) in metallacyclopropene units as well,[18a,c,d] indicating a reduced single bond of Os–Se in complex **4-PH$_3$**. The stability of the selenirene ring can be studied by means of isodesmic reactions,[21] whereby the types and numbers of chemical bonds in the reactants are the same as those in the products (Scheme 2). A negative value by computing the reaction energies is expected when the ring strain is released in the following four equations. Astonishingly, the computed reaction energy (+20.3 kcal mol^{-1}) for **4-PH$_3$** (the fourth equation) becomes positive when an osmapentalene fragment is introduced, whereas the fusing of a benzene ring to selenirene makes it even less stable (the second equation, −52.6 kcal mol^{-1}) in comparison with the first equation. This could be explained by the enhanced ring strain (the Se-C-C angles in **1** and **2** are 71.3° and 69.7°, respectively). Comparing the third equation with the fourth one suggests that the metallapentalene ring in **4-PH$_3$** plays an important role in the achievement of higher stabilization in the unsaturated three-membered ring (3MR). Since the ring strain must be released in these isodesmic reactions, the endothermicity of the last equation demonstrates that the introduction of osmapentalene fragment results in enhanced stability in **4-PH$_3$**. Since σ-aromaticity can be dominant in the osmacyclopropene unit of osmapentalene derivatives,[18a] could it exist in the Se-containing analogue to overwhelm the ring strain?

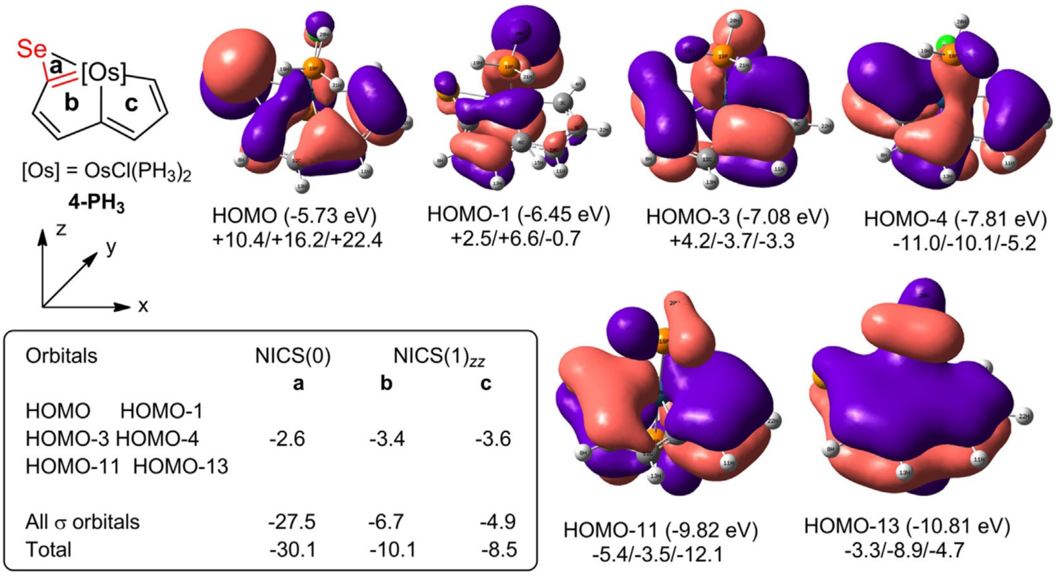


Scheme 2. The isodesmic reactions by breaking the Se–C bonds in different types of 3MRs. The energies, including the zero-point energy corrections, are given in kcal mol^{-1}.

To examine the hypothesis of the aromaticity in the 3MR, we performed canonical molecular-orbital (CMO) nucleus-independent chemical shift (NICS)[22] calculations on model complex **4-PH$_3$**. In general, negative values indicate aromaticity and positive values antiaromaticity. The dissected NICS(0) and NICS(1)$_{zz}$ are chosen to gain an insight into the nature of the possible σ-aromaticity in the 3MR and π-aromaticity in the two five-membered rings (5MRs) (Figure 1 and Figure S1). The total diamagnetic contributions from the six key occupied π MOs (HOMO, HOMO−1, HOMO−3 HOMO−4, HOMO−11 and HOMO−13) for the NICS(0) of 3MR are −2.6 ppm, whereas all the σ orbitals contribution to NICS(0) of 3MR in **4-PH$_3$** is −27.5 ppm, thus indicating σ-aromaticity in the 3MR (Figure S2). However, both the σ and π contributions to the 5MRs are particularly small, suggesting reduced aromaticity or nonaromaticity according to the NICS(1)$_{zz}$ values.

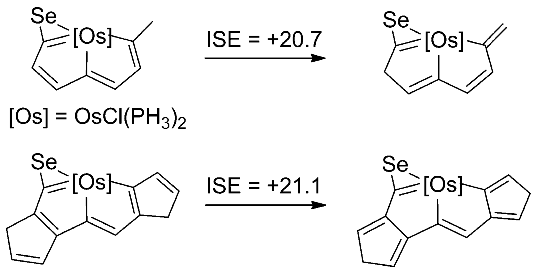
To examine the stabilization of the metal fragment on the fused 5MRs, we further investigated the aromaticity of the fused 5MRs. Two strain-balanced "isomerization stabilization energy" (ISE) methods[23] were used to probe the magnitude of total π aromatic character. As shown in Scheme 3, the calculated positive values, +20.7 and +21.1 kcal mol^{-1}, are close to each other, indicating the reliability of the ISE methods and confirming the stabilizing effect of the metal center. Note that these two values are less than that of the cyclopropaosmapentalene (+27.8 kcal mol^{-1}),[18a] indicating the reduced aromaticity in the fused 5MRs. The reducing of the aromaticity is also essentially supported by the NICS(1)$_{zz}$ values of rings **b** and **c** (−10.1 and −8.5 ppm in Figure 1, respectively), which are approximately half of those for cyclopropaosmapentalene (left and right: −19.1 and −19.7 ppm).[18a]

The reduced NICS and ISE values indicate that appending the strained 3MR could perturb π-electron delocalization in the fused 5MRs and weaken their π aromaticity sharply. It could be ascribed to the interaction of perpendicular p$_z$ lone pair of the Se atom with the conjugated π-electrons in 5MRs, resulting in partial 4*n* π-antiaromatic character. To test the hypothesis, we employed electron-localization function (ELF)[24] analysis. ELF is a powerful method to localize electrons-concentrated regions in the molecular space where significant bonds and lone pairs can be identified. As shown in Figure 2, the perpendicular



Orbitals	NICS(0)	NICS(1)$_{zz}$	
	a	b	c
HOMO HOMO-1 HOMO-3 HOMO-4 HOMO-11 HOMO-13	-2.6	-3.4	-3.6
All σ orbitals	-27.5	-6.7	-4.9
Total	-30.1	-10.1	-8.5

Figure 1. NICS (in ppm) contributions of the six key occupied MOs of osmapentaloselenirene **4-PH$_3$**. The eigenvalues of the MOs are given in parentheses.



Scheme 3. ISE evaluations of the osmapentaloselenirene **4-PH$_3$**. The energies, including the zero-point energy corrections, are given in kcal mol^{-1}.

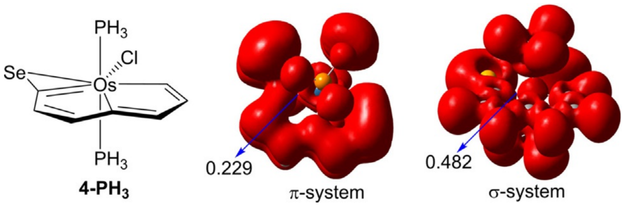


Figure 2. ELF basins separated into the σ and π system with bifurcation values of 0.482 and 0.229 for the Os=C bond, respectively.

basin population on the Se atom in π system is significant, confirming its participation.

The σ-aromaticity in the unsaturated 3MR is further supported by the anisotropy of the induced current density (ACID)[25] analysis. In general, aromatic species exhibit clockwise diatropic circulations, whereas antiaromatics have anticlockwise paratropic circulations. As shown in Figure 3, the diatropic ring currents in the 3MR of **4-PH$_3$** appear in the σ-system (Figure 3 and Figure S3), confirming the σ-aromaticity in the 3MR.

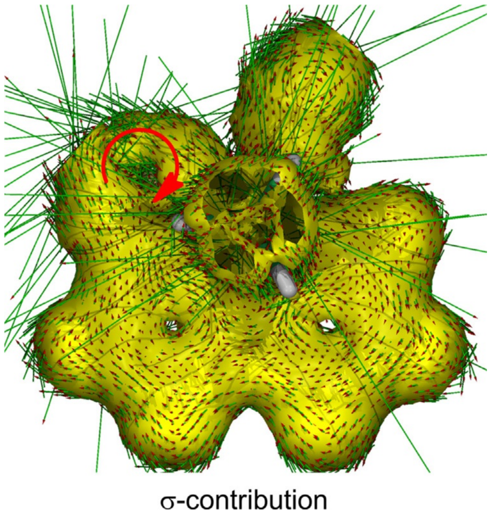
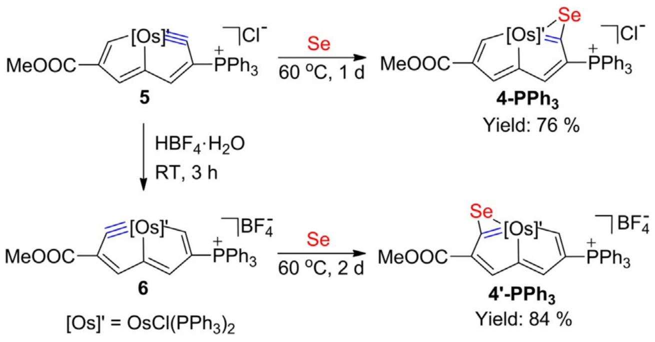


Figure 3. ACID plot of **4-PH$_3$** from σ contribution with an isosurface value of 0.014. The magnetic field vector is orthogonal with respect to the ring plane and points upward (aromatic species exhibit clockwise diatropic circulations).

Synthesis and structural characterization

Motivated by the theoretical results, we tried to synthesize an osmapentaloselenirene. Based on earlier reports that the nucleophilic carbyne carbon of Os(≡CR)Cl(CO)(PPh$_3$)$_2$ (R = *p*-tolyl) can be attacked by the electrophile selenium[26] and osmapentalynes are also reactive toward electrophiles such as acids, ICl, and Br$_2$, leading to the corresponding osmapentalenes,[6,7,27] we reasoned that osmapentaloselenirenes might be prepared by the reaction of osmapentalynes with selenium. As expected, by treating osmapentalyne **5**[7] with element selenium at 60 °C, osmapentaloselenirene **4-PPh$_3$** could be facilely obtained in an isolated yield of 76 % (Scheme 4). Osmapentalyne **6**, which was generated by treatment of **5** with HBF$_4$·H$_2$O through a rare tau-



Scheme 4. Synthesis of osmapentaloselenirenes **4-PPh$_3$** and **4′-PPh$_3$**.

tomeric shift of the Os≡C bond to the other five-membered ring,[7] was also reactive toward selenium, leading to the formation of osmapentaloselenirene **4′-PPh$_3$** in 84% yield. Notably, the two Se-containing metallacycles could be regarded as consequences of this particularly rare tautomeric triple bond shift.

Both the solution and solid states of complexes **4-PPh$_3$** and **4′-PPh$_3$** exhibit remarkable stability toward air, water, and heat. Particularly, the solid state of **4′-PPh$_3$** is even persistent at 150 °C in air or at 200 °C in nitrogen for 3 h. The thermal gravity analysis shows a weight loss over 250 °C (Figure S16), further confirming the thermal stability. The origin of the outstanding stabilities could be mainly attributed to the σ-aromaticity in 3MR, which also confirms the stabilization of the osmium fragment.

Both **4-PPh$_3$** and **4′-PPh$_3$** are characterized by nuclear magnetic resonance (NMR) spectroscopy, high-resolution mass spectrometry (HRMS), and elemental analysis. The structure of complex **4′-PPh$_3$** is further determined by single-crystal X-ray diffraction analysis. As shown in Figure 4, nine atoms (Os1, C1⋯C7, and Se1) construct the metallacycle of complex **4′-PPh$_3$**, which is coplanar with a mean deviation from the least-squares plane of 0.0226 Å. The sums of the internal angles of the two fused 5MRs and 3MR are 539.9°, 540.0° and 180.0°, which are close to the ideal values of 540° and 180°, respectively. The bond lengths (Os1–C1 2.015(5) Å; Os1–C4 2.105(5) Å; Os1–C7 1.986(5) Å), compare well with those in osmapentalene (1.926–2.139 Å).[6] In addition, the Os1–C7 and Os1–C1 bond lengths are shorter than that of Os1–C4, revealing distinct differences between the Os1–C1, Os1–C7 with Os1–C4 and the double-bond characters of Os1–C1 and Os1–C7. The C–C bond lengths (1.369–1.413 Å) in the fused 5MRs are between those of single and double C–C bonds, demonstrating the osmapentalene nature of the fused 5MRs. The bond distance of C7–Se1 is 1.791(5) Å, the Os1–Se1 bond length is 2.6843(6) Å, which is in the range of reported Os–Se single bond (2.266–2.726 Å),[19] supporting the osmaselenirene nature of the three-membered ring.

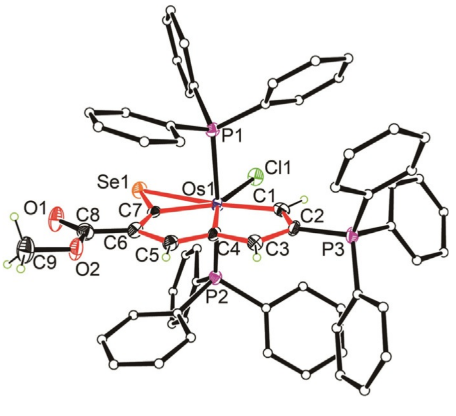


Figure 4. X-ray molecular structure of the cation of **4′-PPh$_3$** drawn with 50% probability. The hydrogen atoms of PPh$_3$ are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C1 2.015(5), Os1–C4 2.105(5), Os1–C7 1.986(5), Os1–Se1 2.6843(6), C1–C2 1.380(6), C2–C3 1.413(7), C3–C4 1.369(7), C4–C5 1.395(7), C5–C6 1.374(7), C6–C7 1.399(7), C7–Se1 1.791(5); Os1-C1-C2 122.2(4), C1-C2-C3 112.0(4), C2-C3-C4 113.5(4), C3-C4-Os1 118.4(4), C4-Os1-C1 73.83(19), Os1-C4-C5 119.5(3), C4-C5-C6 113.7(5), C5-C6-C7 108.8(5), C6-C7-Os1 126.8(4), C7-Os1-C4 71.24(19), Os1-Se1-C7 47.72(16), C7-Os1-Se1 41.86(14), Os1-C7-Se1 90.4(2).

The NMR spectroscopic analysis of complex **4′-PPh$_3$** is consistent with the X-ray structure. In agreement with the trend of bond lengths, the signals of C7 and C1 (252.98 and 241.79 ppm) are more downfield than that of C4 (183.28 ppm), revealing distinct differences between C7, C1 and C4 and the carbene characters of C7 and C1. In short, resonance structures **A** and **B** should be dominant in Scheme S1 according to the crystal and NMR data. In order to examine the effect of substituents on σ-aromaticity of 3MR in **4-PH$_3$**, CMO-NICS and ACID calculations were carried out to probe the σ-aromaticity of model complexes **4-PH$_3$-right** and **4′-PH$_3$-left**, in which PH$_3$ was used to replace the PPh$_3$ in **4-PPh$_3$** and **4′-PPh$_3$** (Figure S4–S6). The results indicate that the substituent effect is very small and the nature of σ-aromaticity is held in both **4-PH$_3$-right** and **4′-PH$_3$-left**.

Ultraviolet-visible (UV/Vis) absorption spectra

The UV/Vis absorption spectrum of complexes **4-PPh$_3$** and **4′-PPh$_3$** are examined (Figure 5). They exhibit broad band spectral absorption ranging from the ultraviolet to the visible region. In particular, the absorption maximum of **4′-PPh$_3$** in low energy

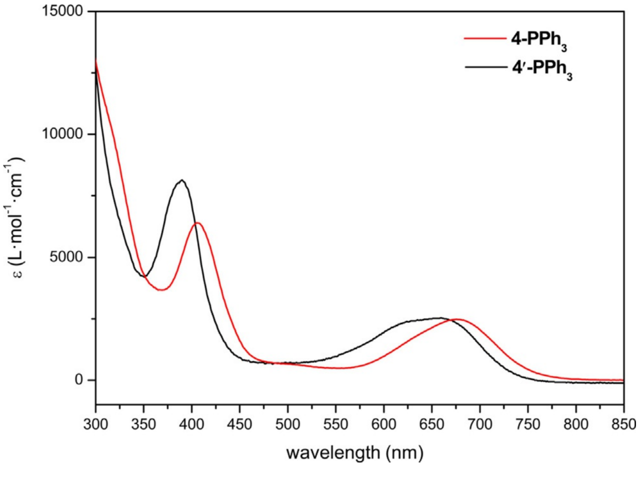


Figure 5. UV/Vis absorption spectra of **4-PPh$_3$** and **4′-PPh$_3$** measured in CH_2Cl_2 at room temperature.

absorption bands is 655 nm (log$\varepsilon = 3.40$, ε is the molar absorption coefficient in $\mathrm{L\,mol^{-1}\,cm^{-1}}$), redshift by 231 nm from that of complex **6** (424 nm).[7] The broad absorption and remarkable stability will significantly facilitate further exploration of their potential applications.

Conclusions

In summary, DFT calculations reveal significant stabilization of pentalene and selenirene simultaneously by the osmium fragment and predict the first example of σ-aromaticity dominating in an unsaturated Se-containing ring. Experimentally realized osmapentaloselenirenes display remarkable thermal stability and planarity, further supporting their aromaticity. As σ-aromaticity is traditionally observed in saturated rings, our findings not only highlight the extraordinary role of a metal fragment in stabilizing multiple antiaromatics but also widen the scope of σ-aromaticity significantly, encouraging further efforts to realize novel σ-aromatic unsaturated systems.

Experimental Section

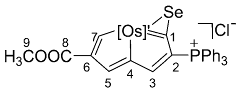
Computational Details

All structures were optimized at the M06 level with keywords Integral (Grid = UltraFine) of density functional theory.[28] In addition, the frequency calculations were performed to confirm the characteristics of the calculated structures as minima. In the M06 calculations, the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) were used to describe the Os atom, whereas the standard 6-311++G(d,p) basis set was used for the C, H, O, P, Cl, and Se atoms[29] for all the compounds. Polarization functions were added for Os (ζ(f) = 0.886).[30] NICS calculations were performed at the same level. All the optimizations were performed with the Gaussian 09 software package,[31] whereas the CMO-NICS and Wiberg bond index[32] calculations were carried out with the NBO 6.0 program[33] interfaced with the Gaussian 09 program. The Mayer bond order[34] and ELF calculations were performed by Multiwfn software[35] and the ELF isosurfaces were visualized with the VMD package.[36] The anisotropy of the induced current density (ACID) calculations were carried out at the B3LYP/6-311++G(d,p)[37] level with the ACID program.[25] In order to examine the reliability of M06 functional, the other M06L,[38] B3LYP, TPSS,[39] PBE,[40] and PBE0[41] have been chosen to optimize the experimental model **4′-PPh$_3$** and calculate its key ^{1}H chemical shifts. The results in Table S1 indicated the reliability of our calculations as the geometry and ^{1}H chemical shifts of **4′-PPh$_3$** were well reproduced by M06 density functional, which can generate the closest data to the experimental ones. In addition, the effect of basis sets has already been examined according to our previous work.[18a] Calculations with all-electron ADZP[42] and ECP60MDF[43] basis sets for the osmium produce a consistent result on the geometry and energetics based on the basis set of LanL2DZ whereas the basis sets for other atoms are unchanged.

General Procedures

Unless otherwise stated, all manipulations were performed at room temperature under an atmosphere of N_2 using standard Schlenk techniques. Hexane and diethyl ether were distilled over sodium/benzophenone, whereas 1,2-dichloroethane and dichloromethane were distilled over calcium hydride under an atmosphere of N_2 prior to use. The osmapentalynes were synthesized according to a previously published procedure.[7] Other reagents were used as received from commercial sources without further purification. Column chromatography was performed on alumina gel (200–300 mesh) in air. Nuclear magnetic resonance (NMR) experiments were performed on a Bruker Advance III 400 spectrometer or a Bruker Ascend 600 spectrometer. The chemical shifts in the ^{13}C NMR and ^{1}H NMR spectra were relative to tetramethylsilane, whereas ^{31}P NMR spectra were relative to 85 % H_3PO_4. Coupling constants were given in Hertz (Hz). Multiplicities were abbreviated as s, d, t, m, and br for singlet, doublet, triplet, multiplet, and broad, respectively. Elemental analyses data were obtained on a Vario EL III elemental analyzer. The HRMS experiments were recorded on a Bruker En Apex Ultra 7.0T FT-MS. The theoretical molecular ion peaks were calculated by Compass Isotope Pattern software supplied by Bruker Company. Thermal gravity analyses (TGA) were carried out on a NETZSCH TG 209F1 Iris analyzer or SDT Q600 at a rate of 10 °C min^{-1} from room temperature to 900 °C under nitrogen atmosphere. Absorption spectra were recorded on a SHIMADZU UV2550 ultraviolet-visible spectrophotometer.

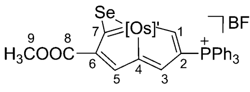
Synthesis and characterization of 4-PPh$_3$



4-PPh$_3$

A mixture of **5** (200 mg, 0.17 mmol) and selenium (671 mg, 8.50 mmol) in 1,2-dichloroethane (10 mL) was stirred at 60 °C in a Schlenk tube for 1 d to give a green solution. The excess selenium was removed by filtration, and the filtrate was evaporated under vacuum to approximately 2 mL. The residue was purified by column chromatography (neutral alumina, eluent: dichloromethane/methanol = 20:1) to give **4-PPh$_3$** as a green solid. Yield: 164 mg, 76 %. ^{1}H NMR plus ^{1}H–^{13}C HSQC (600.1 MHz, CD_2Cl_2): δ = 13.71 (s, 1 H, C^7*H*), 9.08 (s, 1 H, C^3*H*), 8.47 (s, 1 H, C^5*H*), 7.88–7.09 (45 H, other aromatic protons), 3.59 ppm (s, 3 H, C^9*H*). ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2): δ = 9.69 (s, C*P*Ph$_3$), −13.02 ppm (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR plus ^{1}H-^{13}C HMBC and ^{1}H–^{13}C HSQC (150.9 MHz, CD_2Cl_2): δ = 252.62 (m, C7), 242.36 (m, C1), 183.42 (dt, $^2J_{PC}$ = 23.1 Hz, $^3J_{PC}$ = 4.6 Hz, C4), 166.51 (d, $^2J_{PC}$ = 17.4 Hz, C3), 162.27 (s, C5), 162.10 (s, C8), 151.29 (s, C6), 131.92 (d, $^1J_{PC}$ = 92.6 Hz, C2), 135.42–117.40 (other aromatic carbons and the above-mentioned C2), 51.05 ppm (s, C9). Elemental analysis calcd (%) for $C_{63}H_{51}Cl_2O_2OsP_3Se$: C 59.44, H 4.04; found: C 59.27, H 4.18. HRMS (ESI): *m/z* calcd for $[C_{63}H_{51}ClO_2SeOsP_3]^+$ 1237.1557; found 1237.1546.

Synthesis and characterization of 4′-PPh$_3$



4'-PPh$_3$

A mixture of **6** (200 mg, 0.16 mmol) and selenium (631 mg, 8.0 mmol) in 1,2-dichloroethane (10 mL) was stirred at 60 °C in a Schlenk tube for 2 d to give a blue solution. The excess selenium was removed by filtration, and the filtrate was evaporated under vacuum to approximately 2 mL. The residue was purified by column chromatography (neutral alumina, eluent: dichloromethane/methanol = 20:1) to give **4′-PPh$_3$** as a blue solid. Yield: 178 mg, 84 %. ^{1}H NMR plus ^{1}H–^{13}C HSQC (400.1 MHz, CDCl$_3$): δ = 13.69 (d, $^3J_{PH}$ = 14.3 Hz, 1 H, C^1*H*), 8.36 (s, 1 H, C^5*H*), 8.13 (s, 1 H, C^3*H*), 7.80–6.85 (45 H, other aromatic protons), 3.41 ppm (s, 3 H, C^9*H*). ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): δ = 12.35 (s, C*P*Ph$_3$), −16.66 ppm (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR plus ^{1}H–^{13}C HMBC and ^{1}H–^{13}C HSQC (100.6 MHz, CDCl$_3$): δ = 252.98 (t, $^2J_{PC}$ = 6.1 Hz, C7), 241.79 (br, C1), 183.28 (dt, $^2J_{PC}$ = 21.7 Hz, $^3J_{PC}$ = 4.4 Hz, C4), 166.54 (s, C5), 159.92 (s, C8), 153.77 (d, $^2J_{PC}$ = 20.2 Hz, C3), 149.50 (s, C6), 128.76 (d, $^1J_{PC}$ = 81.9 Hz, C2), 135.57–117.78 (other aromatic carbons and the above the mentioned C2), 51.25 ppm (s, C9). Elemental analysis calcd (%) for $C_{63}H_{51}BClF_4O_2OsP_3Se$: C 57.13, H 3.88; found: C 57.09, H 4.08. HRMS (ESI): *m/z* calcd for $[C_{63}H_{51}ClO_2SeOsP_3]^+$ 1237.1557; found 1237.1545.

Crystallographic analysis

Single crystals suitable for X-ray diffraction of **4′-PPh$_3$** was grown from a dichloroethane/methanol 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$_{K\alpha}$ radiation (λ = 0.71073 Å). All of the data were corrected for absorption effects by using the multiscan technique. The structure was solved by the Patterson function, completed by subsequent difference Fourier map calculations, and refined by full matrix least-squares on F^2 using the SHELXTL program package. 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. The CH_3OH solvent molecule in **4′-PPh$_3$** was refined without the addition of H atoms. CCDC 1526688 (**4′-PPh$_3$**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre Crystal Data for **4′-PPh$_3$**: $C_{68}H_{59}BO_3F_4P_3Cl_5SeOs$ (M = 1550.28 g mol^{-1}): monoclinic, space group $P2_1/n$ (no. 14), a = 13.5528(3) Å, b = 11.5707(3) Å, c = 42.3023(10) Å, β = 93.469(2)°, V = 6621.5(3) Å^3, Z = 4, T = 173 K, $\mu(\mathrm{Mo}_{K\alpha})$ = 2.807 mm^{-1}, D_{calcd} = 1.555 g cm^{-3}, 28 961 reflections measured ($5.366° \leq 2\theta \leq 50°$), 11 639 unique ($R_{int}$ = 0.0400, R_{sigma} = 0.0779) which were used in all calculations. The final R_1 was 0.0409 ($I > 2\sigma(I)$) and wR_2 was 0.0828 (all data). GOF = 0.985. Residual electron density (e Å^{-3}) max min^{-1}: 0.98/−1.39.

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Conflict of interest

The authors declare no conflict of interest.

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