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Metallapentalenofurans and Lactone-Fused Metallapentalynes

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Abstract: Metalla-aromatics are attractive species because they exhibit the properties of both organometallics and aromatics. Reported metal-bridged polycyclic aromatic complexes, as well as Möbius aromatic species, are still rare. Herein, we present the construction of two new metal-bridged polycyclic aromatic frameworks, α-metallapentalenofurans and lactone-fused metallapentalynes, by the reactions of osmapentalyne with terminal aryl alkynes in the presence of H_2O or HBF_4/H_2O, respectively. DFT calculations show that the α-metallapentalenofurans possess rare planar Craig-type Möbius aromaticity derived from the 11-center-12-electron d_π–p_π π-conjugation. This study offers a new route for the construction of polycyclic metalla-aromatics as well as planar Möbius aromatic species.

Introduction

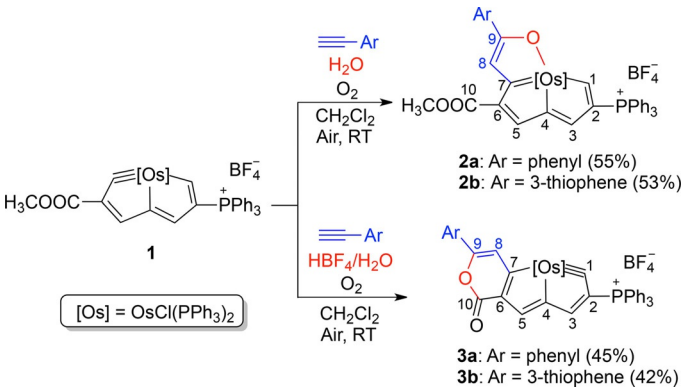
The combination of organometallic chemistry and aromatic chemistry generates metalla-aromatic chemistry, which was first proposed by Thorn and Hoffmann in 1979.[1] Generally, we can predict the reactivities and properties of derivative metalla-aromatics from their organic parents. For examples, metallabenzenes,[2,3] metallabenzynes,[4,5] and other metalla-aromatic species[6] possess aromaticity and analogous reactivities with their organic counterparts.

Recently, we reported a stable metalla-aromatic system, metallapentalyne and metallapentalene,[7,8] the properties of which are totally different from their *anti*-aromatic and unstable organic parents, pentalyne and pentalene.[9] The unexpected stability of osmapentalynes and osmapentalenes is derived from the Möbius aromaticity, which is supported by DFT calculations.[7a,b,8c] The chemistry of this unique Möbius aromatic system still deserves to be explored, although some types of reactivities have been reported in the past few years.[7,8b,c] Furthermore, the reported examples of planar Craig-type Möbius aromaticity are still rare and all of them have *n*-center-*n*-electron (*n* = 8 or 12).[7a,b,8c] Herein we report the reactions of osmapentalyne **1** with terminal aryl alkynes and water under different conditions (without or with acid), leading to the formations of the first α-metallapentalenofurans and the first lactone-fused metallapentalynes. DFT calculations show that the metallapentalenofurans possess planar Craig-type Möbius aromaticity derived from the 11-center-12-electron d_π–p_π π-conjugation. In addition, the examples of metal shared by three aromatic rings are rare.[7c,8a,c]

Results and Discussion

Treatment of osmapentalyne **1** with phenylacetylene and water at room temperature (RT) for one day under air atmosphere, led to the formation of the first α-metallapentalenofuran, **2a**, in 55% isolated yield (Scheme 1). Complex **2b** was also synthesized by the reaction of **1** with 3-ethynylthiophene under the same conditions (Scheme 1).

Complex **2a** was characterized by single crystal X-ray diffraction. As shown in Figure 1, the osmium center of complex **2a** is shared by three fused five-membered rings with a seven-coordinated pentagonal bipyramidal geometry. The three fused five-membered rings constituted by Os1, O1 and C1–C9 are approximately coplanar, indicated by the mean deviation from



Scheme 1. Reactions of osmapentalyne **1** with terminal aryl alkynes.

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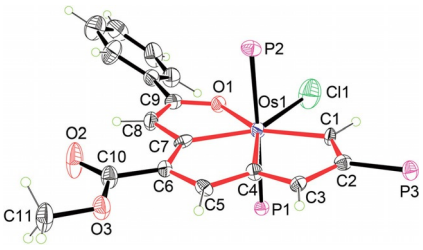


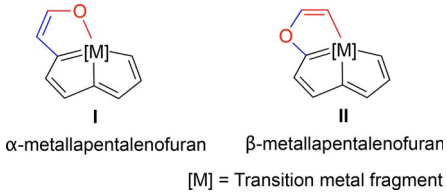
Figure 1. X-ray molecular structure for the cation of complex **2a** drawn with 50% probability level. The phenyl groups in PPh_3 are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C1 2.088(7), Os1–C4 2.156(7), Os1–C7 2.098(8), Os1–O1 2.120(5), C1–C2 1.361(10), C2–C3 1.416(11), C3–C4 1.347(10), C4–C5 1.434(10), C5–C6 1.358(10), C6–C7 1.430(11), C7–C8 1.413(11), C8–C9 1.373(12), C9–O1 1.294(10), Os1-C1-C2 123.3(6), C1-C2-C3 112.4(7), C2-C3-C4 112.6(7), C3-C4-Os1 121.1(6), C4-Os1-C1 70.6(3), Os1-C4-C5 119.4(5), C4-C5-C6 114.0(6), C5-C6-C7 112.1(7), C6-C7-Os1 122.9(6), C7-Os1-C4 71.4(3), Os1-C7-C8 116.3(6), C7-C8-C9 113.6(7), C8-C9-O1 117.0(7), C9-O1-Os1 118.5(5), O1-Os1-C7 73.8(3).

the least-squares plane (0.080 Å) and the sums of the angles in the three five-membered rings (540.0°, 539.8°, and 539.2°). All of the Os–C bond lengths (Os1–C1 2.088, Os1–C4 2.156, Os1–C7 2.098 Å) in complex **2a** are within the range of those reported for osmapentalene derivatives (1.926–2.175 Å).[7b–e,8a,c] The Os1–O1 (2.120 Å) and the C9–O1 (1.294 Å) bond lengths are within the range of those reported for osmafurans (2.082–2.234 Å for Os–O and 1.216–1.295 Å for C–O).[10] All of the C–C bond lengths (1.358–1.434 Å) in the metallacycle are between the typical lengths of a C–C conjugated double (1.34 Å) and single (1.46 Å) bond, suggesting a delocalized structure of **2a**.

Both complexes **2a** and **2b** were characterized by nuclear magnetic resonance (NMR), elemental analysis (EA), and high-resolution mass spectrometry (HRMS). Consistent with the solid state structure, the ^{1}H NMR spectrum of complex **2a** shows a characteristic Os*CH* signal at 13.81 ppm. Other proton signals on the metallacycle are observed at 7.71 (H3), 7.66 (H5), and 8.24 (H8) ppm. In the ^{13}C NMR spectrum, the signals for C1, C4, and C7 are located at 208.3, 181.4, and 226.5 ppm, respectively. These results suggest that C7 shows more carbene character than both C1 and C4.

The structural features and NMR data indicate that the metallacycle in complex **2a** is delocalized. Thus, complex **2a** represents a new framework of polycyclic metalla-aromatic complex, namely α-metallapentalenofuran (**I** in Scheme 2).[11] Although the framework of β-metallapentalenofuran (**II** in Scheme 2)[7c] was reported in 2014, examples of metal-bridged polycyclic aromatic complexes are still rare.[7c,8a,c]

Interestingly, when the reactions of osmapentalyne **1** with phenylacetylene or 3-ethynylthiophene were carried out in the presence of HBF_4/H_2O, complexes **3a** and **3b** were formed in 45 and 42% isolated yield, respectively (Scheme 1). In these reactions, an interesting phenomenon was observed that the Os–C triple bond was shifted from the left five-membered ring to the right with the formation of the lactone unit. Note that only one example of shiftable metal–carbon triple bond in cyclic complexes was reported so far.[7a]



Scheme 2. The structures of α- and β-metallapentalenofuran.

Complex **3a** was characterized by single crystal X-ray diffraction analysis, NMR, EA, and HRMS. As shown in Figure 2, the most interesting structural feature of complex **3a** is that the

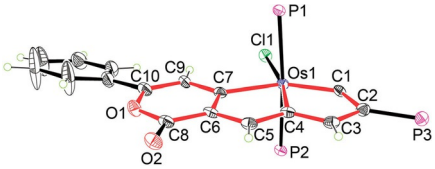


Figure 2. X-ray molecular structure for the cation of complex **3a** drawn with 50% probability level. The phenyl groups in PPh_3 are omitted for clarity. Selected bond lengths [Å] and angles [°]:Os1–C1 1.834 (4), Os1–C4 2.081(4), Os1–C7 2.076(4), C1–C2 1.406(6), C2–C3 1.404(6), C3–C4 1.410(7), C4–C5 1.383(6), C5–C6 1.395(7), C6–C7 1.414(6), C7–C9 1.421(6), C9–C10 1.353(6), C10–O2 1.375(6), O2–C8 1.379(6), C8–C6 1.446(7), C8–O1 1.210(6); Os1-C1-C2 130.6(3), C1-C2-C3 106.9(4), C2-C3-C4 111.8(4), C3-C4-Os1 117.8(3), C4-Os1-C1 72.91(18), Os1-C4-C5 119.3(3), C4-C5-C6 113.6(4), C5-C6-C7 114.4(4), C6-C7-Os1 117.7(3), C7-Os1-C4 75.04(17), C6-C7-C9 116.1(4), C7-C9-C10 121.6(4), C9-C10-O2 121.4(4), C10-O2-C8 122.3(4), O2-C8-C6 116.2(4), C8-C6-C7 122.4(4).

osmapentalyne unit and the fused lactone ring are almost coplanar, reflected by the maximum deviation from the least-squares plane (0.052 Å for the C2 atom in the three fused rings constituted by Os1, O1, C1–C10). The C–C bond lengths in the lactone unit are 1.446 Å for C6–C8, 1.421 Å for C7–C9, and 1.353 Å for C9–C10. The C–C bond lengths in the osmapentalyne unit are in the range of 1.383–1.414 Å. These results suggest that the metallacycle in complex **3a** is delocalized. Therefore, complex **3** represents a new framework of metalla-aromatics, which contains a metallapentalyne unit and a lactone unit.

The NMR data of complex **3a** are consistent with the solid state structure. The three proton signals at 9.71, 8.08, and 6.92 ppm are assigned to H5, H3, and H9, respectively. The ^{13}C NMR spectrum displays the signals in the lactone ring at 147.6 (C10), 119.5 (C9), 145.6 (C6), and 217.2 (C7) ppm. The NMR data of complex **3b** are similar to those of **3a**.

In order to investigate the nature of this reaction, we did some control experiments, which showed that both water and air are indispensable for these reactions (Figure S1 in Supporting Information). To reveal the source of O1 in complexes **2** and **3**, we carried out ^{18}O-labeled experiments. First, we did the reaction of osmapentalyne **1** with phenylacetylene in the presence of ^{18}O-labeled water ($H_2{}^{18}O$) in an O_2 atmosphere. We found that only ^{18}O-labeled complex **2a** was formed, which was confirmed by the HRMS (*m/z* 1279.2873). This result clearly shows that the source of O1 in the metallapentalenofuran is from water. Experimentally, when $HBF_4/H_2{}^{18}O$ was used, the ^{18}O-labeled complex **3a** was formed and confirmed by HRMS

(*m/z* 1247.2572), which supports that the O1 in complex **3** is also from water.

As discussed above, complex **2a** shows a delocalized character. To elucidate its bonding and electronic structure, we performed DFT calculations on an unsubstituted model, **2′**, in which PH_3 groups were used to replace the PPh_3 ligands. First, the isomerization stabilization energy (ISE) was calculated to evaluate the aromaticity.[12] As shown in Figure 3, the ISE values for the three five-membered rings are −17.3, −15.3 and −7.1 kcal mol^{-1}. The sum of these values (−39.7 kcal mol^{-1}) is close to the global ISE value (−42.3 kcal mol^{-1}) for **2′**, which suggests that complex **2** is aromatic.

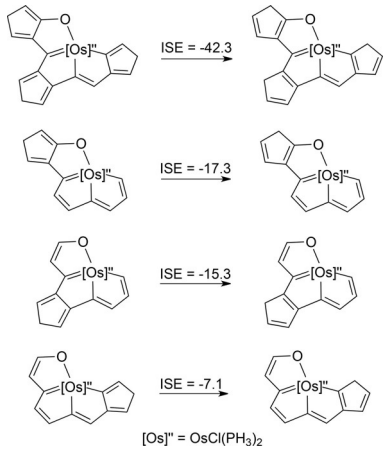


Figure 3. The aromaticity of model **2′** evaluated by the ISE method. The energies (in kcal mol^{-1}, computed by the B3LYP functional with the LanL2DZ basis set for Os, P, Cl and the 6–311++G(d,p) basis sets for C, O, and H) include zero-point energy corrections.

The delocalized structure and aromaticity of model **2′** is further supported by the anisotropy of the induced current density (AICD) analysis.[13] The AICD method is a reliable approach to investigate and visualize electron delocalization. As shown in Figure 4, the clockwise ring current in the π-system is displayed along the periphery of the three fused five-membered rings, confirming the aromaticity of complex **2**.

To further investigate the nature of the aromaticity in complex **2′**, we also analyzed its electronic structure. The seven-coordinated Os center has three electrons in its two unhybridized d_π atomic orbitals (AOs), nine carbon atoms contribute nine electrons and the oxygen contributes two nonbonding electrons. These π-AOs constitute seven occupied π-molecular orbitals (MOs) of **2′** (Supporting Information Figure S28).

Among them, six key occupied π-MOs selected in Figure 5 reflect the π-delocalization along the perimeter of the three fused five-membered ring system. These six occupied π-MOs are derived principally from the orbital interactions between the $p_{z\pi}$ atomic orbitals of the C_9H_7O unit and two of the d orbitals of the Os atom ($5d_{xz}$ and $5d_{yz}$). Accordingly, complex **2′** can be regarded as a Craig-type Möbius aromatic complex derived from 11-center-12-electron d_π–p_π π-conjugation.

DFT calculations (ISE, AICD, and electronic structure analysis) show that the osmapentalyne unit in complex **3** also possesses

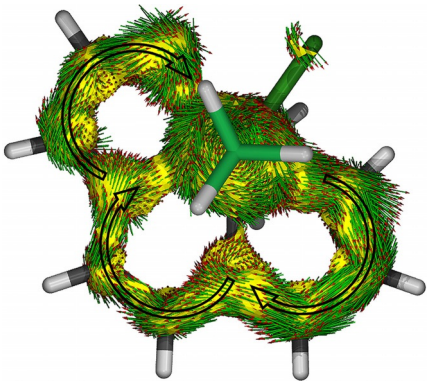


Figure 4. AICD isosurface of the model complex **2′** by π-contribution. Current density vectors are plotted onto the AICD isosurface of 0.030 to indicate diatropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

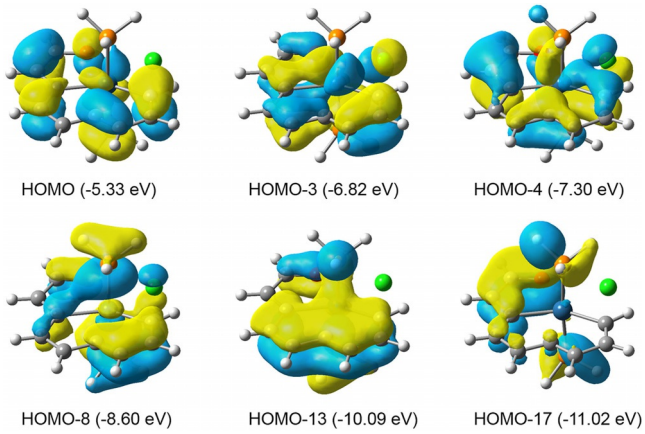


Figure 5. Six key occupied perimeter π molecular orbitals (π-MOs) of the model complex **2′**. The eigenvalues of the MOs are given in parentheses.

Möbius aromaticity, as reported in metallapentalynes.[7a] First, the calculated ISE values for model **3′** (Supporting Information Figure S29) are comparable with the values for metallapentalyne reported early.[7a] Secondly, the ACID analysis was also used to evaluate the aromaticity of complex **3**. The clockwise ring current in the π-system is displayed along the periphery of the two fused five-membered rings, confirming the aromaticity of osmapentalyne unit in complex **3** (Supporting Information Figure S30). In addition, seven occupied π-MOs of **3′** were found (Supporting Information Figure S31), and only four of them (HOMO, HOMO−3, HOMO−11, and HOMO−16) were derived principally from the osmapentalyne unit. Accordingly, osmapentalyne unit in complex **3** is essentially an 8-center-8-electron Möbius aromatic system.

Conclusions

In summary, two types of new metalla-aromatic frameworks, α-metallapentalenofurans and lactone-fused metallapentalynes, have been constructed by the reactions of osmapentalyne with aryl alkynes under different conditions. Interestingly, the metal-carbon triple bond in osmapentalyne **1** was shifted to

another five-membered ring in complex **3** with the new lactone ring was formed. DFT calculations show that the α-metallapentalenofurans possess rare Möbius aromaticity derived from 11-center-12-electron d_π–p_π π-conjugation. This study not only offers the possibility for the construction of metal-bridged polycyclic aromatic systems, but also enriches the family of Möbius aromatics.

Experimental Section

General information

All syntheses were carried out under an inert atmosphere (N_2) using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under N_2 from sodium/benzophenone (diethyl ether) or calcium hydride (dichloromethane). Compound **1** was synthesized according to published literatures.[7a] Other reagents were used as received from commercial sources without further purification. Column chromatography was performed on alumina gel (200–300 mesh), silica gel (200–300 mesh) or polystyrene gel (Bio-Beads ™S-X3 Support, 200–400 mesh) in air. Nuclear magnetic resonance (NMR) spectroscopic experiments were performed on a Bruker AVIII-500 (^{1}H, 500.2 MHz; ^{13}C, 125.8 MHz; ^{31}P, 202.5 MHz) spectrometer or a Bruker AVIII-400 (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{31}P, 162.0 MHz) spectrometer at room temperature. ^{1}H and ^{13}C NMR chemical shifts are relative to tetramethylsilane, and ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. The absolute values of the coupling constants are given in Hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m) and broad (br). High resolution mass spectra (HRMS) experiments were recorded on a Bruker En Apex Ultra 7.0T FT-MS. Elemental analyses were performed on a Vario EL III elemental analyzer.

Synthesis and characterization of 2a

Phenylacetylene (87.7 μL, 0.80 mmol) was added to a solution of compound **1** (200 mg, 0.16 mmol) in 10 mL dichloromethane and 0.2 mL water in air. The mixture was stirred at RT for 1 d to give a red solution. The solution was evaporated under vacuum to a volume of ca. 2 mL, and then purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone = 5:1) to give a red solution. The red solid of **2a** (120 mg, 55%) was collected after the solvent was evaporated to dryness under vacuum. ^{1}H NMR plus ^{1}H–^{13}C HSQC (500.2 MHz, $CDCl_3$): δ = 13.81 (d, J_{P-H} = 15.1 Hz, 1H, H1), 8.24 (s, 1H, H8), 7.71 (s, 1H, H3, confirmed by ^{1}H–^{13}C HSQC), 7.66 (s, 1H, H5, confirmed by ^{1}H–^{13}C HSQC), 3.59 (s, 3H, COOC*H*$_3$), 8.03–6.94 ppm (50H, other aromatic protons); ^{31}P NMR (202.5 MHz, $CDCl_3$): δ = 10.85 (s, C*P*Ph$_3$), −17.25 ppm (s, Os*P*Ph$_3$); ^{13}C NMR plus DEPT-135, HSQC, and HMBC (125.8 MHz, $CDCl_3$): δ = 226.5 (t, J_{P-C} = 6.1 Hz, C7), 208.3 (br, C1), 194.8 (s, C9), 181.4 (dt, J_{P-C} = 22.8 Hz, J_{P-C} = 4.5 Hz, C4), 168.4 (s, C5), 163.4 (s, *C*OOCH$_3$), 144.3 (d, J_{P-C} = 19.9 Hz, C3), 140.4 (s, C6), 120.8 (s, C8), 119.4 (d, J_{P-C} = 89.6 Hz, C2), 50.9 (COO*C*H$_3$), 135.0–125.4 ppm (other aromatic carbons); elemental analysis calcd (%) for $C_{71}H_{57}BClF_4O_3OsP_3$: C 62.54, H 4.21; found: C 62.72, H 4.19; HRMS (ESI): *m/z* calcd for $[C_{71}H_{57}ClO_3OsP_3]^+$, 1277.2814; found 1277.2818.

Synthesis and characterization of 2b

3-Ethynylthiophene (80.2 μL, 0.80 mmol) was added to a solution of compound **1** (200 mg 0.16 mmol) in 10 mL dichloromethane and 0.2 mL water in air. The mixture was stirred at RT for 1 d to give a red solution. The solution was evaporated under vacuum to a volume of ca. 2 mL, and then purified by column chromatography (neutral alumina, eluent: dichloromethane/acetone = 5:1) to give a red solution. The red solid of **2b** (116 mg, 53%) was collected after the solvent was evaporated to dryness under vacuum. ^{1}H NMR plus ^{1}H–^{13}C HSQC (400.1 MHz, $CDCl_3$): δ = 13.77 (d, J_{P-H} = 15.1 Hz, 1H, H1), 7.99 (s, 1H, H8), 7.64 (s, 1H, H3, confirmed by ^{1}H–^{13}C HSQC), 7. 61 (s, 1H, H5, confirmed by ^{1}H–^{13}C HSQC), 3.59 (s, 3H, COOC*H*$_3$), 8.06–6.95 ppm (48H, other aromatic protons); ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 10.57 (t, J_{P-P} = 3.9 Hz C*P*Ph$_3$), −17.40 ppm (d, J_{P-P} = 3.9 Hz Os*P*Ph$_3$); ^{13}C NMR plus DEPT-135, HSQC and HMBC (100.6 MHz, $CDCl_3$): δ = 225.7 (t, J_{P-C} = 6.2 Hz, C7), 208.5 (br, C1), 190.1 (s, C9), 181.2 (dt, J_{P-C} = 22.5 Hz, J_{P-C} = 4.3 Hz, C4), 168.0 (s, C5), 163.3 (s, *C*OOCH$_3$), 143.9 (d, J_{P-C} = 20.0 Hz, C3), 140.1 (s, C6), 121.4 (s, C8), 119.3 (d, J_{P-C} = 89.6 Hz, C2), 50.9 (s, COO*C*H$_3$), 138.9–124.9 ppm (other aromatic carbons); elemental analysis calcd (%) for $C_{69}H_{55}BClF_4O_3OsP_3S$: C 60.51, H 4.05; found: C 60.57, H 4.01; HRMS (ESI): *m/z* calcd for $[C_{69}H_{55}ClO_3OsP_3S]^+$, 1283.2376; found, 1283.2375.

Synthesis and characterization of 3a

Phenylacetylene (87.7 μL, 0.80 mmol) and 0.2 mL $HBF_4{\cdot}H_2O$ (1.6 mmol) were added to a solution of compound **1** (200 mg, 0.16 mmol) in 10 mL dichloromethane. The mixture was stirred at RT for 1 d to give a red solution in air. The solution was evaporated under vacuum to a volume of ca. 2 mL, and then purified by column chromatography (silica, eluent: dichloromethane/acetone = 3:1) to give a red solution. The solvent was evaporated to dryness under vacuum to give a red solid. The solid was further purified by polystyrene gel (Bio-Beads ™S-X3 Support, 200–400 mesh) column eluted by 1,2-dichloroethane to give a red solution. The red solid of **3a** (96 mg, 45%) was collected after the solvent was evaporated to dryness under vacuum. ^{1}H NMR plus ^{1}H-^{13}C HSQC (500.2 MHz, CD_2Cl_2): δ = 9.71 (s, 1H, H5), 8.08 (s, 1H, H3), 6.92 (s, 1H, H9), 7.81–7.05 ppm (50H, other aromatic protons); ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ = 6.15 (s, C*P*Ph$_3$), 0.71 ppm (s, Os*P*Ph$_3$); ^{13}C NMR plus DEPT-135, HSQC and HMBC (125.8 MHz, CD_2Cl_2): δ = 322.4 (td, J_{P-C} = 13.6 Hz, J_{P-C} = 13.5 Hz, C1), 217.2 (t, J_{P-C} = 7.8 Hz, C7), 178.6 (dt, J_{P-C} = 22.5 Hz, J_{P-C} = 3.4 Hz, C4), 161.8 (d, J_{P-C} = 15.4 Hz, C3), 159.4 (s, C8), 155.0 (s, C5), 147.6 (s, C10), 145.6 (s, C6), 119.7 (d, J_{P-C} = 91.6 Hz, C2), 119.5 (s, C9), 135.7–126.1 ppm (other aromatic carbons); elemental analysis calcd (%) for $C_{70}H_{53}BClF_4O_2OsP_3$: C 63.14, H 4.01; found: C 63.29, H 4.31; HRMS (ESI): *m/z* calcd for $[C_{70}H_{53}ClO_2OsP_3]^+$, 1245.2552; found, 1245.2543.

Synthesis and characterization of 3b

3-Ethynylthiophene (80.2 μL, 0.80 mmol) and 0.2 mL $HBF_4{\cdot}H_2O$ (1.6 mmol) were added to a solution of compound **1** (200 mg, 0.16 mmol) in 10 mL dichloromethane. The mixture was stirred at RT for 1 d to give a red solution in air. The solution was evaporated under vacuum to a volume of ca. 2 mL, and then purified by column chromatography (silica, eluent: dichloromethane/acetone = 3:1) to give a red solution. The solvent was evaporated to dryness under vacuum to give a red solid. The solid was further purified by polystyrene gel (Bio-Beads ™S-X3 Support, 200–400 mesh) column eluted by 1,2-dichloroethane to give a red solution. The red solid of **3b** (90 mg, 42%) was collected after the solvent was evaporated to dryness under vacuum. ^{1}H NMR plus ^{1}H–^{13}C HSQC (500.2 MHz, CD_2Cl_2): δ = 9.68 (s, 1H, H5), 8.02 (s, 1H, H3), 6.69 (s, 1H, H9), 7.87–7.02 ppm (48H, other aromatic protons); ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ = 6.03 (s, C*P*Ph$_3$), 0.90 ppm (s, Os*P*Ph$_3$). The attempt to obtain ^{13}C NMR spectroscopic characteri-

zation of complex **3b** failed due to its poor solubility in organic solvents; elemental analysis calcd (%) for $C_{68}H_{51}BClF_4O_2OsP_3S$: C 61.06, H 3.84; found: C 61.08, H 4.22; HRMS (ESI): *m/z* calcd for $[C_{68}H_{51}ClO_2OsP_3S]^+$, 1251.2114; found, 1251.2115.

X-ray crystallographic analysis

All single crystals suitable for X-ray diffraction were grown from dichloromethane solution layered with hexane. Single-Crystal X-ray diffraction data were collected on a Rigaku R-Axis Spider IP CCD area detector for **2a** with a Mo Kα radiation ($\lambda = 0.71073$ Å). Single-Crystal X-ray diffraction data were collected on an Oxford Gemini S Ultra CCD area detector for **3a** with a Cu Kα radiation ($\lambda = 1.54184$ Å). None absorption corrections for **2a** and multi-scan absorption corrections for **3a** were applied. Using Olex2,[14] the structures of **2a** was solved with the XS[15] structure solution program using Patterson Method and refined with the ShelXL[16] refinement package using Least Squares minimization. The structure of **3a** was solved with ShelXT[17] structure solution program using Direct methods and refined with the ShelXL[16] refinement package using Least Squares minimization. All non-hydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were placed at idealized positions and assumed the riding model. Some of the solvent molecules and phenyl groups were disordered and refined with suitable restrains. CCDC1450718 (**2a**) and 1514178 (**3a**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Crystal Data for 2a: $C_{72}H_{59}BCl_3F_4O_3OsP_3$ $[C_{71}H_{57}ClO_3OsP_3]BF_4{\cdot}CH_2Cl_2$ ($M = 1448.46$ g mol^{-1}): monoclinic, crystal dimension 0.10×0.10×0.10 mm space group $P2_1/c$ (no. 14), $a = 13.5171(3)$ Å, $b = 11.7039(2)$ Å, $c = 40.4485(7)$ Å, $\beta = 98.3440(10)^\circ$, $V = 6331.3(2)$ Å^3, $Z = 4$, $T = 173$ K, μ(MoKα) = 2.277 mm^{-1}, $D_{calcd} = 1.520$ g cm^{-3}, 83841 reflections measured ($6.092^\circ \le 2\Theta \le 51.998^\circ$), 12434 unique ($R_{int} = 0.0849$, $R_{sigma} = 0.0507$) which were used in all calculations. The final R_1 was 0.0597 ($I > 2\sigma(I)$) and wR_2 was 0.1462 (all data). GOF = 1.151. Residual electron density (e. Å^{-3}) max/min: 2.61/−2.49.

Crystal Data for 3a: $C_{72}H_{58}BCl_5F_4O_{2.5}OsP_3$ $[C_{70}H_{53}ClO_2OsP_3]BF_4{\cdot}2\,CH_2Cl_2{\cdot}0.5\,H_2O$ ($M = 1510.35$ g mol^{-1}): triclinic, crystal dimension 0.40×0.10×0.04 mm space group $P\bar{1}$ (no. 2), $a = 12.0804(4)$ Å, $b = 13.1020(4)$ Å, $c = 22.7773(6)$ Å, $\alpha = 81.762(2)^\circ$, $\beta = 80.788(2)^\circ$, $\gamma = 65.694(3)^\circ$, $V = 3231.18(18)$ Å^3, $Z = 2$, $T = 175$ K, μ(CuKα) = 6.818 mm^{-1}, $D_{calcd} = 1.552$ g cm^{-3}, 26968 reflections measured ($7.432^\circ \le 2\Theta \le 124.334^\circ$), 10157 unique ($R_{int} = 0.0435$, $R_{sigma} = 0.0499$) which were used in all calculations. The final R_1 was 0.0389 ($I > 2\sigma(I)$) and wR_2 was 0.1030 (all data). GOF = 1.037. Residual electron density (e. Å^{-3}) max/min: 1.83/−1.64.

Computational Details

All the optimizations were performed with the Gaussian 09 software package.[18] All structures were optimized at the B3LYP level of density functional theory.[19] The frequency calculations were performed to confirm the characteristics of the calculated structures as minima. In the B3LYP calculations, the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) were used to describe the Os, P, and Cl atoms, whereas the standard 6–311++G(d, p) basis set for all other atoms.[20] Polarization functions were added for Os (ζ(f) = 0.886), P (ζ(d) = 0.34), and Cl (ζ(d) = 0.514).[21] The ACID calculations were carried out with the ACID program.[13]

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aromaticity · density functional calculations · metallacycles · metallapentalyne · osmium

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