Metallacycles

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Synthesis and Characterization of a Metallacyclic Framework with Three Fused Five-membered Rings

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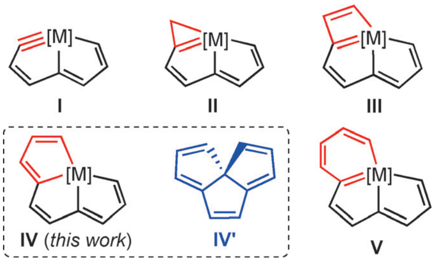
Abstract: *Polycyclic complexes containing a bridgehead transition metal are interesting species because the transition metal is shared by all the rings simultaneously. In this study, we present a novel osmium–bridgehead system with three fused five-membered rings. This novel framework can be viewed as a 10-atom carbon chain coordinating to the osmium center. In sharp contrast to the nonplanar organic analogue, this unique metallacycle exhibits good planarity, which was unambiguously verified by means of X-ray diffraction. Interestingly, preliminary DFT calculations show that the aromaticity in the three 5MRs of these osmatricycles can be easily tuned by the ligand substitution. Finally, the broad UV/Vis absorption spectra of these novel polycyclic complexes were also reported.*

The chemistry of metallacycles has received considerable attention from both experimentalists and theoreticians.[1] Incorporating transition metals into the organic cyclic systems can induce a significant impact on the stability and structural, electronic, and magnetic properties, as the metal center could donate more electrons to the rings than the replaced carbon atom.[2–4] For instance, pentalene, a fused five-membered ring (5MR) bicyclic compound with eight π electrons, is antiaromatic and unstable at room temperature, which was first generated in argon matrices by photocleavage of the corresponding dimer in 1997.[5] However, the metallapentalenes, by replacing one of the carbons in pentalene framework with a transition metal, are much more stable and are characterized by X-ray diffraction.[6]

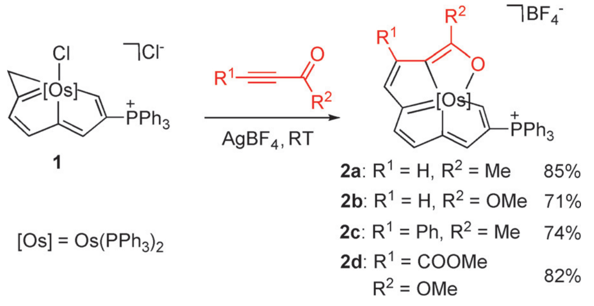
Recently, we reported the formation of a novel polycyclic system that is comprised of fused metallacyclic rings and stabilized by a transition metal positioned at a bridgehead position.[7–11] Specifically, the first fused 5MRs with a metal–carbon triple bond (**I** in Scheme 1), namely metallapentalyne, was reported in 2013.[7] Thereafter, a series of metallapentalene fused with 3MR (**II**),[8] 4MR (**III**),[9] and 6MR (**V**)[10] have been synthesized. All of these species show excellent stability and interesting properties. Thus, the isolation of species with three fused 5MRs (**IV**) seems to be the next logical step.



Scheme 1. A representation of polycyclic complexes with fused five-membered rings.

In organic chemistry, the corresponding three fused 5MRs constituted by carbon atoms (**IV′**) is nonplanar owing to the sp^3 hybridization of the center carbon atom. Therefore, a question was raised whether the three fused 5MRs (**IV**) with a bridgehead transition metal is planar. Herein, we report the synthesis and structural characterization of the first metal–bridgehead three fused 5MRs (**IV**) with good planarity, a "missing link" between **I**, **II**, **III**, and **V**.

A previous study showed that complex **1** reacts with two equivalent alkynes, leading to the formation of complex **V**.[10] A metal-centered 16-electron intermediate with three fused 5MRs was involved in the plausible mechanism of that reaction.[10] We hypothesize that alkynes with coordinating atoms, such as alkynones or alkynoates, may stabilize such an intermediate. With this idea in mind, treatment of complex **1** with 3-butyn-2-one in the presence of $AgBF_4$ resulted in the formation of a blue solution, from which complex **2a** was isolated in 85% yield after column chromatography (Scheme 2).



Scheme 2. The reactions of complex **1** with alkynones and alkynoates.

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In this reaction, the metallacyclopropene unit in complex **1** was expanded to a 5MR. A possible mechanism for the formation of complex **2a** is proposed in the Supporting Information, Figure S1. In the solid state, complex **2a** exhibits remarkable thermal and air robustness, being stable up to 200 °C in air for 10 h. **2a** is the first example of metal-bridgehead fused three-5MR complex constituted of carbon atoms.[11] Furthermore, the stable complex **2b** also was synthesized by the reaction of complex **1** with methyl propiolate in 71% yield under the same conditions (Scheme 2).

The structure of complex **2a** was confirmed by single-crystal X-ray diffraction.[12] As shown in Figure 1, **2a** contains a near-planar tetracyclic framework, as reflected by the small mean deviation from the least-squares plane (0.0685 Å), which is contrast to the nonplanar parent compound **IV′**. The sums of angles in the three 5MRs and the 4MR are 539.9°, 539.7°, 539.8°, and 359.9°, which are close to the ideal values of 540° and 360°, respectively. The nearly equal Os−C bond lengths (Os1−C1 2.078 Å, Os1−C4 2.113 Å, Os1−C7 2.119 Å, Os1−C10 2.109 Å) indicate a delocalized structure. The length of C11−O1 (1.315 Å) was elongated compared with the typical C=O double bond, indicating the σ-bond property between Os1 and O1.

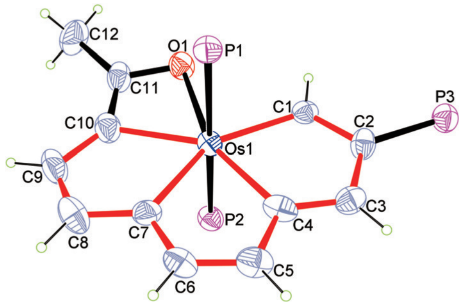
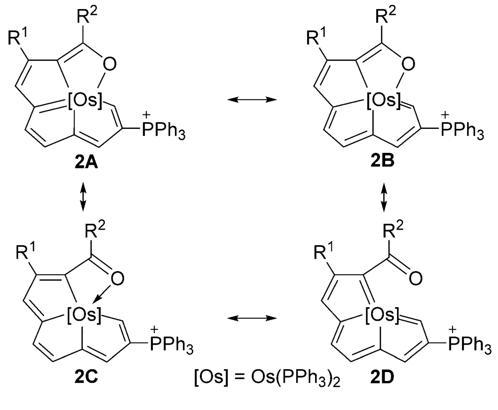


Figure 1. Molecular structure of the cation of **2a** (ellipsoids set at 50% probability). The PPh_3 phenyl moieties are omitted for clarity.

The nuclear magnetic resonance (NMR) spectroscopy and high resolution mass spectrometry (HRMS) data of **2a** are consistent with the solid-state structure. In particular, in the ^1H NMR spectrum, the signal of H1 was observed at 11.50 ppm, which is comparable to the values of Os-C*H* observed in aromatic osmapentalenes (11.93–12.46 ppm).[6c] Other proton signals on the fused 5MRs were observed in the aromatic region. In the ^{13}C NMR spectrum, the signals of metal-bonded C7 (217.5 ppm) and C1 (215.4 ppm) are more downfield than those of C4 (189.4 ppm) and C10 (153.4 ppm), suggesting that C7 and C1 show carbene character. Complex **2b** was also characterized by X-ray diffraction, NMR, and HRMS, in which structural features were similar to those of **2a**. The structural parameters and NMR data indicate that the metallacycle of **2** can be represented by four resonance structures (Scheme 3).

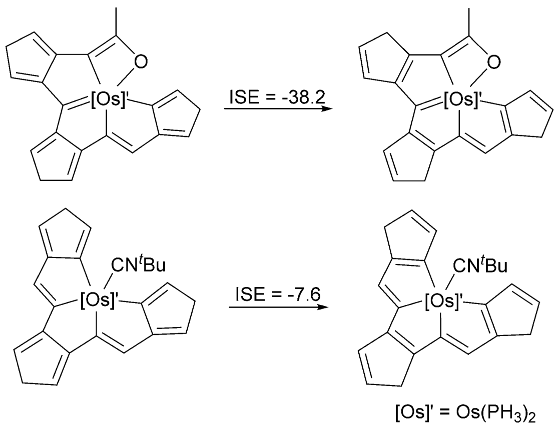


Scheme 3. Proposed resonance structures for the cation of **2**.

To study the scope of the ring-expansion reaction of complex **1**, the reactions of **1** with internal alkynones and alkynoates were also investigated. Treatment of **1** with 4-phenyl-3-butyn-2-one or dimethyl acetylenedicarboxylate in the presence of $AgBF_4$ at room temperature overnight led to the formation of 3MR ring-expanded products **2c** or **2d**, respectively (Scheme 2). The structures of **2c** and **2d** were confirmed by X-ray analysis, which structural features and parameters are close to those of **2a** and **2b**. In solution, the characteristic NMR signals of **2c** and **2d** are also similar to those of **2a** and **2b**.

The observed delocalized bond lengths, the planarity of the fused three 5MRs, and the down-field proton chemical shifts on the rings indicate that complex **2** is aromatic. The aromaticity of complex **2** was evaluated by the isomerization stabilization energy (ISE) calculations.[13] The ISE value was calculated based on a simplified model complex of **2a**, in which the PH_3 groups were used to replace the PPh_3 ligands. As shown in Scheme 4, the negative ISE value (−38.2 kcal mol^{-1}) of the model complex **2a′** is larger than those values for aromatic **V** (−29.0 kcal mol^{-1})[10] and osmapentalene (−31.4 kcal mol^{-1}),[6c] indicating the global aromaticity in complex **2a**.

Furthermore, the aromaticity in **2a′** was further supported by the anisotropy of the induced current density (AICD) analysis.[14] As shown in Figure 2, the clockwise current



Scheme 4. The aromaticity of model complexes of **2a** and **3** evaluated by the ISE method. The energies [kcal mol^{-1}] include zero-point energy corrections.

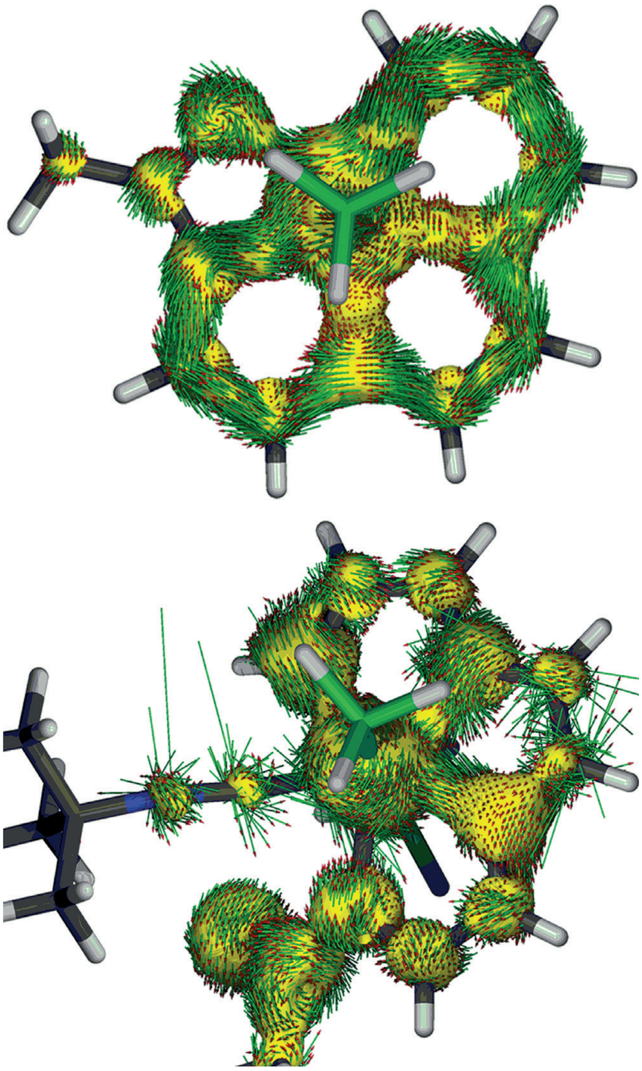
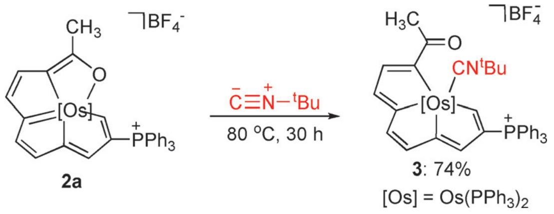


Figure 2. AICD isosurface of **2a′** (upper) and **3′** (lower) from π contribution. Current density vectors are plotted onto the AICD isosurface of 0.040 to indicate dia- and paratropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

density vectors plotted on the AICD isosurface in the π system of **2a′** show a diatropic ring current along the periphery of the three fused 5MRs, further confirming the π-aromaticity in complex **2a**.

Interestingly, the aromaticity in complex **2a** can be easily changed by the ligand substitution reaction (see below). Treatment of **2a** with 2 equiv of *tert*-butyl isocyanide at 80 °C for 30 h results in the formation of a red solution, from which complex **3** was isolated in 74 % yield (Scheme 5). The high reaction temperature and slow process further suggest the strong interaction between the osmium center and the O1 atom in complex **2a**.



Scheme 5. The reaction of complex **2a** with *t*-BuNC.

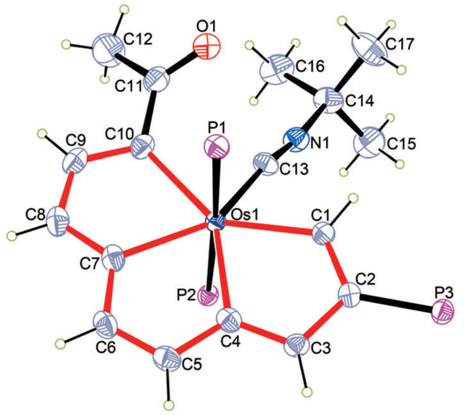


Figure 3. Molecular structure of the cation of **3** (ellipsoids set at 50 % probability). The PPh_3 phenyl moieties are omitted for clarity.

Complex **3** was fully characterized by X-ray diffraction, NMR, HRMS, and elemental analysis. The X-ray crystal structure (Figure 3) shows that the three fused 5MRs constituted of a 10-atom carbon chain (C1–C10) coordinating to the osmium center are planar, as reflected by the mean deviation (0.0568 Å) from the least-squares plane through all of the eleven atoms. Complex **3** is a novel kind of metallacyclic framework with three fused 5MRs, although the hetero-**IV** frameworks (that is, metallapentalenofuran and metallapentalenopyrrole) were reported earlier.[11]

All of the Os–C bonds in the three fused 5MRs of complex **3** (Os1–C1 2.127 Å, Os1–C4 2.155 Å, Os1–C7 2.152 Å, Os1–C10 2.220 Å) are significantly lengthened compared to those observed in **2a** (Os1–C1, 2.078 Å, Os1–C4 2.113 Å, Os1–C7 2.119 Å, Os1–C10 2.109 Å), suggesting the much weaker Os–C bonding in complex **3**. Furthermore, the C–C bond lengths within the metallacycle show a significant alternation (range from 1.341 to 1.433 Å). Also of note is the shortening of C11–O1 bond length (1.232 Å) compared to that of **2a** (1.315 Å). These parameters of complex **3** indicate a more localized structure compared to that of complex **2a**.

The observed localized bond lengths in the fused three 5MRs indicate that the aromatic character of complex **3** might be weakened. Therefore, we carried out DFT calculations to gain a deeper insight into the aromaticity of **3**. The calculated ISE value based on the simplified model of complex **3** is $-7.6\ \mathrm{kcal\,mol^{-1}}$ (Scheme 4), which is tremendously reduced in comparison with that of **2a** ($-38.2\ \mathrm{kcal\,mol^{-1}}$). These experimental data together with the small ISE value imply that complex **3** should be non-aromatic, which was further confirmed by the localization revealed by the AICD isosurface of **3′** (Figure 2). The non-aromatic character of complex **3** is probably due to the weak d_π–p_π π-conjugation between the osmium center and the coordinated carbon chain, as reflected by the single-bond character of all the Os–C bonds in the three fused 5MRs. Therefore, complex **3** is an interesting non-aromatic species that is different from the aromatic character observed in the other metallapentalene derivatives with at least one Os−C multiple bond (**I**, **II**, **III**, and **V**).[7–10]

For organic compounds, red-shifted absorption is observed for larger conjugation. With these novel metal-containing polycyclic complexes in hand, the UV/Vis absorption spectra of complexes **2** and **3** were also examined. In comparison, the absorption spectrum of **1** was also depicted in Figure 4. The absorption maximum of **2a** was observed at 639 nm ($\log\varepsilon = 4.05$, ε: molar absorption coefficient in $\mathrm{L\,mol^{-1}\,cm^{-1}}$) in the visible region, which was red-shifted by 203 nm compared with that of complex **1** ($\lambda_{\max} = 436$ nm). Correspondingly, the absorption maximum of **3** ($\lambda_{\max} = 534$ nm, $\log\varepsilon = 3.85$) was red-shifted by 98 nm compared with that of complex **1**; whereas blue-shifted by 105 nm compared with that of **2a**.

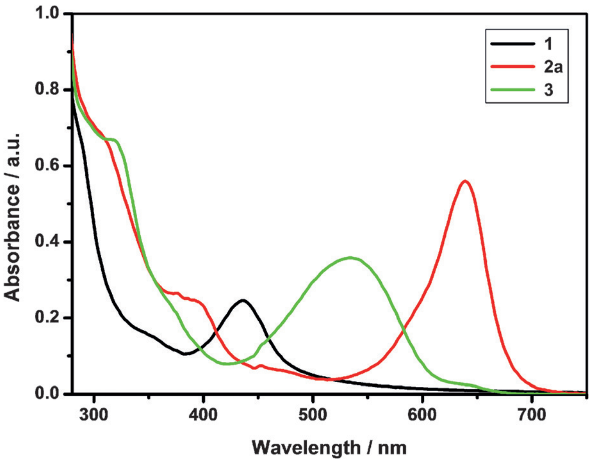


Figure 4. UV/Vis absorption spectra of **1**, **2a**, and **3** (5.0×10^{-5} mol L^{-1}) measured in CH_2Cl_2 at RT.

In summary, a new metallacyclic framework with three fused 5MRs has been constructed by the ring-expanded reactions of complex **1** with alkynones or alkynoates. The novel metallacycles exhibit excellent planarity and thermal stability, which is contrast to the nonplanar parent compound **IV′**. Interestingly, the ligand of the osmium center plays an important role in the aromaticity of the three fused 5MRs. Both experimental results and DFT calculations show that the three fused 5MRs in complex **2** are aromatic, whereas they are non-aromatic in *t*-BuNC substituted complex **3**. This framework can be viewed as a 10-atom carbon chain (carbolong[10]) coordinating to the osmium center, leading to the formation of perfect three fused 5MRs with C_2 symmetry. This study not only enriches the family of metallacyclic chemistry, but also provides a promising route for the construction of a polycyclic system containing a bridgehead transition metal.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aromaticity · DFT calculations · metallacycles · metallapentalene · osmium

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