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Five-Membered Cyclic Metal Carbyne: Synthesis of Osmapentalynes by the Reactions of Osmapentalene with Allene, Alkyne, and Alkene**

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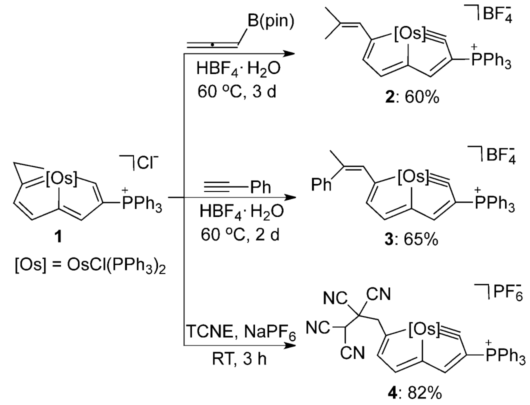
Abstract: *The synthesis of small cyclic metal carbynes is challenging due to the large angle strain associated with the highly distorted nonlinear triple bonds. Herein, we report a general route for the synthesis of five-membered cyclic metal carbyne complexes, osmapentalynes, by the reactions of an osmapentalene derivative with allene, alkyne, and alkene. Experimental observations and theoretical calculations document the aromaticity in the fused five-membered rings of osmapentalynes. The realization of transforming osmapentalene to osmapentalyne through this general route would not only allow further exploration of metallapentalyne chemistry but also show promising applications of this novel aromatic system with broad absorption band and high molar absorption coefficient.*

Small cyclic alkynes and metal carbynes have attracted many interests from chemists for their highly strained structures with the nonlinear triple bonds.[1,2] Not surprisingly, the first example of a cyclic metal carbyne complex, metallabenzyne (six-membered ring), has not been reported until 2001.[2a] In principle, the realization of smaller rings requires more effort to overcome larger ring strain. On the other hand, compared with Hückel aromatic compounds containing $4n+2$ π electrons, Möbius aromatic ones with $4n$ π electrons have proven much more difficult to synthesize and identify.[3,4] So far, the reported Möbius aromatic compounds are limited and most of them have a twisted topology.[5]

Recently, we reported the first five-membered cyclic metal carbyne, metallapentalyne.[6] Density functional theory (DFT) calculations not only confirmed the larger ring strain (24.3 kcal mo1^{-1} in osmapentalyne versus 9.6 kcal mol^{-1} in osmabenzyne) but also revealed planar Möbius aromaticity in osmapentalyne.[6,7] Further study demonstrated that these unique aromatics show aggregation-enhanced near-infrared photoluminescence[6] and the carbyne carbon can be attacked by both electrophile and nucleophile.[7] However, only the alkyl propiolates have been proven to be effective substrates for the synthesis of osmapentalynes so far. Thus, developing alternative synthetic approaches is desirable to explore the chemistry of metallapentalyne, as well as planar Möbius aromaticity. Here, we report a general route to osmapentalynes by the reactions of complex **1**[8] with allene, alkyne, and alkene.

Complex **1** can be facilely prepared and exhibits remarkable stability in the solid state due to σ-aromaticity in the metallacyclopropene unit and π-aromaticity in the fused five-membered rings.[8] In addition, metallacyclopropene species are considered as important intermediates in various reactions.[9] Therefore, we study the reactions of **1** with a series of unsaturated molecules, such as allene, alkyne, and alkene. As shown in Scheme 1, treatment of complex **1** with excess allenylboronic acid pinacol ester in the presence of $HBF_4{\cdot}H_2O$ at 60 °C for 3 days led to the formation of complex **2**, which was isolated in 60 % yield by column chromatography. A plausible mechanism for the formation of **2** was proposed in Scheme S1 in the Supporting Information (SI).



Scheme 1. Synthesis of osmapentalynes **2–4**.

The structure of complex **2** has been verified by X-ray diffraction analysis.[10] As shown in Figure 1, the metallabicycle of **2** is almost planar, which is reflected by the mean deviation (0.0143 Å) from the least-squares plane through the eight atoms (Os1, C1⋯C7). The Os–C1 bond length (1.847 Å) is close to that of the first osmapentalyne (1.845 Å).[6] The C–C bond distances (1.375–1.411 Å) in the fused five-membered rings are between the lengths of C–C single and double bonds without significant bond-length alternation. The planarity as well as the Os–C and C–C bond distances in the fused five-

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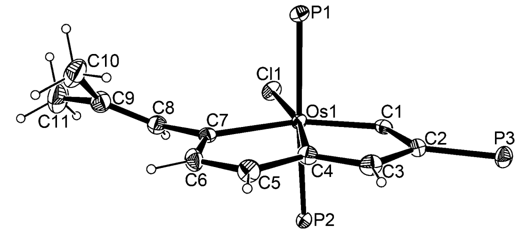
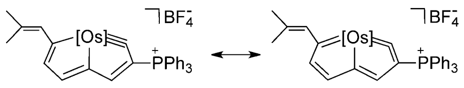


Figure 1. Molecular structure of the cation of **2** (thermal ellipsoids set at 50% probability). Phenyl groups in PPh_3 have been omitted for clarity.

membered ring indicates a delocalized metallabicyclic compound.[11]

Complex **2** has also been characterized by high-resolution mass spectrometry (HRMS), NMR spectroscopy, and elemental analysis. The HRMS showed a molecular ion peak at $m/z = 1155.2817$ with expected isotopic distribution (calculated value for complex **2** $[C_{65}H_{55}ClOsP_3]^+$ at $m/z = 1155.2809$). In the ^{1}H NMR spectrum, the typical H signal of Os–C*H* disappears, which is consistent with the solid structure. The proton signals in the fused five-membered rings of **2** are observed at the aromatic region (i.e. 9.03 ppm for H5, 7.60 ppm for H6, and 7.28 ppm for H3, confirmed by ^{1}H-^{13}C HSQC). In the ^{13}C NMR spectrum, the signal of the carbyne carbon appears at 320.0 ppm, which is close to the signals of the reported osmapentalynes (323.8–330.8 ppm).[6]

The delocalized structure of **2** can be rationalized by two major resonance structures (Scheme 2): osmapentalyne **2 A** (with an Os≡C unit) and osmacycloallene **2 B** (with an Os=C=C unit). The structures with C=C=C unit in five-membered metallacycles, e.g., metallacycloallenes[12] and metallacyclocumulenes,[13] have been reported experimentally and theoretically. In contrast, the similar structure with a M=C=C unit in a five-membered ring has only one example reported by us recently.[14]



2A [Os] = $OsCl(PPh_3)_2$ **2B**

Scheme 2. Two major resonance structures of **2**.

Besides allene, osmapentalene **1** can also react with alkyne. As shown in Scheme 1, treatment of **1** with excess phenylacetylene in the presence of $HBF_4 \cdot H_2O$ at 60 °C for 2 d led to the formation of complex **3**, which was isolated in 65% yield by column chromatography. The structure of **3** was fully supported by NMR spectroscopy, HRMS, elemental analysis, and X-ray diffraction. The structural features of the metallabicycle in **3** are very similar to those of **2** (Figure S6).

Although these reactions provide a new route for the synthesis of osmapentalynes via osmapentalene, they are relatively slow. To target a more rapid reaction, we carried out density functional theory (DFT) calculations to probe the nature of the reaction. Formally, it is the internal sp-hybridized carbons of allene and alkyne that attacked the sp^3-hybridized carbon atom (C8) of osmapentalene **1** (Figure S1). As the B(pin) substituent is electron-deficient, the internal carbon of allene should be electrophilic. Thus the C8 atom of osmapentalene **1** is expected to be nucleophilic. Indeed, the calculation on the model complex **1′** (for which PH_3 was used to replace PPh_3 in **1**) shows that the Mulliken charge on the C8 atom is −0.61 (Figure S1). The charge on the internal carbon atoms in allene, and in alkyne are +0.56 and +1.19, respectively, in line with our hypothesis. If the carbon in a substrate becomes more electrophilic, this reaction should become faster. Interestingly, the Mulliken charge of alkene carbon in tetracyanoethylene (TCNE) is +2.35, indicating that it could be a better substrate.

Therefore, we tried TCNE to react with osmapentalene **1**. Osmapentalyne **4** was produced at room temperature for only 3 h and isolated in 82% yield (Scheme 1). The proton signals of the fused five-membered rings in **4** were located at the aromatic region in the ^{1}H NMR spectrum. Specifically, the signals of H3, H5, and H6 were observed at 7.82, 9.55, and 8.11 ppm, respectively. In the ^{13}C NMR spectrum, the C1 signal (319.7 ppm) was comparable to the signals for osmapentalynes (323.8–330.8 ppm)[6] and osmabenzynes (264.9–316.4 ppm).[2]

The structure of complex **4** was further confirmed by HRMS, elemental analysis, and single-crystal X-ray diffraction. As shown in Figure 2, it contains an Os≡C triple bond in the planar fused five-membered rings (the mean deviation from the least-square plane is only 0.0214 Å). The length of the Os1–C1 (1.795 Å) and the bond angle at the carbyne carbon (130.9°) are comparable to those of Os≡C triple bonds (1.845 and 1.808 Å) and the bond angles (129.5 and 131.2°) in osmapentalynes reported earlier.[6] The bond lengths of C7–C8 (1.512 Å), C8–C9 (1.556 Å), and C9–C12 (1.572 Å) are obviously carbon–carbon single bonds.

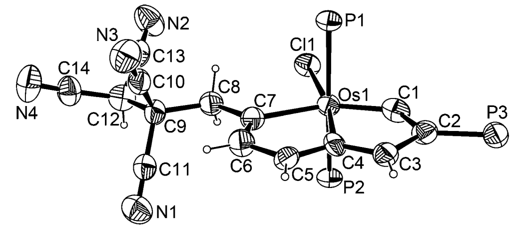


Figure 2. Molecular structure of the cation of **4** (thermal ellipsoids set at 50% probability). Phenyl groups in PPh_3 have been omitted for clarity.

The downfield proton chemical shifts, the planarity of the fused five-membered rings, and the delocalized carbon–carbon bond indicate that the osmapentalynes **2**–**4** are aromatic. To confirm their aromaticity, we employed the “isomerization stabilization energy” (ISE) method, a convenient tool to evaluate the magnitude of aromaticity[15] by DFT calculations. We calculated the ISE values based on the model complexes of **2′**, **3′**, and **4′** for which PH_3’s were used to replace the PPh_3’s. The computed ISE values of **2′**, **3′**, and **4′** are −36.1, −37.6, and −32.6 kcal mol^{-1} ($R = PH_3^+$, Scheme S5), respectively, which are more negative than those of the model complexes **2″** (−24.1 kcal mol^{-1}), **3″** (−25.0 kcal mol^{-1}), and **4″** (−23.9 kcal mol^{-1}) in which the phosphonium substituent was removed (R = H, Scheme S5), further demonstrating the stabilization effect of the phosphonium substituent.[16]

We also performed nucleus-independent chemical shift (NICS) calculations[17] on the model complexes of **2′**, **3′**, and **4′**. In general, negative values indicate aromaticity and positive values mean antiaromaticity. Indeed, the computed NICS(1)$_{zz}$ for the left and right five-membered rings of complexes **2′** (−15.7 and −16.1 ppm), **3′** (−15.3 and −15.9 ppm), and **4′** (−18.1 and −18.0 ppm) are all negative. These larger negative NICS(1)$_{zz}$ values suggest that all these osmapentalynes are aromatic. In addition, the aromaticity in **2′** is further supported by the anisotropy of the induced current density (AICD) analysis.[18] As shown in Figure 3, the clockwise current density vectors plotted on the AICD isosurface indicate that a diatropic ring current in the π system is displayed along the periphery of fused five-membered rings, thus confirming the π-aromaticity in **2′** (see also Figure S2).

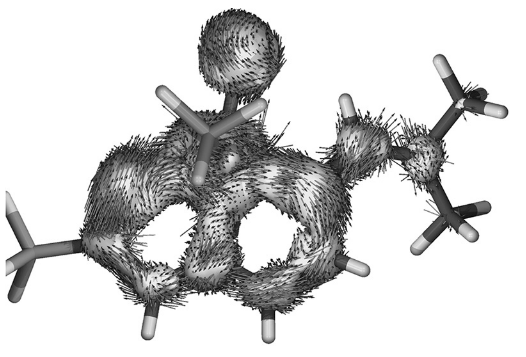
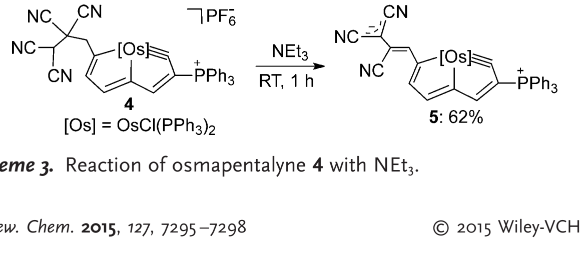


Figure 3. AICD isosurfaces of **2′** by π contribution. Current density vectors are plotted onto the AICD isosurface of 0.035 to indicate diatropic ring currents. The magnetic field vector is orthogonal with respect to the ring plane and points upward (clockwise currents are diatropic).

Note that the cyano group is one of the strongest electron-withdrawing groups, which also induce stronger electron-accepting effects in a conjugated system. However, the four cyano groups in complex **4** are unconjugated with osmapentalyne unit. Fortunately, treatment of complex **4** with excess triethylamine at room temperature for an hour led to the color change from yellow to green. The conjugated product **5** was isolated as a green solid (Scheme 3). A possible mechanism for the formation of **5** is proposed in Scheme S3 in the SI.

Complex **5** was characterized by HRMS, elemental analysis, ^{1}H and ^{31}P NMR spectra. Unfortunately, the poor solubility of complex **5** hampers the characterization by ^{13}C NMR spectroscopy. Nevertheless, the solid structure of **5**, which also contains an osmapentalyne unit, was confirmed by single-crystal X-ray diffraction (Figure 4). The characteristic Os1–C1 bond length (1.855 Å) and the Os1-C1-C2 angle (130.0°) are close to those of osmapentalynes reported earlier.[6] In addition, the three cyano groups in complex **5** are conjugated with the osmapentalyne unit.



Scheme 3. Reaction of osmapentalyne **4** with NEt$_3$.

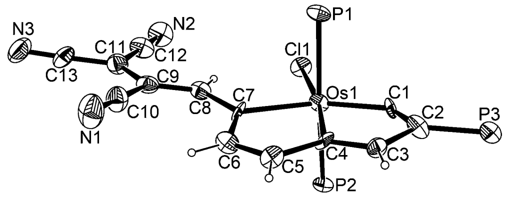


Figure 4. Molecular structure of **5** (thermal ellipsoids set at 50% probability). Phenyl groups in PPh$_3$ have been omitted for clarity.

Structurally, the most distinct feature of complex **5** is that all of the cyano groups are conjugated with the osmapentalyne unit compared with complex **4**, which could lead to the significant difference of the UV/Vis absorption spectra. As shown in Figure 5, with the extended conjugation, the lowest-energy absorption band is red-shifted and the molar extinction coefficient is increased. Specifically, the absorption maximum of complex **5** in the low-energy absorption band located at 694 nm ($\varepsilon = 4.68\times10^4\,\text{M}^{-1}\text{cm}^{-1}$, ε: molar extinction coefficient), which is red-shifted by 242 nm compared with that of **4** ($\lambda_{\max} = 452$ nm, $\varepsilon = 0.84\times10^4\,\text{M}^{-1}\text{cm}^{-1}$) due to the effective conjugation of multicyano groups with osmapentalyne unit (Figure S3). Remarkably, the molar extinction coefficient of **5** ($4.68\times10^4\,\text{M}^{-1}\text{cm}^{-1}$) in the low-energy absorption band is even three times more than that of the classical ruthenium complex N3 ($\varepsilon = 1.42\times10^4\,\text{M}^{-1}\text{cm}^{-1}$).[19] The UV/Vis absorption maximum of **2** ($\lambda_{\max} = 510$ nm, $\varepsilon = 1.73\times10^4\,\text{M}^{-1}\text{cm}^{-1}$) and **3** ($\lambda_{\max} = 526$ nm, $\varepsilon = 1.71\times10^4\,\text{M}^{-1}\text{cm}^{-1}$) are also recorded under the same conditions which are slightly red-shifted by 75 and 91 nm compared with that of complex **1** ($\lambda_{\max} = 435$ nm, $\varepsilon = 0.82\times10^4\,\text{M}^{-1}\text{cm}^{-1}$; Figure S4). The absorption maximum of complexes **4**, **2**, **3**, and **5** are red-shifted gradually, which is consistent with the decreasing HOMO–LUMO gaps (3.45, 3.08, 2.98, and 2.31 eV for **4**, **2**, **3**, and **5**, respectively) from calculations.

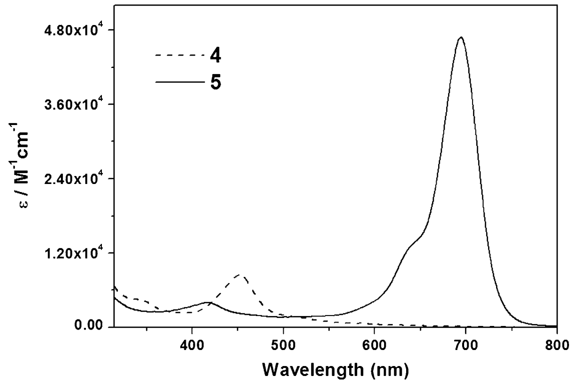


Figure 5. UV/Vis absorption spectra of **4** and **5** measured in CH$_2$Cl$_2$ at room temperature.

Metallapentalyne, containing a metal–carbon triple bond in five-membered ring, is a unique aromatic system. Here, we developed a general and effective method for the synthesis of osmapentalynes via osmapentalene with a metallacyclopropene unit. Such a metallacyclopropene unit can react with allene, alkyne, and alkene to form osmapentalynes. The experimental data together with the computations (the negative ISE, NICS values, and AICD plot) confirm the aromaticity of these fused five-membered rings. Developing such a general method allows us to realize various metalla-aromatics with potential applications in photoacoustic imaging and photothermal therapy.[20]

Keywords: aromaticity · density functional calculations · metal carbynes · osmapentalynes · osmium

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[10] CCDC 1041475 (**2**), 1041476 (**3**), 1041477 (**4**), and 1041478 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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