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Synthesis of Imidazopyridinium-Fused Metallacycloallene via One-Pot Reaction of η^2-Alkynol-Coordinated Osmacycle with 2-Aminopyridine

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Supporting Information

ABSTRACT: Metallacycloallenes are metallacyclic derivatives of cyclic allenes, in which a CH_2 (type **A**) or CH (type **B**) segment is formally replaced by an isolobal transition-metal fragment. In constrast to the well-developed chemistry of metallacycloallenes of type **A**, the synthesis of metallacycloallenes with the structural features of type **B** has met with limited success. In this study, we present the reaction of η^2-alkynol-coordinated osmacycle **1** with 2-aminopyridine in the presence of hypervalent iodine reagent, leading to the formation of imidazopyridinium-fused 4-osmacyclohexa-2,3,5-trienone **2** and 4-osmacyclohexa-2,5-dienone **3**. Two key intermediates, η^2-ethynyl ketone coordinated osmacycle **4** and 4-osmacyclohexa-2,5-dienone **5**, were isolated and fully characterized, which suggest the hypervalent iodine reagent plays an important role in the formation of the fused metallacycloallene **2**.

INTRODUCTION

Allenes are a unique class of unsaturated compounds containing two orthogonal cumulative C═C bonds, which has aroused ever-increasing interest from both experimental and theoretical chemists.[1] The synthesis of small cyclic allenes encounters substantial challenges due to the ring strain associated with the highly distorted cumulative double bonds.[2,3] The incorporation of a metal moiety in cycloallenes has been established as an efficient strategy to release the ring strain,[4] leading to a number of stable metallacycloallenes. As shown in Figure 1, the reported small metallacycloallenes can be classified into two types, in which a CH_2 group (type **A**) or a CH group (type **B**) of the corresponding carbocyclic analogues is formally replaced by a transition-metal fragment. A wide variety of type **A** species has been demonstrated in the past two decades.[5−7] As shown in Figure 1, four-membered (**I**)[5] and five-membered metallacycloallenes (**II**)[6,4b] and five-membered metallacyclocumulenes (**III**)[7] stand out as prominent representatives due to their considerable synthetic advances.

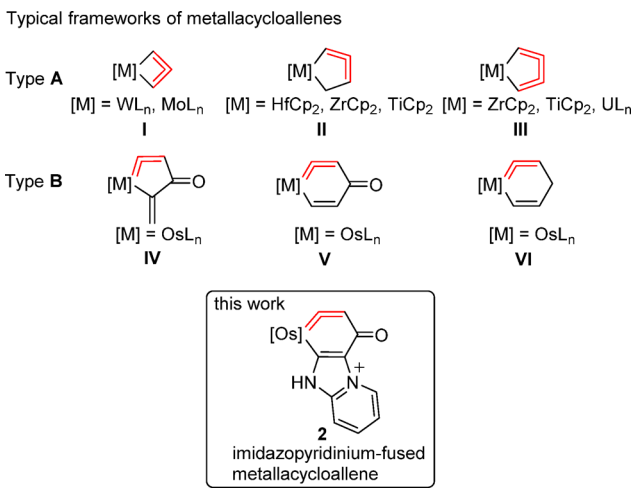

Figure 1. Examples of all-carbon metallacycloallenes: type **A**, metallacycloallenes derived from replacement of a CH_2 group with an isolable metal; type **B**, metallacycloallenes derived from replacement of a CH group with an isolable metal.

In contrast, only a few examples of type **B** have been reported, including five-membered osmacycloallenes (**IV**), six-membered osmacycloallenes (**V**),[8] and iso-osmabenzenes (**VI**).[9,10] The synthetic methods available for their preparation are very limited.[8−10] In this context, our efforts have been directed toward developing new synthetic methods of fused metallacycloallenes. Herein, we describe a direct construction of the first imidazopyridinium-fused metallacycloallene (**2**) from the readily available osmacycle **1**. The isolation of key intermediates provides a deeper understanding of the mechanism for the one-pot synthetic method.

RESULTS AND DISCUSSION

Synthesis of 4-Osmacyclohexa-2,3,5-trienone and 4-Osmacyclohexa-2,5-dienone. When complex **1**[11] was reacted with 4 equiv of (diacetoxyiodo)benzene, 3 equiv of 2-aminopyridine, and 4 equiv of Cs_2CO_3 in dichloromethane at room temperature for 1 h, complex **1** was completely consumed to afford a mixture, as indicated by in situ NMR spectroscopy. When the mixture was further treated with $NaPF_6$, complexes **2**

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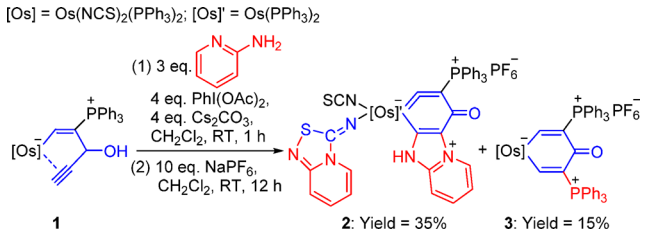
and **3** could be isolated by column chromatography (Scheme 1). Complex **2** was isolated as an orange solid in 35% yield. We think

Scheme 1. Synthesis of Complexes 2 and 3



that **3** is derived from the nucleophilic addition reaction of **1** with in situ formed PPh_3, which may come from the partial decomposition of compound **1**.

Complex **2** was characterized by multinuclear NMR spectroscopy, single-crystal X-ray diffraction analysis, high-resolution mass spectroscopy (HRMS), and elemental analysis (EA). The structure of complex **2** is depicted in Figure 2, which confirmed

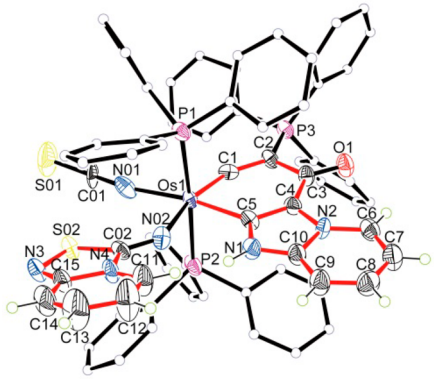
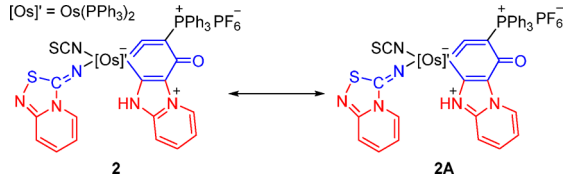


Figure 2. X-ray structure of complex **2** (ellipsoids at the 50% probability level). Hydrogen atoms in PPh_3 are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1−C1 1.754(8), Os1−C5 2.105(8), C1−C2 1.385(13), C2−C3 1.489(13), C3−C4 1.450(12), C4−C5 1.399(12), C4−N2 1.375(12), C5−N1 1.325(12), C10−N1 1.355(13), C10−N2 1.393(12), C3−O1 1.234(11); C1−Os1−C5 80.0(3), C2−C1−Os1 153.5(7), C1−C2−C3 115.0(7), C2−C3−C4 114.7(7), C3−C4−C5 131.0(9), C4−C5−Os1 125.6(6).

that it is a 4-osmacyclohexa-2,3,5-trienone fused with an imidazopyridinium. The metallatricyclic planarity of **2** is reflected by the mean deviation from the least-squares plane of 0.036 Å through the 13 atoms (Os1, C1−C10, N1 and N2). The notable structural feature of **2** is the metal−vinylidene moiety within the six-membered ring. The Os1−C1 bond length (1.754(8) Å) is slightly shorter than all of the reported Os−C double-bond lengths of osmium vinylidenes (1.762−1.909 Å).[13,14] The Os1−C1−C2 angle (153.5(7)°) is comparable to those of the reported six-membered metallacycloallenes **V** and **VI** (152.7(5),[8] 155.1(8),[9] and 158.5(3)°[10]). The structural parameters indicate that **2** could be represented by two resonance structures (Scheme 2). We have previously demonstrated a fused iso-osmapyridinium containing a cyclic vinylidene bond,[12] in which a coordinated nitrogen atom is embedded in the six-membered framework. In this context, **2** can be regarded as the first example of a fused all-carbon metallacycloallene. Interestingly, a unique thiadiazolopyridine imine ligand is coordinated to the metal center. This thiadiazole moiety was supposed to be derived from the [3 + 2]

Scheme 2. Proposed Resonance Structures of Complex 2

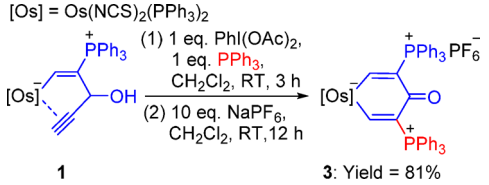


annulation reaction of the thiocyano ligand and 2-aminopyridine (vide infra), which is a brand new synthetic approach to access thiadiazoles.[15]

The solution NMR spectroscopic analysis of complex **2** is consistent with its solid-state structure. The singlet at 10.45 ppm in the ^{1}H NMR spectrum was attributed to N*H*, and the characteristic downfield signal of C1 was observed at 287.96 ppm in the $^{13}C\{^1H\}$ NMR spectrum. The other four carbon signals of the six-membered metallacycle appeared at δ 91.86 (C2), 172.09 (C3), 121.13 (C4), and 161.91 ppm (C5). The $^{31}P\{^1H\}$ NMR spectrum showed two singlets at 7.30 (C*P*Ph_3) and −3.58 ppm (Os*P*Ph_3). The molecular formula of **2** was confirmed by HRMS at 1355.2649 (m/z), which is in agreement with the calculated value for $[\mathbf{2} - PF_6]^+$ (1355.2625).

The yield of complex **3** could be improved to 81% when PPh_3 was added to the solution of complex **1** and (diacetoxyiodo)-benzene (Scheme 3). The structure of **3** was determined by

Scheme 3. Synthesis of Complex 3



X-ray diffraction. As shown in Figure 3, complex **3** is a 4-osmacyclohexa-2,5-dienone, in which the six atoms of the osmacyclohexadienone ring (Os1, C1−C5) are coplanar with a mean deviation from the least-squares plane of 0.01 Å. The Os1−C1 (2.008(8) Å) and Os1−C5 (1.988(9) Å) bond lengths are located in the range of an Os−C single bond (1.897−2.115 Å).[13]

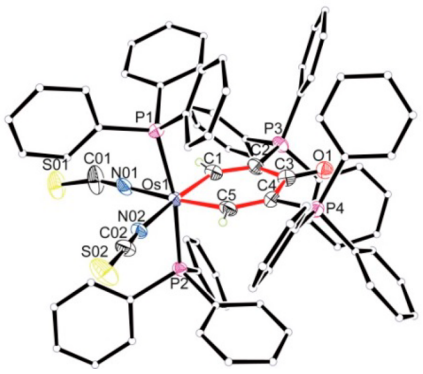


Figure 3. X-ray structure of complex **3** (ellipsoids at the 50% probability level). Hydrogen atoms in PPh_3 are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1−C1 2.008(8), Os1−C5 1.988(9), C1−C2 1.351(12), C2−C3 1.474(11), C3−C4 1.472(11), C4−C5 1.374(11), C3−O1 1.226(10); C1−Os1−C5 86.4(3), C2−C1−Os1 132.9(6), C1−C2−C3 124.1(7), C2−C3−C4 119.7(7), C3−C4−C5 124.1(7), C4−C5−Os1 132.7(6).

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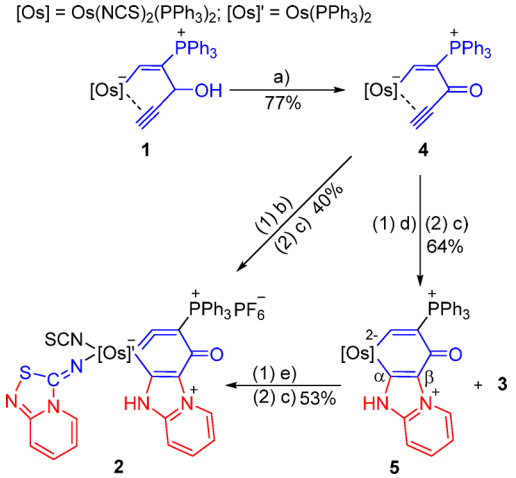
C1−C2 (1.351(12) Å) and C4−C5 bond lengths (1.374(11) Å) are comparable to the standard value of carbon−carbon double bonds. C2−C3 (1.474(11) Å) and C3−C4 bond lengths (1.472(11) Å) are consistent with those of typical carbon−carbon single bonds. The C3−O1 bond length (1.226(10) Å) is typical of a C═O double bond length. Complex **3** is paramagnetic, so that it could not be characterized by NMR. The molecular formula of **3** was confirmed by HRMS at m/z 1434.2884, which is in good agreement with the calculated value for $[\mathbf{3} - PF_6]^+$ (1434.2867).

Isolation of Key Intermediates along the Reaction Pathway Leading to 2. As detected by in situ $^{31}P\{^1H\}$ NMR spectroscopy, several intermediates appear during the transformation from **1** to **2**. A pair of signals at 13.61 and −6.24 ppm was observed within the first 15 min. Fortunately, it could be isolated under controlled conditions. As shown in Scheme 4,

Scheme 4. Isolation of Intermediates[a]



[a]Reaction conditions. (a) 1 equiv of $PhI(OAc)_2$, CH_2Cl_2, room temperature, 15 min; (b) 3 equiv of 2-aminopyridine, 3 equiv of $PhI(OAc)_2$, 4 equiv of Cs_2CO_3, CH_2Cl_2, room temperature, 1 h; (c) 10 equiv of $NaPF_6$, CH_2Cl_2, room temperature, 12 h; (d) 3 equiv of 2-aminopyridine, 1 equiv of $PhI(OAc)_2$, 2 equiv of Cs_2CO_3, CH_2Cl_2, room temperature, 10 h; (e) 3 equiv of 2-aminopyridine, 2 equiv of $PhI(OAc)_2$, 2 equiv of Cs_2CO_3, CH_2Cl_2, room temperature, 1 h.

treatment of complex **1** with 1 equiv of (diacetoxyiodo)benzene in dichloromethane for 15 min afforded compound **4**, which could be isolated as a green solid in a yield of 77%. The structure of **4** was confirmed by single-crystal X-ray diffraction, and the molecular structure is shown in Figure 4. The X-ray diffraction study confirmed that **4** contains a planar osmacycle with a carbonyl group. The planarity of the metallacycle is reflected by the mean deviation from the least-squares plane of 0.031 Å through six atoms (Os1, C1−C5). As a consequence of the coordination, the terminal alkyne is strongly bent with a C3−C4−C5 angle of 166.6(9)°.

The NMR spectroscopic analysis of compound **4** is consistent with the X-ray structure. In the ^1H NMR spectrum, the C^1H signal was observed as a doublet at 13.09 ppm. With the aid of $^1H-^{13}C$ HSQC and $^1H-^{13}C$ HMBC, the signal of C^5H was assigned to 5.56 ppm. In the $^{13}C\{^1H\}$ NMR spectrum, the signals of the alkyne carbon atoms appeared at 96.63 (C5) and 88.19 ppm (C4). The other carbon signals were observed at 240.87 (C1), 192.85 (C3), and 119.80 ppm (C2), respectively. The $^{31}P\{^1H\}$ NMR spectrum showed two singlets at 13.61 (CPPh$_3$) and −6.24 ppm (OsPPh$_3$), which is consistent with the

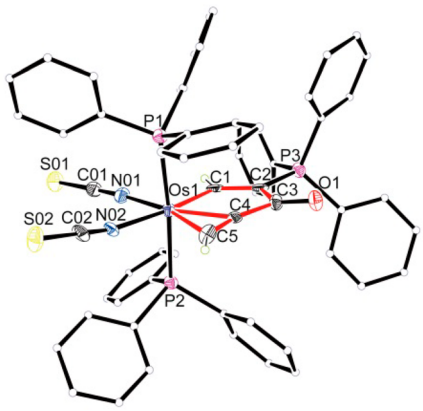


Figure 4. X-ray structure of compound **4** (ellipsoids at the 50% probability level). Hydrogen atoms in PPh_3 are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1−C1 2.064(11), Os1−C5 2.179(10), Os1−C4 2.156(9), C1−C2 1.362(14), C2−C3 1.456(13), C3−C4 1.521(14), C4−C5 1.223(13), C3−O1 1.222(11); C1−Os1−C5 106.2(4), C2−C1−Os1 124.2(7), C1−C2−C3 115.5(10), C2−C3−C4 108.2(8), C3−C4−C5 166.6(9), C3−C4−Os1 118.4(6), C5−C4−Os1 74.6(6), C4−C5−Os1 72.6(6).

signals observed by the in situ $^{31}P\{^1H\}$ NMR spectroscopy mentioned above. The molecular formula of **4** (1172.2005) detected by HRMS is consist with the calculated value for $[\mathbf{4}]^+$ (m/z 1172.1953). As illustrated in Scheme 4, in the presence of (diacetoxyiodo)benzene (3 equiv) and excess Cs_2CO_3, **4** could further converted to **2** by treatment with excess 2-aminopyridine and $NaPF_6$. The conversion strongly indicates that compound **4** is the intermediate of the transformation from **1** to **2**.

In order to further study the mechanism, we tried to isolate other intermediates by reducing the amount of hypervalent iodine reagent. As shown in Scheme 4, when the amount of (diacetoxyiodo)benzene was reduced to 1 equiv, the reaction of complex **4** with Cs_2CO_3 and 2-aminopyridine produced another intermediate, **5**. (Diacetoxyiodo)benzene was considered as an oxidant in this reaction, since we found that other typical oxidants, such as hydrogen peroxide, can also facilitate this transformation. Similar examples utilizing hypervalent iodine(III) as oxidant have been widely investigated in the literature.[16] The structure of compound **5** was confirmed by an X-ray diffraction study, NMR spectroscopy, HRMS, and elemental analysis.

As shown in Figure 5, compound **5** can be described as a 4-osmacyclohexa-2,5-dienone fused with an imidazopyridinium unit. It contains a planar tricyclic framework, as reflected by the mean deviation from the least-squares plane of 0.012 Å through 13 atoms (Os1, C1−C10, N1, and N2). The bond lengths within the osmacyclohexadienone ring were comparable to those of complex **3**. Nucleophilic additions of 2-aminopyridine to **4** were suggested in the formation of **5** (vide infra). Although both the amino and pyridine groups of 2-aminopyridine can act as nucleophiles, the reaction selectively gave **5** rather than the isomer **5′** (in which the nitrogen of the pyridine unit is bonded to the α-carbon and the amino nitrogen atom is connected to the β-carbon). As shown in Figure S18 in the Supporting Information, this may be attributed to the steric hindrance between the bulky imidazopyridinium ring and the SCN ligand, which inhibits the formation of **5′**. Preliminary density functional theory (DFT) calculation results show that **5** is more stable than **5′** by 12.6 kcal/mol.

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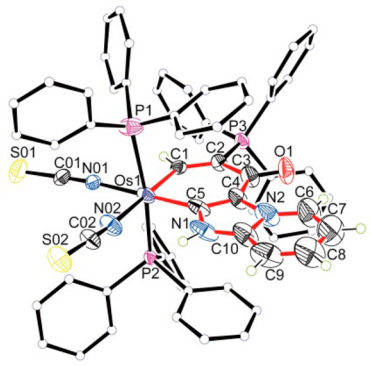
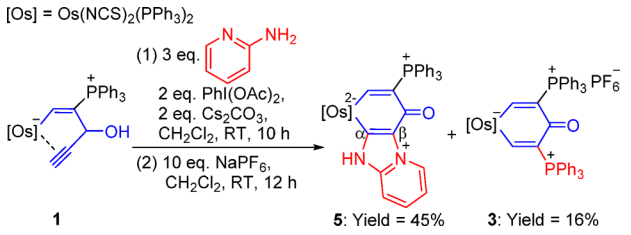


Figure 5. X-ray structure of compound **5** (ellipsoids at the 50% probability level). Hydrogen atoms in PPh_3 are omitted for clarity. Selected bond distances (Å) and angles (deg): Os1−C1 1.995(6), Os1−C5 2.014(8), C1−C2 1.384(9), C2−C3 1.450(10), C3−C4 1.429(10), C4−C5 1.368(11), C3−O1 1.258(9); C1−Os1−C5 87.3(3), C2−C1−Os1 130.0(5), C1−C2−C3 127.0(6), C2−C3−C4 118.2(7), C3−C4−C5 127.2(7), C4−C5−Os1 130.3(5).

As shown in Scheme 4, after treatment of complex **5** with 2-aminopyridine, (diacetoxyiodo)benzene, and Cs_2CO_3 in dichloromethane at room temperature for 1 h, and a subsequent counteranion exchange by treatment of the mixture with $NaPF_6$, **5** could convert to **2** in good yield. It is worth mentioning that 2-aminopyridine is indispensable in this reaction. In the absence of 2-aminopyridine, the oxidative dehydrogenation of **5** cannot take place, which suggests that the newly formed thiadiazolopyridine ligand is vital for the dehydrogenation process.

As shown in Scheme 5, compound **5** could also be obtained from complex **1** under the corresponding reaction conditions.

Scheme 5. Synthesis of Complexes 5 and 3



These experimental observations further established the transformation process from **1** to **4**, **5**, and the final product **2**.

Proposed Reaction Mechanism. On the basis of the experimental observations, a possible mechanism for the formation of osmacycloallene **2** is proposed in Scheme 6. Oxidation of **1** in the presence of (diacetoxyiodo)benzene led to the formation of intermediate **4**. Then, the nucleophilic addition of the 2-aminopyridine to the coordinated alkyne may generate intermediate **A**. The intramolecular nucleophilic attack of an amino group to the α-C atom of osmacyclohexadienone may produce intermediate **B**, which may undergo oxidation by (diacetoxyiodo)benzene to yield complex **5**. With the aid of (diacetoxyiodo)benzene, a [3 + 2] annulation of **5** with 2-aminopyridine may lead to the formation of intermediate **C**, which could eliminate 1 equiv of HOAc to produce intermediate **D**. Subsequent dissociation of PPh_3 from the metal center could give intermediate **E**, which would undergo 1,2-H migration and result in the formation of the hydride intermediate **F**. A similar conversion of alkenyl complexes to hydride−vinylidene complexes by 1,2-H migration has been reported.[12,17] Oxidative dehydrogenation may occur to facilitate the further transformation from **F** to **G**. Finally, the coordination of PPh_3 to the metal center and the subsequent exchange of the counteranion in the presence of $NaPF_6$ would yield the final product **2**. The addition of Cs_2CO_3 to the reaction mixture may assist in the dissociation of HOAc during the reaction (from **B** to **5**, **C** to **D**, and **F** to **G**).

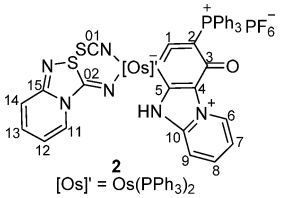
CONCLUSIONS

In conclusion, we introduced η^2-alkynol-coordinated osmacycle **1** as a starting material that could react with 2-aminopyridine to produce the first imidazopyridinium-fused metallacycloallenes. The mechanism of the one-pot reaction was established with aid of the isolation of two key intermediates. A mechanistic study demonstrates that the addition of hypervalent iodine reagent is indispensable for the formation of the fused metallacycloallenes. Our findings provide a new synthetic strategy for fused metallacycloallenes, which may encourage further efforts in the chemistry of strained cycloallenes.

EXPERIMENTAL SECTION

General Procedures. All syntheses were performed at room temperature under a nitrogen atmosphere using standard Schlenk techniques, unless otherwise stated. Solvents were distilled under nitrogen from sodium/benzophenone (tetrahydrofuran and diethyl ether) or calcium hydride (dichloromethane). Reagents were used as received from commercial sources without further purification. Column chromatography was performed on neutral alumina gel (200−300 mesh). The starting material **1** was synthesized according to the literature procedures.[11] The nuclear magnetic resonance (NMR) experiments were performed on a Bruker AVIII-400 spectrometer (^{1}H, 400.1 MHz; ^{13}C, 100.6 MHz; ^{31}P, 161.9 MHz) or a Bruker AVIII-600 spectrometer (^{1}H, 600.1 MHz; ^{13}C, 150.9 MHz; ^{31}P, 242.9 MHz) at room temperature. ^{1}H and ^{13}C NMR chemical shifts (δ) are relative to tetramethylsilane, and ^{31}P NMR chemical shifts (δ) 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). Elemental analyses were performed on a Vario EL III elemental analyzer. High-resolution mass spectrometry (HRMS) experiments were performed on a Bruker En Apex Ultra 7.0T FT-MS. The theoretical molecular ion peak was calculated by Compass Isotope Pattern software supplied by Bruker.

Preparation and Characterization of Complex 2.



Method 1. A mixture of **1** (270 mg, 0.23 mmol), (diacetoxyiodo)-benzene (296 mg, 0.92 mmol), 2-aminopyridine (65 mg, 0.69 mmol), and Cs_2CO_3 (301 mg, 0.92 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 1 h. Then $NaPF_6$ (386 mg, 2.30 mmol) was added, and the mixture was stirred at room temperature for 12 h to give a brown suspension. The solid was removed by filtration, and the filtrate was reduced to about 2 mL under vacuum. Addition of diethyl ether (20 mL) to the solution gave a brown precipitate, which was collected by filtration, washed with diethyl ether (3 × 10 mL), and dried under vacuum. The residue was purified by column chromatography (neutral alumina, eluent acetone and methanol/dichloromethane 1/20) to give **3** as a red solid (yield: 54 mg, 15%) and **2** as an orange solid (yield: 121 mg, 35%)

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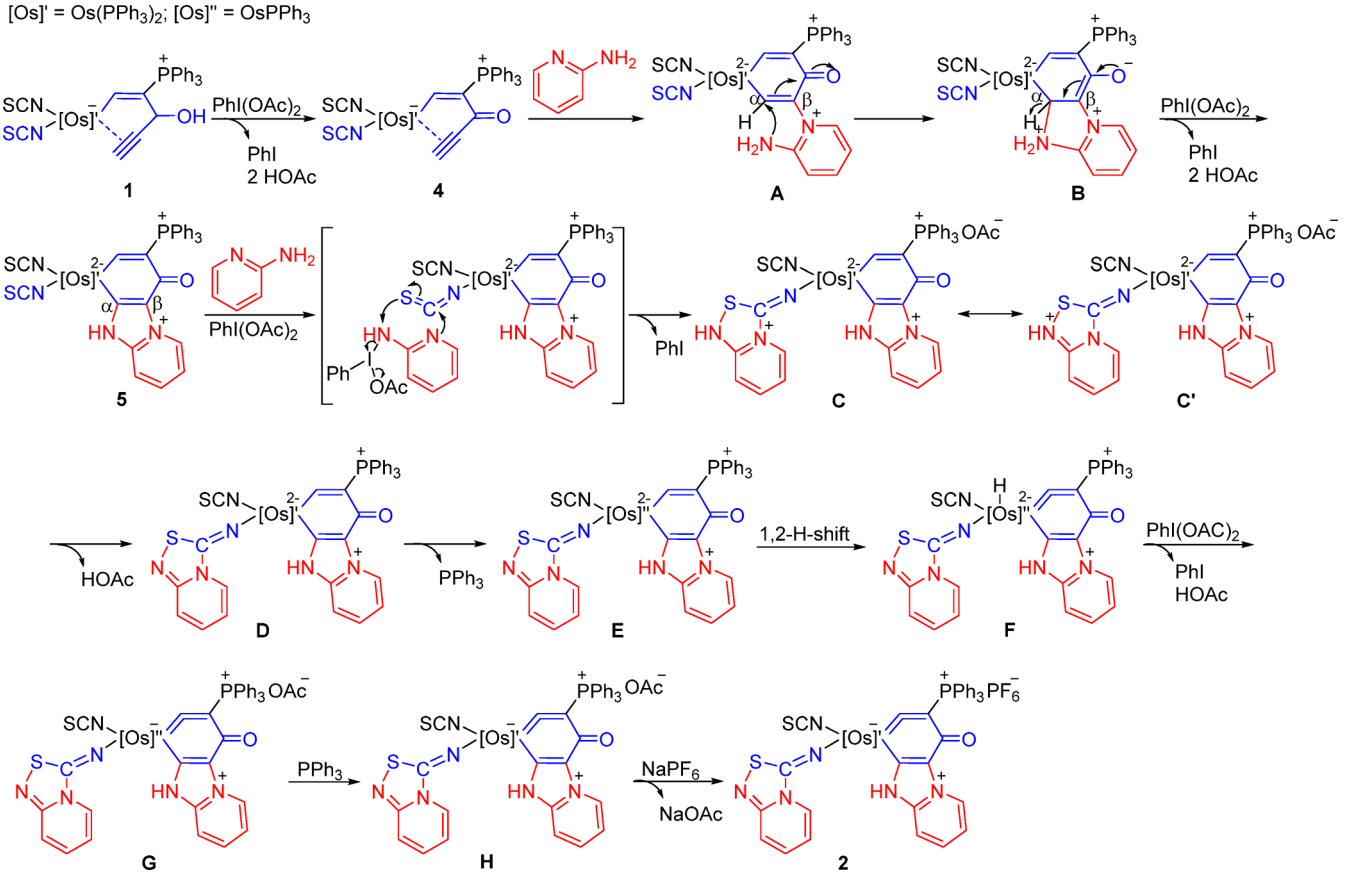
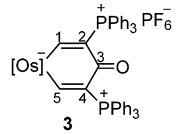
Scheme 6. Proposed Mechanism for the Synthesis of Imidazopyridinium-Fused 4-Osmacyclohexa-2,3,5-trienone 2



Method 2. A mixture of **4** (200 mg, 0.17 mmol), (diacetoxyiodo)-benzene (164 mg, 0.51 mmol), 2-aminopyridine (48 mg, 0.51 mmol), and Cs_2CO_3 (221 mg, 0.68 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for about 1 h. Then $NaPF_6$ (285 mg, 1.70 mmol) was added, and the mixture was stirred at room temperature for 12 h to give a brown suspension. The solid was removed by filtration, and the filtrate was reduced to about 2 mL under vacuum. Addition of diethyl ether (20 mL) to the solution gave a brown precipitate, which was collected by filtration, washed with diethyl ether (3 × 10 mL), and dried under vacuum. The residue was purified by column chromatography (neutral alumina, eluent acetone and methanol/dichloromethane 1/20) to give **2** as an orange solid (yield: 101 mg, 40%)

Method 3. A mixture of **5** (151 mg, 0.12 mmol), (diacetoxyiodo)-benzene (77 mg, 0.24 mmol), 2-aminopyridine (34 mg, 0.36 mmol), and Cs_2CO_3 (78 mg, 0.24 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for about 1 h. Then $NaPF_6$ (201 mg 1.20 mmol) was added, and the mixture was stirred at room temperature for 12 h to give a brown suspension. The solid was removed by filtration, and the filtrate was reduced to about 2 mL under vacuum. Addition of diethyl ether (20 mL) to the solution gave a brown precipitate, which was collected by filtration, washed with diethyl ether (3 × 10 mL), and dried under vacuum. The residue was purified by column chromatography (neutral alumina, eluent acetone and methanol/dichloromethane 1/20) to give **2** as an orange solid (yield: 95 mg, 53%). ^{1}H NMR (400.1 MHz, CD_2Cl_2): δ 10.45 (s, 1H, N*H*), 8.95 (d, 1H, J = 5.2 Hz, C^6*H*), 7.81−6.74 ppm, (52H, Ph, Py). ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ 7.30 (s, C*P*Ph$_3$), −3.58 ppm (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, plus ^{1}H−^{13}C HMBC and HSQC and ^{13}C-dept 135): δ 287.96 (br, C^1), 172.09 (d, ^2J(P,C) = 4.4 Hz, C^3), 171.25 (s, C^{02}), 161.91 (br, C^5), 150.30 (s, C^{15}), 121.13 (d, ^3J(P,C) = 4.2 Hz, C^4), 134.89−119.37 (Ph, Py), 91.86 ppm (d, ^1J(P,C) = 116.2 Hz, C^2). HRMS (ESI): m/z calcd for $[C_{71}H_{54}N_6OOsP_3S_2]^+$, 1355.2625; found, 1355.2649; Anal. Calcd for $C_{71}H_{54}N_6OOsP_4S_2F_6$: C, 56.87; H, 3.63; N, 5.60; Found: C, 57.10; H, 3.52; N, 5.93.

Preparation and Characterization of Complex 3.

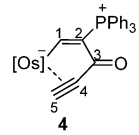


3

[Os] = Os(NCS)$_2$(PPh$_3$)$_2$

A mixture of **1** (305 mg, 0.26 mmol), (diacetoxyiodo)benzene (84 mg, 0.26 mmol), and triphenylphosphine (68 mg, 0.26 mmol) was stirred in CH_2Cl_2 (10 mL) at room temperature for about 3 h. Then $NaPF_6$ (433 mg 2.58 mmol) was added, and the mixture was stirred at room temperature for 12 h to give a red solution. The solution was reduced to about 2 mL under vacuum. Addition of diethyl ether (20 mL) to the solution gave a red solid, which was collected by filtration, washed with diethyl ether (3 × 10 mL), and dried under vacuum to give **3** as a red solid (yield: 334 mg, 81%). HRMS (ESI): m/z calcd for $[C_{79}H_{62}N_2OOsP_4S_2]^+$, 1434.2867; found, 1434.2884. Anal. Calcd for $C_{79}H_{62}F_6N_2OOsP_5S_2$: C, 60.11; H, 3.96; N, 1.77; Found: C, 59.86; H, 4.32; N, 2.16.

Preparation and Characterization of Complex 4.



4

[Os] = Os(NCS)$_2$(PPh$_3$)$_2$

A mixture of **1** (223 mg, 0.19 mmol) and (diacetoxyiodo)benzene (61 mg, 0.19 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for about 15 min to give a red solution. The volume was reduced to about 2 mL under vacuum. Addition of diethyl ether (20 mL) to the solution produced a red solid that was collected by filtration and washed with tetrahydrofuran (2 mL) and diethyl ether (3 × 10 mL) to give **4** as a green solid (yield: 172 mg, 77%). ^{1}H NMR (600.1 MHz, CD_2Cl_2/$(CF_3)_2$CHOH 1/1): δ 13.09 (d, 1H, J(P,H) = 14.4 Hz, C^1*H*),

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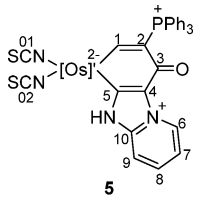
5.56 (s, 1H, C^5*H*) 7.74−6.91 ppm (45H, Ph).^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2): δ 13.61 (s, C*P*Ph$_3$), − 6.24 ppm (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, plus ^{1}H−^{13}C HMBC and HSQC and ^{13}C-dept 135): δ 240.87 (s, C^1), 192.85 (d, ^2J(P,C) = 22.6 Hz, C^3), 119.80 (d, ^1J(P,C) = 90.5 Hz, C^2), 96.63 (s, C^5), 88.19 (d, ^3J(P,C) = 18.1 Hz, C^4), 136.61−119.51 ppm (Ph). HRMS (ESI): *m*/*z* calcd for $[C_{61}H_{47}N_2OOsP_3S_2]^+$, 1172.1953; found, 1172.2005. Anal. Calcd for $C_{61}H_{47}N_2OOsP_3S_2$: C, 62.55; H, 4.04; N, 2.39; Found: C, 62.90; H, 4.44; N, 2.16.

Preparation and Characterization of Complex 5.



5

[Os]' = Os(PPh$_3$)$_2$

Method 1. A mixture of **4** (176 mg, 0.15 mmol), (diacetoxyiodo)-benzene (48 mg, 0.15 mmol), 2-aminopyridine (42 mg, 0.45 mmol), and Cs_2CO_3 (98 mg, 0.30 mmol) was stirred in CH_2Cl_2 (10 mL) at room temperature for 10 h. Then $NaPF_6$ (250 mg 1.49 mmol) was added, and the mixture was stirred at room temperature for 12 h to give a brown suspension. The solid was removed by filtration, and the filtrate was reduced to about 2 mL under vacuum. Addition of diethyl ether (20 mL) to the solution gave a brown solid, which was collected by filtration, washed with diethyl ether (3 × 10 mL), and dried under vacuum. The residue was purified by column chromatography (neutral alumina, eluent acetone/dichloromethane = 1/20 and acetone) to give **5** as a green solid (yield: 121 mg, 64%) and **3** as a red solid (yield: 24 mg, 10%).

Method 2. Hydrogen peroxide (113 μL, 1.12 mmol, 30% in water) was added to a suspension of **4** (328 mg, 0.28 mmol) and 2-amino-pyridine (131 mg, 1.40 mmol) in CH_2Cl_2 (10 mL). The solution was stirred at room temperature for about 10 h to give a brown suspension. The solution was reduced to about 2 mL under vacuum. Addition of ether (20 mL) to the solution gave a brown solid, which was collected by filtration and washed with diethyl ether (3 × 10 mL). The residue was purified by column chromatography (neutral alumina, eluent acetone/dichloromethane 1/20) to give **5** as a green solid (yield: 192 mg, 54%).

Method 3. A mixture of **1** (246 mg, 0.21 mmol), (diacetoxyiodo)-benzene (135 mg, 0.42 mmol), 2-aminopyridine (59 mg, 0.63 mmol), and Cs_2CO_3 (137 mg, 0.42 mmol) was stirred in CH_2Cl_2 (10 mL) at room temperature for about 10 h. Then $NaPF_6$ (350 mg 2.08 mmol) was added, and the mixture was stirred at room temperature for 12 h to give a brown suspension. The solid was removed by filtration, and the filtrate was reduced to about 2 mL under vacuum. Addition of diethyl ether (20 mL) to the solution gave a brown solid, which was collected by filtration, washed with diethyl ether (3 × 10 mL), and dried under vacuum. The residue was purified by column chromatography (neutral alumina, eluent acetone/dichloromethane 1/20 and acetone) to give **3** as a red solid (yield: 53 mg, 16%) and **5** as a green solid (yield: 119 mg, 45%). ^{1}H NMR (600.1 MHz, CD_2Cl_2): δ 14.66 (d, J(P,H) = 23.1 Hz, 1H, C^1*H*), 9.44 (d, J = 6.7 Hz, 1H, C^6*H*), 8.22 (s, 1H, N*H*), 6.60 (d, J = 8.4 Hz, 1H, C^8*H*), 7.53−6.76 ppm (47H, Ph, C^7*H*, C^9*H*). ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2): δ 18.55 (s, C*P*Ph$_3$), −1.20 ppm (s, Os*P*Ph$_3$). ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, plus ^{1}H−^{13}C HMBC and HSQC and ^{13}C-dept 135): δ 232.92 (br, C^1), 182.48 (d, ^2J(P,C) = 15.0 Hz, C^3), 179.86 (br, C^5), 142.27 (s, C^{10}), 139.72 and 137.56 (s, C^{01} and C^{02}), 128.37 (s, C^6), 124.56 (d, ^3J(P,C) = 10.6 Hz, C^4), 115.59 (s, C^7 and C^9), 111.84 (d, ^1J(P,C) = 83.0 Hz, C^2), 109.33 (s, C^8), 136.38−123.66 ppm (Ph). HRMS (ESI): *m*/*z* calcd for $[C_{66}H_{51}N_4OOsP_3S_2]^+$, 1264.2328; found, 1264.2336. Anal. Calcd for $C_{66}H_{51}N_4OOsP_3S_2$: C, 62.74; H, 4.07; N, 4.43; Found: C, 62.70; H, 4.38; N, 4.15.

Crystallographic Details. Single-crystal X-ray diffraction data were collected on an Oxford Gemini S Ultra CCD area detector or a Rigaku R-AXIS SPIDER IP CCD area detector with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.54184 Å). All of the data were corrected for absorption effects using the multi-scan technique. The structure was solved and refined using full-matrix least squares based on F^2 with the programs SHELXS-2014[18] and SHELXL-2014 within Olex2.[19] Non-H atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were introduced at their geometric positions and refined as riding atoms unless otherwise stated. Crystals suitable for X-ray diffraction was grown from CH_2Cl_2 or $C_2H_4Cl_2$ solutions layered with *n*-hexane for all compounds. CCDC-1532084 (**2**), CCDC-1532089 (**3**), CCDC-1532106 (**4**), and CCDC-1532088 (**5**) contain supplementary crystallographic data for this paper. Further details on the crystal data, data collection, and refinement are summarized in Table S1 in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00629.

Crystallographic data for complexes **2**−**5** and ^{1}H, ^{31}P, and ^{13}C NMR spectra of all new products (PDF)

Cartesian coordinates of the calculated structures (XYZ)

Accession Codes

CCDC 1532084, 1532088−1532089, and 1532106 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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